Universidad de
Oviedo

EPM
ESCUELA
POLITÉCNICA DE
MIERES

TRABAJO FIN DE GRADO

GRADO EN INGENIERÍA FORESTAL Y DEL MEDIO NATURAL

Mención en Explotaciones Forestales

Soil Analysis of a Waste Dump in La Soterraña mine

Caracterización de una escombrera en la mina de La Soterraña

Autor: **Miguel Menéndez Rodríguez**

Tutor: Elias Afif Khouri

Cotutor: Rubén Forján Castro

Junio, 2024

Declaración de Originalidad del Trabajo Fin de Grado

D. Miguel Menéndez Rodríguez, estudiante del Grado en Ingeniería Forestal y del Medio Natural de la Escuela Politécnica de Mieres de la Universidad de Oviedo, declaro bajo mi responsabilidad que:

El Trabajo de Fin de Grado aquí presentado con título *Soil Analysis of a Waste Dump in La Soterraña mine* ha sido realizado bajo mi autoría, es original y que todas las fuentes utilizadas para su realización han sido debidamente citadas en el mismo.

Para que así conste, firmo la presente declaración.

En Mieres, a 9 de junio de 2024.

Miguel Menéndez Rodríguez

Relación del TFG con los Objetivos de Desarrollo Sostenible

Breve justificación:

La salud del suelo juega un papel clave en la consecución de los Objetivos de Desarrollo Sostenible (ODS). Esto se debe a que los suelos prestan servicios esenciales para las actividades humanas y la sostenibilidad de los ecosistemas, tales como: producción de alimentos, producción de biomasa, hábitat y reserva de la biodiversidad, almacenamiento, filtrado y transformación de nutrientes, agua y carbono, secuestro de carbono, plataforma de actividades humanas y elementos del paisaje.

A continuación, se enumeran algunos de los objetivos relacionados con el trabajo de fin de grado:

- Agua Limpia y Saneamiento (ODS 6): presenta relación al promoverse el restablecimiento de un emplazamiento contaminado, capaz de dañar ecosistemas relacionados con el agua.

- Acción por el Clima (ODS 13) y Vida en los Ecosistemas Terrestres (ODS 15): también presentan relación con el trabajo por razones similares, al clamar por la restauración de un suelo degradado, exponiendo sus carencias y aportando información para su recuperación.

Resumen / Abstract

En este apartado se incluye un resumen y palabras clave en castellano en cumplimiento con el BOLETÍN OFICIAL DEL PRINCIPADO DE ASTURIAS núm. 62 de 30-03-2020 que aprueba el reglamento sobre la asignatura Trabajo Fin de Grado en la Universidad de Oviedo.

🇪🇸

Palabras clave: Degradación del suelo, mercurio, arsénico, contaminación química.

Para conocer las necesidades y estado general de la escombrera situada en La Soterraña se realiza una caracterización edáfica de la misma. Datos previos muestran indicios de contaminación por arsénico y mercurio en toda el área de la antigua explotación minera. La escombrera se encuentra sin restaurar y carece de vegetación, siendo considerada como un tecnosol espólico. Una muestra representativa de varios puntos de la escombrera es tratada en laboratorio siguiendo diversas metodologías para conocer sus principales características físico-químicas. Los resultados exponen un claro desequilibrio en sus propiedades físicas y químicas con respecto a un suelo sano, así como indicios de una alarmante contaminación por arsénico y mercurio. Su estado presenta consecuencias graves como la dispersión de contaminantes que amenazan a la salud de las personas y ecosistemas cercanos o la incapacidad de desarrollar vegetación con normalidad debido factores como la escasez de nutrientes, falta de estructura, déficit de materia orgánica o contaminación por As y Hg. Se enumeran las posibles fases de un necesario trabajo de restauración sobre la escombrera para solucionar las problemáticas anteriormente mencionadas que presenta la misma.

🇬🇧

Keywords: Soil degradation, mercury, arsenic, chemical contamination

To understand the needs and general condition of the waste dump located in La Soterraña, a soil characterization is conducted. Previous data shows signs of metal(loid) contamination throughout the area of the former mining site. The waste dump remains unrestored and lacks vegetation, with its material considered as spolic technosol. A representative sample of the waste dump is treated in the laboratory following various methodologies to expose its physiochemical properties. The results reveal a clear imbalance in its properties when compared to a healthy soil, as well as signs of alarming arsenic and mercury contamination. Its condition has serious consequences such as the dispersion of contaminants threatening human health and ecosystems or the inability to develop vegetation normally due to factors such as nutrient scarcity, lack of structure, organic matter deficit, or contamination by As and Hg. The possible phases of a necessary restoration work on the waste dump are listed to address the issues it presents.

INDEX

TABLES

FIGURES

EQUATIONS

1. Introduction

1.1. Mining and soil pollution

Mining is an economic activity that extracts minerals and other geological materials from the earth's crust which are then used as raw materials to fuel other economic activities (Candeias et al., 2019). Mining activities carry environmental consequences with a ranging impact as the extraction and processing of geological materials is often a source of contaminant elements that slip into the soil, air or water streams flowing off-site (Boente et al., 2022; FAO, 2021; Panza et al., 2024). The leftover residues from the mining activity are often settled in dumps after the activity is stopped, some remaining on-site decades after closure (Candeias et al., 2019; Luque Cabal & Gutiérrez Claverol, 2006).

In Europe, there were more than 3 million contaminated sites in 2015, with industrial areas and mining sites among them (Montanarella, 2015). According to the *Inventario de instalaciones de residuos mineros clausuradas y peligrosas en España* (2022), there were 109 closed mining facilities in Spain that had a negative environmental impact on its surroundings. 86 of them were identified as waste dumps, with La Soterraña being among them. The rest of the identified sites are tailing ponds.

The need to combat soil pollution is deemed important by many countries around the globe as it compromises food security, promotes land degradation and poses a threat to human health (FAO, 2021). Mining activities pose the risk of soil degradation and are closely related with the reduction of ecosystemic services (Boldy et al., 2021; Zhang et al., 2024). Within the multiple negative consequences of land degradation also lie, climate stability, environmental sustainability, and economic prosperity. For the last case alone, it is estimated that the global economic impact of land degradation, assessed through the loss of ecosystemic services, could total the astonishing cost of 6.3–10.6 trillion US dollars annually (Prăvălie et al., 2024).

The 31 % of all areas polluted by heavy metals in Europe are deemed in a critical state of contamination (Figure 1), with Spain having almost a 50 % of its heavy metals contaminated areas with the same classification (Prăvălie et al., 2024). North-western Spain is among the areas in Europe with the highest levels of heavy metals contamination (Figure 1). Arsenic (As) and mercury (Hg) are among the contaminant elements most frequently detected in the region according to Ballabio et al. (2021) (Figure 2). It also specifically provides a clear look at the mercury (Hg) contamination (Figure 3) product of well-known mining activities, coal combustion industries or local diffuse contamination. Some of Spain's hotspots are in close proximity to old mercury mining sites such as Almadén (Castilla-La Mancha) or La Soterraña (Asturias).

