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

THE INFLUENCE OF NATURAL OIL SEEPS ON THE CHEMICAL PROPERTIES OF THE SURROUNDING SURFACE SOIL LEVELS.

Master's Thesis

Desmond Kwayela SAMA

SUPERVİSOR
Assoc. Prof. Dr. Tomasz ZALESKİ

II. Supervisor

Prof. Dr. Orhan DENGİZ

SAMSUN
2024

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ONDOKUZ MAYIS ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM
ENSTİTÜSÜ

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.ACCEPTANCE AND APPROVAL OF THE THESIS

The study entitled **"THE INFLUENCE OF NATURAL OIL SEEPS ON THE CHEMICAL PROPERTIES OF THE SURROUNDING SURFACE SOIL LEVELS"** prepared by **Desmond Kwayela SAMA**, and supervised by **Assoc. Prof. Dr. Tomasz ZALESKİ and Prof. Dr. Orhan DENGİZ**, was found successful and unanimously accepted by committee members as Master thesis, following the examination on the date 14.8.2024.

	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
Member	Prof. Dr. Coşkun GÜLSER Ondokuz Mayıs University Department of Soil Science and Plant Nutrition	☒ Accept ☐ Reject
Member	Doç. Dr. Ammar A. ALBALASMEH Jordan University Science and Technology, Jordan Department of ………………	☒ Accept ☐ Reject

This thesis has been approved by the committee members that already stated above and determined by the Institute Executive Board.
.

Prof. Dr. Ahmet TABAK
Head of Institute of Graduate Studies

DECLARATION OF COMPLIANCE WITH SCIENTIFIC ETHIC

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.

Is Ethics Committee Necessary?

Yes ☐ (If it necessary, please add appendices.)

No ☒

27 /06 / 20...
Desmond Kwayela SAMA

DECLARATION OF THE THESIS STUDY ORIGINALITY REPORT

Thesis Title: THE INFLUENCE OF NATURAL OIL SEEPS ON THE CHEMICAL PROPERTIES OF THE SURROUNDING SURFACE SOIL LEVELS

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ÖZET

PETROL SIZINLTILARININ ÇEVRESİNDEKİ YÜZEY TOPRAĞIN KİMYASAL ÖZELLİKLERİ ÜZERİNDEKİ ETKİSİ

Desmond Kwayela SAMA

Ondokuz Mayıs Üniversitesi
Lisansüstü Eğitim Enstitüsü
Adli Bilimler Ana Bilim Dalı
Toprak Bilimi ve Bitki Besleme Ana Bilim Dalı
Yüksek Lisans, **Temmuz/2024**
Danışman: **Assoc. Prof. Dr.Tomasz ZALESKİ**
II. Danışman: **Prof. Dr. Orhan Dengiz**

Doğal petrol sızıntıları, yer kabuğundan sızan, kabarcıklar, su ve yağ ile koyu viskoz sıvı olarak görülebilen sıvı veya gaz halindeki hidrokarbonlardır. Polonya, özellikle Zmiennica-Brzózow, Ropianka ve Płowce'nin Subcarpathia Voyvodalığı bölgelerinde önemli petrol sızıntılarına ev sahipliği yapıyor. Bu sızıntılar jeolojik bilgiler sunar ancak çevresel riskler oluşturur. Bu çalışmanın amacı, bu bölgelerdeki üst toprak kimyası üzerindeki doğal sızıntı etkilerini araştırmaktır.

Toprak örnekleri 0-20 cm derinlikte, sızıntılara yakın ve daha uzakta toplanmıştır. Yağ içeriği değişmiştir: Zmiennica-Brzózow'da% 0.885 -% 3.540, Ropianka'da% 0.695 -% 44.126 ve Płowce'de% 1.756 -% 19.660. Yağ içeriği yüksek olan alanlar, toprak organik karbon, azot ve C/N oranlarında artış gösterdi. pH, yüksek yağ içerikli alanlarda pH'ta (KCl) hafif bir artışla hafif asidik ila hafif alkali arasında değişiyordu. Silt/kil oranı 0.3 ile 8.2 arasında değişmektedir. Kalsiyum, potasyum, magnezyum, sodyum, fosfor, bitkide bulunan potasyum, serbest demir oksit, kristal demir, amorf demir ve toplam demir gibi elementler daha yüksek yağ içeriği ile azalmıştır. Kristal demir, Zmiennica-Brzózow'da 7531 mg / kg ila 11439 mg / kg, Ropianka'da 5509 mg / kg ila 9738 mg / kg ve Płowce'de 3353 mg / kg ila 6021 mg / kg arasında değişen her üç yerde de en yüksekti.

Anahtar Sözcükler: Subcarpathia Voyvodalığı, hidrokarbonlar, üst toprak, kimyasal özellikler ve toprak kirliliği

ABSTRACT

THE INFLUENCE OF NATURAL OIL SEEPS ON THE CHEMICAL PROPERTIES OF THE SURROUNDING SURFACE SOIL LEVELS.

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Master, February/2022
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Natural oil seeps are liquid or gaseous hydrocarbons that leak from the earth's crust, visible as dark-viscous liquid with bubbles, water, and oil. Poland hosts significant oil seeps, particularly in the Subcarpathia Voivodeship areas of Zmiennica-Brzózow, Ropianka, and Płowce. These seeps offer geological insights but pose environmental risks. This study's aim was to investigate natural seep effects on topsoil chemistry in these regions.

Soil samples were collected at 0-20 cm depth, near and further from the seeps. The oil content varied: 0.885%-3.540% in Zmiennica-Brzózow, 0.695%-44.126% in Ropianka, and 1.756%-19.660% in Płowce. Areas with high oil content showed increased soil organic carbon, nitrogen, and C/N ratios. The pH ranged from slightly acidic to slightly alkaline, with a mild increase in pH (KCl) in high oil content areas. The silt/clay ratio ranged from 0.3 to 8.2. Elements such as calcium, potassium, magnesium, sodium, phosphorus, plant-available potassium, free iron oxide, crystalline iron, amorphous iron, and total iron decreased with higher oil content. Crystalline iron was highest in all three locations, ranging from 7531 mg/kg to 11439 mg/kg in Zmiennica-Brzózow, 5509 mg/kg to 9738 mg/kg in Ropianka, and 3353 mg/kg to 6021 mg/kg in Płowce.

Keywords: Subcarpathia Voivodeship, hydrocarbons, topsoil, chemical characteristics, and soil contamination.

ACKNOWLEDGEMENT

Desmond Kwayela SAMA

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1. INTRODUCTION

Natural oil seeps are liquid or gaseous hydrocarbon substances that leak to the surface of the Earth from the crust. They are organic occurrences that have been there for millions of years and may be found all over the planet (Etiope, 2015). Those seeps are characterized by a very dark color, a viscous dark liquid that shows the presence of oil, water, and bubbles (a sign of gas emission). These seeps are distributed globally in terrestrial and marine environments [Etiope 2009].

These seeps can affect human activity and the environment in both beneficial and non-beneficial ways. They can be used as a source of energy and useful information about the geology and petroleum prospects of a region since their composition depends on the source rock, geological conditions, and the maturity of the hydrocarbon reservoir (Adeola et al., 2022). Soil contamination usually arises from Transport mechanisms such as diffusion and oil volatilization from the seep sources (Etiope, 2015). The soil's chemical composition can be changed because the hydrocarbons in the soil can be transformed via microbial activities, redox processes, and other processes, influencing the availability of nutrients and the mobility of heavy metals (Sama et al., 2023; Adesipo et al., 2020; Ossai et al., 2020). Changes in soil composition have ecological consequences, affecting plant growth, soil fauna, and overall ecosystem health.

Natural Crude oil leaks are prevalent in Poland, particularly in regions of the Carpathians mountain range. According to Wołkowicz et al., (2017), the first known accounts of these seeps date from the first half of the 16th century. In Poland, the oil from these naturally occurring seeps is used to paint wood, used for house construction to slow down its degradation.

According to Ossai et al., (2020), the physical and chemical characteristics of soil may be affected by pollution caused by oil presence. Extensive research has been carried out to elucidate the degree of surrounding surface soil pollution in oil seep sites. For example, a study conducted by Saikai et al., (2023) on the impact of crude oil on soil physiochemical properties, reported the following changes in the surrounding soil as a result of the crude oil: soil organic carbon, soil organic matter, pH, phosphorus, calcium, and nitrogen content were higher in oil drilled site compared to the surrounding soils, while total iron content, moisture, electrical conductivity, bulk density were found to be low in oil drilled site compared to surrounding soils.

This work aim to look into the impact of natural oil seeps on the chemical properties of top soils in the surrounding area of the regions of Zmiennica-Brzózow, Ropianka, and Płowce, in the Subcarpathia Voivodeship (in Polish: województwo podkarpackie) of Poland. Several amounts of these oil seeps are situated on an agricultural site, or the area may be used for forestry and other purposes in the future. Moreover, the topsoil is an important section of soil especially when it concerns agricultural activities. This has made it important to confirm if the land will be acceptable for these kinds of operations or, if it is not, what steps can be taken to improve the land's condition to fit the intended use. So is it of utmost importance for continuous monitoring of natural oil seeps for the essential understanding of their dynamics and potential impacts?

2. LITERATURE REVIEW

2.1 Natural Oil Seeps

Natural oil seeps are liquid or gaseous hydrocarbon substances that leak to the surface of the Earth from the crust (Etiope, 2015). Oil seeps may generate oil that oozes episodically from rocks, soils, or oil-impregnated landscapes, or they can create black pools filled with oil. Oil may be seen in aquatic settings as drips, oily patches, slicks (layers of buoyant oil), diffuse iridescences, or all three.

According to geological data, the extensive petroleum extraction that started in the 1800s has resulted in the disappearance of several historical oil seeps or a significant reduction in their fluid activity (Etiope, 2015; Ali, 2017). Reduced fluid pressure inside reservoirs leads to a reduction in oil flow. Although the precise number of onshore seeps (including; Oil seeps, Gas seeps, Mud Volcanoes, and Springs) worldwide is unclear, it is estimated to be more than 10,000 (Etiope et al., 2015), and they are dispersed across the petroliferous basins on every continent. Some of the most active and large onshore oil seeps can currently be observed in Poland (Carpathian Mountain range), Azerbaijan (near Dashgil), Alaska (Samovar Hills), California (e.g., the McKittrick and Sargent oil fields), Pulkhana (Iraq), Kuwait (e.g., Burgan), and New Zealand (Kōtuku) (Etiope, 2009; Idczak et al., 2020; Baliński et al., 2022).

Table 1. Summary of the total number of natural oil seeps globally (Modified from Etiope, 2015)

Continent	Oil seeps	Number of countries	Countries
Europe	207	19	Albania, Armenia, Azerbaijan, Croazia, Denmark, Georgia, Greece, Ireland, Italy, Poland, Portugal, Romania, Russia, Spain, Sweden, Switzerland, Turkey, United Kingdom, Ukraine

Asia	123	31	Bahrain, Bangladesh, Brunei, Cambodia, China, India, Indonesia, Iran, Iraq, Israel, Japan, Jordan, Korea North, Kuwait, Kyrgyzstan, Laos, Malaysia, Mongolia, Myanmar, Nepal, Oman, Pakistan, Philippines, Syria, Taiwan, Thailand, Timor-Leste, Turkmenistan, United Arab Emirates, Vietnam, Yemen
Africa	36	14	Angola, Egypt, Ethiopia, Ghana, Madagascar, Morocco, Mozambique, Nigeria, Sao Tome, Somalia, Tanzania, Tunisia, Uganda, Zaire
North America	115	2	Canada, United States of America
Central South America	107	19	Argentina, Barbados, Belize, Bolivia, Brazil, Chile, Colombia, Costa Rica, Dominican Republic, Ecuador, Guatemala, Jamaica, Mexico, Nicaragua, Panama, Perù, Puerto Rico, Trinidad, Venezuela
Oceania	46	4	New Zealand, Papua New Guinea, Tonga, Australia
Total	634		

2.2 Oil Seeps History in Poland

Seeps of crude oil occur naturally across southeast Poland, particularly in areas where the Carpathian Flysch series (Kotarba et al., 2021; Więcław et al., 2022). These leaks have been documented since the early sixteenth century. It has been cited in connection with a failed attempt at gold mining by Seweryn Boner (1486–1549), a nobleman who held positions as the Treasurer of the Crown under King Sigismund I the Old, the castellan (Burggraf) of Kraków, and the head of the Biecz District (Wołkowicz et al., 2017). In the town of Ropa, which means oil in Polish, at the foot of Mount Chełm, powerful seeps of rock oil (petroleum) from bedrock were released in 1530 as a consequence of massive excavations nearby (Wołkowicz et al., 2017).

Additionally, the oil business in Poland grew quickly when Ignacy Łukasiewicz discovered a method for distilling kerosene from seep oil and created an effective

contemporary kerosene lamp in 1853 (Wołkowicz et al., 2017). In 1859, several wells in the Carpathians were already producing oil (Kotarba et al., 2021). Oil production and exploration continued eastward when major oil deposits were discovered in Schodnica and Borysław, initially concentrating in the districts of Gorlice, Jasło, and Krosno (De Cizancourt, 1931; Wołkowicz, et al., 2017). Famous places where these natural oil seeps occur in Poland include; Węglówka, Stara Sól, Łacko, Nahajowice, Bóbrka, Ropa, Potok, Ropianka, Kobylanka, Brzozow, Libusza, Iwonicz, Klimkówka, Harklowa, Wietrzno Rogi, Wieliczka, Pokucie, Maramures, Gorlice, Krosno, Sanok, Ustrzyki, Drohobycz and Płowce (Wołkowicz et al., 2017; Kotarba et al., 2021; Baliński et al., 2022).

Nevertheless, the information that is currently accessible does not specifically state how many oil leaks are there in Poland in total. While the specific count of oil seeps in Poland remains elusive, their presence underscores the geological significance of the region (Wołkowicz et al., 2017). Some observations on the presence and usage of this oil from these seeps, as well as descriptions of simple hand-dug trenches that were in use by the end of the eighteenth century for obtaining this oil, were documented in a report by Kluk, Staszic, and Zejszner (Dowgiałło and Kozerski, 2012). Even in the present day, some of those hand-dug trenches can be still seen in the field near the natural oil seeps.

2.3 General Composition of Crude Oil

The chemical composition of crude oil depends on the source rock, the geological formation, and the processes involved in the formation and migration of the oil (McCarthy et al., 2011; Xia et al., 2019)**.** When oil is exposed to the atmosphere, its gas content diminishes and is then followed by oxidation, biodegradation, and solidification (Ossai et al., 2020; Ambaye et al., 2022).

