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SCHOOL OF CIVIL, ENVIRONMENTAL AND LAND MANAGEMENT ENGINEERING
MASTER OF SCIENCE IN ENVIRONMENTAL AND LAND PLANNING ENGINEERING

TREATMENT AND RECYCLING OF OXIDIZED SULPHIDE SOIL

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Acronyms

AASS – Actual acid sulphate soil

ASS – Acid sulphate soil

EC – Electrical conductivity

HC – Hydrochar

HTC – Hydrothermal carbonization

ICP – Inductively Coupled Plasma

L/S 10 – liquid to solid ratio of 10

LOD – limit of detection

LT – leaching test

OES – Optical Emission Spectroscopy

PASS – Potential acid sulphate soil

SIS – Swedish Institute of Standards

SS – Swedish Standard

TS – total solids

VS – volatile solids

WHC – water holding capacity

XRF – X-ray fluorescence

Sintesi

Si stima che nel mondo i suoli solfurei ricoprano una superficie di 12-14 milioni di ettari. Questo tipo di suolo, quando viene scavato ed entra in contatto con l'ossigeno, si ossida raggiungendo pH molto acidi (da 2 a 4), una condizione che favorisce la lisciviazione dei metalli e quindi l'inquinamento della falda e dei corsi d'acqua nelle vicinanze. Il trattamento più utilizzato è lo smaltimento in discarica, che è la soluzione più sicura ma anche quella più costosa ed impattante a livello ambientale, perché implica la perdita di suolo, una soluzione non sostenibile al giorno d'oggi.

Lo scopo del lavoro di tesi è quello di studiare un nuovo metodo per trattare e riciclare questo tipo di terreni. Esso è stato svolto nell'ambito del progetto "Senior design project in Waste Science" sviluppato da Jurate Kumpiene e Ivan Carabante, durante il periodo Erasmus svolto presso l'università di Luleå (Svezia).

Lo studio è stato svolto su campioni di suolo prelevati dall'area rurale di Luleå.

Il trattamento è stato condotto su terreno solfureo ossidato e consiste nell'aggiunta di additivi in grado di migliorare le sue caratteristiche. Gli additivi usati sono bioash, residuo della combustione di biomassa, alcalino e in grado di innalzare il pH del suolo; biochar, residuo della pirolisi di biomassa, alcalino e con proprietà adsorbenti per i metalli; torba, per aumentare la porosità e con proprietà adsorbenti per i metalli, e infine compost, dal centro di compostaggio di Luleå, che apporta materia organica e nutrienti.

Tramite esperimenti in laboratorio sono stati individuati i mix più idonei, testando poi il possibile riciclo e impiego del materiale trattato mediante un esperimento in serra, durante il quale sono stati monitorati la crescita di biomassa vegetale, il pH, il potenziale redox, la conducibilità elettrica specifica e la concentrazione dei metalli nell'acqua interstiziale.

I risultati mostrano che il trattamento e il riciclo sono possibili ricorrendo ad uno dei mix testati (suolo, 20% ash, 4% char, 8% torba, 5% compost), che ha riportato buoni risultati sotto tutti gli aspetti, soprattutto per quanto riguarda la concentrazione dei metalli nell'acqua interstiziale.

Abstract

It is estimated that sulphide soils cover an area of 12-14 million hectares worldwide. This type of soil, when it is excavated and get in contact with oxygen, oxidized to a very acidic pH (2 to 4), a condition that favors the leaching of metals and therefore the pollution of the groundwater and nearby watercourses. The most used treatment is landfilling, which is the safest solution but also the most expensive and environmentally impactful, as it involves the loss of soil, an unsustainable solution nowadays.

The aim of this thesis is to study a new method for treating and recycling this type of soil. It was carried out as part of the Senior design project in Waste Science developed by Jurate Kumpiene and Ivan Carabante during the Erasmus period at the Luleå University of Technology (Sweden).

The study was carried out on soil samples taken from the rural area of Luleå.

The treatment was carried out on oxidized sulphide soil and consisted of adding additives to improve its characteristics.

The additives used are bioash, a residue from biomass combustion, which is alkaline and raises the pH of the soil; biochar, a residue from biomass pyrolysis, which is alkaline and adsorbs metals; peat, which is used to increase porosity and adsorbs metals; and compost, from the Luleå composting center, which provides organic matter and nutrients.

The most suitable mixes were identified through laboratory experiments, and the possible recycling and use of the treated material was tested through a greenhouse experiment, during which the growth of plant biomass, pH, redox potential, specific electrical conductivity, and the concentration of metals in the interstitial water were monitored.

The results show that treatment and recycling is possible using one of the tested mixes (soil, 20% ash, 4% char, 8% peat, 5% compost), which performed well in all respects, especially with regard to the concentration of metals in the interstitial water.

Chapter 1
Introduction

1.1 Background

It is estimated that there are about 12-14 million hectares of sulphide-rich soils worldwide (Beek et al., 1980). In Sweden, this figure amounts to 1,400 km^2 hectares and these lands are found mainly along the Norrland coast but also in the Mälardalen valley (Öborn, 1994). Through land uplift and anthropogenic interventions such as ditching or construction, these soils can become problematic as they, when in contact with oxygen, convert the sulphide into sulphate and reach a very low pH. The acidic conditions increase the risk of metals being released and mobilized and can, in turn, lead to not only acidified but also contaminated soil and watercourses.

Sulphide soils often have a high-water content due to a large amount of organic material, which makes them very prone to subsidence with poor bearing capacity. If one is to build on such soil, it must be strengthened or replaced with other more suitable substrate (Larsson et al., 2007). Today, the excavated soil masses are handled, among other things, by placing them below the groundwater surface. In some cases, the soil is placed above the groundwater surface but with a cover layer that protects against further reaction. Sometimes a combination of these methods is used. When laid below the groundwater surface, the sulphide soil returns to becoming anaerobic. In this way, the oxidation stops, and the soil becomes virtually harmless again. When laying above the groundwater surface, it is very important that the soil is covered properly to further reduce oxidation of the soil. However, excavated sulphide soils often end up in landfill, as a waste, which can involve high costs (Pousette, 2010).

The Swedish Environmental Code adopts an EU directive called the waste ladder or the “waste hierarchy”, which governs how to handle waste in the first and last place (1998: 808). Figure 1.1 shows an overall picture of what the steps of the waste ladder look like. The first step is to minimize the amount of waste from the beginning - if there has been no waste, it does not need to be taken care of either. Thereafter, the product should, if possible, be reused as much as possible, and after that recycled to save resources. If it cannot be recycled, it must be incinerated and converted into energy and heat that can be used, and the last choice is to place the waste in a landfill.

Figure 1.1. The waste ladder (Environmental cooperation Norrbotten, 2017).

For sulphide soil, the possibilities for reuse and energy recovery disappear because this soil can not be used in the condition it is after getting in contact with oxygen and there is no energy to be extracted at present from this type of soil (Environmental cooperation Norrbotten, 2017; Swedish Society for Nature Conservation, 2017).
Prevention should be preferred, by choosing not to alterate and dig in areas of sulphide soil or by choosing methods where the soil is largely unaffected, so the risk of creating waste is minimized. In any case, this is hardly possible and therefore the land can at best be recycled or at worst must be disposed of (Bark, 2017).

1.1.1. Sulphide soil and acid sulphate soil, definition

Sulphide soils are formed under reducing conditions, but since the properties of the soil change in connection with changing oxygen conditions, a distinction is made between aerobic (oxidized) and anaerobic (reduced) sulphide soils. A distinction is usually made between potential acidic sulphate soil and actual acid sulphate soil, as problems with acidification only occur when the soil is oxidised. Potential acid sulphate soil (PASS) is found in the reduced zone of a sulphide soil (anaerobic sulphide soil) and actual acid sulphate soil (AASS) is found in the oxidized zone (aerobic sulphide soil), see table 1.1 below (County Administrative Board Västerbotten, 2017; Pousette, 2010).

Table 1.1. Classification and designation of sulphide soil and acid sulphate soil (Pousette, 2010).

Zone	Conditions about oxygen supply	Conditions about water saturation	Geotechnical designation	Geological and international name
not defined			sulphide soil	ASS
oxidized zone	Aerobic	Unsaturated	aerobic sulphide soil	AASS
transition zone	aerobic/anaerobic			
reduced zone	Anaerobic	water saturated	anaerobic sulphide soil	PASS

ASS = acid sulphate soil, AASS = actual acid sulphate soil, PASS = potential acid sulphate soil.

1.1.2. Sulphide soil formation and distribution

The Swedish and Finnish sulphide soils were formed about 3000-8000 years ago as sediment at the bottom of the Littorina Sea, now the Baltic Sea (Boman et al., 2010; Pousette, 2010). With a warm climate, higher salinity than today together with poor circulation, the Littorina Sea was favourable for high bio production. The high production led to oxygen-free bottoms. In the oxygen-free conditions, climate, higher salinity than today together with poor circulation, the Littorina Sea was favourable for high bio production. The high production led to oxygen-free bottoms. In the oxygen-free conditions, anaerobic bacteria thrived which extracted energy by reducing sulphate ions (SO_4^{2-}) to hydrogen sulphide (H_2S). Iron sulphide was formed as a by-product due to the high supply of dissolved iron. Pyrite, which is a form of iron sulphide, dominates in the Mälardalen sediment. The coast of Norrland, on the other hand, is dominated by iron monosulphide, which makes the soil black, which is why the sulphide soils here have been named black suede (Pousette, 2010; Sohlenius, 2011). Due to the land uplift, these sediments formed on the seabed have eventually ended up above sea level and now make up a large part of the soils along the current coast (figure 1.2).

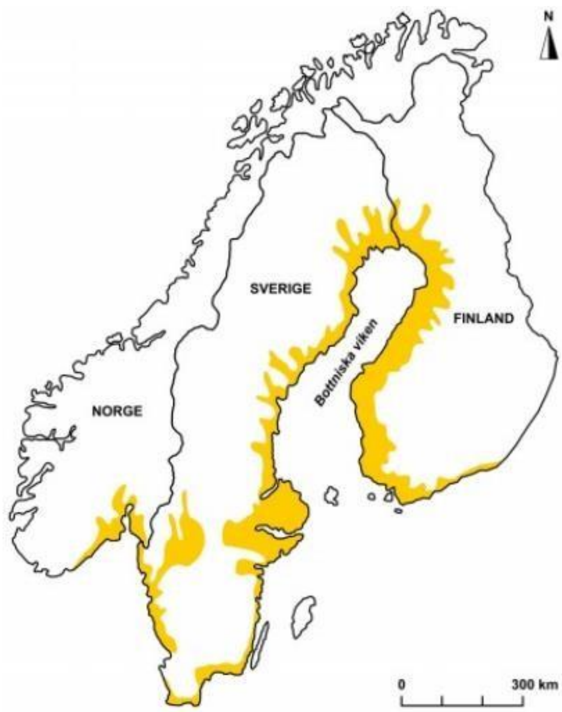

Figure 1.2. Maximum extent of the Littorina Sea about 7000 years ago and thus where sulphide soil can occur (Boman, 2010).

Acid sulphate soils (ASS) are formed when they come in contact with oxygen and then oxidize, following the lowering of the groundwater surface. The progressive uplift of the soil is an influencing factor, but studies have shown that the greatest impacts are given by anthropogenic interventions, such as excavations, because the surface of the water table lowers very slowly during the natural process of soil uplift (Boman et al., 2010).

During these rapid changes, due to human intervention, the pH drops very sharply and becomes a greater shock to the surrounding environment compared with the natural groundwater lowering due to land uplift. In addition, some construction work in the vicinity of sulphide soil areas can also affect surrounding land, i.e., create a drainage effect, which can lead to acidification with devastating consequences for the surrounding land and water (Bernes and Lundgren, 2009; County Administrative Board Västerbotten, 2017).

1.1.3. Chemical reactions

When the sulphide soils are oxidized, the pH is greatly lowered due to the sulphuric acid that is formed. The acidification effect obtained by oxidation of sulphide soils depends on the amount of acid produced and the soil's buffer capacity (Pousette, 2010). A simplified formula of the reaction looks like this:

Pyrite: $$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

Iron monosulphide: $$2FeS + \frac{18}{4}O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

Upon contact with oxygen, iron monosulphide oxidizes faster than pyrite, due to grain size distribution and porosity, that is why soils along the Norrland coast tend to have a higher acidification effect than soils to the south (Larsson et al., 2007; Pousette, 2010). When the sulphide soil oxidises, sulphuric acid is formed, it is not uncommon for the pH to drop all the way down to 2-4. These acidic conditions lead to increased chemical weathering (Boman et al., 2010; Öborn, 1994). An acid sulphate soil is often characterized by clear rust deposits of iron and the yellowish mineral jarosite (Pousette, 2010; Sohlenius, 2011).

A sulphide soil seldom has a higher metal content than in a sulphide-free soil, but due to the acidic conditions, leaching to the surroundings increases (Öborn, 1994). During drier periods, soil drains, and deep cracks can form. At the same time, the groundwater surface is further lowered, which leads to the oxidation reaching greater depths and even more soil being acidified. During heavy rain or melting snow, water can be quickly transported through the cracks and carry large amounts of the metals released by the pH lowering to adjacent watercourses (Sohlenius, 2011). Metals can also precipitate further down into the earth, in the so-called transition zone, where oxidation has not yet reached. Elevated levels of mentals, e.g., copper, nickel and zinc have been measured in the transition zone in sulphide soils in western Finland (Sohlenius, 2015; Åström, 1998).

1.1.4 Characterization

Figure 1.3 shows an illustrated picture of a typical pH profile for sulphide soil where the non-oxidized potential acid sulphate soil can be identified in the lower part of the figure. The PASS has the characteristic black colour, but variations of different colours may occur, especially in southern Sweden when the sulphide soils there are dominated by pyrite. It is iron monosulphide that gives the black colour that is more common in northern Sweden (County Administrative Board Västerbotten & Norrbotten, 2017).

Above, there is the transition zone where it is possible to distinguish the pale from the dark soil, which indicates that no oxidation has taken place to a greater extent. In the transition zone, the pH increases considerably with depth as the light layer above with precipitates of iron hydroxide is actual acid sulphate soil.

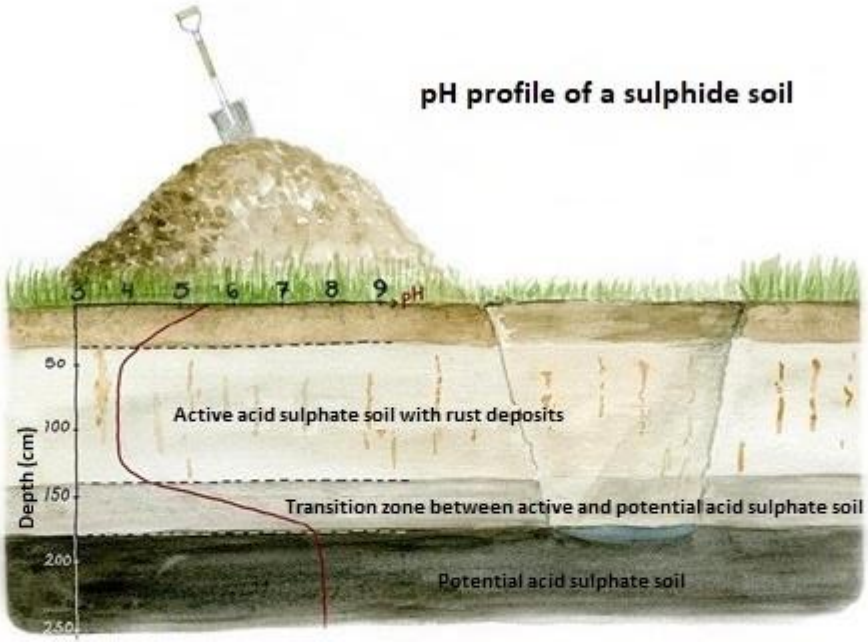

Figure 1.3. Sulphide soil profile that describes how the pH varies with depth (SGU, 2019b).

Actually, acid sulphate soil can be identified in the field using relatively simple methods thanks to its characteristic properties (SGU, 2019b). It is possible to measure the pH of the soil directly in the field to investigate whether there is actual acid sulphate soil in the area, as the pH meter should indicate a low pH (2-4). Check watercourses and ditches in the immediate area to see if there are deposits of iron/aluminium hydroxide. Sulphide soils often occur in clay and silt soils, there can be large cracks in the soil when these are dried out. There could be precipitates of iron hydroxides in actual acid sulphate soil. Identifying a potentially acidic sulphate soil can most easily be done if it has a characteristic black or dark grey colour, but this characteristic can vary depending on where in Sweden the soil is located. All black soil is not a potential acidic sulphate soil, but it is a characteristic. The smell of sulphide soil can be reminiscent of rotten eggs from its high sulphur content; however, the pH of the soil can be around neutral. About it after field observations concerning a potential acid sulphate soil, the soil should be further analysed in a laboratory for examination of pH and the leaching potential of substances should be performed.

1.1.5 Problems with sulphide soil

Sulphide soils are problematic in several ways. Partly due to the low pH that can occur and leads to the leaching of metals and strongly acidifies and pollutes watercourses in the vicinity. The deteriorating water quality can damage animals and vegetation (Pousette, 2010). There are several documented cases of fish deaths in watercourses in connection with sulphide soils (Sohlenius et al., 2015). The mobilized metal ions are taken up and enriched in plants and animals and can thus be dangerous to human health if they are consumed as food (Environmental cooperation Norrbotten, 2017). With its high-water content and amount of organic material, sulphide soil is very prone to sedimentation and has poor bearing capacity. To build on such soil, it must be reinforced or replaced with another more suitable substrate (Larsson et al., 2007).

Oxidized sulphide soil can also cause problems in drainage pipes through iron deposits that clog and can cause blockages and moisture damage, and the low pH can cause corrosion of concrete and iron (Environmental cooperation Norrbotten, 2017; Pousette, 2010).

In Sweden, the Parliament has adopted 16 national environmental goals to address current environmental issues (Environmental Goals, 2020). Several of these environmental goals are affected by the properties of sulphide soils. The environmental goal *Only natural acidification* is one of the environmental goals that is affected. Many forest lands and watercourses are naturally acidic, but many times precipitation and changed land use led to increased acidification which has a negative effect on nature, including the acid sulphate soils which are highly anthropogenic. The environmental goal *Non-toxic environment* is affected by the sharply lowered pH which means that heavy metals are mobilized and heal into the watercourses. Examples of metals are cadmium, nickel, zinc, and copper. Despite low levels in the soil from the beginning, the pollution can become significant when the metals are released. *Living lakes and watercourses* is another environmental goal that the problems of sulphide soils affect. Today, acid sulphate soils contribute to many watercourses being acidified and containing dissolved metals, and this has a negative effect on aquatic life. Finally, the environmental goal *Groundwater of good quality* is also affected by the fact that surface water and wells are negatively affected by human activity in acid sulphate soils (County Administrative Board, 2017; Environmental Goals, 2020).

