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ANALYSIS OF SOILS LEACHATES TREATED WITH DIFFERENT SULFUR BASED PRODUCTS

Analisi dei percolati di suoli trattati con differenti prodotti a base
di zolfo

TIPO TESI: sperimentale

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1. INTRODUCTION

1.1 SOIL DEFINITION

Soil is considered as the fine earth that covers land surfaces in which plant grows and provides to them with physical support, water, and nutrients. It is the result of the *in situ* weathering of rocks or the accumulation of mineral matter transported by water, wind, or ice. The weathered soil is added with organic material inherited by the degradation of dead material or by the activity of living organisms. The dead organic matter includes little altered and freshly added dead plant roots and leaf and other plant litter, dead fauna, and organic material in various stages of decomposition from little modified relatively fresh materials to the complex decomposed material called humus. As a result, soil differs from its parent material in texture, structure, consistency, color, chemical, biological and physical characteristics (Northcliff et al., 2012).

Due to these characteristics, soil is a multifunctional ecosystem since provides food purifies water, fiber and fuel and support animal and human activities, these include functions related to natural ecosystems, agricultural productivity, environmental quality, soil as source of raw materials and as base for buildings, other human infrastructure and cultural heritage.

It has an important role in the climate regulation, soil in fact can be a trap for the CO₂ and other gasses that cause the rising of temperature, this particular activity leads to another important function that is the accumulation of carbon, “the quantity of accumulated carbon in soils can space between 30 to 580 t/ha” (Freppaz M. 2019).

Without any doubt among these, the agricultural productivity function is probably the most widely recognized and understood.



Fig. 1 Soil functions scheme

1.1.2 SOIL HORIZONS

Soil is characterized by a vertical sequence, parallel to the surface of the soil, distinguishable from adjacent layers by a distinctive set of properties produced by the soil-forming processes. The term “horizon” is used to define these layering, differentiated by physical, chemical, or biological characteristics. This sequence of horizons is normally described as the soil profile (Owens and Rutledge, 2005).

The horizons are classified by:

- **Capital letters** (H, O, A, E, B, C, R, I, L, W), used to designate the master horizons and layers;
- **Lowercase letters:** used as suffixes to indicate specific characteristics of master horizons and layers;
- **Numbers:** used both as suffixes to indicate vertical subdivisions within a horizon or layer and as prefixes to indicate discontinuities;
- **Special symbols:** used to indicate layers formed in human-transported material or sequences of horizons having otherwise identical designations. (Soil Survey staff. 1999)

- The first horizons that we encounter is the “H” one, this particular horizon is mostly composed by organic material originated from the non-decomposition of organic matter.
- Then there is the “O” horizon which composition consists of undecomposed or partially decomposed organic material such as leaves, lichens, twigs and moss. They can be on top of both mineral and organic soils, these horizons aren’t saturated with water for long periods.
- “A” horizons are mineral based and they can be find at the surface or below “O” horizons; in these ones all of the original rock structure has been dislodged. They are characterized by the mix of organic matter and mineral fraction or by the resulting of cultivation and pasturing.

Generally, the O and A horizons are considered the biologically most active part of the soil and are also subject to considerable changes as a result of the weather, being frequently exposed to wetting and drying cycles and to a wide range of temperatures, which results in high rates of activity in physical and chemical processes (Northcliff et al. 2012).

- “E” horizons are also mineral based, particularly they are characterized by the loss of silicate clay and metals like aluminum and iron which means that their main structure is made up of sands and silt particles; due to this characteristic, these types of horizons are less dark than the following “B” horizons.
- Originally subsurface horizons, “B” horizons are the result of illuvial concentration of silicate clay, iron, aluminium, humus and residual concentration of sesquioxides, that make these horizons lower

in value and higher in chroma and also brittle. They represent the balance shift from predominantly biological processes to predominantly chemical and physical processes. This is the most important zone for the pedological or soil-forming processes, in fact this zone is considered by the pedologists, the one with the peak activity for the formation of soil, and for this reason they pay attention to the B horizon for the allocation of soils to classes.

- “C” horizons, called also layers, aren’t so much affected by the pedogenetic processes, they are mineral layers that can include coral and diatomaceous earth. These layers can be modified even if there is no evidence of pedogenesis.
- “R” layers are made of hard bedrock characterized by granite, basalt, quartzite and either limestone or sandstone. Bedrock can contain cracks but they are very small and only few roots can penetrate.
- “T” layers are ice lenses constituted by 75 percent of ice by volume. The “T” isn’t used in horizon designations.
- ”L” layers, are subaqueous layers made of both organic and inorganic materials (limnic material), the “L” symbol like the “T” isn’t used to classify the horizons.
- “W layers, are water layers or submerging soils that can permanently or cyclic surface in the time frame of 24 hours.

1.2 MAJOR THREATS OF SOIL DEGRADATION

Soil is subjected to degradation processes and threats such as erosion, loss of organic matter, contamination, sealing, compaction, biodiversity decrease, floods and salinisation, all together these risks can lead to the desertification. This thesis is focused on one of these threats, the salinisation.

In the following section it is explained what salinisation is and how it is fought.

1.2.1 SALINISATION

Salinity is an increasing environmental problem in agricultural ecosystems.

It is a promoter and a consequence of desertification, that is the progressive degradation of fertility in the surface layer of the soil and of the production capacity of arid, semiarid and dry sub-humid lands, which can be attributed to stresses due to climate and to the unsustainable pressure of human activity on the environment (UNEP 1994).

1.2.2 A VIEW ON THE SALINISATION WORLDWIDE

Soil salinisation is a term that includes saline, sodic and alkaline soils (van Beek and Tóth, 2012), respectively defined as (a) high salt concentration, (b) high sodium cation (Na^+) concentration, and (c) high pH, often due to high CO_3^{2-} concentration, in the soil.

Soil salinisation is a widespread phenomenon and one of the major soil degradation threats worldwide, with Europe contributes about 30.7 Mha or 3.3% of the global saline and sodic soils (Rengasamy, 2006).

Global soil salinisation hotspots include Pakistan, China, United States, India, Argentina, Sudan and many countries in Central and Western Asia, while at European scale the Mediterranean coastline stands out. Effectively, this soil threat has gained worldwide attention in the State of the Art, as concern has grown about irrigation mismanagement , organic and inorganic amendment selection and quantification, and the role of plant tolerance and soil fauna in the adaptation and soil reclamation process.

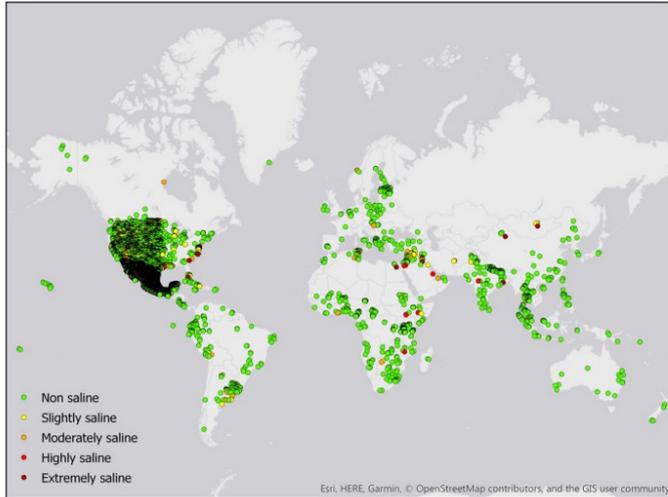


Fig. 2 Global map of salinisation

SALIC HORIZONS IN SOILS

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Fig. 3 Map salinisation in USA