Hydrocarbons are the $1°$ constituents of crude oil (Olah and Molnár, 2003). The hydrocarbons are classified into different forms based on their molecular structure such as alkanes like methane, ethane, propane, butane, etc. The alkanes are the most abundant class of hydrocarbons in crude oil. The next is aromatics hydrocarbons such as benzene, toluene, and xylene which contain one or more benzene rings. Moreover, they are the alkenes and alkynes, unsaturated hydrocarbons containing double and triple bonds respectively. The alkenes and alkynes are generally present in smaller

quantities compared to alkanes. (Olah and Molnár, 2003). Some oils may contain compounds such as hydrogen sulfide, Mercaptans, thiophenes, and sulfides (Saji 2021). To add to this, Nitrogen-containing compounds like pyridines, indoles, and quinolones are found in crude oil but in very minute quantities compared to hydrocarbons and Sulfur compounds (Zhang et al., 2018). Furthermore, we can have organic acids, alcohols, ketones, and esters. Finally, some metals like iron, nickel, vanadium, and copper; may come from the source rock or geological formations (Shahbaz et al., 2023).
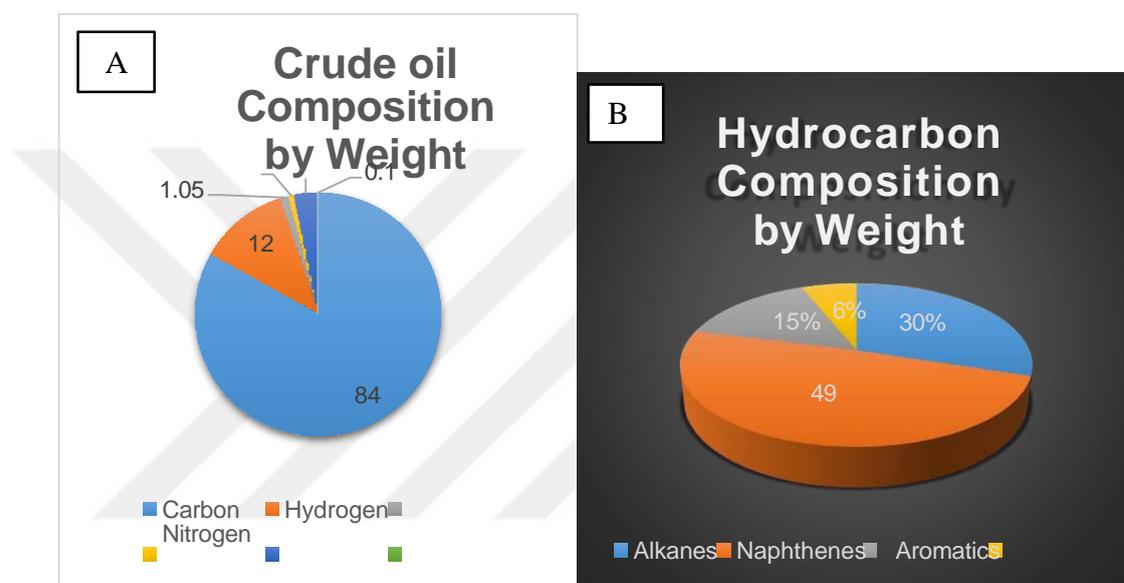
Figure 1. A- Percentage composition of elements by weight in crude oil; B- Percentage composition of the various hydrocarbons by weight in crude oil (Source of data; Hyne, 2001)

2.3.1. Global Variations in Crude Oil Composition

Due to variations in tectonic settings, geological processes, and source rock features, crude oil compositions range greatly around the globe (Peters and Fowler, 200; McCarthy et al., 201; Caineng et al., 2013). It observed that every crude oil or petroleum comes from a source rock. These source rocks are fine-grained, organic-rich rocks capable of generating oil when exposed to sufficient heat and pressure under the earth's crust (McCarthy et al., 2011). As a result of exposure of the source rock to heat and pressure, it is transformed into an insoluble organic matter known as Kerogen. The type of kerogen formed depends on the source of the materials (McCarthy et al., 2011). From the table below we can see the kind of kerogen based on the source material;

Table 2. The type of kerogen formed depends on the source of the materials

Kerogen Type	Source material	Environment of deposition	Description
I	Mainly algae	Lacustrine setting	Very rich in hydrogen and low in oxygen, oil sensitive and sometimes produce gas. Account for <3% of the world's oil and gas reserves. We can find it in Green River, Western USA.
II	Mainly plankton, algae	Marine setting	It is low in carbon and high in hydrogen, with considerable sulfur incorporation in certain places(Term as Type II-S kerogen), and produces gas and oil as well. The North Sea's Kimmeridge clay, Siberia's Bazhenov Formation, California's Monterey Formation, and Venezuela's La Luna Formation are a few examples.
III	Mainly higher plants	Terrestrial setting	Low in Hydrogen but rich in Oxygen content compared to type I or II. Produces dry gas.
IV	Reworked, oxidized residual materials	Varied setting	Has high Carbon content but is low in Hydrogen. This type of Kerogen almost does not have the potential to generate oil or gas.

Source (Modified from McCarthy et al., 2011)

2.3.2 Composition of Crude Oil in Different Areas in Poland

In Poland especially in the Carpathian region, the source rocks of crude oil are Black shale, the Paleocene Majdan beds, and the Lower Oligocene Menilite beds (Kruge et al., 1996). According to the study by Kruge et al., (1996) carried out in the Carpathian region on these bed rocks, it reported that the black shale (Aptian-Albian Spaskie) beds were made of Type III Kerogen, the Paleocene Majdan beds were made of Type I kerogen, and the Oligocene Menilite beds rocks were made of reworked materials (Type IV Kerogen). Moreover, the result of the oil analysis he obtained shows that the Manilite beds rocks have predominantly $C_{15} - C_{31}$ n-alkanes with some low amount of organic sulfur contents, the Majdan Black Shale is predominantly made of short-chain C_{17} and C_{18} n-alkanes, and the Spaskie black Shale was dominated by n-alkanes C_{25} to C_{33}.

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2.4 Soil Contamination by Oil

The presence of oil in the soil can lead to contamination, affecting its physical and chemical properties of the soil (Ossai et al., 2020). Limited studies have been conducted to explain the extent of surrounding surface soil contamination in oil seep areas. However, a lot of studies have been carried out to explain the impact of oil spills on soil's physical and chemical properties. The difference between oil seeps and oil spills is; that the oil from oil seeps moves upward in the soil while for oil spills, it moves downward (McDonald, 1998; Essien and John, 2010; Michel and Fingas, 2016). Since both involve crude oil, they may have a similar impact on the soil's physical and chemical properties. Soil contamination usually arises from Transport mechanisms such as diffusion, advection, and volatilization of the oil from the seep sources (Etiope, 2015).

When gas and/or crude oil are often dumped over agricultural soils and the mixture is allowed to build up, the resulting soil becomes toxic and useless, particularly in the uppermost layer. Because of the oil's decrease in soil fertility, most of the essential nutrients for plant growth and development are no longer accessible (Adesipo et al., 2020; Sama et al., 2023). Due to its density, crude oil plugs soil pores, reduces permeability, and drives air and water out of the soil, depriving soil microbes and plant roots of oxygen (Ossai et al., 2020). Oil's impact on soil's chemical characteristics is summarized in the table below.

Table 3. Effect of Crude oil on soil chemical properties

Soil chemical properties	Effect of oil on the soil's chemical properties	Remark	Reference

		The increased pH values may be due to the hydrophobic nature of crude oil that potentially causes drought in surface and subsurface layers, leading to salinization and increased pH.	(Njoku et al. 2009).
pH	Crude oil pollution increased pH values.		
Total Soil organic carbon content	Increase soil organic carbon	- Most likely as a result of the much greater TPH and/or slow decomposition by microorganisms due to poor aeration.	(Wang et al., 2010; Agbogidi et al., 2007).
Total Calcium carbonate content	It does not directly influence oil on Calcium carbonate in soil.		
Cation Exchange Capacity (CEC)	-Overall it decreased the total CEC of soils. - lower levels of K^+ and Na^+. -increased Ca^{2+}.	Lower Na and K may be the result of nutrient immobilization, which happens when complexes are formed in the soil after absorption and breakdown.	(Wang et al., 2013).
Total nitrogen	-By some authors, oil contamination decreased nitrogen levels.	-possibly due to the slow-down actions of microorganisms involved in the breakdown of organic materials, such as nitrogen-fixing bacteria.	(Ezeigbo et al., 2013).
	-To some, an increase in oil increases total nitrogen in soils.	The oil promotes the organic carbon content in the soil.	(Saikia et al., 2023).
Total Phosphorus	Increases with increased oil content in the soil.	As a result of the increased pH and high Ca^{2+} turn to precipitate P in soil	(Agbogidi et al., 2007).

Iron	Increased concentration of iron. Fe^{2+} turns out to be more in oil-polluted soil.	might be related to the conversion of Fe^{3+} to Fe^{2+} as a result of the favorable reducing conditions brought forth by oil pollution.	(Akubugwo et al., 2009).
Heavy metals	Increased concentration of copper, Manganese, chromium, and lead.		(Akubugwo et al., 2009).

2.5 Iron Forms in Soils

Analysis of iron forms in soil is one of the commonly acknowledged techniques in soil genesis and soil classification investigations that rely on the direction, kind, and intensity of soil-forming processes (Różański, 2013). There are many different forms of iron in the soil, and they largely depend on the following factors: pH, soil moisture, temperature, and redox potential, particularly in anaerobic environments. These forms are the outcome of intense metabolic changes that occur in soils high in organic matter (Waychunas et al., 2005; Weber et al., 2006; Orzechowski et al., 2018). Furthermore, Iron serves as a gauge for both the length and strength of pedogenic processes, as well as the intensity of geological processes (Chardon et al., 2018).

If larger iron distribution values are found in the surface soil compared to the parent material horizon, this might indicate pedogenesis (Orzechowski et al., 2018). While there is a weak negative link between iron level and organic carbon content, other research indicates that there is no substantial relationship between iron content and soil humus content (Różański 2013). On the other hand, Orzechowski et al., (2018) found a substantial positive correlation between the amount of clay and the levels of total iron, including its silicate, crystalline, and free forms.

According to Shui-Sheng, (2016), free iron forms (Fe_d) are iron forms that have been adsorbed or coated on the surface of soil particles but are not present in the lattice structure. One of the most important fundamental aspects of soil is its analytical measurement of free iron, which helps researchers understand the behavior of soil dispersion, soil genesis, and soil categorization (Shui-Sheng, 2016). When the clay

proportion and Fe_d content are correlated, the high concentration of Fe_d in the sub-surface soil horizon is probably the consequence of illuviation rather than weathering. This is because hydrous Fe oxides have very tiny particle sizes and are often found in conjunction with clay. If the surface horizon has high Fe_d content the lower horizon, can be due to intense weathering (Orzechowski et al., 2018).

Studies have shown the importance of iron oxide minerals in controlling the biogeochemical cycles of carbon on Earth's surface and stabilizing organic carbon (Yu et al., 2021; Song et al., 2022). For example, iron-bound organic carbon may make up a significant amount of total organic carbon in forest soils, highlighting the significance of both sorptive and incorporative interactions between iron and organic matter (Song et al., 2022). These interactions are regulated by several variables, including soil physicochemical qualities and Eco geographical variables, and are not only reliant on the content of reactive iron. Compared to non-iron-bound organic carbon, iron-bound organic carbon has different properties, such as being richer in carbon-13 and often less aliphatic, organic-bond iron is black while non-iron-bond organic is grey (Lalonde 2014; Zhao et al., 2016).

In addition to free iron (Fe_d), Iron is also present in the soil as amorphous Iron oxides (Fe_o), with amorphous iron oxides being the most labile and active form of iron (Rezapour et al., 2010; Rabajczyk and Namieśnik, 2014). Non-persistent anaerobic state and high organic materials in the soil increased the amorphous iron oxide form (Büyükkılıç et al., 2022; Chen et al., 2022).

The sum of the Free iron oxide Fed and amorphous oxides Fe_o gives the value of the crystalline iron (Fec). The Fe_c value tells the state of iron crystallization in the soil. Higher values of Fe_c indicate favorable conditions for iron crystallization in soil and vice versa (Orzechowski et al., 2018). The silicate form of iron (Fes) is indirectly connected to the free iron in the soil. Lower levels of free iron are undoubtedly indicated by a greater Fes value, which points to a more active weathering process in the soil (Orzechowski et al., 2018).

One method for researching how iron is changed in the soil is to look at the iron activity index (Fe_o/Fe_d) (Pawłowski and Kobierski, 2023). A study by Orzechowski et al., (2018) stipulated that greater Fe_o/Fe_d ratios indicate increased activity of soil-forming processes and younger soil material age in the humus layer. High Fe_o/Fe_d ratios in the soil indicate a predominance of low-structure iron species with a slow crystallization of iron oxide rate, which decreases with soil age. The weathering index (Fe_d/Fe_t)

readings may be used to reflect the age of the soil (Pawłowski and Kobierski, 2023). The rate at which soil weathering intensifies with age is connected with identical soil and climate variables. Furthermore, according to Orzechowski et al., (2018), low Fe_d/Fe_t ratio readings indicate that the soil under study is young, with characteristics of the soil-forming processes being visible.