Today's management of these sulphide soils (storage and placement in landfills) is not sustainable in a society that strives for sustainability, where recycling and reuse are two important prerequisites (County Administrative Board, 2017). By converting these acidic soils into recyclable soils, it could reduce the contribution to the problems that affect the relevant national environmental objectives at several different levels.

1.1.6 Treatment

Advice and recommendations on how sulphide soil should be handled and considered about the environmental geotechnical properties have been developed by the Swedish Transport Administration, with the help of Kerstin Pousette (Pousette, 2007). To assess which measure is suitable for the situation, the geotechnical properties of the sulphide soil, acidification properties, the volume of the excavated masses and surrounding factors such as surface water, groundwater, soil conditions and protection value/sensitivity must be taken into account. The Swedish Transport Administration also recommends a hierarchy for which measure should be prioritized if the sulphide soil is acidifying and the volume is considered large as follows:

1. In situ method, excavation is avoided.
2. Excavation with installation below the groundwater surface.
3. Excavation with installation above or partially above groundwater.
4. Excavation and disposal at waste landfill.

Excavated sulphide soil needs to be treated to reduce the environmental impact it can have (Pousette, 2010). It is convenient to cover the sulphide soil with a cover layer for several reasons, such as preventing oxidation, dehydration, infiltration of rainwater and being a good breeding ground for vegetation.

Coverage can cause the oxidized sulphide soil to return to a reduced environment when the soil becomes water saturated and an anaerobic environment can occur when oxygen is consumed (Pousette, 2010). This inhibits the acidifying oxidation of the sulphides and thus also the leaching of metals.

Liming is a method that can be applied to reduce acidification if the sulphide soil is already oxidized and aerobic, where the lime acts as a pH buffer and accelerates the leaching of sulphur (Pousette, 2010). This alternative can be applied when the sulphide soil has already oxidized as the addition of lime means that the sulphide soil will not return to an anaerobic state. This is a common method in agriculture as the topsoil is placed aerobically above the groundwater level and is processed annually (Bång et al., 2012). It should be highlighted that the pH increase is not the only reason why lime is added to agricultural land, but it has more favourable properties such as reduced phosphorus losses and coarser aggregate formations.

At present, it is most common for sulphide soil to be disposed in construction projects because of its problematic, previously described, properties (Ecoloop, 2017). This corresponds to a management that is at the bottom of both the Swedish Transport Administration's hierarchy and the waste hierarchy that appears in the Environmental Code.

On previous occasions, storage has been carried out above the groundwater surface with excavated masses consisting of sulphide soil, where the results showed that the leached water was influenced by acid sulphate soil, a low pH was measured on the leached water (Pousette, 2010). During the implementation of the work, only an existing plant in operation in the country has been identified that neutralizes and stabilizes sulphide soil for reuse purposes (Sweco, 2016).

1.2 Project description

1.2.1 Objectives and purpose

The purpose of the thesis is to find a new way to treat the sulphide soil and recycle it, giving a “second life”, instead of using the treatments seen in paragraph 1.1.6.

First, it is necessary to find a way to neutralize the acidity of the soil, using some alkaline additives, understand which ones are the best and which is the suitable amount. This step is crucial to reach a pH that guarantees the immobilization of metals.

Then, the goal is to find the perfect mix to plant and grow some beans, to understand if the soil can allow the development of crops. To do that is necessary to improve the structure and porosity of the soil and reach the suitable amounts of nutrients necessary for growth. So, it will be necessary to add other additives that can help the process.

In Sweden, the treatment of sulphide soil is a very popular topic since there is an urgent need to find alternative treatments for this widespread soil.

1.2.2 Method

The execution of the project consists of literature studies, some theoretical lessons, many comparisons with the project supervisor, a visit on site to take the samples of soil and several laboratory experiments, including the creation of a small greenhouse where plants can grow.

The literature study is carried out to provide an overview of the sulphide soils and the actual situation in Sweden, some of the projects done on this topic to better understand which additives to use, the standard procedures for laboratory experiments and the Swedish and Italian legislation in terms of soil remediation to understand and comment the results obtained.

The laboratory experiments are essential to characterize the soil and the additives used, to know their properties and, relying on the literature data, understand how to mix them to obtain the desired characteristics to grow plants in the best way.

1.2.3 Delimitation of the project

Obviously, the limitations to the project must be taken into consideration. They are given by the time available, the inexperience and the difficulties encountered that slowed down some steps. But also, the machinery and equipment available to the laboratory which allowed to focus only on some aspects even if the potentiality of the project would allow further investigations, which could be developed in PhD projects.

Only some nutrients have been studied (Ca, Fe, K, S) because they are the most important to characterize this type of soil and because they are more related to crop growth. Also, for pollutants, we have focused only on some metals (As, Cd, Cu, Pb, Zi) because they are the ones that limit the growth of plants the most and are subject to more stringent limits.

The work does not investigate the metal content in crops, so it is not responsible for use in the food sector. The leaf area, stem length, fresh weight and dry weight of the plant were examined.

The geotechnical properties of the treated soil are not studied to a greater extent than visually observed.

The additives are limited to bioash, biochar, peat, and compost for the work, subject to the time required for the evaluation of the results and the availability of additives.

Chapter 2
Additives and pollutants

To contrast the acidification and leaching of metals that sulphide soils can cause, the pH should be raised and have a high buffer capacity, as previously described in paragraph 1.1.5, “Problems with sulphide soils”.

In addition, the particle size distribution of the sulphide soil is usually dominated by clay particles that maintain a low permeability. Water that enters the soil thus remains for a longer period, which prevents oxygen from penetrating the soil and reaching the roots. The small cavities in the soil limit roots to develop which affects plant establishment when nutrients and water cannot be absorbed to the same extent as in soils with larger cavities (Pierret et al., 1999).

The additives that have been chosen for the work are described below. The result of the choice should be an increase in pH, a reduced content of dissolved trace elements, plant establishment should benefit from increased porosity and the addition of nutrients.

One of the objectives of the project is to check whether the interstitial water, contained in the mixes created, respects the concentration limits for metals, which are the only pollutants studied in this project. We studied only the metals most critical to the health of soil and vegetation growth, i.e., arsenic, cadmium, copper, lead, and zinc.

2.1 Additives

The selection of additives is made based on the criteria described in the paragraph above where the bioash will increase the pH, biochar will adsorb dissolved metals and trace elements, peat will increase the porosity, and compost will add some nutrients and organic matter. The choice has also been based on the availability of the substances. Other substances with similar properties could have been investigated, but bioash, biochar, peat, and compost were considered suitable to achieve the desired results.

2.2 Bioash

Ash is the solid residue of the combustion process, when it is “biological” ash, it is referred to the combustion of biomass. The ashes are considered waste and as such should be disposed of in landfills, representing a problem and a considerable cost. According to Mastrolonardo and Nati (2014), in many countries, there is a strong interest in the reuse and enhancement of ashes, which can be considered:

a fertilizer, as they provide the soil with nutrients useful for plant growth, such as potassium, phosphorus, magnesium, and calcium, reducing the consumption of artificial fertilizers; a corrective, because the ashes are strongly alkaline due to the presence of basic cations in the form of oxides, hydroxides, and carbonates, this property increases the pH of the soil.

2.2.1 Definition and composition of the ashes

The quantity and composition of the ash change mainly according to the type of biomass burned and the combustion temperature. The major elements present in the ashes are calcium (Ca), potassium (K), magnesium (Mg), silicon (Si), aluminium (Al), iron (Fe), and phosphorus (P), while carbon (C) and nitrogen (N) are almost totally absent because they volatilize during combustion.

As for the pollutant content, ash contains some elements considered dangerous for humans and the environment, such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), and chlorobenzenes, therefore the use of ash should be carried out in appropriate doses (Mastrolonardo and Nati, 2014).

2.2.2 Effects of ashes on soil and plants

The main effect of the ashes on the soil is the correction of the pH towards more basic values, which in a range of values close to neutrality can immobilize heavy metals and prevent them from leaching into the soil.

As a fertilizer, however, it must be borne in mind that the solubility of the various minerals contained in the ash varies considerably in the soil. Potassium, for example, is rapidly dissolved in water and must be readily used by plants, otherwise, it will be lost from the soil. Calcium and magnesium have an intermediate solubility, while phosphorus is the least soluble mineral. The availability of these elements, therefore, influences the methods and the choice of timing of any fertilization with ashes. On crops, the positive effects of the use of ash can be recorded both in terms of growth and increase in fruit productivity (Mastrolonardo and Nati, 2014).

2.2.3 Integration of ash with manure and compost

The ash is particularly suitable for adding to manure and compost. In fact, it absorbs humidity and therefore favours the aeration of the biomass in fermentation. The minerals contained in them are used by microorganisms for the formation of organic substances which can then be released into the soil more easily and more gradually. Consequently, the ash improves both the fermentation of manure and compost and the availability of the elements contained in the ash itself, thus forming a higher quality fertilizer (Mastrolonardi and Nati, 2014).

2.2.4 Bioash for Italian legislation

The ashes deriving from biomass combustion processes are classified as "special non-hazardous waste" pursuant to Legislative Decree 152/2006 (part IV). This standard establishes various possibilities for recovering "ashes from the combustion of biomass" with simplified procedures which concern the production of cement conglomerates or the production of compost and fertilizers. Direct spreading, on the other hand, is not required by law. However, the ashes are configured as waste, and distributing them on the ground would mean illegally disposing of waste. It is, therefore, necessary to qualify the ashes as a "by-product", thus opening new possibilities for their use. It is Article 184-bis, introduced by Legislative Decree 205/2010 which transposes Directive 2008/98/EC which indicates the various conditions that must be met to configure a material as a by-product. It should be noted that to date there is no regulation concerning the chemical composition of the ashes, nor is there any mention of the presence of metallic elements or other pollutants. A final observation concerns the EC regulation 2092/1991, which allows the use in organic farming of "wood ash" as a fertilizer, placing the only limit that it derives from "wood not chemically treated after felling".

2.2.5 Bioash for Swedish legislation

The Swedish Environmental Code (DS 2000:61) gives general guidance for the protection of the environment in Sweden, definitions of waste and provisions for environmental permits that could have bearing on the disposal or reuse of bioash. EU directives such as end-of-waste criteria and REACH are applicable in Sweden according to Bjurström et al. 2009. Some other pieces of Swedish legislation that they indicate to have bearing on the governance of bioash are: Building Product Directive (EU) (which also exists in Finland), guidelines for contaminated soil (Swedish EPA) and criteria for the utilization of waste as construction material (Swedish EPA).

Table 2.1. Limits for elements in ash used for fertilizer in Finland, Sweden, and Denmark (Karltun et al. 2008, Nurmesniemi et al. 2012).

		Finland		**Sweden**		**Denmark**	
Parameter	Unit	Limit Value		Limit Value		Limit Value	
		Agri/Forest				Straw+ mix/wood ash	
Ca	%	10/6.0	min	12.5	min	-	
Mg	%	-		1.5	min	-	
K	%	-		3.0	min	-	
P	%	-		0.7	min	-	
P+K	%	2.0	min	-		-	
Zn	%	-		0.05	min		
As	mg/kg	25/40	max	30	max	-	max
B	mg/kg	-		800	max	-	
Cd	mg/kg	2.5/25	max	30	max	5/20	max
Cr	mg/kg	300/300	max	100	max	100	max
Cu	mg/kg	300/700	max	400	max	-	max
Hg	mg/kg	1.0/1.0	max	3	max	0.8	max
Pb	mg/kg	100/150	max	300	max	120/250	max
Ni	mg/kg	100/150	max	70	max	30	max
V	mg/kg	-		70	max	-	max
Zn	mg/kg	1500/4500	max	7000	max	-	max

2.3 Biochar

Biochar is a vegetable carbon obtained following the thermochemical conversion in the absence of oxygen of different types of vegetable biomass using three main technologies: pyrolysis, gasification, and hydrothermal carbonization (HTC) (Zhang et al., 2019).

The biochar used in this project is produced through the hydrothermal carbonization process, so its technical name would be hydro char, but for convenience, we will always call it with the more general term of biochar.

2.3.1 Hydrothermal carbonization

Hydrothermal carbonization is a thermochemical process for the conversion of biomass at relatively low conditions of temperature (100-200 °C) and pressure (10-20 bar) in the presence of liquid water. During the HTC reaction, water, carbon dioxide, and other compounds are broken down from the biomass, generating, in less than 10 hours, a carbonaceous solid, biocarbon (or hydrochar - HC), with characteristics like lignite, and a residue aqueous rich in nutrients present in the raw material.

The HTC process simulates those conditions that in nature caused the plant material to become peat or lignite. The factors are in fact water, temperature, and pressure. The HTC process on organic substrates thus produces HC which has the typical characteristics of lignite.

Since the process takes place in water, hydrothermal carbonization is also suitable for treating biomass with a high level of humidity. The starting material for this transformation can therefore be a vegetable and biological waste from agricultural, industrial, and commercial activities, as well as from the municipal waste separate collection service.

2.3.2 Hydrochar

As regards the main product of the process, the carbonaceous solid has characteristics like those of lignite, with the following possible applications (Kambo and Dutta, 2015).

- Bio-fuel: at present, its use as fuel represents one of the main and technologically more mature ways of enhancing HC. The application as a fuel has already been demonstrated and is currently underway with the HC produced in the Ingelia plant in Valencia starting from mowing and pruning, suitably dried and pelletized (Tasca et al., 2020).
- Soil amendment: HC is placed, by characteristics, in an intermediate position between compost and biochar. The application of hydro-char on silos can respond to fertilization and/or carbon sequestration objectives for the purpose of (direct and/or indirect) mitigation of carbon dioxide emissions and constitutes a research area of considerable interest at the international level, also for the purpose of reviewing the legal regulations for the application of chars on its files that guarantee the achievement of the safety and sustainability objectives.
- Adsorbent: HC possesses the characteristics of a precursor for the production, after appropriate physical-chemical activation, of activated carbons to be used as adsorbents both in liquid and aeriform medium. The fields of use proposed in the literature include the purification of wastewater (removal of heavy metals, organic dyes, contaminants, and

pollutants in general) and gaseous emissions (removal of atmospheric pollutants such as hydrogen sulphide), as well as the capture/sequestration of CO_2, storage of CH_4 or H_2.

2.3.3 Biochar in Swedish legislation

In Sweden, biochar has been used as a fertilizer for years according to the requirements of European Biochar Certificate for Agriculture (EBC-Agro). Furthermore, Sweden has defined limits beyond the EU regulation, which are covered by the Sweden Annex of the EBC (EBC, 2012-2022).

2.3.4 Biochar in Italian legislation

In Italy, there is the ICHAR Association, which in 2012 acted by submitting to the Ministry of Agriculture, Food and Forestry Policies (MIPAAF) an application for the inclusion of biochar in the Italian legislation on fertilizers (Legislative Decree 75/2010 and subsequent amendments), since 2015 biochar is included in the list of soil improvers that can be used in the soil (Annex 2 of Legislative Decree 75/2010).

Subsequently, in December 2018, the ICHAR association presented a new application to the competent Ministry to include biochar in the list of products that can be used as a component of cultivation substrates (Annex 4 of Legislative Decree 75/2010) and, again as a soil improver, in the list of fertilizers allowed in organic farming (Annex 13 of Legislative Decree 75/2010).

To date (March 2022) the application has not yet been successful. Therefore, in the current state of Italian legislation, biochar can be used in the soil as a soil improver, but not in organic farming, despite the Commission Implementing Regulation (EU) 2019/2164 (December 17, 2019), amending the Regulation (EC) 889/2008, has officially included it in the list of soil improvers that can be used in organic farming (authorization pursuant to EC regulation 834/2007).

As regards the cultivation substrates sector, biochar cannot be used as a component, but could be added as a soil improver during use by the end user (ICHAR, 2022).

2.4 Peat

Peat soil consists of partially decomposed organic material that is formed when wetlands and lakes grow again or when the solid ground becomes swampy and forms oxygen-free environments (Ciarimboli and Draguhn, 2012). The most common formation environments are marshes and bogs where the different formation environments give rise to different vegetation and the availability of nutrients looks different for the environments (SGU, 2020). For marshes, nutrients are obtained via groundwater, while bog's water supply takes place via precipitation, which provides a nutrient-poor environment. The kind of vegetation where the peat is created affects the components of the peat, which may affect pore water quality depending on the type of peat used. Sweden's surface consists of about 15% peat with approximately 6.4 million hectares available for extraction, where peat is currently used for, among other things soil improvement (SGU, 2019a).

The high organic content of peat and its high porosity with large cavities form the basis for the choice of this additive. The cavities are judged to have the capacity to promote increased porosity even when mixed with loam. In addition, peat is well established in tillage to topsoil and is found to a large extent easily accessible in Sweden.

2.5 Compost

Compost is the result of the bio-oxidation and humification of a mixture of organic materials (such as pruning residues, kitchen waste, manure, slurry, or garden waste such as leaves and mown grass) by macro and microorganisms in particular conditions: the presence of oxygen and equilibrium between the chemical elements of the matter involved in the transformation.

Within the so-called organic cycle, composting, or bio stabilization, is an aerobic and man-controlled biological process that leads to the production of a mixture of humified substances (compost) starting from both green and woody biodegradable plant residues or even animals through the action of bacteria and fungi.

Once produced, it can be used as a soil improver, then destined for agronomic uses or for horticulture.

Compost, in addition to the amending function, determines the promotion of the microbiological activity in the soil, and the reduction of losses caused by erosion, the decrease in density, the improvement of structural stability, the availability of nutrients, the absorption by of plants, as well as the increase of water retention.

2.6 Pollutants

This section describes the Italian and Swedish guidelines from which the limits on metal concentrations for interstitial water were taken and explains the main characteristics of the metals considered.

In Italy, the protection of soil quality is dealt with in the fourth part of Legislative Decree 152/06 where under title V, in the regulation on remediation, the thresholds concentration of contamination (CSC) for groundwater are defined and then reported in table 2 of Annex 5.

In Sweden, the Swedish Environmental Protection Agency has published a report on contaminated sites containing the Method of Surveying Contaminated Sites (MIFO) guidelines. Contamination limits for groundwater are reported in the fourth appendix, table 3.

Cadmium

Cadmium is strongly absorbed by the organic matter in the soil; when it is present in soils it can be extremely dangerous, as it increases absorption through food. Acidified soils increase the absorption of cadmium by plants which poses a potential danger to animals that depend on plants for survival. Cadmium can build up in their bodies, particularly when they eat multiple plants.

Earthworms and other essential soil organisms are extremely susceptible to cadmium poisoning. They can die at very low concentrations, and this has consequences on the structure of the soil. When cadmium concentrations in the soil are high, they can affect the processes of soil microorganisms and threaten the entire soil ecosystem (Lenntech, 2022).

For groundwater, cadmium is the metal subject to stricter limits, i.e., 5 µg/l in both Italian and Swedish legislation.

Arsenic

Arsenic can be found naturally on earth in small concentrations. It occurs in soil and minerals and may enter the air, water, and land through wind-blown dust and water run-off. Arsenic in the atmosphere comes from various sources: volcanoes release about 3000 tonnes per year and microorganisms release 20.000 tonnes per year, but human activity is responsible for much more: 80.000 tonnes of arsenic per year are released by the burning of fossil fuels. It cannot be destroyed once it has entered the environment so that the amounts that we add can spread and cause health effects to humans and animals in many locations on earth.