1.2.3 DRIVERS AND TYPES OF SALINISATION

1.2.3.1. Primary salinity

Primary salinisation is the development of salts through natural processes, mainly including physical or chemical weathering and transport from parent material, geological deposits or groundwater (Fig. 1). Soil may be rich in salts due to parent rock constituents such as carbonate minerals and/or feldspar. Closely related to this, geological events or specific formations can increase salt concentration in groundwater and therefore in superimposed soil layers. This can occur when, after capillary effects or evapotranspiration cause salinity affected groundwater to rise, previously dissolved salts accumulate at or near the surface (Chari et al., 2012, Geeson et al., 2003). These drivers affect the soil depending on aquifer architecture and hydraulic conductivity of geological layers and soil characteristics such as porosity, structure and texture, clay mineral composition; compaction rate, infiltration rate, water storage capacity, saturated and unsaturated hydraulic conductivity and finally potential salt content. In total, the types of saline or saline prone soil formed as listed by WRB (2014) are shown in Table 1; the **World Reference Base for Soil Resources (WRB)** is an international soil classification system for naming soils and creating legends for soil maps. The WRB is edited by a working group of the International Union of Soil Sciences (IUSS). The current chair of the working group is Peter Schad (Technical University of Munich, Germany, since 2010). The current vice-chair is Stephan Mantel (International Soil Reference and Information Centre, The Netherlands, since 2018). Chairs of the WRB working group and responsible first authors of the WRB editions are: Seppe Deckers (Belgium, 1st edition 1998), Erika Michéli (Hungary, 2nd edition 2006) and Peter Schad (Germany, 3rd edition 2014).

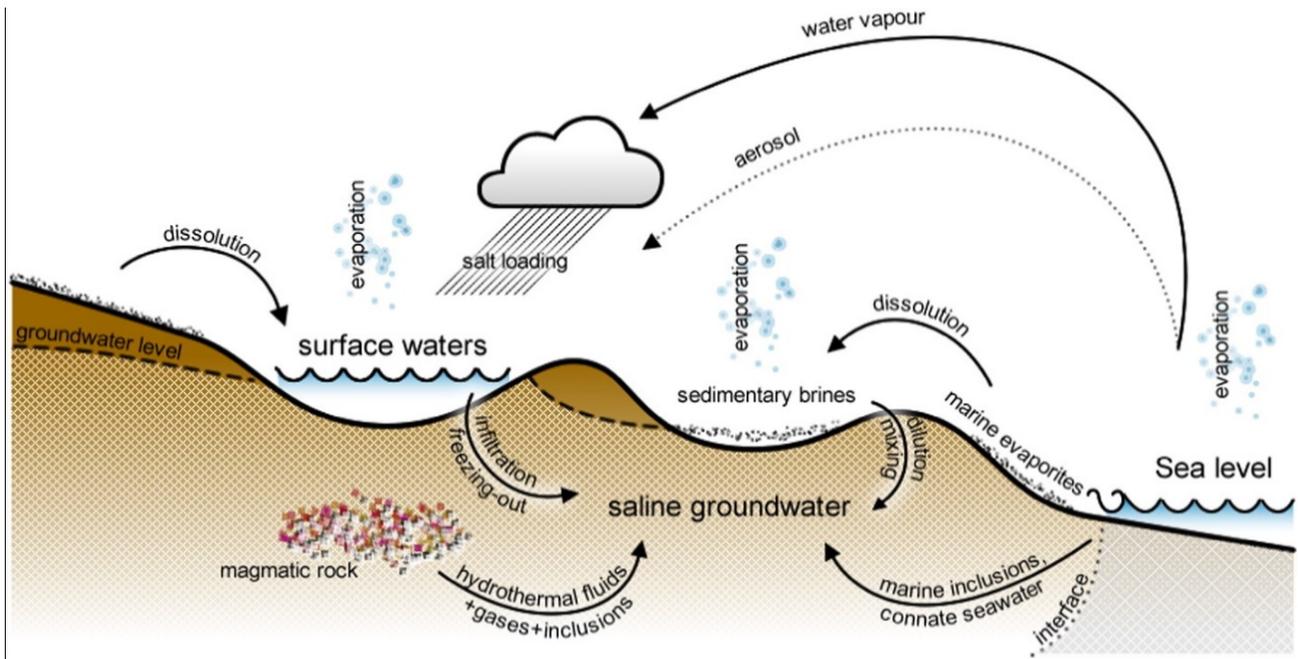


Fig. 4 Primary soil salinity mechanisms.

Table 1. Types of saline or saline prone soil formed as listed by WRB (2014).

Soil types	Main characteristics	Saline	Saline Prone
Solonetz	Subsurface clay accumulation, rich in sodium	x	
Solonchak	Strongly saline	x	
Acrisol	Subsurface accumulation of low-activity clays and low base saturation		x
Alisol	Subsurface accumulation of high-activity clays, rich in exchangeable aluminium		x

Soil types	Main characteristics	Saline	Saline Prone
Calcisol	Accumulation of secondary calcium carbonates		×
Fluvisol	Relatively young in alluvial deposits		×
Gleysol	Permanent or temporary wetness near the surface		×
Luvisol	Subsurface accumulation of high-activity clays		×
Vertisol	Dark-coloured cracking and swelling clays		×

Apart from the long-term accumulation of salts in the soil profile, natural soil salinisation can also pre-exist due to once submerged soils under seawater. During this period, seawater fills the voids of the sediments and remains enclosed within the marine deposits, even after the seawater incursion. Besides historical marine waters, contemporary sea level rises may cause seawater to flood coastal land, either for long (marine transgressions) or short (storm flood events, tsunamis) periods. In addition, these rises may boost lateral seawater intrusion into coastal areas that are hydraulically connected to the sea, causing wide-spread soil salinity problems across regions near the coast, as observed in Western Netherlands, Denmark, Belgium, North-eastern France, and South-eastern England (Raats, 2014, Trnka et al., 2013, van Weert et al., 2009).

1.2.3.2. Secondary salinity

Contrary to primary salinisation, secondary salinisation is introduced by human interventions; mainly irrigation with saline water or other ill-suited irrigation practices often coupled with poor drainage conditions. With a climate predominated by little rainfall and adverse evapotranspiration rates, and soil characteristics that restrain salt leaching, arid irrigated lands are prominent salinisation hotspots. While constant or increasing salt accumulation in the upper soil layers is primarily the result of irrigation sourced from highly saline water such as seawater contaminated groundwater, moderate problems are observed even when sufficient quality water is used. As such, salinisation is a major factor limiting crop production and land development in arid coastal areas.

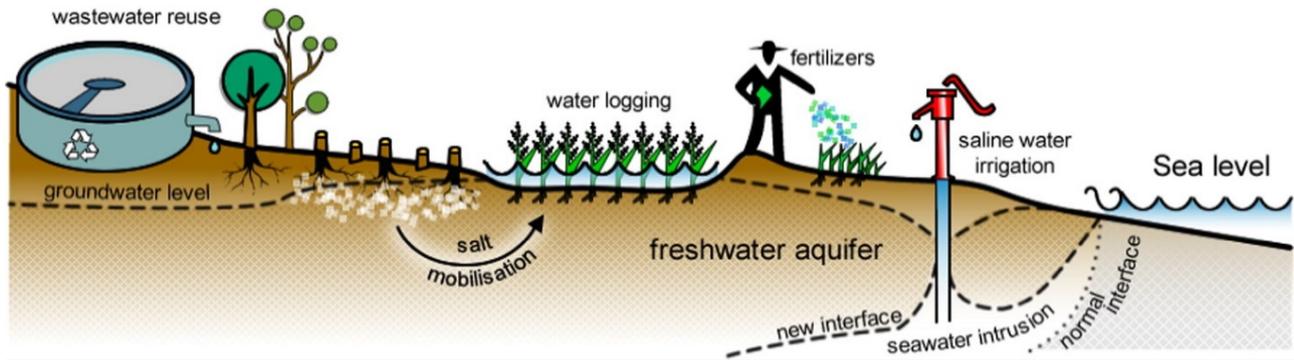


Fig. 5 Secondary soil salinity mechanisms.