3.0. MATERIAL AND METHODS

3.1. Study Area

Three sites were used to conduct the research; Zmiennica-Brzózow, Ropianka, and Płowce in the Subcarpathian Voivodeship (Fig. 2). Those regions are well reknown for oil production in Poland and possess numerous natural oil seeps. Coordinates that enable us to pinpoint the exact position of the oil seeps were acquired by analyzing a relief map to discover the natural oil seep in those locations (Table 3). A portion of those areas were chosen for our inquiry in all three locations. In Zmiennica-Brzózow (Figure 3), the soil class identified was Gleysol, the oil seeps area is made of an abandoned oil well that was sealed but oil and gases were seeping from the sides and around. The oil seep is located in a forest made of coniferous trees typically found in the Carpathian mountains and shrubs. In Ropianka (Fig. 4), the soil class identified was also Gleysol. The natural oil seep is located in a Ranch field. The main vegetation is nutsedge grasses (*Cyperus rotundus*). Lastly in Płowce (Fig. 5), the soil class identified is Cambisol. During the time of sampling, the primary vegetation in the area, where the natural oil seep is situated was grass, with the predominant plant variety being nutsedge grass (*Cyperus rotundus*). Additionally, earthworms were seen in this location, indicating that the soil conditions there are healthy.
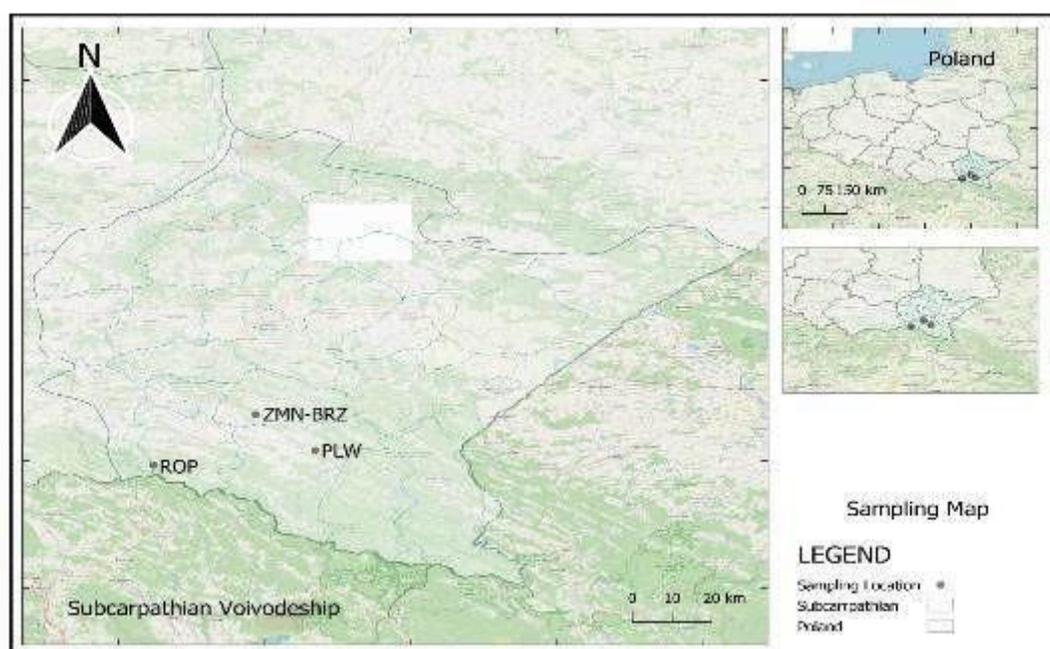
Figure 2. Map of various Locations (Zmiennica-Brzózow, Ropianka and Płowce)

Table 4.Geo-localization of sample places

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Locaion	Latitude	Longitude
Zmiennica-Brzozów	49°41'00.4"N	21°58'04.6"E
Ropianka	49°29'01.3"N	21°37'07.3" E
Płowce	49°32'31.21" N	22°10'18.72"E
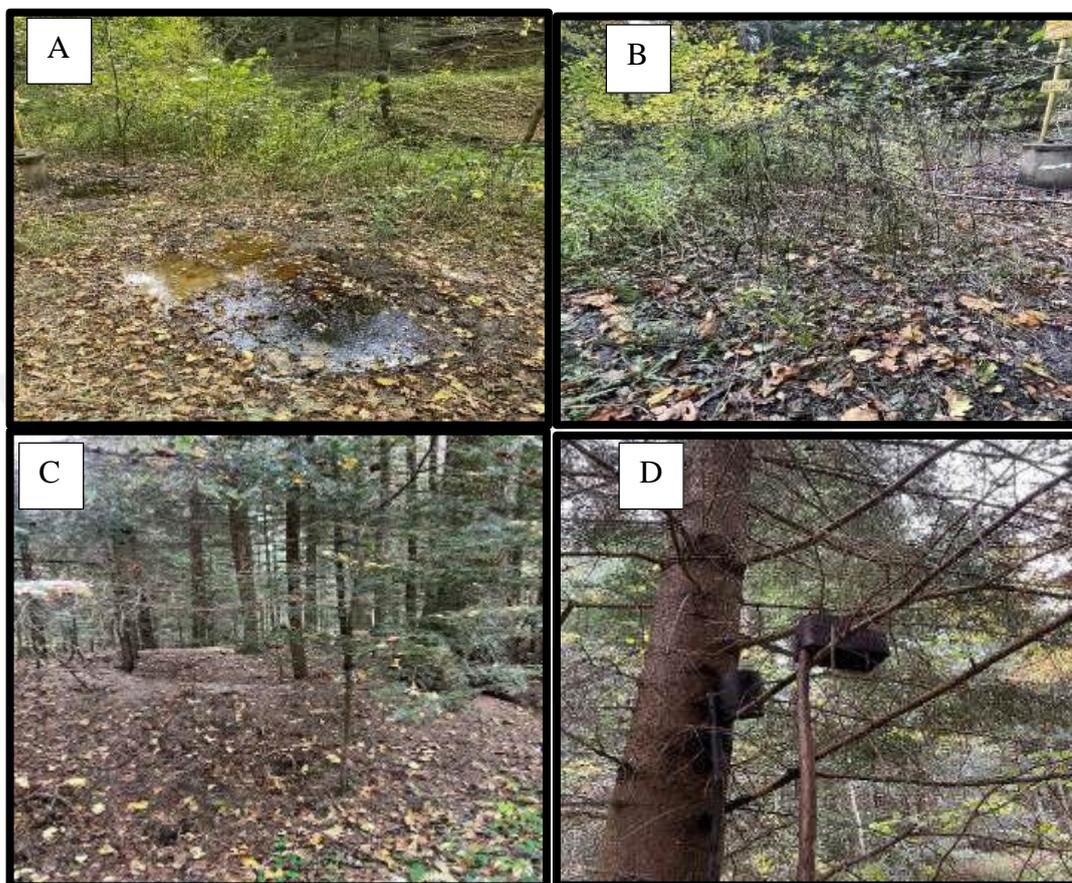
Figure 3. Pictures from Zmiennica-Brzózow. Picture A- oil seep source; B- Surrounding area; C- Abandoned dug holes where oil gotten from the seep is stored; D- Some sort of a cup that is used to pick up the oil from the natural oil seeps
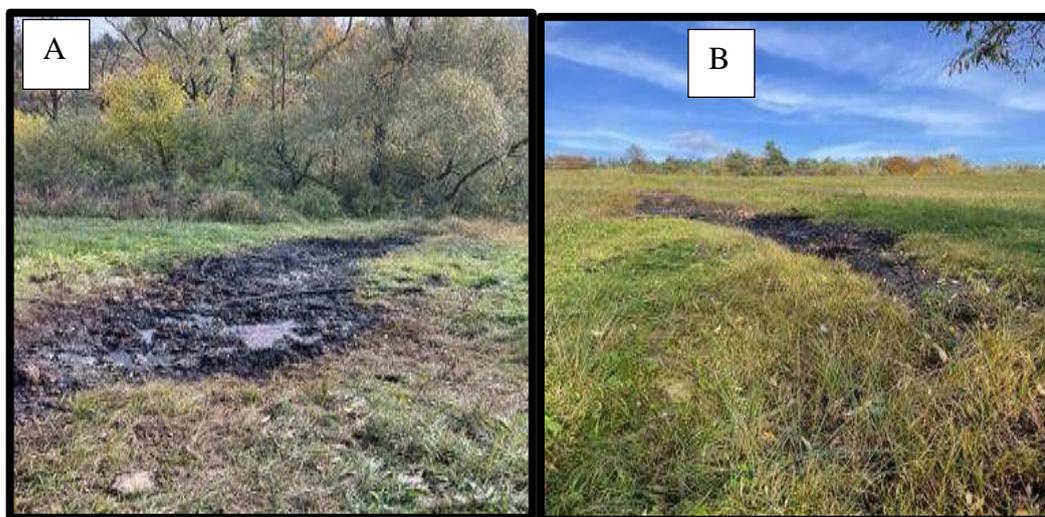
Figure 4. Picture A and B shows the Natural Oil Seep from Ropianka
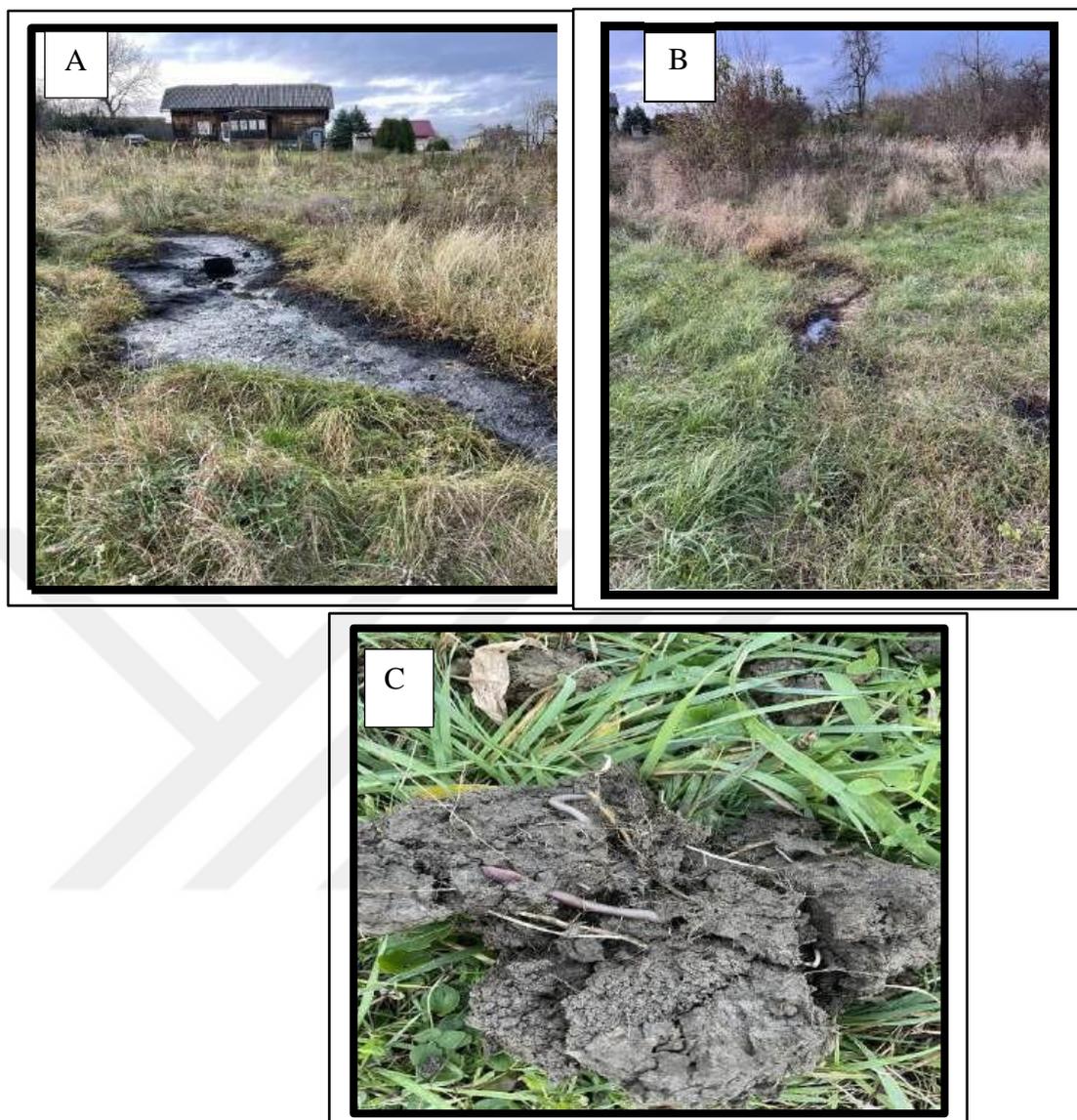
Figure 5. Pictures A and B- show natural oil seep; Picture C- showing earthworm from the soil in Płowce.

3.2. Soil Sampling and Measurement

In each site, a soil profile was dug near the oil seeps, and soil samples from the surface horizon (0 – 20cm) and the surrounding surface samples were collected about 5 to 10cm from the oil seep. In the Zmiennica-Brzózow area (Fig. 6), 4 soil samples were collected from the surrounding surface. Two samples were collected in the south direction (BRZ1 and BRZ3), one in the west (BRZ2), and one in the North (BRZ4) from the seep source. In Ropianka, 3 soil samples were collected from the surrounding surface (Fig. 7). One in the North (ROP2), one in the West (ROP1), and one in the

East (ROP3). In Płowce (Fig. 8), 3 soil samples were collected from the surrounding surface soil (PL1, PL2, and PL3). All soil samples were taken from the South direction along the flow of the oil from the seep.

A spade was used to dig the profile, and samples were gathered. To identify the generic horizon, the cross-section morphology of the soil profiles was described on the spot. Testing for pH and calcium carbonates was done on horizon samples laid out on the ground. From the onsite testing of $CaCO_3$, no effervescent was observed indicating the absence of calcium carbonate. Following that, they were placed in a plastic bag, and tagged with the date, place, and brought to the lab for drying and analysis.
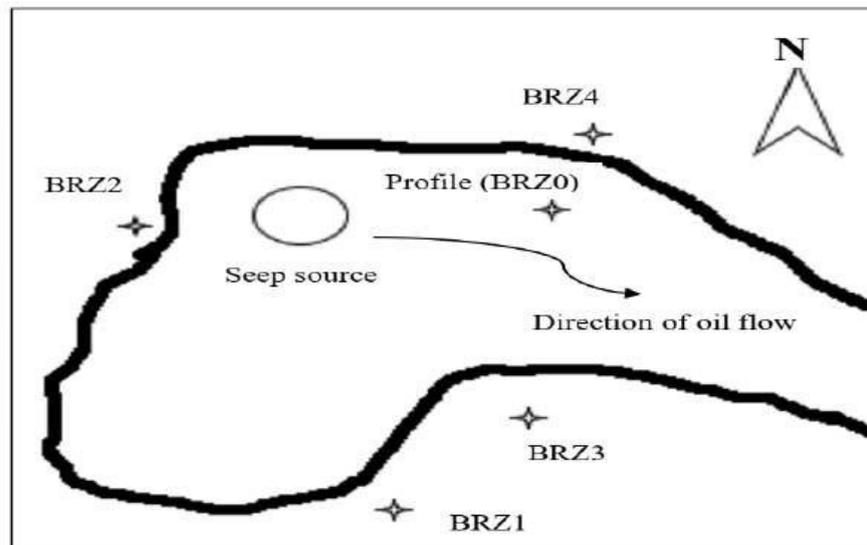
Figure 6. Seep shape and sampling area in Zmiennica-Brzózow
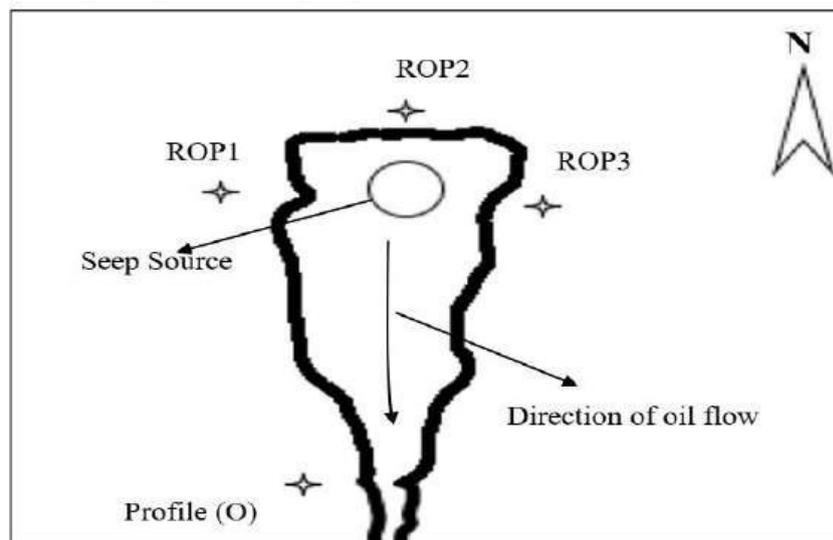
Figure 7. Seep shape and sampling area in Ropianka
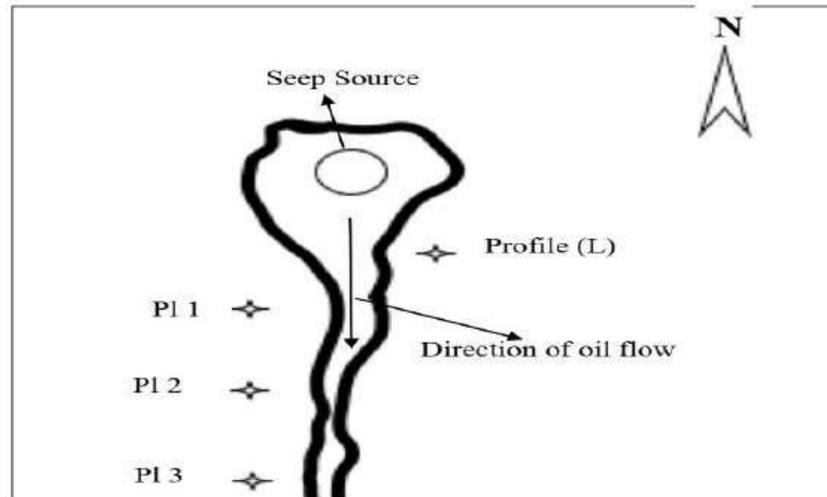
Figure 8. Seep shape and sampling area in Płowce

