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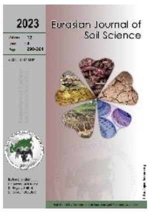

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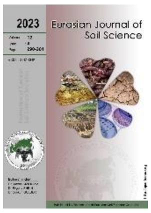

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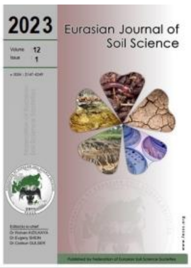

Comprehensive assessment and information database on saline and waterlogged soils in Kazakhstan: Insights from Remote Sensing Technology

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Abstract

Soil salinity and waterlogging are significant challenges in agricultural regions worldwide, including Kazakhstan. Understanding the characteristics and distribution of saline and waterlogged soils is crucial for developing effective strategies to mitigate their negative impact on crop productivity and environmental sustainability. This study aims to provide a comprehensive assessment of saline and waterlogged soils in various zones of the Republic of Kazakhstan, including the desert, foothill semi-desert (vertical), semi-desert (latitudinal), and dry-steppe areas. By examining the genetic horizons, chemical composition, ionic composition, salt content, and granulometric composition of these soils, this research contributes to the knowledge base necessary for implementing targeted soil management practices and restoration techniques. Fieldwork was conducted at 66 designated base points, where detailed descriptions of the genetic horizons of these soils were made. The data collected from these surveys were utilized to create an extensive information database, encompassing various indicators such as nomenclature, profile structure morphology, chemical composition, ionic composition of water extracts, salt content, absorbed cations, and granulometric composition. The findings reveal that saline soils cover a significant area of 16.7% (35,817.4 thousand hectares) of the agricultural land, while waterlogged soils occupy 0.5% (1,083.4 thousand hectares). The study highlights the poor fertility of saline soils due to high concentrations of water-soluble salts, predominantly sodium chlorides and sulfates, throughout the soil profile. Conversely, waterlogged soils exhibit distinct features such as gleyed horizons and a greenish-grayish color, with variations in fertility. The information presented in this study contributes to the understanding of the characteristics and distribution of saline and waterlogged soils in Kazakhstan, facilitating the development of strategies to restore soil fertility and implement appropriate management practices.

Keywords: Information base, salinity, waterlogging, remote sensing, solonchak soil, peat-bog soil, GIS technology.

Introduction

The classification and understanding of soil salinization play a crucial role in managing agricultural lands and ensuring sustainable productivity. This study focuses on the identification and assessment of saline and swampy soils in Kazakhstan, aiming to provide valuable insights into the distribution, severity, and potential mitigation strategies for these soil types.

Kazakhstan exhibits diverse soil conditions, with varying degrees of salinization (Funakawa et al., 2000; Saparov, 2014; Pachikin et al., 2014; Otarov, 2014; Laiskhanov et al., 2016; Suska-Malawska et al., 2019; Zhang

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et al., 2019; Ma et al., 2019; Yertayeva et al., 2019; Kussainova et al., 2020; Liu et al., 2022; Suska-Malawska et al., 2022). Soil salinity is categorized into three gradations based on the level of salinization and solonchak complexes:

i. Slightly saline: This category includes solonchak soils and their complexes with solonchaks up to 10%, covering an area of 11.5 million hectares.
ii. Medium-saline: Encompassing solonchak soils and their complexes with solonchaks ranging from 10% to 30%, this category extends over 7.3 million hectares.
iii. Highly saline: Comprising highly solonchak soils and their complexes with solonchaks exceeding 30% salinity, this category occupies 14.2 million hectares.

These gradations provide insights into the extent of soil salinization and facilitate a comprehensive understanding of the distribution and severity of salinity in specific regions.

Solonchaks, characterized as saline soils, cover approximately 2.8 million hectares of land in Kazakhstan. These saline soils are found in various soil zones, with a significant proportion (more than 58%) occurring in brown and gray-brown soils. Within this group, approximately 64% of the saline soils exhibit medium to strong salinity. The largest concentration of solonchaks, accounting for over 50% of the total area, is observed in the zone of brown and gray-brown soils. Additionally, saline soils are identified on 1.6 million hectares of land in the chernozem (black soil) zone, 6.2 million hectares in the dark-chestnut and chestnut soil zones, and 2.7 million hectares in the light-chestnut soil zone. Furthermore, 2.5 million hectares of saline lands are present within arable land (Funakawa et al., 2000; Saparov, 2014; Pachikin et al., 2014; Otarov, 2014; Laiskhanov et al., 2016; Suska-Malawska et al., 2019; Zhang et al., 2019; Ma et al., 2019; Yertayeva et al., 2019; Kussainova et al., 2020; Liu et al., 2022; Suska-Malawska et al., 2022).

The utilization of saline soils varies depending on their salinity levels and land usage. Weakly saline soils and their complexes (covering 1.8 million hectares) are predominantly utilized in non-irrigated arable land. In irrigated agriculture, slightly saline soils and complexes consisting of unsalted and slightly saline soils with salt marshes up to 30% (covering 190.1 thousand hectares) are utilized. These slightly saline soils require relatively simple desalination and leaching measures, taking into account the presence of a collector-drainage network. On the other hand, medium and highly saline soils with salt marshes reaching up to 30% and salt marshes covering 510.2 thousand hectares necessitate comprehensive reclamation measures. Therefore, it is recommended to exclude them from agricultural use and convert them into grazing land.

Swampy soils cover an area of 1.1 million hectares in Kazakhstan, with 23.9 thousand hectares designated as arable land, including 15.3 thousand hectares of irrigated arable land. These soils are predominantly composed of swamp and meadow-swamp soils, forming in areas with excessive moisture. Although distributed across all regions of Kazakhstan, except for Mangystau, their utilization as part of arable land is impractical due to the need for extensive drainage measures. Furthermore, waterlogged soils cover 2.9 million hectares in the country, with 224.9 thousand hectares used for agriculture. This group primarily consists of hydromorphic and semi-hydromorphic soils, including floodplain lands (1.1 million hectares) and non-floodplain lands (1.8 million hectares). The Karaganda region exhibits the most significant extent of waterlogged lands, covering 0.6 million hectares, while Kostanay, West Kazakhstan, Pavlodar, Aktobe, and Almaty regions have 0.2-0.3 million hectares of waterlogged lands. Excessive meltwater and prolonged flooding pose challenges to planting, maturation, and crop yields in these areas, making it more suitable to utilize these soils for hayfields (Funakawa et al., 2000; Saparov, 2014; Pachikin et al., 2014; Otarov, 2014; Laiskhanov et al., 2016; Suska-Malawska et al., 2019; Zhang et al., 2019; Ma et al., 2019; Yertayeva et al., 2019; Liu et al., 2022; Suska-Malawska et al., 2022).

The primary objective of this research is to utilize remote sensing techniques and conduct comprehensive fieldwork to assess soil properties and vegetation cover in the semi-desert (latitudinal) and dry steppe zones. Furthermore, the study aims to develop a robust database and evaluate the extent of waterlogging and salinization, ultimately facilitating the formulation of effective strategies for mitigation and improvement of these soil conditions.

Material and Methods

Kazakhstan, located in Central Asia, is the world's largest landlocked country, encompassing an area of over 2.7 million square kilometers. Its strategic geographic position places it between Europe and Asia, with Russia to the north, China to the east, and the Caspian Sea and the Caucasus to the west (Figure 1). Most of the country's territory is lowlands and plains, with mountainous areas only in the east and southeast (Pilifosova et al., 1997). The country's diverse geography, climate, and land resources contribute to a wide range of soil covers and altitudes, making it an ideal case study for assessing saline and waterlogged soils.

Kazakhstan's geographic location spans across the northern hemisphere, extending from approximately 40°N to 55°N latitude and 46°E to 88°E longitude. The country's vast territory experiences diverse climatic conditions due to its considerable size. The climate of Kazakhstan is highly continental. In the north of the country, 250–350 mm of precipitation falls annually, and in the southern regions, only 100–120 mm. The average January temperature is −15 °C, while the minimum value reaches −40 °C. The summers are fairly hot, with a maximum mean July temperature of up to 40 °C in low-lying steppes and desert steppes (Salnikov et al., 2015). According to the Koppen–Geiger climate classification, the northern and eastern regions of Kazakhstan belong to cold climates with hot summer (Dfa) and warm summer (Dfb). Areas with dry steppe (BSk) and desert (BWk) climates are located in the southern and western regions (Peel et al., 2007). The arid regions are characterized by low precipitation and high evaporation rates, contributing to the formation of saline and waterlogged soils. Kazakhstan's climate exhibits a diverse range of classifications according to the Köppen-Geiger climate classification system (Figure 2). The country experiences various climate types, including arid (BW) in the southern and central regions, continental (D) in the northern parts, and subarctic (Dfc) in the extreme north. These classifications reflect the variations in precipitation, temperature, and vegetation patterns across different regions of Kazakhstan.

Figure 1. Location map of the study area - Kazakhstan

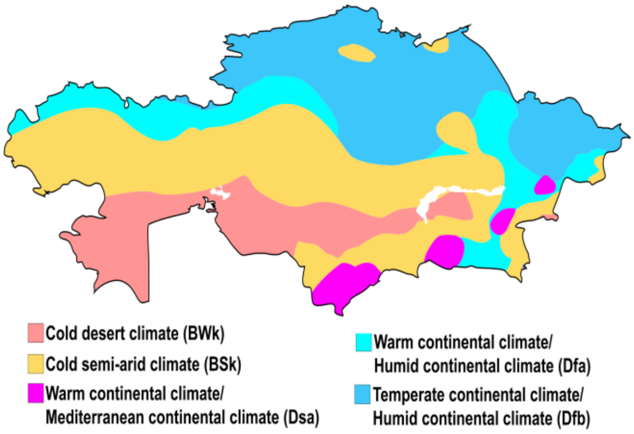

Figure 2. Kazakhstan map of Köppen climate classification

Kazakhstan boasts rich land resources, including vast steppes, deserts, mountains, and forests. Steppes, covering more than two-thirds of the country, are the dominant land cover, consisting of grasslands and shrublands. The desert regions, such as the Betpak-Dala and the Kyzylkum Desert, exhibit specific soil challenges, including salinity and waterlogging, which impact agricultural productivity.

The country's topography varies from low-lying plains to high mountain ranges. The Altai, Tien Shan, and Dzungarian Alatau mountain systems dominate the eastern and southeastern parts of Kazakhstan. These mountain ranges are characterized by high-altitude plateaus, deep valleys, and steep slopes. The altitudes range from below sea level in the Karagiye Depression (-132 meters) to the peak of Khan Tengri in the Tien Shan Mountains (7,010 meters).

Kazakhstan's unique geographic position, diverse climate, vast land resources, and varying altitudes contribute to a wide range of soil covers and challenges, including saline and waterlogged soils. Remote sensing technology provides valuable insights for comprehensive assessment and the development of an information database on these soils. By leveraging this technology, researchers can gain a better understanding of the spatial distribution, extent, and dynamics of saline and waterlogged soils in Kazakhstan, paving the way for effective land management strategies, agricultural planning, and sustainable development in the region.

The digital processing and classification of multispectral space scanning (MSS) data method is a modern and highly effective approach for mapping saline and saline soils (Singh and Dwivedi, 1989; Mulders and Girard, 1993; Dwivedi, 2001). The survey of saline and saline soils consisted of three stages: preparatory, field, and office.

Preparatory Stage

The preparatory stage involved collecting and organizing information on soil and natural conditions, existing soil maps, and digital data related to soil composition. A preliminary list of soil types was developed based on the expected structure of the soil cover. Remote sensing data, such as high-resolution satellite images or aerial photography, were used to create a preliminary map of the soil cover. The primary direct decoding features of saline and saline soils in arid desert, semi-desert, and dry steppe territories were identified, characterized by a relatively light tone across most spectral ranges and a complex contour image pattern. The phytoindication technique, which involves analyzing multispectral space scanning (MSS) data obtained from high and ultra-high spatial resolution satellites, was used as an effective indirect mapping method for identifying saline soils (Murphy, 1986; Dwivedi and Sreenivas, 1998a,b; Dwivedi, 2001). A generally accepted algorithm was employed for the mapping of saline and saline soils, involving systematic, radiometric, atmospheric, and geometric corrections, as well as radiometric calibration, contrast enhancement, spatial filtering, and general statistical analysis to determine the optimal number of classes for image classification. The outcome of the digital processing and classification was a georeferenced hypothetical map representing the spatial arrangement of distinct ranges exhibiting significant variations in optical properties across the Earth's surface.

Field Stage

The field stage of the survey included interpreting a map derived from remote sensing methods to study the Earth's surface. It involved a preliminary survey to determine the relationships between soil and landscape and refine the list of soil types. Soil sections were established based on the boundaries depicted on the soil cover map, and the initial identification of solonetz and solonchak soil complexes was carried out by analyzing the physical structure of the soil profiles, supported by subsequent analysis to determine their genetic status (USDA, 2012; 2015; 2022). For this purpose, 66 monitoring points were selected from the diverse ecological conditions of Kazakhstan, which is the research area (Figure 3).

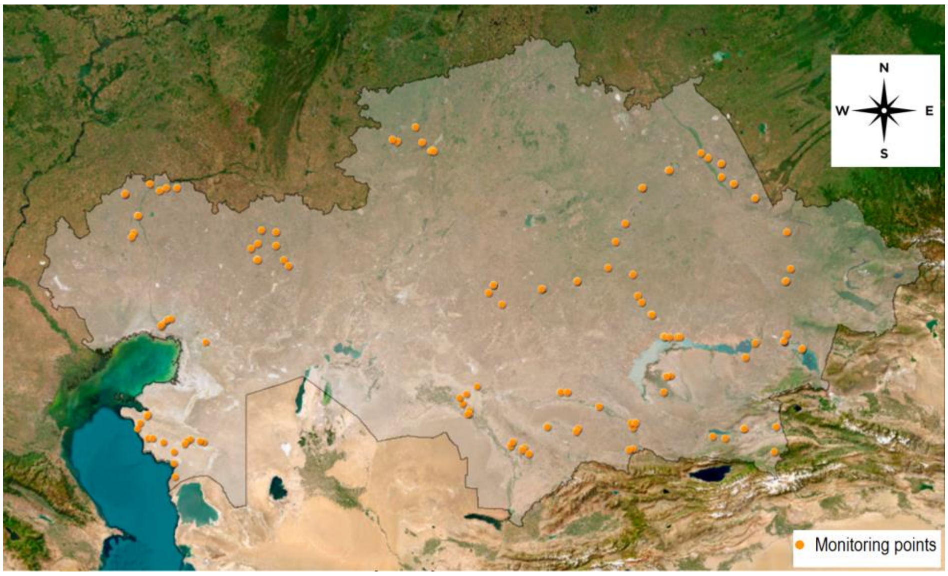

Figure 3. Monitoring points of the study area - Kazakhstan

Laboratory Analysis

Samples of saline and saline soils were collected and analyzed in the laboratory. The analysis focused on determining the humus content, granulometric composition, absorption capacity, amount of absorbed sodium, and cationic-anionic composition of water extracts. Based on the analysis results, specific names of soils were determined, and a final nomenclature list of soils was compiled. Additionally, a soil map, along with its corresponding legend, was prepared as a foundation for future recommendations regarding the reclamation of saline and saline soils (USDA, 2014; 2017; 2022).

Salinity and Waterlogging Determination

The determination of salinity and waterlogging of the soil was carried out using remote sensing data of the Earth. The Geographic Information System (GIS) of the project was created using available soil and geobotanical maps and supplemented with processed satellite images. Medium-resolution satellite data from Landsat 8, Sentinel 2, and Modis TERRA were used for sub-satellite studies, detailed classification of key areas, and verification of ground and space information. Remote sensing data, along with vector data in the form of digitized thematic maps and field survey data recorded using GPS receivers, were utilized. The method of remote sensing of the Earth involved the application of two spectral indices (LDI-NDVI, LDI-TCW) specifically developed to assess soil salinity and waterlogging. These indices considered various parameters, including vegetation cover (NDVI), surface moisture levels (TCW), and the brightness of the satellite image's red channel, where bare soils exhibit the highest brightness properties. Consistent ranges of index values for different satellite data were determined, enabling the identification of areas with saline and waterlogged soil cover in the images, regardless of the acquisition time or year. Seasonal variations in soil cover, such as the drying up of coastal areas, temporary reservoirs, and marshes, were also described using distinct index value ranges.

Methodology for Surface Classification

To determine salinity and waterlogging, special spectral brightness indices were utilized based on the specific wavelengths of the visible and infrared spectra. The primary satellite indices used included NDVI, SAVI, BareSoil Index, Salinity Index, and Top-Soil Grain Size Index. These indices allowed the distinction of various surface types, such as dense, sparse, moderate, bunched, and near-water vegetation, different soil types (clayey, sandy, lkali flat, and solonchaks), battered soils, water, marshes, and shoals.

Results and Discussion

Description of the Soil Profiles

The solonchak profile observed in the study area shows weak differentiation into genetic horizons. It primarily consists of a 10-cm thick humus horizon A, transitional horizons B, and a structureless parent rock. However, a notable feature of this soil profile is the presence of a moist clayey gley horizon with a grayish color. Upon drying, the soil surface and its upper horizon exhibit whitish patches formed by readily soluble salts.

Research Point No.1 - Sasykkol 1: The study site for this research is located adjacent to Sasykkol lake, within the Urzhar district of Abay region in Kazakhstan. The transect was established 200 meters north of the Semey-Almaty highway. The precise coordinates of the transect are N46°40'50.9, E080°35'06.3. The surveyed area is used as pasture land for cattle grazing. The landscape exhibits a greenish aspect. The dominant vegetation community in this area consists of various species of saltwort. These saltwort plants contribute to the formation of saline soils known as solonchaks-solonets. In the following sections, we provide a detailed morphogenetic description of the genetic horizons observed in these saline soils.

The morphogenetic description of the genetic horizons observed in the saline soils of Sasykkol 1 is as follows:

0-10 cm: The topmost layer is light gray in color, dry, loose, and dusty. It has a loamy texture with visible salt deposits on the soil surface. When treated with hydrochloric acid (HCl), it shows boiling, indicating the presence of carbonates. Roots are present in this layer, and the transition to the next horizon is clear.

11-28 cm: This layer is brownish-gray and fresh, with a weakly compacted and medium loam texture. It appears lumpy in structure. Boiling occurs more vigorously when treated with HCl. Small roots are observed, and the transition to the underlying horizon is clear in color.

29-60 cm: The soil in this horizon has a bluish color and is moist. It is weakly compacted and has a clayey texture. The soil structure is unstructured, and brown spots are noted within this layer. Boiling is observed vigorously when treated with HCl. The transition from the previous horizon to this one is gradual.

61-120 cm: This layer is slightly darker than the previous horizon. It is weakly compacted and unstructured, with a moist and clayey texture. Boiling occurs vigorously when treated with HCl. There are few visible spots of carbonates and gypsum within this layer.

These morphogenetic descriptions provide insights into the physical and chemical characteristics of the different soil horizons found in the Sasykkol 1 research site.

Chemical composition analysis of the solonchak - solonetz reveals a relatively low humus content of 0.83%. However, in the lower horizon, this value slightly increases to 1.21% (Table 1). Within the upper 0-10 cm layer, the mobile forms of nitrogen, phosphorus, and potassium exhibit concentrations of 33.6, 83.0, and 750 mg/kg of soil, respectively. As we move deeper into the soil, the nitrogen and potassium content increase to 47.6 and 1000 mg/kg of soil, respectively, while the phosphorus content decreases to 65.0 mg/kg of soil. The concentration of carbonate gradually increases with depth, ranging from 4.61% to 8.72%. It reaches its maximum concentration in the 40-50 cm layer at 11.39%.

Table 1. Chemical Composition of Solonchak-Solonetz Soils

Depth, cm	Humus content, %	Available nutrient contents, mg/kg			Total nitrogen, %	Total carbonates, %
		Nitrogen	Phosphorus	Potassium		
0-10	0.83	33.6	83.0	750	0.098	4.61
10-25	1.21	47.6	65.0	1000	0.098	7.29
25-50	-	-	-	-	-	11.39

The soil being investigated exhibits typical characteristics of saline soils, characterized by the accumulation of neutral salts that result in the formation of salt deposits on the surface. The dominant salt component in the soil composition is the sulfate ion. In the upper layer of the soil, the concentration of sulfate ions reaches its highest level, measuring 52.27 meq 100 g^{-1}. However, as we move deeper into the soil, this concentration sharply decreases to 14.41 meq 100 $g^{-1}$and then gradually increases again to 28.18 meq 100 g^{-1}. Despite these variations, the sulfate ion concentration remains above the threshold of salt toxicity, which is 1.7 meq 100 g^{-1}. In contrast, the chloride ion content increases as we progress deeper into the soil, ranging from 0.95 to 17.1 meq 100 g^{-1} in comparison to the sulfate ion concentration. This elevated chloride ion concentration is known to be toxic to plants. Furthermore, significant amounts of carbonate and bicarbonate ions are present in the salt composition, particularly in the soil's depth of half a meter. The soil composition is characterized by a predominance of sodium as a cation, particularly in the 0-10 cm and 25-50 cm layers, where its content is significantly high at 52.54 and 49.46 meq 100 g-1, respectively. The elevated levels of sodium ions are also reflected in the overall salt content of the soil. In the 0-10 cm and 25-50 cm layers, the salt content reaches its highest levels at 3.871% and 3.436%, respectively. In the other layers, the salt content ranges from 1.3% to 1.5%, classifying them as solonchaks and indicating moderate salinity. Moreover, the soil exhibits remarkably high pH values ranging from 9.5 to 10.46, signifying an extremely alkaline soil environment (Table 2).