Interventions that increase time of ponding or limit sufficient drainage can also lead to salinisation. An increased water table level due to filtration from unlined canals, reservoirs and waterlogging (Barros et al., 2012), uneven distribution of irrigation water, land clearing, and improper drainage may mobilise salts that have accumulated in the soil layers (Chesworth, 2008, Eckelmann et al., 2006). Salty groundwater may reach the upper soil layers and, thus, supply salts to the root zone. Additional hurdles to good drainage may be posed by coastal protection infrastructure aiming to reducing seawater encroachment into the aquifers but ergo blocking natural drains of rich in salts discharges. In arid regions, poorly drained soils, also allow for too much evaporation leading to salt residuals on the soil surface. Salinisation origins can also be relevant to soil pollution. The use of fertilizers and other inputs in association with irrigation and insufficient drainage cause soil salinisation, markedly in cases of intensive agriculture in compacted and limited leaching soils (Eckelmann et al., 2006). Wastewater treatment, or mining operation effluents are often rich in salts, therefore their mismanaged subsurface injection, surface disposal or use for irrigation, can also lead to soil salinisation. Finally, the use of traditional salt based de-icing agents in excess contributes to the accumulation of salt in the soil and water (Mateo-Sagasta and Burke, 2011).

According to Stanners and Bourdeau (1995), secondary salinisation affects around 3.8 Mha in Europe. Using expert judgement, van Camp et al. (2004) assessed that approximately 4 Mha of European soils have a moderate to high level of degradation due to secondary salinisation. Artificially induced salinisation is affecting significant parts of Italy (e.g. Campania and Sicily), Spain (e.g. the Ebro Valley), Hungary (e.g. Great Alfold), Greece, Cyprus, Portugal, France (West coast), the Dalmatian coast of the Balkans, Slovakia and Romania. In addition, North Europe countries (e.g. Denmark, Poland, Latvia, and Estonia) are facing similar issues. Road and bridge snow and ice control in Europe contribute 20 to 25 Mt of de-icing salt per year (Houska, 2007). Soil salinity is a major cause of desertification along the Mediterranean coast, mainly due to human activities, especially with the extension of irrigation and undisciplined use of saline water which has caused over-pumping, and the consequent sea-water infiltration into the groundwater layer. In the Mediterranean region, soil salinisation affects 25% of irrigated agricultural land at a significant level. For example, about 3% of the 3.5 Mha of irrigated land in Spain now has a significantly reduced agricultural potential due to soil salinity, with another 15% facing the same risk. Also, about 9% of the 1.4 Mha of

irrigated land in Greece is affected by soil salinisation due to seawater intrusion (Jones et al., 2003, OECD, 2009). In addition to seawater intrusion, in several areas like Cyprus, the excess use of fertilizers and municipal wastewater has contributed to the soil salinity (FAO, 2011, Huber et al., 2008, Mateo-Sagasta and Burke, 2011).

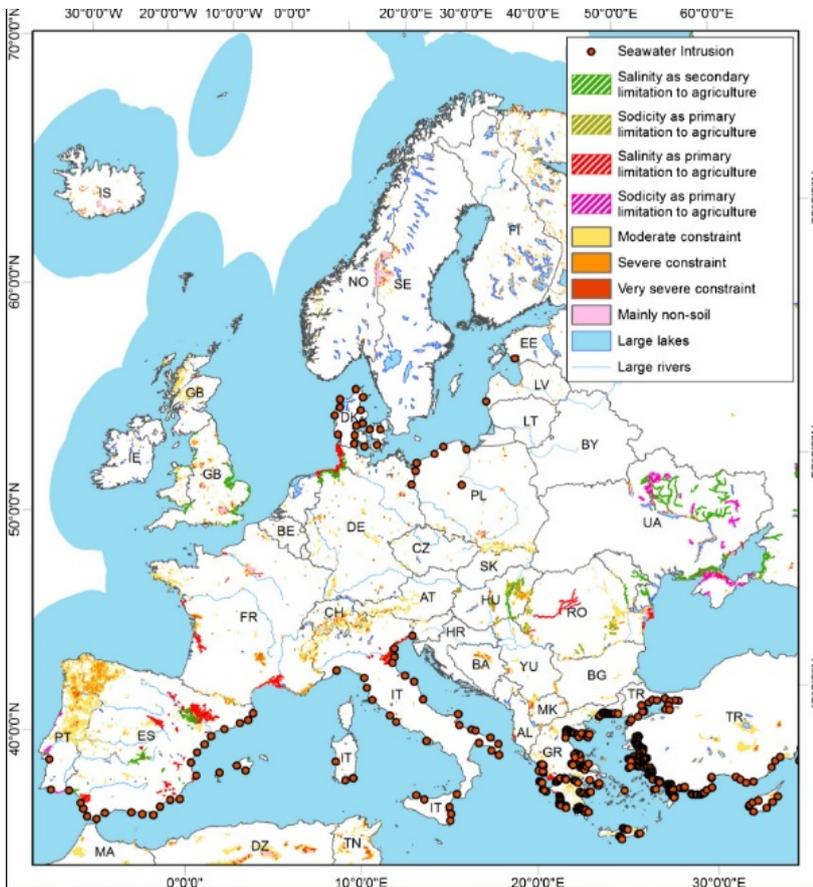


Fig. 6 Saline ($EC > 4 \text{ dS m}^{-1}$ within 100 cm of the soil surface) and sodic ($ESP > 6\%$ within 100 cm of the soil surface) soils as agricultural constraint and as primary and secondary limitations to agricultural use, and areas of seawater intrusion in Europe. Compiled from SGDBE, EEA (1999), Daskalaki and Voudouris (2008) and Fischer et al. (2008).

1.3 SULFUR

Historically speaking the Sulfur is known by men since thousands of years and probably his name comes from the Arabic word “sufra” which means “yellow”.

Only from the end of the 18th century it is been recognized as pure element and not as a compound.

The Sulfur, whose chemical symbol is “S”, is considered one of the native elements, it is found in a lot of different minerals but it is also possible find it at his pure state, not bonded to anything else. It can be found in crystalline clusters or rhombic crystals, in both cases it is bright yellow when it’s pure or brownish if there are some impurity in it.

The sulfur can be found all over the world, mostly it’s located near thermal sources and volcanic areas. In Italy we can find important deposits in Sicily (Agrigento, Catania, Palermo), Marche (Pesaro Urbino, Ancona) and Emilia-Romagna (Forli, Cesena).

1.3.1 SULFUR CYCLE

Sulfur cycles is between the atmosphere, lithosphere, and hydrosphere; but it has major reservoirs in both the atmosphere and the lithosphere.

The process begins with geochemical and meteorological processes such as the weathering of rock. When sulfur is released from the rock and comes in contact with air, it is converted into sulfate (SO_4), which is taken up by plants and microorganisms and converted into organic forms. Animals acquire these organic forms of sulfur from their foods. When organisms die and decompose, some of the sulfur enters the tissues of microorganisms and some is released again as sulfate. There is, however, a continual loss of sulfur from terrestrial ecosystems as some of it drains into lakes and streams and eventually into the ocean as runoff. Additional sulfur enters the ocean through fallout from the atmosphere.

Once in the ocean, some of the sulfur cycles through marine communities as it moves through food chains, some reenters the atmosphere, and some is lost to the ocean depths as it combines with iron to form ferrous sulfide (FeS), which is responsible for the black color of marine sediments. Sulfur reenters the atmosphere naturally in three major ways: sea spray releases large amounts of the element from the ocean into the atmosphere; anaerobic respiration by sulfate-reducing bacteria causes the release of hydrogen sulfide (H_2S) gas especially from marshes, tidal flats, and similar environments in which anaerobic microorganisms thrive; and volcanic activity releases additional but much smaller amounts of sulfur gas into the atmosphere.