3.3 Sample Preparation

For a few weeks, the soil samples were allowed to air dry at room temperature. The samples were cleared of any undesired debris, such as leaves and stones, before being put through a 2-mm mechanical sieve machine. From the sieved soil, about 1kg was taken and put in a small box, labeled, and taken for laboratory analysis.

3.4 Laboratory analysis

A typical combination of a glass electrode and a CPI-551 Elmetron pH meter were used to determine the potentiometric values of soil pH in a mixture of 1:1 soil:1 mol·dm−3 KCl solution. In Cassagrande Prószynski's modification, the Bouyoucos aerometric technique was used to examine the particle size distribution of sands (2.00 – 0.05 mm), silt (0.05 – 0.002 mm), and clay (<0.002 mm) by the Polish Standard (PN-R 04032., 1998). Using the USDA Soil Texture Triangle, the data were represented as a percentage to determine the soil textural class (Soil Science Division Staff 2017). The Tiurin technique was used to determine soil organic carbon (SOC) in Oleksynowa's modification (Oleksynowa 1993), without the calcium carbonate being removed. With the assumption that organic matter includes 58% of organic carbon, the soil organic matter (SOM) content was computed by multiplying the value of soil organic carbon by 1.7248. The content of total nitrogen was determined using the Kjeldahl method (Lityński et al., 1976) on a FOSS Kjeltec TM 8100 apparatus.The soxhlet extraction method was used to determine the oil content in contaminated soils.

$$\% \ \square\square\square\square\square \ \square\square\square = \frac{\square\square - \square\square}{\square} * \ \square\square\square$$

W1= Weight of empty flask (g), W2= Weight of flask and extracted fat (g), and S= Weight of sample. Assessment of the sum of individual basic cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) 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 were expressed in mmol/kg. The total phosphorus content was determined using the Colorimetric method with ammonium molybdate and a spectrometer at 660nm.

The content of free iron oxides (Fed) was determined in sodium citrate dithionite extract (Mehra, Jackson 1960). Using Tamm's approach (Schwertmann, 1964), ammonium oxalate extraction was used to identify the amorphous form of iron (Feo). The goal was to eliminate sesquioxide compounds from the ground (Courchesne, 2008). The quantity of organic-complexed iron (Fep) was determined using the sodium pyrophosphate extraction technique described in McKeague, (1967). Crystalline iron oxide was determined by adding free iron oxide and amorphous iron oxide. Total Iron (Fet) was determined by adding free iron oxide, amorphous iron oxide, crystalline iron oxide, and organically-bond iron forms. The iron activity was strongminded by dividing free iron oxide and amorphous iron (Fed/Feo). The weathering index was calculated by dividing free iron oxide and total iron. The values were expressed in mg/Kg. The values obtained in the measurement of cation exchange capacity, soil organic carbon, total nitrogen, Silt/clay ratio, and soil organic matter were classified according to Metson, (1961); Hazelton and Murphy, (2016).

4. RESULT AND DISCUSSION

4.1. Profile description

In Zmiennica-Brzózow, the soil was classified as Epistaggnic Reductic Gleysol (Fig. 9). The vegetation was shrubs and trees. The loamy texture suggests a blend of silt, clay, and sand may be due to the varied mineral makeup that may have been caused by Parent materials. The parent material is predominantly made of clay stones. Gley indicates some water saturation. Both the "epistagnic" and "reductic" qualifiers attest to some times of waterlogging that result in less favorable circumstances. According to Skiba, (2009), the water saturation or waterlogging condition is attributed to the structural features of the Flysch bedrock. The humic properties point to a substantial buildup of organic materials. The A horizon's granular texture and dark olive hue might be caused by the high amount of organic materials. Changes in hue and structure along the profile indicate varied degrees of waterlogging and root penetration. The massively structured, gray-to-olive-gray color change in the Cg horizon displays protracted water saturation and reduction. Similar findings of the soil type were obtained by Skiba et al., (2003), in a study to determine the soil cover of the Magurskiego Parkucially reported some Gleysol occupying the area, especially in springs.

In Ropianka the profile was classified as Reductic Gleysol (Fig. 10). There was grass and pasture for the vegetation type. The difference in texture between the top and lower horizons might be attributed to regional geomorphological factors, such as distinct sediment accumulation patterns or processes involved in soil development. The same is true for "reductic" and "abruptic" natures, which denote waterlogging. According to Skiba, (2009), the waterlogging condition is a result of the structural features of the Flysch bedrock. Sudden textural changes in the horizon, sloped terrain's influence on water circulation, and humic natures suggest the presence of organic materials although probably less than in forest regions. The olive-gray hue and granular texture of the Apg horizon may be the consequence of strong root penetration and organic materials from grazing animals and other pastoral activities. There may be more water effects and fewer organic materials in the G and Cg horizons, which is why the hue gradually changed to a lighter gray. Similar findings of the soil type were obtained by Skiba et al., (2003), in the study to determine the soil cover of the Magurskiego Parkucially reported some gleysol occupied the area, especially in

springs. In a study by Tchounke, (2023), he got a similar soil type when evaluating the level of soil contamination by oil production sites in this area.

Epifragic Cambisol was the profile classified in Płowce (Fig. 11). The term "epifragic" denotes the existence of a hard, impermeable layer called fragipan at the surface, which hinders root penetration and water transport. Cambisols often occur in places with considerable leaching. The textures of the loam to sandy clay loams suggest worn parent material with a high clay percentage. The pasture vegetation may be the cause of the moderate organic matter at the higher horizon. The dark Ap horizon denotes a moderate build-up of organic materials. The color of the AB and B layers gradually changes from grayish olive to yellow, showing weathering and leaching as well as iron oxidation and a decrease in organic content. This progressive change in color is indicative of soil development processes. The BC hoizon, which has an angular blocky structure and a light gray color, finally suggests more clay and a change to less worn parent materials. Similar findings of the soil type was obtained by Skiba et al., (2001); Skiba et al., (2004); Skiba et al., (2006), from the studies they made mention of Cambisol been the predomant soil type in the studied areas.

tion; ; Zmiennica-Brzózow o41"0.004', E 21°58"4.6' tation; Shrubs/tress sification (WRB); Epistagnic Reductic Gleysol mic, Humic, Vitric)	
10cm A- dark olive (2.5Y 3/3) moist; loam; ular, abundant very fine roots, diffuse boundary.	
18cm Cg1- gray (2.5Y 4/6) moist; subangular ; loam; few very fine roots; diffuse boundary	
40cm Cg2- olive gray (10Y 4/1) moist, massive; ;few roots; diffuse boundary	
m Cg3- olive gray (10Y 5/1) moist, massive; ; no roots; diffuse boundary.	

Figure 9. Profile description of Zmiennica- Brzózow

	Location; Ropianka N 49o29"01.3', E 21o37"0.7.3' Vegetation; Pasture/Grass Classification (WRB); Reductic Gleysol (Loamic, Humic, Abruptic, Inclinic)
	0 – 12cm Apg- olive gray (7.5Y 3/2) moist; sand; granular, abundant very fine roots, diffuse boundary.
	12 – 25cm G- gray olive (5Y 4/2) moist; sandy loam; granular; common very fine roots; diffuse boundary
	25 – 50cm Cg- gray olive (7.5Y 5/2) moist, loam; granular; few very fine roots; diffuse boundary
	>50cm C- olive gray (10Y 4/2) moist, loam; subangular blocky; no roots; diffuse boundary.

Figure 10. Profile description of Ropianka

	Location; Płowce N 49o32"31.21', E 22o10"18.72' Vegetation; Pasture/Grass Classification (WRB); Epifragic Cambisol (Loamic, Profundic)
	0 – 20cm Ap, olive black (5Y 3/2) moist; loam; angular blocky;, abundant very fine roots, diffuse boundary.
	20 – 30cm AB, grayish olive (5Y 4/2) moist; sandy clay loam; angular blocky; few very fine roots; diffuse boundary
	30 – 50cm B1, yellow (5Y 7/6) moist, sandy clay loam; angular blocky; no roots; diffuse boundary
	50 – 75cm B2, yellow (5Y 5/6) moist; sandy clay loam; angular blocky; no roots, diffuse boundary
	>75cm BC, light gray (10Y 7/2) moist, clay loam; angular blocky; no roots; diffuse boundary.

Figure 11. Profile description of Płowce

4.2. Soil Chemical Properties

The pH in all three locations with both water and KCl was moderately acidic except for Płowce where the pH in water ranges from moderately acidic to neutral based on Hazelton and Murphy's, (2016) classification (Table 5). At Zmiennica-Brzózow, pH in both water and KCl the lowest was at BRZ2 with 4.67 and 3.63 respectively, and highest at BRZ0 (6.86) and BRZ4 (6.61) respectively. Ropianka's lowest was 5.44 at 1O and highest was 6.47 at ROP1 for water, while in KCl, the

lowest value was recorded at ROP2 (4.79) and highest value at ROP1 (5.56). Płowce in water the lowest value was recorded at PL3 (6.77) and highest at PL2 (7.38), while in KCl lowest recorded value was at 1L (5.85) and the highest recorded value at PL2 (6.83). Moreso, there is less variability in the pH values from all three locations. The observed variation of the pH in water and KCl, with pH values in KCl lower than that of water, may be attributed to the salt presence in KCl, which increases the H^+ ion in the solution. It was observed that area with high oil content has a slightly high pH value (in KCl), supporting the findings by Njoku et al., (2009) increased oil, increased pH.

Table 5. Summary result of soil pH.

Location	Sample code	pH (1:2 water)	pH (1:2 KCl)
Zmiennica-Brzózow	BRZ0	6.86	5.57
	BRZ0	6.73	5.55
	BRZ1	5.47	4.19
	BRZ2	4.94	3.63
	BRZ2	4.67	4.18
	BRZ3	6.4	5.59
	BRZ4	6.05	6.61
	Mean	5.87	5.04
	Standard deviation	0.866	1.061
Ropianka	1O	5.44	4.92
	2O	6.05	5.28
	ROP1	6.47	5.56
	ROP2	5.69	4.73
	ROP3	6.38	5.43
	Mean	6.00	5.18
	Standard deviation	0.440	0.349
Płowce	1L	6.8	5.85
	PL1	7.13	6.53
	PL2	7.38	6.83
	PL3	6.77	6.16
	Mean	7.02	6.34
	Standard deviation	0.290	0.428

From the textural classification, 56.25 % of the soil types were loam soils, 25 % Silty loam, 12.5 % sandy loam, and 6.25 % sand. Points 1 to 7 are sample points from Zmiennica-Brzózow, 8 to 12 from Ropianka, and 13 to 16 from Płowce (Fig. 12). We can ascribe the loamy nature of most of the surrounding soil surfaces to result from high organic matter in the soil surface [Burke et. 1989]. The majority of the sampling areas recorded a high sil/clay ratio except for 1O (0.3) in Ropianka which recorded a low value and 1L (1,4) in Płowce which recorded a moderate value (Table 5). The high

sil/clay results in most of the sampled areas might be explained by the clay particles' eluviation from the surface horizon to the lower horizon of the soil.