Plants absorb arsenic easily, so high-ranking concentrations may be present in food. The concentrations of the dangerous inorganic arsenic that are currently present in surface waters enhance the chances of alteration of the genetic materials of fish. This is mainly caused by the accumulation of arsenic in the bodies of plant-eating freshwater organisms. Birds eat fish that already contain eminent amounts of arsenic and will die because of arsenic poisoning as the fish is decomposed in their bodies (Lenntech, 2022).

For groundwater, the Italian limit is 10 µg/l, while the Swedish limit is 50 µg/l.

Copper

Copper is a very common substance that occurs naturally in the environment and spreads in it through natural phenomena. Humans use copper extensively, in industry and agriculture, its production has increased during the last decades and due to this, the amount of copper present in the environment has increased.

When it ends up on the ground, it strongly attaches itself to organic matter and minerals. As a result, it does not go very far after release and hardly enters the groundwater. In surface water, copper can travel great distances, either suspended on mud particles or as free ions. It does not decay in the environment and because of this, it can accumulate in plants and animals when it is present in the soil. On soils rich in it, only a limited number of plants have a chance to survive, so it poses a serious threat to the production of arable land, depending on the acidity of the soil and the presence of organic matter. Despite this, fertilizers containing copper are still used.

Copper can disrupt the activity of soils, as it negatively affects the activity of microorganisms and worms, the decomposition of organic matter can seriously slow down due to this.

When arable land is polluted, the animals absorbed concentrations that were harmful to their health. Sheep especially suffer greatly from copper poisoning, since the effects of copper occur in reasonably low concentrations (Lenntech, 2022).

For groundwater, the Italian limit is 1000 µg/l, the Swedish limit is 2000 µg/l.

Lead

Lead occurs naturally in the environment, however, most of what is found in the environment is produced by human activities.

Thanks to the past application of lead in gasoline, an artificial lead cycle was formed, and this has made lead pollution a worldwide problem. Also, it was widely used for application in metal products, cables, and pipelines, but also in paints and pesticides. It can enter drinking water through pipe corrosion, and this is more likely to happen when the water is slightly acidic.

Lead is one of the four metals that have the most negative effects on human health and, as far as we know, it does not perform any essential function in the human body, it can only cause damage following the absorption of food, air, or water.

When it is in the environment, it cannot be destroyed but only be converted to other forms. Lead is a particularly dangerous chemical element since it can accumulate not only in different organisms but also in the entire food chain (Lenntech, 2022).

For groundwater, the Italian and Swedish limits are the same, equal to 10 µg/l.

Zinc

Zinc is a very common substance found in nature; many foods contain certain concentrations of zinc. Drinking water also contains certain amounts of zinc, but industrial sources or toxic waste dumps can cause the zinc in drinking water to reach levels that can cause health problems. World zinc production is still on the rise, which basically means that more and more ends up in the environment.

The water is polluted with zinc, due to the presence of large quantities in the wastewater of industrial plants, these waste waters are not adequately purified. One consequence is that rivers deposit zinc-polluted sludge on their banks, which can also increase the acidity of the water.

Some fish can accumulate zinc in their bodies when living in zinc-contaminated waterways and thus bioaccumulate on the food chain. Large amounts of zinc can also be found in the soil. When agricultural land is polluted by it, animals have absorbed concentrations that are harmful to their health.

Zinc may not only be a threat to livestock, but also to plant species. Plants often have zinc uptake that their systems cannot handle, due to the accumulation of zinc in the soil. Only a limited number of plants can survive on zinc-rich soils. Due to its effects on plants, zinc poses a serious threat to agricultural production. Despite this, zinc-based fertilizers are still applied.

Finally, zinc can disrupt the activity of the soil, as it negatively affects the activity of microorganisms and earthworms (Lenntech, 2022).

The Italian limit for groundwater is 3000 µg/l, while the Swedish limit was not reported in Table 3 of Appendix 4th of the MIFO document.

Chapter 3
Analytical methods

3.1 Laboratory methods for characterization of soil and additives

The study for the characterization of the materials was mainly carried out through laboratory work following established standards from the Swedish Institute for Standards (SIS). Some of the procedures have been modified based on the existing conditions for the experiments, and for some others, it was necessary to use the LTU laboratory guidelines because no standard has been found.

Most of the experiments have been carried out on each material, the procedures adopted are explained in paragraphs 3.2 to 3.8, while the results are reported in chapter 4.

3.2 XRF

The XRF, or X-ray fluorescence, is the emission of characteristic “secondary” (or fluorescent) X-rays from a material that has been excited by being bombarded with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials. (Beckhoff et al., 2006)

In this project, the portable X-ray system "ThermoScientific™ Niton™ XL3t XRF Analyzer" has been used to evaluate the concentration of the main macro-nutrients (Ca, Fe, K, S) and of the most interesting pollutants for the purpose of the work (As, Cd, Cu, Pb, Zi). Thanks to this analysis, it is possible to have a first overview of the chemical composition of the materials.

The procedure is simple: after calibrating the device and setting on soil analysis mode, it is only necessary to place the tip of the device, which is in the shape of a gun, on the material to be analysed, wait for sufficient time, about 2 minutes and read the results on the screen. In output there will be the concentration values and the standard deviation values for each chemical element.

3.3 Total and volatile solids

The total solids (TS), or dry matter, represent the amount of solids contained in the material sample, they are determined according to the standard SS 028113, while the volatile solids (VS), which represent the content of organic matter, are evaluated in accordance with the standard SS-EN 15935:

2012. All materials were tested in triplicate to calculate the mean and the standard deviation for both TS and VS.

For the TS, it is necessary to mix well the material, take three ceramic crucibles, weigh them, and put a sample of the material in each and weigh again. Then they are placed in an oven that maintains a temperature of 105 °C for 24 hours to remove the moisture from the beakers. In the end, they are placed in a desiccator for a few hours to cool them down until they reach room temperature. At this point, it is possible to weigh them and calculate the percentage of TS in the samples, according to the equation:

$$TS\ (\%) = \frac{[(weight\ dry\ sample + container) - (weight\ empty\ container])}{(weight\ wet\ sample + container) - (weight\ empty\ container)} \times 100$$

The moisture content can be calculated with the following equation:

$$Moisture\ (\%) = 100 - TS(\%)$$

The same dried samples are now used to determine VS, they are placed in a 550 °C oven for 24 hours and then in a desiccator. When the samples are back to room temperature, the weight is recorded and then VS is calculated according to equation 3, where "$Weight_{105}$" is the sample weight after the first oven and "$Weight_{550}$" is the weight of the sample after the second warmer oven:

$$VS\ (\%) = \frac{Weight_{105} - Weight_{550}}{Weight_{105}} \times 100$$

3.4 Total bulk density

The bulk density is another important parameter to characterize the additives, the procedure is taken from the LTU laboratory guidelines and the steps are: take a graduated glass beaker of known volume (e.g. 100 ml), weigh it on a scale, add some material to the beaker, lightly shake it to levelized the surface, note down the volume reached and the total weight, then calculate the density with this equation:

$$\rho_t = \frac{[(weight\ sample + weight\ beaker) - weight\ beaker]}{volume\ sample}$$

repeat this procedure several times to get a more accurate value.

3.5 Leaching test

The leaching test is a particular type of chemical extraction, generally used as a preparatory activity for subsequent analysis. The test consists of a "washing", designed to allow the passage inside a liquid (a solution called leachate), of the mobile substances present in a solid sample. The leachate produced will be subjected to a set of chemical analysis that will allow the evaluation of the "release potential" of the initial sample.

The standard SS-EN 12457-2 explains the procedure. The test has a L/S 10 (liquid to solid ratio of 10), this means that the ratio between the TS of the solid sample and the leaching liquid must be equal to 10, and the liquid used is distilled water. Practically, after a well mixing of the material, a sample is taken, weighed and placed in a HDPE plastic container, then water is added until it reaches a L/S of 10 and the container is placed in a rotating machine for 24 hours. At the end of the period, the leachate is sucked with sterile syringes and filtered through a 0.45 µm membrane. When enough leachate has been filtered, a part of it is analyzed for pH and 9.8 ml of leachate is placed in test tubes along with 0.2 ml of nitric acid which preserves the samples for metal analysis (ICP-OES) which takes place at a later stage.

3.6 pH

To measure the pH of a solid material it is necessary to have previously generated the leachate with a leaching test and preferably to have filter it with a 0.45 µm membrane (paragraph 3.5) to have a homogeneous sample and a better execution of the test. A pH meter is a precise instrument that weighs the hydrogen-ion movement in water-based suspensions, showing its acidity or alkalinity expressed as pH, it is also called a “potentiometric pH meter” because it measures the variation in electrical potential between a pH electrode and a reference electrode. The variation in electrical potential links to the acidity or pH of the suspension (Covington et al., 1985).
For a realistic result, the temperature of the suspension must be about 20 °C and the pH meter needs to be calibrated often.

3.7 ICP-OES

The ICP-OES, or “Inductively Coupled Plasma – Optical Emission Spectroscopy”, identifies an analytical instrument capable of measuring the light (optical emission) produced by a liquid sample when introduced into an inductively coupled argon gas plasma. Through this mechanism it is possible to quantify the metals contained in the sample by measuring, for each, the intensity of the light emitted with a specific optical bench (system of mirrors, lenses, and gratings). For the determination in ICP-OES it is necessary to have samples in liquid form. For solid matrices it is possible to proceed with a preliminary phase of mineralization, that is a technique of disintegration of the solid matrix in liquid solution.

The ICP-OES (or ICP-AES) allows to determine metals in highly variable concentrations and in multiple matrices, which is why it is today the most versatile technique for determining metals in water, soils, sediments or even in food and petroleum products.

The inputs to this instrument are the tubes containing 9.8 ml of filtered leachate from the LT test and 0.2 ml of nitric acid, as already mentioned in the paragraph 3.3. The tubes can be stored in the refrigerator if they are not immediately analyzed.

3.8 Water holding capacity

The water holding capacity (WHC) is a hydrological constant of the soil. It defines the water content in the soil, in terms of percentage humidity, in optimal conditions as regards the ratio between water and air in the soil. These conditions occur when the soil humidity is at the field capacity all the micropores are saturated with water while in the macropores there is only air.

The water holding capacity is determined according to the following layout.

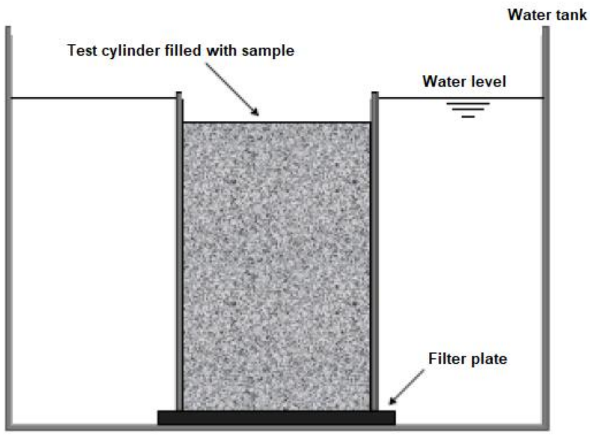

Figure 3.1. Layout used for the determination of the WHC.

Three plastic columns are prepared with a filter at the bottom. A known amount of the material is put into each of the tubes, whereupon the tubes will be covered with parafilm to avoid evaporation. The columns are placed in a container which then is filled with water up to a level slightly above the material surface. Under these conditions the material can slowly saturate with water. Let it saturate for about 24 hours.

After saturation, remove the columns from the container and place them on a bed of sand in order to allow the surplus water to drip off. Note for how long water is dripping. As soon as the dripping stops, determine the gravimetric water content of the samples.

The water holding capacity is calculated by the ratio of water trapped in the sample, and the dry mass of the sample, according to:

$$WHC = \frac{mass\ of\ water}{dry\ mass} = \frac{wet\ mass - dry\ mass}{dry\ mass}$$

Chapter 4
Characterization for soil and additives

4.1 Soil

The soil has been sampled from a rural area of Luleå, in four different spots of the same site, that is because the soil is never homogeneous in large areas so that different locations could have different concentrations of sulphur and metals. They have been stored in four different buckets, as seen in figure 4.1, while, in figure 4.2, it is possible to see the first appearance of the wet soil, it is mainly clay, very compact, it has dark grey colour with some yellowish areas where oxidation has already occurred or is in progress.

Figure 4.1. Buckets containing the four soil samples.

Figure 4.2. Wet soil after sampling.

The first thing to do is to verify if this soil is a sulphide soil; the experiments to do are the XRF, that shows the sulphur concentration, and the pH measurement that shows the acidification potential.
The XRF device is used directly on the four wet samples. For all of them, the sulphur concentration results below the limit of detection (LOD) and approximately 600 ppm for two of the four samples and approximately 800 ppm for the other two. Therefore, the oxidation process was carried out on those with higher concentrations, to evaluate their behavior. About 300 grams of material per bucket are taken and placed in a oven for 24 hours at 100 °C.

The XRF results on dry samples are reported in the tables 4.1 and 4.2 and the values are the averages of two identical tests. Table 4.1 shows the concentrations (ppm) of the most important nutrients, including the sulphur (S), and their standard deviations, here the S concentration is much higher than before the drying process and its value is characteristic of a sulphide soil. While, in table 4.2, the pollutant concentrations are reported; where there is “<LOD” it means that the concentration value is below the limit of detection (LOD), so that the XRF the device does not return the standard deviation.

Table 4.1. XRF: concentrations of nutrients in soil.

Chemical element	Concentration (ppm)	+-2sigma (ppm)
Fe	30300	500
K	5702	318
S	**4798**	1061
Ca	4092	189

Table 4.2. XRF: concentrations of pollutants in soil.

Chemical element	Concentration (ppm)	+-2sigma (ppm)
Zn	53	19
Cu	44	28
Pb	17	10
Cd	14	<LOD
As	12	<LOD

For the pH, it is necessary to do previously a leaching test L/S 10; to compare the results, it is done on both a wet soil sample and a dried soil sample. For the wet soil, the pH is 5.3 ± 0.3, for the dry soil it is 3.1 ± 0.1, these results show a significant decrease of pH after the drying process so that the soil has good acidification potential, which is characteristic of sulphide soils, moreover the pH after the oxidation is within the range of values typical of actual acid sulphate soils (pH: 2-4).
So, it is possible to conclude by saying that the soil is sulphide soil.

The next step is to dry all the suitable soil available, so about 20 kg of wet soil of containers 1 and 2, to speed up the oxidative process that in nature would occur naturally due to contact with the ambient air but in longer times, proportionally to the degree of exposure of the soil to atmospheric oxygen. Since it is a considerable amount of material, it is put in 11 baking trays and let it dry for about 48 hours in an oven at 50 °C, with ventilation at 50%. The images of the soil after drying are shown in appendix A, some characteristics such as jarosite deposits can be seen.

With the use of a hammer, we tried to reduce the size of the agglomerates as much as possible and obtain a powder that could be homogenized. Since the ground was sampled in two different points of the site, although they have similar characteristics, it is good to homogenize the content as much as possible to be able to conduct tests on representative samples of the entire soil.

A "splitter" was used, capable of dividing the incoming material into two subsamples, which were then mixed again and again divided into two by the machine; this procedure was repeated numerous times and for all the dried soil available, equal to about 14 kg, combining, in turn, the subsamples with each other.

To evaluate the residual moisture, the total solids (TS), volatile solids (VS), and the total bulk density (ρ_t) the steps seen in paragraph 3.3 and 3.4 are carried out, in table 4.3 the results are reported.

Table 4.3. Total solids, moisture, volatile solids, and total bulk density of the soil after drying process.

Parameter	Value	Standard Deviation
TS (%)	92	1
Moisture (%)	8	1
VS (%)	5	1
ρ_t (kg/m^3)	860	15

These values change a bit over time because the moisture tends to decrease, that is why the standard deviation of values is limited to units and not to decimals, to give to the reader a general idea; of course, during the project the values are updated every month to be more accurate.

4.2 Additives used

- **Bioash**: a mix of fly ash and bottom ash was used in this project. We have chosen to sift the ashes with a 2 mm sieve and use only the under-screen to obtain a mixture with the soil and other additives as homogeneous as possible, moreover, by working with finer grain sizes, a better chemical-physical interaction is obtained between the materials involved.
- **Biochar**: hydrochar was used as a soil improver to improve the physical, chemical, and biological characteristics of the soil; as an acidity corrector because, like bioash, it has a strongly basic pH that counteracts the acidic pH of the soil; finally, as an adsorbent medium, for the adsorption of some heavy metals. Also, for the biochar a dimensional cut of less than 2 mm was chosen, for the same reasons indicated for the ash.
  We had two bags of hydrochar from France, but only one was pure material, the other contained impurities. We had about 500 g of pure material available, so char was the limiting element for the tests, and this influenced the choices made.
- **Peat**: peat pellets from the Swedish brand *Geogen* were used, a particular type of peat invented in the 1980s by the Geotechnical Department of the University of Luleå**.** This peat is very porous and is used as an adsorbent material in case of oil or petrol spills both on land and in the sea. Also, in this case we did not use the original material but the residue of the production, that is the undercut deriving from the production of pellets.
  The goal of using peat is to bring organic substance to the soil and increase its porosity, as it makes the soil less heavy and compact, favouring ventilation. Furthermore, the adsorbing effect could have benefits on some heavy metals.
  We have chosen to use a dimensional range between 1 mm and 2 mm, not less than one to guarantee the aeration effect and not more than two to have a matrix as homogeneous as possible and maximize the interaction with the other additives.
- **Compost**: the compost used is a mixed composted soil conditioner produced by the controlled transformation and stabilization of the organic fraction of solid urban waste and vegetable waste; it was taken directly from the composting centre in Luleå.
  It was not possible to define the best granulometric fraction for the compost, being a material of high humidity and very similar to soil, it was therefore preferred to manually eliminate foreign bodies larger than a centimetre, such as food remains or wooden sticks, which could need more time to degrade.

In this paragraph are reported means and standard deviations values of the parameters for each additive. The following tables also show the values for the soil, already seen in paragraph 4.1, to have a complete overview.

Table 4.4. pH of soil and additives.

Material	pH	Temperature (°C)
Soil	2.97	19.7
Ash	12.15	20.7
Char	9.3	19.5
Peat	4.52	20.2
Compost	8.45	19.7

In table 4.4, the pH values are precise, because they are referred to a single measurement made at the same time for all materials. However, the pH varies over time, so these are indicative values, and they were updated periodically.

Table 4.5. Total solids (TS) and volatile solids (VS) of soil and additives.

Material	TS (%)	St. Dev. (%)	VS (%)	St. Dev. (%)
Soil	92	1	5	1
Ash	89	1	3	1
Peat	87	1	95	1
Compost	57	2	47	2

This analysis was not conducted on biochar in order not to waste it, as we did not have much available for subsequent experiments. The moisture content of zero percent was therefore assumed, so TS was equal to 100%. Note the high percentage of volatile solids contained in the peat.

Table 4.6. Total bulk density (ρ_t) of soil and additives.