Since the Industrial Revolution, human activities have contributed significantly to the movement of sulfur from the lithosphere to the atmosphere as the burning of fossil fuels and the processing of metals have

occasioned large emissions of sulfur dioxide. Oxides of sulfur and nitrogen contribute to the acid rain that is common downwind from these industrial activities (*see acid rain*).

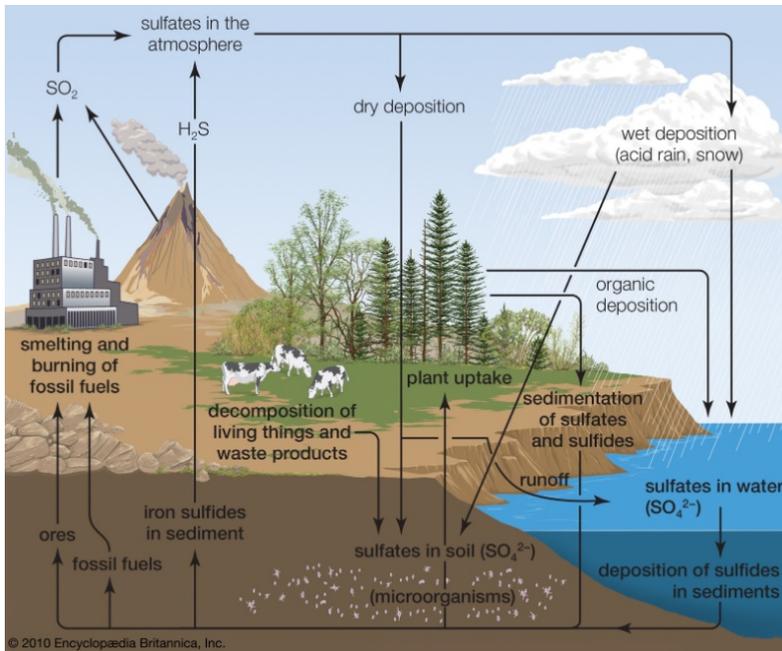


fig. 7 Sulfur cycle (The Editors Encyclopaedia Britannica)

In the soil portion explored by the plant roots, the major quantity of sulfur is contained in the organic matter (about 93-95% of the total sulfur). (Bucci V. 2018). This element in agricultural land is important for fertility and has effects on the photosynthesis, but what was studied for this thesis is the impact that sulfur has on the soil pH. In the next portion of the elaborate it is described the type of experiments conducted and what kind of materials were used, also it is documented what particular analysis were performed.

2. AIM OF THE RESEARCH

The current thesis is part of an experimental project focused on the investigation of the effects of sulfur treatments on different soils. Since these sulfur products were derived from industrial processes, with less known properties, the first steps of investigation were performed in laboratory, in order to have a controlled environment. Specifically, this research work analyzed the elemental, cation and anion content of the leachate of three different soils (volcanic, alkaline and alkaline-saline soils) treated with six different sulfur products. The interpretation of the results was implemented with the analysis of chemical, biochemical and mineralogical properties of the respective soil. For details of the setting of the experimental design see the chapter below (“Material and Method”). The intent was to observe what are the effects that sulfur has on soils and if it can represent a good resource for the correction of degraded saline soils.

3. MATERIALS AND METHODS

3.1 LOCATIONS AND SOIL TYPE

The soils used for the experimentation were:

- Volcanic (V); from Monte Amiata (Abbadia San Salvatore, SI), this soil is originated from a trachytic rock (it is testified from the presence of the plagioclase in the mineralogical composition), this soils is currently used for pasture with a good forest cover made mostly of beech trees.

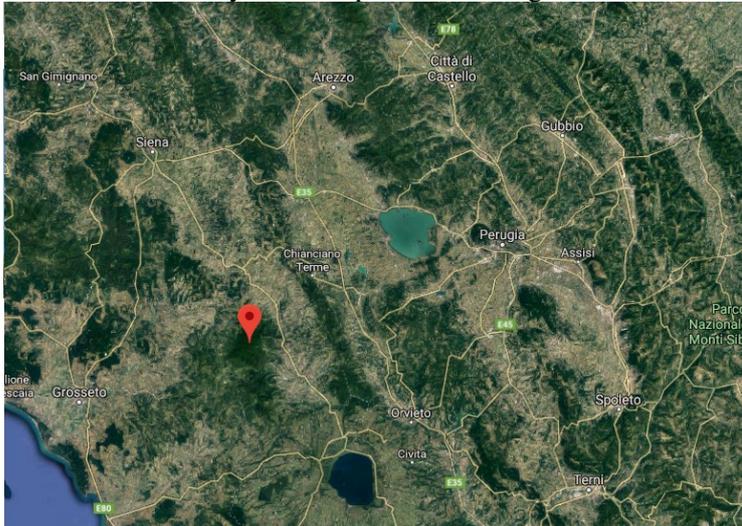


Fig. 1 Localization of the volcanic soil in Monte Amiata

- Alkaline (A1); calcareous soil used for arable from the UNIVPM’s didactical-experimental farm “P. Rosati” (Agugliano, AN)

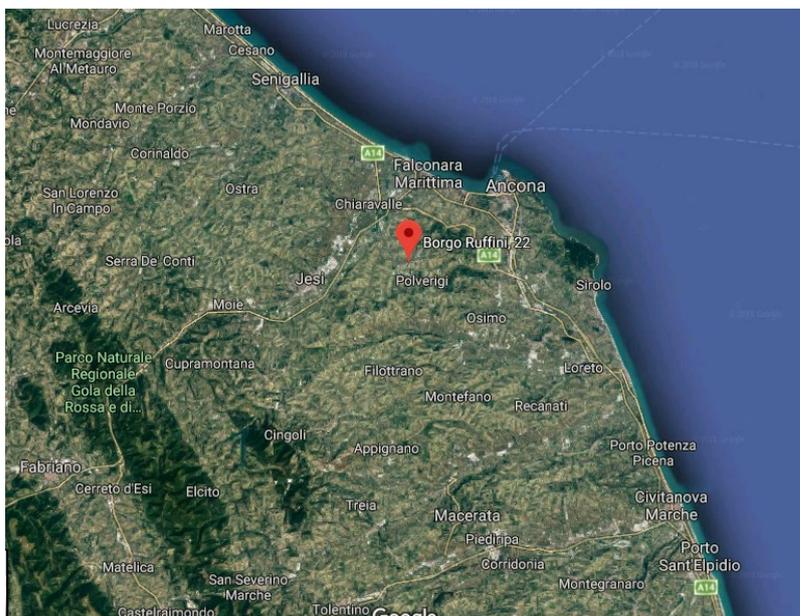


Fig. 2 Localization of alkaline soil from farm “P. Rosati” in Agugliano (AN)

- Saline-Alkaline (S1); originated from evaporitic rocks sedimentation, which salinization is the result of lithological causes. It is basically naked (minimal vegetation due to the excessive salt concentration, testified from whitening efflorescence on the surface (Saline di Volterra, PI).

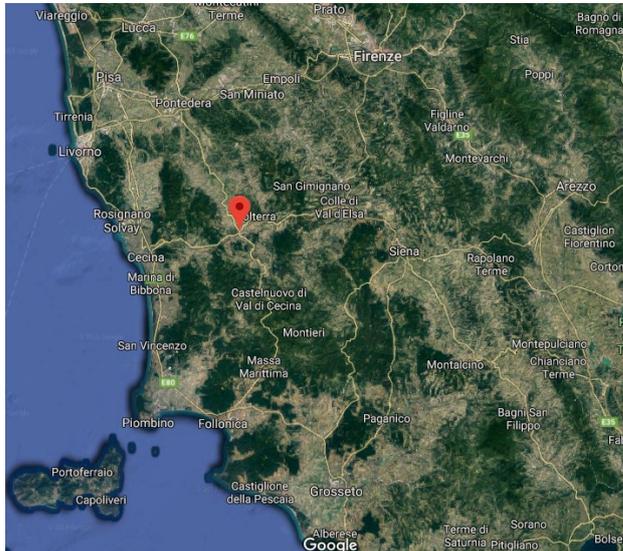


Fig. 3 Localization of Saline-Alkaline soil in Volterra (PI)

3.1.2 PRE-TREATMENTS SOIL CHARACTERIZATION

Analysis of soil characterization were performed in order to know the properties of soil before the sulfur treatments and, successively, compare the results obtain with the same analysis on soil post-treatments.