Table 6. Summary result of soil texture from the three different locations

| Location	Sample code	Sand (2.0 - 0.02) [%]	Silt (0.02 - 0.002) [%]	Clay (>0.002) [%]	Silt/clay ratio	Textural Class
	BRZ0	43	36	21	1.7	Loam
	BRZ0	48	35	17	2.1	Loam
	BRZ1	29	48	23	2.1	Loam
Zmiennica -Brzózow	BRZ2	20	53	27	2.0	Silty Loam
	BRZ2	45	49	6	8.2	Sandy Loam
	BRZ3	29	54	17	3.2	Silty Loam
	BRZ4	31	44	25	1.8	Loam
	1O	96	1	3	0.3	Sand
	2O	38	44	18	2.4	Loam
Ropianka	ROP1	28	53	19	2.8	Silty Loam
	ROP2	30	50	20	2.5	Loam
	ROP3	42	43	15	2.9	Loam
	1L	52	28	20	1.4	Loam
Płowce	PL1	47	43	10	4.3	Loam
	PL2	20	57	23	2.5	Silt Loam
	PL3	70	22	8	2.8	Sandy Loam
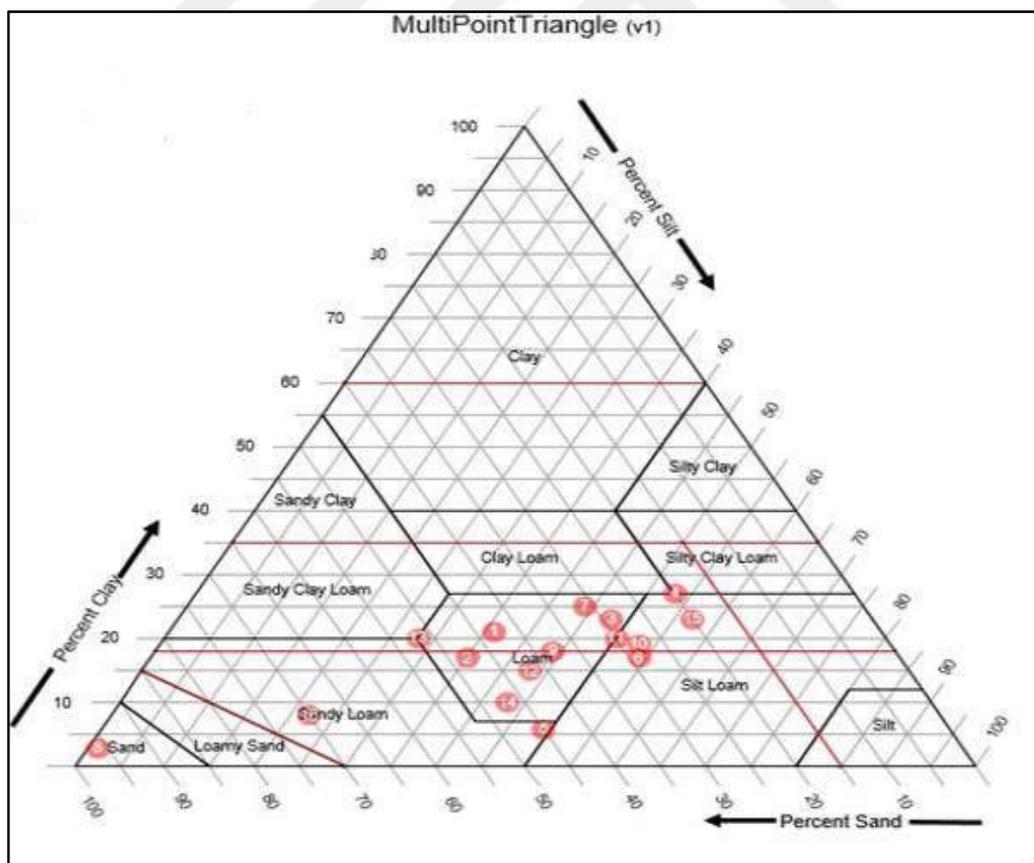
Figure 12. Soil textural data points plotted on the USDA Soil Textural Triangle

Overall nitrogen content (N) was high in all three locations with Płowce having 0.389%, Ropianka 0.372%, and Zmiennica-Brzózow 0.264%. There was significant difference in the means of the sample areas at Zmiennica-Brzózow, no significant difference in Ropianka, and significant difference in Płowce (Table 6). In Zmiennica-Brzózow (Fig. 13), the highest N value of 0.5166% was acquired at BRZ2 and the lowest value of 0.1323% at BRZ1. In Ropianka (Fig. 14), the highest N value of 0.4438 was acquired at ROP2 and the lowest value of 0.2688% at ROP3. In Płowce (Fig. 15), PL1 had the highest value of 0.4732% while 1L had the lowest value of 0.2422%. In all three locations except for the sample area ROP3 in Ropianka, the nitrogen content turns out to be higher in areas with high oil content. This can be attributed to the crude oil from the seeps supporting the findings by Saika et al., (2023), Essien and John, (2010); Fayemi, (1975), who reported that nitrogen increases with increased crude oil in the soil. The increased N in the oil-rich areas could be the activities of nitrogen-fixing bacteria and other microorganisms that decomposed organic matter, which may accompany areas polluted with crude oil.

The soil organic carbon (SOC) and soil organic matter (SOM) were found to be high in areas with higher oil content (Fig, 13, 14, and 15). Averagely Zmiennica-Brzózow had the lowest SOC and SOM values (2.148%, 3.70%), Ropianka and Płowce medium with values (3.778%, 6.510%) and (4.477%, 7.719%) respectively. All sample areas from the three locations showed significant differences in the mean values of the SOC and SOM (Table 6). In general, soil organic carbon is derived from the decomposition of organic matter such as plant/animal remains, microbial biomass, and other carbon-rich sources, by microorganisms in soil. Therefore, the crude oil from the natural oil seeps might have contributed to the high SOC and SOM in those areas, because there was a highly significant association between oil content and SOC (Table 10). A similar finding was gotten by Saika et al., (2023); Wang et al., (2010); and Agbogidi et al., (2007). The high values in the two areas may be attributed to the organic input from farmers and animals.

There was a significant difference in the means of oil content in the sample areas in all three locations: Zmiennica-Brzózow, Ropianka, and Płowce (Table 6). In Zmiennica-Brzózow (Figure 13), the highest oil content value of 3.540% was seen at BRZ0 and the lowest value was 0.885% at BRZ1. In Ropianka (Figure 14) the highest oil content value of 44.126% was seen at ROP2 and the lowest value of 0.695% at ROP1. In Płowce (Figure 15), PL3 had the highest value of 19.660% while PL2 had

the lowest value of 1.647%. From observation of the results obtained, areas not close to the seep source but located down the gradient of the flow of the crude oil turn to have higher amounts of crude oil. This can be attributed to the terrain of the area. The critical level for remediation of crude oil-contaminated soils varies with countries. For example, In Holland, they set 0.5% and 1% of total petroleum hydrocarbon (TPH) for residential areas and industrial areas respectively (Franken et al., 1999).

C/N ratio ranges from 7.75 to 16.82 at Zmiennica-Brzózow, Ropianka 5.96 to 20.32, and Płowce 8.04 to 15.98 (Table 7). The C/N ratio of all samples from the three locations recorded values less than the threshold value of 25 (Fig. 17, 18, 19). A C/N ratio of <25 is best for the decomposition of organic material by microorganisms (Hoyle, 2013).

Table 7. Summary result of oil content, N, SOC, SOM, and C/N ratio

Location	Sample Code	Sample size (N)	Oil Content [%]	N [%]	SOC [%]	SOM [%]	C/N Ratio
Zmiennica-Brzózow	BRZ0	2	1.792^b	0.3598^c	2.65^e	4.58^e	7.38^{abc}
	BRZ0	2	3.540^c	0.3178^{cb}	2.79^f	4.80^f	8.77^{bc}
	BRZ1	2	0.885^a	0.1323^a	1.51^b	2.61^b	11.44^c
	BRZ2	2	1.105^{ab}	0.1449^a	1.10^a	1.89^a	7.58^{ab}
	BRZ2	2	1.805^b	0.5166^d	2.50^d	4.32^d	4.85^a
	BRZ3	2	2.483^b	0.1694^a	2.85^f	4.91^f	16.82^d
	BRZ4	2	1.230^{ab}	0.21^{ab}	1.63^c	2.81^c	7.75^{ab}
	Mean		1.834	0.264	2.148	3.703	9.226
	Standard deviation		0.925	0.141	0.714	1.231	3.878
Ropianka	1O	2	44.126^c				
	2O	2	2.225^a	0.399^a	4.66^a	8.03^a	11.67^a
	ROP1	2	0.695^b	0.3773^a	2.25^b	3.87^b	5.96^b
	ROP2	2	2.225^a	0.4438^a	2.74^c	4.72^c	6.17^b
	ROP3	2	8.099^b	0.2688^a	5.46^d	9.42^d	20.32^c
	Mean		3.311	0.372	3.776	6.510	11.029
	Standard deviation		3.272	0.074	1.531	2.640	6.736
Płowce	1L	2	1.790^a	0.2422^a	1.95^a	3.36^a	8.04^a
	PL1	2	7.756^b	0.4732^b	7.56^b	13.04^b	15.98^a
	PL2	2	1.647^a	0.4242^b	3.92^c	6.76^c	9.24^a
	PL3	2	19.660^c				
	Mean		3.731	0.380	4.477	7.719	11.089
	Standard deviation		3.486	0.122	2.849	4.912	4.281

Mean values with the same letters are not significantly different
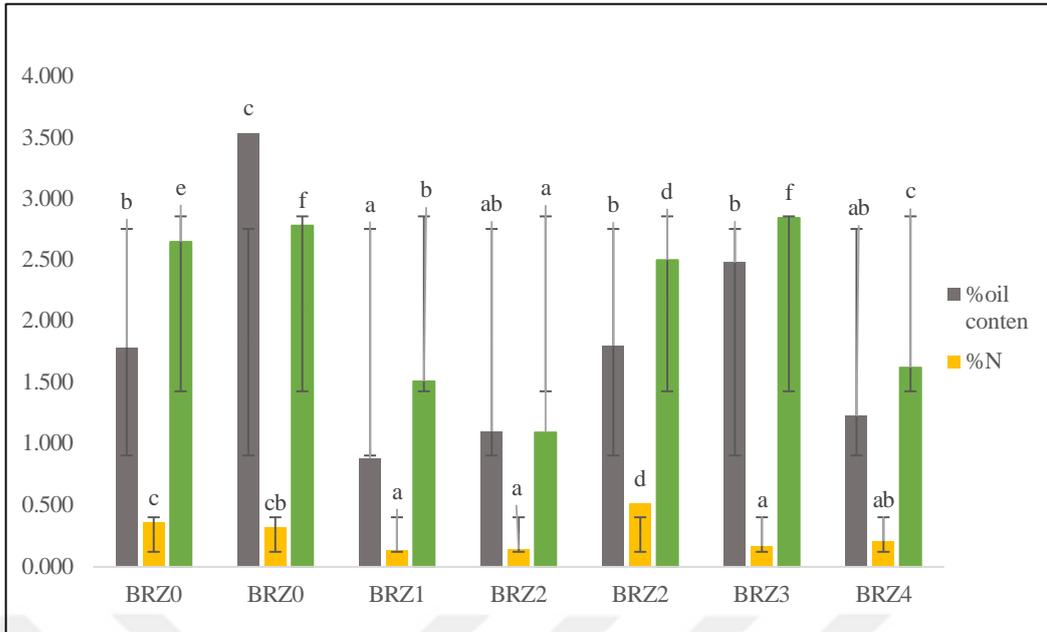Mean values with different letters are significantly different

