T.R.
ONDOKUZ MAYIS UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF SOIL SCIENCE AND PLANT NUTRITION

THE SOILS OF MOFET SPRINGS IN THE VICINITY OF MUSZYNA

Master's Thesis

Christian Dave Roque ALONZO

Supervisor
Prof. Dr. Orhan DENGIZ

II. Supervisor
dr hab. inż. Tomasz ZALESKI, Prof. URK

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ACCEPTANCE AND APPROVAL OF THE THESIS

The study entitled **"THE SOILS OF MOFET SPRINGS IN THE VICINITY OF MUSZYNA"** prepared by **Christian Dave Roque ALONZO**, and supervised by **Prof. Dr. Orhan DENGIZ**, was found successful and unanimously accepted by committee members as Master thesis, following the examination on the date 21.8.2023 .

	Title Name SURNAME **University** **Department/Art**	**Final Decision**
Chairman	Prof. Dr. Orhan Dengiz Ondokuz Mayıs University Department of Soil Science and Plant Nutrition	☒ Accept ☐ Reject
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This thesis has been approved by the committee members that already stated above and determined by the Institute Executive Board.

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I hereby declare and undertake that I complied with scientific ethics and academic rules in all stages of my Master's Thesis , that I have referred to each quotation that I use directly or indirectly in the study and that the works I have used consist of those shown in the sources, that it was written in accordance with the institute writing guide and that the situations stated in the article 3, section 9 of the Regulation for TÜBİTAK Research and Publication Ethics Board were not violated.

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No ☒

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ÖZET

MUSZYNA CİVARINDAKİ MOFET YAYLARININ TOPRAKLARI

Christian Dave Roque ALONZO
Ondokuz Mayıs Üniversitesi
Lisansüstü Eğitim Enstitüsü
Toprak Bilimi ve Bitki Besleme Bölümü
Erasmus Mundus Master in Soil Science (emiSS) Program
Yüksek Lisans, Temmuz/2023
Danışman: Prof. Dr. Orhan DENGIZ
Danışman: dr hab. inż. Tomasz ZALESKI, Prof. URK

Mofettler, ana özelliklerinden biri gazla zenginleştirilmiş suyun çıkışı olan dağınık jeolojik yapılardır. Mofettlerle yer değiştiren karbondioksit, alt kabuktan veya üst mantodan çatlaklar veya tektonik faylar yoluyla yukarı doğru ve toprak örtüsü aracılığıyla yüzeye doğru hareket eder. İncelenen alanlar, Polonya'nın güneyindeki Küçük Polonya voyvodalığında, Nowy Sącz semtindeki Muszyna civarında yer almaktadır. Bu çalışmanın amacı, 1) mofettleri çevreleyen toprakların fiziksel ve kimyasal özellikleri hakkında veri sağlamak 2) oluşumlarıyla ilişkili pedojenik süreçlerin yoğunluğu ve süresine ilişkin seçilmiş demir oksit formlarını ölçmekti.

İncelenen profiller Gleyik topraklar olarak sınıflandırılmıştır. Bu topraklar, killerin veya siltli killerin tane boyutu ile karakterize edildi. Mofetta 2 dışındaki hemen hemen tüm topraklar, çoğu özellikte, yani % SOC, % N, EC ve değişebilir baz katyonlarında yukarıdan aşağıya doğru azalan değerler göstermiştir. Bu özellikler Mofetta 2'nin profilinde değişiklik gösteriyordu. Analiz edilen demir formları - amorf demir ve organik olarak bağlı demir - hiçbir korelasyon göstermedi. Feo ve Fep'in dikey dağılımları her toprak profili için farklıdır. Bu gleyik topraklar için Feo ve Fep içeriği toprak derinliği ile azalmıştır. Mofetta 3'ün Gox horizonu, Feo formlarının en yüksek değerlerini (13.41 g/kg), ancak Fep formlarının en düşük değerlerini (0.89 g/kg) gösterdi.

Anahtar Sözcükler: Mofette, Toprak Demiri, Gleysoller, Dağ toprakları

ABSTRACT

THE SOILS OF MOFET SPRINGS IN THE VICINITY OF MUSZYNA

Christian Dave Roque ALONZO
Ondokuz Mayıs University
Institute of Graduate Studies
Department of Soil Science and Plant Nutrition
Erasmus Mundus Master in Soil Science (emiSS) Program
Master, July/2023
Supervisor: Prof. Dr. Orhan DENGIZ
Supervisor: dr hab. inż. Tomasz ZALESKI, Prof. URK

Mofettes are diffuse geological structures, one of the main features of which is the outflow of gas-enriched water. Carbon dioxide displaced by mofettes moves upwards from the lower crust or upper mantle through fractures or tectonic faults and further to the surface through the soil cover. The studied sites are located in the vicinity of Muszyna, in the Nowy Sącz district, in the Lesser Poland voivodeship, southern Poland. The aim of the present study was 1) to provide data on physical and chemical properties of soils surrounding the mofettes 2) to quantify selected forms of iron oxides on the intensity and duration of pedogenic processes associated with their formation.

The profiles studied were classified as Gleyic soils. These soils were characterized by the grain size of clays or silty clays. Almost all soils, with the exception of Mofetta 2, showed decreasing values from upper to lower horizons in most properties, i.e., %SOC, %N, EC and exchangeable base cations. These properties varied in the profile of Mofetta 2. The analyzed forms of iron - amorphous iron and organically bound iron - showed no correlation. The vertical distributions of Feo and Fep are different for each soil profile. For these gleyic soils, Feo and Fep content decreased with soil depth. The Gox horizon of Mofetta 3 showed the highest values of Feo forms (13.41 g/kg), but the lowest values of Fep forms (0.89 g/kg).

Keywords: Mofette, Soil Iron, Gleysols, Mountain soils

CONTENTS

SYMBOLS AND ABBREVIATIONS

Fet	: Total iron content
Fes	: Silicate form of iron
Fed	: Free iron (non-sillicate form)
Fec	: Crystalline form of iron
Fep	: Organically-bound iron
μS/cm	: microSiemens per centimeter

FIGURES LEGENDS

TABLE LEGENDS

1. INTRODUCTION

Mofettas or mofettes are defined as diffuse degassing structures (Chiodini, 2001). The volcanic carbon dioxide exhaled by these mofettes travels upward from the lower crust or upper mantle through cracks or tectonic faults (Kämpf, 2007; Pfanz, 2019) and further into the soil atmosphere (Rennert T. E., 2012). They are found in several regions of quaternary volcanism across Europe (e.g., the French Massif Central, the Italian Tuscany, the German Eifel Mountains or the Czech Eger Rift) (Rennert T. E., 2012). The ascending CO_2 may fully displace the soil atmosphere affecting not only the soil development but also the flora and fauna diversity surrounding such sites (Rennert T. E., 2012) that is why, mofettes can be observed not only by the bubbling gas streams but also as a semi-circular features with limited vegetation (Beulig, 2015).

The migrating CO_2 gas may appear at the surface as either dry features or as CO_2-rich mineral water determined by the local hydrogeological condition (Pfanz, 2019). The soil development and properties of the soils in mofette sites are affected by the ascending geogenic CO_2 (Rennert T. E., 2012). In fact, the effect of these CO_2 to soil phase has already been described by several researches (Pfanz, 2019). Additionally, some studies suggest that mofette soils exhibit low pH, high content of carbon, and anoxic or oxygen deficient condition (Rennert T. E., 2011; Ross DJ, 2000). However, in soil science literature, there are limited studies available about the soils surrounding mofette sites especially those in Muszyna region. There are however studies on the water chemistry of its natural spring and the geochemistry of its geological formation (Klojzy-Kaczmarek B., 2021) and, Ciężkowski et al. 2002 as cited by (Cąplak, 2022).