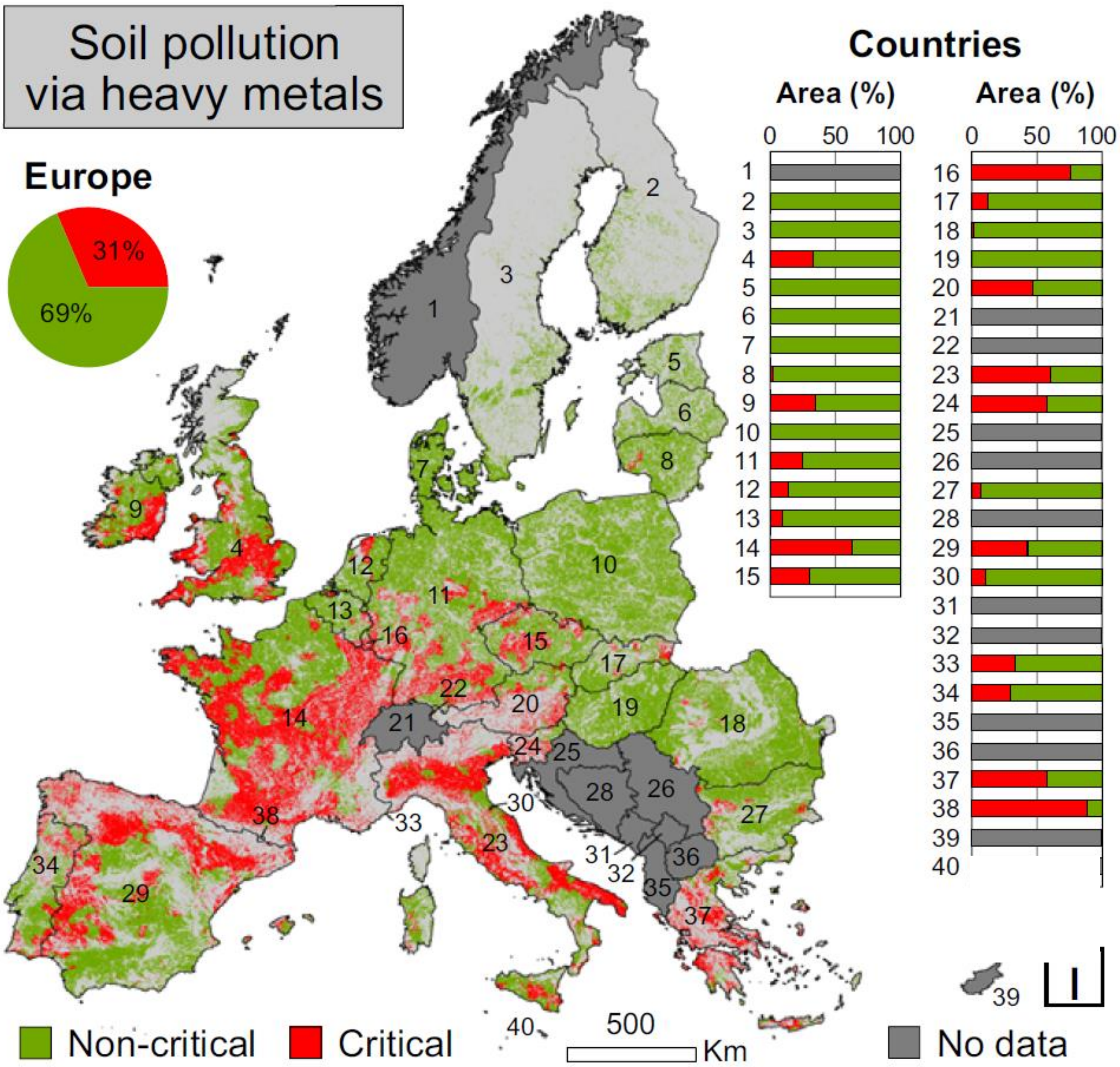

Figure 1: Soil Pollution by heavy metals in Europe. Extracted from Prăvălie et al. (2024)

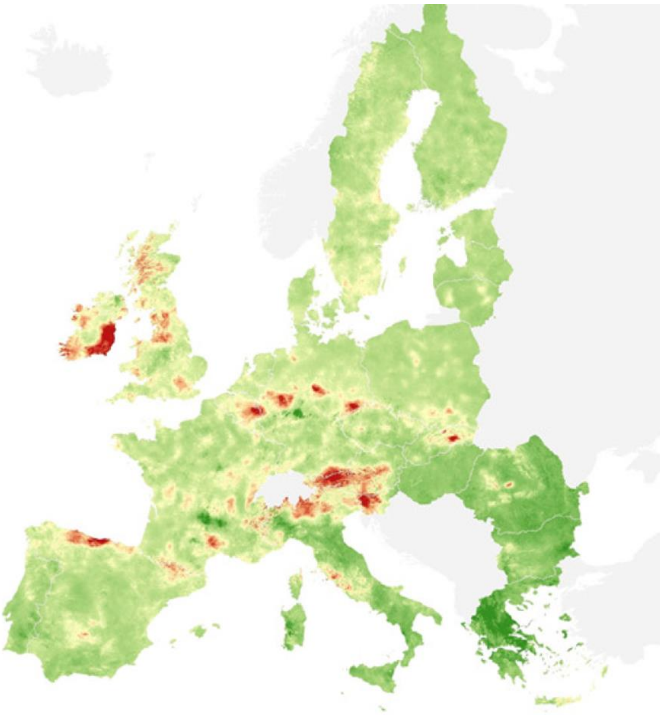

Figure 2: Presence of Contamination by Elements such as As, Cd, Hg, and Pb in calcareous soils (Toth et al., 2016)

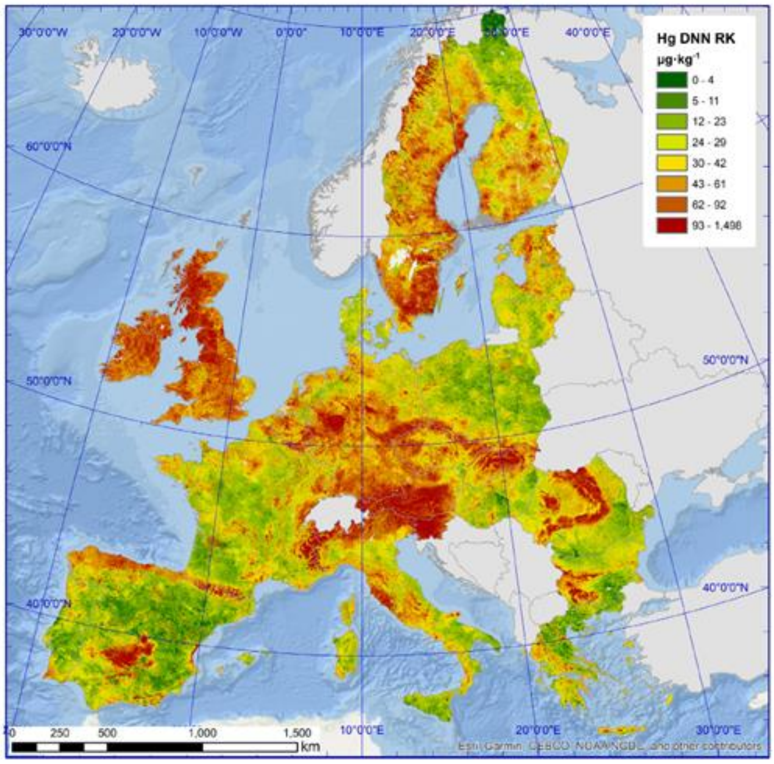

Figure 3: Mercury contamination in Europe (Ballabio et al., 2021)

1.2.La Soterraña

La Soterraña is an abandoned mining complex situated in Lena, Asturias, Spain (Figure 4). The village Muñón Cimero is situated in close proximity, with other settlements located downhill. This proximity poses a problem as toxic pollutants have dispersed out of the site throught the years with close-by areas presenting high concentrations of As and Hg (Boente et al., 2022).

The book *La minería del mercurio en Asturias Rasgos históricos* dives into the story of the mining settlements of Lena, among others (Luque and Gutiérrez, 2006). The first recorded mining activity in the area next to Muñón Cimero started in the year 1844. The extraction of minerals was intermittent until its final closure in the decade of 1970. It is recognised in said book that the on-site metallurgical treatments were considered high risk regarding the workers' health and environment even while the site was still active.

Two identified sources of pollution in La Soterraña are the chimneys that released pollutants into the air while they were active and the dumps nowadays present (Boente et al., 2022). Even though the chimneys are not active today, the mercury (Hg) vapors emitted propagated toxic particles all over the site and the abundant precipitation of the region still favor the mobilization of metals and metalloids (as Arsenic) from the waste dump and surroundings (Loredo et al., 2006).

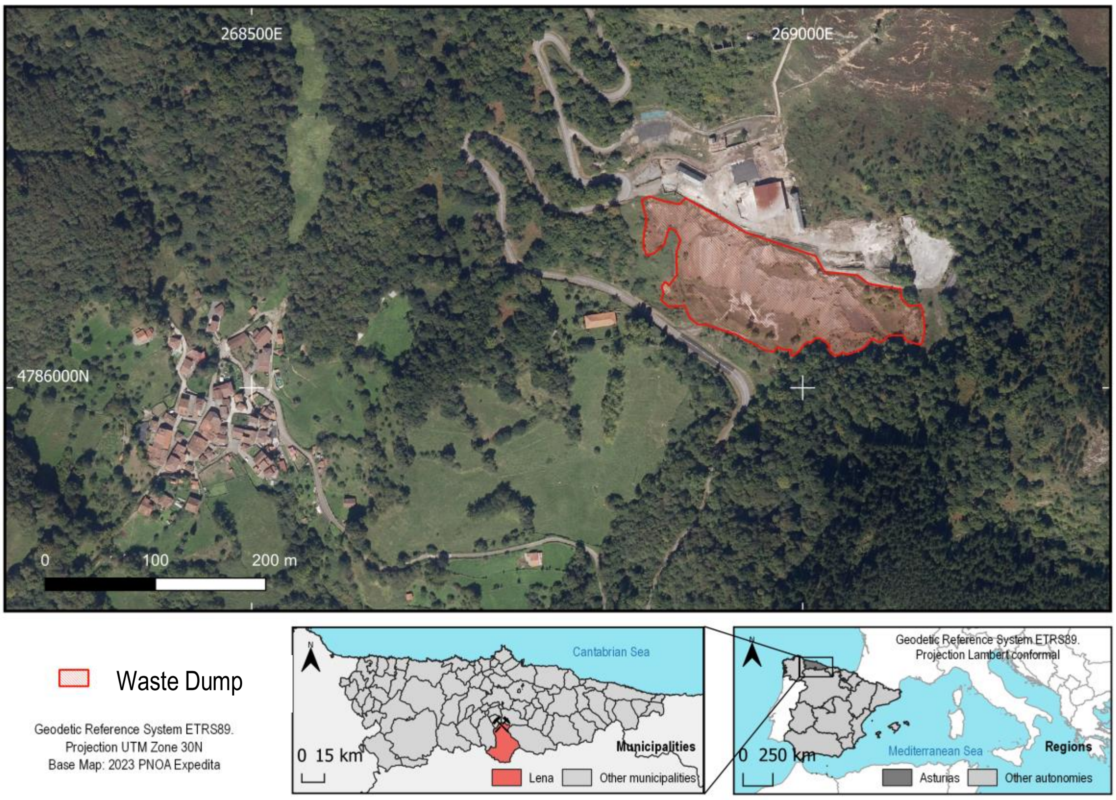

Figure 4: Location of the waste dump. La Soterraña.