Figure 13. Bar chat displaying oil content, N, and SOC in Zmiennica-Brzózow
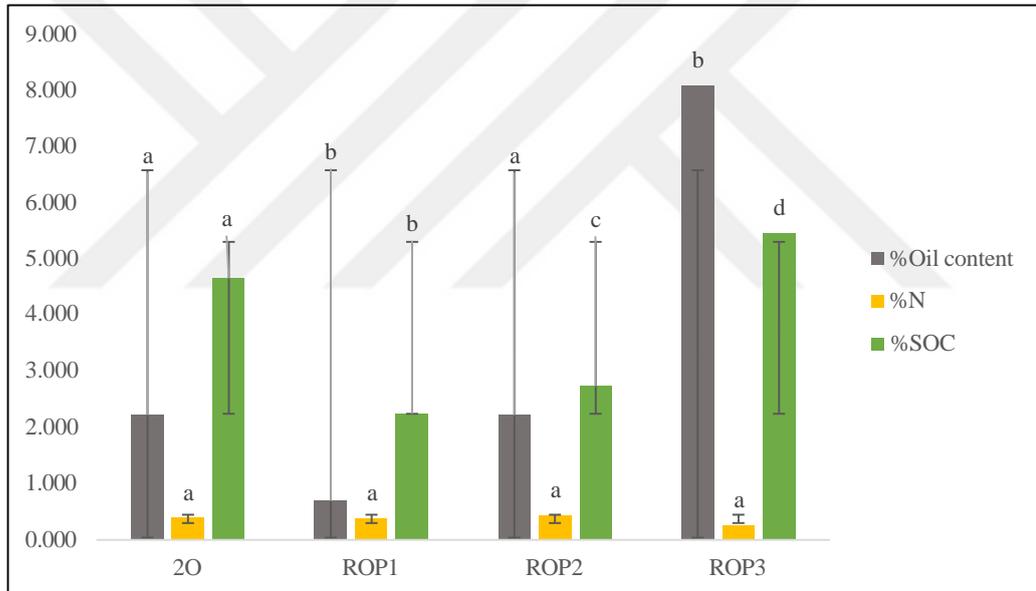
Figure 14. Bar chat displaying oil conaten, N, and SOC in Ropianka
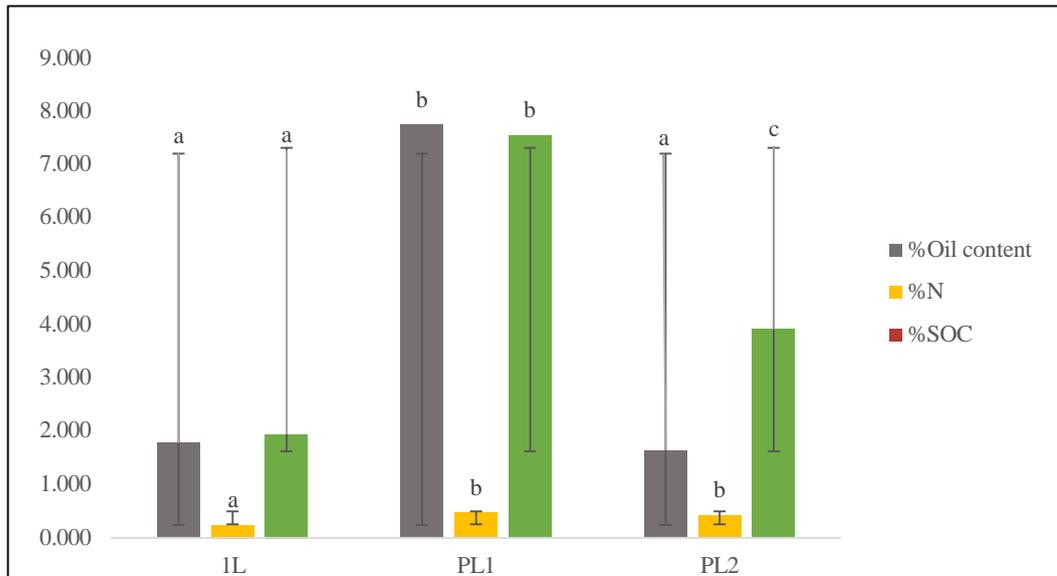
Figure 15. Bar chat displaying oil content, N, and SOC Ratio in Płowce
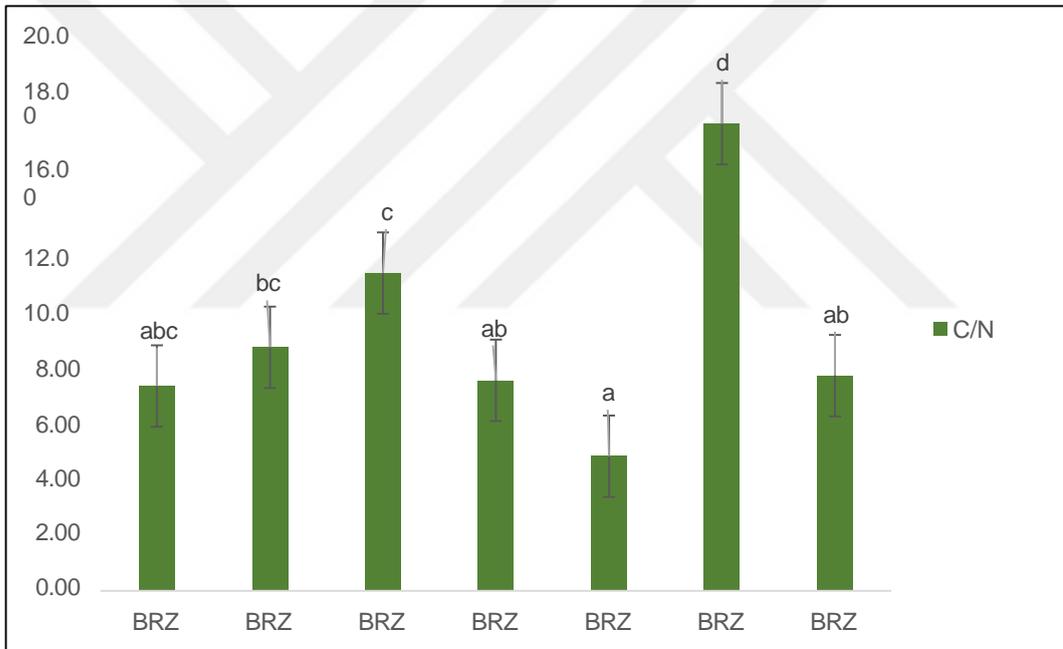
Figure 16. Bar chart displaying the C/N ratio in Zmiennica-Brzózow
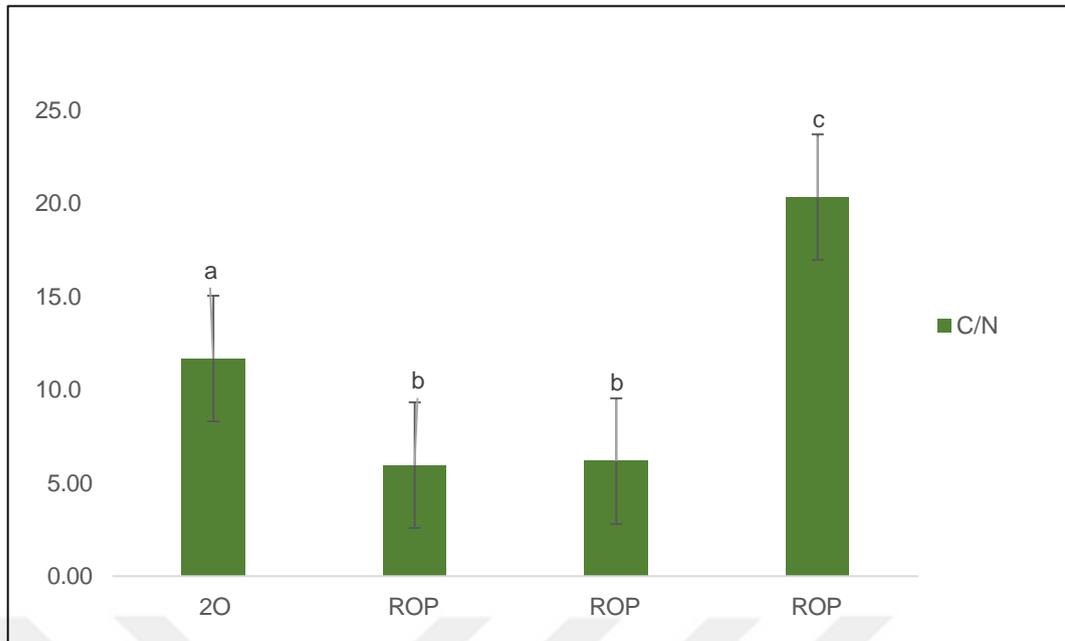
Figure 17. Bar chart displaying the C/N ratio in Ropianka
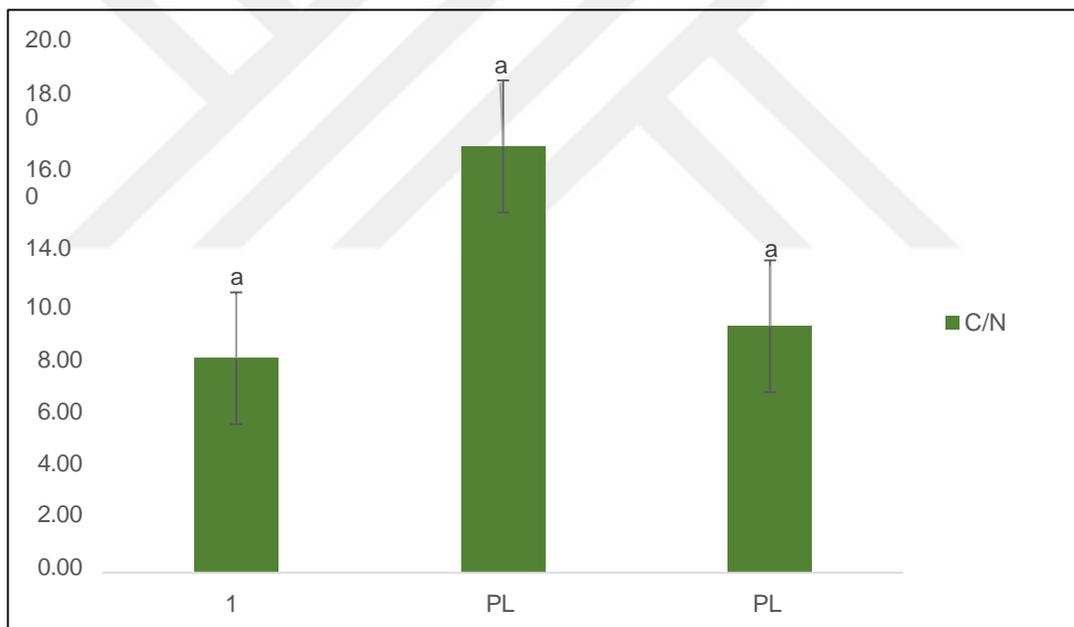
Figure 18. Bar chart displaying the C/N ratio in Płowce

Calcium in the soil comes from various sources; first is present in abundant amounts as primary and secondary minerals in the soil that are insoluble for plants, they are also present in soluble forms as exchangeable cations on the surface of colloidal complexes [Agbogidi et al. 2007]. From the investigation, Calcium levels were very high in all 3 locations; with the lowest value of 3.85 mmol/100g at BRZ1 and the highest value of 8.47 mmol/100g at BRZ3 in Zmiennica-Brzózow, the lowest

value of 4.18 mmol/100g at 1O and highest value of 7.47 mmol/100g at ROP1 in Ropianka, and in Płowce the value ranges from 6.24 mmol/100g to 16.82 mmol/100g at 1L and PL2 respectively (Table 7). Results showed that oil content slightly lowers calcium (but insignificant) in the surrounding soil surfaces (Table 10). This result opposes the findings by Wang et al., (2010); Agbogidi et al., (2007) who reported that high calcium content was recorded in areas that were highly contaminated with crude oil but supported the findings by Onojake and Osuji, (2012).

Potassium being an important element for plant growth plays a key role in a numerous part in the physiological processes of plants. For example, protein synthesis and osmotic pressure (Agbogidi and Eshegbey, 2006). Potassium was very high in all three locations ranging from 0.13 mmol/100g to 0.739 mmol/100g in Zmiennica-Brzózow, 0.216 mmol/100g to 0.45 mmol/100g in Ropianka and 0.433 mmol/100g to 0.903 mmol/100g in Płowce (Table 7). Potassium decreases with increased oil content but is insignificant (Table 9) which supports the findings by Agbogidi et al., (2007); Wang et al., (2013). According to Agbogidi et al., (2007), the reduced potassium with increased oil content may be as a result of nutrient immobilization due to the formation of complexes in the soil after degradation and uptake.

Magnesium levels were very high in all 3 locations; with the lowest value of 2.73 mmol/100g at BRZ4 and the highest value of 3.68 mmol/100g at BRZ2 in Zmiennica-Brzózow, the lowest value of 0.41 mmol/100g at 1O and highest value of 0.86 mmol/100g at ROP2 in Ropianka, and in Płowce the value ranges from 1.9 mmol/100g to 2.89 mmol/100g at 1L and PL1 respectively (Table 7). The investigation shows oil content slightly decreases Magnessium level but is insignificant (Table 10).

Sodium is not considered too much as an important nutrient for plant growth but plays the role of counter-ion in the soil where potassium concentration is very low. Variation was recorded in the sodium concentration in the different locations. Sodium was very high in Zmiennica-Brzózow and Płowce with average values of 0.38 mmol/100g and 0.33 mmol/100g respectively, while high in Ropianka value of 0.088 mmol/100g (table 7). Observed sodium decreases with increased but insignificant oil content in the soil in line with Wang et al., (2013) studies.

Overall, It is observed that the total CEC is very high. Not much influence of oil on the total CEC in the surface soil (Table 10). The difference in CEC value in the different locations might be agricultural practices, soil properties, or geological

factors. High Base saturation values indicate higher proportion of exchangeable base cation relative to total Excahngeable capacity and good soil fertility (Table 7).

Table 8. Summary of cation exchange capacity (CEC)

| Location | Sample code | Cation exchange capacity | | | | | |
		Ca^{2+} mmol/100g	K^+ mmol/100g	Mg^{2+} mmol/100g	Na^+ mmol/100g	Sum CEC mmol/100g	Base sat. me/100g
Zmienni ca- Brzózow	BRZ0	8.22	0.13	3.11	0.452	11.912	23.6
	BRZ0	7.4	0.431	3.22	0.5	11.551	22.2
	BRZ1	3.85	0.664	3.07	0.253	7.837	14.8
	BRZ2	4.34	0.452	3.68	0.193	8.665	16.7
	BRZ2	5.69	0.242	0.86	0.245	7.037	13.6
	BRZ3	8.47	0.739	3.09	0.209	12.508	24.1
	BRZ4	5.28	0.396	2.73	0.832	9.238	17.3
	Mean	6.179	0.436	2.823	0.383	9.821	18.9
	Standard deviation	1.72	0.20	0.84	0.21	2.16	4.01
Ropiank a	1O	4.18	0.302	0.41	0.082	4.974	9.6
	2O	7.16	0.216	0.75	0.096	8.222	16.1
	ROP1	7.47	0.325	0.73	0.114	8.639	16.8
	ROP2	6.17	0.45	0.86	0.078	7.558	14.6
	ROP3	6.47	0.283	0.82	0.073	7.646	14.9
	Mean	6.29	0.3152	0.714	0.0886	7.408	14.4
	Standard deviation	1.29	0.09	0.18	0.02	1.43	2.83
Płowce	1L	6.24	0.483	1.9	0.578	9.201	17.3
	PL1	10.86	0.519	2.89	0.082	14.351	28.1
	PL2	16.82	0.903	2.52	0.127	20.37	39.7
	PL3	6.9	0.433	2.08	0.543	9.956	18.9
	Mean	10.21	0.58	2.35	0.33	13.47	26.00
	Standard deviation	4.86	0.22	0.45	0.26	5.13	10.30

The earth's crust is made largely of iron which plays an important role in the conscription of toxic elements in the environment, acts as an electron carrier in redox processes, and co-factor of many enzymes in plants (Saikia et al., 2023). Crystalline Fe (Fec) had the highest in the sampled soils followed by amorphous Fe (Feo), then organically bound Fe, and the least being free Fe oxide (Fed) in all three locations (Table 9). Moreover, the was a significant variation in the distribution of all the iron forms from the sample areas except at Płowce. Free iron oxide ranges from 440 mg/kg (BRZ0) to 2012 mg/kg (BRZ2) in Zmiennica-Brzózow, 279 mg/kg (ROP3) to 1343 mg/kg (2O) in Ropianka, and 323 mg/kg (1L) to 446 mg/kg (PL1) in Płowce. For organically-bound iron, the value range from 920 mg/kg(BRZ0) to 3284 mg/kg

(BRZ2) in Zmiennica-Brzózow, 1169 mg/kg (ROP3) to 2538 mg/kg (2O) in Ropianka and 920 mg/kg (1L) to 1226 mg/kg (PL1) in Płowce. Amorphous iron ranges from 5908 mg/kg (BRZ2) to 10,078 mg/kg (BRZ3) in Zmiennica-Brzózow, 5230 mg/kg (ROP3) to 6646 mg/kg (ROP1) in Ropianka and 3353 mg/kg (1L) to 6021 mg/kg (PL2) in Płowce. Lastly, for crystalline iron, it ranges from 7531 mg/kg (BRZ2) to 11,439 mg/kg (BRZ3) in Zmiennica-Brzózow, 5503 mg/kg (ROP3) to 9738 mg/kg (2O) in Ropianka and 3676 mg/kg (1L) to 6453 mg/kg (PL2) in Płowce. The overall high amount of Crystalline Fe (Fec) in all three locations can result from good aerobic conditions in all 3 locations that favor the crystallization of iron (Alamdari et al., 2010). Free iron oxide being the least in the surface soils may be attributed to the fact that with their close association with clay particles (especially hydrous iron oxide), they may have been illuviated with the clay particles to the subsoil. In addition to a positive link between clay concentration and free iron oxide, a study by Orzechowsji et al., (2017) reported low free iron oxide in the surface but high in the lower horizon. Across all locations, the highest mean total iron content is observed in Zmiennica-Brzózow had the value of 10236 mg/kg, followed by Ropianka with the value of 8348 mg/kg and then Płowce with the value of 6423 mg/kg. Zmiennica-Brzózow samples exhibit the highest mean Fe activity and weathering index, followed by Ropianka and Płowce (Table 9). The high weathering index in Zmiennica-Brzózow and Ropianka may indicate a more intensive weathering process and potentially higher levels of iron availability in these soils. It can be observed that the oil content in the soil does not strongly influence the total iron in the surface soil.