Material	ρ_t (kg/m^3)	Standard Deviation (kg/m^3)
Soil	861	12
Ash	989	12
Char	173	11
Peat	283	4
Compost	442	17

It is noted that char is the lightest and certainly the most porous as it has a strong adsorption potential, followed by peat, which is also used as an adsorbent material (for oils). Compost is the most heterogeneous material and therefore with the highest standard deviation, while peat is the most homogeneous since it maintains a size range between 1 and 2 mm and therefore reports the lowest standard deviation. Ash is the material with the highest density.

In the next page, figure 4.3 shows the results of the XRF test, i.e., the concentrations of nutrients in the materials. Soil contains a very high amount of iron compared to additives and char contains very little. For sulphur, the soil always contains more, because it is a sulphide soil, while for potassium and calcium it is the ashes that are richest.

In general char provides the least macronutrients, while ash provides the most. Peat is rich in iron, while compost is rich in calcium and potassium, which are the components in which the soil is most deficient.

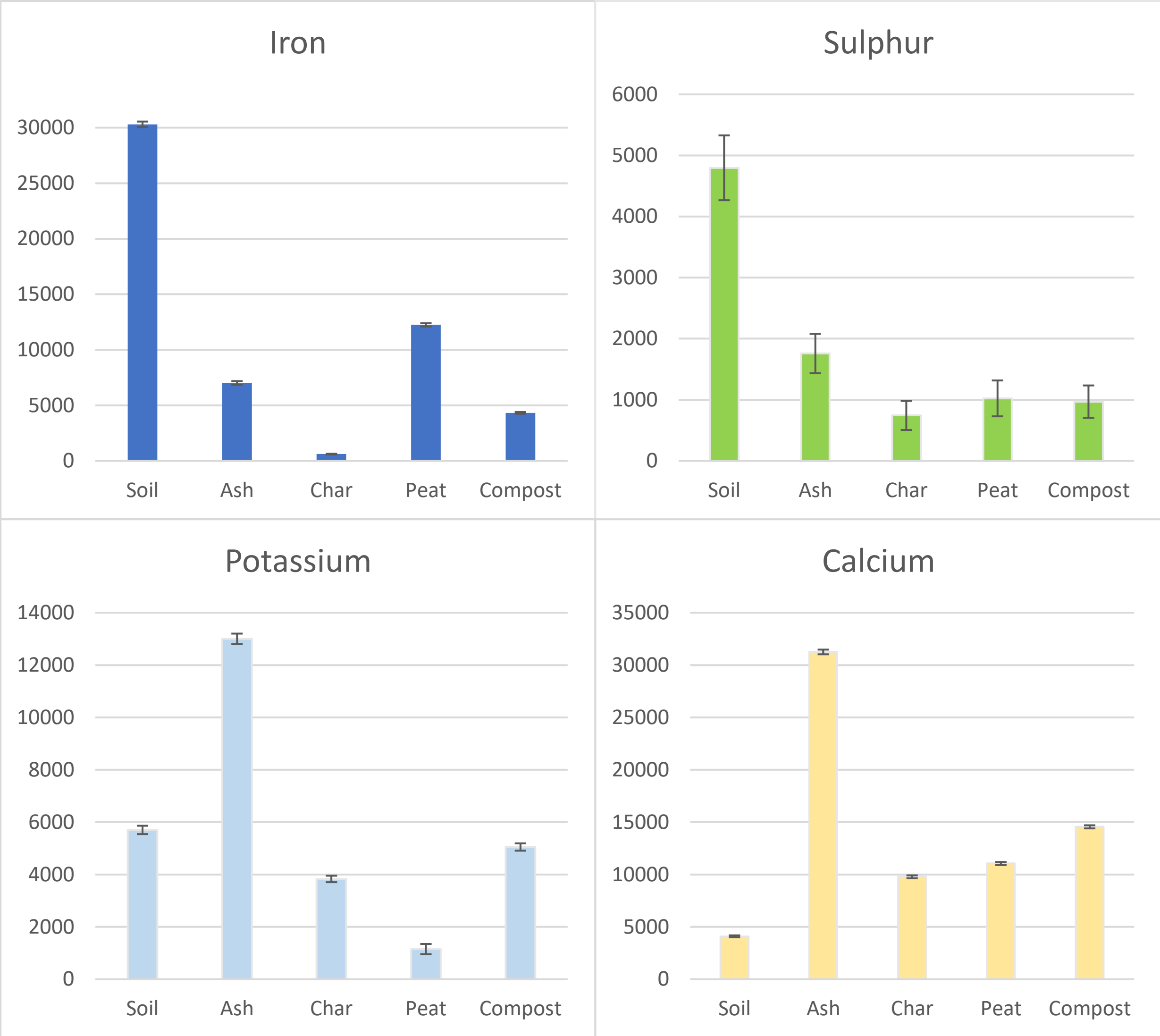

Figure 4.3. XRF: Concentrations of nutrients (ppm) and standard deviation for each material.

The concentrations of polluting metals resulting from the XRF test are shown in Figure 4.4.

The ashes contain the highest concentration of pollutants, recording the highest value for each.

For copper, ash always has the highest concentration, followed by soil and compost, then char and peat.

For arsenic, ash has a high content compared to other materials.

Also, for lead, the highest concentration is recorded in ash, while the other materials have lower and similar concentrations.

For cadmium, ash and soil have similar values, while compost, peat and char are lower.

Finally, zinc has extremely high values in the ashes, while the others have values an order of magnitude lower.

Again, it can be said that char always has the lowest values, while ash has the highest.

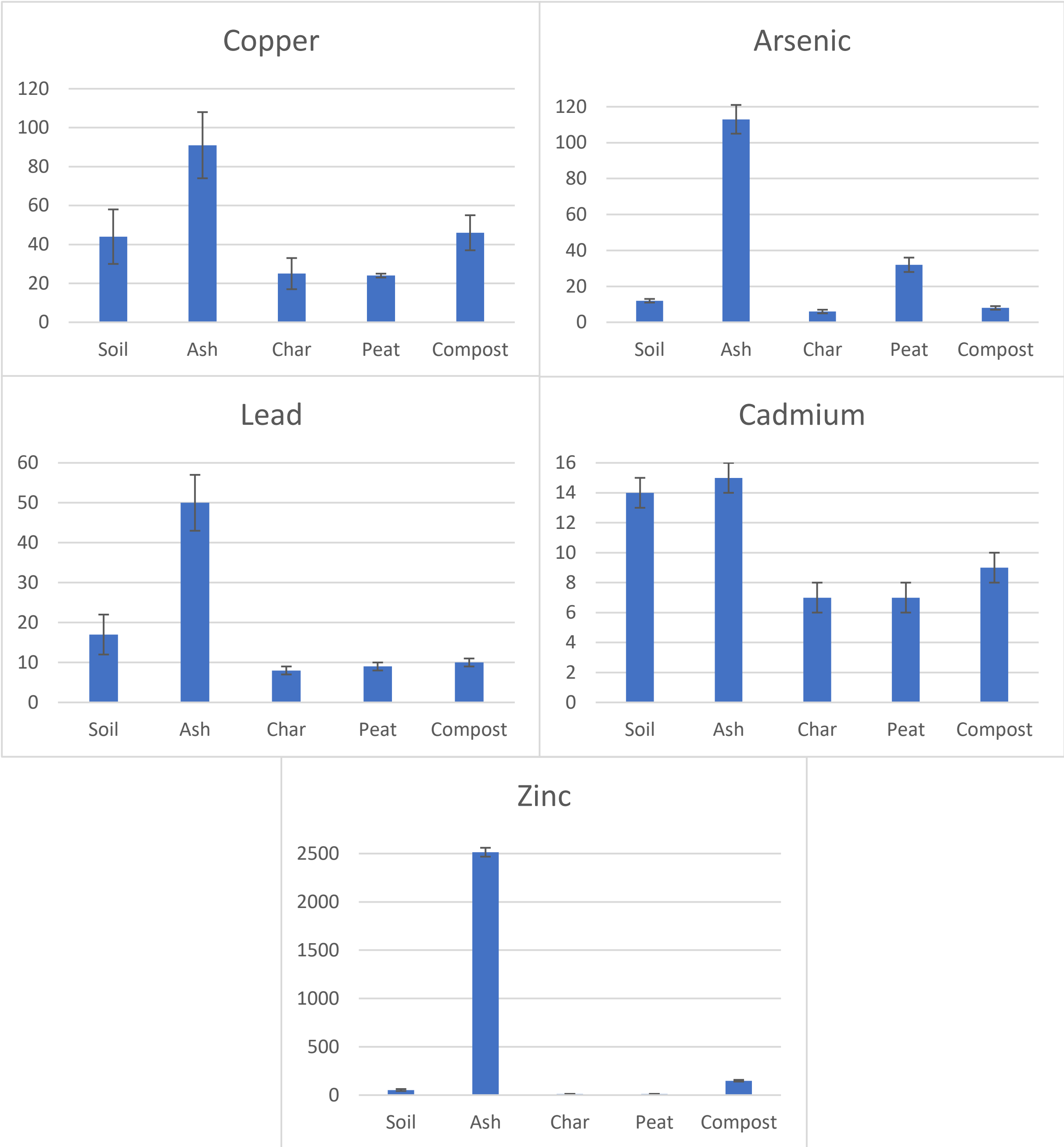

Figure 4.4. XRF: Concentrations of pollutants (ppm) and standard deviation for each material.

4.3 Leaching tests

Some leaching tests were carried out to understand in which quantities it is better to use the additives, to obtain a higher yield during the pot experiments.

4.3.1 Leaching test with soil and bioash

The first leaching test was performed combining soil and bioash. This is because the bioash, among all the materials available, is the main responsible for raising the pH given its high buffering power which allows counteracting the acidity of sulphide soils. Furthermore, the bioash improves the texture and water retention of the soil and immobilizes some trace components, especially cationic species, while anionic elements such as arsenic may not have these benefits, their mobility will greatly depend on the final pH of the soil.

A liquid/solid ratio of 10 was used and it was decided to gradually increase the percentages of bioash and consequently decrease those of soil, as reported in the appendix. It was decided to work with reduced quantities of solids, therefore, to use bottles of 50 ml because they are quicker to prepare, easy to manage, and sufficient for the quantity of filtrate necessary for subsequent analyses. Having average residual moisture in the soil of 8%, this was considered for the respect of the ratio L/S = 10, so the moisture present in the soil was subtracted from the theoretical quantity of water to be added, while for the ashes have been assumed to have a zero-humidity value because they are stored in a dry environment.

Figure 4.5. Rotating machine for the LT.

Once the bottles were prepared, they were rotated for 24 hours on the roller machine in figure 4.5, and at the end the pHs were measured. The results are shown in table 4.7, and the pH trend curve in relation to the increasing percentage of ash is shown in figure 4.6.

Table 4.7. pH results of the LT with soil and ash.

Results LT (L/S=10)		
soil, dry (%)	ash, dry (%)	pH
100	0	3.1
95	5	3.97
90	10	4.77
85	15	6.33
80	20	6.93
60	40	8.83
20	80	10.99
0	100	11.95

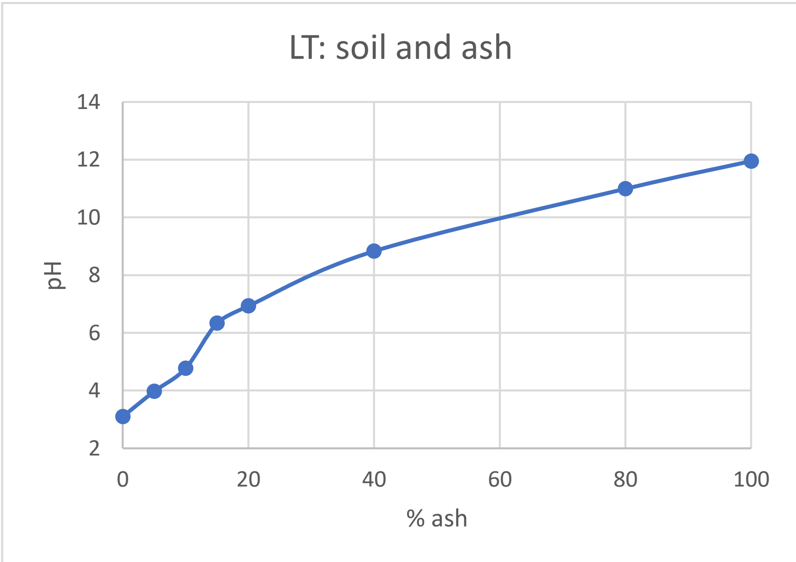

Figure 4.6. Soil and ash LT results: increase in pH as the percentage of ash increases.

It is noted that bioash strongly influences the pH.

This experiment is crucial because it allows us to understand which percentages of material to fix and then proceed with the addition of biochar. Knowing that biochar is also responsible for a small part of the pH increase and that for values close to or above neutrality, metals such as arsenic are immobilized, the choice falls on bioash percentages of 10 and 15%, therefore percentages of soil 85 and 90%.

Finally, the samples were prepared to conduct the metal analysis (ICP analysis).

Figure 4.7. Steps to prepare samples for ICP analysis: collection, filtration, and dosage.

4.3.2 Leaching test with soil, bioash and biochar

Based on the results of the first leaching test, it was decided to set the percentages of 10% and 15% of ash. The second test was then carried out (L/S = 10, 24 h), fixing the quantity of soil and varying only the percentages of ash and char, precisely to focus attention on the role that these two components play in modifying the soil, for which 4 different mixes were prepared for a percentage of 1% of ash, containing respectively 5, 10, 20 and 40% of char, equal for the percentage of ash of 15%, as described in the appendix.

Results of the test in table 4.8 and graphical representation of the results in figure 4.9.

Figure 4.8. Biochar before sieving.

Table 4.8. pH results of the LT with soil, ash, and char.

	pH	
% char	10% ash	15% ash
5	4.71	5.80
10	5.12	6.20
20	5.71	6.23
40	5.63	6.50

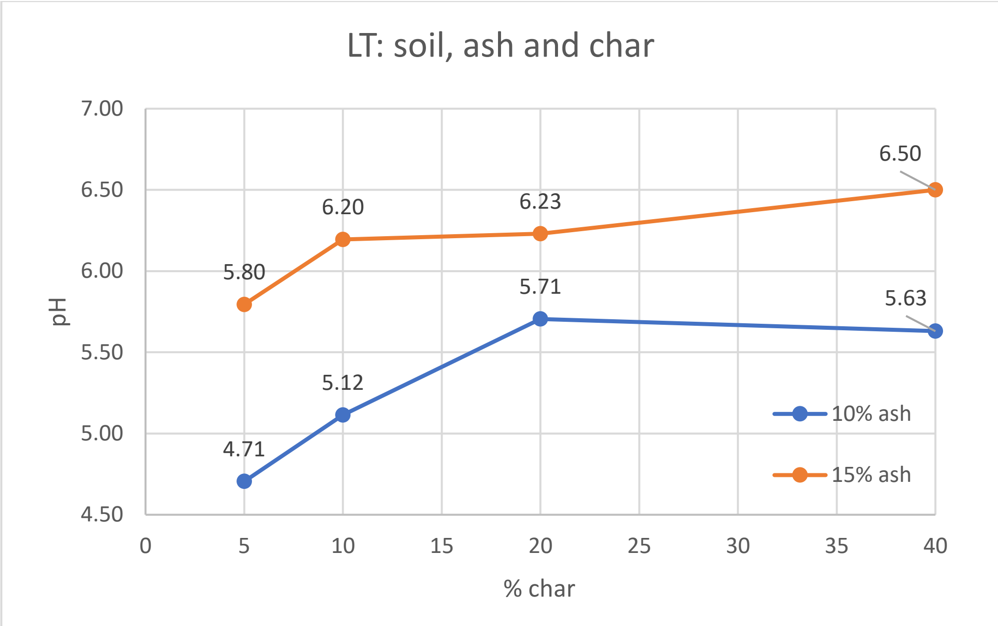

Figure 4.9. Trend of pH for fixed percentages of ash (10 and 15%) as the percentages of char increase.

In general, an increasing trend in pH can be affirmed with the increase in the percentage of biochar, a more marked trend for low percentage values, less marked as the char content by weight increases.

These tables are useful if integrated with the knowledge of the metals present in the filtrates, these are reported in the appendix, and they are the results of the ICP test.

The results of the ICP test show how in the first leaching test, in which there was only soil and ashes, as the ash weight content increases, there follows an increase in the concentration of arsenic (up to 3 orders of magnitude more), chromium (2 orders of magnitude more), and cadmium (1 order of magnitude. This shows that the ashes play a crucial role in increasing the alkalinity and therefore in raising the pH of the soil, but they also involve the consistent contribution of heavy metals, so it is advisable not to exceed the dosage.

With the addition of biochar, it is noted that as the dose of char increases, the adsorption of metals significantly increases, and therefore their concentration in the leached product decreases, this is especially true for aluminium, cadmium, chromium, nickel. For arsenic and lead, values close to the detection limit threshold were detected, this is because fairly low percentages of ash were chosen (10 and 15%).

4.3.3 Leaching test with soil, bioash, biochar and peat

After measuring the pH of the peat which turned out to be 4.52, therefore acidic, and having to use small amounts of char, due to limited availability, it was considered necessary to increase the ash content to obtain the desired pH values, so the quantities of ash to be tested were 15 and 25%.

Table 4.9. pH results of the LT with soil, ash, char, and peat.

#	Ash (%)	Char (%)	Peat (%)	pH
1	15	0.1	2	5.49
2	15	0.1	8	5.22
3	15	4	2	5.55
4	15	4	8	5.38
5	25	0.1	2	6.6
6	25	0.1	8	6.81
7	25	4	2	6.79
8	25	4	8	6.65
9	20	2.05	5	6.36

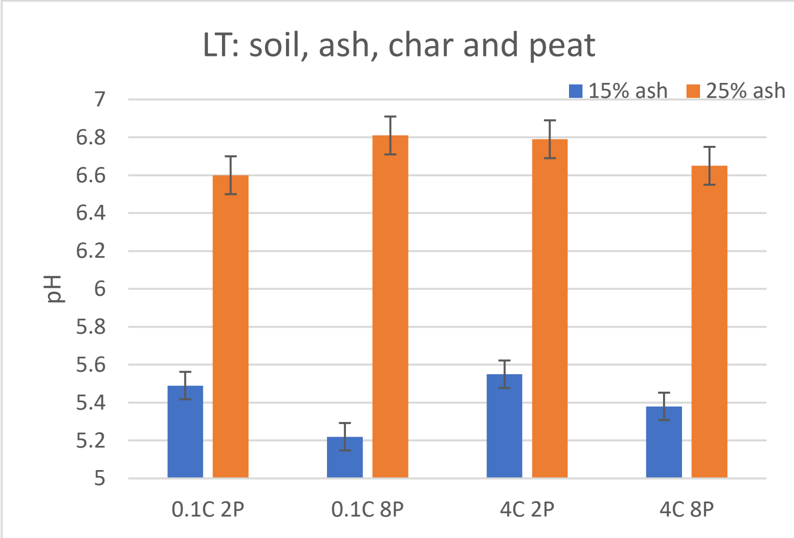

Figure 4.10. pH in relation to the quantities of ash, char (C), peat (P).