The effects of mining in La Soterraña are intense both in waters and the local atmosphere, whose Hg content was established as 10 times higher than the background level in the area, exceeding the target carcinogenic risk for arsenic (As) and mercury (Hg) (Loredo et al., 2006). The whole region is located in a mercury (Hg) hotspot as seen in Figure 3. High concentrations of antimony (Sb) and lead (Pb) were also detected (Matanzas et al., 2017).

According to Boente et al. (2022), the maximum concentrations of arsenic (As) and mercury (Hg) detected were two or up to almost three orders of magnitude above the RBSSLs (Risk-based Soil Screening Levels). Other elements that surpassed the legal limits at least once were Ba, Pb, Sb and V. However, Hg and As were the only elements whose mean concentration notably exceeded the limits in, at least, more than one order of magnitude. These values indicate the necessity for restoration to halt soil degradation and foster positive impacts on the ecosystem services previously disrupted (Boldy et al., 2021).

1.3. Toxic elements and human health

Many routes of exposure to toxic elements are possible within polluted mining sites (Jiménez O. et al., 2020). One example of a route of exposure in La Soterraña could be the regular consumption of plants by the locals, as tuber crops have shown evidence of high Arsenic content when grown in proximity to the site, being able to cause health problems (Loredo et al., 1999). Candeias et al. (2019) offers data on how toxic elements affect human health. Important facts regarding some of the metal(loids) found in La Soterraña is presented here:

Arsenic (As) is spread onto the environment by volcanic activity, microorganisms or through human activities. Its inorganic forms are very toxic and mobile. Accumulation in plants and freshwater organisms is common. Arsenic can make its way into a human's organism through contaminated water, food, inhalation or through dermal contact. Arsenic and its inorganic compounds are regarded as highly carcinogenic. Poisoning occurs fast and carries serious health effects that range from irritation to death.

Mercury (Hg) spreads through wind and water after normal breakdown of the minerals and soils. Fossil fuels, mining and smelting are some human activities that spread mercury. In the context of mining operations, runoff can be easily contaminated from leftover material containing mercury, spreading it into the environment. Methyl mercury can be synthesized by microorganisms, contributing to the spread by creating a compound that can be absorbed by other organisms. The effects of mercury poisoning depend on the route of exposure and the chemical form, being methyl mercury the most common exposure route for humans through ingestion of contaminated animals or plants. Exposure to mercury has toxicological effects that include damage to organs, the nervous system and DNA.

2. Objective

The main objective of this project is to conduct a soil edaphic characterization of a representative sample from the primary dump in the old mine La Soterraña, which is currently unrestored. For this purpose, a physiochemical characterization of a representative sample of this dump will be carried out to know the possible affections of the soil (technosol). The data obtained will shed light into the total and available concentrations of the major metal(loid)s (As and Hg) of the dump and the most important deficits regarding restoration. Some solutions adapted to the sample's needs are to be suggested in face of the results.

A look at the past and the present state of the site is deemed crucial to shape the future solution.

3.Methodology

The sample collection and the laboratory procedures used to obtain the different soil parameters are described in the following section.

3.1.Description of study area and identification of pollution sources

The facilities at La Soterraña in Lena (Asturias, NW Spain, Fig. 1) were used for the underground exploitation of Hg and the pyrometallurgical processing of ores from the mines on the region (Loredo et al., 2006). The exploited minerals were cinnabar (HgS), orpiment (As2S3), realgar/pararealgar (AsS), and arsenopyrite (FeAsS), which originated from a low-temperature hydrothermal process that occurred in fractured limestones, shales, and sandstones (Loredo et al., 1988). These dumps have a high content of sulfide/oxide minerals susceptible to reacting with water and/or air. The analyzed dump is defined as a spolic technosol located at 624 m above sea level. This dump has a steep slope and is located in a hilly terrain. Most of the dump is devoid of vegetation except for a few small inconsistent islands of herbaceous plants (Table 1).

Table 1: Sample information

Dump sample	
Sample type:	Spolic Technosol
Sampling depth:	0 - 20 cm
Location:	Soterraña (Asturias). 43°11'32"N 5°50'37"W
Altitude:	624 m
Surrounding terrain:	Hilly terrain
Steepness:	Strong slope
Vegetation:	Practically non-existent

3.2.Experimental design

The S sample is collected manually, and it contains materials from the first 20 cm of depth extracted from various points of the dump’s surface. The sample gets sieved with a 2 mm sieve to separate the coarse material from the rest of the soil. **Three repetitions** are used to analyze each category and the mean value is then taken to tackle other calculations and report the results.

3.3. pH analysis

S pH is determined using a Mettler Toledo Seven-Compact multimeter. The preparation consists in creating a 25 ml 1:2.5 soil/water suspension. The multimeter is calibrated with two buffer solutions with pH values of 7.00 and 9.21. The electrode is submerged in the suspension and the data is taken (Guitián and Carballas, 1976).

3.4. Salinity

Salinity is determined by electrical conductivity. The same suspension and equipment done for the pH analysis is used immediately afterwards for this procedure. An additional 25 ml of deionized water are added into the suspension to create a 1:5 soil/water ratio. The multimeter was calibrated using a 0,001 M potassium chloride solution. The multimeter's electrode is then submerged in the supernatant and the data is collected (Porta et al., 1986).

3.5. Effective cation exchange capacity and limiting factors for plant production

Exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} + Al^{3+}) and the effective cation exchange capacity (ECEC) were determined using the method proposed by Pansu and Gautheyrou (2006). The sample preparation involved adding soil into 25 ml of 1N ammonium chloride (NH_4Cl), shaking and then filtering. Three additional 25 ml aliquots of 1N ammonium chloride were added sequentially. For the analysis, 2 ml of the soil extract was mixed with 2 ml of lanthanum chloride (LaCl) and 16 ml of distilled water. The concentrations of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and Al^{3+} were measured using atomic absorption spectrophotometry using a spectrophotometer (Perkin Elmer AA200) (Figure 5). Specific multipliers were applied to the measured concentrations to calculate their values in $cmol_{(+)}\ kg^{-1}$. The ECEC was then determined by summing the $cmol_{(+)}\ kg^{-1}$ of all exchangeable cations plus exchangeable Al^{3+}.

Figure 5: Perkin Elmer AA200 Spectrometer and Perkin Elmer HGA900 graphite furnace

A series of critical values were assigned to each of the chemical parameters, based on the model of the soil fertility capability classification (SFCC) proposed by Buol et al. (1975) and adapted by Calvo et al. (1987) and Macias and Calvo (1983). These were used to evaluate the limiting factors for plant production:

- The K factor signifies low potassium (K) content and considers a soil deficient in K if the content is less than 0.2 $\text{cmol}_{(+)}$ kg^{-1}.
- Mg factor addresses magnesium (Mg) deficiency, which can arise from either a low Mg content (less than 0.4 $\text{cmol}_{(+)}$ kg^{-1}) or an imbalance in the Ca/Mg (greater than 50) and K/Mg (greater than 10) ratios.
- The Ca factor examines calcium (Ca) deficiency, defined by a Ca content smaller than 1.5 $\text{cmol}_{(+)}$ kg^{-1} or a Ca/Mg ratio less than 0.5.
- The N factor attends to the presence of high sodium (Na) content in the exchange complex. Soil exceeding 15% Na are considered problematic.
- The C factor evaluates soil acidity, considering a pH of less than 3.5 as problematic.
- The E factor assesses the effective cation exchange capacity (ECEC) of the soil. A value below 4 $\text{cmol}_{(+)}$ kg^{-1} suggests inadequate ECEC.