The purpose of this study aimed to 1) provide data on the physical and chemical characteristics of soils surrounding mofette 2) quantify the profile distribution of selected forms of iron oxides and assess its relationship to other physical and chemical properties. Information on the transformation of iron (i.e., mobilization, migration, and immobilization) along the soil profile is useful to determine the soil-forming processes that shaped the mofette soils of Muszyna. This kind of research resolve challenges related to soil taxonomic classification (Miechówka, 2015). The forms of iron being investigated were limited only to amorphous form (Feo) and organically-bound iron (Fep).

The present work is a continuation of research on the genesis and impact of mofette phenomenon on the formation and chemical properties of soils, begun by (Cąplak, 2022).

2. REVIEW OF LITERATURE

2.1. Iron and its forms

Iron is the third most abundant element in soils after silicon and aluminum. Depending on the type of the parent material, iron content differs from place to place between one to hundreds of grams per kilogram (Shui-Sheng, 2016). In soil science studies, iron can be categorized into groups based on its forms or species such as the total iron, free iron – which is subsequently classified into crystalline and amorphous – silicate, and organically-bound iron (Shui-Sheng, 2016). To date, the environment is known to be composed of sixteen iron oxides, oxide hydroxides, and hydroxides. Among the iron oxides, Hematite, α-Fe_2O_3 is considered to be the oldest and widely spread in rocks and soils. Other oxide forms such as Fe_2O_3 (γ form), Fe_3O_4, and Fe-OOH (α and γ form) also gained interest due to its distribution in soil and industries (Shui-Sheng, 2016). Iron is used as an indicator of geological, and also of the intensity and duration of pedogenic processes (Orzechowski, 2018).

2.2. Soil formation in mofetta

The study of pedogenic oxides on mofette soils is limited to determination of aluminum and iron (Blume, 2009; Stephens, 2002). Mofette soils belong to Reduktosol in the German soil classification system according to (Ad-hoc-AG Boden, 2005). The redox condition is visible in Reduktosol. For instance, the reduction of ferric oxides is typically evident in its subsoil, and oxidation is clearly observed in pore spaces in the top soil (Blume, 2009). There are cases however, that reducing environment and reducing gases are observed in Y horizon despite lacking an aquic moisture regime (Ad-hoc-AG Boden, 2005).

Gleyzation is favored in a water abundant condition with limited aeration and the presence of swelling clay minerals. Gleyic process, being common in mofette soils is also confirmed by the redoximorphic features. Current knowledge on iron minerals in mofette soils noted that Fe (II) and/ or Fe (III) may co-exist. Although the different Fe minerals are not uniformly distributed but disturbed in the precipitation zones such as in pore spaces (Rennert, 2012). Precipitation of iron oxides in mofette soils such as gleysols takes place in macropores (root channels) (Rennert, 2012).

Fe (II) in mofette soils is not oxidized because of the geogenic CO_2 displacing O_2 and therefore causing O_2 deficiency. Fe (II) in non-mofette and saturated soils, the presence of Fe (II) is the result of microbial reduction of Fe (III) and oxygen consumption (Rennert, 2012).

2.3. Outflow of CO2 as a soil forming factor in mofette soils

Exhalation of CO2 and outflow of carbonated water are one of the main features of a mofetta (Modelska, 2015) which are considered to be factors on its soil formation (Rennert T. E., 2011). The soil chemistry of mofette sites is affected by an intense CO2 degassing through lowering the pH thus, inducing acidification in soil (Beulig, 2015; Rennert T., 2018). A study of (Pfanz, 2019) showed correlation of CO2 to pH and soil conductivity. Moreover, CO2 outflow slows down the mineralization and transformation of SOM resulting to accumulation of SOC content (Rennert T. E., 2011); this makes a mofette soil a natural laboratory in investigating SOM dynamics (Rennert T. , 2018). Another study about a gleysol mofette in New Zealand showed increased in carbon sequestration and labile carbon pool in the mineral soil (Ross DJ, 2000). Microbial respiration and communities (Beulig, 2015) may also be suppressed by partial CO2 pressure affecting the fate and humification of SOM (Pansu, 2010; Rennert T. E., 2011). Lastly, SOM formation is indirectly influenced when oxygen level is affected by the outflowing CO2 (Pfanz, 2019).

Furthermore, CO2 plays a key role in the soil redox potential by causing variation in the quantity and quality of the speciation of iron (Beulig, 2015; Rennert T. E., 2012). It hinders the formation and further development of pedogenic Fe oxides, which however may adversely affect SOM storage (Rennert T. E., 2011). When the temperature and pressure are favorable, soils on mofette sites may form clay minerals. For instance, carbonates, muscovite, and kaolinite are formed under the weathering of primary minerals when exposed to carbon dioxide (Haszeldine et al., 2005). Aside from the widely known soil-forming factors, soil formation and development on mofette sites also depend on the properties of soil atmosphere thus, it is recommended that the composition of soil atmosphere be taken into account in soil classification system (Rennert T. E., 2011).

2.4. Iron forms under different soil-forming processes

One of the fundamental challenges in the field of soil science is the study of soil genesis and soil classification, since soils are initially classified on-site according to its morphogenetic characteristics and the results are seldom confirmed through laboratory analyses (Różański, 2013). Depending on the direction, type, and intensity of soil-forming processes, the analysis of iron forms is one of the generally accepted methods in studies of soil genesis. Iron forms are the result of biochemical transformations, where organic matter plays an important role (Wheeler D.B., 1999). Aside from the total content of iron in soil, it is also important to take into account the vertical distribution of different forms of iron. Under various soil-forming processes, transformations of iron occur along the soil profile (Orzechowski, 2018). Sometimes, the groundwater gleization associates the lithogenic accumulation of iron in Haplic Gleysol and Gleyic Chernozem (Orzechowski, 2018)

Distribution of iron maybe a result of pedogenesis if higher values is observed in upper horizon than in the parent material horizon (Orzechowski, 2018). Some studies suggest that iron content has no significant relationship to soil humus content, although exhibits low negative correlation with organic carbon content (Różański, 2013). In contrast, contents of total iron, and its silicate, crystalline and free forms were significantly positively correlated with the clay content (Orzechowski, 2018). This study confirmed the soil processes involved according to the profile distribution of iron forms on the basis of morphological and textural properties affirmed the importance of this kind of research (Różański, 2013).

2.5. Total Iron (Fe_t) and its Forms: Free iron (Fe_d), Amorphous Iron (Fe_o), Crystalline Iron (Fe_c), and Silicate Iron (Fe_s)

Total iron content is influenced by the geological origin of parent material (Kobierski M. D.-N. H., 2012). The parent material influences the total amount of iron while the iron forms are influenced by the soil forming processes which is a function of pH, soil moisture and temperature, redox condition, etc. (Straub K., 2001; Waychunas G.A., 2005).