Table 2. Ionic Composition of Water Extract from Solonchak-Solonetz

Depth, cm	Total Soluble salt, %	Anions, meq 100 g^{-1}				Cations, meq 100 g^{-1}				pH
		HCO_3^-	CO_3^{2-}	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	
0-10	3.871	1.20	0.40	0.95	52.27	52.54	0.70	0.69	0.49	9.50
10-25	1.480	2.80	1.68	3.71	14.41	19.75	0.58	0.29	0.29	10.00
25-50	3.436	5.12	4.24	17.1	28.18	49.46	0.55	0.10	0.29	10.36
50-90	1.304	3.84	2.96	14.01	2.30	19.13	0.33	0.20	0.49	10.46

The analysis of absorbed bases data reveals that the proportion of absorbed sodium constitutes a significant portion, ranging from 65.67% to 77.00% of the total cation exchange capacity. This indicates that the soil under investigation is saline. Conversely, the absorbed calcium content is found to be insignificant, accounting for only 8.40% to 11.03% of the total. The soil exhibits a high cation exchange capacity, measuring 29.13 meq 100 g-1 in the 10-25 cm layer. In other soil horizons, the cation exchange capacity is classified as very high (>40 meq 100 g-1) (Table 3).

Table 3. Content of Absorbed Bases in Solonchak-Solonetz

Depth, cm	Cations, meq 100 g^{-1}				CEC, meq 100 g^{-1}	Adsorbed Cations, %			
	Na^+	K^+	Ca^{2+}	Mg^{2+}		Na^+	K^+	Ca^{2+}	Mg^{2+}
0-10	31.68	0.78	4.95	7.43	44.84	70.65	1.74	11.03	16.57
10-25	19.13	1.09	2.97	5.94	29.13	65.67	3.74	10.20	20.40
25-50	31.68	1.21	3.47	4.95	41.31	76.70	2.90	8.40	12.00
50-90	30.84	0.79	3.96	4.46	40.05	77.00	1.97	9.88	11.13

Solonchaks within a half-meter thickness exhibit a granulometric composition primarily consisting of light clay, comprising 52.9% to 58.7% of the soil. This composition is supported by the morphogenetic characteristic descriptions. The mechanical fractions of these solonchaks are predominantly composed of fine sand, with depth-dependent variations ranging from 24.48% to 41.24% (Table 4).

Table 4. Granulometric Composition of Solonchak-Solonets

Depth, cm	Fraction size, mm						
	1,0-0,25	0,25-0,05	0,05-0,01	0,01-0,005	0,005-0,001	<0,001	<0,01
0-10	1.255	41.243	0.810	23.487	19.842	13.363	56.692
10-25	0.795	31.899	8.566	24.883	6.119	27.738	58.740
25-50	0.472	24.482	22.145	7.382	19.684	25.836	52.901
50-90	0.326	35.289	20.375	7.742	15.892	20.375	44.010

Research Point No. 2 - Sasykkol 2. A cutting was established in the Urzhar district of the Abay region, starting from the lowering of the plain of Sasykkol lake, extending 200 meters to the north from the Semey-Almaty highway. The coordinates of the section are N46°43'27.0, E080°33'39.1. The area is characterized by boggy soils covered with reed vegetation and saltwort. The grassland plant community is dominated by reedy vegetation, giving the landscape a dark green appearance. The following are the peculiarities of the morphology of the genetic horizons observed in the studied soils. The morphology of the genetic horizons observed in the studied soils at Research Point No. 2 - Sasykkol 2 are described as follows:

0-15 cm: The horizon appears gray with a greenish tint and has a granular and lumpy structure. It exhibits vigorous boiling when treated with hydrochloric acid (HCl). The presence of roots, both living and decomposed cane roots, can be observed. The soil is dry, loamy, and loose. A noticeable transition is observed.

16-28 cm: This horizon also appears gray with a greenish tint and is fresh in nature. It has a clumpy structure that is weakly compacted. The texture is characterized as light loam. Roots are present, and the soil exhibits vigorous boiling when treated with HCl. A noticeable transition is observed.

29-54 cm: This horizon is characterized by buried humus, giving it a black-brown color. It appears fresh and has a granular-lumpy structure that is weakly compacted. The texture is loamy. Boiling is observed with HCl treatment. Roots, including single larger reed roots, are present. The transition is gradual.

55-100 cm: This horizon is identified as subhumus buried. It is lighter in color compared to the previous horizon and appears fresh. The structure is weakly compacted and clumpy. The texture is loamy. Roots are present, and the boiling response to HCl is weak.

The bog soil profile consists of several distinct horizons that exhibit noticeable variations. The uppermost horizon, known as the organogenic horizon, extends from a depth of 0-15 cm and displays a gray color with a greenish tint. It is characterized by the presence of both living and decomposed reed roots. Similar horizons are also observed at depths of 29-54 cm and 55-100 cm, but they are considered buried horizons compared to the upper organogenic horizon. These buried horizons were once located near the soil surface but became covered by subsequent material accumulation, resulting in their burial.

This interpretation is supported by the distribution of humus content throughout the soil profile, as shown in Table 5. The upper humus horizon has a humus content of 1.38%. The underlying horizons (29-54 cm and 55-100 cm) also contain significant levels of humus, with values of 1.65% and 2.17% respectively.

Table 5. Chemical Composition of Swamp soil

Depth, cm	Humus content, %	Available nutrient contents, mg/kg			Total nitrogen, %	Total carbonates, %
		Nitrogen	Phosphorus	Potassium		
0-15	1.38	33.6	27	400	0.070	3.42
16-28	0.38	16.8	15	160	0.084	2.65
29-54	1.65	-	-	-	-	1.34

The chemical composition of the swamp soil is as follows:

In the upper layer (0-15 cm), the mobile nitrogen content is relatively low, measuring 33.6 mg/kg of soil. Moving deeper into the soil, in the lower layer (16-28 cm), the concentration of mobile nitrogen decreases to 16.8 mg/kg of soil. Regarding mobile phosphorus availability, the soil is considered to have average levels. In the upper horizon, the concentration of mobile phosphorus is 27 mg/kg of soil, while in the lower horizon, it decreases to 15 mg/kg of soil. In terms of carbonate content, the swamp soil exhibits slight levels. In the 0-28 cm layer, the carbonate content ranges from 2.65% to 3.42%. In the deeper layer (29-100 cm), the carbonate content is very slight, ranging from 0.25% to 1.34%. These values indicate the nutrient availability and carbonate content in the studied swamp soil.

The analysis of the ionic composition of the aqueous extract from the marsh soils indicates that they share similarities with solonchak soils. These soils contain soluble salts in concentrations that can potentially hinder plant growth, particularly at depths of 0-15 cm and 29-54 cm. In the latter depth range, the total salt concentrations were measured at 0.789% and 0.440% respectively, as shown in Table 6. The dominant anionic component contributing to the salinity of these soils is sulfate, while the cationic composition reveals a high concentration of sodium. This suggests that the salinity is primarily influenced by the presence of sulfate and sodium ions. Furthermore, the soil solution extracted from these soils displays a strongly alkaline pH, ranging from 8.62 to 8.93. This high alkalinity further contributes to the challenging conditions for plant growth in the marsh soils.

Table 6. Ionic Composition of Water Extract from bog soil

Depth, cm	Total Soluble salt, %	Anions, meq 100 g^{-1}				Cations, meq 100 g^{-1}				pH
		HCO_3^-	CO_3^{2-}	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	
0-15	0.789	0.68	0.08	1.64	9.10	8.66	0.30	1.57	0.88	8.93
16-28	1.480	0.48	0.00	0.40	1.96	1.07	0.10	0.69	0.98	8.92
29-54	0.192	0.60	0.00	0.95	4.87	4.35	0.11	0.98	0.98	8.62
55-100	1.304	3.84	2.96	14.01	2.30	19.13	0.33	0.20	0.49	8.30

The absorbed bases in the soil column show that calcium is the dominant component, constituting a range of 51.38% to 71.06% of the cation exchange capacity. Following calcium, absorbed magnesium occupies the second position, accounting for a varying share of 26.66% to 44.53% in the soil column, as indicated in Table 7. The substantial presence of magnesium suggests the potential solonetization of the soil, indicating the likelihood of solonetz formation.

Table 7. Content of Absorbed Bases in bog soil

Depth, cm	Cations, meq 100 g^{-1}				CEC, meq 100 g^{-1}	Adsorbed Cations, %			
	Na^+	K^+	Ca^{2+}	Mg^{2+}		Na^+	K^+	Ca^{2+}	Mg^{2+}
0-15	0.01	0.21	13.37	6.93	20.52	0.04	1.02	65.15	33.77
16-28	0.38	0.21	7.43	6.44	14.46	2.62	1.45	51.38	44.53
29-54	0.44	0.19	19.80	7.43	27.86	1.58	0.68	71.06	26.66
55-100	0.92	0.21	14.85	6.44	22.42	4.10	0.93	66.23	28.72

The granulometric composition of bog soils displays heterogeneity across their profiles. In the depths of 0-10 cm and 35-45 cm, the predominant soil composition is light loam, with a physical clay content ranging from 21.5% to 22.4%. However, between these layers, there exists a distinct sandy horizon (15-25 cm) characterized by a lower physical clay content of 9.26%. It is likely that this sandy horizon originated from sediment deposited by a sandy lake and has gradually been buried over time, as indicated in Table 8.

Table 8. Granulometric Composition of bog soil

Depth, cm	Fraction size, mm						
	1,0-0,25	0,25-0,05	0,05-0,01	0,01-0,005	0,005-0,001	<0,001	<0,01
0-15	1.441	66.903	10.146	3.653	10.552	7.305	21.510
16-28	0.624	85.688	4.428	1.208	4.428	3.623	9.259
29-54	1.610	58.863	17.115	8.965	2.037	11.410	22.412
55-100	0.630	64.026	1.625	4.063	29.250	0.406	33.719

The surveys conducted between 2021 and 2022 in various regions of Kazakhstan, including Almaty, Zhambyl, Turkestan, Karaganda, Ulytau, Pavlodar, Abay, and East Kazakhstan, have yielded a digital information database on saline and waterlogged soils. These regions encompass different zones such as the desert, foothill semi-desert (vertical), semi-desert (latitudinal), and dry-steppe zones. The database incorporates data from both satellite and ground surveys, providing comprehensive information on the characteristics and distribution of saline and waterlogged soils in these areas. Using ArcGIS software, an interactive online map has been developed to visualize the collected data. This map allows users to explore the chemical and granulometric compositions of the 66 monitoring points located across the eight oblasts of Kazakhstan. ArcGIS is a powerful system that enables the creation and analysis of online maps and related geographical information (https://arcg.is/DqXba). The findings obtained from previous studies conducted on saline and waterlogged soils in different regions of Kazakhstan (Laiskhanov et al., 2016; Issanova et al., 2017; Funakawa et al., 2020; Smanov et al., 2023) exhibit significant similarities with the results obtained in this study as well.

By utilizing this interactive map, researchers, land managers, and policymakers can access valuable insights into the properties and distribution of saline and waterlogged soils in the surveyed regions. This information can contribute to informed decision-making, land use planning, and the development of strategies for sustainable soil management in Kazakhstan.

Conclusion

Based on the final findings of this study, the following points can be concluded:

- The study reveals that saline soils cover an extensive area of 35,817.4 thousand hectares in the Republic of Kazakhstan, accounting for approximately 16.7% of the total agricultural land area, which is 214,348.8 thousand hectares. Additionally, waterlogged soils occupy 1,083.4 thousand hectares, representing 0.5% of the agricultural land area.
- The assessment of saline and waterlogged soils encompassed various zones in the republic, including the desert, foothill semi-desert (vertical), semi-desert (latitudinal), and dry-steppe areas. Fieldwork was conducted at 66 designated base points, where thorough descriptions of the genetic horizons of saline and waterlogged soils were made, providing a comprehensive understanding of their nomenclature.
- The collected data on the condition of saline and waterlogged soils in different zones of Kazakhstan allows for a comprehensive assessment of their status in specific areas. This assessment contributes to the development of technologies aimed at restoring soil fertility and implementing appropriate management practices.
- The information database compiled as part of this study includes crucial indicators such as the nomenclature of soils, profile structure morphology, chemical composition (NPK, carbonate content), ionic composition of water extracts, salt content, composition and quantity of absorbed cations, and granulometric composition of soils. This comprehensive database provides valuable insights into the characteristics and properties of saline and waterlogged soils in the desert, foothill semi-desert (vertical), semi-desert (latitudinal), and dry-steppe zones of Kazakhstan.
- Field and camera studies conducted on the soil cover of various zones in the Republic highlight the poor fertility of saline soils, which contain high concentrations of water-soluble salts that are detrimental to plant growth. These salts are present throughout the soil profile, exceeding an average concentration of 1.0%. Sodium chlorides and sulfates are the predominant salt compositions found in most cases. Waterlogged soils, characterized by close proximity to the groundwater and reductive processes, exhibit distinct features such as gleyed horizons with iron oxide rusts and a greenish-grayish color. These soils generally have low fertility, but meadow areas may exhibit differences, showing a sufficient supply of humus compared to peat or turf horizons.

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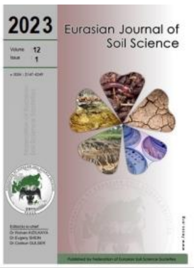

Prediction of some selected soil properties using the Hungarian Mid-infrared spectral library

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Abstract

Routine soil chemical and physical laboratory analysis provides a better understanding of the soil by evaluating its quality and functions. Demands for the development of national Mid-infrared (MIR) spectral libraries for predicting soil attributes with high accuracy have risen substantially in the recent past. Such MIR spectral library is usually regarded as a fast, cheap and non-destructive technique for estimating soil properties compared to laboratory soil analysis. The main objective of this research was to assess the performance of the Hungarian MIR spectral library in estimating four soil properties namely: Cation Exchange Capacity (CEC), Exchangeable Mg and Ca and pH water at different scenarios. Archived soil samples were scanned and spectra data were saved in the Fourier transform infrared spectrometer OPUS software. Preprocessed filtering, outlier detection and calibration sample selection methods were applied to the spectral library. MIR calibration models were built for soil attributes using partial least square regression method and the models were validated with sample predictions. R2, RMSE and RPD were used to assess the goodness of calibration and validation models. MIR spectral library had the ability to estimate soil properties such as CEC and exchangeable Ca and Mg through various scale models (national, county and soil type). The findings showed that the Hungarian MIR spectral library for estimation of soil properties has the ability to provide good information on national, county and soil type scales at different levels of accuracy.

Keywords: Mid-infrared spectroscopy, soil information monitoring system, partial least square regression, fourier transform infrared spectrometer, coefficient determination.

Introduction

Soil is an important element of agricultural production especially in agroecology. Food security, water security, energy sustainability, climate stability, biodiversity preservation, and the provision of ecosystem services all depend on soil (McBratney et al., 2014). It is critical to recognize and monitor soil physical and chemical attributes using innovative approaches. Routine soil chemical and physical laboratory analysis must be performed to evaluate soil functions. Conventional laboratory techniques are widely regarded as accurate methods for characterizing soil attributes, however, they sometimes have been viewed as impractical due to their time-consuming, and occasional imprecision (Demattê et al., 2019). Many new soil analysis techniques have recently been developed, in particular, diffuse reflectance spectroscopy. In essence, an Infrared (IR) spectrum provides a chemical profile of the sample. Soil infrared spectroscopy techniques have demonstrated several advantages over wet chemistry methods. This approach is cheap, utilizes tiny subsamples and have the advantage that a single spectrum of soil sample integrates many attributes with high precision (Raphael, 2011; Waruru et al., 2015). It permits rapid acquiring of soil data, does not require the use of chemical extracts

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that might harm the environment and allows for the scanning diverse of soil types without samples dilution (Siebielec et al., 2004; Viscarra Rossel et al., 2006; Seybold et al., 2019). The IR spectroscopy is a repeatable and reproducible analytical approach for predicting soil properties (Soriano-Disla et al., 2014).

The electromagnetic spectrum of infrared radiation ranges from 0.7 µm to 1 mm that contains: near-infrared (0.70 - 2.5 µm), mid-infrared (2.5 - 25 µm) and far-infrared (25 - 1000 µm) (Nocita et al., 2015). The two most important spectral ranges for soil investigation and analysis are mid-infrared and near-infrared (Wijewardane et al., 2018). The mid-infrared (MIR) spectroscopy spectrum contains a high reflectivity, useful spectral features and gives greater information on soil attributes (Shepherd and Walsh, 2007; Bo Stenberg et al., 2010). This is due to the fact that MIR range results are based on fundamental molecular vibrations that are absorbed at the specific wavelengths of electromagnetic radiation, while vis-NIR spectra result from overtones and combination bands which are complex and more difficult to describe than those recorded in the MIR region. The type of molecular motions, functional groups, or bonds present in the soil sample can be identified through mid-infrared spectroscopy since every frequency correlates to a certain quantity of energy and a specific molecular motion such asstretching, bending, etc (Tinti et al., 2015). The MIR range shows high-density peaks (Shepherd and Walsh, 2007; Soriano-Disla et al., 2014), containing much mineral composition information on soils such as Si-bearing minerals and iron forms. The basic vibrations of functional groups in minerals and organic matter of soil samples are used to explain the strong absorption of mid-infrared spectra (Shepherd and Walsh, 2007). MIR has been confirmed to show better results and high predictions for several soil properties across soil types in comparison to near-infrared spectroscopy (Pirie et al., 2005; Minasny and McBratney, 2008). In order to build predictive models, data from mid-infrared spectroscopy can be grouped into spectral libraries (harmonized point-dataset with coupled reflectance and analytical reference measurements) with the progress of mid-infrared spectroscopy in soil science. Many publications show soil attributes have been efficiently estimated based on the mid-infrared spectral library with high accuracy. It has been usefully applied to predict various physical (Kasprzhitskii et al., 2018), biological and chemical soil properties (Reeves and Smith, 2009; Acqui et al., 2010). On the other hand, traditional soil surveys and fresh soil sampling campaigns are costly and time-consuming. Legacy soil samples have an abundance of spectral information that can be utilized to improve the calibration models of the mid-infrared spectral library. The majority of large soil spectral databases are built from archived historical soil samples (Rossel and Webster, 2012).

Multivariate statistical techniques have given a powerful approach for soil component discrimination, such as partial least square regression (PLSR). PLSR has been used for soil attributes prediction from the spectral library and can quantify varied soil attributes with a high level of accuracy (Seybold et al., 2019). PLSR is easy to compute and understand (Wijewardane et al., 2018), and commonly integrates PCA and multiple regression (Wold et al., 2001).

Although soil spectroscopy methods have been used in previous years in literature to predict some soil attributes in Hungary, the potential use of an extensive national MIR spectral library that contains different soil types for estimating soil properties is yet to be intensively explored. Therefore, the present study objectives were: i) to build a multivariate statistical models using PLSR based on Hungarian MIR spectral libaray and ii) to test the predictive capacity of the Hungarian spectral library in the spectral based estimation of key some chemical soil properties (CEC, exchangeable Ca and Mg and pH in water).

Material and Methods

Hungarian MIR spectral library and soil samples

The spectral library consists of 2200 soil samples, corresponding to horizons of 543 soil profiles. The soil samples collected from the laboratory bank archives of Soil Information Conservation and Montoring System (SIMS), representing 10 Hungarian counties which are: Baranya, Fejer, Komarom_Esztergom, Nograd, Pest, Tolna, Bacs-Kiskun, Bekes, Csongrad and Jasz-Nagykun-Szolnok (Figure 1). These samples belong to the first SIMS project survey of 1992. The MIR spectral library was built at the Hungarian University of Agriculture and Life Sciences, Szent István Campus.

Previously, all soil samples were dried, mashed, and filtered via a two-millimetre sieve, with the remaining part stored in SIMS archives in plastic containers at room temperature. Three hundred gram from each sample were packaged in plastic sacs and shipped out to the Department of Soil Science, Godollo. Coning and quartering was done to obtain 20 g of soil subsamples, which were then grinded to less than 0.5 (fine powdered particle size between 20 and 53um) by hand using an agate pestle and mortar. Through a micro spatula, the fine soil samples were put into aluminium sample cups, and one by one the loaded samples were placed in the sample holding tray. Excess soil was removed to reduce sample surface roughness and the surface was leveled with a straight-edged tool. The Bruker Alpha II with a spectral range of 2500 – 25000 nm (4000 – 500 cm^{-1}) was used to scan the 2200 soil samples given for this study under DRIFT mode. A scan of the gold background was taken before the measurement of each sample to account for variations in temperature and moisture content. Gold background is used as a reference material in mid-infrared spectroscopy methods since it does not absorb infrared light (Nash, 1986). Every soil sample was read three times using three subsamples, and each spectrum was produced from 47 scans. Soil spectra were measured following the protocol proposed by the World Agroforestry Centre (Dickens, 2014). The collected information of all spectra was saved with the Fourier Transform Infrared Spectrometer (FTIR) spectrometer OPUS software.