3.6.Texture

The methodology of the texture is based on Stokes' law. 25 g of sample are treated with 6 % hydrogen peroxide (H_2O_2) to eliminate any organic matter. 50 ml of 1N hydrochloric acid (HCl) are then used to dissolve the oxides. The clay dispersion is performed with a 20 ml solution of sodium hexametaphosphate ($Na_6[(PO_3)_6]$). The fractions larger than 50 µm (fine sand and coarse sand) are separated by wet sieving. The smaller fractions (fine silt, coarse silt, and clay) are collected using a Robinson pipette, following Stokes' law regarding the different sedimentation velocities of particles in a liquid medium based on their size (Guitián and Carballas, 1976). USDA (2017) criteria was then followed to determine the percentages of silt, clay and sand.

3.7.TOC and carbon stocks

Total carbon (TC) and inorganic carbon (IC) were determined using a TOC-V CSH (Shimadzu) equipped with a solid sample module. Total organic carbon (TOC) was calculated as the difference between TC and IC. They are all expressed in percentages of the total mass of the soil.

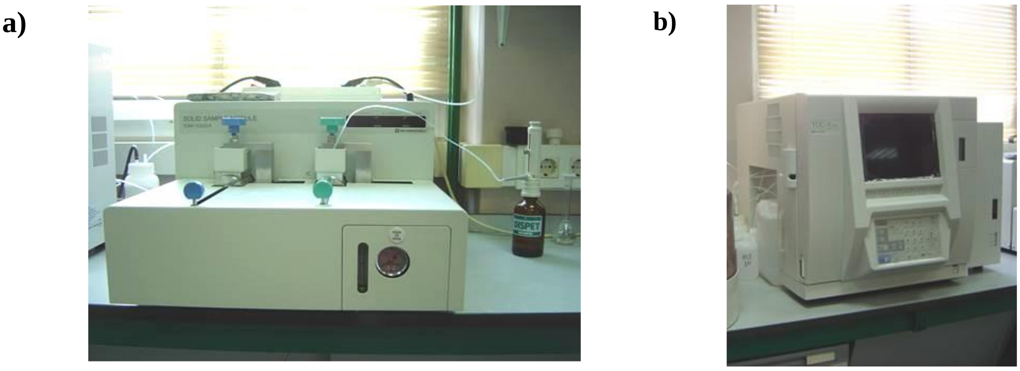

Figure 6: (a) TOC module for solid samples (TNM-1, Shimadzu), (b) TOC module for liquid samples (TNM-1, Shimadzu).

To estimate soil organic carbon stocks, the protocol proposed by Calvo de Anta et al. (2015) has been followed. The equation and parameters used in the stock calculation are detailed below. (Anta et al., 2015). The result is expressed in tons of carbon (C) per hectare.

$$OCSL(tC\ ha^{-1}) = OC(\%) \times BD(g\ cm^{-3}) \times \left(1 - \frac{VG\ (\%)}{100}\right) \times LT(cm)$$

Equation 1: Soil Organic Carbon Stocks

Where OC is the organic carbon content for the given depth in percentage of total soil mass, BD is dry bulk density in grams per cubic centimeter, VG is the amount of coarse material sieved in percentage of the total mass of the sample and LT is the thickness of the soil layer expressed in centimeters.

The organic matter is estimated through the Bremmer factor (Nelson and Sommers, 1996). It is calculated multiplying the OM content by the factor 1.724. The reliability of this method is established as low, but the calculation of OM is regarded as relevant to characterize the soil.

3.8.Hydraulic properties

The following hydraulic properties are obtained through the methodology contained in Saxton et al. (1986). They were calculated using the tool provided by CDM Smith*, unlesss stated otherwise.

- Permanent Wilting Point (PWP) is expressed in units of water per units of soil and represents the water content at a matric potential of -1,500 kPa (-15 bars). This point roughly corresponds to the lower limit of Available Water.

- Field Capacity (FC) is expressed in units of water per units of soil and represents the water content at the upper limit of Available Water or the drained upper limit. This point corresponds to a matric potential of approximately -30 kPa (-0.3 bars) in most soils and -10 kPa (-0.1 bars) in sandy soils.

- Hydraulic conductivity refers to the ease with which water can move through pore spaces in the soil. It is calculated through the model contained in Saxton et al. (1986) and represented in centimeter per hour.

- Bulk Density (BD) is used to determine soil porosity and it was calculated through the formula (1 - Saturation) * 2.65 using the saturation value provided by the CDM Smith tool. It is expressed in grams of soil mass per cubic centimeter of soil volume.

- Available soil water-holding capacity (ASWC) is the water held between -8 and -60 kpa (Hazelton & Murphy, 2016), obtained through the formula AWC = (FC – PWP) * BD * sampling depth. The result is expressed in cubic meters per hectare. The available water (AW) which is the difference between the field capacity and permanent wilting point is also calculated.

3.9.Nitrogen content

Total nitrogen concentration is determined by the Kjeldahl method (Sáez-Plaza et al., 2013), modified by Bremmer (1982). This particular methodology reduces the organic nitrogen into ammonia nitrogen to then be analysed through colorimetry. A digester (DK 20 Heatinh) and a spectrophotometer (Thermo Spectronic Genesys20) were used.

The sample is introduced into a dry Kjeldahl flask, followed by the addition of the catalytic mixture of K_2SO_4 and Selenium powder. Concentrated sulfuric acid is added and the mixture is stirred to ensure thorough wetting by the acid, resulting in a dark-colored solution. The sample is later subjected to high temperatures in the digestion apparatus until the liquid attains a clear appearance, signaling the completion of mineralization. The mineralized sample is later filtrated to eliminate potential impurities

---

*http://www.dynsystem.com/netstorm/soilwater.html and diluted with distilled water. The sample solution, and the following solutions are mixed in a test tube for the colorimetry analysis:

- Buffer solution: comprised of sodium potassium tartrate tetrahydrate ($C_4H_4KNaO_6 \cdot 4H2O$), disodium phosphate (Na_2HPO_4) and sodium hydroxide (NaOH).
- Reagent salicylate solution: comprised of Sodium salicylate ($C_7H_5NaO_3$) and Sodium nitroprusside ($Na_2Fe(CN)_5NO \cdot 2H2O$).
- 5% sodium hypochlorite reagent.

Following calibration of the equipment, the absorbance of the sample contained in the test tube is measured at the spectrophotometer at a 660 nm wavelength. The following formula is employed to calculate the mg/kg concentration of nitrogen in the sample:

$$\mathrm{N}(mg\ kg^{-1}) = \frac{A_m}{\bar{b}(\mu g\ ml^{-1})} \times \frac{T_v(ml)}{S_v(ml)} \times \frac{F_v(ml)}{S_m(g)}$$

Equation 2: Nitrogen concentration

A_m represents the absorbance value of the sample given by the colorimeter; $\bar{b}$ is the slope of the calibration curve; T_v is the total volume in the test tube for measuring absorbance; S_v, the initial volume of the sample in the test tube; F_v, the volume of the volumetric flask where the S_v sample was taken for the test tube; and S_m, the amount of sieved soil sample introduced into the Kjeldahl flask for digestion.

3.10. Phosphorus content

Mehlich 3 method was used to colorimetrically determine available phosphorus (Mehlich, 1984) using a spectrophotometer (Thermo Spectronic Genesys20).

An extract solution is made by mixing soil and Mehlich solution into a plastic container and stirring, later filtering the supernatant into another container. A portion of the extract solution is then introduced into a test tube together with a working solution* and distilled water. The calibration of the device is performed. A fraction of the solution contained in the test tube is introduced and measured at a wavelength of 880 nm. The resulting phosphorus content is expressed in mg/kg using the following formula:

$$P(mg\ kg^{-1}) = \frac{\frac{A_m}{\bar{b}(\mu g\ ml^{-1})} \times \frac{S_v(ml)}{E_v(ml)} \times M_v(ml)}{S_m(g)}$$

Equation 3: Available phosphorus

A_m is the absorbance detected at λ 880nm, $\bar{b}$ is the mean slope of the calibration curve, S_v is the volume of the sample where the measured fraction is extracted from, E_v is the volume of the extract solution (Soil and Mehlich supernatant) added to the sample, M_v

is the volume of Mehlich reagent solution used to prepare the extract solution and S_m is the mass of the soil added into the extract solution.

*The working solution is comprised of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot4H_2O$), potassium antimony tartrate ($C_8H_4K_2O_{12}Sb_2\cdot3H_2O$), sulfuric acid ($H_2SO_4$), and ascorbic acid (vitamin C) ($C_6H_8O_6$).

3.11. Soil fertility index

The Soil Fertility Index (SFI) sheds light into the general quality of a soil and allows for comparison. It was calculated following the method described in Lu et al. (2002). The formula has the following structure:

$$SFI = pH + OM + P + K + Ca + Mg - Al$$

Equation 4: Soil Fertility Index

OM is organic matter (% dry soil basis), P is the available P in dry soil (mg/kg dry soil) and K^+, $Ca2^+$ and Mg^{2+} are the exchangeable cation concentration in soil ($cmol_{(+)}kg^{-1}$) minus the exchangeable acidity, Al^{3+} ($cmol_{(+)}kg^{-1}$).