Free iron is adsorbed or coated form of iron on the surface of soil particles but is excluded in the lattice structure (Shui-Sheng, 2016). Analytical determination of free iron is a crucial soil basic properties for it guides researchers in understanding the behavior of soil distribution, soil genesis, and classification (Shui-Sheng, 2016). When the Fed content correlates with the clay fraction, the high amount of Fed in soil horizons are likely resulted by illuviation process and not a cause of weathering. This reason is due to the hydrous Fe oxides having a very small particle sizes and oftentimes associated with the presence with clay (Orzechowski, 2018). In cases that the surface horizons have higher values of Fed content than the horizon of parent material suggests it was because of an intensive weathering (Orzechowski, 2018).

Amorphous oxides (Feo) which is the most labile and active form of iron, occurs as a free iron (Fed) together with crystalline (Fec) (Schwertmann, 1964). High amounts of Feo may be due to non-permanent anaerobic condition and soil organic matter (Alamdari P., 2010).

Crystallization of iron oxides depend on Fec values. Horizons with the higher Fec content suggests favorable condition for crystallization (Orzechowski, 2018). Meanwhile, the silicate form of iron (Fes) is inversely proportional to free iron. The higher the Fes, the lower the amount of free iron suggesting how intensive the weathering is (Orzechowski, 2018).

2.6. Iron indices derived from the measured iron forms

Iron activity index is one way to study the transformation of iron in the soil. This is determined based on the ratio or relationship of the most active form of iron and its non-silicate forms (Schwertmann, 1964). That is, the higher Feo/Fed values indicates higher activity of soil forming processes, and in humus horizons a younger age of soil material (Orzechowski, 2018). High values of Feo/Fed ratio in different horizon suggest dominance of iron forms of poor structure and slow rate of crystallization. With the soil age, Feo/Fed ratio values have the tendency to decrease (Moody L.E., 1995). Consequently, lower value of Feo/Fed ratio of the parent material horizon than in upper or overlying horizons suggest higher crystallization of iron. In contrast, higher values of Feo/Fed states lower crystallization of iron oxides (Orzechowski, 2018). Iron activity index values can also be explained by other factors like redox processes and organic matter content (Orzechowski, 2018).

The age of soil can be represented by the values of the weathering index or Fed/Fet. Under similar soil and climatic conditions, the intensity of soil weathering is correlated with its age. (Arduino E., 1986). Low values of Fed/Fet ratio reveals that the studied soil is young where features of the soil forming processes are evident (Orzechowski, 2018). Additionally, high mobility index values (Fed/Fet) and a high percent of crystalline iron in an illuvial horizon confirms the occurrence of lessivage as the only soil forming process in Luvisols (Kobierski M., 2010; Różański, 2013). In such iron distribution and its forms in the profile indicate a moderate rate of silicate mineral decomposition while the crystallization of iron compounds gained favor of this condition (Różański, 2013).

3. MATERIALS AND METHODS

3.1. Geological setting of the study site

The examined sites are located in Muszyna in Nowy Sącz County, Lesser Poland province, in southern Poland. The Muszyna region lies in the southern part of the Polish Outer Carpathians (Kania, 2010). The Carpathians are divided by the younger Outer Carpathians and the older Inner Carpathians Figure 3.1. (Ślączka, 2006). The Polish Outer Carpathians rose from thrust-sheets and nappes – these are (from North to the South) Skole Nappe, the Sub-Silesian Unit, the Silesian Nappe, the Fore-Magura-Dukla group of units, and the Magura Nappe (Kania, 2010). Muszyna is seated in the south-eastern part of the Magura Nappe at the Krynica faces zone comprising of two subunits named the Upper Cretaceous and Oligocene deposits (Kania, 2010). The oldest deposits of Krynica faces zone are found in the area of Muszyna-Złockie, while the thick-bedded Magura Fm (Middle Oligocene) is the youngest deposit in the Muszyna region (Kania, 2010).

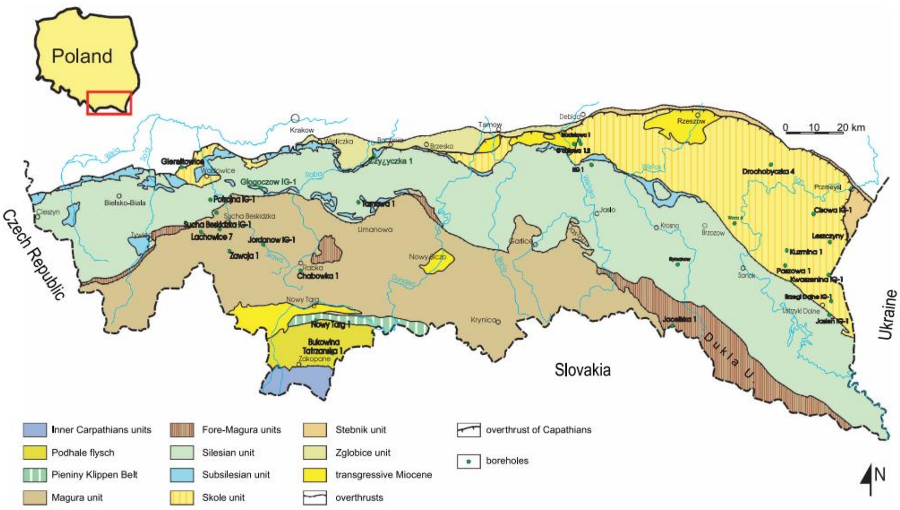

Figure 3.1 Tectonic illustration of the Polish Carpathians where the study sites are located (Ślączka, 2006)

3.2. Soil Sampling and Measurements

The studied soil profiles were selected within the proximity of mofette locations. The five soil profiles taken from three different mofette sites were tagged with the name Mofetta 1 to Mofetta 5 for this study. Figure 3.2 shows that Mofetta 1 is located near the border of two villages Złockie and Jastrzębik. Mofetta 2 and Mofetta 3 are located in Powroźnik, while Mofetta 4 and Mofetta 5 are located in Jastrzębik. The cross-section morphology of the soil profiles was characterized on site to identify the genetic horizons. Soil sampling was done in each horizon instead of by depth, because sampling by depth is characterized with more variability considering that the sample is a mixture of soil material of different properties (Patterson, 2008). Soil samples of Mofetta 1 to Mofetta 3 were taken in 2021, thus soil morphology and other physical and chemical properties have been described prior to the commencement of this study. Soil samples of Mofetta 4 and Mofetta 5 were collected in November 2022.