Previously the analysis, a pedological survey and sampling were made for each site.

It was taken about 90-100 kg of soil for each location.

- Based on this, the realization of the profiles, of the examined places, it was made with a manual excavation of the surface horizons with the help of both shovel and spade. The profile samples were taken from bottom to top and kept in plastic bags with recognition label which defined: sampling date, identification sign, progressive number and observed horizons. During the sampling, were discarded the roots if present, coarse fragment, stones and leaves. In laboratory, the samples were:
- dried at open air for about one month, which aim is to reduce to the minimum the biological activity and to limit the sample alteration during lab analysis.

- Disintegrated with pestle and ceramic mortar, necessary to obtain a soil fraction useful for the next step, specifically a more reactive and homogeneous one.
- Sieved and passed through the 2mm sieve to obtain the fine grained soil, the fraction that conventionally is retained more homogeneous and representative of the sample and because of that useful for the next experimental tests.

The experimental implant was built on glass columns (with an inside diameter of 8cm, and height of 18cm), each column had a sink and a sample-carrier strut. Also, each column had a filtering system for the leachate made of filter paper and glass wool in which it has been deposited 0,600 kg of soil.

The three soils investigated were treated with, six different sulfur based products (Table 1):

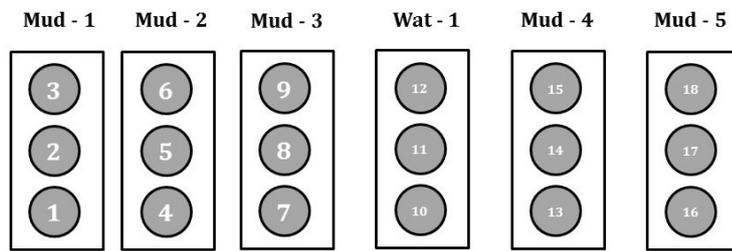
Table 1 – Identification number and label of sulfur treatment and their composition	
ID	Traatmens
Mud-1	Liquid sulfur decanted for ageing
Mud-2	Liquid sulfur with flocculant reagent I
Mud-3	Liquid sulfur with iron-based flocculant reagent
Mud-4	Liquid sulfur with high biological activity
Mud-5	Liquid sulfur with flocculant reagent II
Wat-1	Water fraction of the liquid sulfur

For each soil, three repetition for each treatment were considered, for a total of eighteen columns per soil. (Fig.4)

For each column was assigned a progressive number from 1 to 54, which indicated the type of soil related to the type of treatment.

Successively, the treatment were added 5 g of sulfur, that were corresponding to 67 ml of liquid sulfur, in the alkaline and alkaline-saline soils; instead in the V soil were added 2 g of sulfur (equalizing 25ml of slurry sulfur). The soils were saturated with water to constantly collect leachate. On leachate, were conducted specific chemical analysis like pH, electrical conductivity, cations and anions. The leachate were collected

every five days for three months, with a pause of ten days after one month and half to simulate the summer drought.



6 treatments X 3 replicas X 3 soils = 54 columns

Fig. 4 Treatments distribution scheme

Table 2 – Percentages of sand, silt and clay with the respective soil texture classification of each of the examined soil before the treatments with water (C), powdered Sulfur (Sp) and slurry Sulfur (Ss). Numbers between parentheses are the standard deviation (n=2).

Suolo	Sabbia	Limo	Argilla	Classe tessiturale
	%			
A1	19 (1)	80 (1)	1(1)	Franco limoso/limoso
S1	8 (1)	91 (2)	1 (1)	Limoso
v	84 (1)	15 (0)	1 (0)	Sabbioso franco

Table 3 – pH values, electrical conductivity (σ) and amount of humic carbon, total organic carbon (TOC) and total nitrogen (TN) contained in the studied soils before the treatments with water (C), powdered Sulfur (Sp) and slurry Sulfur (Ss). Numbers between parentheses are the standard deviation (n=2).

Suolo	pH	σ	C umico	TOC	TN
		dS m ⁻¹	g kg ⁻¹		
A1	8.33 (0.03)	0.44 (0.02)	3.93 (0.35)	6.57 (0.75)	0.00 (-)
S1	8.09 (0.04)	6.23 (0.06)	6.07 (0.21)	9.75 (0.21)	0.00 (-)
V	5.47 (0.36)	71.03 (7.48)	56.22 (0.76)	0.05 (0.00)	

Table 4 –Semi-quantitative mineralogical analysis of the studied soils before the treatments with water (C), powdered Sulfur (Sp) and slurry Sulfur (Ss).

A1								
Calcite	Quarzo	Plagioclasti	Argille 2:1	Mica	Dolomite	Caolinite	Serpentino	
+++ (+)	++ (+)	+ (+)	+	(+)	(+)	tr	tr	
S1								
Calcite	Dolomite	Quarzo	Mica	Caolinite	Argille 2:1	Albite	Gesso	Clorite
+++	(+)	++	+	+	+	(+)	+	tr
V								
Plagioclasti	Ortoclasio	Quarzo	Mica	Caolinite	Pirosseni	Olivina	Clorite	
+ (+)	+ (+)	+	+++	tr	+ (+)	+	tr	
+ = ~10%; (+) = ~5%; tr = tracce.								

Table 5 – Enzyme activity analysis of the studied soils before the treatments with water (C), powdered Sulfur (Sp) and slurry Sulfur (Ss).

	AryS	α -gluco	β -gluco	Xilo	Uroni	Chit	Leu	AcPME	BisP	PiroP	AlkPME	Nona
	nanomoles of 4-methylumbelliferone (7-amino-4-methyl coumarine) • g ⁻¹ dry soil • hour ⁻¹											
A1	1.0	0.3	1.1	0.3	0.4	0.8	3.2	11.1	2.8	13.8	39.3	15.6
S1	0.4	0.4	4.1	0.5	0.2	1.2	4.4	3.8	0.4	2.1	11.5	16.0
V	137.8	8.6	46.0	10.4	14.8	28.1	113.2	388.3	44.5	48.9	149.5	324.5

AryS=Arylsulfatase; α -Gluco= α -glucosidase; β -Gluco= β -glucosidase; Xilo=xylosidase; Uroni=glucuronidase; Chit=chitinase; Leu=leucina-aminopeptidase; AcPME=fosfatase acida; BisP=fosfodiesterase; PiroP=pirofosfatase-fosfodiesterase; AlkPME=fosfatase alcalina; Nona=Nonanoate-esterase.

3.2 CHEMICAL ANALYSIS

3.2.1 ELEMENTAL AND CATIONS CONTENT

This type of analysis is carried out by the ICP (Inductively Coupled Plasma) Spectroscopy (Fig. 5). It's used for the analysis of the elements present on the soil samples. The process is based on the ionization of a sample by an extremely hot plasma, usually made from argon gas.

In an ICP spectroscopy unit, argon gas (fig. 6) streaming through a torch apparatus is charged with an electromagnetic coil and lit with a Tesla unit that produces a quick discharge arc through the argon flow to trigger the ionization sequence. As soon as the plasma is "lit", the ICP spectroscopy unit is switched off the Tesla device.

It is generated a fireball made mostly of argon atoms and a small part of free electrons and argon ions. Then a channel is created by the passage of a gas flow in the middle of the plasma, samples to be tested are released into this channel, they are usually a mist of liquid created by driving the liquid into a nebulizer.