3.12. Arsenic (As) and mercury (Hg) concent

Pseudototal metal(loid) contents were extracted with aqua regia by acid digestion in a microwave oven (Milestone ETHOS 1, Italy), and the concentrations were measured by ICP-MS (Milestone ETHOS 1, Italy). Available concentrations of metal(loid)s were determined by means of TCLP extraction (Toxicity Characteristic Leaching Procedure) following the USEPA Method 1311 (1992), and the concentrations were determined by ICP-OES (Perkin-Elmer Optima 4300 DV).

The Generic Reference Levels (GRLs) for the region were extracted from the Boletín Oficial del Principado de Asturias, núm 91, April 21, 2014. They are expressed in miligrams of substance per kilogram of soil. Other sources that provide relevant thresholds are Prăvălie et al. (2024) and Real Decreto 3/2023.

4. Results

Every valorization of the data presented in this chapter is done using the book *Interpreting Soil Test Results: What Do All the Numbers Mean?* by Hazelton and Murphy (2016), unless stated otherwise with another citation.

4.1. Soil physical properties

The sample contains a percentage of 8.04% clay, 6.93% silt and 85.03% sand; represented in the figure 2. According to the percentages and USDA (2017), the soil is classified as **loamy sand**.

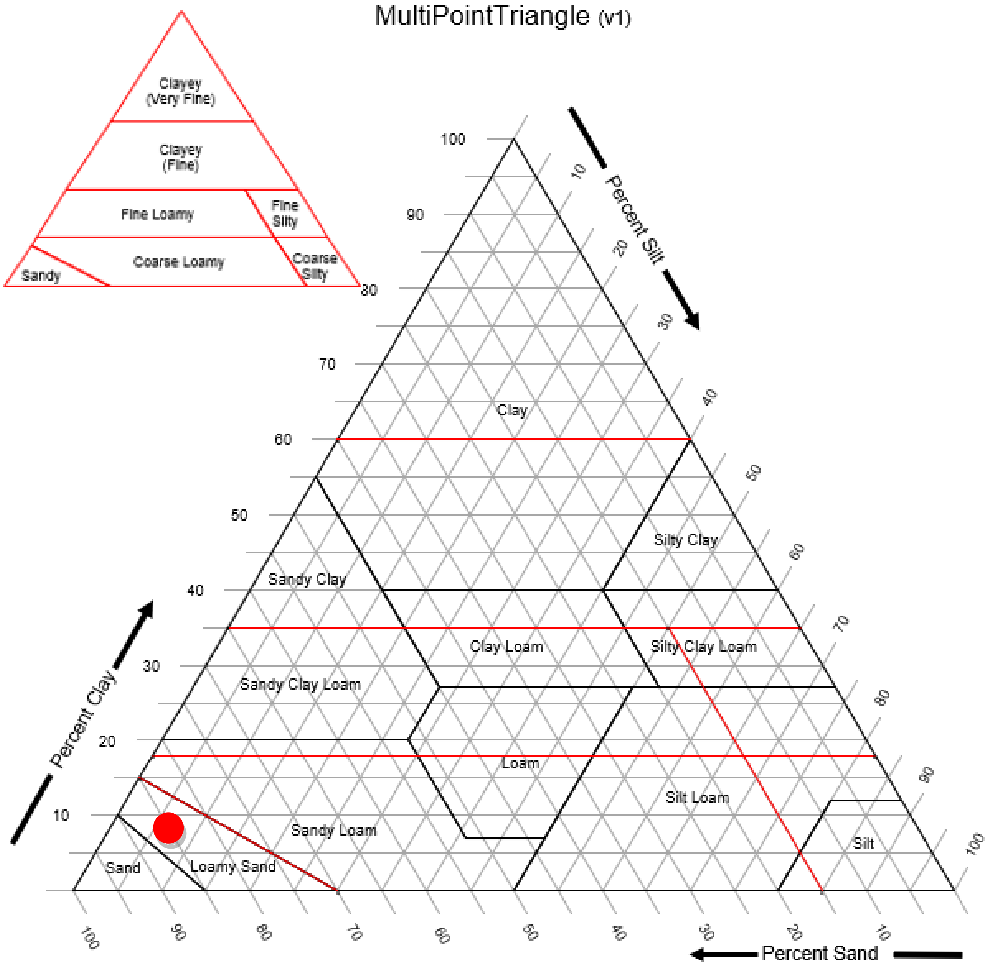

Figure 7: Texture Triangle (USDA Soil Texture Calculator).

The bulk density (Table 2) is low, situated under the threshold for restricting plant growth considered for loamy sands (1,8 g/cm^3). Permanent wilting point and field capacity (Table 2) can be compared to the common values in loamy sands for each variable, being 4 % and 20 % respectively, showing a higher than normal permanent wilting point and a low field capacity, constraining the available water into a low value. For a depth of 20 cm, the soil available water-holding capacity is then considered severely limited. Consequently, the hydraulic conductivity is moderate (Table 2).

Table 2: Resulting soil physical properties.

	Sample values	**Common loamy sands values**
Bulk density	1.67 g/cm^3	1.80 g/cm^3
Permanent wilting point	7.60 %	4.00 %
Field capacity	15.50 %	20.00 %
Hydraulic conductivity	4.20 cm/h	6.00 – 12.00 cm/h
Available water	7.90 %	16.00 %
Soil available water-holding capacity	257.54 m^3/ha	-

4.2. Soil chemical properties

The sample’s chemical properties, including some useful indexes for determining the state of the soil, are laid out in the following tables.

The pH of 8.85 (Table 3) exposes the strongly alkaline nature of the sample, the electrical conductivity analysis pictures it as non-saline. The value for nitrogen (N) is considered medium while available phosphorus (P) is extremely high (more than 10 times the upper threshold to obtain a very high rating). The C and N ratio (C/N) is considered low (Table 3) and in terms of carbon, although the total carbon (TC) value is 4.02%, it can be observed that more than 60% of this value is due to inorganic carbon (IC). The value of organic carbon (OC) in S is 1.46% (Table 3). The OCSL is low regarding inside data from the Carbon2mine project.

Table 3: Chemical properties of the sample and C/N index.

pH	8.85
EC	1.32 dS/m
TC	4.02 %
IC	2.56 %
OC	1.46 %
OCSL	8.53 tC/ha
OM	2.52 %
N	0.19 %
C/N	7.56
P	297.85 mg/kg

The levels of Ca^{2+}, Na^{+} and Mg^{2+} are deemed low attending the general levels of exchangeable cations (Table 4), while potassium K^{+} is classified as very low. In consequence, the ECEC is considered very low all around. The calcium-magnesium ratio (Ca/Mg, Table 4) further indicates a deficiency in magnesium in the sample. The soil fertility index (SFI) is perverted by the phosphorus (P) value in table 3

Table 4: ECEC and relevant indexes.

Ca^{2+}	79.70	% ECEC
	4.28	cmol$_{(+)}$/kg
Mg^{2+}	10.36	% ECEC
	0.56	cmol$_{(+)}$/kg
K^{+}	1.90	% ECEC
	0.10	cmol$_{(+)}$/kg
Na^{+}	5.00	% ECEC
	0.27	cmol$_{(+)}$/kg
Al^{3+}	3.03	% ECEC
	0.16	cmol$_{(+)}$/kg
ECEC	5.37	cmol$_{(+)}$/kg
Ca/Mg	7.68	
K/Mg	0.19	
SFI	313.99	

4.3.Metal and metalloids concentrations

The total arsenic (As) and mercury (Hg) concentrations are extremely high (Table 5). As concentrations exceed the Generic Reference Levels (GRLs) for Asturias for all the uses analyzed (BOPA, 2014), even the available concentrations would exceed these limits for residential limits and other land uses (Table 5). Hg concentrations exceed GRLs for residential soils and other uses (Table 5).

Table 5: Arsenic (As) and mercury (Hg) total and available concentrations together with GRLs for Asturias (BOPA, 2014).

	As (mg/kg)	**Hg** (mg/kg)
Total	910 ± 9.00	15.00 ± 1.40
Available	72.09 ± 0.32	22.42 ± 12.32 (µg/kg)
GRL industrial	200	100
GRL residential	40	10
GRL other	40	1

5. Discussion

5.1. Soil physical properties

Hazelton and Murphy (2016) proposed critical bulk density values for plant growth, beyond which root penetration is likely to be severely restricted. The bulk density of the dump is very close to the proposed value for loamy sand soils (Table 2). This may be one of the factors contributing to the near absence of vegetation in the dump

The texture of the dump was loamy sand (Figure 7), which is logical given that the material primarily originates from mineral beneficiation process residues. In the absence of organic matter and structural integrity, finer particles such as clays are washed away, leaving behind the greater than 2 mm fractions, along with silt and sand (Jensen et al., 2017).