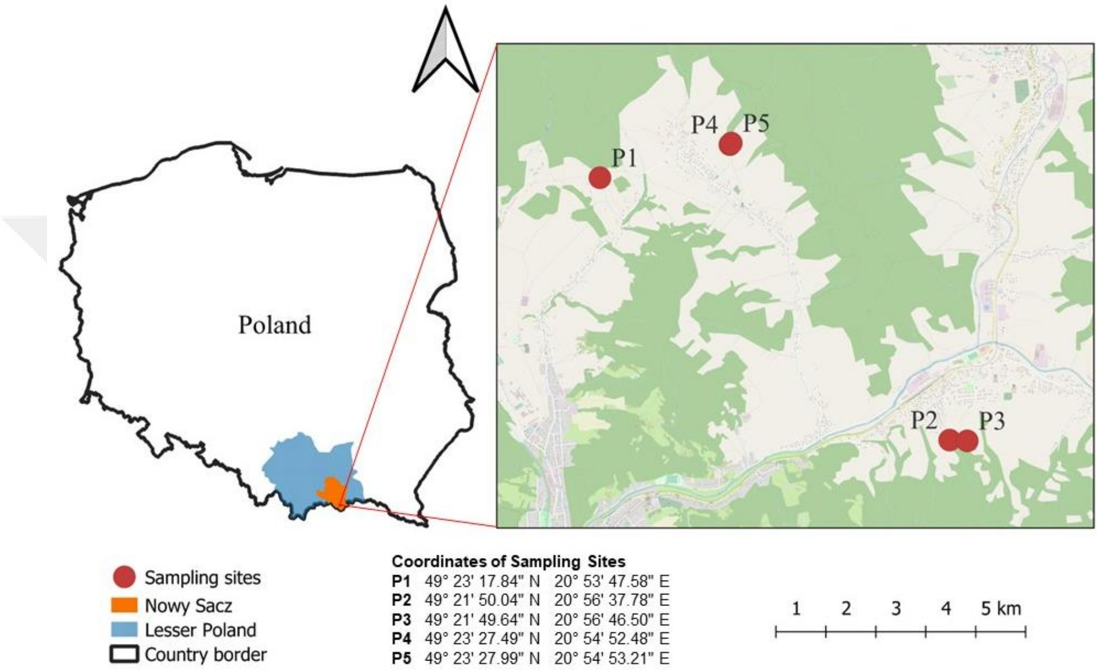

Figure 3.2. Research area and location of soil profiles

3.3. Soil Physical and Chemical Analyses

The soil samples were air-dried at ambient temperature for few weeks. Leaves, pebbles, and other unwanted materials were cleaned out from the samples before passing through a 2-mm sieve. These 24 soil samples were examined for physical and chemical analysis. The particle size distribution of sands (2.00 – 0.05 mm), silt (0.05 – 0.002 mm), and clay (<0.002 mm) was analyzed using the Bouyoucos aerometric method in Cassagrande in Prószynski’s modification according to Polish Standard (PN-R 04032., 1998). The results were expressed in percentage to identify the soil textural class using the USDA Soil Texture Triangle (Soil Science Division Staff, 2017). The potentiometric measurements of soil pH were determined using a standard combination glass electrode and a CPI-551 Elmetron pH meter in a mixture of 1:1 soil:1 mol·dm^{-3} KCl solution, and H_2O. Electrical Conductivity (EC) analysis was done by obtaining the soil extract from a saturation paste left overnight and filtered using a Buchner funnel and Whatman 42. Filtration was aided by a vacuum pump at a pressure of -0.5 to 0.8 atm and the extract was measured in the EC meter expressed in µS/cm. The soil organic carbon (SOC) determination was performed according to the Tiurin method in Oleksynowa's modification (Oleksynowa K., 1993) using the potassium dichromate and Mohr's salt, without removing the calcium carbonate. The percent organic matter content was calculated from the result of % SOC multiply to 1.7248 with the assumption that organic matter contains 58% of organic carbon. Percent total nitrogen content was measured using the Kjeldahl method (Lityñski T., 1976) on a FOSS Kjeltec TM 8100 apparatus. The values obtained in the measurement of EC, % SOC, %SOM, and total nitrogen were classified according to (Hazelton, 2016) while the result of pH measurement was classified according to (Hazelton, 2009). Evaluation of the sum of individual basic cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{2+}) were extracted in 1 M NH_4Cl at pH 7.0 (Kociałkowski et al. 1984) and analyzed with ICP-OES (Optima 7300 DV); the results are expressed in mmol/kg.

The amorphous form of iron (Feo) was determined using ammonium oxalate extraction according to Tamm's method (1964). It was intended to remove the products of sesquioxide from the soil (Courchesne, 2008). The sodium pyrophosphate extraction method in reference to (McKeague, 1967) was used to measure the amount of organic-complexed iron (Fep).

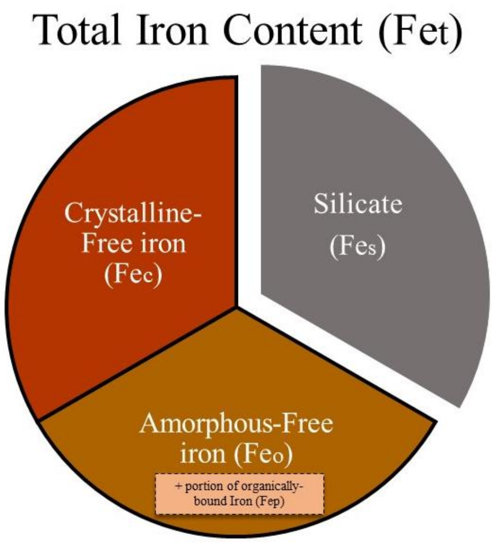

Figure 3.3. Schematic representation of different forms of iron composition in the total iron content

3.4. Statistical Analyses

The correlation coefficients of different forms of iron to other soil properties were calculated in *R software*. Regression analysis was done for statistically correlated properties. Moreover, the Analysis of Variance (ANOVA) using Completely Randomized Design (CRD) was performed to determine the variances of soil properties based on pH, SOC, and Nitrogen level.

4. RESULTS AND DISCUSSION

4.1. Soil Description

Mofetta 1 is located 700 meters west of the largest mofette in Poland named after Henryk Świdziński. It is seated on the slope of a small stream and surrounded by lush grassy vegetation. Mofetta 1 is characterized as Gleysol delineated with three horizons Ah-Abg-Gox (Cąplak, 2022).

Several minor gas exhalations are observed in Mofetta 2, as well as the presence of carbonates on the surface. The site is saturated with few grasses around. Mofetta 2 is characterized as Gleysol and exposed to possible anthropogenic contamination (Cąplak, 2022).

Mofetta 3 is situated along the valley of a stream around 200 meters below Mofetta 2. It is characterized by a large number of different plant and tree species. The soil is described as Gleysol (Cąplak, 2022).

Mofetta 4 is positioned along the stream where gas exhalations are also present in Figure 4.1. In horizon 25-30 cm, 50% of rock fragments were observed and becomes greater in deeper horizon. Since the soil profile is cut off from the stream bank, four to five points of water is seen coming out from the profile phase. The organic horizon, Oi, was taken from 0-30 cm depth, around 20 m above the Mofetta 4. The soil is characterized as Gleysol.

Mofetta 5 is located 15 meters above of Mofetta 4 and is classified as Cambisol. The soil is positioned at the shoulder of the hillslope showing 20% of sandstone rock fragments in BC1 layer and 40% of sandstone rock fragments in a deeper horizon.

Figure 4.1. Photo of gas exhalation in Mofetta 4 (a) and Organic horizon with recognizable dead plant material (b).

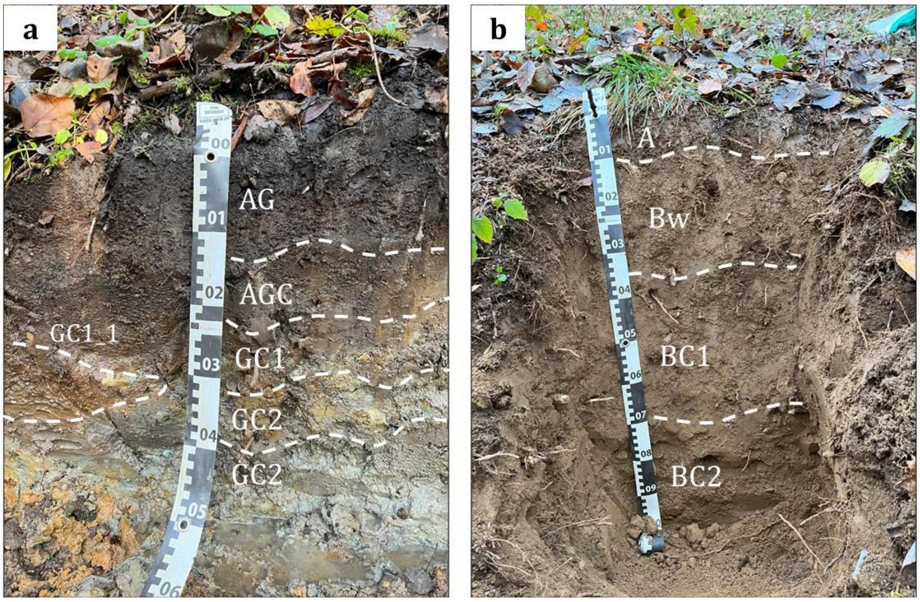

Figure 4.2. Soil horizon designation of Mofetta 4 (a) and Mofetta 5 (b), delineated by a dashed line. Mofetta 4 shows additional horizon.