Temperatures in an ICP spectroscopy unit are capable of ionizing the atoms of many chemical elements because their most-loosely linked electron it's dropped and it create a charged ion. The sample ions are then evaluated using a spectroscopy instrument. With this type of analysis elements such as S, Cu, Fe, Ca, Mg, Zn... can be analyzed.

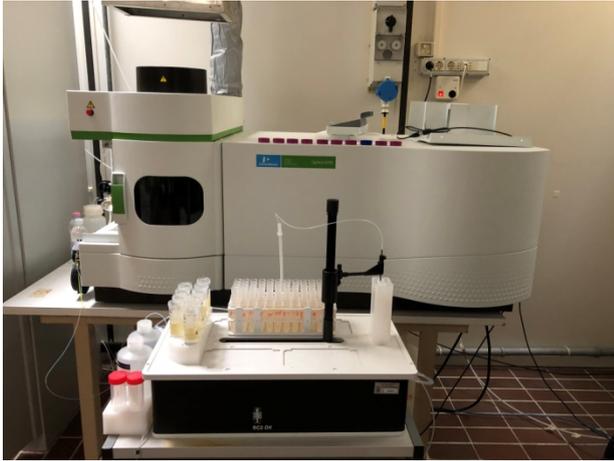


Fig. 5 Inductively Coupled Plasma Spectroscopy



Fig. 6 Gas tanks

3.2.2 HOW SAMPLES HAVE BEEN PREPARED FOR THE ICP ANALYSIS

There were took 16 collections for each type of soil. For each sample were prepared test tubes to be used at the ICP Spectrometry device. The test tubes were labeled with a number and a letter between A,S or V based on what type of soil they were referred to. When necessary, the samples were filtered with a syringe to make sure that all the coarse material was removed, this particular process was done to avoid the eventual malfunction of the machine caused by all the dirty deposited on the torch.

When all the samples were ready, they were placed on a sample-holder which carried 48 tubes at time and then the sampler of the machine proceeded by sucking a portion of liquid from each sample and it took about 2/3 minutes for each one to be analyzed.

3.3 ANIONS ANALYSIS

The Ionic Chromatography is the machine used for this analysis. (fig. 7)

Ion chromatography (IC) is an analytical technique that separates ionic species by combining chromatographic and ion equilibrium theory into one application. In theory, IC can be used to analyze any ionic species. The most common ion exchange systems used today combine high performance liquid chromatography (HPLC) technology with ion exchange capability (Fig. 8).

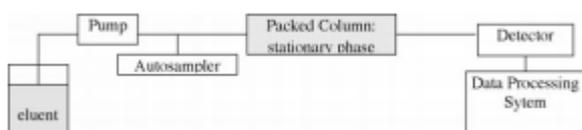


Fig. 8

A stationary phase of uniform small-diameter particles is packed into a column. Eluent is passed through the column with a high-pressure pump. A fixed volume injection loop is placed between the pump and column for sample introduction. The components of the sample are separated on the column and flow to a detector. Data from the detector are collected on a data station, where quantification of the analyte is calculated and stored. Modern IC systems generally include an integrated package of pumps, detectors, autosampler, and column oven, and are completely computer automated. Ion exchange is capable of identification and quantification of several ions, which include halides, alkali metals, alkaline earths, transition metals and oxyanions. Depending on the detector response of the analytes, ion exchange detection limits for most common ions is 1–5 parts per billion (ppb). For routine analysis, accuracy is around 3% relative standard deviation (RSD), and with the use of an internal standard, RSDs of less than 1% can be achieved (Small 1989). (J.P.Lemmon)

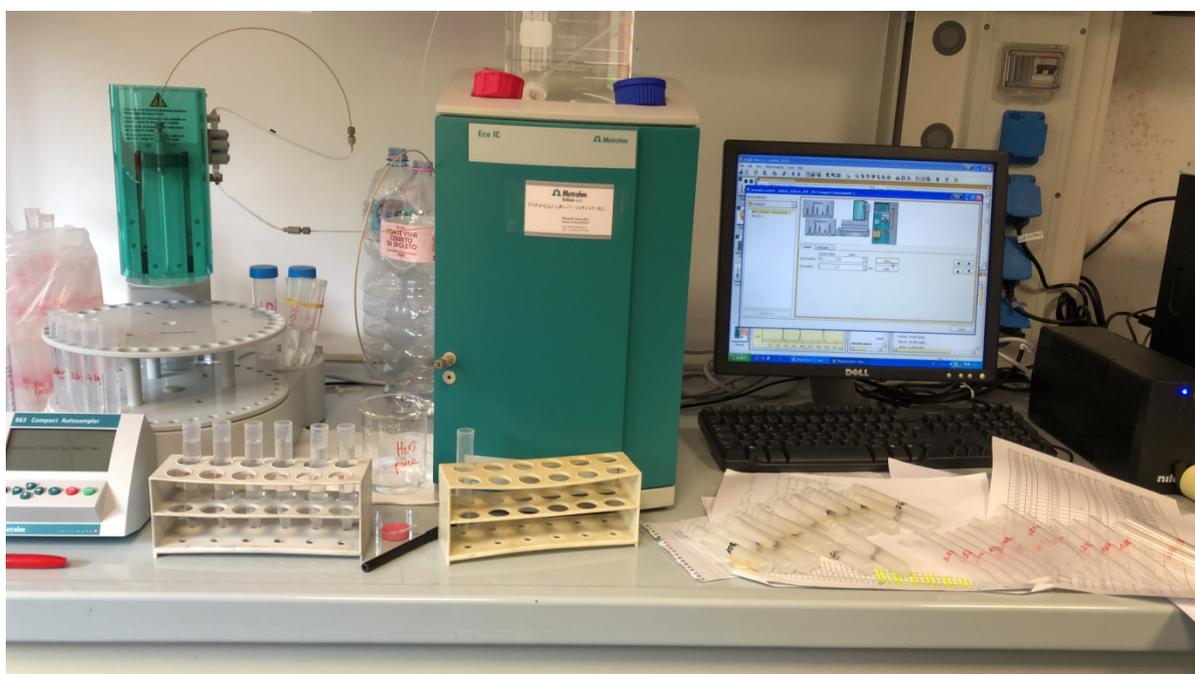


Fig. 7 Ionic Chromatography

3.3.1 HOW SAMPLES WERE PREPARED

In the same way as the ICP analysis, the samples were put into test tubes of 10ml capacity, each tube was labeled with the letter correspondent to the type of soil (A,S,V) and a progressive number. The dilutions for the analysis were made with ultrapure water. Based on what kind of soil the leachate was from, there were done two different dilutions, the first one made of 9,9ml of water and 0,1ml of filtered sample and the second one made of 9,5ml of water and 0,5ml of sample. The process was made by using the automatic pipettes.

3.4 TOTAL CARBON (TC) AND TOTAL NITROGEN (TN) ANALYSIS

This analysis is done with an instrument called CN elemental analyzer. (fig. 9)

The samples are dropped in a tube in the presence of external oxygen flash combustion occurs at a temperature of 1800 °C. The gaseous combustion products N_2 , NO_x , H_2O , SO_2 , O_2 and CO_2 are carried by the helium as carrier gas through a column filled with copper oxide and from there to a Cu-column where nitrogen oxides are reduced to elementary nitrogen, and O_2 to CuO. Water can be absorbed in another column. The remaining gasses are introduced into a TPD (Temperature Programmed Desorption) column where N_2 is going right through it and the other gases are bound to the column. With a programmed temperature raise in the column the gases are released separately. They flow along a thermal conductivity detector (TCD) which produces an electrical signal proportional to the concentration of nitrogen, carbon, hydrogen and sulfur.



Fig.9 CN elemental analyzer

For sample preparation, soil was weighed into tin capsules using analytical micro-balance (fig. 10). The usage of this type of capsule allowed the right combustion and the gases produced are not recognized by the analyzer.