Various factors related to soil moisture and water are clearly affected and do not fall within the normal values of a loamy sand, such as the permanent wilting point, field capacity, available water, and hydraulic conductivity (Table 2). The available water-holding capacity's threshold for considering a soil as severely limited in its water content is 100 mm/m, with our sample's value being 25.75 mm/m when translated into the correct units, meaning that there is very little plant-available water in reserve (Hazelton & Murphy, 2016). Paired with a moderate conductivity resulting from other physical factors, these alterations impact soil microbiology, vegetation development, and the dispersion of contaminants.

5.2. Soil chemical properties

The high pH value of the dump (Table 3) results from the significant limestone content in the area where mining operations were conducted, composed mainly of calcium carbonate and magnesium carbonate (Loredo et al., 1988). Although the effective cation exchange capacity is low, the Mg content was greater than 10 %, and the Ca content was 79,70 % (Table 3). This clearly demonstrates the influence of the parent material on the pH of the dump. Based on the pH values proposed by Calvo et al. (1987) and Macías and Calvo (1983) for plant production, the pH of the dump (Table 3) is significantly above the threshold for the occurrence of acidity issues, indicating their absence. However, according to authors such as Hazelton and Murphy (2016), the optimal pH range for many plants is between 5.0 and 7.8. Therefore, the pH in the landfill would create conditions not suitable for the growth of various plant species.

The TC value is clearly influenced by the IC content derived from the presence of carbonates (Table 3). The OC value (Table 3) is low because the dump is entirely inorganic, and the little OC it contains is due to runoff from upper areas and the very sparse vegetation it supports (Boente et al., 2022). The estimated OM appears to be higher than it should be judging by the OC value (Table 3). The method employed for the estimation of OM is acknowledged to carry a low accuracy in the results it yields (Nelson & Sommers, 1996). It should be noted that the dump is composed of waste material from the host rock (limestone, shales, sandstones) and residues from the mineral beneficiation process (Loredo et al., 1988). Furthermore, no restoration work has been carried out on the dump, so no topsoil layer was deposited on it when mining activities ceased.

The low OC value (Table 3) reflects the similarly low organic matter (OM) content in the dump, tampering the formation of organo-mineral complexes, aggregates and soil development (Six et al., 2002). Additionally, organic matter is directly related to cation exchange capacity (CEC) (Elliott et al., 1986), and the low organic matter content may be one of the reasons for the low ECEC in the dump (Table 4). However, soil organic carbon content in technosols is generally very high in comparison to less anthropized soils (Allory et al., 2021). The Carbon2mine project associated to the University of Oviedo has provided data of similar dumps with a mean OSCL value of 20 tC/ha, making our dump fall short with 8.53 tC/ha (Table 3), evidencing again the low organic matter content.

Due to the low organic carbon content and medium nitrogen content, the C/N ratio (Table 3) being less than 10 further supports the idea that any organic matter present in the landfill can decompose rapidly (Hazelton and Murphy, 2016). Consequently, the resilience of these elements is low, making them unavailable to microorganisms and vegetation. This rapid decomposition results in limited availability of organic matter for sustaining microbial activity and plant growth, thereby reducing the overall fertility and ecological sustainability of the landfill environment, falling in line with the low estimated organic carbon stocks.

According to Hazelton and Murphy (2016) the ECEC in our sample (Table 4) is considered low, indicating a low capacity to retain nutrients which creates a problem in terms of plant production. Furthermore, according to the factors for plant production proposed by Calvo et al. (1987) and Macías and Calvo (1983), the dump would be affected by factor K, factor Mg, factor Ca, and factor N although these deficiencies in exchangeable cations are within the values proposed by other authors such as Hazelton and Murphy (2016). This discordance between authors may be the result of the establishment of upper thresholds without lower thresholds or vice versa in the factors evaluating chemical properties, creating ranges to evaluate plant production could seem more appropriate. According to these authors, the dump would also present an imbalanced Ca/Mg ratio.

The high content of available phosphorus (P) (Table 4) is clearly attributable to the P content of the parent material, as no phosphorus additions were made to the dump. The elevated P levels are possibly also a result of the high pH of the dump, given that phosphorus is highly influenced by it, as at high pH levels, the mobility of phosphorus can be significantly increased (Szogi et al., 2024). The Soil Fertility Index (SFI) value was clearly altered by the phosphorus content in the dump. The phosphorus value was 297.87 mg/kg, representing 94% of the SFI value.

5.3. Arsenic (As) and mercury (Hg) content

The concentrations of As and Hg inside of the waste dump are worrying due to the possibility of displacing harmful particles into other soils, underground waters or water bodies in general (Boente et al., 2022).

Total As concentrations in the dump (Table 5) overshoot the GRLs established in the region (BOPA, 2014) for all land uses (Table 5) by 455%, creating a need for restoration if any changes in land use are sought-after in La Soterraña. The boundaries selected in Prăvălie et al. (2024) for considering a soil in a critical state of contamination were also exceeded by a 18.200% for the total concentration of As.

Although legislatively the focus is on the total concentrations of elements, from an ecological perspective, it is essential to consider the available values of the elements, as these directly impact fauna and flora. The dump presented a considerable available As concentration (Table 5). This mobility of As can be attributed to its nature as an anion, which becomes mobile at basic pH levels (Bissen and Frimmel, 2003). Additionally, the presence of other anions with a higher affinity for soil binding sites, such as phosphorus, displaces As into the soil solution (Baragaño et al. 2020a; Bolan et al. 2013; Fleming et al. 2013; Hartley et al. 2009).

Regarding Hg and according to Spanish legislation, specifically Real Decreto 3/2023, the maximum allowable concentration of mercury in drinking water is 1.00 µg/L. This regulation aligns with the European Union's standards as outlined in the Directive (EU) 2020/2184, which aims to ensure that water intended for human consumption is free from contaminants that could pose a risk to human health. Extrapolating the limit values in water to those obtained through the TCLP extraction, the Hg values pose a threat to adyacent water bodies as it posseses an available mercury concentration of approximately 37.44 µg/L when translating the units from the total Hg value in Table 5. The soil can be classified as critically polluted as it exceeded the threshold established in Prăvălie et al. (2024) by a 3.000 % in its total mercury concentration.

The mobility of Hg in the dump may be due to its low organic carbon content, as Hg typically binds to organic matter, reducing its mobility (Skyllberg et al., 2006; Ravichandran, 2004). Another factor influencing Hg mobility is soil texture; organic matter forms complexes with clay particles that can adsorb Hg. As previously mentioned, the dump had very low clay values (Wang et al., 2020). The lack of vegetation is also related with the high concentration of Hg, as soils in land covers with various structures of vegetation tend to present lower Hg values than sparsely vegetated spaces (Ballabio et al., 2021).

5.4.Restoration options

When considering options for restoring this soil, it is essential to highlight the complexity it presents. On one hand, there is a clear lack of organic matter, and on the other, the soil is contaminated by two elements that exhibit distinct chemical behaviors, as arsenic (As) behaves as an anion while mercury (Hg) behaves as a cation. This dual contamination poses unique challenges for remediation efforts, as strategies effective for one contaminant may not be suitable for the other.

For a soil to be considered fully restored, it must be capable of supporting stable and self-sustaining vegetation (Frérot et al., 2006). Here is an example of the phases needed to reach that objective.:

- The dump should be re-sloped to reduce the gradient and increase stability, facilitating the application of treatments later.
- An iron-based amendment is applied to the soil to reduce the arsenic content and reduce its mobility (Baragaño et al., 2020a, 2020b). The kinds of suitable amendments can range from by-products of other mines containing iron and fine granularity to iron micro or nanoparticles (Baragaño et al., 2022; Forjan et al., 2024). Additionally, these iron-based amendments will also decrease the mobility of phosphorus.
- An organic, nutrient-rich amendment will follow. These amendments can be applied individually or in combination with each other. Some types of suitable amendments include vermicompost, vermichar, biochar, and, in some cases, hydrochar. Each one of these amendments offer unique advantages and can be tailored to specific soil rehabilitation needs, thereby increasing the overall effectiveness of the treatment strategy. They will serve several functions such as fixing the high mercury concentrations by reducing its mobility (Bandara et al., 2020; Wang et al., 2020) and improving the cation exchange capacity (CEC) while providing nutrients (Forján et al., 2017; Forján et al., 2019).
- The introduction through plantation of a mixture of herbaceous species will serve as the initial phase for vegetation to develop in the surface of the dump. The ideal scenario would be for the chosen species to already be growing in the area (Matanzas et al., 2021). These plants, with their roots, will help stabilize the treatments and structure the new soil (Ford et al., 2016). The selected species should possess phytostabilization characteristics.
- The last phase involves planting tree species, such as *Betula pubescens* Ehrh. which posseses phytoremediation properties, particularly phytostabilization (Mleczek et al., 217; Rosselli et al., 2003; Sanchez et al., 2024).