4.2. Soil physical and chemical characteristics

The physical and chemical characteristics of mofetta profiles are summarized in Table 4.1. Measurement of pH in soil samples from Mofetta 1 to Mofetta 3 were classified as neutral to moderately alkaline, while Mofetta 4 and Mofetta 5 exhibit slightly to strongly acid pH. There is an evidence of increasing pH values in Mofetta 1, Mofetta 3, and Mofetta 5 as soil depth increases. The case is different for Mofetta 2, and Mofetta 4 although the differentiation in pH values is almost negligible.

As observed, the resulting pH values measured in 1M KCl are much lower than the same samples measured in water. The presence of salts in the KCl solution moderates the changing soluble salt concentration in the soil samples and thus increasing the concentration of H^+ ions (FAO, 2021). Bw horizon of Cambisol marked with the lowest pH measurement of 3.64, very strongly acid, in KCl suspension while Gox layer of Mofetta 1 was noted with the highest pH value of 7.37, moderately alkaline.

In terms of soil texture, Mofetta 1 has the highest clay content all throughout its profile where each particle size shares the same percentage when plotted in the soil textural triangle. Mofetta 1 has clay loam to loam texture making its silt/clay ratio values the lowest among the five studied soils. Mofetta 4 contains the highest sand fraction and lowest clay content on its profile making each horizon generally loamy sand to sandy loam.

Aside from this, Mofetta 1, Mofetta 3, and Mofetta 4 have relative increasing clay content, additional 5 to 20% clay from the upper horizons going to lower horizons. This can be explained as a result of clay illuviation process or clay enrichment in the deeper layers. Mofetta 5 is a Cambisol and a young soil, so the increase in clay content from upper to lower horizons is low though already observable. Mofetta 2 shows an equal distribution of clay on its profile, and decreases in the parent material.

Another trend that can be observed is the nitrogen distribution of all the soil profiles except for Mofetta 2. The mineral horizons of these soils have moderate to high nitrogen content which decreases in soil depth. The Mofetta 2 displays mixed nitrogen distribution ranging from low to moderate (0.0378 to 0.1400 %).

The humus horizons of Mofetta 3 to Mofetta 4 have extremely high amounts of organic carbon and organic matter content. The AG horizon of Mofetta 4 contains the highest OC and OM content (6,36% and 10,97%). Owing to its location in the forest, the organic material in AG horizon was able to decompose and accumulate through time without much disturbance. The soil of Oi layer of Mofetta 4 despite being an organic horizon does not contain the highest OC and OM content due to its water saturated condition, rendering a slow rate decomposition of the plant material. Generally, the studied soil profiles exhibit decreasing OC and OM trend with increased soil depth where the top 15 cm accounted for 45% to 61% of the total SOC profile except for Mofetta 2.

The relative nitrogen content of organic materials was also calculated based on the carbon to nitrogen ratio, wherein the soil carbon has lower values as compared to the organic materials (Hazelton, 2016). The C/N ratio of all soil samples resulted to <25 threshold, which means the nitrogen is released more rapidly (Hoyle, 2013). The Cg horizon of Mofetta 3 is the only sample with high C/N ratio of 64.29 resulting to the lowest nitrogen content (0.042%) among the soil samples. On the other hand, the Abg horizon of Mofetta 1 reveals the lowest C/N ratio and resulted to the highest percent of total N (0.6692%).

The sum of exchangeable base cations was also analyzed. The trend vary for each soil profile since this property is affected by several factors such as clay content (Hazelton, 2016) and pH (WRB, 2022). Mofetta 1 and Mofetta 3 being mildly to moderately alkaline contain higher average of exchangeable bases (155.27 to 477.96 mmol/kg) in the soil profiles. The average exchangeable bases of Mofetta 2 and

Mofetta 4 range from 65.47 to 112.14 mmol/kg. Mofetta 5 having the lowest pH has also the lowest exchangeable bases of 44.15 mmol/kg.

The EC values of all soil samples though vary from 139.91 to 1873.30 µS/cm do not exhibit signs of salinity.

Mofetta 4 range from 65.47 to 112.14 mmol/kg. Mofetta 5 having the lowest pH has also the lowest exchangeable bases of 44.15 mmol/kg.

The EC values of all soil samples though vary from 139.91 to 1873.30 µS/cm do not exhibit signs of salinity.

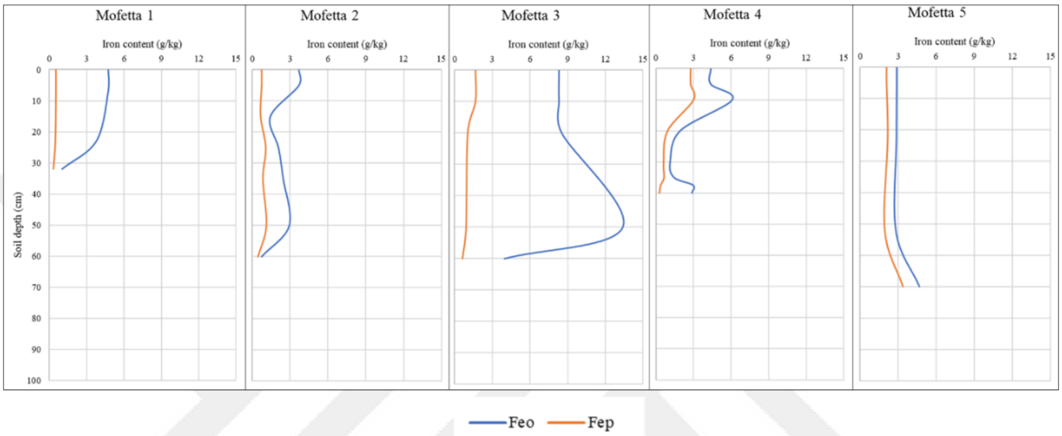

Figure 4.3. Distribution of iron in five soil profiles

The distribution of Feo and Fep in five soil profiles is highly diversified. For this reason, no correlation was found between these two forms of iron. The Feo ranges from 0.74 – 13.41 g/kg, while the Fep ranges from 0.27 – 3.37 g/kg. Each soil however, shows its own iron distribution trend. Generally, the content of Feo and Fep in Mofetta 1 to Mofetta 4 decrease in soil depth if the result is solely based on the difference of the surface and parent material horizon, the case is different for Mofetta 5 which is the only Cambisol among the studied soils.

The sudden increase of amorphous iron in Gox horizon of Mofetta 3 also draws attention. This horizon has the highest Feo (13.41g/kg) but has one of the lowest Fep (0.89 g/kg).