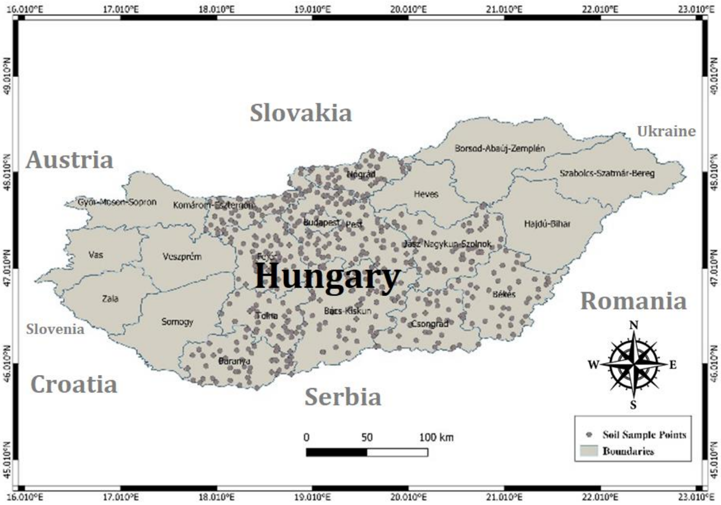

Figure 1. Spread of sampling points according to counties in Hungary

In terms of soil reference data, physical and chemical soil parameters were determined at the horizon level using conventional laboratory methods in the frame of the SIMS project and have been stored in the project database since 1992. TIM (1995) gave details for reference laboratory methods used in the conventional database of SIMS. The conventional database was subjected to quality and consistency checks before being used as soil reference data for calibration models.

Spectral data mangement

Initially, the transformation of measured spectral reflectance to absorbance value was performed using the equation:

$$\text{Absorbance} = \log(1/\text{Reflectance})$$

Absorbance spectra were preprocessed with a moving average window of 17 bands and Savitzky-Golay filtering methods (Savitzky and Golay, 1964).

Principal Component Analysis (PCA) was applied to reduce the dimension of the spectral library and improve computational efficiency for different model scenarios of our data. Mahalanobis distance outlier detection method was carried out on principal component scores of spectral data to identify samples that deviate from the average population of spectra (Shepherd and Walsh, 2002; Waruru et al., 2014). Based on standard arbitrary threshold methods, the samples with a Mahalanobis dissimilarity larger than one were considered outliers. Detected outlier samples were filtered away from the mid-infrared spectral library dataset at different levels of the scenarios then further investigation and calibration were performed on the remaining soil samples.

Kennard-Stone Sampling method (Kennard and Stone, 1969) was applied to the spectral library data to define how many observations (samples) should be listed in calibration. Optimal calibration sample sets was selected and the remaining samples were retained for the validation set.

Spectroscopic modeling for soil properties prediction

The mid-infrared spectral library and soil reference data, including the depths of horizons, were merged into one dataset. Three modelling scenarios were used. Consequently, the dataset was split according to 10 counties, 6 soil types and the national scenario that included the whole dataset. Furthermore, depending on the KSS method, the dataset of each sub-scenario was split into a calibration dataset and validation datasets. In this research, PLSR (Lorber et al., 1987) statistical models were fitted between latent variables (mid-infrared spectral library) and response variables (soil attributes) based on calibration data using the highest number of principal components and oscorespls method (Wadoux et al., 2020). For each soil property, the PLSR regression coefficients were plotted using the number of components. The built PLSR models and the appropriate number of components were used to predict soil properties using spectra on the calibration and validation datasets. Four soil properties in the frame of this study were predicted, including, exchangeable calcium (Ca^{++}), exchangeable magnesium (Mg^{++}), pH water, and Cation Exchange Capacity (CEC). R software (R Core Team, 2022) was used for spectral displaying, analysis and modelling processes. Models development and predictions were performed using the caret package interface (Max et al., 2016) and PLSR function from pls package (Liland et al., 2016).

Models performance and accuracy

Coefficient of determination (R2), ratio performance to deviation (RPD) and root mean square error (RMSE) were used to determine the goodness and inaccuracy of the model's predictions.

$$\mathrm{R2} \quad = \frac{\sum_{i=1}^{n}(\hat{y}_i - \bar{y}_i\ )^{\,2}}{\sum_{i=1}^{n}(Y_i - \bar{y}_i\ )^{\,2}}$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{y}_i - Y_i)^{\,2}}$$

$$\mathrm{RPD} = \quad \mathrm{s_y/RMSE}$$

ŷ indicates the spectral library's predicted value, while ȳ and y represent the observed value average and observed value of reference soil database respectively n represents the sample number where *I* is equivalent to 1, 2, ..., while, s_y the observed values' standard deviation.

eval function of R was used to derive the goodness measurement of prediction and validation models.

Results and Discussion

Summary statistics of spectral library soil attributes

In this study, the predictability of 4 soil attributes were assessed at different scenarios. Figure 2 shows the distribution of the dataset for soil attributes at the national level. The soil attributes of the spectral library dataset showed wide-ranging distributions, as well as based on frequency histograms, many of them were skewed from the normal distribution (Figure 2). These factors were expected in this database, since the samples were derived from different depths and horizons of soil types at wide spatial variability covering several variations of climatic conditions, geological formation and parent material, land cover and human activities.

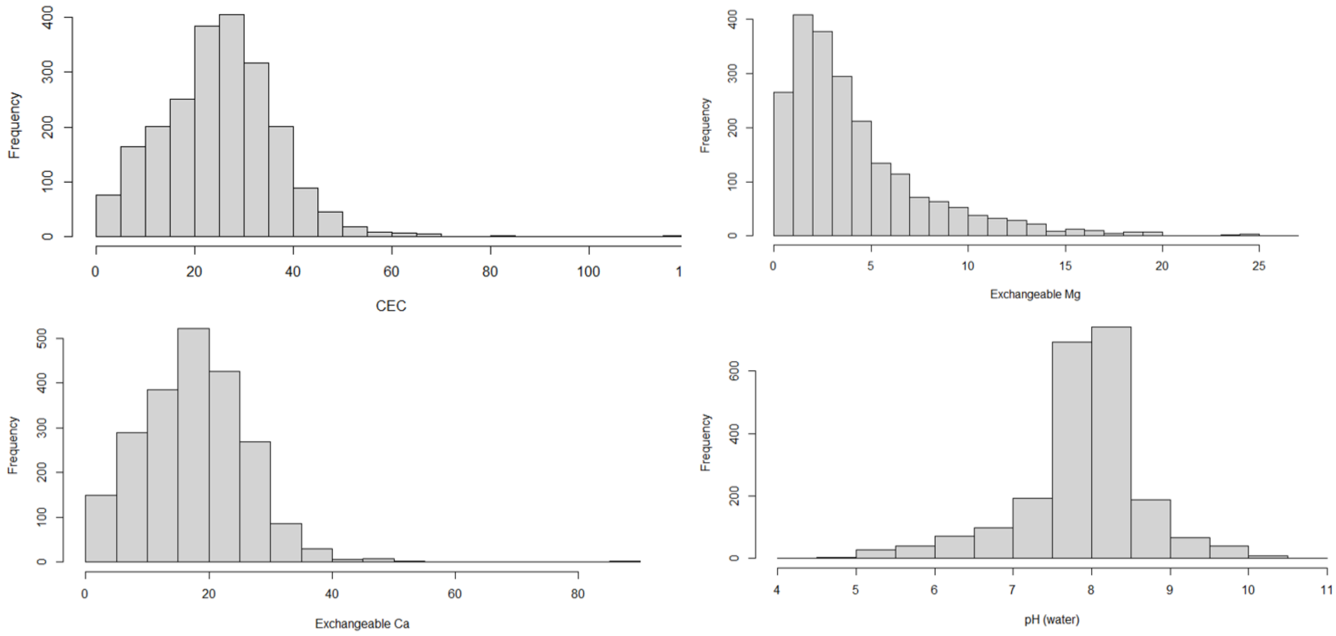

Figure 2. Distribution of dataset for soil properties

Mid-Infrared spectral signature and regression coefficient of PLSR models

Absorbance signatures in the MIR spectral library were due to fundamental molecular vibrations described by peaks related to different compounds (Figure 3), mainly minerals and organic constituents. Despite, the overlapping bands and exchangeable cations are not spectrally active, several absorption bands linked to certain functional groupings were identified (Figure 3). For example, many exchangeable cations influence the position and strength of the wide band around 3400 1/cm. Its position falls in the order of K^+, Na^+, Ca^{2+} and Mg^{2+}, which corresponds to the cation's increasing polarizing strength (charge/radius). These findings are in agreement with the results of some earlier authors such as Madejová (2003) and Tinti et al., (2015).

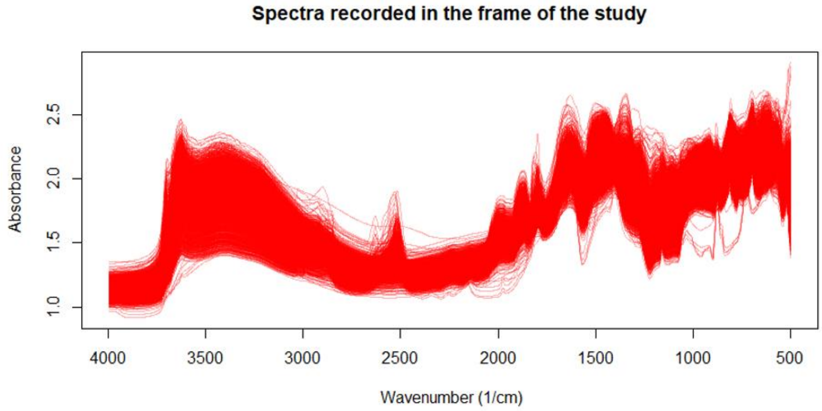

Figure 3. Absorbance mid-infrared spectral library of different Hungarian soil types using Bruker alfa II

On ther hand, the regression coefficient of PLSR illustrated the association between the mid-infrared frequencies and the soil constituents. The plots of PLSR regression coefficients vs wavelength for calibration models of the 4 soil attributes at national levels data are shown in figure 4. In this context Viscarra Rossel et al. (2006) stated that the positive peaks belong to the interest components, whilst negative peaks refer to interfering components. It's worthwhile to mention that some important wavelengths for the CEC prediction model are almost similar to those of the clay. For instance, the weak bands at 400 1/cm and significant broad wavelengths between 1000 to 1500 1/cm. The important bands for predicting exchangeable calcium are those near 400, 900, 1300, 720 and 1800 1/cm with the latter two bands attributed to diagnostic peaks for calcite (Figure 4) which may consistent with the result obtained by Nguyen et al. (1991). The peak bands for models prediction of exchangeable magnesium are those near 400 and 1200 1/cm, in addition to bands near 1440, 1470, and 875 1/cm which are representative of carbonate and may be caused by the presence of magnesium carbonate and dolomite (Figure 4). Figure 4 also showed that the regression coefficients for exchangeable Ca and Mg prediction models are identical in many spectral regions to those of the clay and organic matter, indicating that these soil properties are associated with each other.

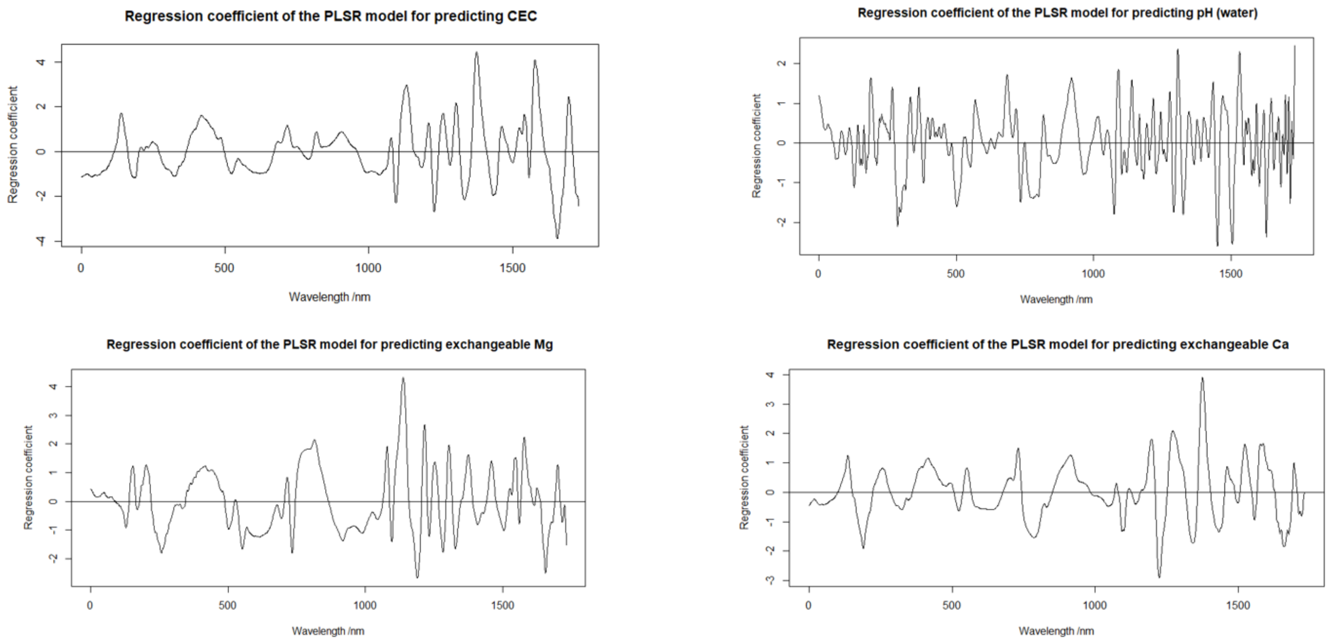

Figure 4. PLSR models' standard regression coefficient for predicting CEC, Exch. Mg, Ca, and pH water

Hungarain Spectral Library Model Performance

Cation Exchange Capacity

The calibration model of CEC at the national scale reached a R2 of 0.61 and RMSE of 8.24 and the validation set reached respective R2 and RMSE of 0.57 and 7.78 (Table 1). At the counties level, Baranya and Tolna showed a R2 ≥ 0.90, while Fejer had R2 of 0.83, and three counties showed R2 of 0.68 (Bekes, Csongrad and Jasz-Nagykun-Szolnok) while only one county showed R2 below 0.55 (Bacs-Kiskun) in the calibration models. Validation sets showed only four counties had R2 ≥ 0.60, while the remaining six counties had R2 ≤ .051. At the soil type scenarios, brown forest soils and alluvial and colluvial soils showed the best calibration results (R2 of 0.86 and RMSE of 3.96 and 4.29 respectively) whereas Chernozem soils had R2 of 0.47 and RMSE of 7.08 and were the worst result (Table 1). Validation sets showed two soil types had R2 ≥ 0.70 (brown forest and Skeletal soils). Four soil types showed R2 ≤ 0.50. The poor results were expected since CEC is not spectrally active, while the other good results were due to the contribution of clay minerals and organic carbon matter to the prediction of CEC and they are correlated with each other (Stenberg et al., 2010). Demattê et al. (2019) showed similar prediction accuracy ranges (R2 0.97 – 0.11) for CEC in the Brazilian spectral library. In addition, several studies with good predictions were observed by Pirie et al. (2005) that showed prediction reached a R2 of 0.82 in small spectral library (415 soil samples). Terhoeven-Urselmans et al. (2010) also achieved the good accuracy (R2 = 0.83) for 4438 global soil samples.

Table 1. PLSR model values, descriptive statistics and results of calibration and validation prediction models of CEC

		Calibration set							Validation set						
	CEC cmol(+)/kg	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	1.48	119.9	26.14	0.61	8.24	1.60	1959	1.64	116.5	24.94	0.57	7.78	1.53
Counties	Pest	98	2.38	59.63	22.69	0.76	5.68	2.05	294	2.15	67.40	25.14	0.65	7.00	1.70
	Baranya	70	3.85	67.94	25.05	0.90	3.39	3.24	141	5.61	42.61	24.07	0.80	2.67	2.23
	Fejer	49	4.76	66.80	27.76	0.83	5.35	2.42	186	8.34	83.12	27.74	0.38	8.25	1.27
	Komarom-Esztergom	35	7.73	60.28	23.13	0.65	6.38	1.72	125	8.39	46.40	22.03	0.61	4.90	1.60
	Nograd	55	3.33	57.22	28.56	0.77	6.82	2.11	88	2.95	49.82	27.64	0.73	5.42	1.93
	Tolna	39	5.50	119.9	29.48	0.96	4.73	4.96	153	5.55	53.00	24.86	0.51	5.41	1.44
	Bacs-Kiskun	98	2.25	54.47	16.44	0.50	7.71	1.42	186	1.48	84.21	11.63	0.28	7.58	1.18
	Bekes	70	11.2	57.66	34.09	0.68	5.51	1.77	132	3.41	58.39	33.71	0.45	6.72	1.35
	Csongrad	50	4.38	48.00	25.04	0.68	7.67	1.77	116	5.66	49.67	28.19	0.31	11.41	1.21
	Jasz-Nagykun-Szolnok	40	1.68	42.44	24.14	0.68	6.37	1.78	179	5.42	61.73	29.33	0.49	5.79	1.41
Soil types	Chernozem	149	2.89	46.40	23.56	0.47	7.08	1.38	530	3.41	61.73	26.99	0.32	6.93	1.22
	Brown forest	99	3.85	57.22	23.66	0.86	3.96	2.73	395	2.95	49.82	23.83	0.77	4.22	2.09
	Alluvial & colluvial	55	2.86	59.63	26.47	0.86	4.29	2.70	153	2.25	53.00	22.31	0.48	6.51	1.40
	Meadow	149	1.68	119.89	32.64	0.55	11.84	1.49	261	4.51	68.16	32.32	0.50	7.44	1.42
	Skeletal	99	2.38	61.57	16.45	0.50	8.25	1.43	200	1.48	49.33	11.31	0.70	4.84	1.84
	Salt-affected	27	6.70	66.83	32.51	0.68	8.11	1.81	64	4.20	84.21	29.75	0.04	13.6	1.03

Exchangeable Mg and Ca

The exchangeable Mg and Ca of both calibration and validation models showed decrease and variance results. The calibration results at national level were good for exchangeable Mg but were satisfactory for exchangeable Ca with respective R2 values being 0.77 and 0.54 and RPD values 2.09 and 1.48. Whereas validation model sets had R2 values of Mg and Ca of 0.52 and 0.48, respectively (Tables 2 and 3). Calibration prediction at county levels for exchangeable Mg showed 4 counties had R2 ≥ 0.90 and 3 counties had R2 lower than 0.55 (Table 3) while, exchangeable Ca showed 6 counties had R2 ≥ 0.80 and only Csongrad county had R2 lower than 0.55 (Table 2). However, the validation prediction results had R2 ranging from 0.14 to 0.66 for exchangeable Mg and ranging from 0.18 to 0.74 for exchangeable Ca (Tables 2 and 3).

Calibration predictions for exchangeable Mg were satisfactory (R2 lower than 0.75) for all soil types except Alluvial and colluvial soils (R2 of 0.94 and RPD of 4.01) and Meadow soils (R2 of 0.82 and RPD of 2.37; Table 9) whereas calibration predictions for exchangeable Ca were poorer (R2 ≤ 0.50 and RPD ≤ 1.42) for three soil types, but was excellent for brown forest soils (R2 of 0.96 and RMSE of 1.56) and alluvial and colluvial soils (R2 of 0.83 and RMSE of 3.32; Table 2). Validation results of soil types had R2 ranging from 0.33 to 0.60 for exchangeable Mg and ranging from 0.32 to 0.71 for exchangeable Ca except salt-affected soils had R2 of 0.01 (Tables 2 and 3).

The poor model results were not expected but we posit that exchangeable Ca and Mg may be present in low concentrations, not have particular MIR absorption features as well as the lack of correlation with spectrally active properties. Ng et al., (2022) concluded that the high correlation with spectrally active elements or the element concentration itself in soils is primarily responsible for prediction accuracy of the elemental concentrations. Furthermore, inverse links with carbon content may also justify the low prediction results, suggesting less sites for exchangeable cations on soil charges (from organic matter) that may be filled by H^+. TIM (1995) reported that soil conditions in Hungary show soil nutrient use stagnated between 1985 and 1990, and reduced sharply after 1990. Soil nutrient balance became negative compared to the period of 1981 to 1986. These reasons, in addition to different land nutrition management conditions, may justify the low exchangeable (Ca^{++} and Mg^{++}) predictions and CEC in various areas, counties and soil types in Hungary. Exchangeable Ca was predicted with fairly good accuracy (R2 = 0.85) by Rossel et al. (2008) followed by exchangeable Mg (R2 = 0.78). Similarly, study by Stenberg and Rossel (2010) observed good predictions for exchangeable Ca (R2 = 0.89) and Mg (R2 = 0.76). Pirie et al. (2005) however, reported lower performance for exchangeable Mg (R2 = 0.69) and exchangeable Ca (R2 = 0.64). Similarly, study by Terhoeven-Urselmans et al. (2010) observed lower predictions for exchangeable Mg (R2 = 0.54) and exchangeable Ca (R2 = 0.78).