The samples weight depends on the main characteristics of the soil in exam, for these thesis, the weight was between 10 and 15 mg.

Resuming, the phases of the process were:

1. Weigh of the tin container was weighed for the tare;
2. Soils weighted with a tiny spatula and poured into the container;
3. Then the container filled of soil was weighed and manually closed;

and round-shaped (this shape is the best to make sure that samples are not going to be stuck in the machine), it is important also to check that the capsule doesn't break during the manipulation with the forceps, if this occur, it has to be replaced with a new one before introduced into the stove.



Fig. 10 Analytical micro-balance

4 RESULTS AND DISCUSSION

4.1 ICP analysis Results

In this analysis, the results show how the concentration of sulfur and sulphates in the first collection are plentiful, but gradually they run out, it's possible to notice that already from the second column.

The course of the sulfur and sulphates, especially in the S1 soil, it is fluctuating, probably with the addition of an acid substance, that melted the calcium, it was formed chalk that may be the cause of the insolubilization of sulphates, so for this reason we can see this alternate peaks.

For example we can see that in the treatments done with the WAT1, which is basically the water fraction of the liquid sulfur, we have high values of both sulfur and sulphates caused by the fact that this product completely pass through the column because it's formed by very small particles that can't be held by the soil and make this product extremely reactive.

On the contrary with another product, the MUD5, we have lower values, because this product is formed by liquid sulfur with flocculant reagent.

The figure 1 and 2 show the different values that sulfur and sulphates present from the first to just the second collection of the treatments done to S1 soil, we can see that in the first collection S is almost 1500,000 mg kg⁻¹ instead in the second collection it is around 700,000 mg kg⁻¹.

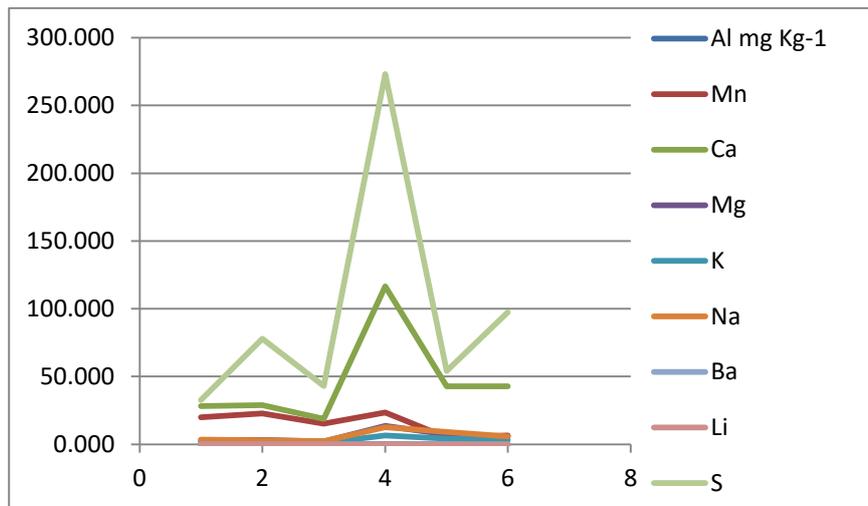


Fig. 1 S1 soil 1st collection

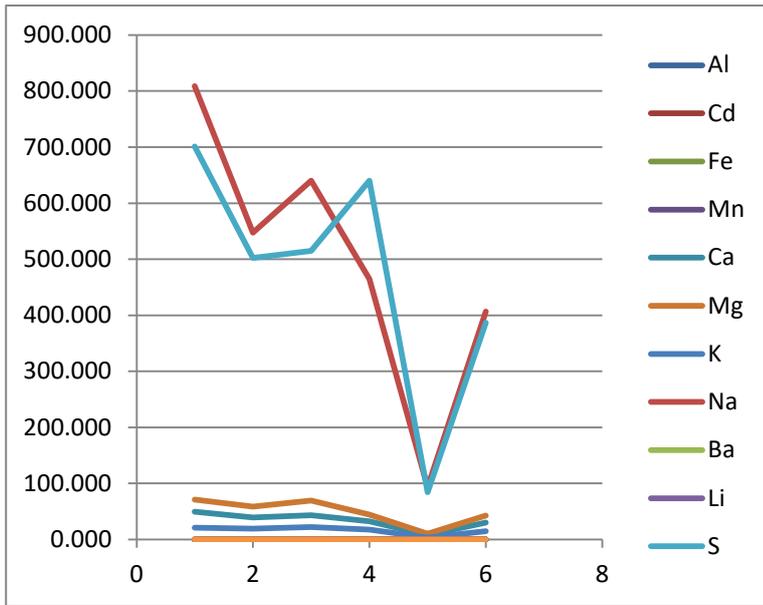


Fig. 2 S1 soil 2nd collection

If we consider one of the last collection for example the 12th one, we can see how the values go down a lot compared to the first collection. (Fig. 3)

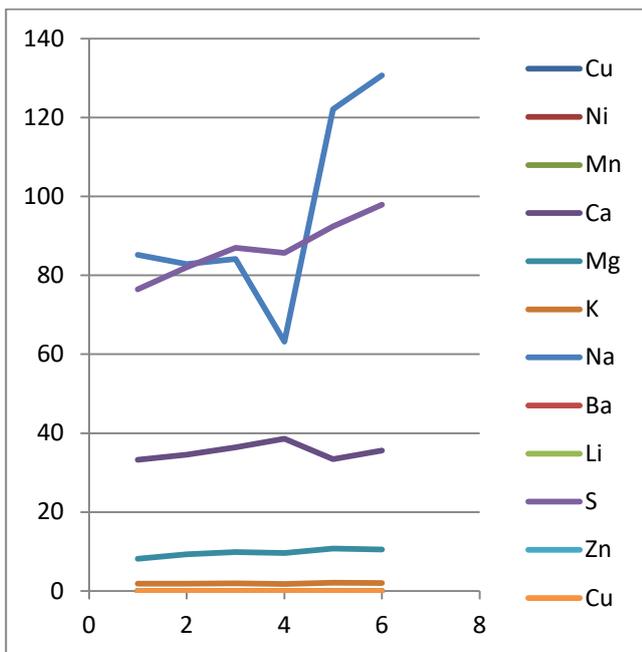


Fig. 3 S1 soil 12th collection

4.2 Anion Analysis Results

For this part the analysis were conducted only for half of the treatments.

In the V soil we can see from the graphics (fig. 1), how the sulphate especially for the treatments with WAT1, MUD4 and MUD5 reaches around 80-160 mg kg⁻¹, but the values remains low in comparison to the other soils.

In fact the S1 soil (fig. 2) reaches peaks of over 1200 mg kg⁻¹ for the WAT1 treatment.

In the A1 soil (fig. 3) the sulphate reach 300 mg kg⁻¹.

Nitrate and chloride are low levels for basically each of the three soils, with only small differences, especially for the S1 soil.

Phosphate also reach high values in comparison to the other elements, however they are smaller than the sulphate ones.