4.3. Results of Statistical Analyses

Different SOC ratings for soil carbon to assess soil health and condition proposed by (Hazelton, 2016) were grouped in to three: Low (extremely low, very low, and low), Moderate, and High (extremely high, very high, high). SOC and N level have treatment effect to the mean of silt/clay ratio values. The silt/clay ratio is a measure of the soil material uniformity and may confirm the differentiation of two layers (Wagner, 2007). For instance, Figure 4.4a shows that the silt/clay ratio of high

SOC and N level is both significantly different to low and moderate SOC levels with 95% confidence (*p-values 0.0013 and 0.0156, respectively*). The silt/clay ratio of low and moderate SOC levels are statistically the same.

Another treatment effect of SOC levels is observed in Na and Fep content of mofette soils. The Na and Fep content under moderate SOC level are statistically the same to either high or low SOC level. However, comparing the Na and Fep content of high and low SOC level, they are significantly different with probability of 95% (*p-values 0.0206, and 0.00627 respectively*).

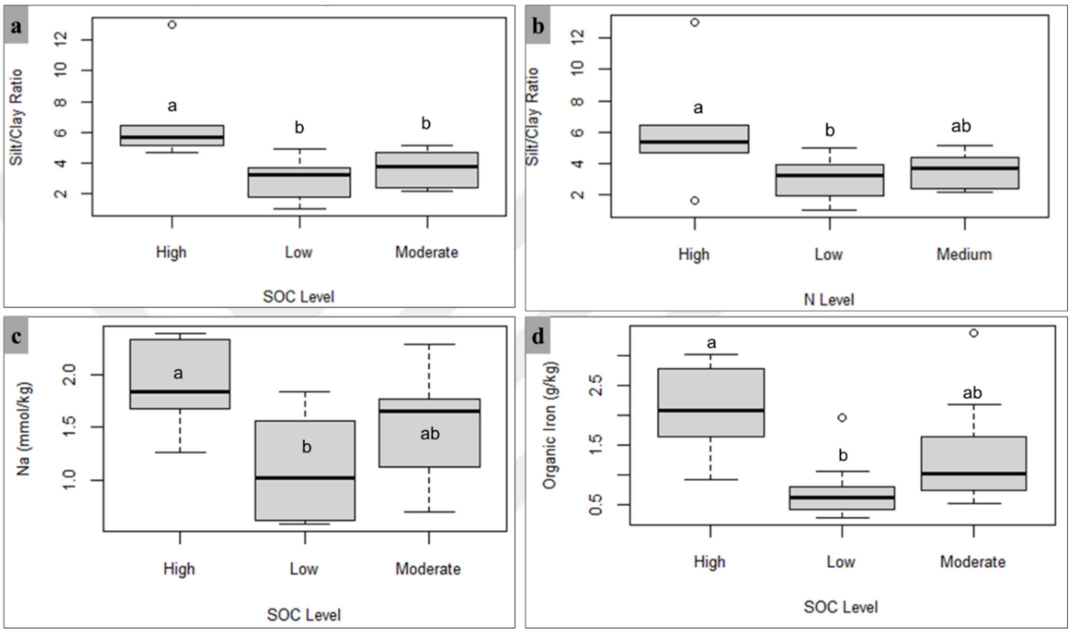

Figure 4.4. Boxplot showing the treatment effect of SOC level to (a) Silt/ Clay Ratio, (c) Na content, and (d) organically bound iron (Fe_p). (b) Silt/ Clay Ratio based on N level.

Table 4.1. Summary of the physical and chemical properties of mofette soils

Mofette number and soil type	Horizon	Depth (cm)	pH		EC (µS/cm)	Particle Size Distribution (%)			Soil textural class	Silt/Clay Ratio
			H_2O	KCl		Sand	Silt	Clay		
1. Mollic Stagnic Eutric GLEYSOL (Humic)										
	Ah	0-14	7.72	7.21	1873.30	36	45	19	Loam	2.37
	Abg	14-32	7.86	7.22	1171.80	23	48	29	Clay loam	1.66
	Gox	>32	8.08	7.37	882.50	25	40	35	Loam	1.14
2. Mollic Stagnic Eutric GLEYSOL (Humic)										
	Ahg	0-10	7.71	7.19	346.30	60	31	9	Sandy loam	3.44
	BCg1	10-20	7.54	6.68	725.70	59	32	9	Sandy loam	3.56
	BCg2	20-30	7.37	6.52	356.00	52	38	10	Sandy loam to Loam	3.80
	Gox	30-40	7.42	6.56	678.20	61	30	9	Sandy loam	3.33
	GC1	40-60	7.10	6.21	456.80	46	44	10	Loam	4.40
	GC2	>60	7.09	6.29	693.00	69	25	6	Sandy Loam	4.17
3. Mollic Stagnic Eutric GLEYSOL (Humic)										
	Ah	0-10	7.30	7.10	1317.70	45	46	9	Loam	5.11
	Abg	10-40	7.75	7.30	811.20	40	41	19	Loam	2.16
	Gox	40-60	7.76	7.30	768.80	46	38	16	Loam	2.38
	Cg	>60	7.92	7.17	552.40	42	29	29	Clay loam	1.00
4. Dystric Folic GLEYSOL (Loamic, Ochric, Uterquic)										
	Oi	0-30	5.09	4.73	1210.00	80	17	3	Loamy Sand	5.67
	AG	0-15	5.87	5.17	577.35	86	13	1	Loamy Sand	13.00
	AGC	15-25	5.72	4.96	486.50	83	14	3	Loamy Sand	4.67
	GC1	25-35	5.56	4.85	280.05	81	15	4	Loamy Sand	3.75
	GC1_1	30-40	5.95	5.05	266.85	75	19	6	Sandy Loam	3.17
	GC2	35-40	5.79	4.83	349.05	79	14	7	Sandy Loam	2.00
	GC2	>40	6.13	5.23	293.40	77	15	8	Sandy Loam	1.88
5. Dystric, Folic CAMBISOL (Colluvic, Loamic)										
	A	0-10	4.99	4.13	288.55	48	45	7	Loam	6.43
	Bw	10-35	4.64	3.64	168.30	45	46	9	Loam	5.11
	BC1	35-70	4.94	3.87	143.67	47	44	9	Loam	4.89
	BC2	>70	5.10	4.09	139.91	40	50	10	Loam to Silt Loam	5.00