Table 2. PLSR model values, descriptive statistics and results of calibration and validation prediction models of exchangeable Ca

		Calibration set							Validation set						
	Ca cmol(+)/kg	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	0.67	87.46	18.52	0.54	6.72	1.48	1959	0.60	85.52	17.54	0.48	6.21	1.39
Counties	Pest	0.87	49.06	16.34	0.75	4.51	2.00	294	0.67	45.89	18.39	0.63	5.15	1.66	1.70
	Baranya	2.00	54.03	18.13	0.91	2.74	3.36	141	4.44	35.05	17.21	0.74	2.65	1.98	2.23
	Fejer	3.29	48.05	18.58	0.91	2.67	3.36	186	5.36	53.92	20.92	0.37	5.53	1.26	1.27
	Komarom-Esztergom	5.18	45.79	17.41	0.63	5.29	1.67	125	5.30	34.85	16.57	0.59	3.99	1.57	1.60
	Nograd	1.67	38.40	18.56	0.80	4.60	2.26	88	1.35	30.72	18.04	0.73	3.74	1.95	1.93
	Tolna	3.83	87.46	21.78	0.95	3.84	4.46	153	3.79	39.07	19.33	0.42	4.65	1.32	1.44
	Bacs-Kiskun	1.51	40.89	11.36	0.84	2.86	2.54	186	0.82	59.07	8.71	0.36	5.25	1.26	1.18
	Bekes	4.96	41.52	21.97	0.98	1.23	6.48	132	5.74	42.32	22.57	0.18	6.78	1.11	1.35
	Csongrad	1.76	45.13	16.44	0.09	9.50	1.06	116	2.67	39.17	18.78	0.34	8.49	1.24	1.21
	Jasz-Nagykun-Szolnok	0.60	31.33	15.51	0.57	5.44	1.55	179	3.12	45.31	18.76	0.36	6.01	1.26	1.41
Soil types	Chernozem	1.54	33.76	17.50	0.34	6.15	1.23	530	4.46	45.31	21.13	0.40	5.51	1.29	1.22
	Brown forest	1.68	38.40	16.95	0.96	1.56	5.34	395	1.35	35.43	16.45	0.67	3.62	1.75	2.09
	Alluvial & colluvial	2.28	40.46	19.33	0.83	3.32	2.45	153	1.51	39.07	16.25	0.50	4.91	1.41	1.40
	Meadow	0.60	87.46	20.85	0.66	7.39	1.73	261	2.92	53.92	20.57	0.32	6.83	1.21	1.42
	Skeletal	0.87	45.13	12.11	0.50	6.00	1.42	200	0.67	40.24	8.65	0.71	3.67	1.86	1.84
	Salt-affected	2.91	45.89	17.04	0.43	8.07	1.35	64	2.07	59.07	14.31	0.01	9.51	0.96	1.03

Table 3. PLSR model values, descriptive statistics and results of calibration and validation prediction models of exchangeable Mg

		Calibration set							Validation set						
	Mg cmol(+)/kg	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	0.67	87.46	18.52	0.54	6.72	1.48	1959	0.60	85.52	17.54	0.48	6.21	1.39
Counties	Pest	0.87	49.06	16.34	0.75	4.51	2.00	294	0.67	45.89	18.39	0.63	5.15	1.66	1.70
	Baranya	2.00	54.03	18.13	0.91	2.74	3.36	141	4.44	35.05	17.21	0.74	2.65	1.98	2.23
	Fejer	3.29	48.05	18.58	0.91	2.67	3.36	186	5.36	53.92	20.92	0.37	5.53	1.26	1.27
	Komarom-Esztergom	5.18	45.79	17.41	0.63	5.29	1.67	125	5.30	34.85	16.57	0.59	3.99	1.57	1.60
	Nograd	1.67	38.40	18.56	0.80	4.60	2.26	88	1.35	30.72	18.04	0.73	3.74	1.95	1.93
	Tolna	3.83	87.46	21.78	0.95	3.84	4.46	153	3.79	39.07	19.33	0.42	4.65	1.32	1.44
	Bacs-Kiskun	1.51	40.89	11.36	0.84	2.86	2.54	186	0.82	59.07	8.71	0.36	5.25	1.26	1.18
	Bekes	4.96	41.52	21.97	0.98	1.23	6.48	132	5.74	42.32	22.57	0.18	6.78	1.11	1.35
	Csongrad	1.76	45.13	16.44	0.09	9.50	1.06	116	2.67	39.17	18.78	0.34	8.49	1.24	1.21
	Jasz-Nagykun-Szolnok	0.60	31.33	15.51	0.57	5.44	1.55	179	3.12	45.31	18.76	0.36	6.01	1.26	1.41
Soil types	Chernozem	1.54	33.76	17.50	0.34	6.15	1.23	530	4.46	45.31	21.13	0.40	5.51	1.29	1.22
	Brown forest	1.68	38.40	16.95	0.96	1.56	5.34	395	1.35	35.43	16.45	0.67	3.62	1.75	2.09
	Alluvial & colluvial	2.28	40.46	19.33	0.83	3.32	2.45	153	1.51	39.07	16.25	0.50	4.91	1.41	1.40
	Meadow	0.60	87.46	20.85	0.66	7.39	1.73	261	2.92	53.92	20.57	0.32	6.83	1.21	1.42
	Skeletal	0.87	45.13	12.11	0.50	6.00	1.42	200	0.67	40.24	8.65	0.71	3.67	1.86	1.84
	Salt-affected	2.91	45.89	17.04	0.43	8.07	1.35	64	2.07	59.07	14.31	0.01	9.51	0.96	1.03

pH in water

Overall, the predictions for soil chemical reaction within the different scenarios were poor. Soil pH in water at the national level had the poorest results in both groups of calibration and validation datasets (Table 4). In general, many counties pH models were better than the national and soil type levels. Four counties including Baranya, Bacs-Kiskun, Bekes and Jasz-Nagykun-Szolnok had high predictions (R2 = 0.91– 0.98 and RMSE = 0.12 – 0.32) in calibration sets, while two counties included Tolna and Csongrad represented the worst results (R2 = 0.09 and 0.04, respectively; Table 4) in the calibration data sets. Three counties had R2 raning from 0.59 to 0.78, while other counties had R2 ≤ 0.51 in validation sets.

With reference to the soil types and with regard to calibration sets only brown forest had the highest results (R2 of 0.94 and RMSE of 0.28). Salt-affected soils and alluvial and colluvial soils represented satisfactory models (R2 of 0.69 and 0.62, respectively; Table 4), while all the validation datasets results had R2 ≤ 0.38. The poor model results were expected because this attribute lacked direct spectral responses, while others good results may be due to correlation between pH and soil organic carbon and carbonates (Minasny et al., 2009; Reeves, 2010; Sarathjith et al., 2014). Terhoeven-Urselmans et al. (2010) obtained a higher prediction of water pH (R2 = 0.81) at a global level of spectral library compared to our results. Generally, Figure 4 and the descriptive statistics tables showed some soil attributes had small datasets that may have affected the prediction's accuracies. Reeves and Smith (2009) found that dataset diversity, parent materials, land uses, and climate such as our spectral library can lead to poor model prediction results.

Table 4. PLSR model values, descriptive statistics and results of calibration and validation prediction models of pH (water)

		Calibration set							Validation set						
	Mg cmol(+)/kg	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	4.80	9.84	7.90	0.29	1.17	1.19	1959	4.00	10.51	7.88	0.18	1.02	1.10
Counties	Pest	98	5.19	10.4	7.75	0.47	0.97	1.38	294	4.92	10.5	7.94	0.51	0.57	1.43
	Baranya	70	4.21	9.12	7.65	0.91	0.32	3.28	141	5.28	8.84	7.68	0.78	0.40	2.15
	Fejer	49	6.54	9.57	8.01	0.65	0.33	1.70	186	6.08	9.77	7.99	0.17	0.88	1.10
	Komarom-Esztergom	35	4.92	8.92	7.69	0.70	0.53	1.84	125	5.09	8.78	7.81	0.43	0.81	1.34
	Nograd	55	4.77	8.41	1.48	0.16	1.48	1.10	88	4.80	8.45	6.94	0.69	0.45	1.81
	Tolna	39	5.12	8.72	7.76	0.09	1.37	1.06	153	5.01	8.51	7.88	0.05	0.99	1.03
	Bacs-Kiskun	98	6.62	10.0	8.19	0.97	0.14	5.45	186	6.37	9.84	8.09	0.59	0.37	1.57
	Bekes	70	5.92	9.88	8.09	0.91	0.24	3.43	132	6.25	9.52	8.00	0.19	0.81	1.11
	Csongrad	50	6.87	9.90	8.32	0.04	2.28	1.03	116	4.00	10.1	8.17	0.13	2.76	0.94
	Jasz-Nagykun-Szolnok	40	6.14	9.92	8.01	0.98	0.12	6.67	179	5.88	9.96	7.93	0.32	0.57	1.21
Soil types	Chernozem	149	6.19	9.92	8.16	0.18	1.28	1.11	530	5.85	9.97	8.02	0.02	1.12	1.01
	Brown forest	99	4.21	9.12	7.41	0.94	0.28	3.94	395	4.77	8.73	7.26	0.38	0.96	1.28
	Alluvial & colluvial	55	6.65	9.57	7.99	0.62	0.31	1.63	153	5.50	9.28	7.94	0.33	0.49	1.23
	Meadow	149	6.52	10.1	8.13	0.13	1.05	1.08	261	4.00	9.88	7.99	0.16	1.04	1.10
	Skeletal	99	5.21	8.89	7.82	0.17	0.99	1.10	200	5.25	8.92	7.97	0.15	0.87	1.09
	Salt-affected	27	5.92	10.5	8.98	0.69	0.67	1.83	64	7.22	10.51	8.89	0.34	0.68	1.24

Conclusion

Based on the final findings of this study, the following points can be concluded:

1. The MIR spectral library reported with 2200 soil samples based on legacy soil samples of the Hungary SIMS project as well as, predicting an array of four soil chemical properties.
2. Models were built using PLSR for national level, ten counties and six soil types using the SIMS reference soil database and the spectral library data.
3. The results were logical for the CEC, exchangeable Ca and Mg which are not spectrally active but correlated with other active elements.
4. For soil properties that are not spectrally active with low content in the soil or have small sizes of samples, the prediction can turn out to be inaccurate, like pH water.
5. The results showed that legacy soil samples can be used to generate a spectral library with good quality information.
6. The developed Mid-infrared spectral library therefore can provides a way for rapid soil properties estimation at low cost and with short time compared to the conventional method.

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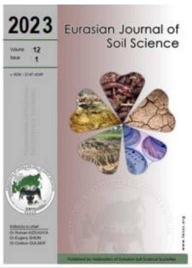

Soil fertility evaluation and land-use effects on soil properties, carbon and nitrogen sequestration in the rainforest of Nigeria

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Abstract

This study investigates changes in soil properties, specifically soil organic carbon (SOC) and total nitrogen (TN), associated with different land use systems derived from forests in the rainforest zone of Nigeria. The land use systems examined include mature oil palm plantation (OP), bush fallow or secondary forest (BF), alley cropping with multi-purpose trees (AC), and continuous cassava cropping with and without fertilizer (FC and UC). Converting forests to cultivated land led to a decrease in SOC and TN content and storage across all soil depths (0-10 cm, 10-20 cm, and 20-40 cm). In the top 0-10 cm depth, the average decrease in SOC and TN storage was 63% and 62%, respectively, while for 0-40 cm, the decrease was 48% and 46%, respectively, for all land use systems derived from forests. Furthermore, the study reveals that even after 5, 10, and 30 years of secondary forest regrowth (BF), alley cropping (AC), and oil palm plantation (OP), respectively, the fertility levels were not restored to those observed in the primary forest. These findings underscore the capacity of forest soils to conserve and enhance soil SOM (soil organic matter), which in turn plays an essential role in SOC sequestration, TN storage, and soil nutrient conservation.

Keywords: Carbon sequestration, land uses, nitrogen sequestration, soil fertility, vegetation.

Introduction

Primary forests and forest derived land uses play vital roles in global carbon cycles and nutrients dynamics in terrestrial ecosystems (Sharma and Rai, 2007; Don et al., 2007; Nair et al., 2009), particularly in the tropics, where forest vegetations are converted to agricultural and other land uses have been on the increase over the past few decades (Fernandes et al., 1997; Lal, 2005). Clearing primary forest for agriculture leads to unsustainable land use with resultant effect on the decline in soil fertility, soil quality and the overall alteration in the global biogeochemical cycles (McGrath et al., 2001; Schrot et al., 2002; Sharrow and Ismail, 2004; Celik, 2005; Sharma and Rai, 2007). Forest conversion into cultivated land affects soil fertility due to its effect on SOM content, which influences ecosystem cycles of nitrogen, carbon, as well as on soil physical properties (Kong et al., 2006; Jelinski and Kucharik, 2009; Nair et al., 2009). Loss of SOC stock when converted from forest to arable land has been documented in several works (Carter et al., 1998). Murty et al., (2002) reported the decline in SOC stock in crop land soils as 16%. It has been shown that about 42% SOC is lost in soil when forest land is turned to crop land and about 59% SOC is lost in soil when grassland is turned to crop land (Guo and Gifford, 2002). For a Mollisol in central Ohio, Puget and Lal (2005) reported that cultivated farm lands had 51+ 4 (equivalent mass) Mg ha^{-1} lesser SOC and lesser 3.5 + 0.3 (equivalent mass) Mg ha $^{-1}$ N within 30 cm soil layer of soil than under forested land. Research findings on the effects of conversion of forest into

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agricultural land and other soil properties like bulk density, total porosity and C:N ratio etc. have been contradictory. For example, while Bayer et al. (2000), Puget and Lal (2005) and Celik (2005) reported significant change in soil bulk density between forest and cultivated sites, Brown and Lugo (1990) found no change in bulk density after forest conversion in Puerto Rico and US Virgin Islands. However, majority of the studies showed that soils under forest had lower bulk density than nearby soils under cultivation. Franzluebbers et al. (2000) and Puget and Lal (2005) reported that forest soils had higher C:N ratio than cultivated soils and the C:N ratio showed the different amount of organic residues in the organic matter pool as a result of contrasting vegetation covers. On the other hand, Jelinski and Kucharik (2009) reported that SOC/TN ratios for 25-cm sampling depth did not differ between the land use systems. Similarly, It has been reported by Geissen et al. (2009) that there was no significant change in the C:N ratio of soils under current land system and also the C:N ratio of soils from 1988 – 2003 were not influenced by land use systems for a wide range of soil groups (Cambisols, Gleysols, Leptosols, Luvisols, Regosols and Vertisols).

The study of the effect of conversion of natural ecosystems e.g. forest to agriculture on soil properties and SOC sequestration has continued to remain a major global issue, especially in recent times because of our collective concern of environmental degradation and climate change. With the renewed emphasis on deforestation and its effect on CO_2 and other greenhouse gases (GHGs) emissions into the atmosphere, there is a need to intensify scientific research in this area, especially in the different ecological zones of the tropics, where such information are limited. Such information is lacking in the rainforest zone of Nigeria and need to be generated from research. This work therefore was undertaken to assess the effects of natural forest and forest derived land uses on changes in soil physico-chemical properties, SOC sequestration and TN storage in an ultisol in the rainforest area of Nigeria. The aim of the study is to investigate specific objectives related to soil properties and nutrient dynamics under different land use systems. The study seeks to determine changes in key soil parameters, including bulk density, porosity, pH, exchangeable bases and acidity, CEC (cation exchange capacity), base saturation and aluminium (AI) saturation in the topsoil. Additionally, the study aims to assess the depth distribution (0 – 40 cm) of soil organic carbon (SOC) and total nitrogen (TN) content, storage, and the carbon-to-nitrogen (C:N) ratio.

The inclusion of TN data alongside SOC data is important due to recent studies highlighting the influence of soil nitrogen dynamics on the sequestration of SOC. It is therefore recommended that investigations into SOC changes incorporate TN data, as suggested by previous research conducted by Kucharik (2007) and Jelinski and Kucharik (2009). In summary, this study aims to provide valuable insights on soil properties, nutrient dynamics, and carbon sequestration resulting from effects of land utilization types. Specifically, it aims to elucidate the inter-relationship between nitrogen and OC (organic carbon) in the soil under varying land uses.

Material and Methods

Description of the Location Site

We collected soil samples from Umudike Abia State (50 25^1 N and 70 35^1 and 125 m elevation) in south-eastern Nigeria. The study area lies within the humid tropical environment, supporting lowland rainforest vegetation and is known by two distinctive seasons, namely, the raining months (April - October) and the dry months (November - March). Annual rainfall average is 1800 and 2200 mm with a bimodal pattern (early April to end of July and middle of August to the end of October). The monthly mean rainfall of the area is optimum between 250 – 300 mm and is recorded in September, while minimum monthly rainfall varies between 0.5 – 1.0 mm and is recorded in February. November and March always experiences the highest mean monthly temperature (30 - 40°C) while the highest mean sunshine hours (5.5 – 6.5) and lowest mean sunshine hour (2 – 2.5) are recorded in December and August respectively. Though all the year round, the relative humidity is generally high but the highest relative humidity is recorded during the wet seasons. The soils originate from coastal sediments and have been classified as acrisol (FAO/UNESCO) and ultisol (USDA). The soil has soil related constraints to the productivity of soil such as low organic matter content and low inherent fertility (Onwudike et al., 2017), high soil acidity (both natural and fertilizer induced), low activity clay (Onwudike et al., 2015), poor water holding capacity of soil, nutrient depletion and high vulnerability to erosion (Opara-Nadi, 2000).

Description of the Land Use Systems

Eleven land use systems were studied which include natural or primary forest (NF) and bush fallow or secondary forest (BF), alley cropping (AC), oil palm plantation (OP), alley cropping with bread fruit (*Treculia Africana L.*) alone (TA), alley cropping with mango (*Magifera indica L.)* alone (MI), alley cropping with acioa (*Dactyldenia barteri L.*) alone (DB), alley cropping with African oil bean (*Pentaaclethra macropylla L.*) alone (PM), continuous Cassava (*Manihot esculenta Crantz*) cropping with fertilizer (FC) and continuous Cassava

(*Manihot esculenta Crantz*) cropping without fertilizer (UC) plots. Sample collections were replicated three times within the same geographic location and of the same geologic material. Details of site and vegetation characteristics of these land use systems are summarized here.

1. Natural forest (NF)- complex with predominant species of acioa (*Dactyldenia barteri L.*) and African oil bean (*Pentaclethra macrophylla L.*) plus shrubs and grasses.
2. Bush fallow (BF)- secondary regrowth (5years) with acioa (*D. barteri* L.), shrubs e.g. Siam weed (*Chromolaena adorata* L.). African marigold (*Aspilia Africana* L.) and grasses e.g. guinea grass (*Panicum maximum* L.) as predominate species. The land use prior to bush fallow was 4 years continuous cassava maize intercropping.
3. Alley cropping with MPTs (AC)- mature (10 years) of fruits trees of bread fruit (*Treculia africana* L.), irvingia (*Irvingia gabonensis L.*) and African pear (*Dacroydes edulis L.*) planted in 8 m row arrangement and this was the distance between cultivated alleys. The land use prior to alley cropping was 4 years continuous cassava (uninterrupted) cropping.
4. Oil palm plantation (OP) mature (30 years) of palm trees (*Elaeis guinensis L.*).
5. Alley cropping with bread fruit (*Treculia Africana L.)* alone (TA)- same age and arrangement as 3.
6. Alley cropping with irvingia *(Irvingia gabnensis L.*) alone (IG)- same as 3.
7. Alley cropping with mango (*Magnifera indica L.)* alone (MI)- same as 3.
8. Alley cropping with acioa (*Dactyldenia barteri L.)* alone (DB) - same as 3.
9. Alley cropping with African Oil bean (*Pentaaclethra macropylla L.*) alone (PM) - same as 3.
10. Sole cropping of cassava (*Manihot esculenta Crantz*), without inorganic fertilizer (UC) -7 years.
11. Same as 10 but with inorganic fertilizer application (FC).