6. Conclusiones / Conclusions

🇪🇸

En este apartado se incluye una síntesis de las conclusiones en castellano en cumplimiento con el BOLETÍN OFICIAL DEL PRINCIPADO DE ASTURIAS núm. 62 de 30-03-2020 que aprueba el reglamento sobre la asignatura Trabajo Fin de Grado en la Universidad de Oviedo.

La escombrera de La Soterraña está fuertemente contaminada por arsénico y mercurio, lo que representa una amenaza para la salud humana y los ecosistemas. Además, el vertedero presenta una clara deficiencia de potasio, mientras que otros nutrientes como el magnesio, calcio y sodio están dentro de rangos aceptables para el crecimiento de la vegetación, pero en niveles relativamente bajos. El pH fuertemente alcalino dificulta la colonización del suelo por parte de especies vegetales. La baja cantidad de materia y carbono orgánicos afecta directamente a la capacidad de intercambio catiónico efectiva, y por ende a la disponibilidad de nutrientes y el desarrollo de vegetación y microorganismos. Finalmente, el valor del fósforo es extremadamente alto, lo que posiblemente aumenta la movilidad del arsénico dentro de la escombrera.

🇬🇧

The characterization of the dump in La Soterraña highlights significant environmental challenges. These findings collectively emphasize the urgent need for restoration efforts to mitigate the ecological and health risks associated with the site:

- The dump in La Soterraña is heavily polluted by As and Hg, posing a threat to the health of humans and ecosystems.

- The dump exhibits a clear potassium deficiency, while other nutrients such as magnesium, calcium, and sodium are within acceptable ranges for plant production, but remain generally low.

- The strongly alkaline pH level makes it hard for plant species to colonize the soil.

- The low organic matter and organic carbon directly affect the effective cation exchange capacity, nutrient availability, and the development of vegetation and microorganisms.

- The phosphorus value is found to be extremely high, possibly providing a higher mobility for arsenic (As).

7. Bibliography

Anta, R., Calvo, E., Sabarís, F., Costa, J., Mosquera, N., F, M., Camps Arbestain, M., & García, N. (2015). Soil organic carbon in northern Spain (Galicia, Asturias, Cantabria and País Vasco). *Spanish Journal of Soil Science, 5*, 41-53. https://doi.org/10.3232/SJSS.2015.V5.N1.04

Allory, V., Séré, G., & Ouvrard, S. (2021). A meta-analysis of carbon content and stocks in Technosols and identification of the main governing factors. *European Journal of Soil Science, 73*. https://doi.org/10.1111/ejss.13141

Bandara, T., Franks, A., Xu, J., Bolan, N., Wang, H., & Tang, C. (2019). Chemical and biological immobilization mechanisms of potentially toxic elements in biochar-amended soils. *Critical Reviews in Environmental Science and Technology, 50*(9), 903–978. https://doi.org/10.1080/10643389.2019.1642832

Baragaño, D., Forján, R., Álvarez, N., Gallego, J. R., & González, A. (2022). Zero valent iron nanoparticles and organic fertilizer assisted phytoremediation in a mining soil: Arsenic and mercury accumulation and effects on the antioxidative system of *Medicago sativa* L. *Journal of Hazardous Materials, 433*, 128748.

Baragaño, D., Forján, R., Fernández, B., Ayala, J., Afif, E., & Gallego, J. L. R. (2020). Application of biochar, compost and ZVI nanoparticles for the remediation of As, Cu, Pb and Zn polluted soil. *Environmental Science and Pollution Research, 27*, 33681–33691. https://doi.org/10.1007/s11356-020-09586-3

Baragaño, D., Forján, R., Welte, L., & Gallego, J. L. R. (2020). Nanoremediation of As and metals polluted soils by means of graphene oxide nanoparticles. *Scientific Reports, 10*, 1896. https://doi.org/10.1038/s41598-020-58852-4

Bissen, M., & Frimmel, F. H. (2003). Arsenic—A review. Part I: Occurrence, toxicity, speciation, mobility. *Acta hydrochim. hydrobiol.*, 31, 9-18. https://doi.org/10.1002/aheh.200390025

Boente, C., Baragaño, D., García-González, N., Forján, R., Colina, A., & Gallego, J. R. (2022). A holistic methodology to study geochemical and geomorphological control of the distribution of potentially toxic elements in soil. *CATENA, 208*, 105730. https://doi.org/10.1016/j.catena.2021.105730

Bolan, N., Mahimairaja, S., Kunhikrishnan, A., & Choppala, G. (2013). Phosphorus-arsenic interactions in variable-charge soils in relation to arsenic mobility and bioavailability. *Science of The Total Environment, 463*, 1154–1162. https://doi.org/10.1016/j.scitotenv.2013.04.016

Boldy, R., Santini, T., Annandale, M., Erskine, P. D., & Sonter, L. J. (2021). Understanding the impacts of mining on ecosystem services through a systematic review. *The Extractive Industries and Society, 8*(1), 457-466. https://doi.org/10.1016/j.exis.2020.12.005

Boletín Oficial del Principado de Asturias (BOPA), 91, April 21, 2014. (2014). Generic Reference Levels for Heavy Metals in Soils from Principality of Asturias, Spain.

Buol, S.W., Sanchez, P.A., Cate, R.B., Granger, M.A. (1975). Soil fertility capability classification. In E. Bornemizza & A. Alvarado (Eds.), *Soil Management and the Development Process in Tropical America* (pp. 126-146). NCS University, Raleigh.

Calvo, R., Macías, F., Buurman, P. (1987). Procesos de Alteración y Neoformación mineral en medios serpentínicos de Galicia. *Cuad. Lab. Xeolóxico Laxe*, 11, 161–170.

Candeias, C., Ávila, P., Coelho, P., & Teixeira, J. P. (2019). Mining Activities: Health Impacts. In J. Nriagu (Ed.), *Encyclopedia of Environmental Health* (Second Edition) (pp. 415-435). Elsevier. https://doi.org/10.1016/B978-0-12-409548-9.11056-5

CDM SMITH. (n.d.) Soil Hydraulic Properties Calculator. Retrieved from http://www.dynsystem.com/netstorm/soilwater.html

Directive (EU) 2020/2184. (2020). Retrieved from https://eur-lex.europa.eu/legal-content/ES/ALL/?uri=CELEX%3A32020L2184

Fao, U. (2021). Global assessment of soil pollution. *FAO ; UNEP*. https://openknowledge.fao.org/handle/20.500.14283/cb4827en

Fleming, M., Tai, Y., Zhuang, P., & McBride, M. B. (2013). Extractability and bioavailability of Pb and As in historically contaminated orchard soil: Effects of compost amendments. *Environmental Pollution*, *177*, 90–97. https://doi.org/10.1016/j.envpol.2013.02.013

Ford, H., Garbutt, A., Ladd, C., Malarkey, J., & Skov, M. W. (2016). Soil stabilization linked to plant diversity and environmental context in coastal wetlands. *Journal of Vegetation Science*, *27*(2), 259-268. https://doi.org/10.1111/jvs.12367

Forján, R., Arias-Estévez, M., Gallego, J. L. R., Santos, E., & Arenas-Lago, D. (2024). Biochar-nanoparticle combinations enhance the biogeochemical recovery of a post-mining soil. *Science of The Total Environment*, *930*, 172451.

Forján, R., Asensio, V., Guedes, R. S., Rodríguez-Vila, A., Covelo, E. F., & Marcet, P. (2017). Remediation of soils polluted with inorganic contaminants: Role of organic amendments. In N. A. Anjum, S. S. Gill, & N. Tuteja (Eds.), *Enhancing cleanup of environmental pollutants: Volume 2: Non-biological approaches* (pp. 313-337). Springer International Publishing. https://doi.org/10.1007/978-3-319-55423-5_10

Forján, R., Asensio, A., Rodriguez-Vila, A., & Covelo, E. F. (2016). Contribution of waste and biochar amendment to the sorption of metals in a copper mine tailing. *Catena*, *137*, 120–125.

Forján, R., Rodríguez-Vila, A., & Covelo, E. F. (2019). Increasing the nutrient content in a mine soil through the application of technosol and biochar and grown with *Brassica juncea* L. *Waste and Biomass Valorization*, *10*(1), 103–119.

Forján, R., Rodríguez-Vila, A., Cerqueira, B., & Covelo, E. F. (2017). Comparison of the effects of compost versus compost and biochar on the recovery of a mine soil by improving the nutrient content. *Journal of Geochemical Exploration*, *183*, 46–57.