Continuation of Table 4.1

Mofette number and soil type	Horizon	SOC (%)	SOM (%)	Total Nitrogen (%)	C/N Ratio	Exchangeable bases (mmol/kg)					Iron Forms (g/kg)	
						Ca^{2+}	K^{2+}	Mg^{2+}	Na^{2+}	Sum	Feo	Fep
1. Mollic Stagnic Eutric GLEYSOL (Humic)												
	Ah	1.52	2.62	0.1624	9.36	617.27	2.94	133.31	2.28	755.80	4.74	0.52
	Abg	0.91	1.57	0.6692	1.36	448.35	2.47	100.82	1.84	553.48	3.79	0.47
	Gox	0.09	0.15	0.0392	2.30	94.46	6.36	22.97	0.81	124.60	1.04	0.31
2. Mollic Stagnic Eutric GLEYSOL (Humic)												
	Ahg	0.72	1.25	0.1400	5.14	57.63	3.31	8.74	0.59	70.27	3.70	0.74
	BCg1	0.51	0.87	0.1113	4.58	51.15	1.51	7.08	0.61	60.35	1.43	0.66
	BCg2	0.6	1.04	0.1379	4.35	32.42	0.64	5.41	0.63	39.10	2.08	1.06
	Gox	0.41	0.70	0.0378	10.85	39.22	0.86	9.53	0.63	50.24	2.45	0.84
	GC1	1.17	2.01	0.1260	9.29	56.09	0.92	11.47	0.71	69.19	2.94	1.11
	GC2	0.19	0.33	0.0308	6.17	86.78	1.01	15.07	0.80	103.66	0.74	0.46
3. Mollic Stagnic Eutric GLEYSOL (Humic)												
	Ah	4.28	7.38	0.4032	10.62	92.27	2.02	18.45	1.27	114.01	8.32	1.64
	Abg	1.25	2.15	0.1918	6.52	82.63	1.02	10.03	1.04	94.72	8.53	1.02
	Gox	1.19	2.05	0.0896	13.28	144.31	1.45	14.88	1.21	161.85	13.41	0.89
	Cg	0.27	0.47	0.0042	64.29	230.54	1.62	17.10	1.23	250.49	3.97	0.60
4. Dystric Folic GLEYSOL (Loamic, Ochric, Uterquic)												
	Oi	4.54	7.84	0.3220	14.11	140.72	1.70	30.82	2.33	175.57	4.38	2.77
	AG	6.36	10.97	0.4984	12.76	224.25	2.41	44.56	2.38	273.59	6.09	3.01
	AGC	2.92	5.04	0.2814	10.38	92.93	1.18	20.64	1.68	116.43	1.94	0.92
	GC1	1.60	2.77	0.1484	10.81	54.52	1.33	13.56	1.65	71.06	1.14	0.60
	GC1_1	0.89	1.53	0.0784	11.31	43.54	1.01	12.20	1.64	58.40	1.44	0.64
	GC2	0.53	0.91	0.0448	11.83	32.81	0.96	9.78	1.45	44.99	2.96	0.37
	GC2	0.40	0.69	0.0224	17.98	32.07	1.04	10.12	1.74	44.96	2.88	0.27
5. Dystric, Folic CAMBISOL (Colluvic, Loamic)												
	A	2.74	4.72	0.2562	10.69	66.16	2.12	10.58	1.84	80.70	2.89	2.08
	Bw	1.21	2.08	0.1610	7.49	20.80	0.97	3.76	1.69	27.21	2.87	2.17
	BC1	0.93	1.60	0.0896	10.36	32.10	0.86	4.14	1.48	38.57	2.84	1.95
	BC2	1.14	1.97	0.0812	14.05	24.32	0.76	3.18	1.85	30.12	4.67	3.37

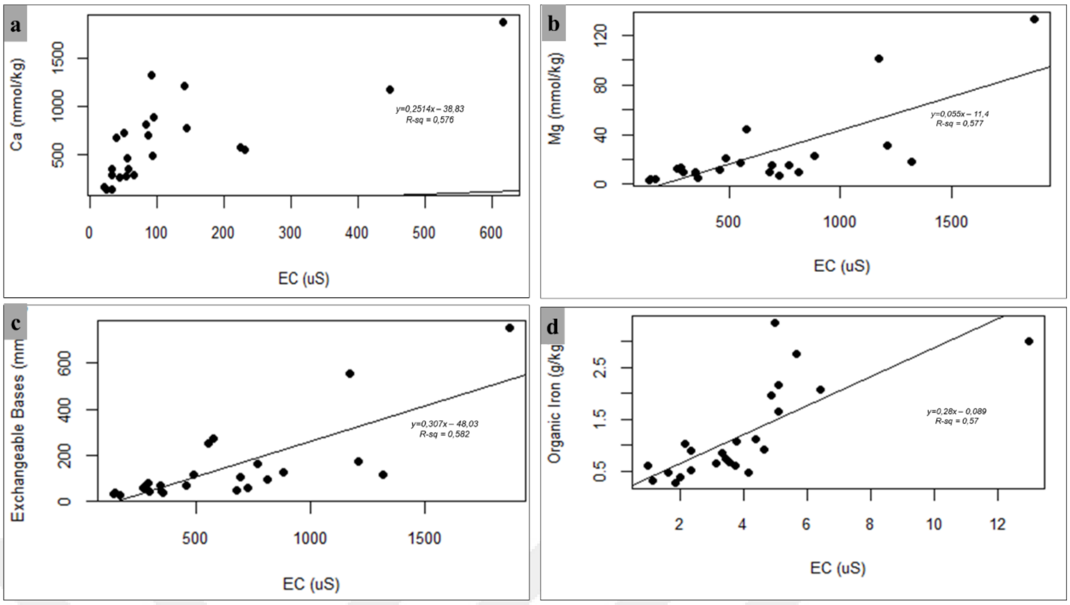

Figure 4.5. Linear regression model showing different content of soil properties as affected by EC values.

The electric conductivity of the soil reveals strong positive association with exchangeable bases and organically-bound iron as noted in Figure 4.5, showing high R^2 values (coefficient of determination). Analysis of each cation also revealed direct proportional relationship to EC especially Ca, and Mg. In fact, the Ah horizon of Mofetta 1 noted with the highest EC values and sum of exchangeable bases. This information is useful in such a way that, the results of EC field test may already give a fair estimation of the availabilities of exchangeable bases and Fe content in organic complexes.

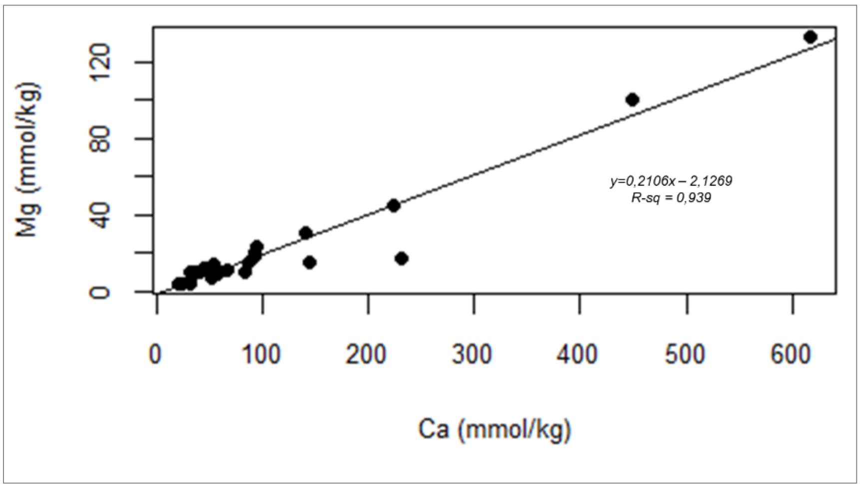

Figure 4.6. Linear regression model showing the relationship of Ca and Mg content in soil

Ca and Mg are basic cations sharing several similarities in terms of their properties. In mofette soil samples, Ca and Mg are directly proportional with each other. The results are highly significant even at 99% confidence level (*p-value* $7.571e^{-15}$).