Table 9. Summary result of Iron forms from the three different locations

Location	Sample code	Free Fe Oxides mg/kg	Organically-bound Fe mg/kg	Amorphous Fe mg/kg	Crystalline Fe mg/kg	Total Iron mg/kg
Zmiennica-Brzózow	BRZ0	440	920	7758	8197	9117
	BRZ0	488	969	8155	8643	9612
	BRZ1	735	1784	7246	7981	9765
	BRZ2	663	1885	6868	7531	9415
	BRZ2	2012	3284	5908	7920	11204
	BRZ3	1364	1090	10075	11439	12529
	BRZ4	545	1455	8008	8553	10008
	Mean	892	1627	7717	8609	10236
	Standard deviation	583	825	1295	1878	2703
	1O					
	2O	1343	2538	8395	9738	22015

Location	Sample code					
Ropianka	ROP1	404	1563	6646	7051	8613
	ROP2	704	2411	6638	7341	9752
	ROP3	279	1169	5230	5509	6678
	Mean	463	1714	6171	6634	8348
	Standard deviation	218	635	815	1033	1668
Płowce	1L	323	962	3353	3676	4637
	PL1	446	1226	5379	5825	7051
	PL2	432	1128	6021	6453	7581
	PL3					
	Mean	400	1105	4918	5318	6423
	Standard deviation	67	134	1393	1457	1569

Table 10. Fe acitivity and Weathering Index of the sampling locations

Location	Sample code	Fe acitivity	Weathering Index
Zmiennica-Brzozow	BRZ0	0.06	0.05
	BRZ0	0.06	0.05
	BRZ1	0.10	0.08
	BRZ2	0.10	0.07
	BRZ2	0.34	0.18
	BRZ3	0.14	0.11
	BRZ4	0.07	0.05
	Mean	0.12	0.09
	Standard deviation	0.45	0.22
Ropianka	1O		
	2O	0.16	0.06
	ROP1	0.06	0.05
	ROP2	0.11	0.07
	ROP3	0.05	0.04
	Mean	0.07	0.06
	Standard deviation	0.27	0.13
Plowce	1L	0.10	0.07
	PL1	0.08	0.06
	PL2	0.07	0.06
	PL3		
	Mean	0.08	0.06
	Standard deviation	0.08	0.06

Phosphorus is one of the key macronutrients required by plants for it growth and development. It acts as a component in adenosine diphosphate (ADP) and Adenosine triphosphate (ATP), substances involved in biochemical reactions such as photosynthesis and respiration. The level of plant-available phosphorus in soil guides

us to know if phosphate fertilizer is required for plant growth (Hazelton and Murphy 2016; Saikia et al., 2023). This study had a variation in the plant available phosphorous in various sampled areas from the three locations (Table 9). In Zmiennica-Brzózow, plant available phosphorous ranges from low with a value of 0.64 mg/100g at BRZ1 to moderate with a value of 1.8mg.100g at BRZ3 except at BRZ2 which recorded a very high value of 9.19 mg/100g. In Ropianka, plant available phosphorous from very low at 2O (0.34 mg/100g), ROP1 (0.35 mg/100g) and ROP3 (0.29 mg/100g) and moderate at 1O (1.08 mg/100g) and ROP2 (1.42 mg/100g). There was a very weak inverse relationship between crude oil content and plant-available phosphorus (Table 10). This may be attributed to the slightly reduced pH, caused in low pH phosphorus becomes unavailable due to immobilization in the soil. This opposes a report on the study carried out by Saikia et al., (2023), from the study the report of phosphorus increases at the oil drilling site compared to 500m and 1000m from the site.

Potassium supplied to plants for their growth comes from two sources: non-exchangeable-available potassium which is released slowly into the soil solution for absorption and exchangeable potassium which is ready and available for plant both in solution or loosely held on soil colloids (Hazelton and Murphy, 2016). From this study, the was little variation in the plant-available potassium across the sampled areas in the three different locations (Table 9). Zmiennica-Brzózow recorded a mean value of 21.59 mg/100g, Ropianka 12.66 mg/100g, and Płowce 22.20 mg/100g. According to Gourley, (1999), the critical level of potassium in soil which limits plant growth ranges from 8.0 mg/100g – 20.0 mg/100g. Ropianka recording mean value within critical value may be due to the intensive use of the land for ranching, where potassium is continuously being uptake by the grasses and not replaced after harvesting or the animals feed on the grasses. There was also a very weak inverse relationship between crude oil content and plant-available potassium (Table 10).

Table 11. Summary result of phosphorus and plant-available potassium

Location	Sample code	P_2O_5 mg/100g	K_2O mg/100g
	BRZ0	1.05	23.1
	BRZ0	1.01	19.53
	BRZ1	0.64	28.72
Zmiennica-Brzózow	BRZ2	0.68	19.7
	BRZ2	9.19	10.83
	BRZ3	1.28	31.52

	BRZ4	0.93	17.73
	Mean	2.11	21.59
	Standard deviation	3.13	6.95
Ropianka	1O	1.08	10.7
	2O	0.34	8.17
	ROP1	0.35	13.34
	ROP2	1.42	19.24
	ROP3	0.29	11.86
	Mean	0.70	12.66
	Standard deviation	0.52	4.14
Płowce	1L	3.56	20.9
	PL1	1.67	19.6
	PL2	0.52	32.28
	PL3	1.31	16.03
	Mean	1.77	22.20
	Standard deviation	1.29	7.03

4.3. Result of Statistical Analysis

Oil content	pH water	pH KCl	clay	N	SOC	C/Nratio	Ca	K	Mg	Na
Cor.	-0.104	0.003	-0.71*	0.22	0.851**	0.762**	-0.215	-0.184	-0.374	-0.153
P-value	0.702	0.99	0.002	0.451	0	0.002	0.495	0.495	0.154	0.572
N	16	16	16	14	14	14	16	16	16	16

Table 12. Correlation coefficients between oil content and the soil chemical properties
*- significance $\alpha = 0.05$, ** - significance $\alpha = 0.01$, N - Sample size.

Continuation of Table 12

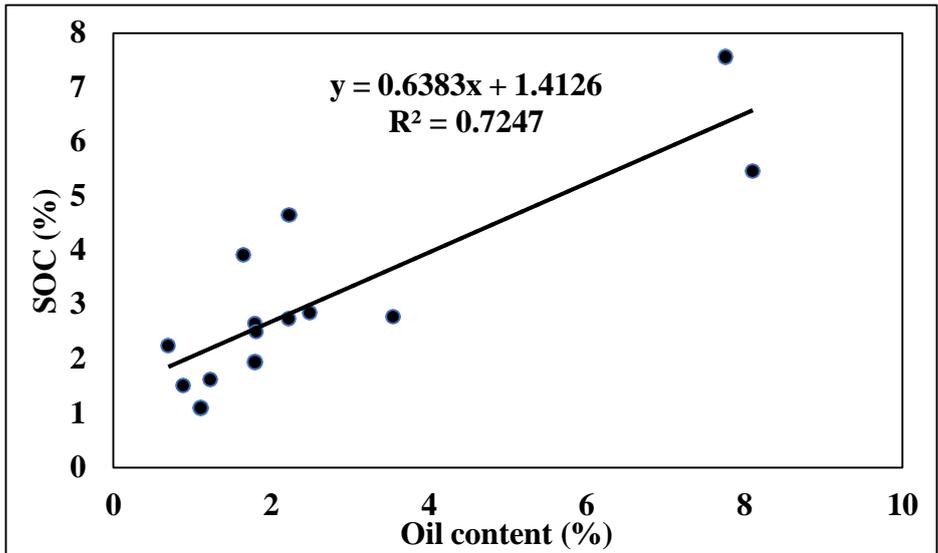| % Oil cotent	Sum CEC	Bas.sat	Fed	Organically-bound Fe	Fec	Feo	P_2O_5	K_2O
Cor.	-0.322	-0.318	-0.388	-0.355	-0.3327	-0.313	-0.088	-0.363
P-value	0.224	0.231	0.17	0.212	0.275	0.745	0.1676	0.125
N	16	16	14	14	14	14	16	16

Figure 19. Linear regression showing oil content and SOC

The strong association between oil content and soil organic carbon was seen (Fig. 19). It further explains that there was some sort of breakdown of the oil in the soil by microorganisms. Soil organic carbon is a result of microbial activities on organic matter in soil and oil is an example of organic matter and a rich source of carbon for some microbes.
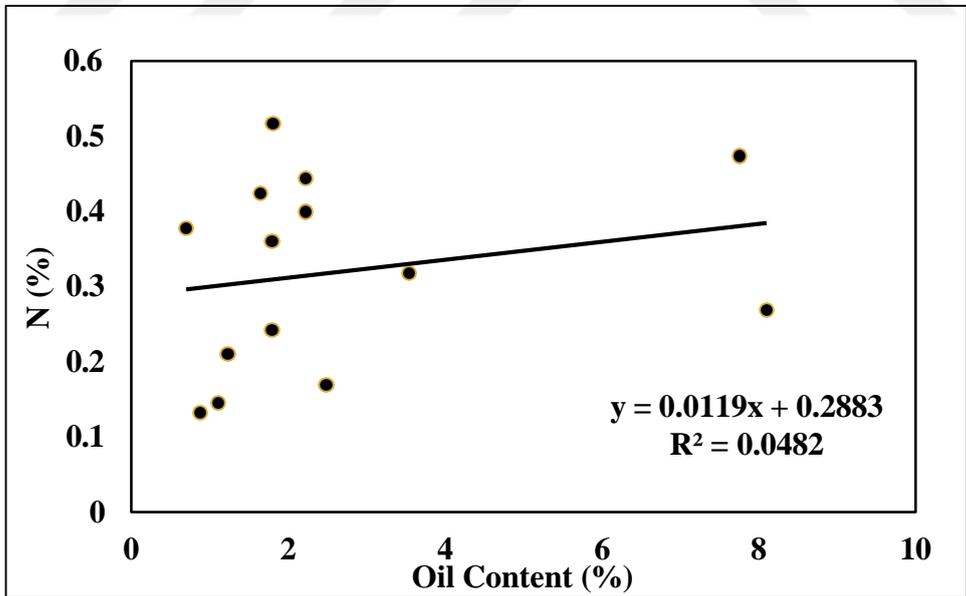

Figure 20. Linear regression showing oil content and nitrogen

There was a positive relationship between oil and nitrogen (Fig. 20). This is in line with Saikia et al., (2023) findings that demonstrate a positive relationship.

Attributing to the fact that the oil promotes the organic carbon content in the soil (Saikia et al., 2023)
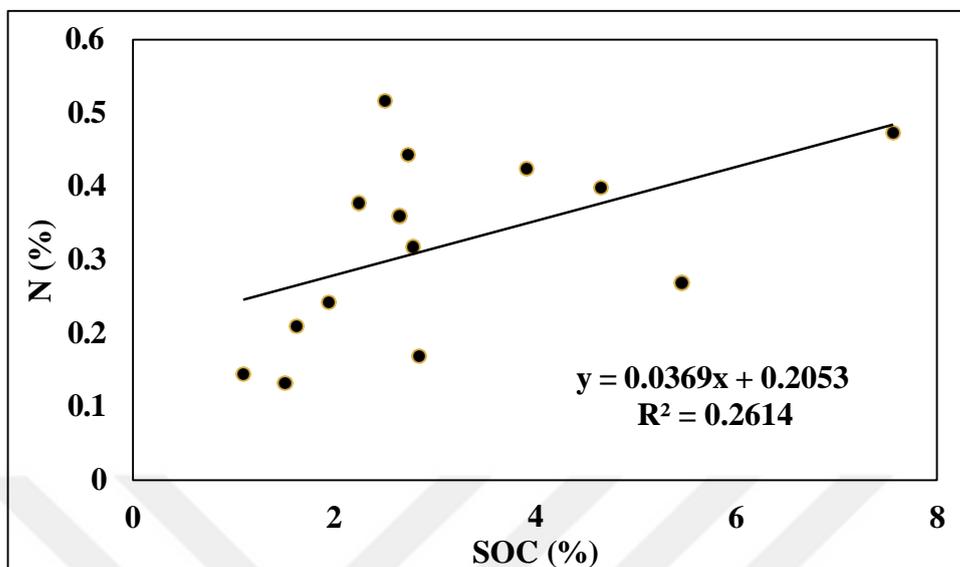

Figure 21. Linear regression showing between SOC and nitrogen

Also, there was a positive relationship between soil organic carbon and nitrogen (Fig. 21). This is in line with earlier research by Lei, (2013) and Yan, (2016), that demonstrates a correlation between SOC and nitrogen. One straightforward explanation is that organic material contributes to availability of nitrogen in the soil [Abegaz 2016].
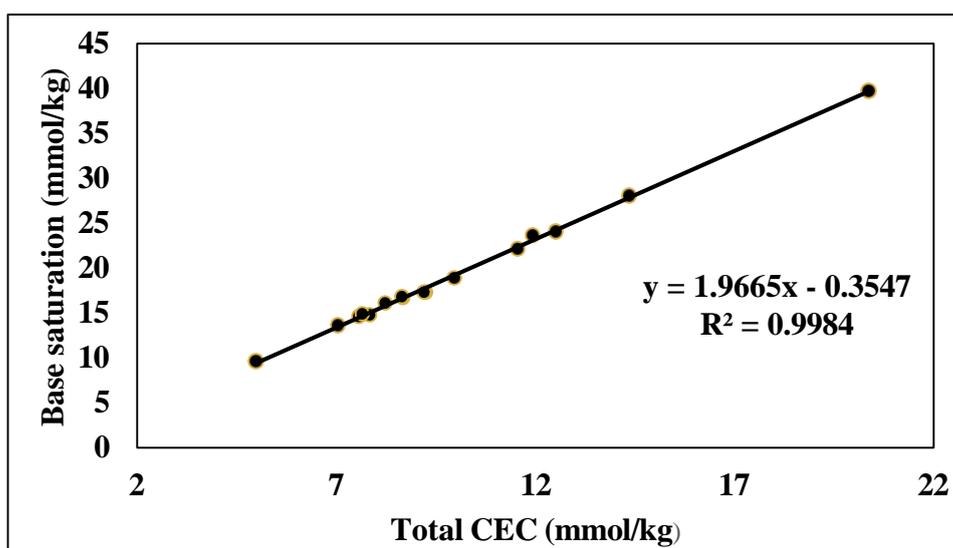

Figure 22. Linear regression showing total CEC and base saturation

There was a strong direct proportionality between the total CEC and base saturation in the surface soils (Fig. 22). This may be due to the high Ca^{2+} presence

(Rippy et al., 2007). There was a positive correlation between clay content and total CEC in the surface soils, increase in clay increases the CEC (Fig. 23).
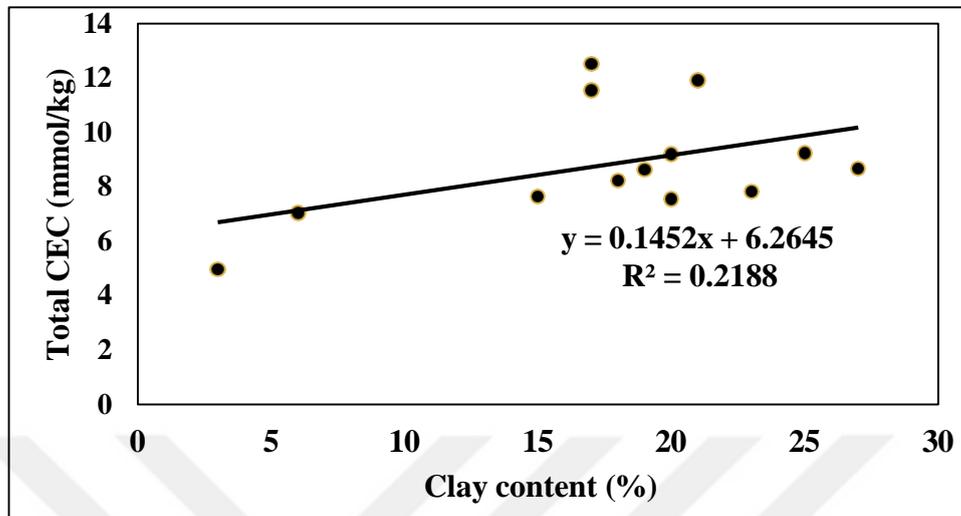