Observing the results, it is noted that for higher quantities of peat (8%), the pH is slightly lower, except for specimen #6, which is the only exception. This indicates that peat has a slightly acidifying effect. On the other hand, increasing the amount of ash also increases the concentration of metals and this is a risk that we do not want to run.

Since the crops we will use for the pot experiments should withstand a slightly acid environment, between the two percentages of ash, it is preferable to work closer to 15%. 25% of ash might seem better because it brings us closer to neutrality but on the other hand brings too high concentrations of polluting metals.

4.3.4 Leaching test with soil, bioash, biochar, peat, and compost

From a leaching test conducted on fresh compost, it was found to have a pH of 8.45. Due to the growing complexity of the problem, for the last LT it was decided to simplify everything by setting the maximum values for peat and compost that would have been added in the experiment in pots, therefore 8% for peat (acid pH) and 5% for compost (basic pH) in order to study the pH response to the variation of the ash content only. The char was not considered because, for the quantities decided above (0.1% and 4%), it did not involve a significant variation of the pH.

The results are shown in the table, it is noted that the range of pH variation is quite narrow and that it is possible to obtain a value close to 6 even with a percentage of 10% ash. Since the ashes are rich in heavy metals and the aim of the project is to use the ashes to raise the pH but not to enrich the soil with metals, it is preferable to stay on lower ash percentages.

Table 4.10. pH results of the LT with soil, ash, peat, and compost.

#	ash (%)	peat (%)	compost (%)	pH
1	10	8	5	5.8
2	15	8	5	6.26
3	20	8	5	6.49
4	25	8	5	6.66

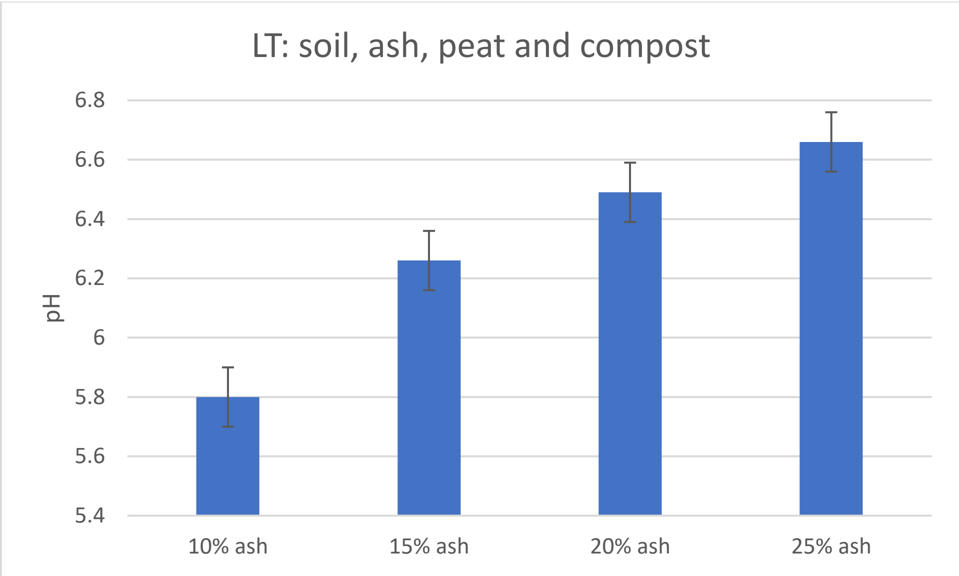

Figure 4.11. pH at constant amount of peat (8%) and compost (5%).

It was therefore decided to set as percentages 10% and 20% of ashes, this is because it has been seen that with 10% it is still possible to guarantee a pH that could be suitable for the growth of beans, with the presence of lower amounts of heavy metals, and 20% of ash because it brings us closer to neutrality and this could favour greater growth.

The choice of 15% of ash as the maximum value was excluded because it is too close to 10%, so 15% will be used as a median point and studied in a single combination.

4.4 Final combinations in preparation for growth experiment

Table 4.11. Total weights and percentages used for growth experiments.

#	soil (g)	ash (%)	ash (g)	char (%)	char (g)	peat (%)	peat (g)	compost (%)	compost (g)
1	250	10	25	0.1	0.25	2	5	5	12.5
2	250	10	25	0.1	0.25	8	20	5	12.5
3	250	10	25	4	10	2	5	5	12.5
4	250	10	25	4	10	8	20	5	12.5
5	250	20	50	0.1	0.25	2	5	5	12.5
6	250	20	50	0.1	0.25	8	20	5	12.5
7	250	20	50	4	10	2	5	5	12.5
8	250	20	50	4	10	8	20	5	12.5
9	250	15	37.5	2.05	5.125	5	12.5	5	12.5
10	250	0	0	0	0	0	0	0	0
11	250	0	0	0	0	0	0	5	12.5

Table 4.11 shows the mixes selected as case studies during the growth experiment.

Mix 9 represents the midpoint between the two levels of values used for combinations from 1 to 8.

Combination 10 is also called blank and serves as a verification of the behaviour of the sulphide soil, while 11 is soil with the addition of 5% of compost to monitor the effect of the compost.

All percentages and weights given in the table are related to the total weight, including moisture, while percentages and weights relating to dry weight are given in the appendix B.

Chapter 5
Pot experiment, methodology and results

In chapter 5 the whole vegetation growth experiment will be explained in detail, starting with the description of the methods adopted and the parameters analysed, concluding with the results and possible sources of error.

This is the most practical part because it shows the results on a real scale of the experiments conducted in the laboratory and that will demonstrate if the chosen mixes will be suitable for the treatment of the soil and therefore if they can be implemented as a soil treatment and recycling technology.

5.1 Materials and methods

In section 5.1 we will first describe the methods used to conduct the pot experiment, then the methods for the evaluation of biomass growth, the layout used for the sampling of the interstitial water from the pots, the definition of the redox potential and the electrical conductivity, which are the parameters measured on the interstitial water, in addition to the pH and ICP analysis, already described in chapter 3.

5.1.1 Growth experiment

The growth experiment is based on a method described by Vangronsveld and Clijsters (1994) where beans from the genus Phaseolus Vulgaris are used, in this laboratory work, yellow beans are chosen ("Maxidor" beans).

First, each soil mixture is kept moist for a week so that the biological processes could be established and stabilized. Then the vernalization begins (the beans are exposed to cold to induce flowering) where the beans are left in the fridge for 24 hours and then the beans are covered with distilled water underneath for four hours (Figure 5.1).

Four beans are planted in each pot where a total of 33 pots are used, three pots for each soil being examined. The growing season lasts for two weeks where the soil's water content is maintained between 57% and 63% of the water holding capacity for each soil mixture. Control is performed by weighing the pots daily to record the respective weight and compensating for the water loss.

Figure 5.1. Beans covered with water for four hours before sowing.

Figure 5.2. Layout of the greenhouse used for the growth experiment.

Figure 5.3. Layout with lit lamps.

During the plant experiment, the beans are fed with light from the plant lamps (230 V, 50 Hz) placed at about 40 cm above the beans, these run 12 hours a day and turn off for the remaining 12 hours. The pots are placed indoors, on a shelf with 3 layers, covered with plastic all around to recreate a greenhouse and protect it from unexpected phenomena, see figure 5.2 and 5.3 for the layout. On the top shelf all pots were placed with the number of the mixture followed by "_1", on the second shelf the pots "_3" and on the lowest shelf the pots "_2". This is because three identical pots were produced for each mixture, as mentioned above.

After 14 days the aboveground plant parts (shoots) are cut to about 1 cm from the soil surface and the following morphological parameters are measured for each plant and the data recorded:

- weight of the fresh shoot,
- length of the shoot,
- leaf area.

The roots of the plants from the soil are carefully removed, washed to remove all soil particles (the roots should be white), the access water is removed with absorbent paper and the roots are weighed. Finally, the weight of the fresh root is recorded.

Measuring Leaf Area by Tracing Technique (Dr. Saupe's method)

The Tracing Technique is a simple, low-budget method that compares a paper replica of the surface to be measured to a standard of known area (Saupe, 2009).

1. Accurately trace on paper the outline of the leaflet. Be sure to keep the leaf flat during tracing.
2. Cut out the tracing(s) and accurately weigh.
3. Weigh a piece of paper of known dimension (100 mm x 100 mm is convenient; the size isn't too important if it isn't too small, and you know it's area).
4. Calculate the conversion factor by dividing the area of the paper by its weight. The units will be mm^2/g.
5. Using the conversion factor, determine the leaf area by multiplying the conversion factor times weight of the paper tracing according to the following equation:

$$\text{leaf area } (mm^2) = \text{weight of leaf tracing (g) x conversion factor } (mm^2/g)$$

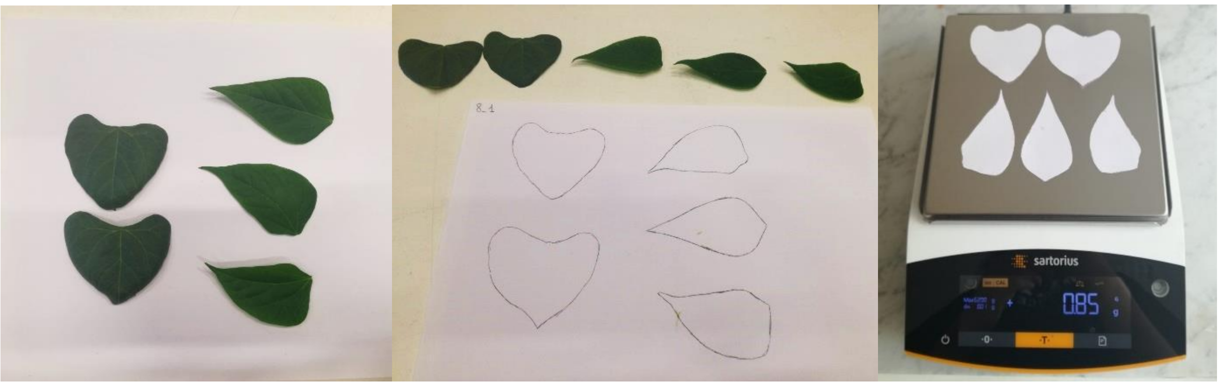

Figure 5.4. Steps for determining the leaf area in mm^2.

5.1.2 Sampling of interstitial water

The examination of the interstitial water is carried out to check the variation in the concentration of trace elements (analysed with the ICP test) and the variation in pH, redox potential, and conductivity during the two weeks of the experiment.

To extract the water from the pores, rizhoners are used, which are visible in the figure 5.5. The rizhoner has one end consisting of a filter with a pore size of approximately 0.15 µm, this end is inserted into the ground and the other end consists of an opening into which a cannula is connected.

Vacuum bottles are created which, once connected to the rizhoners by means of a needle, can extract the water from the ground (see figure 5.6). To have enough filtrate to do the subsequent analyses (about 15 ml) it is necessary to carry out the sampling for at least 24 hours. Sampling is done on the first, seventh and fourteenth day to evaluate the temporal trend of the analysed parameters.

The pH, redox and conductivity measurements are made immediately after the cannula was disconnected, while the samples for the ICP test were stored in the refrigerator as already explained in chapter 3.

Figure 5.5. Layout used to sample the interstitial water.

Figure 5.6. Phase of extraction of the interstitial water.

5.1.3 Redox potential

According to Franco Ajmone Marsan, the measure of redox potential provides, in practical terms, an indication of soil aeration, or how much a soil is aerobic or anaerobic. More specifically, the potential indicates the intensity of the oxidation and reduction reactions and allows to relate this to the biological processes that occur in the soil.

The redox potential (Eh) is measured in Volts or millivolts and, generally, in a well-aerated soil it assumes values between +400 and +700 mV; with the removal of oxygen, for example due to submersion, the value can drop to around -300 mV. In aerobic conditions, in fact, microorganisms use O_2 as the final electron acceptor; in the absence of this, the aerobes are replaced by facultative or obliged anaerobic microorganisms which use other substances as acceptors with consequences both on the general metabolism of the soil and on its relations with other environmental compartments. Usually, it is the organic substance that supplies the electrons and its evolution is altered since almost exclusively substances with a lower molecular weight are used. The reduction of nitrates can produce greenhouse gases and that of the compounds of Mn and Fe causes an increase in their solubility and the release of substances, including pollutants, which are normally associated with them.

According to the Nernst equation, the redox potential increases as the activity of the oxidized compound increases, decreases as the activity of the reduced one increases and increases as the pH decreases.

The measurement is of the electrometric type, like that of the pH. A pH meter equipped with a Pt electrode and a calomel or Ag: AgCl reference electrode is used; combined electrodes which also allow temperature detection are widespread. The measurement is carried out by immersing the combined electrode in the suspension under examination, taking care to slightly shake the container to facilitate the achievement of a stable reading (Ajmone Marsan).

5.1.4 Electrical conductivity

According to Marno Fourie (2017), the electrical conductivity (EC) of a soil is a measure of the ability to conduct an electrical current. Most importantly to fertility, EC is an indication of the availability of nutrients in the soil. The higher the EC, the more negatively charged sites (clay and organic particles) there must be in the soil, and therefore the more cations (which have a positive charge) there are that are being held in the soil.

As with most things in the soil, it is important that the EC does not get too high either, as too many of these nutrients, especially Na and Mg, can be detrimental to soil health. Optimal EC levels in the soil therefore range from 110-570 milli siemens per meter (mS/m). Too low EC levels indicate low available nutrients, and too high EC levels indicate an excess of nutrients.

Usually, sand has a low EC (1-10mS/m), silt has a medium EC (8-80 mS/m) and clay has a high EC (20-800 mS/m). This means that sandy soils have a poor capacity to store and hold onto cations and lose nutrients easier than silty and clayey soils. Silty and clayey soils thus have a much better ability to store and hold onto cations, and the loss of nutrients would be much less so than in sandy soils.

Understanding this, something to consider is that less fertiliser can/should be applied on soils with higher EC, as less of what is applied will be lost through leaching. In sandy soils, improving the organic matter levels can lead to an improvement in the ability of the soil to hold cations, thereby improving the EC levels.

Soil EC, much like pH, is a good overall indicator of soil fertility. It can be used to show the capacity of the soil to store nutrients, as an indicator of soil texture and as an indication of an excess of soil nutrients.

Measurement

The conductivity meter is equipped with a probe, usually portable, for field or on-site measurements. After the probe is placed in the liquid to be measured, the meter applies a voltage between the two electrodes inside the probe. The electrical resistance of the solution causes a voltage drop, which is read by the meter. The meter converts this reading into milli Siemens per centimetre, this value indicates the total dissolved solids (Cozzi et al., 2013).

The EC is influenced by the temperature. When temperature varies, follow variations of the ionic concentration (which depends on the equilibrium of dissociation, complexation, and solvation of each ion in solution) and the speed at which the individual ions move (which depends on the viscosity of the solvent). Consequently, the specific conductivity increases by approximately 1-3% for each degree of temperature (Cozzi et al., 2013).

5.1.5 Study of additional mixes

During the first week of growth, it was noticed that combinations number 4 and 9 were growing more than the others, so it was decided to create two more mixes (numbers 12 and 13) that started from the percentage values of mixes 4 and 9 and improved some features, notably by adding larger amounts of char, peat, and compost to see if these changes could have a good effect. Table 5.1 shows all tested mixes as a percentage of the total weight of soil.

Table 5.1. Percentages on total soil weight of all tested mixes.

number	ash (%)	char (%)	peat (%)	compost (%)
1	10	0.1	2	5
2	10	0.1	8	5
3	10	4	2	5
4	10	4	8	5
5	20	0.1	2	5
6	20	0.1	8	5
7	20	4	2	5
8	20	4	8	5
9	15	2.05	5	5
10	0	0	0	0
11	0	0	0	5
12	10	6	10	10
13	15	6	10	10

5.2 Results

Section 5.2 will describe the results of the methods described in section 5.1. The biomass growth will be described in terms of number of seeds grown per pot, total leaf area per stem, biomass weight per stem, stem length and root weight. Then we will focus on the parameters of pH, redox and conductivity of the interstitial water, finally on the concentrations of heavy metals measured in the interstitial water, through ICP analysis.

5.2.1 Biomass growth

The following pictures show the plants after two weeks of growth. Attention is paid only to the stems, and thus to the pots, which achieve sufficient growth. A hierarchy of importance has therefore been defined between the growth parameters calculated to be able to define from which values onwards the growth can be defined as sufficient:

leaf area > biomass weight > stem length

Therefore the main parameter is the leaf area, which by convention has been assumed to be at least 300 mm^2. Many of the beans sprouted but gave no leaves and were therefore not considered to have grown sufficiently.

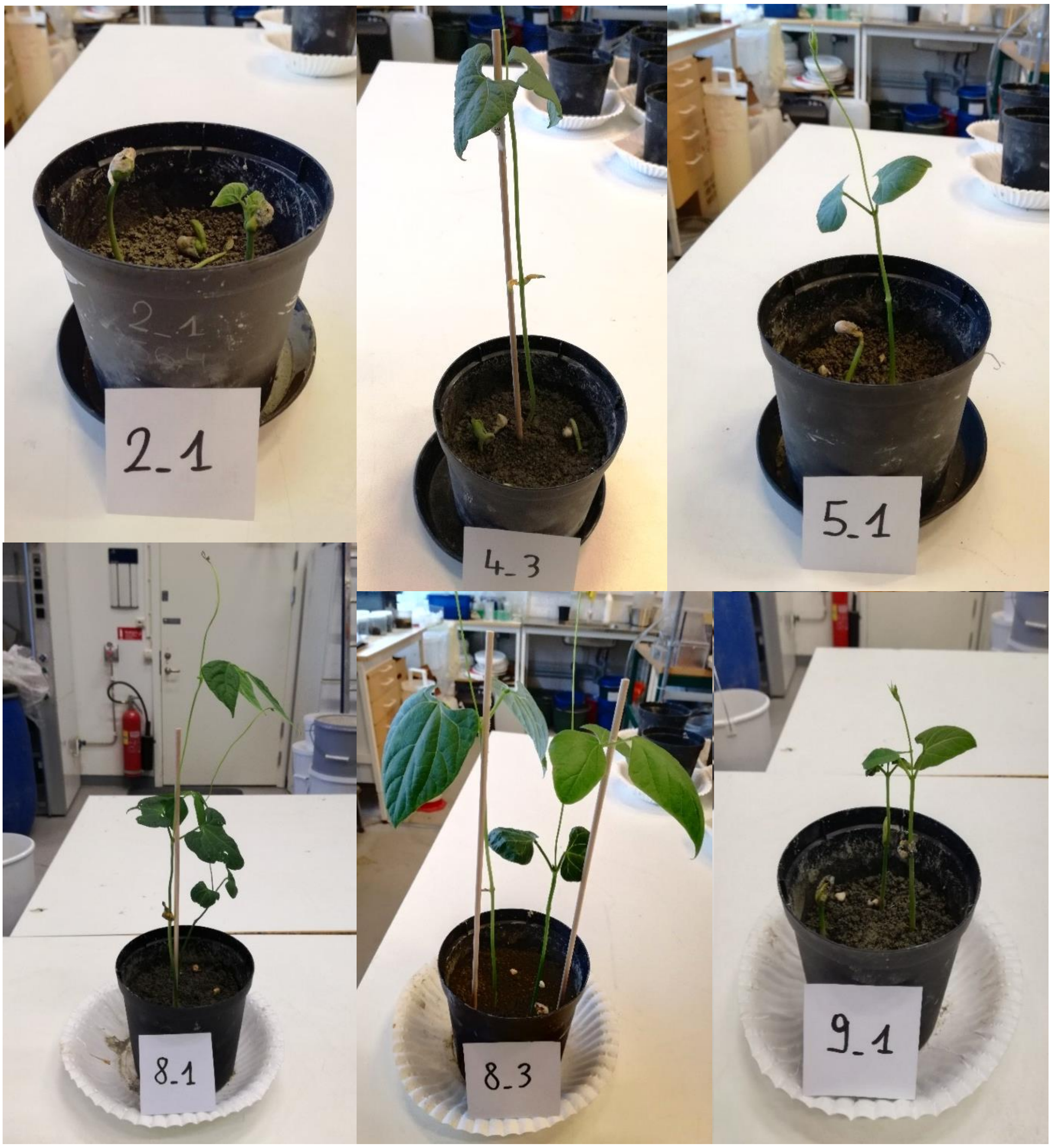

Figure 5.7. Pots that have reported sufficient growth (from 2_1 to 9_1).