Soil Sampling and Chemical Analysis

For all land use systems, soil texture of the topsoil and slope position (middle slope) within transect were used as criteria to locate sampling areas. This was necessary in order to minimize error in data interpretation arising from spatial variability. Soil sampling was done in replicated 100 m by 100 m quadrants in each land use type and in each sample location. Each quadrant was subsequently divided into 10 sub quadrants, each measuring 10 m by 10 m from which three cores samples were randomly selected. Soil sampling sites were selected on the basis of uniformity in characteristics which included slope, elevation, soil type and texture as well as present land use. Disturbed (composite) samples and undisturbed (core) samples were sampled with the use of cylindrical metal core with diameter of 5 cm and 5cm height and these were taken in three replicate from each of 0- to 10, 10- to 20 and 20- to 40 cm depths. The core samples were taken with a hammer-driven sampler. Physical properties (bulk density and total porosity) were obtained using core sampler as described by Grossman and Reinsch (2002), while the augar soils were used to determine chemical properties (pH), organic C, total N, exchangeable acidity and cations (K, Ca, Mg, Na, Mn and Al). Chemical analyses were done in the Soil Science laboratory of Buesgen-Institute of Temperate and Boreal Ecosystems, University of Goettingen, Germany. The pH soil was measured in deionized 1:1 soil-water-extract using ICP-Mass spectrometry. Organic C and concentrations of total N were obtained by high-temperature catalytic combustion using a Heraeus-CHN Analyzer (Vario Max, Elementar Analysen systeme, Germany). Exchangeable cations were measured using ICP-Mass spectrometry after displacement in I M NH_4CI solution, CEC by summation of exchangeable cations and base saturation from CEC and cation values. The masses of SOC and TN on an area basis (Mg ha^{-I}) were obtained by multiplying SOC and TN in grams per 100 g by the bulk density (Mg m^{-3}), soil depth (m) and area (10,000 m^2). The C:N ratio was gotten by dividing the soil organic carbon the values of total nitrogen. Significance of differences for the different soil parameters among land uses and the depths was determined using analysis of variance (ANOVA) with Statistical Analysis Systems (SAS, 2001). Significance was assigned to probability level of $p = 0.05$.

Results

Soil Bulk Density

Forest and forest derived land use systems had significant effect on soil bulk density (Table I) in the 0 to 10, 10 to 20 and 20 to 40 cm depths. In all these depths, lowest bulk density was obtained for cassava based systems (UC and FC). In the 0- to 10- cm depths, the NF, TA, PM, UC and FC systems had bulk density values lower than 1.40 g cm^{-3}, while the BF, AC, OP, IG, MI, and DB systems had 21 values higher than 1.40 g cm^{-3}. In the 10 to 20 and 20 to 40 cm depths, bulk density did not differ significantly between the NF, BF, AC, OP, IG, MI, DP, and PM systems. Generally, bulk density increased with soil depths.

Table 1. Soil bulk density of 0–10, 10 – 20 and 20 – 40 cm depths under different land use system

Land use system	Soil bulk density (Mg m^{-3}) Soil depth (cm)		
	0 – 10 cm	10 – 20 cm	20 – 40 cm
Natural forest (NF)	1.37 ± 0.06	1.52 ± 0.11	1.56 ± 0.18
Bush fallow (BF)	1.53 ± 0.10	1.59 ± 0.13	1.71 ± 0.12
Alley cropping with MPTs (AC)	1.48 ± 0.08	1.62 ± 0.09	1.67 ± 0.15
Oil palm plantation (OP)	1.42 ± 0.11	1.64 ± 0.09	1.69 ± 0.09
Alley cropping (TA)	1.36 ± 0.07	1.43 ± 0.10	1.49 ± 0.06
Alley cropping (IG)	1.43 ± 0.09	1.53 ± 0.12	1.62 ± 0.11
Alley cropping (MI)	1.53 ± 0.15	1.66 ± 0.18	1.69 ± 0.12
Alley cropping (DB)	1.55 ± 0.13	1.62 ± 0.14	1.64 ± 0.12
Alley cropping (PM)	1.35 ± 0.08	1.57 ± 0.10	1.58 ± 0.09
Unfertilized cassava (UC)	1.25 ± 0.06	1.29 ± 0.08	1.44 ± 0.06
Fertilized cassava (FC)	1.34 ± 0.10	1.35 ± 0.07	1.47 ± 0.10

MPTs(AC) = Alley cropping with multi-purpose trees, TA= *Treculia Africana .L.*, IG =*Irevingia ganensis L.*, MI = *Magnifera indica. L.*, DB = *Dactyldenia barteri. L*, PM = *Pentaclethra macropylla. L*, UC = cassava Cropping without fertilizer application, FC= cassava cropping with fertilizer application

Soil pH

The pH values of the soil over the total sampled depths were acidic and significantly different among the different land use systems (Table 2, 3, 4). In all three depths, soil pH was highest for OP system and lowest for NF system. Generally, soil pH for the 0 to 10, 10 to 20 and 20 to 40 cm depths did not show any definite trend and did not differ appreciably for each land use.

Table 2. Soil characteristics of the 0 – 10 cm depth under land uses

Soil characteristics	NF	BF	AC	OP	TA	IG	MI	DB	PM	UC	FC	LSD$_{0.05}$
pH (H$_2$O)	4.10	4.48	4.50	5.45	4.28	4.80	4.55	4.58	4.50	4.63	4.37	0.30
Potassium, cmol kg^{-1}	0.41	0.13	0.13	0.23	0.087	0.095	0.087	0.11	0.13	0.13	0.17	0.10
Calcium, cmol kg^{-1}	1.55	0.40	1.09	2.20	0.16	1.42	0.75	1.96	1.15	0.49	0.81	0.85
Magnesium, cmol kg^{-1}	0.66	0.082	0.27	0.62	0.070	0.034	0.17	0.44	0.23	0.10	0.078	0.27
Sodium, cmol kg^{-1}	0.17	0.067	0.090	0.059	0.043	0.027	0.028	0.047	0.055	0.041	0.061	0.022
Manganese, cmol kg^{-1}	0.084	0.017	0.046	0.039	0.025	0.096	0.060	0.054	0.017	0.020	0.015	0.056
Aluminium, cmol kg^{-1}	3.77	1.99	1.81	0.030	2.58	0.88	1.58	1.26	1.50	2.28	2.34	1.26
Exch. Acidity, cmol kg $^{-1}$	4.10	2.05	1.99	0.030	2.69	0.92	1.65	1.50	2.20	2.36	2.42	1.56
CEC, cmol kg^{-1}	7.05	2.76	3.57	3.16	3.10	2.59	2.78	4.14	3.09	3.15	3.55	1.76
Base saturation, %	39.57	24.00	43.83	97.75	11.61	64.67	36.51	61.76	28.33	24.16	31.24	12.21
Al saturation, %	53.58	72.10	50.70	0.95	83.23	30.13	56.83	30.43	61.83	72.38	65.92	21.02

LSD = least significant difference, CEC =cation exchange capacity, NF = Natural forest BF= bush fallow, AC = alley cropping, OP = oil palm plantation, TA= *Treculia Africana .L.*, IG =*Irevingia ganensis L.*, MI = *Magnifera indica. L.*, DB = *Dactyldenia barteri. L*, PM = *Pentaclethra macropylla. L*, UC = Cropping without fertilizer application, FC= cropping with fertilizer application

Table 3. Soil characteristics of the 10 – 20 cm depth under land uses

Soil characteristics	NF	BF	AC	OP	TA	IG	MI	DB	PM	UC	FC	LSD$_{0.05}$
pH (H$_2$O)	4.13	4.52	4.44	5.53	4.21	4.71	4.53	4.66	4.37	4.54	4.51	0.36
Potassium, cmol kg^{-1}	0.27	0.092	0.11	0.18	0.082	0.090	0.063	0.10	0.069	0.15	0.19	0.12
Calcium, cmol kg^{-1}	0.25	0.29	0.65	2.18	0.067	0.160	0.24	0.47	0.10	0.13	0.44	0.55
Magnesium, cmol kg^{-1}	0.13	0.038	0.095	0.58	0.030	0.041	0.045	0.097	0.042	0.063	0.042	0.17
Sodium, cmol kg^{-1}	0.092	0.091	0.048	0.060	0.019	0.049	0.026	0.050	0.028	0.068	0.079	0.024
Manganese, cmol kg^{-1}	0.013	0.016	0.010	0.029	0.010	0.013	0.018	0.014	0.004	0.012	0.018	0.023
Aluminium, cmol kg^{-1}	4.72	2.08	3.76	0.12	3.10	2.60	2.73	2.30	2.27	2.70	3.05	1.47
Exch. Acidity, cmol kg $^{-1}$	4.88	2.13	0.91	0.12	3.20	2.20	2.78	2.36	2.37	2.78	3.12	1.22
CEC, cmol kg^{-1}	5.68	2.62	3.84	3.14	3.14	2.70	3.17	3.06	2.60	3.38	3.89	1.01
Base saturation, %	13.01	17.76	23.62	94.26	5.56	18.00	11.93	23.20	9.33	20.06	19.05	9.42
Al saturation, %	83.10	79.39	71.88	3.82	90.91	78.80	86.12	74.68	82.27	79.88	78.41	19.46

LSD = least significant difference, CEC =cation exchange capacity, NF = Natural forest BF= bush fallow, AC = alley cropping, OP = oil palm plantation, TA= *Treculia Africana .L.*, IG =*Irevingia ganensis L.*, MI = *Magnifera indica. L.*, DB = *Dactyldenia barteri. L*, PM = *Pentaclethra macropylla. L*, UC = Cropping without fertilizer application, FC= cropping with fertilizer application

Table 4. Soil characteristics of the 20 - 40 cm depth under land uses

Soil characteristics	NF	BF	AC	OP	TA	IG	MI	DB	PM	UC	FC	$LSD_{0.05}$
pH (H_2O)	4.14	4.42	4.55	5.46	4.32	4.51	4.69	4.59	4.40	4.60	4.45	0.39
Potassium, cmol kg^{-1}	0.25	0.12	0.058	0.16	0.060	0.090	0.053	0.061	0.051	0.11	0.13	0.09
Calcium, cmol kg^{-1}	0.16	0.47	0.63	1.40	0.020	0.16	0.34	0.32	0.040	0,33	0.34	0.76
Magnesium, cmol kg^{-1}	0.080	0.062	0.055	0.43	0.021	0.041	0.030	0.053	0.028	0.074	0.038	0.16
Sodium, cmol kg^{-1}	0.099	0.068	0.038	0.050	0.012	0.050	0.033	0.042	0.016	0.039	0.093	0.026
Manganese, cmol kg^{-1}	0.008	0.022	0.004	0.016	0.009	0.013	0.012	0.010	0.005	0.007	0.011	0.091
Aluminium, cmol kg^{-1}	4.86	3.29	3.20	0.33	2.63	2.60	2.58	2.49	2.52	2.79	3.41	1.44
Exch. Acidity, cmol kg $^{-1}$	4.97	3.37	3.31	0.33	2.70	2.64	2.64	2.69	2.59	2.87	3.49	1.36
CEC, cmol kg^{-1}	5.59	4.13	4.10	2.38	2.18	2.98	3.11	3.10	2.73	3.42	4.05	1.71
Base saturation, %	10.63	17.49	18.99	85.26	3.99	11.28	14.78	15.49	4.97	15.80	13.72	8.16
Al saturation, %	86.94	79.66	78.05	13.87	93.59	86.62	82.96	80.32	92.31	81.58	84.20	24.06

LSD = least significant difference, CEC =cation exchange capacity, NF = Natural forest BF= bush fallow, AC = alley cropping, OP = oil palm plantation, TA= *Treculia Africana .L.*, IG =*Irevingia ganensis L.*, MI = *Magnifera indica. L.*, DB = *Dactyldenia barteri. L*, PM = *Pentaclethra macropylla. L*, UC = Cropping without fertilizer application, FC= cropping with fertilizer application

Exchangeable Potassium, Calcium, Magnesium, Sodium, Manganese and Aluminium

Significant differences among land uses were found in the measured soil characteristics in the 0 to 10 cm depth (Table 2), 10 to 20 cm depth (Table 3), and 20 to 40 cm depth (Table 4). In addition, differences between the highest and lowest values of each of these characteristics ranged widely. For example, in the 0 to 10 cm layer, the highest value of K was 0.41 cmol kg^{-1} (NF) and the lowest was 0.076 cmol kg $^{-1}$ (IG), showing a difference of 439% for the variability in K content that existed within land uses. Similarly, the highest value of Ca was 2.20 cmol kg^{-1} for OP and the lowest was 0.16 for TA system, showing in difference of 128% and also illustrating a high variability in Ca content among the different land use systems.

Exchangeable K, Na and Al in all three depths were highest for NF, while Ca was highest for OP, when compared with the other land use systems. Exchangeable Ca and Mg in all three depths were lowest for TA, while exchangeable Al was lowest for OP system in comparison to the other systems. The study found that the content of exchangeable K, Ca, Mg, Na and Mn decreased with increase in the depth of the soil, while the content of exchangeable Al increased with depth. For example, under the NF system, exchangeable K, Ca, Mg, Na and Mn showed a decrease of 39.90, 88, 42 and 90 percent respectively from the 0 to 10 cm to the 20 to 40 cm depth. Exchangeable Al showed an increase of 22 percent between these two depths. Similarly, for the OP systems, the decrease in the concentrations of exchangeable K, Ca, Mg, Na and Mn was 30, 42, 31, 44 and 59 percent respectively, while the increase in Al concentration was 91 percent from the 0 to 10 cm to the 20 to 40 cm depth. These results showed that nutrient dynamics under the land use systems varied considerably.

Exchangeable Acidity, Al saturation, CEC and base saturation

Exchangeable acidity and CEC were significantly highest in the NF system in the 0 to 10, 10 to 20 and 20 to 40 cm depths when compared with the other land use systems (p=0.05) (Tables 3, 4, 5). Similarly, base saturation and Al saturation were higher in the OP and TA systems respectively in all three depths than in any of the other land use systems (Table 2, 3, 4). On the other hand, in all three depths, exchangeable acidity, CEC and Al saturation were lowest in the OP system, while base saturation was lowest in the TA system, when compared with the other systems. Averaged over the three depths, exchangeable acidity was 4.65, 3.01, 2.86, 2.67, 2.52, 2.36, 2.21, 2.18, 1.92 and 0.16 cmol kg^{-1} for NF, FC, TA, AC, UC, BF, MI, PM, DB, IG and OP systems respectively. Similarly, averaged over the three depths, CEC was of the order NF > AC > FC > DB > UC > BF > TA > MI > PM > IG > OP systems. As with exchangeable acidity and CEC, base saturation and Al saturation averaged over the three depths did not follow any definite trend among the different land systems. Base saturation and Al saturation values varied between 7.05% (TA) to 92.50% (OP) and 6.22% (OP) to 89.24% (TA) respectively.

Soil C and N Concentration, C: N ratio and C and N Storage

Conversion of natural forest to agricultural land use led to a decrease in soil organic carbon (SOC) and total N content in the 0-to 10- cm depth (Table 5), 10- to 20- cm depth (Table 6) and 20- to 40- cm depth (Table 7) but the largest contrasts between the land use systems were found in the top depth increment (0 – 10 cm) than the last two increments (p = 0.05). In the 0 to 10 cm depth, SOC concentration was highest (33.7 gkg^{-1}) for NF system and lowest (9.5 g kg^{-1}) for IG system. In the 10- to 20- cm depth, SOC content was highest (17.6 g kg^{-1}) for NF system and lowest (8.2 gkg^{-1}) for DB system. Similarly, in the 20- to 40- cm depth, SOC content was highest (14.7 gkg^{-1}) for both the NF and BF systems and lowest (6.6 gkg^{-1}) for MI system. As with SOC content, TN content was significantly different among the land use systems (p= 0.05), also decreased with depth and with largest contrasts among the land use systems found in the 0 to 10 cm depths than in the other two depth increments.

Table 5. Soil C and N content, C:N ratio and C and N storage of the 0 – 10 cm depth under different land use systems

Land use system	Carbon content g kg^{-1}	Nitrogen Content g kg^{-1}	C:N	C storage Mgha^{-1}	N Storage Mgha^{-1}
Natural Forest (NF)	33.7	2.6	12.9	46.9	3.6
Bush fallow (BF)	10.8	0.8	12.7	16.5	1.3
Alley cropping with MPTs (AC)	13.7	1.1	12.9	19.8	1.5
Oil palm plantation (OP)	13.7	1.1	12.9	19.8	1.5
Alley cropping (TA)	12.8	0.9	13.8	16.8	1.1
Alley cropping (IG)	9.5	0.7	13.0	13.6	1.1
Alley cropping (MI)	10.3	0.8	12.9	15.8	1.3
Alley cropping (DB)	15.9	1.1	14.3	24.8	1.7
Alley cropping (PM)	13.3	1.2	11.4	18.0	1.6
Unfertilized cassava (UC)	12.9	1.0	12.5	16.1	1.3
Fertilized cassava (FC)	12.6	1.0	12.5	17.0	1.4
LSD (0.05)	3.9	0.6	3.1	6.8	0.5

NF = Natural forest BF= bush fallow, MPTs(AC) = Alley cropping with multi-purpose trees, OP = oil palm plantation, TA= Treculia Africana .L., IG =Irevingia ganensis L., MI = Magnifera indica. L., DB = Dactyldenia barteri. L, PM = Pentaclethra macropylla. L, UC = Cropping without fertilizer application, FC= cropping with fertilizer application

Table 6. Soil C and N content, C:N ratio and C and N storage of the 10 – 20 cm depth under different land use systems

Land use system	Carbon content g kg^{-1}	Nitrogen Content g kg^{-1}	C:N	C storage Mgha^{-1}	N Storage Mgha^{-1}
Natural Forest (NF)	17.6	1.3	13.2	26.7	2.1
Bush fallow (BF)	9.2	0.7	12.5	14.6	1.1
Alley cropping with MPTs (AC)	11.3	1.1	10.0	18.4	1.4
Oil palm plantation (OP)	12.6	1.0	13.0	19.1	1.5
Alley cropping (TA)	12.3	1.0	12.7	17.6	1.3
Alley cropping (IG)	9.2	0.8	12.1	14.1	1.1
Alley cropping (MI)	8.9	0.8	11.7	14.8	1.3
Alley cropping (DB)	8.2	0.7	12.4	13.2	1.1
Alley cropping (PM)	9.3	0.8	12.2	14.8	1.3
Unfertilized cassava (UC)	10.3	0.8	11.2	14.8	1.3
Fertilized cassava (FC)	12.9	1.0	12.9	16.4	1.3
LSD (0.05)	2.4	0.4	3.5	5.3	0.5

NF = Natural forest BF= bush fallow, MPTs(AC) = Alley cropping with multi-purpose trees, OP = oil palm plantation, TA= *Treculia Africana .L.*, IG =*Irevingia ganensis L.*, MI = *Magnifera indica. L.*, DB = *Dactyldenia barteri. L*, PM = *Pentaclethra macropylla. L*, UC = Cropping without fertilizer application, FC= cropping with fertilizer application

Table 7. Soil C and N content, C:N ratio and C and N storage of the 20 – 40 cm depth under different land use systems

Land use system	Carbon content g kg^{-1}	Nitrogen Content g kg^{-1}	C:N	C storage Mgha^{-1}	N Storage Mgha^{-1}
Natural Forest (NF)	14.7	1.1	13.3	46.0	3.5
Bush fallow (BF)	14.7	1.0	14.7	50.1	3.5
Alley cropping with MPTs (AC)	8.6	0.7	12.8	28.6	2.3
Oil palm plantation (OP)	7.6	0.6	12.4	26.2	2.1
Alley cropping (TA)	11.2	0.8	13.4	33.2	2.5
Alley cropping (IG)	8.3	0.6	13.2	27.0	2.1
Alley cropping (MI)	6.6	0.7	10.0	22.3	2.2
Alley cropping (DB)	8.1	0.6	13.6	26.7	2.0
Alley cropping (PM)	7.5	0.7	11.2	23.6	2.2
Unfertilized cassava (UC)	7.6	0.6	12.3	22.0	1.9
Fertilized cassava (FC)	11.0	0.9	12.7	32.3	2.6
LSD (0.05)	7.1	0.7	4.4	7.9	0.8

NF = Natural forest BF= bush fallow, MPTs(AC) = Alley cropping with multi-purpose trees, OP = oil palm plantation, TA= *Treculia Africana .L.*, IG =*Irevingia ganensis L.*, MI = *Magnifera indica. L.*, DB = *Dactyldenia barteri. L*, PM = *Pentaclethra macropylla. L*, UC = Cropping without fertilizer application, FC= cropping with fertilizer application

In the 0 to 10 cm depth, TN content was highest (2.6 g kg^{-1}) for NF and lowest (0.7g kg^{-1}) for IS system. In the 10 to 20 cm depth, TN concentration was highest (1.3 g kg^{-1}) for NF and lowest (0.7g kg^{-1}) for BF and DB systems, while in the 20 to 40 cm, TN content was highest (1.1 g kg^{-1}) for NF and lowest (0.6 g kg^{-1}) for OP, IG, DB and UC systems. Soil organic C storage was significantly greater (p = 0.05) in NF system than in any of the forest derived land use systems in the 0 to 10 and 10 to 20 cm depths (Tables 5 and 6 respectively) while in the 20 to 40 cm depth (Table 7), SOC storage was greater in the BF system than in any of other land use systems. For example, in the 0 to 10 cm depth, SOC storage was highest (46.9 Mgha^{-1}) in the NF system and lowest (13.6 Mg ha^{-1}) in the IS system. Compared to the NF system, decrease in SOC storage in this depth was 47.1, 57.8, 57.8, 61.6, 63.8, 64.8, 65.7, 66.3 and 70.6 percent for DB, AC, OP, PM, FC, TA, BF, UC, MI and IG systems respectively. In the 10- to 20- cm depth, SOC storage was highest (26.7 Mg ha^{-1}) for NF and lowest (13.2 Mg ha^{-1}) for DB system, while in the 20- to 40- cm depth, SOC storage was highest (50.1 Mgha^{-1}) for BF and lowest (22.0 Mgha^{-1}) for UC system.