Figure 23. Linear regression showing %clay content and total CEC

The SOC and Nitrogen levels were classified into low, moderate, and high according to Hazelton and Murphy, (2016). Nitrogen level has a treatment effect on silt/clay ration, plant available phosphorus, and potassium (Fig. 24, 25, and 26 respectively), and SOC level has a treatment effect on organically bound iron (Fig. 27). The silt/clay ratio, plant available phosphorus, and potassium of high nitrogen levels are significantly different from low but insignificant with moderate Nitrogen level, at $\alpha = 0.05$. Looking at the treatment effect of SOC level on organically bound iron, there was a significant difference between a high SOC level to a moderate level at $\alpha = 0.05$.
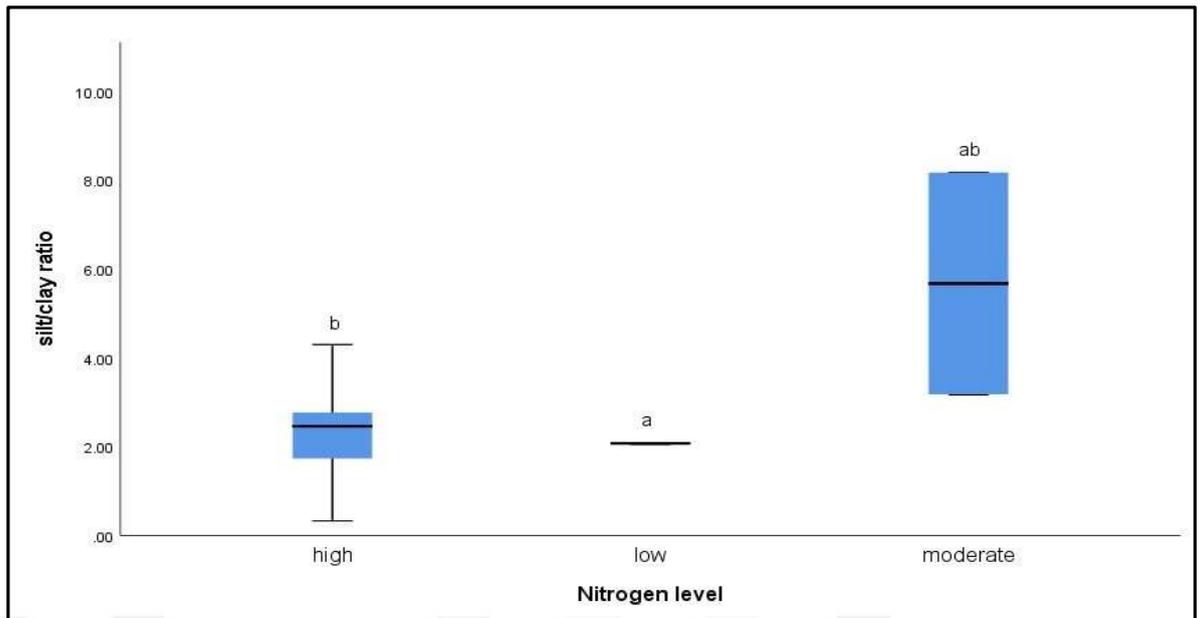
Figure 24. Boxplot showing treatment effect of Nitrogen level to silt/clay ratio
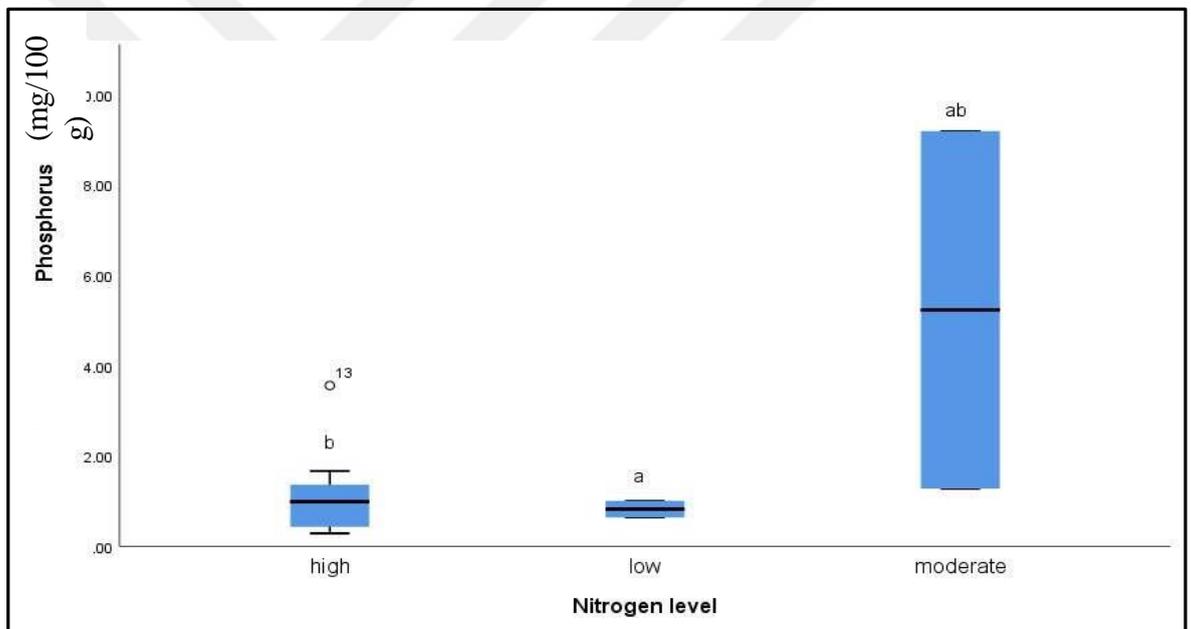

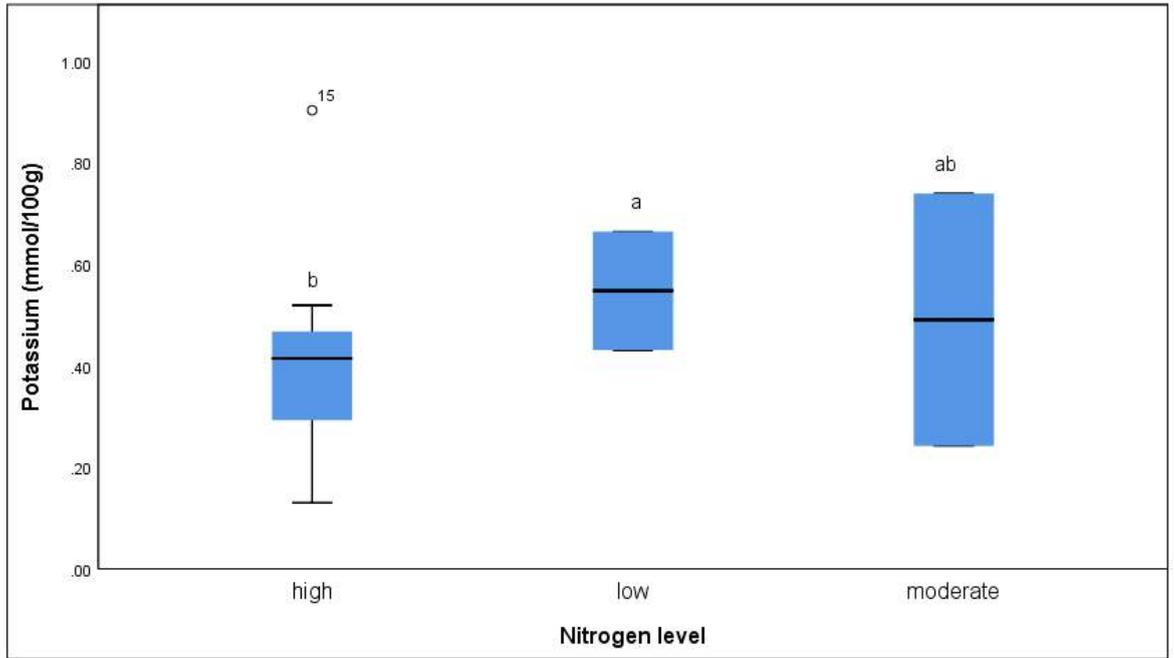Figure 25. Boxplot showing nitrogen level to phosphorus

Figure 26. Boxplot showing nitrogen level to potassium
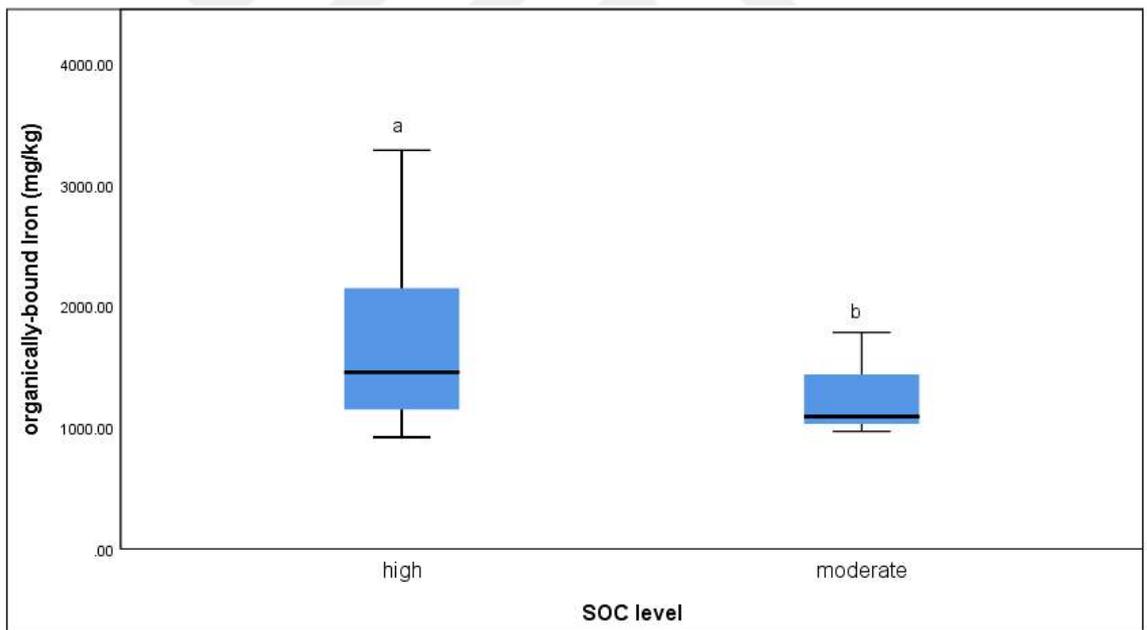
Figure 27. Boxplot showing SOC level to organically-bound iron

5. CONCLUSION

1. The soil in Płowce is classified as Cambisol, Zmiennica-Brzózow as Gleysol, and Ropianka as Gleysol.

2. The reaction of the surrounding soils ranges from weakly acidic to weakly alkaline.

3. The oil content varied greatly in the surrounding surface soils, especially in the location of Ropianka and Płowce.

4. The majority of the soil texture falls in the loam class

5. The C/N ratio being <25 in the soils tells of a good humification process in the surrounding surface soils.

6. In all, the physical observation of the natural seep sites and lab results obtained indicate less negative influence of the oil from these seeps in the surrounding surface soils.

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Master of Science in Soil Science and Plant Nutrition   Oct 2022 - Sept 2024

Ondokuz Mayis University, Samsun, Turkey | CGPA: 3.8 / 4.0

Thesis: The Influence Of Natural Oil Seeps On The Chemical Properties Of The Surrounding Surface Soil Levels.

Supervisor: Assoc. Prof. Tomasz Zaleski

Bachelor of Agriculture   Oct. 2014 – Aug. 2018

University of Buea, Buea, Cameroon

Research Interests :

- Soil contamination and remediation   - Soil fertility management

- Environmental impact assessment   - and environmental biogeochemistry

-Soil-plant-microbe interaction

Publications :

1. Georgieva, R., Steinkellner, S., Manolov, I., Pangilinan, P. J. M., & Desmond, K. S. (2024). Effect of organic pest control products on Arbuscular Mycorrhizal colonization in Bulgarian rose plantations: A two-year field study. *Eurasian Journal of Soil Science*, *13*(2), 161-166.

2. Sama, D. K., Agbor, D. T., Maningas Pangilinan, P. J., Sunjo, T. E., & Sama-Lang, P. (2023). CUTTING EDGE USE OF MICROBIAL CONSORTIA FOR BIOREMEDIATION OF CONTAMINATED SOIL. *Agricultural Sciences/Agrarni Nauki*, *15*(39).

3. SAMA, D. K., PANGILINAN, P. J. M., DENGIZ, O., & ZALESKI, T. (2023). Soil reclamation after the oil extraction industry. *EEDINGS*, 59.

4. SAMA, D. K., AGBOR, D. T., DOHNJI, J. D., & KIZILKAYA, R. (2022, December). Exploring the soil fertility and plant nutrition potential of LAB isolated from palm wine and sha'. In *International Soil Science Symposium on Soil Science and Plant Nutrition* (pp. 2-3).

5. Agbor, D. T., Eboh, K. S., Sama, D. K., Teche, L. M., Tanyi, G. T., & Nkongho, R. N. (2023). Maize-legume intercropping and botanical piper mitigating effect on pest populations while enhancing the yield of maize. *Journal of Natural Pesticide Research*, *6*, 100060.

6. Eboh, K. S., Agbor, D. T., Sama, D. K., Bambe, B. A., Tanyi, G. T., & Tening, A. S. (2023). ENHANCING THE EFFICACY OF ALLIUM (GARLIC) EXTRACT AND MAIZE-LEGUME INTERCROPPING AGROECOLOGICAL PRACTICES IN MITIGATING THE FALL ARMYWORM DAMAGE ON MAIZE. *Agricultural Sciences/Agrarni Nauki*, *15*(38).

Won Awards, Incentives and Scholarships

1. Fully Funded Erasmus Mundus Master's Degree (EMJMD) Scholarship 2022
2. Fully Funded Erasmus Blended Intensive Training Program   2024
3. 1st place in my class (form 4B)   2011
4. 1st position in my class (form 3B)   2021
5. **1**st position in my class (form 2B)   2009
6. Best Biology Student   2009
7. 2nd position in my class (form 1B)   2008

TECHNICAL SKILLS

- Microsoft Office   -Soil sampling /analysis - QGIS   - Remote sensing   - R-programming - Data anylusis and visualisation - SPSS

EXTRA CURRICULAR ACTIVITIES

- Community development services   - Playing Games   - Internet surfing