Figure 5.8. Pots that have reported sufficient growth (from 9_3 to 13_3).

The first thing to notice from the pictures is that mixes 12 and 13 gave better results in terms of the number of seeds grown, with more homogeneous results than the other mixes. This is because, having started a week later, the experience on the cure and on the quantity and modality of the water to be added had improved, and they were also the best mixes selected to study.

Mix number 8 has seen an important growth, but late compared to the others, it was a very rapid growth but concentrated in the second week of monitoring. Mix 2_1 recorded a visibly lower growth than the others, at the limit of sufficiency (leaf area of 360 mm^2).

Figure 5.9 shows the number of seeds per pot that have achieved sufficient growth.

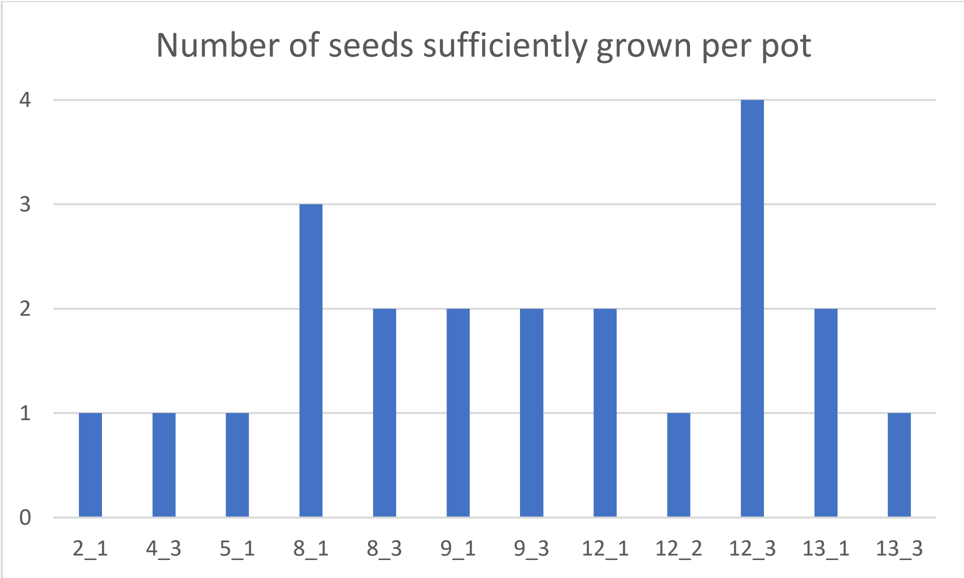

Figure 5.9. Number of seeds sufficiently grown per pot.

The mix 12_3 is the only one that reports significant growth for all four seeds planted. Furthermore, it is noted that almost all the reported mixes belong to the upper shelves, of the top floor are 6, of the intermediate floor are 5, while of the lower floor is only 1. Therefore, it can be deduced that greater exposure to sunlight has helped in growth.

In figure 5.10 is reported the main parameter, the leaf area. It is evident that the mixes 8_1 and 8_3 are the ones that show the largest leaf area per stem, and this is also clearly visible from the photos. These mixes record values 3 to 5 times higher than other mixes. In the second position is the mix 4_3 and then the others which are around 1000-2000 mm^2.

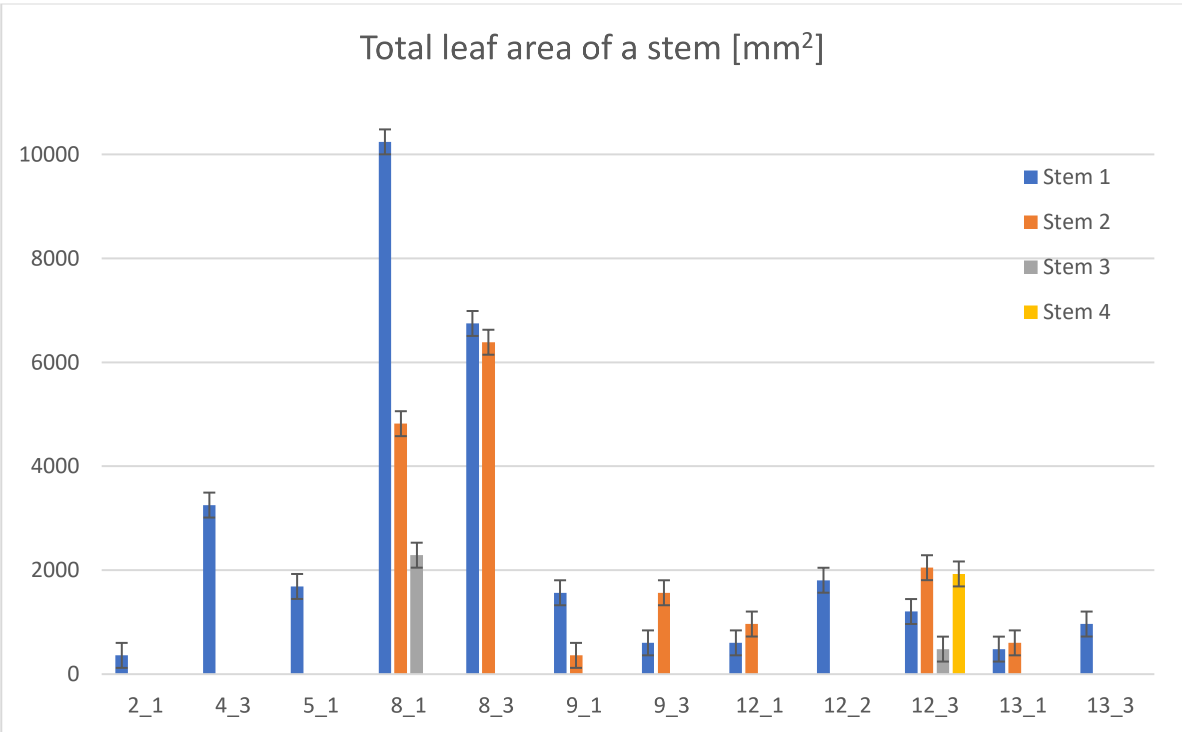

Figure 5.10. Total leaf area of a stem [mm^2].

As for the weight, second most important parameter, 8_1 and 8_3 record the highest values, but with less variation than the other mixes. The 12_3 mix also recorded good values, especially homogeneous for all four stems (figure 5.11)

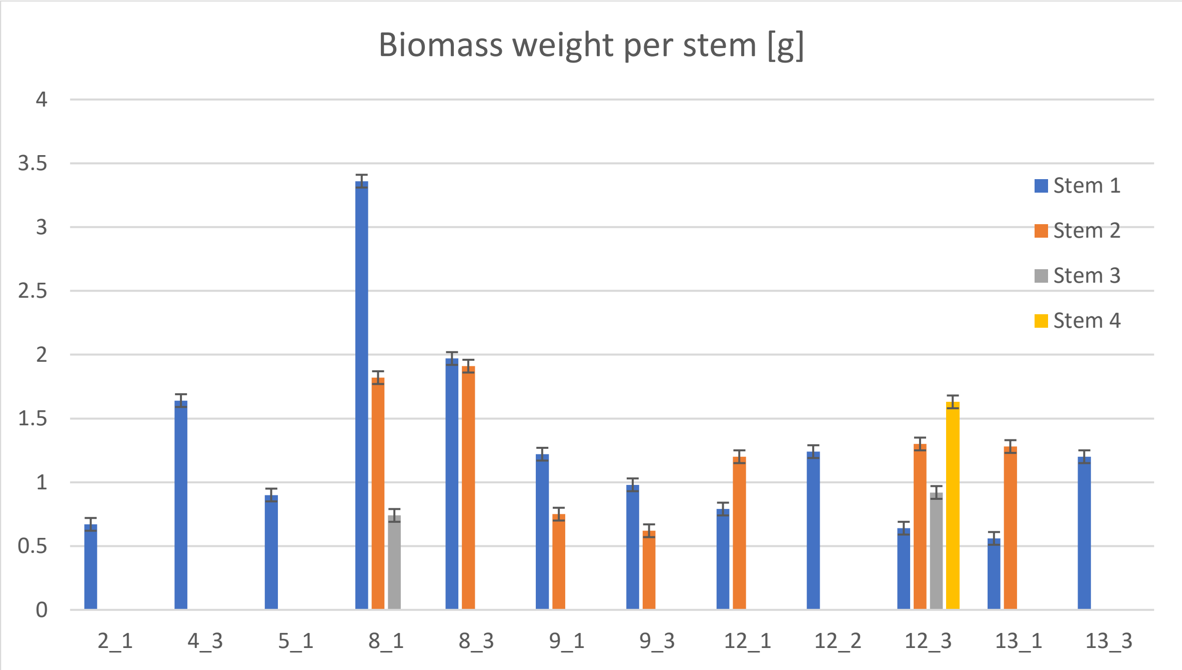

Figure 5.11. Biomass weight per stem [g].

The third parameter is the length, which is much greater for mixes number 8, followed by 4, then 12, 9, and 5.

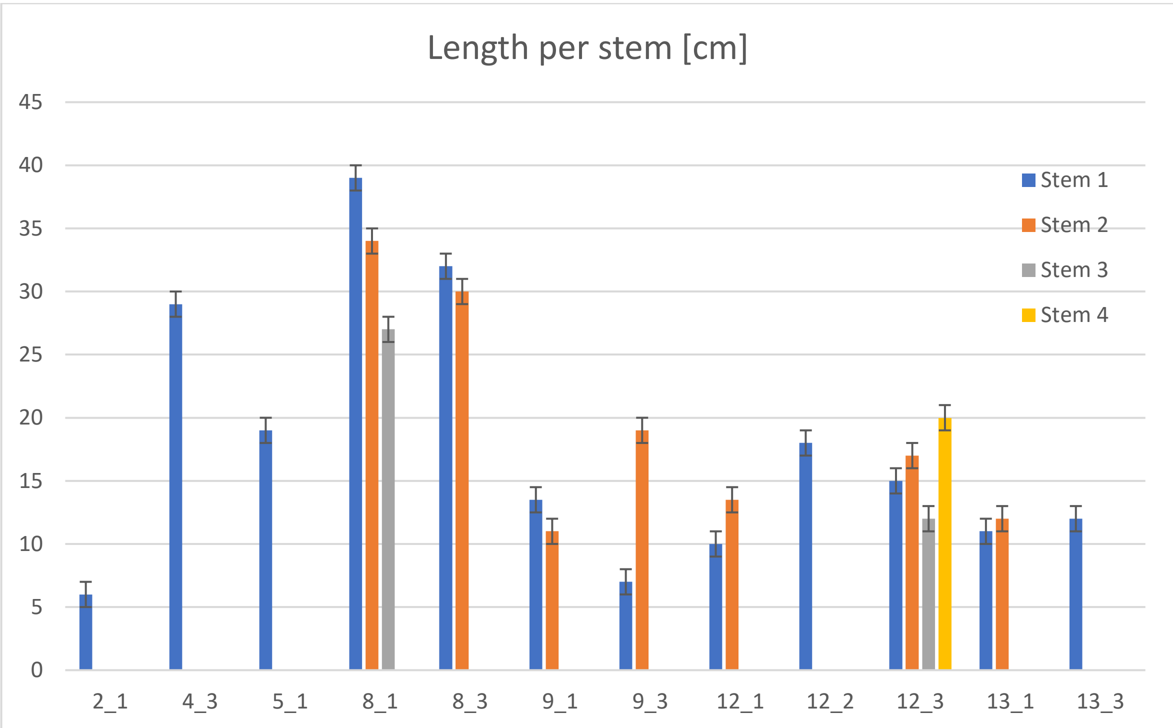

Figure 5.12. Length per stem [cm].

The weight of the roots is also reported. A more homogeneous trend is noted in this case, this could mean that the roots have developed in a more similar way and that therefore the difference could lie in the speed of growth, probably for some mixes it would have taken longer to grow.

Furthermore, the error bars are wider than the other parameters because the roots were washed and then left to dry in the air, but the level of drying was not the same for all, so the values could vary based on the presence or not of water.

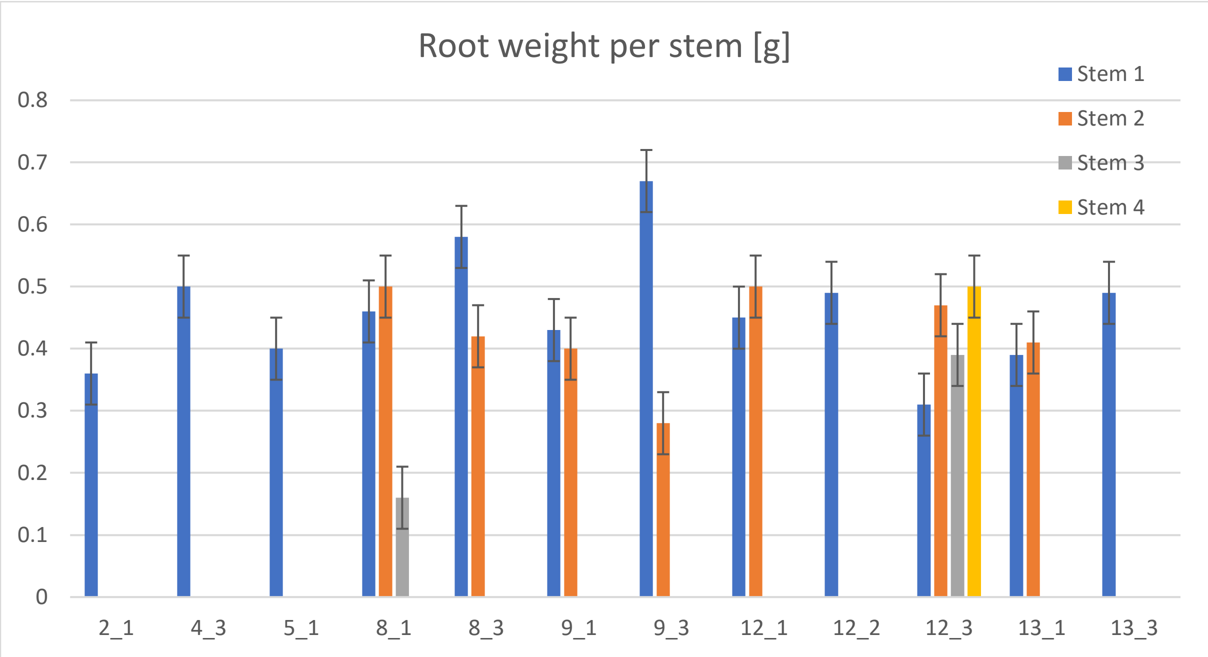

Figure 5.13. Root weight per stem [g].

In general, the best results are recorded in terms of biomass growth for mixes 8 and the most homogeneous results for mixes 12. Now let's see the situation in terms of pH, conductivity, redox, and finally the concentrations of metals in the interstitial water that could give us a completely different perspective on the situation.

5.2.2 pH, redox, conductivity

The pH, redox and conductivity data are those on days 1, 7, and 14 of the growth experiment, following the sampling of the interstitial water. We tried to understand if there might be some temporal, or spatial or general trend in these parameters, the results are shown below.

Temporal trend

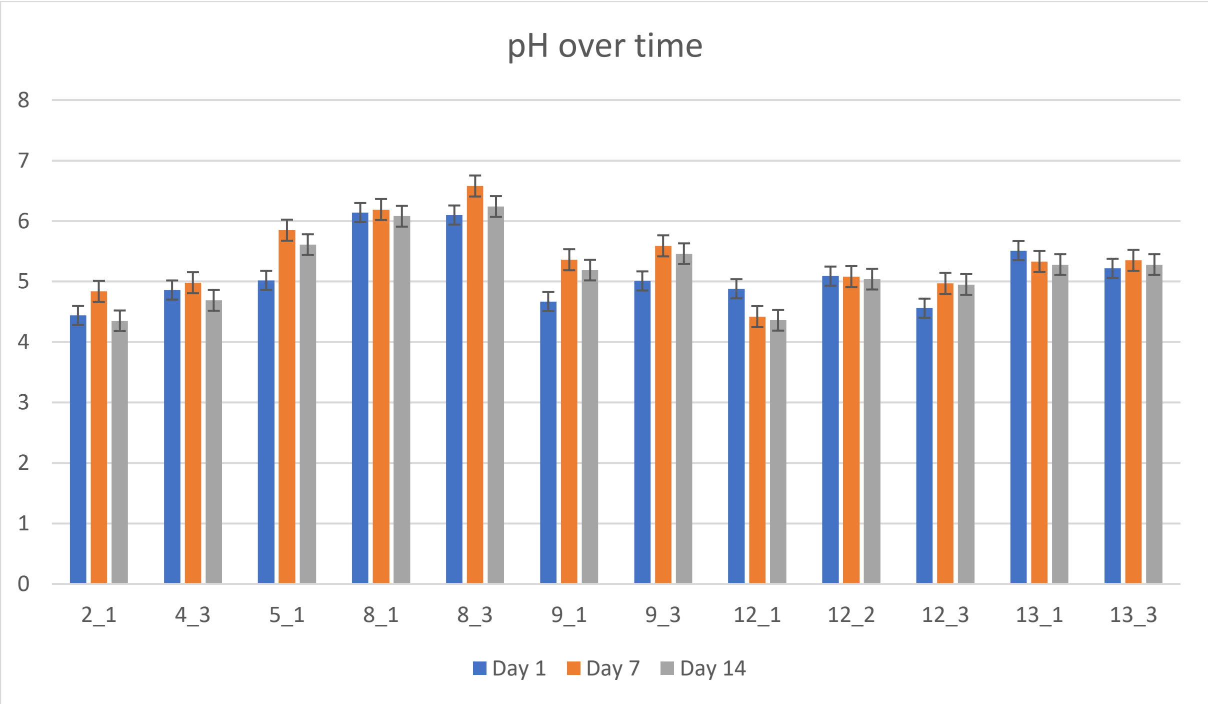

Figure 5.14. Temporal trend for the pH of the interstitial water.