These results showed that SOC storage in 0 to 10 and 10 to 20 cm depths was significantly higher than in five years of bush fallow (BF), eight years of alley cropping with MPTs (AC) and thirty years of oil palm plantation (OP). In contrast, SOC storage in 20- to 40- cm depth was insignificant in NF and BF systems, while SOC storage in these systems was higher than in any of the other systems. Soil organic C storage in the 0 to 10 and 10 to 20 cm depths did not differ between UC and FC plots but in the 20 to 40 cm depth, the FC plot had significantly higher SOC stock than the UC plot (32.3 vs. 22.0 Mgha^{-1}).

Soil TN storage was higher ($p = 0.05$) in NF system than any of the other land use systems in the 0 to 10 and 10 to 20 cm depths (Tables 5 and 6 respectively), but in the 20 to 40 cm depth (Table 7), TN storage was equal in the NF and BF systems and was higher in these two systems than in any of the other land uses. In the 0 to 10 cm depths, total N storage ranged from 1.1 Mg ha^{-1} in the TA and IS systems to 3.6 Mg ha^{-1} in the NF system, in the 10 to 20 cm depth, the range was from 1.1 Mg ha^{-1} (BF, IS and DB systems) to 2.1 Mg ha^{-1} (NF system), while in the 20 to 40 cm, it ranged from 1.9 Mg ha^{-1} in the UC system to 3.5 Mg ha^{-1} in both the NF and BF systems. For the 0 to 10 cm depth, TN storage decreased by 69.4, 69.4, 66.7, 63.9, 61.1, 58.3, 55.6, and 52.8 percent for the TA, IG, MI, BF, UC, FC, OP, AC, PM and DB systems respectively when compared to the NF system. In the 0 to 10 and 10 to 20 cm depths, TN storage in NF was significantly higher than in five years bush fallow, eight years of alley cropping and thirty years oil palm plantation but in the 20 to 40 cm TN storage was the same for BF and NF systems. Total C decreased with depth (with 10 cm depth increment) in all the land uses, while total N mass did not follow this trend but was more or less uniform in the depth increments. Thus, a difference in total N mass was less detectable as with total C mass.

The C: N ratios for the 0 to 10 cm depth (Table 5), 10 to 20 cm depth (Table 6) and 20 to 40 cm depth (Table 7) did significantly differ ($p = 0.05$) when compared to the different land uses and did not follow any definite trend. The C: N ratios ranged from 11.4 (PM system) to 13.8 (TA system) in 0 to 10 cm depth, 10.0 (AC system) to 13.2 (NF system) in 10 to 20 cm depth and 10.0 (MI system) to 14.7 (BF system). The results also showed that C: N did not correlate with either C and N content or SOC and TN storage in the land use systems, even though detectable changes in these soil properties were very high, ranging between 47% to 71% for SOC storage and between 52% to 69% for TN storage in the 0 to 10 cm depth for example.

The total SOC and TN storage (Mg ha^{-1}) in the whole soil pedon (0 - 40 cm) are presented in Table 8. When compared to NF system, total SOC and TN storage showed a decrease in percent of 32.1 and 35.9 respectively for BF, 44.1 and 43.5 for AC, 45.6 and 44.6 for OP, 43.5 and 46.7 for TA, 54.3 and 53.3 for IS, 55.8 and 48.9 for MI, 45.9 and 47.8 for DB, 52.2 and 44.6 for PM, 52.9 and 51.1 for UC and 45.3 and 42.4 for FC. On the average, the total SOC and TN storage in the 0 – 40 cm depth decreased by 48 and 46 percent respectively due to forest conversion to agricultural land use systems.

Table 7. Total C and N storage for the 0 – 40 cm depth under different land use systems

Land use system	C storage, Mgha^{-1}	N Storage, Mgha^{-1}
Natural Forest (NF)	119.6	9.2
Bush fallow (BF)	81.2	5.9
Alley cropping with MPTs (AC)	66.8	5.2
Oil palm plantation (OP)	65.1	5.1
Alley cropping (TA)	67.6	4.9
Alley cropping (IG)	54.7	4.3
Alley cropping (MI)	52.9	4.7
Alley cropping (DB)	64.7	4.8
Alley cropping (PM)	57.2	5.1
Unfertilized cassava (UC)	52.9	4.5
Fertilized cassava (FC)	65.4	5.3
LSD (0.05)	13.1	0.9

NF = Natural forest BF= bush fallow, MPTs(AC) = Alley cropping with multi-purpose trees, OP = oil palm plantation, TA= *Treculia Africana .L.*, IG =*Irevingia ganensis L.*, MI = *Magnifera indica. L.*, DB = *Dactyldenia barteri. L*, PM = *Pentaclethra macropylla. L*, UC = Cropping without fertilizer application, FC= cropping with fertilizer application

Discussion

The lower bulk density and higher porosity in the 0 to 10, 10 to 20 and 20 to 40 cm depths of soils under continuous cassava cultivation than soils under forest plantation and alley cropping might be ascribed to the loosening of the topsoil by the tuberous roots of cassava over time. This effect might have overshadowed the effect of continuous cultivation on loss of SOC and reduction in the aggregation of soil both of which would otherwise result in increased bulk density. Opara-Nadi and Lal (1987) observed that the development of tuberous roots under cassava in the topsoil (0-20 cm) led to a decrease in bulk density which is intimately connected with increased porosity and alteration of pore size distribution.

The acidic nature of the soils under all the land uses was more a reflection of the nature of the parent material (quartz rich, coarse textured and strongly leached) as reported by Onwudike (2015) than the effect of land use systems. The higher soil pH in the 0 to 10, 10 to 20 and 20 to 40 cm depths under oil palm plantation than any of the other systems may be attributed to high calcium content, high base saturation and low aluminium content. The long-term inorganic fertilizer input in the FC system did not affect the soil pH as there was no effect in pH between the fertilized and unfertilized and cassava plots.

The higher values of exchangeable K, Na and AI, CEC and acidity under forest soil than soils under any of the other land use systems as well as the relatively high values of Ca and Mg under forest soil demonstrate the high capacity of forest soils to conserve and enhance SOM, which in turn, has positive implications on the conversation of nutrients. The result of this study confirms those of other studies on tropical ecosystems and other ecosystems (Fernandez et al., 1997; Sanchez, 2000; McGrath et al., 2001; Lal, 2005; Jelinski and Kucharik, 2009; Nair et al., 2009). The relatively lower levels of exchangeable nutrients and acidity as well as CEC under bush fallow, agro-forestry and oil palm plantation than primary forest demonstrate the fact that the recovery of these systems in terms of nutrient addition is a rather slow process. Similar studies showed that the rate of recovery of bush fallows following forest clearing in terms of nutrient build-up and fertility status is rather a slow process have been reported (Brown and Lugo, 1990; Szott and Palm, 1996). These studies also showed that rate of recovery of bush fallows and fertility status depends on a number of factors such as climate, type of secondary vegetation, rate of turn-over of SOM as well as nutrient and fertility levels at the onset of fallow regeneration. These factors were not examined in study but it may suffice to mention here that the tree species in the alley cropping systems were not leguminous tress capable of fixing atmospheric nitrogen and also having high rate of SOM turn-over in the soil. The very high base saturation in the 0–40 cm depth of soil under OP system demonstrates the high levels of exchangeable acidity and AI saturation under this system. Exchangeable Ca, Mg and K in that order contributed to the high base saturation of soil under OP system. Both Ca and Mg distributions in the OP system as well as K distribution in the NF system were strongly stratified with depth in these two systems, which had the highest concentrations of these elements in the top 40 cm depth in comparison to the other land use systems. These three elements were dominant in the CEC level in the soil. The effect of CEC was perhaps a more important action than exchangeable cations and acidity in determining the nutrient status and overall fertility of soils under most of the land use systems.

As was reported in previous studies (Ellert and Bettany, 1995; Blanco-Canqui and Lal, 2005; Jelinski and Kucharik, 2009), SOC, TN content and storage were calculated on an area basis rather than on mass basis. Thus, differences in soil bulk density which was large and significant had a large influence on SOC and TN content and storage under the different land use systems in the study area. The potentially high SOC and TN storage in the entire topsoil (0–40 cm), ranging from 52.9 to 119.6 Mgha^{-1} for SOC and 4.3 to 9.2 Mgha^{-1} for TN showed that between land use systems different soil bulk density values dramatically affected calculations of differences in SOC and TN storage. Similar observations have been made by other workers (Brown and Lugo, 1990; Puget and Lal, 2005; Blanco-Canqui and Lal, 2008; Jelinski and Kucharik, 2009; Geissen, 2009) in studies involving land use alone, tillage alone or land use and tillage in the US forest and cropland soils and also in studies involving mulching and tillage, tillage and organic amendments or soil and crop management practices in south-eastern Nigeria (Ohaneje, 2002, Kirby and Potvin, 2007). When natural forest was converted into cultivation, SOC and TN storage for a depth of 0- to 10- cm was reduced significantly with an average of 63 and 62 percent respectively relative to SOC and TN storage of the natural forest land. In the whole soil pedon (0–40 cm), total SOC and TN storage decreased by an average of 48 and 46 percent respectively for all forest derived land use systems due to forest change to agriculture. Similar results showing a drop of SOC and TN stock or storage have been reported for other studies in different ecological zones. For example, Kern and Johnson (1993) and Murty et al. (2002) evaluated the decrease of SOC stock in the major US cropland soils at approximately 16% and 22 – 25% respectively upon conversion from forest to crop. Similarly, Guo and Gifford

(2002) reported that soils lost 42% of their SOC stock upon forest conversion. Carter et al. (1998) reported that cultivation decreased the mass of organic C (35%) and total N (10%) in the soil profile of Podzolic soils.

The non-significant effect of land use systems on C:N ratio in the study area is in agreement with the findings of Jelinski and Kucharik (2009) and Geissen et al. (2009) in other locations even though the result of land use change from forest to agriculture on SOC and TN content and storage in all three depths was very detectable and significant. However, the result of this study deviated from the findings of Franzluebbers et al. (2002) and Puget and Lal (2005) which reported that forest soils have higher C:N ratios than agricultural soils.

Conclusion

The findings of this study demonstrate a consistent decrease in soil organic carbon (SOC) and total nitrogen (TN) concentrations and storage when natural forests are converted to agriculture in south-eastern Nigeria. These results are in agreement with previous studies conducted in different ecological zones. The study reveals that forest ecosystems possess a higher capacity to retain exchangeable potassium (K), sodium (Na), aluminum (AI), cation exchange capacity (CEC), and acidity compared to other land systems. Moreover, the relatively high concentrations of calcium (Ca) and magnesium (Mg) under the forest indicate the forest's ability to conserve and enhance soil organic matter (SOM) and nutrient content.

The research also demonstrates a significant decline in total SOC and TN storage (0 – 40 cm depth) by an average of 48% and 46%, respectively, for all forest-derived land use systems following conversion to agriculture. These results highlight the substantial capacity of natural forests to sequester and store large amounts of SOC and TN, surpassing the values observed in forest-derived land uses. Additionally, the study reveals that 5, 10, and 30 years of forest regrowth (bush fallow), alley cropping with multipurpose trees (MPTs), and oil palm plantation, respectively, were insufficient in restoring fertility levels similar to those found in the natural forest.

Based on the findings, it can be concluded that continuous cultivation of cassava, with or without inorganic fertilizer inputs, leads to a decrease in SOC and TN stocks in the soil. Overall, the conversion of forest to agriculture in the study area significantly impacted key soil chemical attributes associated with fertility of soil, including SOC, CEC and total nitrogen. These results emphasize the need for further research on the potential of agroforestry systems in storing SOC and TN in the rainforest zones. Additionally, long-term comparative studies investigating carbon and nitrogen sequestration under natural forests, grasslands, and agroforestry systems are warranted.

In conclusion, this study sheds light on the consequences of land use change from forest to agriculture on soil chemical properties and nutrient dynamics. It underscores the importance of preserving natural forests for their significant role in carbon and nitrogen storage, while also emphasizing the potential of agroforestry systems as viable alternatives. The findings provide valuable insights for sustainable land management practices in similar ecological zones and suggest avenues for future research.

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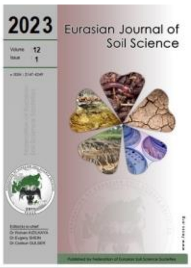

Assessing the biomass yield and nitrogen fixation of Lupinus angustifolius varieties as green manure in Jalisco, Mexico

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Abstract

Limited information is available in Mexico regarding the use of *Lupinus angustifolius* L. as a green manure. This study aimed to assess the effectiveness of six *Lupinus angustifolius* varieties as green manure in terms of above-ground biomass production, expressed as dry matter (DM), and total nitrogen (N) accumulation at successive harvest dates. Additionally, the study aimed to estimate N_2 fixation 110 days after sowing (DAS). The varieties Haags Blaue, Boregine, Borlu, Probor, Sonate, and Boruta were sown during the winter season of 2018-2019 using a randomized block factorial design. The N difference method was employed to estimate N_2 fixation, with wheat serving as the reference crop. Data on above-ground biomass production, N concentration, and total N accumulation were recorded at different harvest times: 80, 95, and 110 DAS. The biomass yield of all varieties significantly increased from the first to the last harvest, with the highest yield observed at the final harvest (ranging from 7,632 to 10,200 kg ha^{-1}). The highest total N accumulation from biomass was recorded at the last harvest. On average, the Borlu, Boregine, Haags Blaue, and Boruta varieties accumulated 195.4 kg ha^{-1} of total N (ranging from 195.6 to 221.2 kg ha^{-1}). The proportion of N derived from the atmosphere (%Ndfa) through N_2 fixation averaged 80.09% (ranging from 72% to 93%), resulting in an average N fixation of 160 kg ha^{-1} (ranging from 106 to 185 kg ha^{-1}) in above-ground biomass. All six varieties demonstrated potential as green manure, considering their above-ground biomass production, total N accumulation, and ability to fix N_2.

Keywords: Dry matter, harvest date, legumes, lupins, N_2 fixation, Rhizobia.

Introduction

Leguminous green manure crops have been widely reported to play an important role in managing soil health and recently received greater attention for improving soil fertility and agricultural sustainability (Meena et al., 2018). In favorable conditions, legumes can produce up to 8-10 t ha^{-1} of dry matter (DM) as manure crops, adding up to 300 kg ha^{-1} of nitrogen (N) to soil (Talgre et al., 2012). Green manures may also provide other benefits, such as a nutrient source for future crops, conservation of soil water, and control of plant pests, pathogens, and weeds (McSorley, 1999; Ross et al., 2001).

The genus *Lupinus* belongs to the family Leguminosae and is well known in several parts of the world for its economic value as a food source, fodder, and green manure due to its ability to obtain atmospheric N through biological nitrogen fixation (BNF) (Carranca et al., 2013). In such a scenario, the BNF process is considered an important route of N entry to agricultural and forestry systems (Ridley et al., 2004). Compared to other legumes, lupin species are considered to be highly efficient at fixing atmospheric N (Unkovich et al., 2010). The genus *Lupinus* includes 200 to 500 species, but only *L. albus*, *L. angustifolius*, *L. luteus,* and *L. mutabilis*) are

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cultivated for different purposes (Gladstones, 1974; Drummond et al., 2012). *L angustifolius* first appeared in an agricultural context as a spring-sown green manure and forage crop in the acidic sands of northern Europe in the nineteenth century (Hondelmann, 1984; Kurlovich, 2002). The cultivar "Lupi" was bred especially for use as green manure in Estonia (Bender and Tamm, 2014).

The incorporation of plants of these species in soils as green manure and their beneficial effects have been reported in different countries (Hanly and Gregg, 2004; Fowler et al., 2013). Although these species are not yet economically important in Mexico, some recent research in narrow-Leafed lupin (*L. angustifolius*), a winter legume, has been carried out in Jalisco Mexico, to determine their potential as winter grain crops (Lara-Rivera et al., 2017). However, no information is available on the potential of lupin to provide green manure in terms of biomass yield and N accumulation throughout the growing season. In this regard, Wivstad and Naetterlund (2008) reported that an important aspect of management associated with green manuring is choosing the development stage of the plant at which a green manure crop is incorporated into the soil. Therefore, the objective of this research was to determine the value of six *L. angustifolius* varieties as green manure in terms of aboveground biomass production and N accumulation at successive harvest dates. Additionally, this research aimed to estimate N fixation in these varieties 110 days after sowing (DAS)

Material and Methods

Plant material

Seeds of the Haags Blaue, Boregine, Borlu, Probor, Sonate, and Boruta varieties were used in this experiment.

Site description

The field experiment was conducted during the winter season of 2018–2019 in the experimental agricultural station at the University of Guadalajara in Zapopan, Jalisco, Mexico (20° 44' 47" N and 103° 30' 43" W) at an altitude of 1523 m.a.s.l. Climatic characteristics of this site were previously reported by Zapata et al. (2019). The experiment was established on loamy sandy soil, Regosol, according to the FAO/UNESCO classification. The chemical and physical properties of the soil were analyzed (Table 1).

Table 1. Basic chemical characteristics of the soil used in the experiment.

Depth (cm)	pH (KCl)	Organic matter (%)	N (%)	P (mg kg^{-1})	K (cmol kg^{-1})	Mineral components of soil (%)			Soil Texture
						Sand	Clay	Silt	
0-30	5.13	1.81	0.12	68.53	0.84	56	16	28	Sandy loam

Treatments and experimental design

On 7 November 2018, all six *L. angustifolius* varieties were planted following complete disking and plowing of the field in an experimental randomized block design with five replicates. Individual plots were 6.0 m long and four rows (75 cm between rows) wide in each replication. Lupin seeds were planted at a rate of 20 per meter of row with a target plant population of 120 000 plants ha^{-1}. Table 2 shows the treatments and characteristics of the lupin cultivars used in the experiment. The experimental design was a randomized block factorial design (factor A is the variety, and factor B is the time of harvest of the green manure biomass). At the time of sowing, no inoculum was added with the seed, but inspections showed that all plants were well nodulated during the growing season. A 2–m strip of spring wheat (*Triticum aestivum* cv Salamanca) was planted adjacent to each variety plot to serve as a non–N–fixing reference plant, with a target plant population of 320 000 plants ha^{-1}.

Table 2. Treatments used in the experiment and characteristics of the varieties.

Treatments	Variety	Type	Origin
Lupin cultivars	Haags Blaue	Early	Germany
	Boregine	Medium early	Germany
	Borlu	Medium early	Germany
	Probor	Medium early	Germany
	Sonate	Late	Germany
	Boruta	Early	Germany
Wheat	Salamanca	Medium early	México
Harvest dates: 80, 95, and 110* days after sowing			

*Assessment of N_2 fixation

Agronomic practices

Approximately 30 days after sowing, the plants in the four rows in each plot were thinned to 10 plants m^{-1}. The two rows located in the central part were then used for plant sampling during the experiment. After seeding, drip irrigation was performed at field capacity; this was repeated every 15 days but suspended 10 days before the last measurement. The weeds were removed manually during cultivation. Fertilizer was not applied, and pesticide application was not necessary because of the low incidence of pests and diseases. The meteorological data for the experimental area during the growing season and harvest date sowing are provided in Table 3.

Table 3. Harvest dates, temperature (T), and precipitation data during crop growth.

Month	Harvest date	Days after sowing	T max (°C)	T min (°C)	T mean (°C)	Rainfall (mm)
November	Seeds sown	----	23.40	9.30	16.35	0.80
December	----	----	17.60	5.40	11.50	5.00
January	1st (01–2019)	80	15.60	5.70	10.65	1.20
February	2nd (15–2019)	95	20.60	8.80	14.70	0.00
March	3rd (01–2019)	110	26.20	10.30	18.20	0.00

Data collection and nitrogen analysis

Sequential aboveground biomass samples were collected from a 1.0–m–long row (0.75 cm spacing) throughout the growing season. A chronological period was used because the varieties had different phenologies and it was not possible to make their flowering times coincide. The first sampling was done on 1 January, the second on 15 February, and the last on 15 March when plants were still immature to minimize the loss of leaves due to senescence. We used pruning scissors to cut plants approximately 3–5 cm above the ground level. The harvested material was washed with water and placed on absorbent paper for 30 min. The plants were dried in a forced air oven at 70 °C until constant weight (48 h). After registering the dry weights, we ground each whole plant in a mill for N analysis. The Kjeldahl method was used to quantify the percent N in each sample (whole plant). The total N content per plant was calculated using the following equation:

$$\text{N content (g plant}^{-1}) = [\text{DM (g plant}^{-1}) \times \%\ \text{N in whole plant}^{-1}] / 100$$

N_2 fixation

Symbiotic N_2 fixation in all six varieties of lupin was estimated 110 days after sowing. The N difference between fixing and non-fixing crops was used to quantify N_2 fixation (Hardarson et al., 1984; Evans et al., 1987). Reference plants (wheat) were cut in the third sampling and the amount of symbiotically fixed N was calculated according to the following equation:

$$\text{Fixed N} = \text{total N (fixing crop)} - \text{total N (non–fixing crop)}$$

Statistical analysis

To analyze the data, the statistical software Statgraphics Centurion, version XVII (Statgraphics Technologies Inc., USA) was used. Analysis of variance (ANOVA) was carried out on the parameters evaluated for the treatments. Means were compared using the Tukey test at $p \leq 0.05$.