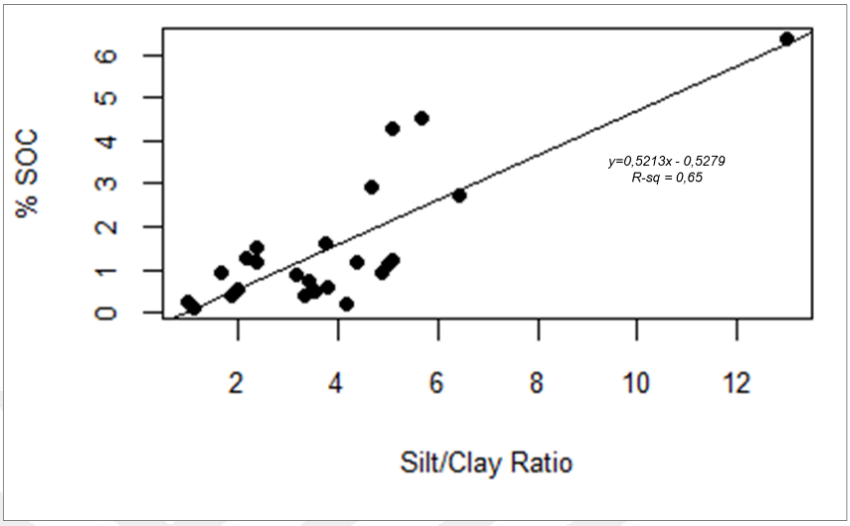

Figure 4.7. Linear regression model showing the relationship of Silt/Clay Ratio and SOC

The ratio of silt/clay and % SOC shows high positive correlation that is, SOC content in the soil increases as the silt/clay ratio increases.

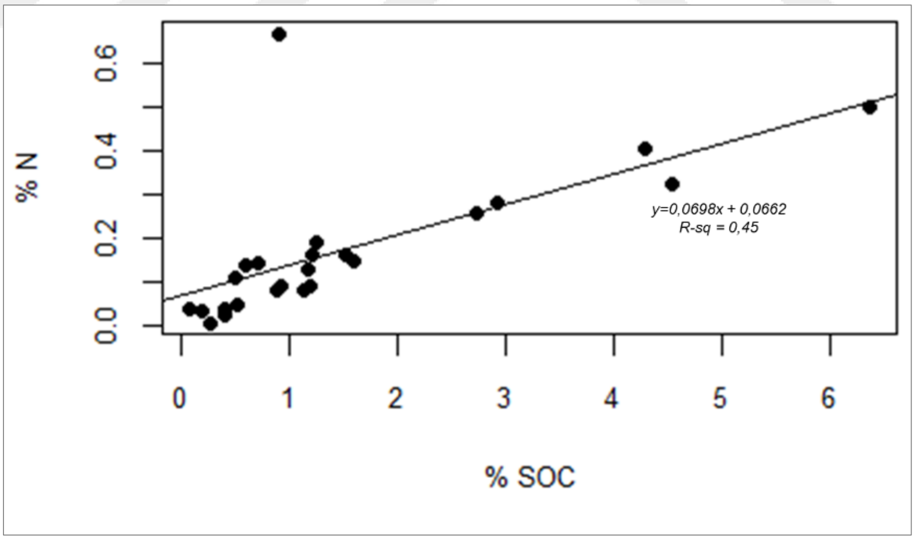

Figure 4.8. Linear regression model showing the relationship of %SOC and %N in soil

Result of Figure 4.8 is consistent with the other studies showing significant relationship between % SOC and % N (Lei, 2013; Yan, 2016). One simple reason is that organic matter is a key provider of total nitrogen (Abegaz, 2016).

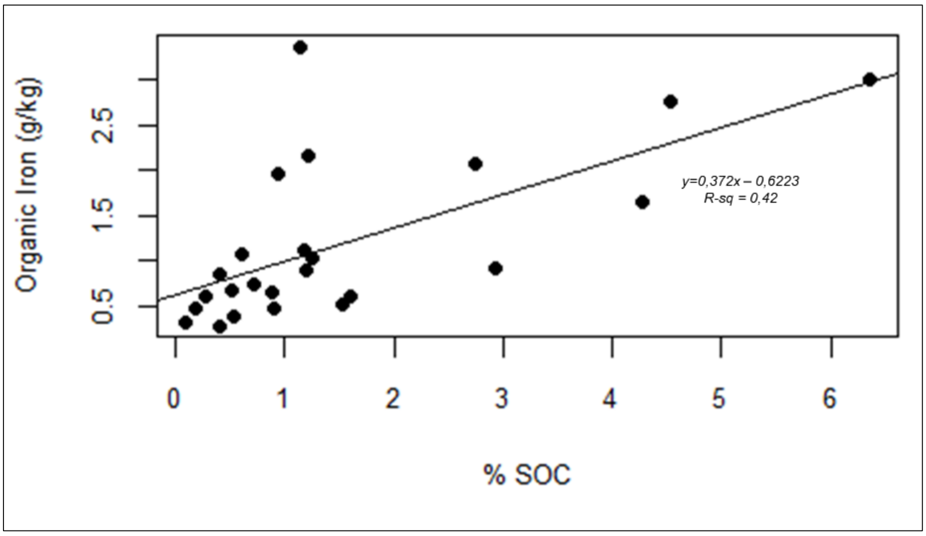

Figure 4.9. Linear regression model showing the relationship of %SOC and organically bound iron

Fep is the form of iron bound to organic complexes of the soil. That being said, the association of these two chemical properties, Fep and %SOC, is expected. Such result is in line with the findings of (Zanelli, 2007) showing positive correlation between these two properties. This information may give insights on the stability of SOC against biodegradation since according to (Singh, 2018), the mechanism of Fe minerals and SOC association is important to stabilize SOC.

5. CONCLUSIONS

For this study, mofette soils are commonly classified as gleysols attributed to the presence of carbonated mineral water spring and reducing soil condition. The pH of Mofetta 1 to Mofetta 3 were close to being neutral and moderately alkaline, while Mofetta 4 and Mofetta 5 exhibit slightly to strongly acid. Bw horizon of Cambisol marked with the lowest pH measurement of 3.64, very strongly acid, in KCl suspension while Gox layer of Mofetta 1 was noted with the highest pH value of 7.37, moderately alkaline.

Mofetta 1 contained the highest clay fraction on its soil profile while the highest sand fraction was recorded in Mofetta 4. The likelihood of clay enrichment in the subsoil was observed in Mofetta 1, Mofetta 3, and Mofetta 4 having clay content difference of 5 to 20% from the upper and lower horizons. Except for Mofetta 2, the rest of the studied soil profiles exhibit decreasing content in the majority of the properties, that is higher composition of silt/clay ratio, % SOC, % N, EC, and exchangeable base cations. The physico-chemical properties of Mofetta 2 are diverse along its profile.

The treatment effect of SOC level shows statistically significant differences to silt/clay ratio, Na content, and organically-bound iron (Fep). On the other hand, different N levels render significant differences silt/clay ratio. The electric conductivity of the studied soils shows high positive correlation with the sum of exchangeable bases especially with Ca and Mg, as well as to the availability of Fep.

The analyzed iron forms – amorphous and organically-bound iron – did not show any correlation. The vertical distribution of Feo and Fep vary for each soil profile. For gleysols, Feo and Fep content decrease in soil depth. Gox horizon of Mofetta 3 displays the highest Feo (13.41g/kg) but has one of the lowest Fep (0.89 g/kg).

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CURRICULUM VITAE

Contact Information:

ORCID ID : https://orcid.org/0009-0004-1667-1586

Publications :

Rice Crop Manager Advisory Service: Operations Manual, volume 2: Research

Won Awards, Incentives and Scholarships

1. Department of Science and Technology - Science Education Institute (DOST-SEI) Undergraduate Scholarship

2. Erasmus Mundus Joint Masters Degree Scholarship