Studying all the pH data, no temporal trends were noted. Figure 5.14 shows the pH values measured on days 1, 7, and 14 for the twelve mixes that provided good growth values. These mixes have been taken as an example just to show that there is no definite trend, but all the pots have reported the same behaviour.

As regards the redox potential, no temporal trend was recorded.

As regards conductivity, there was a decreasing trend over time, reported in figure 5.15. Since this trend was found in each pot, the average values were calculated for each mix (therefore mix 1 is equal to the conductivity average of vessel 1_1, 1_2, 1_3). A strong descent trend is noted especially during the first week. We have defined conductivity as a measure of the total dissolved solids, therefore of the quantity of present ions (paragraph 5.1.4). These ions represent both metals and nutrients, so the decrease over time could be given both by the adsorption of metals by biochar and peat and using nutrients by the growing biomass. To verify, these results will be integrated with the results of the ICP test.

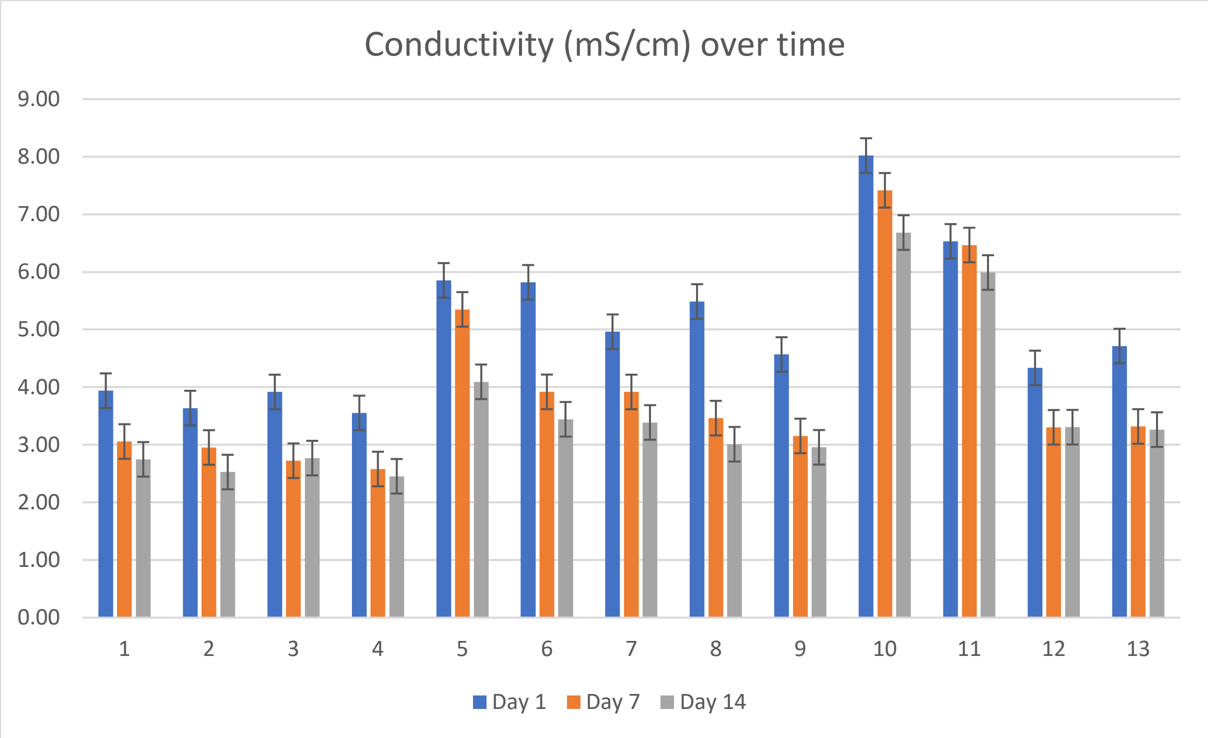

Figure 5.15. Temporal trend for the conductivity [mS/cm] of the interstitial water.

Spatial trend

We tried to demonstrate if there could be a spatial trend, based on the arrangement of the pots on the shelves, since all the pots "_1" were on the top shelf, "_3" on the intermediate one, and "_2" on the lower one. None of the parameters reported a significant spatial trend, although, in terms of biomass, only one pot over twelve managed to grow on the bottom shelf.

General trend

We also wanted to study the general trend, that is to understand which average values are assumed by each mix, to highlight the differences more easily. These values, shown in figures 6.10, 6.11, and 6.12, represent the temporal averages for each triplet, therefore they are representative average values of each mix.

As for the pH, figure 5.16, it reflects the characteristics of the additives, already studied with the leaching tests. We note how bioash is the additive that most affects the total pH value, in this case, there are values of 2.5-2.6 for the mixes with no ash, 4.5-4.8 for the mixes containing 10% ash, 5.3-5.4 for the mixes with 15% ash, and 5.7-6.5 for mixes with 20% ash.

Biochar also slightly affects the pH, raising it, this can be seen because mixes 3, 4, 7, 8 have a higher char content than mixes 1, 2, 5, and 6.

The effect of peat is also noticeable, especially in mixes 5 to 8. Peat has an acid pH, in fact, the mixes 6 and 8 which have a higher content, record a lower pH.

The compost percentages are constant, so no substantial differences can be deduced. In general, the results reflect what was already expected, from the results of the leaching tests.

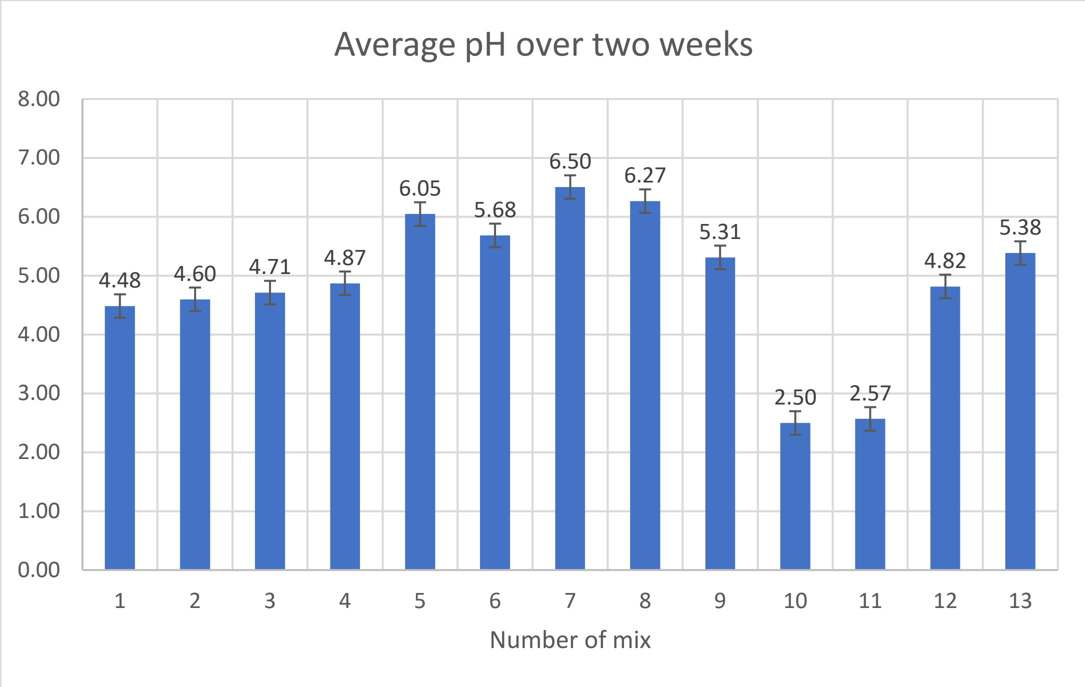

Figure 5.16. Average pH values during the two weeks of growth.

For the redox potential, for mixes without ash it is around 340-360 V, for 10% ash around 180 mV, for 15% ash around 130-150 mV, for 20% ash around 110-130 mV. Hence the redox potential decreases as the ash content increases.

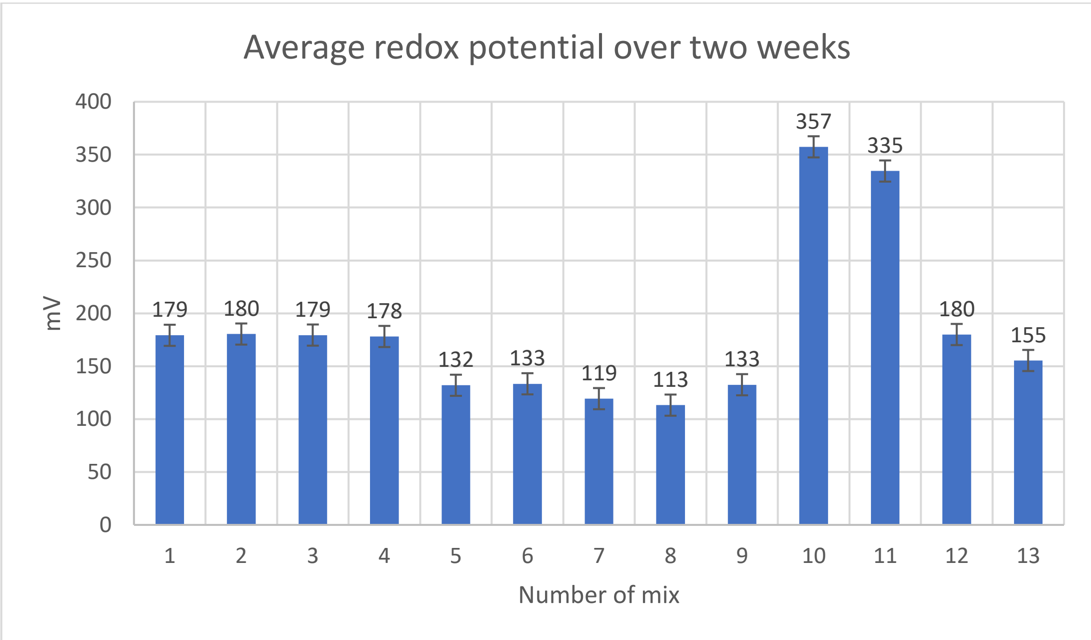

Figure 5.17. Average redox potential values during the two weeks of growth.

For conductivity (figure 5.18), the effects of peat and biochar are quite evident due to their adsorbing properties; where there is more peat, the conductivity is lower (see 2vs1, 4vs3, 6vs5, 8vs7), and where there is more char, the conductivity is lower (see 3-4 vs 1-2, 7-8 vs 5-6).

Furthermore, it should be noted that where there is more ash, the conductivity is higher (see 5vs1), even if in any case the conductivity is lower than in untreated soil (number 10). Therefore, the addition of additives, in any case, decreases the conductivity.

It should also be noted that in mixtures 12 and 13, although there is a difference in the ash of 5%, the difference in conductivity is not so marked, this could be due to the adsorbing properties of peat and char which are present in higher percentages than the other mixes.

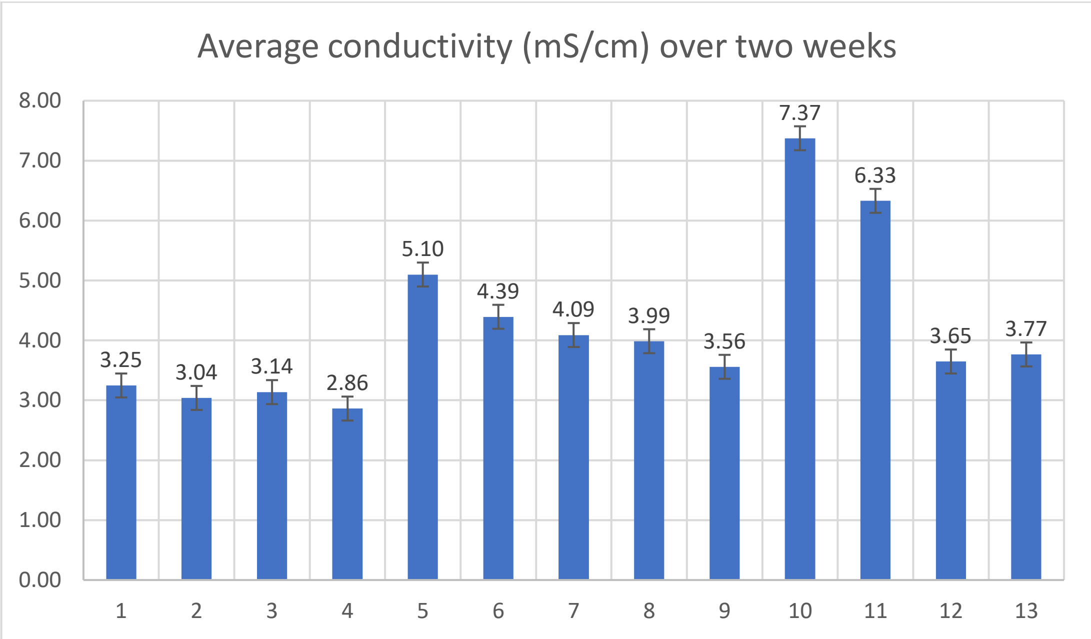

Figure 5.18. Average conductivity values during the two weeks of growth.

5.2.3 Heavy metals in interstitial water

In this section, we will analyse the concentrations of heavy metals detected through the ICP analysis conducted on the samples of extracted interstitial water. We will focus only on the pots that have reported sufficient growth of vegetation and compare the results with the Italian and Swedish limits in terms of underground waters, already seen in section 2.6.

Cadmium

For groundwater, cadmium is the metal subject to stricter limits, i.e., 5 µg/l in both Italian and Swedish legislation. In figure 5.19, the cadmium concentration in the interstitial water is reported and the black line is the limit.

It is noted that the pots that always respect the limit are 8_1, 8_3, and 13_1, so even though the "8" mixes were the ones with the highest ash content and from which the highest content of heavy metals was expected, they are instead those that report the lesser content.

The pot reporting the highest concentration on average is 2_1 and this may also have limited biomass growth.

There is no trend over time common to all pots, in some cases, there is even an increase in concentration over time. This is likely due to the uncertainty of sampling and measurement, not a real increase in concentration. At most, the concentration could be stable over time.

Taking as a reference the blank, that is the untreated soil, an average cadmium value of 80 µg/l is recorded in it, so it is noted that the addition of additives has led to much lower concentrations of cadmium, probably thanks to the increase in pH and metal immobilization.

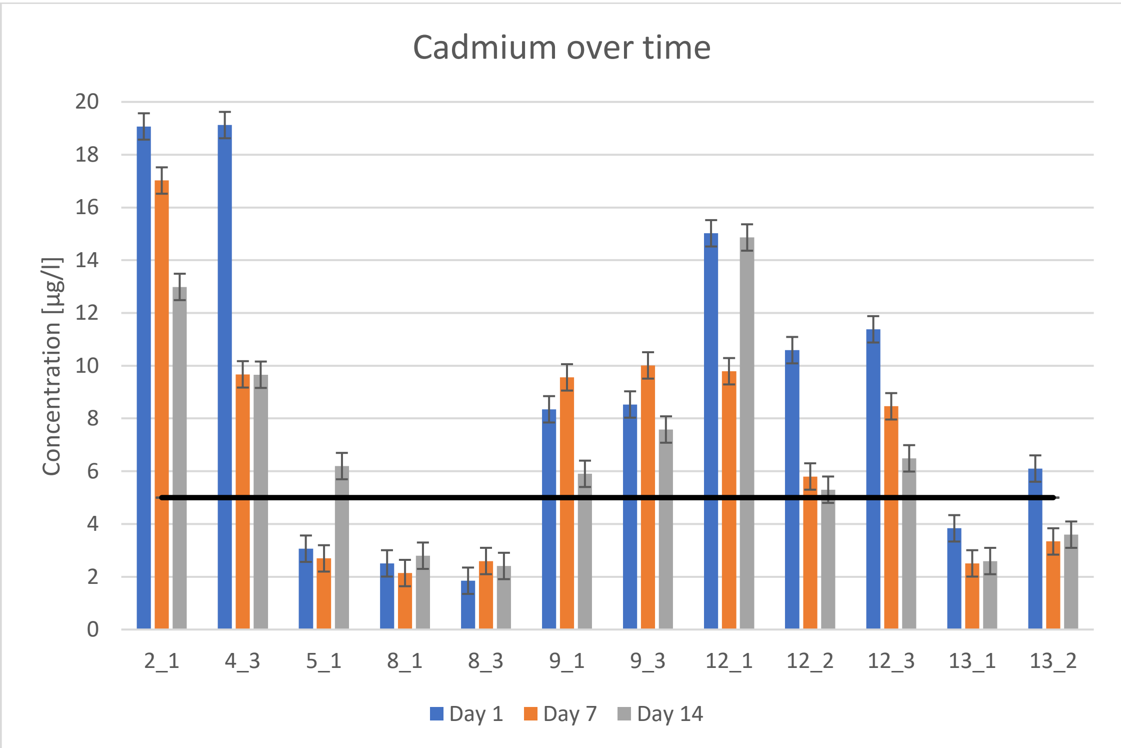

Figure 5.19. Cadmium concentration over time, the blank has an average value of 80 µg/l.

Arsenic

For groundwater, the Italian limit is 10 µg/l, while the Swedish limit is 50 µg/l. In figure 5.20, the arsenic concentration over time is reported, and the blue line represents the Swedish limit, while the yellow line represents the Italian limit.

No pot can respect the Italian limit, while the Swedish limit is almost always respected, apart from the 8_1 mix on day 7. In general, arsenic is the metal, among those studied, that is most tolerated by plants, so obviously not respecting the limits is a health problem, but this should not have affected the growth of biomass too much. In reference to the blank, it records an average arsenic value of 420 µg/l, much higher than the others mix.