Results and Discussion

Above-ground biomass yield

The effect of *L. angustifolius* varieties and harvest date on the above-ground biomass yield was significant ($p<0.05$). Variety × harvest date interactions were also observed (data not shown). Above-ground biomass yields expressed as the Kg ha^{-1} of DM for all six varieties at different harvest dates are presented in Table 4. As expected, we measured a significant increase in biomass DM yield for all varieties from the first to the last harvest date. In the first sampling, the values ranged from 1867 Kg ha^{-1} for the Sonate variety to 2964 Kg ha^{-1} for the Borlu variety. At the second harvest date, the yield varied from 3616 for Boruta to 5662 Kg ha^{-1} for Haags Blaue, whereas at the last harvest date, the yield ranged from 7632 Kg ha^{-1} for the Sonate variety to 10 200 Kg ha^{-1} for the Borlu variety (average 7864 Kg ha^{-1}).

Table 4. Change in dry matter yield of *L. angustifolius* varieties at successive harvest dates.

Days after sowing	Aboveground biomass yield (kg ha^{-1})					
	Haags Blaue	Boregine	Borlu	Probor	Sonate	Boruta
80	2412c	2765b	2964a	3098a	1949d	1867d
95	5662a	4116c	4887b	5465a	4082c	3616d
110	8568c	9132b	10200a	7956c	7632d	9096b

Values in the same row with different letters were significantly different ($p<0.05$) according to Tukey test.

Our results revealed that, in general, aboveground DM progressively increased in all six varieties with increasing maturity, which is considered a natural phenomenon in favorable conditions new tissues and organ are formed with the progression of maturation. A similar trend has already been reported in other species of legumes with potential as green manures and forage (Matos et al., 2008; Odhiambo, 2010; Perdigão et al., 2012; Prusiński, 2014; Solati et al., 2017; Dhamala et al., 2017; Zapata et al., 2019; Hernández et al., 2022). On the other hand, the aboveground biomass yields measured in this study were in the range of those reported by other authors, who reported values up to 8000-10 000 Kg ha^{-1} of DM in different legumes under favorable conditions (Dubrovskis et al., 2011; Talgre et al., 2012; Dhamala et al., 2017). In particular, the above-ground biomass yield of *Lupinus* species under different climatic and soil conditions reported in the reference varies; for example, in Portugal, *Lupinus luteus* harvested 5 months after sowing has a yield of 4900 to 4930 Kg ha^{-1} in the first year of cultivation and from 5330 to 6370 Kg ha^{-1} in the second year of cultivation (Perdigão et al. 2012). In Poland, the DM yields of this species ranges from 5820 to 6190 Kg ha^{-1} (Pietrzykowski et al., 2017). In New Zealand, the above-ground DM yield of the *L. angustifolius* variety "Fest" harvested at 150 days reached 4850 Kg ha^{-1} (Fowler et al., 2004). In another study in New Zealand with *L. angustifolius* sampled 6 months just before being incorporated into the soil, the above-ground biomass ranged from 7400 to 8200 Kg ha^{-1} (Hanly and Greeg, 2004). The progressive and gradual accumulation of above-ground DM as the maturation period increased indicate that all six *L. angustifolius* varieties tested as green manure showed good adaptation to sandy and acidic soils and the moderately cool winter temperatures in the central region of Jalisco, Mexico (Figure 1). This can also be attributed to the plants having access to adequate amounts of moisture, nutrients, temperature, and sunlight.

Figure 1. *Lupinus angustifolius* varieties cultivated in Zapopan, Jalisco, México

The results indicate that the accumulation of DM could continue for a few more days, but there is a risk that the quality of the biomass used as a green manure decreases in terms of chemical composition (decreased N content and increased lignin concentration in the tissues). Delaying the harvest date and subsequent incorporation of green manure into the soil may affect its decomposition due to greater lignification of plant tissues. Although the lignin content was not quantified in the *L. angustifolius* varieties tested during the growing season in the present study, the results of other studies have shown that lignin concentrations on legume and non-legume species can consistently increase with successive harvest dates (Abiven et al., 2011; Markovi et al., 2012). On the other hand, the differences in DM accumulation between varieties can be explained in terms of varietal differences, as well maturation time (early and late maturation). Under the environmental conditions of the experimental site for the current study, the late maturing varieties (Boregine, Borlu, and Boruta) showed potential for producing more biomass than the early maturing varieties (Haags Blaue, Sonate, and Probor). In addition, inspections at each harvest date showed that all plants were well-nodulated during the growing season; therefore, the increase in aboveground biomass from the first to the third sampling date is probably due to increased N fixation by the six lupin varieties.

Nitrogen concentration and total accumulation in above-ground biomass

Significant differences in the N concentration and total N accumulation in the aboveground biomass were observed among the varieties at each sampling date ($p<0.05$). The N concentration expressed percentage decreased significantly in all six varieties across the growing season (Table 5). From the first to the third harvest date, the N concentration (as the average of six varieties) was 2.95%, 2.62%, and 2.30%, respectively. Among all six varieties, Probor accumulated significantly higher N concentrations at the first harvest date (3.6%), whereas the highest N concentration was registered at the second and third harvest date with the Haags Blaue variety (3.1% and 2.6%, respectively).

Table 5. Nitrogen (N) concentration and total accumulation in six *Lupinus angustifolius* varieties at different harvest dates.

Variety	N concentration (%) Days after sowing			Total N accumulation (kg ha^{-1}) Days after sowing		
	80	95	110	80	95	110
Haags Blaue	3.0b	3.1a	2.6a	74.5b	179.2a	193.7b
Boregine	3.0b	2.4b	2.4a	90.4a	102.6c	197.5b
Borlu	2.4b	2.0c	2.1a	49.9c	100.9c	212.2a
Probor	3.6a	2.7b	2.3a	58.5c	152.4b	166.5c
Sonate	2.8b	2.5b	1.9b	44.6c	105.3c	126.1d
Boruta	2.6c	2.6b	2.2a	49.6c	97.0c	195.6b
Mean	2.95	2.62	2.30	61.25	122.9	181.9

Values in the same column with different letters were significantly different ($p<0.05$) according to Tukey test.

The N concentrations found in the tested varieties were well within the reported values in the literature for similar types of green manures and forage crops at different locations and conditions. For example, in New Zealand, *L. angustifolius* variety “Fest” harvested 150 DAS recorded an N concentration of 3.39%, whereas in South Africa, *L. angustifolius* (variety name was not mentioned) at 3.5 months, just before incorporation into the soil, had an N concentration of 3.0% (Van Antwerpent et al., 2002; Fowler et al., 2004). However, lower N concentrations (1.4% and 1.5%) than those found in this experiment were reported in another study carried out at two sites in New Zealand (Hanly and Greeg, 2004). A decrease in N concentration with successive harvest dates was reported in other studies with different species and conditions, possibly due to the dilution effect of greater above-ground biomass. Similarly, a decreasing trend in N content has been reported for different forage crops and green manures in one season of growth as the plant matured beyond flowering (Odhiambo 2010; Dhamala et al., 2017; Zapata et al., 2019; Hernández et al., 2022). According to Müller et al. (1988), the biomass production of a green manure is important when incorporating it into the soil, but it is necessary to also consider its concentration of N, as this is an important chemical characteristic that governs the rate of decomposition and mineralization into the soil. The pattern in DM accumulation of green manures with increasing maturity is important for proper timing of incorporation into the soil; however, even though delaying the harvest will increase the DM yield of the crop significantly, the quality will probably decrease (Odhiambo and Bomke, 2001). In general, the quality of a green manure in terms of chemical composition varies a great deal due to a number of factors, such as species, stage of growth, soil conditions, fertilizer application, availability of water, and climatic conditions.

In the current research, the amount of total N that can return to the soil through the biomass produced varied greatly among the six varieties evaluated and the harvest dates, with a tendency to increase the total yield of N accumulated in the biomass throughout the growth period. The highest total N yields were found in the biomass produced at the last harvest date, with an average of 181 Kg ha^{-1} (range 126.2–212.1 Kg ha^{-1}). Borlu was the variety that exhibited the highest amount of total N accumulation, followed by Boregine, Borlua, and Boruta varieties. As expected, the lowest total N accumulation was recorded at the first harvest date (range 44.6–90.4 Kg ha^{-1}). This general tendency of increased total N yield in the biomass of the *L. angustifolius* varieties tested during the growth period is consistent with the literature for different legume species used as forage and green manure (Wivstad, 1999; Odhiambo and Bomke, 2001; Unkovich et al., 2010; Bhardwaj et al., 2010). Previous research in different environmental and growth conditions has shown a close association between total N accumulated and biomass yield throughout the growth period (Carranca et al., 2013; Zapata; et al., 2019). Although we did not observe a decrease in the N content in the harvested biomass as the sampling dates increased in this study, different studies with species of the genus *Lupinus* and other legumes have observed that the N content in the biomass can decrease during the growth cycle (from vegetative to pod-filling phases). In the current research and considering that the N concentration decline and C/N ratio probably increase as the plant matures, it is convenient to cut and incorporate the green manure at the last harvest date tested.

Atmospheric nitrogen fixation

The lupin varieties evaluated in this study were able to fix atmospheric N in symbiosis with the native soil bacteria 110 days after planting and under the climatic conditions of Zapopan, Jalisco (Mexico). The genus *Lupinus* has been known for some time to be nodulated by *Bradyrhizobum* sp. in the soil (Jordan, 1982). Observations during the growing season (all sampling dates) showed that plants were well nodulated. However, significant (p<0.05) differences were observed in the amount of N fixed and percentage of N derived from the atmosphere (Ndfa) between lupin genotypes (Figure 2).

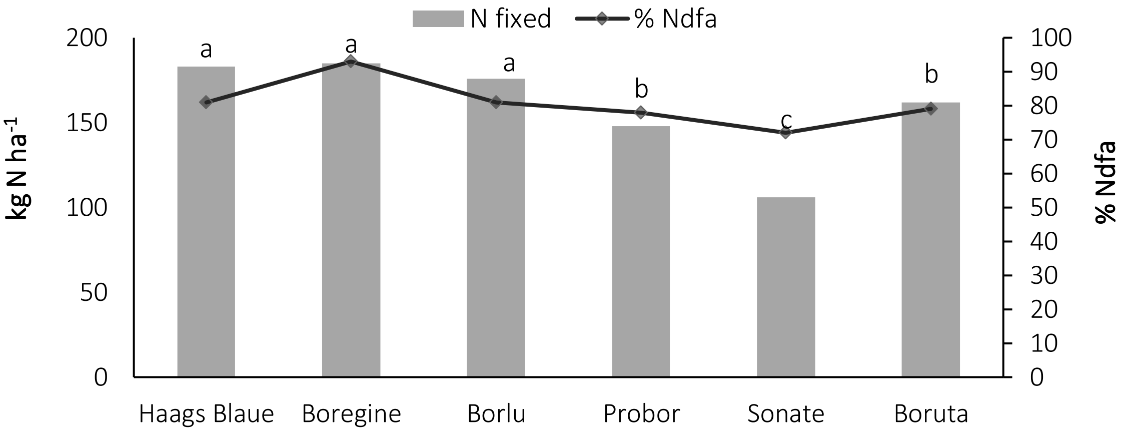

Figure 2. Amount of nitrogen (N) fixed and proportion of N derived from the atmosphere (Ndfa)

The Ndaf averaged 80.9% (range 72.1–93.2%), with a corresponding N_2 fixation input in aboveground biomass of 162 Kg ha^{-1} (range 106–185 Kg ha^{-1}). Boregine, Haags Blaue, and Borlu varieties showed a better response in fixing ability with 185, 183, and 176 Kg N ha^{-1} (Figure 2). The highest percentage of Ndfa 110 days after sowing was achieved with Haags Blaue, Boregine, Borlu, and Boruta varieties (up to 84%). Sonate and Probor varieties were found to have the worst adaptive ability in regard to the biomass yield and N fixation, but the average N_2 fixation values found in this study are generally within the ranges reported by other researchers for *L. angustifolius* varieties. For example, in one of the first studies to measure N fixation in *L. angustifolius,* Pálmason et al. (1992) reported 117 DAS and at a mean temperature below 10°C in Iceland that lupin derived an average of 92% or 195 Kg N ha^{-1}. Later, in an Andisol soil of southern Chile, Barrientos et al. (2002) reported that *L. angustifolius* cv. Gungurru fixed 197 Kg N ha^{-1} 80 days after planting, which was equivalent to 91% Ndfa. However, in some cases, our values for fixed N_2 were higher than those reported by other studies, with the exception of the Sonate variety. Kelstrup et al. (1996) reported that the total amount of N derived from N_2 fixation was 119 Kg ha^{-1} for the Feste variety harvested in New Zealand when plants were judged to be physiologically mature. In comparison to other studies, our results were slightly lower. In Iceland, for example, Pálmason et al. (2004) reported that *L. angustifolius* cv Uniharvest reached symbiotic N yields as high as 185 to 212 Kg ha^{-1} at seeding rates of 200 Kg ha^{-1}. On the other hand, Denton et al. (2017) reported maximum symbiotic N fixation values in Australia of 225 Kg ha^{-1} N. These differences may be due to the conditions established before and during the experiments, such as the evaluated varieties, inoculant application, climatic and soil conditions, sampling dates, and methods used to evaluate N_2 fixation, among others. On the other hand, the present study revealed variation between genotypes in the ability to fix N_2. These and other results obtained with different legumes and using different methods showed that genetic variability exists between genotypes in regard to their ability to support N_2 fixation (Hardarson et al., 1984; Zimmer et al., 2016; Akter et al., 2018; Diatta et al., 2020). These results should be useful to growers and researchers interested in selecting management practices that optimize N fixation and increase the aboveground biomass yield of *L angustifolius* used as green manures.

Conclusion

All *L. angustifolius* varieties showed good adaptation to acidic soils and moderately cool winter temperatures in central Jalisco, Mexico, with a rapid accumulation of DM (up to 8700 Kg ha^{-1} on average) and little damage from pests or disease. The N concentration in the plants decreases with maturity from 2.95 to 2.30 %, but the total N accumulated in the aboveground biomass of *L. angustifolius* varieties increased significantly from the first to the last harvest. The varieties with major potential as green manure for agricultural soils in Zapopan, Jalisco, were Haags Blaue, Boregine, Borlu, and Boruta in terms of aboveground biomass production, total N accumulated and ability to fix N_2. At 110 days after sowing, Haags Blaue and Boregine were the varieties with the highest ability to fix atmospheric N, with 180 kg ha^{-1} on average.

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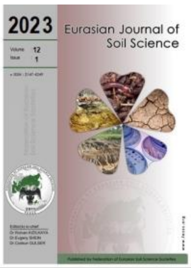

Assessing the efficacy of ameliorants on saline-sodic soils: Laboratory insights for reclamation strategies

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Abstract

This study presents the combined findings of laboratory experiments conducted to assess the efficacy of various ameliorants on saline-sodic soils in the foothill plain of Ile Alatau in the Northern Tianshan region. The investigation focused on the influence of phosphogypsum, elemental sulfur, nano sulfur, and sulfuric acid on the ionic composition of the soil solution and their impact on the soil-absorbing complex. Different doses of these ameliorants were applied to saline-sodic soil samples, and their incubation period was observed. The analysis of the aqueous extract of the soil emphasized the presence of bicarbonate, carbonate, sulfate, calcium, and sodium ions. The results revealed that sulfuric acid was the most effective ameliorant, rapidly neutralizing extreme alkalinity, reducing bicarbonate and carbonate ion content, and increasing sulfate and sodium ion concentrations. Elemental sulfur ranked second in effectiveness, significantly decreasing bicarbonate and carbonate ions and increasing sulfate and sodium ions. Phosphogypsum exhibited the lowest effectiveness, causing reductions in bicarbonate and carbonate ions and modest increases in sulfate and calcium ions. The study demonstrated that the introduction of phosphogypsum led to an increase in calcium and sulfate ions in the soil solution, while elemental sulfur and sulfuric acid significantly increased the sulfate ion content. Sulfuric acid exhibited the highest efficacy among the ameliorants, completely neutralizing normal carbonates and reducing alkalinity in the soil solution. The formation of subsoil gypsum through the interaction of sulfuric acid with calcium carbonates facilitated the displacement of sodium from the soil-absorbing complex. These findings contribute to our understanding of the processes involved in the amelioration of saline-sodic soils and provide insights into effective soil management practices. They serve as a theoretical basis for developing strategies for the reclamation of such soils worldwide. The research highlights sulfuric acid as the most effective ameliorant for saline-sodic soils, resulting in a significant rearrangement of the soil's ionic composition. Further research and field studies are necessary to validate and refine these laboratory findings for practical applications in soil improvement methods.

Keywords: Saline-sodic soils, ameliorants, soil reclamation, Soil management.

Introduction

Soil salinization is a widespread issue, particularly in arid and semi-arid regions, and it poses a significant challenge to global agricultural production (El hasini et al., 2019). Saline soils are prevalent in arid areas due to limited rainfall, which hinders the leaching and transport of salts, and the high evaporation rates that lead to salt concentration in soils and surface waters. The expansion of salinity-affected land is estimated to increase at a rate of approximately 1-2% annually, attributed to factors such as global climate change and improper irrigation and tillage practices. These saline soils contain high concentrations (> 0.25%) of soluble salts in all soil layers, which are toxic to plants and hinder their growth (Shaygan and Baumgartl, 2022).

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Sodic and saline-sodic soils exhibit poor physical properties and fertility issues that negatively impact the growth and yield of most crops (Rengasamy, 2002; 2006). Saline-sodic soils are found across various continents, ranging from tropical to polar zones, but they are most common in the Northern Hemisphere. In the Commonwealth of Independent States (CIS), the area covered by saline-sodic soils amounts to 120 million hectares, and the escalating expansion of these soils has made their reclamation a prominent concern in modern soil science (Yertayeva et al., 2019).

Kazakhstan, a country located mostly within the largest drainless part of the plain, faces an uneven distribution of saline soils. Approximately 70% of the saline soils in the Commonwealth of Independent States are located in Kazakhstan, covering an area of 111.55 million hectares, which accounts for 41% of the national territory. Central Asia, including Kazakhstan, is situated in the most saline part of the planet's land, with 191 million hectares of saline soils, equivalent to the combined area of soils in Africa and America. Salty soils in Kazakhstan are widespread, with solonetzes and solonetsous soils predominant in the northern and central parts, and solonchaks and solonchak soils dominating the southern, southwestern, and southeastern regions. Based on salt accumulation, four halogeochemical regions have been identified, namely the Caspian Sea basin (accumulation of sulfate-chloride and chloride salts), the Aral Sea basin (accumulation of chloride-sulfate salts), the Karsk Sea basin (accumulation of chloride-sulfate salts), and the Balkash Lake basin (accumulation of sodic-sulfate salts). In the southern, southwestern, and southeastern regions of Kazakhstan, the area covered by saline-sodic soils is approximately 7.095 million hectares, with distribution percentages of 18.6% in Almaty, 47.7% in Dzhambul, 27.3% in South Kazakhstan, and 21.7% in Kyzylorda. The presence of sodic-salinity among the highly fertile soils of the foothill color of the Northern Tien Shan, including meadow, meadow-serozem, and meadow-chestnut soils, accentuates the significance of addressing soil fertility issues. Crop losses due to sodic salinity in these areas range from 15% to 45% (Funakawa et al., 2000; Saparov, 2014; Pachikin et al., 2014; Otarov, 2014; Laiskhanov et al., 2016; Suska-Malawska et al., 2019; Zhang et al., 2019; Ma et al., 2019; Yertayeva et al., 2019; Kussainova et al., 2020; Liu et al., 2022; Suska-Malawska et al., 2022). Peasant farms annually apply various agricultural practices, from plowing to harvesting, to address saline-sodic soil patches. However, the low yields from these patches result in significant depreciation of material, monetary, and labor resources. Hence, the urgent need for saline-sodic soil reclamation in irrigated agricultural zones is evident.

The reclamation of saline or saline-sodic soils is a crucial global objective. Successful reclamation for agricultural purposes depends on understanding sodium dynamics and the chemical interactions that govern nutrient availability. Various methods are employed for the reclamation of saline soils, including physical techniques such as deep plowing, subsoiling, sanding, and profile inversion; chemical approaches involving amendments with substances like gypsum, calcium chloride, limestone, sulfuric acid, sulfur, and iron sulfate; and electro-reclamation techniques that utilize electric current treatment. The most effective methods involve the removal and exchange of soluble sodium, as well as modifying the ionic composition of soils through the addition of chemicals while simultaneously leaching sodium salts from the soil profile (Shaygan and Baumgartl, 2022).