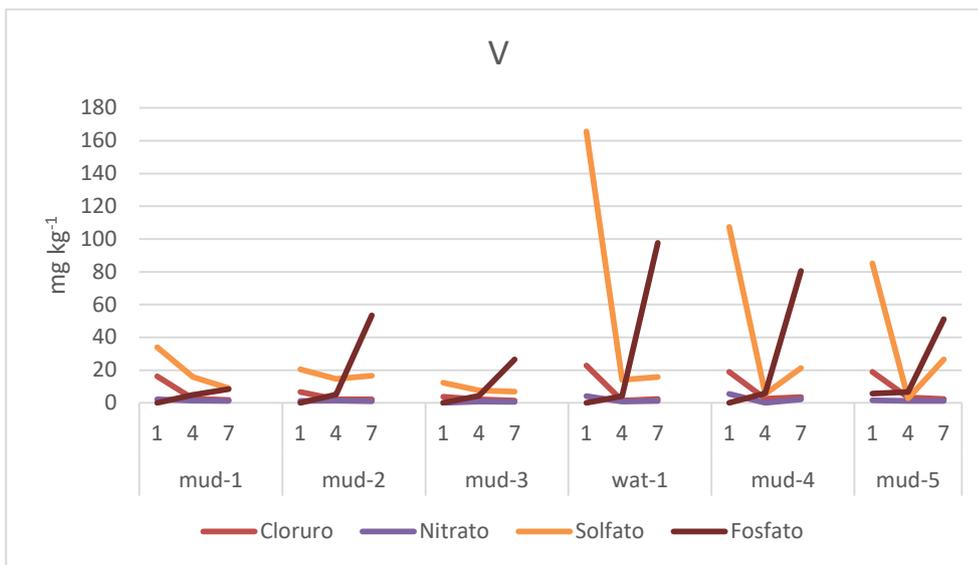


Fig. 1 Anions analysis results V soil

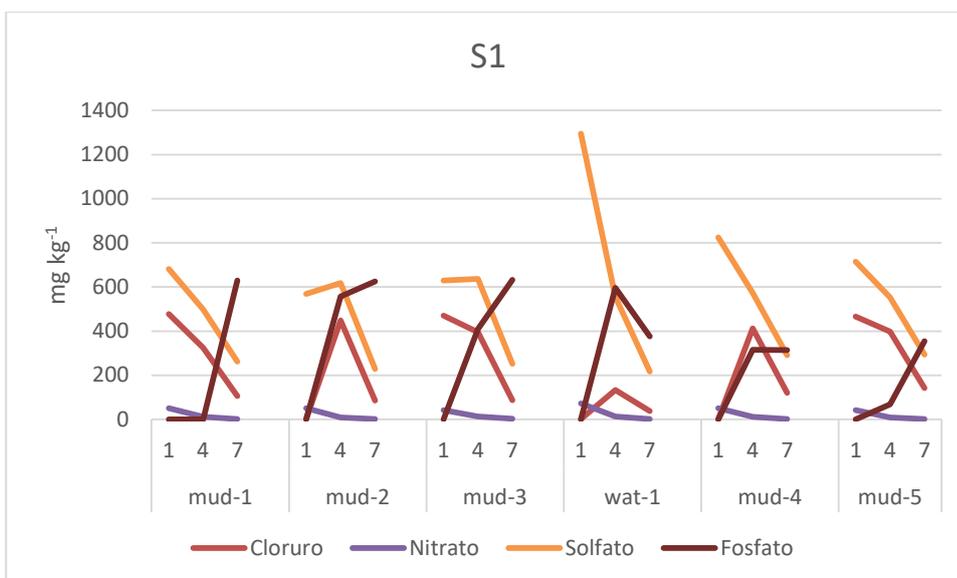


Fig. 2 Anions analysis results S1 soil

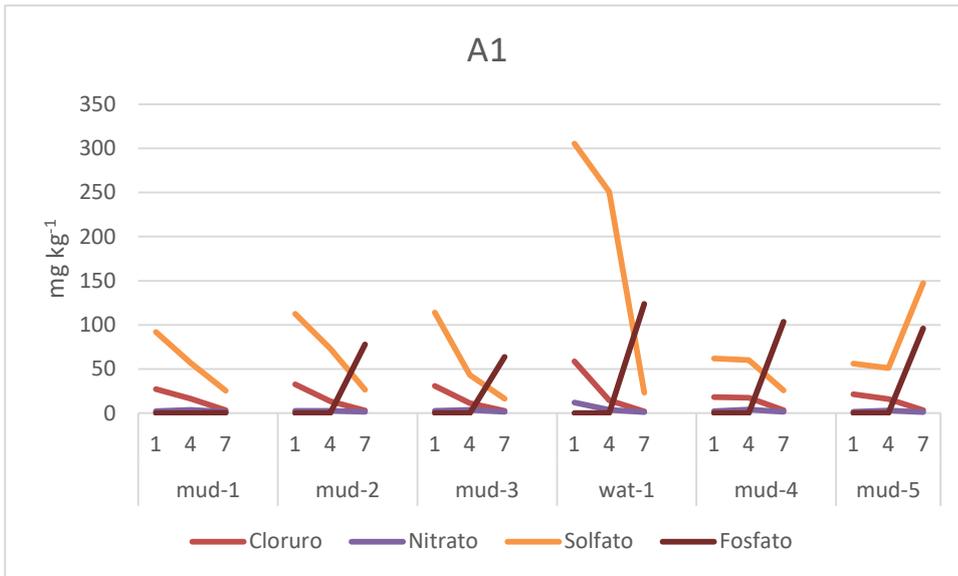


Fig. 3 Anions analysis results A1 soil

4.3 Total Carbon (TC) And Total Nitrogen (TN) Analysis

With this type of analysis we've been able to quantify the level of humification of organic substance.

5. CONCLUSION

In conclusion we can say that doing this treatments to this soils, the acidity will change only partially, we can't say with absolute security that this represents the right solution to improve the soil pH.

6. BIBLIOGRAFIA

- Bannick C.G., Bredemeier M., Hulpke H., Knoop G., Northcliff S., Schulte-Bisping H., Terytze K., *Soil, 1. Definition, Function, and Utilization of Soil, in Ullmann's Encyclopedia of Industrial Chemistry*, University of Reading, Department of Soil Science, Reading, United Kingdom Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2012.
- Bartholomeus H., Bregt A. K., de Sousa L., Ivushkin K., Kempen B., Pulatov A., *Remote Sensing of Environment Volume 231 article 111260*, Published by Elsevier Inc. 2019
- Bockheim J. G., Hartemink A. E., *Pedosphere Volume 23, Issue 5 Pages 600-608*, Published by Elsevier B.V. and Science Press October 2013
- Cecchi S., Zanchi C. *Coastal Water Bodies: Nature and Culture Conflicts in the Mediterranean* 2010
- Daliakopoulos I.N., Karatzas G.P., Kourgialas N.N., Koutroulis A., Ritsema C. J., Tsanis I. K., Varouchakis A. E., *The threat of soil salinity: A European scale review Science of The Total Environment Volume 573 Pages 727-739*, Polestar Wheatons, Ltd., Exeter, UK 15 December 2016
- Feitz, A.J. & Lundie, S. *Int J LCA Soil salinisation: a local life cycle assessment impact category Volume 7, Issue 4, pp 244–249* Springer Berlin Heidelberg July 2002.
- Frausto Da Silva J.R.R., Williams R.J.P., *The biological chemistry of the elements*, Oxford, Oxford University Press, 1991; d. voet, j.g. voet, *Biochemistry*, New York, Wiley, 1990 (trad. it. Bologna, Zanichelli, 1993).
- Owens, P.R., Rutledge E.M., *Horizons Encyclopedia of Soils in the Environment, 511-520*, 2005.
- Soil Survey staff. *Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys*, 2nd edition. U. S. Department of Agriculture Handbook 436, Natural Resources Conservation Service 1999
- Zhang W., Wang C., Wang L., Xue R., *Journal of Integrative Agriculture Volume 18, Issue 6 Pages 1360-1368*, Published by Elsevier Ltd. June 2019

7 SITOGRAFIA

- <https://www.ru.nl/science/gi/facilities-activities/elemental-analysis/cn-elemental/>
- <https://www.britannica.com/science/biosphere/The-cycling-of-phosphorus-and-other-essential-nutrients>
- <http://www.treccani.it/enciclopedia/>
- https://it.wikipedia.org/wiki/World_Reference_Base_for_Soil_Resources
- <https://www.xrfscientific.com/what-is-icp-spectroscopy/>
- <https://www.ru.nl/science/gi/facilities-activities/elemental-analysis/cn-elemental/>
- <https://coltureprotette.edagricole.it/featured/lo-zolfo-elemento-essenziale-per-le-piante/>

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