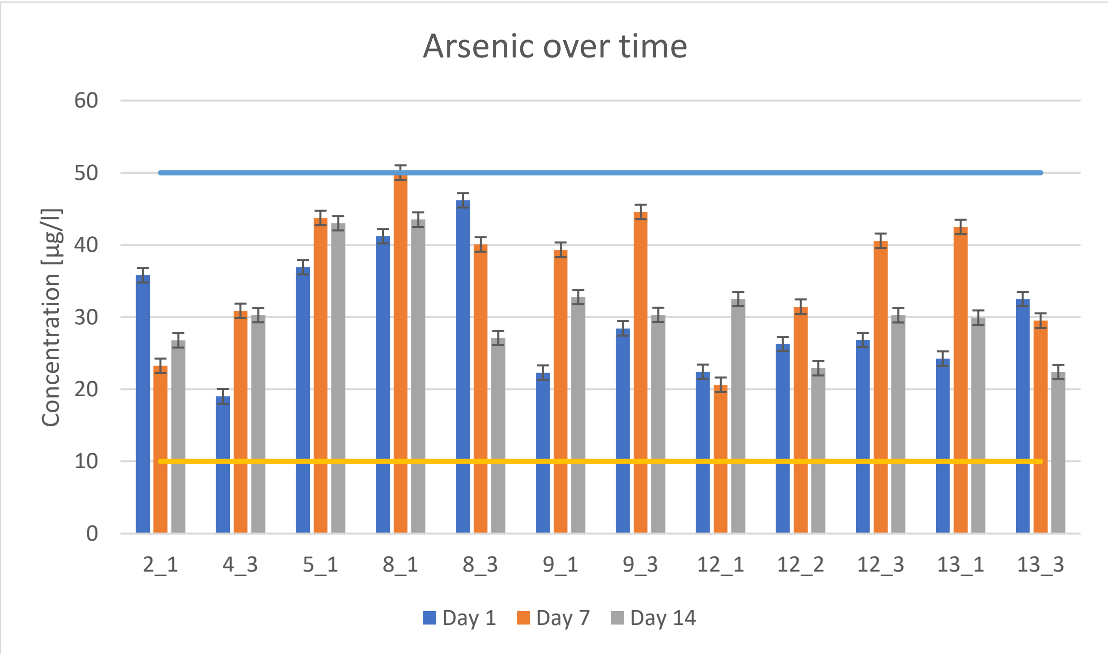

Figure 5.20. Arsenic concentration over time, the blank has an average value of 420 µg/l.

Copper

For groundwater, the Italian limit is 1000 µg/l, the Swedish limit is 2000 µg/l. Its trend is reported in figure 5.21, where the limits are not shown because they are too high.

In this case, all recorded values are much lower than the limits. There are two values much higher than the others as regards day 1 of the 12_1 and 12_2 mixtures, which however record a strong decrease on day 7. For the others, they register homogeneous values, and, in most cases, there is a decrease in concentration over time.

Also, in this case the blank records an average value of copper much higher than the mixes, it is 3700 µg/l, which is much higher than the limits.

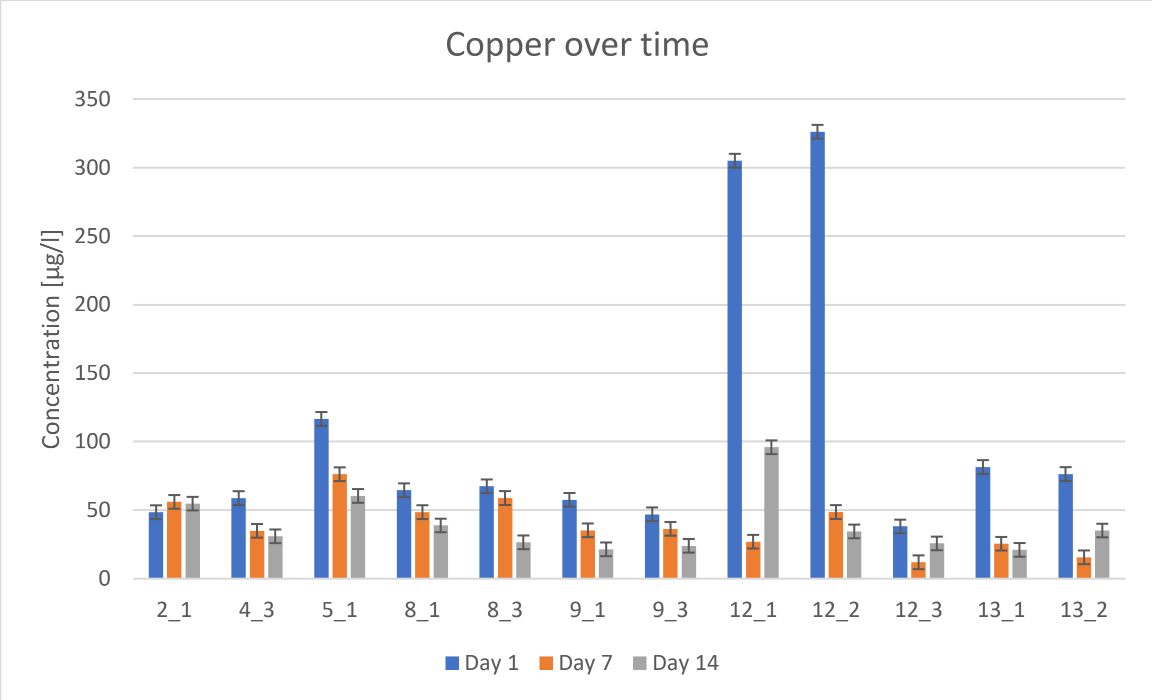

Figure 5.21. Copper concentration over time, the blank has an average value of 3700 µg/l.

Lead

The Italian and Swedish limits are the same, equal to 10 µg/l; data and limit are reported in figure 5.22. Also in this case, the mixes 8_1 and 8_3 have values well below the limit, which is unexpected given that they are the ones with the highest percentage of ashes. The mix 13_1 has very high values: 850 µg/l on the first day, 51 µg/l on day 7 and 37 µg/l on the last day. Also, in this case the blank records an average value of copper much higher than the other mixes, it is 660 µg/l, which is much higher than the limit.

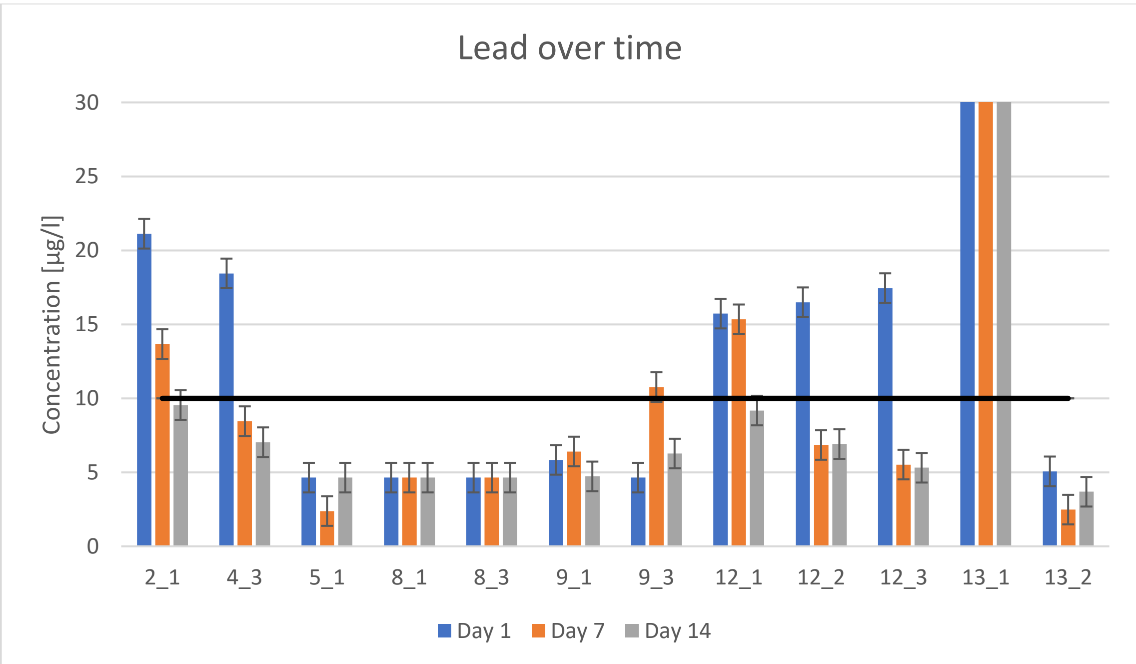

Figure 5.22. Lead concentration over time, the blank has an average value of 660 µg/l.

Zinc

Figure 5.23 shows the zinc concentrations and the Italian limit of 3000 µg/l, while the Swedish limit was not reported in Table 3 of Appendix 4th of the MIFO document.

Again, the lowest concentrations are reported from mixes 8_1 and 8_3 and the highest from 2_1 and 4_3. Also 13_1, 13_2 and 5_1 largely respect the limit, while the others do not.

Here too, blank pot shows an average value that is extremely higher than the others, equal to 22700 µg/l.

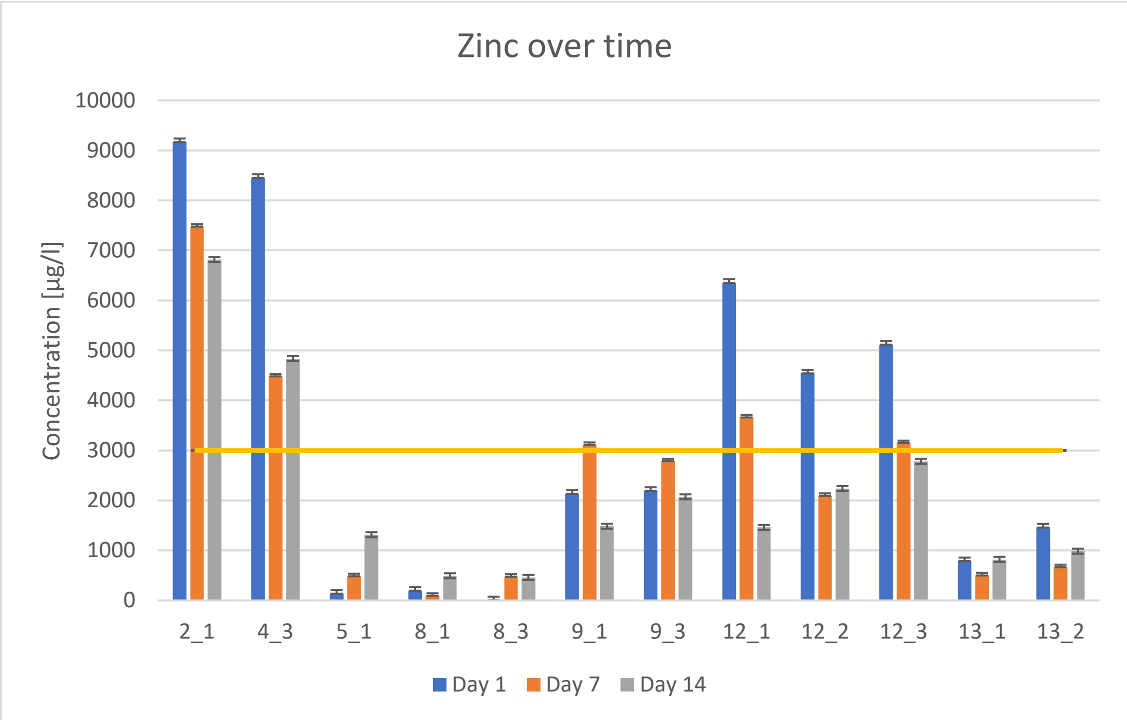

Figure 5.23. Zinc concentration over time, the blank has an average value of 22700 µg/l.

It can be concluded that, although against all odds, the mixes 8_1 and 8_3 are those that reported the lowest concentrations of metals, except for arsenic, for which all the mixes had concentrations beyond the Italian limit, and in general 8_1 and 8_3 they were the ones with slightly higher values. However, comparing these results with those of biomass growth, the mixes 8_1 and 8_3 are confirmed as the most successful mixes for both parameters.

5.3 Sources of errors

One of the main sources of error that might potentially affect the results is to assume that the mixtures created are homogeneous.

Furthermore, during the growing season, an attempt was made to maintain a water content of 60% of the WHC, with a range of variation of 3%. This was obviously not easy and was not always respected. There were nights during which there was more evaporation and consequently it could be as low as

50% of the WHC. The next morning there was again integration of the missing water, but the fluctuations may have affected the growth.

Also, during the interstitial water sampling period, lasting two weeks, the daily temperature fluctuated a lot, from 20-25°C in the first week to 15-20°C in the second week. This may have affected the growth but especially the sensitivity of the measuring instruments, such as the pH-meter, which is quite affected by the temperature.

In general, the most common sources of error are related to the sensitivity of the instruments for sampling, weighing, and measuring, combined with the experience of the performer.

In addition, the choice of standards/methods can also be considered as a source of error when it has not been possible to carry them out completely due to laboratory conditions.

Finally, the inexperience related to the bean growth experiment certainly influenced the execution, in fact pots 12 and 13 which were created a week later, gave more homogeneous growth results, this is also due to more manual and experienced bean care.

Chapter 6
Conclusion

When the sulphide soil is excavated and gets in contact with oxygen, it oxidizes reaching very acid pH (from 2 to 4), which favour the mobilization of metals that can leach up to pollute the groundwater and nearby water courses and making the land incompatible with its reuse, so in most cases it is disposed of in landfills, which is the safest, but also the most expensive and impactful solution, because it implies the loss of land. The problem of sustainable treatment of sulphide soils is very topical and Sweden is investing heavily in the search for alternative treatments.

The aim of the project was to investigate if it was possible a way to recycle this soil, to guarantee it a second life. To do this, we studied how the soil could respond to the addition of some additives that would restore and improve its pre-oxidation characteristics.

The addition of additives had to serve to counteract the acidity of the soil, raising its pH, to reduce the leaching of metals, and create the suitable conditions for the development of vegetation, thanks to an increase in porosity and concentration of nutrients in the soil.

The materials used were bioash, residue from the combustion of biomass, alkaline and capable of strongly raising the pH of the soil; biochar, residue of hydrothermal carbonization of biomass, alkaline and with adsorbent properties for some metals; peat, from the production undercut, with the aim of increasing the porosity of the soil and for the adsorption of some metals; finally compost, directly from the composting centre of Luleå, with the aim of providing organic matter and nutrients to the soil to improve the development of vegetation.

The methods used were a series of laboratory tests to characterize the materials used (XRF, TS, VS, bulk density, pH, WHC) and numerous leaching tests to understand what the best quantities of additives were to add to the soil to pursue the purpose. Once the most suitable mixes were identified for the project, a growth experiment was carried out, where the seeds of the bean were planted, and the growth was monitored for two weeks. Finally, a comparison was made based on the grown biomass, the pH, redox and conductivity characteristics of the mixes and the concentrations of polluting metals in the interstitial water.

It was therefore possible to identify a better mix than all the others. This is mix number 8, consisting of soil, ash (20% by weight), char (4% by weight), peat (8% by weight), compost (5% by weight).

Biomass growth was the best for all parameters and, as for the heavy metal concentration in the interstitial water, they were always respected, except for arsenic, compared with the Swedish legislation (MIFO guidelines, appendix 4, table 3) and the Italian legislation for groundwater quality (D. Lgs. 152/06, 4th part, Annex 5, table 2).

However, what could be done in a real application is to select ash with lower arsenic content compared to what used in performed tests.

Mix 8 (soil, 20% ash, 4% char, 8% peat, 5% compost) had an average pH value overtime of 6.3, a pH close to neutrality that certainly contributed to the immobilization of the metals, and which consequently reported the lowest values of metals in the interstitial water.

A doubt to be verified is whether this ability to buffer the acidity of soil can be kept in the long term, under equilibrium conditions.

6.1 Full scale recycling

If this solution had to be implemented in the field, it would be necessary to dry the soil, to shorten the oxidation process which naturally brings the soil pH at 2.5-3.

Another reason why the drying was carried out is that in the sampling conditions the soil was clayey, very compact, and difficult to work, so mixing it with the other additives would have been extremely difficult and a very heterogeneous matrix would have formed, losing the goal of the experiment, that is the creation of soil as homogeneous as possible, to have an effective interaction between the components.

A drying phase would require certain energy expenditure. The treatment could be carried out on-site, through a mobile rotating drum kiln, or in an ex-situ plant. However, in this last case, costs due to the transport of the solid matrix should be accounted for.

After drying, a phase of crashing of the agglomerates would be necessary to create a homogeneous powder. In our case, it was done manually but for large quantities of soil, it must be done with suitable machinery.

As for in the lab, a mechanical mixing phase between materials should be also performed.

Finally, the irrigation phase would be required to favour the balancing processes between the components and then to planting.

As far as costs are concerned, it should be remembered that all used additives can be considered as waste. Bioash is the residue of incineration, the biochar used is the residue of hydrothermal carbonization, the peat used is the by-product of the production of floating peat for oil adsorption and the compost comes from the Luleå composting plant. No raw material was used for this treatment technology, so the real costs can only be attributed to the pre-treatments just described to prepare the soil as a new growth substrate.

6.2 Future research

The work consisted of laboratory experiments using simple methods and during a short period, analysing only metal and nutrient concentrations, measuring pH, conductivity, redox and plant growth.

The geotechnical properties of the soil were not studied in this work, which is an important aspect of soil in construction work.

Furthermore, the problem of arsenic concentration not respecting the limits needs to be solved, try to see if using other ashes, with a lower arsenic content, the result would be different.

It is recommended to test a pilot plant to study how the method works on a real scale.

In addition, the long-term effects of this technology should be studied, i.e., whether the characteristics of the interstitial water change over time and how the geotechnical properties of the soil may respond over time.

The work shows that there are good conditions for the implementation of this treatment, but further research should be done, also on the best type of vegetation to be used.

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Appendix A
Special features of the soil after drying

Appendix B
Total weight, dry weight (or total solids TS) and percentages referred to dry weight

Mix number	1	2	3	4	5	6	7	8	9
Soil total (g)	250	250	250	250	250	250	250	250	250
Soil TS (g)	230	230	230	230	230	230	230	230	230
Ash total (g)	25	25	25	25	50	50	50	50	37.5
Ash TS (g)	22.25	22.25	22.25	22.25	44.5	44.5	44.5	44.5	33.38
Ash (%)	9.67%	9.67%	9.67%	9.67%	19.35%	19.35%	19.35%	19.35%	14.51%
Char total (g)	0.25	0.25	10	10	0.25	0.25	10	10	5.13
Char TS (g)	0.25	0.25	10	10	0.25	0.25	10	10	5.13
Char (%)	0.11%	0.11%	4.35%	4.35%	0.11%	0.11%	4.35%	4.35%	2.23%
Peat total (g)	5	20	5	20	5	20	5	20	12.5
Peat TS (g)	4.35	17.4	4.35	17.4	4.35	17.4	4.35	17.4	10.88
Peat (%)	1.89%	7.57%	1.89%	7.57%	1.89%	7.57%	1.89%	7.57%	4.73%
Compost total (g)	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
Compost TS (%)	7.13	7.13	7.13	7.13	7.13	7.13	7.13	7.13	7.13
Compost (%)	3.1%	3.1%	3.1%	3.1%	3.1%	3.1%	3.1%	3.1%	3.1%

Mix number	10	11	12	13
Soil total (g)	250	250	250	250
Soil TS (g)	230	230	230	230
Ash total (g)	0	0	25.9	38.8
Ash TS (g)	0	0	23.05	34.53
Ash (%)	0.00%	0.00%	10.02%	15.01%
Char total (g)	0	0	13.9	13.9
Char TS (g)	0	0	13.9	13.9
Char (%)	0.00%	0.00%	6.04%	6.04%
Peat total (g)	0	0	26.4	26.4
Peat TS (g)	0	0	22.97	22.97
Peat (%)	0.00%	0.00%	9.99%	9.99%
Compost total (g)	0	12.5	40.8	40.8
Compost TS (%)	0	7.13	23.26	23.26
Compost (%)	0.0%	3.1%	10.1%	10.1%