Frérot, H., Lefébvre, C., Gruber, W., Collin, C., Dos Santos, A., & Escarré, J. (2006). Specific interactions between local metallicolous plants improve the phytostabilization of mine soils. *Plant and Soil*, *282*, 53-653. https://doi.org/10.1007/s11104-006-0007-z

Guitián Ojea, F., & Carballas, T. (1976). Técnicas de análisis de suelos. *Pico Sacro*. Retrieved from https://digital.csic.es/handle/10261/59235

Hartley, W., Dickinson, N. M., Riby, P., & Lepp, N. W. (2009). Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with *Miscanthus*. *Environmental Pollution*, *157*, 2654–2662. https://doi.org/10.1016/j.envpol.2009.05.011

Hazelton, P., & Murphy, B. W. (2016). Interpreting soil test results: What do all the numbers mean? Retrieved from https://doi.org/10.1071/9781486303977

Inventario de instalaciones de residuos mineros clausuradas y peligrosas en España. (2022). *Ministerio para la Transición Ecológica y el Reto Demográfico*. Retrieved from https://www.miteco.gob.es/es/energia/mineria-explosivos/mineria.html

Jensen, J. L., Schjønning, P., Watts, C. W., Christensen, B. T., & Munkholm, L. J. (2017). Soil texture analysis revisited: Removal of organic matter matters more than ever. *PLOS ONE*. https://doi.org/10.1371/journal.pone.0178039

Jiménez O., S., García-Martínez, M. J., Ortega, M., Bolonio, D., Rodríguez Salgado, C., Esbrí, J., Llamas, J., & Higueras, P. (2020). Multi-pathway human exposure risk assessment using Bayesian modeling at the historically largest mercury mining district. *Ecotoxicology and Environmental Safety, 201*, 110833. https://doi.org/10.1016/j.ecoenv.2020.110833

Loredo, J., Ordóñez, A., & Álvarez, R. (2006). Environmental impact of toxic metals and metalloids from the Muñón Cimero mercury-mining area (Asturias, Spain). *Journal of Hazardous Materials, 136*(3), 455-467. https://doi.org/10.1016/j.jhazmat.2006.01.048

Loredo, J., Ordóñez, A., Gallego, J. R., Baldo, C., & García-Iglesias, J. (1999). Geochemical characterisation of mercury mining spoil heaps in the area of Mieres (Asturias, northern Spain). *Journal of Geochemical Exploration, 67*(1), 377-390. https://doi.org/10.1016/S0375-6742(99)00066-7

Lu, D., Moran, E., & Mausel, P. (2002). Linking Amazonian secondary succession forest growth to soil properties. *Land Degradation & Development, 13*, 331-343. https://doi.org/10.1002/ldr.516

Luque Cabal, C., & Gutiérrez Claverol, M. (2006). La minería del mercurio en Asturias: Rasgos históricos. Retrieved from https://dialnet.unirioja.es/servlet/libro?codigo=268653

Macías, F., Calvo, R.: El análisis del medio físico y su aplicación a la ordenación del territorio: una experiencia piloto en el área de Padrón (La Coruña). *Trab. Compostelanos Biol. 10*, 179–208 (1983)

Matanzas, N., Afif, E., Díaz, T. E., & Gallego, J. L. R. (2021). Screening of pioneer metallophyte plant species with phytoremediation potential at a severely contaminated Hg and As mining site. *Environments, 8*(7), 63.

Matanzas, N., Sierra, M. J., Afif, E., Díaz, T. E., Gallego, J. R., & Millán, R. (2017). Geochemical study of a mining-metallurgy site polluted with As and Hg and the transfer of these contaminants to *Equisetum sp. Journal of Geochemical Exploration, 182*, 1-9. https://doi.org/10.1016/j.gexplo.2017.08.008

Mehlich, A. (1984). Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. https://doi.org/10.1080/00103628409367568

Mleczek, M., Goliński, P., Krzesłowska, M., Gąsecka, M., Magdziak, Z., Rutkowski, P., Budzyńska, S., Waliszewska, B., Kozubik, T., Karolewski, Z., & Niedzielski, P. (2017). Phytoextraction of potentially toxic elements by six tree species growing on hazardous mining sludge. *Environmental Science and Pollution Research, 24*, 22183–22195.

Montanarella, L. (2015). Agricultural policy: Govern our soils. *Nature, 528*(7580), 32-33. https://doi.org/10.1038/528032a

Nelson, D. W., & Sommers, L. E. (1996). Total Carbon, Organic Carbon, and Organic Matter. In *Methods of Soil Analysis* (pp. 961-1010). John Wiley & Sons, Ltd. https://doi.org/10.2136/sssabookser5.3.c34

Pansu, M., & Gautheyrou, J. (Eds.). (2006). *Handbook of soil analysis: Mineralogical, organic and inorganic methods*. Springer.

Panza, G., Frigeri, A., Jr, J., Gomez, F., Cavalazzi, B., Rocchini, D., Altieri, F., & Sanctis, M. (2024). Remote sensing observations of sulfides and sulfates for the geologic mapping of the extreme acidic environment of Rio Tinto, Spain. https://doi.org/10.5194/egusphere-egu24-506

Porta, J. (1986). Técnicas y experimentos de edafología. *Collegi Oficial D´enginyers Agronoms de Catalunya*. Barcelona.

Prăvălie, R., Borrelli, P., Panagos, P., Ballabio, C., Lugato, E., Chappell, A., Miguez-Macho, G., Maggi, F., Peng, J., Niculiță, M., Roșca, B., Patriche, C., Dumitrașcu, M., Bandoc, G., Nita, I.-A., & Birsan, M.-V. (2024). A unifying modelling of multiple land degradation pathways in Europe. *Nature Communications*, *15*(1), 3862. https://doi.org/10.1038/s41467-024-48252-x

Ravichandran, M. (2004). Interactions between mercury and dissolved organic matter—a review. *Chemosphere*, *55*(3), 319-331.

Real Decreto 3/2023, de 10 de enero, por el que se establecen los criterios técnico-sanitarios de la calidad del agua de consumo, su control y suministro. Retrieved from https://eur-lex.europa.eu/legal-content/ES/ALL/?uri=CELEX%3A32020L2184

Rosselli, W., Keller, C., & Boschi, K. (2003). Phytoextraction capacity of trees growing on a metal contaminated soil. *Plant and Soil*, *256*(2), 265–272.

Sáez-Plaza, P., Navas, M., Wybraniec, S., Michałowski, T., & Garcia Asuero, A. (2013). An overview of the Kjeldahl method of nitrogen determination. Part II. Sample preparation, working scale, instrumental finish, and quality control. *Critical Reviews in Analytical Chemistry*, *43*. https://doi.org/10.1080/10408347.2012.751787

Sánchez, S., Baragaño, D., Gallego, J. R., López-Antón, M. A., Forján, R., & González, A. (2024). Valorization of steelmaking slag and coal fly ash as amendments in combination with *Betula pubescens* for the remediation of a highly As- and Hg-polluted mining soil. *Science of The Total Environment*, *927*, 172297. https://doi.org/10.1016/j.scitotenv.2024.172297

Saxton, K. E., Rawls, W. J., Romberger, J. S., & Papendick, R. I. (1986). Estimating generalized soil-water characteristics from texture. *Soil Science Society of America Journal*, *50*(4), 1031-1036. https://doi.org/10.2136/sssaj1986.03615995005000040039x

Skyllberg, U., Bloom, P. R., Qian, J., Lin, C.-M., & Bleam, W. F. (2006). Complexation of mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. *Environmental Science & Technology*, *40*(13), 4174-4180.

Tóth, G., Hermann, T., Szatmári, G., & Pásztor, L. (2016). Maps of heavy metals in the soils of the European Union and proposed priority areas for detailed assessment. *Science of The Total Environment*, *565*, 1054-1062. https://doi.org/10.1016/j.scitotenv.2016.05.115

USDA. (2017). *Soil survey manual*. In Soil Survey Division Staff; Soil Conservation Service (Chapter 3, Volume Handbook 18). U.S. Department of Agriculture.

USEPA. (1992). *Method 1311: Toxicity characteristic leaching procedure*. Retrieved from https://www.epa.gov/hwsw846/sw-846-testmethod-1311-toxicity-characteristic-leaching-procedure

Vareda, J. P., Valente, A. J. M., & Durães, L. (2019). Assessment of heavy metal pollution from anthropogenic activities and remediation strategies: A review. *Journal of Environmental Management*, *246*, 101-118. https://doi.org/10.1016/j.jenvman.2019.05.126

Wang, L., Hou, D., Cao, Y., Ok, Y. S., Tack, F. M. G., Rinklebe, J., & O'Connor, D. (2020). Remediation of mercury contaminated soil, water, and air: A review of emerging materials and innovative technologies. *Environment International*, *134*, 105281. https://doi.org/10.1016/j.envint.2019.105281

Zhang, S., Xia, M., Pan, Z., Wang, J., Yin, Y., Lv, J., Hu, L., Shi, J., Jiang, T., & Wang, D. (2024). Soil organic matter degradation and methylmercury dynamics in Hg-contaminated soils: Relationships and driving factors. *Journal of Environmental Management*, *356*, 120432. https://doi.org/10.1016/j.jenvman.2024.120432