To gain better control over soil fertility, it is crucial to understand the mechanisms underlying physicochemical and biological processes during the reclamation of saline-sodic soils under strictly controlled conditions. Laboratory research aimed at assessing the comparative effectiveness of different ameliorative techniques employing various rates of phosphogypsum, elemental sulfur, and sulfuric acid on saline-sodic soils can contribute to the development of effective soil amelioration technologies for saline-sodic soils.

Material and Methods

Site description

The soil sampling and laboratory experiment were conducted in the Talgar area of the Almaty region in Kazakhstan. The field plot was selected based on small, medium, and large-scale soil maps and soil reports, focusing on the distribution of alkaline soda-saline soils in the region. The specific coordinates of the site are N 43°39'7858, E 77°18'2917 (Figure 1). The selected region belongs to the halogeochemical province of accumulation of sodic-sulfate salts of the Balkhash Lake basin. The climate in the area is characterized by continentality and drought, with dry and hot summers. The average temperature in July ranges from 22-25°C, while in January, it is 9-12°C. The annual precipitation is 250-300 mm, and the average annual air temperature is 9.8˚C. The main background soils in the field plot are light meadow gray soils, but the focus of the study was on the small and medium semi-hydromorphic heavy loamy solonetzes with sulfate-sodic, sodic-sulfate, and pure sodic chemism. These soils occupy approximately 10% of the field.

Figure 1. Partial Snapshot of the Experimental Site Showing Soil Sample Locations

Soil sampling and lab experiment

Soil samples were taken from the upper layers (0-40 cm) of the identified spots of semi-hydromorphic heavy loamy solonetzes. The laboratory experiment involved the following ameliorative techniques: phosphogypsum, elemental sulfur (powdered and nano), and sulfuric acid (1%, 3%, and 5%). These ameliorants were thoroughly mixed with the soil and placed in plastic cups with a volume of 175 cm^2. The samples were kept at room temperature (23°C), and the soil moisture was maintained at 21%, corresponding to 70% of the field's water-holding capacity.

The calculations for the application of ameliorants were based on the initial physicochemical composition of the soil, and the doses were determined according to the formulas and coefficients specific to each ameliorant. The equivalent doses of ameliorants applied to the saline-sodic soils are presented in Table 1.

Table 1. The equivalent doses of ameliorants applied to soda-saline soils

Variants		Doses of introduced ameliorants	
		g $100g^{-1}$	ton/ha
Control		-	-
Phosphogypsum	$PG_{1.0}$	0.218 (estimated)	11.67
	$PG_{1.5}$	0.327	17.50
	$PG_{2.0}$	0.436	23.34
Elemental sulfur	$S_{1.0}$	0.041 (estimated)	2.217
	$S_{1.5}$	0.062	3.325
	$S_{2.0}$	0.082	4.434
Nanosulfur	$NS_{1.0}$	0.041 (estimated)	2.217
	$NS_{1.5}$	0.062	3.325
	$NS_{2.0}$	0.082	4.434
Sulfuric acid	$SA_{1\%}$	0.124/16 g H_2O (estimated)	6.652
	$SA_{3\%}$	0.124/15.65g H_2O	6.652
	$SA_{5\%}$	0.124/15.31g H_2O	6.652
Leaching with water		150 ml	

The laboratory experiment lasted for 60 days, and four blocks of the experimental scheme were used to assess the ameliorative efficiency of different doses and incubation periods of the ameliorants. After 15, 30, and 60 days of incubation, each block was eliminated, and the ionic composition (HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+), total salts, and pH of the water extract from the soils were determined (USDA, 2014; 2022). The experiment was replicated three times. Statistical analysis was performed using one-way ANOVA and Tukey's multiple comparison tests to determine the significance of differences between the different ameliorants. The analysis was conducted in the R statistical software version 4.3.0.

Results and Discussion

The laboratory experiment aimed to evaluate the effectiveness of different ameliorants, including phosphogypsum, elemental sulfur (both powdered and nano), and sulfuric acid, on saline-sodic soils in the foothill plain of Ile Alatau. The soil samples, taken from semi-hydromorphic heavy loamy solonetzes, were subjected to various doses and incubation periods of the ameliorants. The analysis of the soil solution emphasized the presence of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), calcium (Ca^{2+}), and sodium (Na^+) ions (Table 2).

Table 2. Effect of equivalent doses of phosphogypsum, sulfur, nanosulfur, and sulfuric acid on the salt regime of saline-sodic soils

	Days after leaching		Total Salt, %	HCO$_3^-$, me 100g^{-1}	CO$_3^{2-}$, me 100g^{-1}	Cl$^-$, me 100g^{-1}	SO$_4^{2-}$, me 100g^{-1}	Ca^{2+}, me 100g^{-1}	Mg^{2+}, me 100g^{-1}	Na$^+$, me 100g^{-1}	K$^+$, me 100g^{-1}	pH
		Control	0.48±0.066ef	0.86±0.093a	0.17±0.071a	0.11±0.035bc	5.64±0.093fg	0.41±0.035d	0.51±0.012bc	5.43±0.084cd	0.26±0.031cdef	9,25
Phosphogypsum	15 days	PG$_1$	0.56±0.019cd	0.67±0.018abc	0.13±0.036ab	0.12±0.018bc	7.07±0.287bcd	0.82±0.218bcd	0.46±0.044bc	6.26±0.001b	0.32±0.022b	8,03
		PG$_{1.5}$	0.51±0.009def	0.61±0.018bc	0.16±0.001ab	0.10±0.018c	6.38±0.122def	0.82±0.151bcd	0.42±0.044c	5.54±0.001cd	0.31±0.013bcd	8,06
		PG$_2$	0.57±0.03cd	0.59±0.040bc	0.09±0.020ab	0.08±0.020c	7.32±0.500bcd	1.08±0.200bc	0.56±0.090bc	6.02±0.320bc	0.33±0.010b	7,96
	30 days	PG$_1$	0.46±0.024fg	0.68±0.027abc	0.11±0.036ab	0.10±0.0108c	5.64±0.327fg	0.52±0.044cd	0.52±0.044bc	5.08±0.378d	0.29±0.004bcdef	8,08
		PG$_{1.5}$	0.48±0.024efg	0.64±0.00abc	0.11±0.036ab	0.11±0.001bc	5.88±0.336efg	0.78±0.064bcd	0.46±0.044bc	5.08±0.378d	0.31±0.004bcde	8,02
		PG$_2$	0.53±0.010de	0.59±0.020bc	0.11±0.040ab	0.10±0.040c	6.76±0.160cde	0.91±0.090bcd	0.56±0.110bc	5.65±0.001cd	0.32±0.001b	7,97
	60 days	PG$_1$	0.62±0.012bc	0.76±0.080abc	0.13±0.036ab	0.21±0.0108a	7.61±0.198bc	0.57±0.111bcd	0.46±0.044bc	7.22±0.276a	0.33±0.018b	8,18
		PG$_{1.5}$	0.64±0.016b	0.72±0.027abc	0.16±0.001ab	0.17±0.040ab	8.03±0.178b	0.67±0.111bcd	0.69±0.067ab	7.22±0.276a	0.34±0.018b	8,18
		PG$_2$	0.73±0.020a	0.59±0.040bc	0.08±0.001bc	0.14±0.020abc	9.62±0.320a	1.83±0.310a	0.86±0.110a	7.22±0.280a	0.42±0.001a	7,99
	After 60 days	PG$_1$	0.28±0.017h	0.79±0.222ab	0.11±0.036ab	0.08±0.0108c	2.96±0.356g	0.40±0.133d	0.46±0.044bc	2.73±0.276f	0.24±0.044	8,05
		PG$_{1.5}$	0.34±0.005h	0.77±0.044abc	0.08±0.001bc	0.07±0.001c	3.84±0.129h	0.47±0.044d	0.42±0.044c	3.55±0.001ef	0.25±0.018	8,02
		PG$_2$	0.41±0.010g	0.53±0.020c	0.00±0.001c	0.10±0.020c	5.17±0.110g	1.10±0.200b	0.62±0.11abc	3.76±0.001e	0.32±0.00bc	7,84
Sulfur	15 days	S$_{1.0}$	0.52±0.016def	0.63±0.036b	0.16±0.001ab	0.11±0.001ab	6.46±0.184efg	0.65±0.109de	0.46±0.044d	5.78±0.320bcd	0.31±0.011ef	8,03
		S$_{1.5}$	0.62±0.032bcd	0.59±0.044bcd	0.11±0.036abc	0.08±0.018ab	8.02±0.393cde	0.69±0.131de	0.42±0.089d	7.22±0.640ab	0.36±0.018cd	8,05
		S$_{2.0}$	0.73±0.038abc	0.51±0.036cdef	0.11±0.036abc	0.11±0.027ab	9.69±0.600abc	1.44±0.304cde	0.75±0.28bcd	7.70±0.001a	0.42±0.02ab	7,87
	30 days	S$_{1.0}$	0.71±0.017abc	0.47±0.018ef	0.00±0.001d	0.14±0.036a	9.58±0.227abc	1.93±0.089ab	1.40±0.173a	6.50±0.001abc	0.35±0.007cd	7,86
		S$_{1.5}$	0.62±0.024cd	0.48±0.001def	0.08±0.001bcd	0.08±0.018ab	8.23±0.340bcd	1.30±0.044bcd	1.20±0.044ab	5.93±0.378abcd	0.34±0.004de	7,86
		S$_{2.0}$	0.56±0.030de	0.57±0.018def	0.11±0.036abc	0.08±0.018ab	7.21±0.442def	0.95±0.044cde	0.65±0.109cd	5.93±0.378abcd	0.33±0.004def	7,91
	60 days	S$_{1.0}$	0.71±0.032abc	0.60±0.027ef	0.08±0.001bcd	0.15±0.024a	9.26±0.502abc	1.23±0.178bcde	1.15±0.173ab	7.22±0.276ab	0.39±0.013bc	8,01
		S$_{1.5}$	0.74±0.026ab	0.52±0.053f	0.03±0.036cd	0.14±0.018a	9.90±0.373ab	1.80±0.333bc	1.12±0.151abc	7.22±0.276ab	0.41±0.011ab	7,91
		S$_{2.0}$	0.81±0.020a	0.45±0.018f	0.00±0.001d	0.14±0.018a	10.92±0.298a	2.73±0.489a	1.12±0.107abc	7.22±0.276ab	0.44±0.004a	7,79
	After 60 days	S$_{1.0}$	0.43±0.003f	0.59±0.044bcd	0.03±0.036cd	0.08±0.018ab	5.39±0.124g	0.67±0.222de	0.52±0.111d	4.58±0.271d	0.29±0.016fg	7,90
		S$_{1.5}$	0.47±0.039ef	0.53±0.018bcdef	0.00±0.001d	0.08±0.018ab	5.97±0.538fg	1.43±0.378bcd	0.66±0.111cd	4.17±0.818d	0.32±0.004def	7,79
		S$_{2.0}$	0.62±0.081bcd	0.52±0.027bcdef	0.07±0.018cd	0.06±0.013b	8.29±1.131bcd	1.97±0.111ab	1.22±0.084ab	5.33±1.196cd	0.36±0.016cd	7,73
Nanosulfur	15 days	NS$_{1.0}$	0.5±0.022bc	0.83±0.018a	0.19±0.036a	0.10±0.018abc	6.04±0.351ab	0.36±0.107	0.29±0.064cd	6.02±0.320abc	0.29±0.004ab	8,24
		NS$_{1.5}$	0.49±0.020c	0.84±0.053a	0.21±0.036a	0.07±0.001bc	5.90±0.331b	0.39±0.001	0.36±0.089bcd	5.78±0.320abc	0.29±0.004abc	8,26
		NS$_{2.0}$	0.52±0.009abc	0.81±0.071a	0.19±0.036a	0.10±0.036abc	6.24±0.227ab	0.39±0.067	0.20±0.064cd	6.26±0.001abc	0.30±0.013ab	8,26
	30 days	NS$_{1.0}$	0.44±0.026cde	0.84±0.053a	0.16±0.001a	0.07±0.024bc	5.13±0.347bc	0.32±0.044	0.39±0.00abcd	5.08±0.378cde	0.24±0.016bcd	8,30
		NS$_{1.5}$	0.47±0.021c	0.75±0.098a	0.19±0.071a	0.08±0.018bc	5.63±0.271b	0.42±0.089	0.42±0.089abcd	5.37±0.378c	0.25±0.016bcd	8,21
		NS$_{2.0}$	0.46±0.025c	0.80±0.053a	0.24±0.001a	0.08±0.018bc	5.48±0.278bc	0.39±0.067	0.36±0.044bcd	5.37±0.378c	0.24±0.013bcd	8,26
	60 days	NS$_{1.0}$	0.61±0.034a	0.67±0.120a	0.19±0.036a	0.12±0.018ab	7.64±0.567a	0.57±0.089	0.62±0.111ab	7.02±0.276a	0.33±0.027a	8,24
		NS$_{1.5}$	0.6±0.003ab	0.65±0.044a	0.16±0.001a	0.13±0.042ab	7.62±0.062a	0.60±0.067	0.66±0.044a	6.81±0.001ab	0.34±0.016a	8,14
		NS$_{2.0}$	0.6±0.017ab	0.67±0.071a	0.13±0.036a	0.17±0.013a	7.57±0.207a	0.63±0.178	0.62±0.178ab	6.81±0.411ab	0.34±0.022a	8,15
	After 60 days	NS$_{1.0}$	0.35±0.023de	0.81±0.089a	0.16±0.001a	0.06±0.013bc	4.02±0.347c	0.27±0.044	0.49±0.001abc	3.93±0.267de	0.20±0.018d	8,26
		NS$_{1.5}$	0.45±0.074cd	0.75±0.089a	0.19±0.036a	0.07±0.024bc	5.39±1.107bc	0.37±0.111	0.46±0.044	5.13±0.929cd	0.25±0.022bcd	8,22
		NS$_{2.0}$	0.34±0.030de	0.76±0.107a	0.13±0.036a	0.04±0.001c	3.92±0.527c	0.33±0.156	0.42±0.044abcd	3.73±0.267e	0.22±0.029cd	8,29
Sulfuric acid	15 days	SA$_{1\%}$	0.78±0.294abcd	0.56±0.107cde	0.08±0.053bc	0.10±0.018abcd	10.42±4.482abcd	2.71±2.571bc	0.98±0.782cd	6.98±0.960abc	0.41±0.069bcde	7,83
		SA$_{3\%}$	0.81±0.174abcd	0.49±0.062de	0.05±0.092bc	0.07±0.001cd	10.89±2.607abcd	2.65±1.304bc	0.91±0.416cd	7.46±0.800ab	0.44±0.044abcd	7,74
		SA$_{5\%}$	1.08±0.067a	0.45±0.018bcd	0.00±0.001c	0.08±0.018bcd	14.87±1.024a	5.55±0.678ab	1.40±0.282cd	7.94±0.320a	0.51±0.004a	7,62
	30 days	SA$_{1\%}$	0.53±0.020cd	0.65±0.036bcd	0.16±0.001ab	0.10±0.018abcd	6.61±0.236cd	0.56±0.089c	0.59±0.067d	5.93±0.378bcd	0.28±0.009fgh	8,10
		SA$_{3\%}$	0.87±0.017abc	0.41±0.036cd	0.00±0.001c	0.10±0.018abcd	12.05±0.282abc	2.84±0.067abc	2.55±0.262ab	6.78±0.378abcd	0.39±0.001cde	7,73
		SA$_{5\%}$	1.03±0.019a	0.39±0.0108d	0.00±0.001c	0.14±0.036ab	14.56±0.293a	4.31±0.329ab	3.59±0.238a	6.78±0.378abcd	0.40±0.009cde	7,69
	60 days	SA$_{1\%}$	0.64±0.016bcd	0.69±0.062abc	0.16±0.08ab	0.16±0.013a	8.12±0.276bcd	0.63±0.244c	0.99±0.001cd	7.02±0.276abc	0.34±0.027efg	8,19
		SA$_{3\%}$	0.94±0.053ab	0.45±0.036e	0.03±0.046c	0.16±0.013a	12.90±0.784ab	4.13±0.756ab	1.48±0.133bcd	7.43±0.001ab	0.47±0.018abc	7,78
		SA$_{5\%}$	1.09±0.061a	0.44±0.027e	0.00±0.001c	0.10±0.018abcd	15.19±0.909a	6.17±1.111a	1.84±0.240bc	7.22±0.276ab	0.5±0.016ab	7,64
	After 60 days	SA$_{1\%}$	0.45±0.071d	0.81±0.089ab	0.21±0.036a	0.05±0.013cd	5.39±1.091d	0.37±0.089c	0.52±0.111d	5.13±0.929de	0.24±0.022h	8,26
		SA$_{3\%}$	0.54±0.074cd	0.44±0.053e	0.03±0.046bc	0.06±0.015cd	7.18±1.167cd	2.27±0.644bc	1.12±0.151cd	3.93±0.267e	0.34±0.022defg	7,77
		SA$_{5\%}$	0.64±0.054bcd	0.43±0.036e	0.00±0.001c	0.06±0.013d	8.68±0.820bcd	3.10±0.600abc	1.58±0.200bcd	4.13±0.001e	0.36±0.013def	7,72

In terms of phosphogypsum, the 15-day incubation had minimal impact on the soil's salt regime, with a slight decrease in HCO_3^- ions from 0.86 to 0.67-0.59 meq $100g^{-1}$. The CO_3^{2-} ions also decreased from 0.17 to 0.16-0.09 meq $100g^{-1}$. However, the CO_3^{2-} ion content remained above the toxicity threshold for plants. The introduction of phosphogypsum led to an increase in SO_4^{2-} ions from 5.64 to 7.07-9.62 meq $100g^{-1}$ and Ca^{2+} ions from 0.41 to 0.57-1.83 meq $100g^{-1}$. The Na^+ ion content in the soil solution increased from 5.43 to 7.22 meq $100g^{-1}$ after 60 days of incubation. Leaching the phosphogypsum-treated soil resulted in decreased SO_4^{2-} and Na^+ ion concentrations compared to the control.

For elemental sulfur, the calculated dose effectively reduced HCO_3^- ions from 0.86 to 0.51 meq $100g^{-1}$ after 15 days of incubation. CO_3^{2-} ions decreased from 0.17 to 0.11-0.08 meq $100g^{-1}$. The SO_4^{2-} ion content increased from 5.64 to 6.46-11.0 meq $100g^{-1}$, and Ca^{2+} ions increased from 0.41 to 0.65-2.73 meq $100g^{-1}$. Na^+ ions in the soil solution increased from 5.43 to 7.22 meq $100g^{-1}$. Leaching the elemental sulfur-treated soil resulted in decreased SO_4^{2-} and Na^+ ion concentrations compared to the incubation period.

Nanosulfur application caused noticeable decreases in HCO_3^- ions from 0.86 to 0.82-0.65 meq $100g^{-1}$ after 15 to 60 days of incubation. CO_3^{2-}ions decreased to 0.13-0.11 mgE. The SO_4^{2-} ion content increased to an average of 7.5 meq $100g^{-1}$, and Ca^{2+} ions increased compared to the control. Leaching did not significantly affect the HCO_3^- and CO_3^{2-} ion content.

Sulfuric acid, particularly at concentrations of 1%, 3%, and 5%, exhibited significant effects on the soil solution. After 15 days of incubation, HCO_3^- ions decreased to 0.45-0.56 meq $100g^{-1}$, and CO_3^{2-} ions dropped to 0.00-0.08 meq $100g^{-1}$. The SO_4^{2-} ion content increased to 10.42-14.87 meq $100g^{-1}$, and Ca^{2+} ions significantly increased compared to the control. Na^+ ions in the soil solution averaged 7.00 meq $100g^{-1}$ before leaching and decreased to 3.93-5.13 meq $100g^{-1}$ after leaching. Sulfuric acid effectively neutralized alkalinity, resulting in a rearrangement of the soil's ionic composition.

Overall, sulfuric acid demonstrated the highest effectiveness among the ameliorants, followed by elemental sulfur. Phosphogypsum exhibited the lowest effectiveness in terms of its impact on the soil's ionic composition. The findings highlight the ability of sulfuric acid to neutralize alkalinity, decrease HCO_3^- and CO_3^{2-} ion content, and increase SO_4^{2-} ion concentrations, leading to significant changes in the soil's chemical properties.

These results provide valuable insights into the mechanisms involved in the amelioration of saline-sodic soils and can guide the development of effective soil improvement strategies. However, further research and field studies are necessary to validate these laboratory findings and optimize their practical applications in soil reclamation and management.

The results of the experiment demonstrate that the application of phosphogypsum, elemental sulfur, nanosulfur, and sulfuric acid, as well as their incubation duration, have a significant impact on the ionic composition of the aqueous extract of soda-sulfate soil. This impact is particularly noticeable in the bicarbonate, carbonate, and sulfate ion content throughout the entire incubation period of the ameliorants in soda-sulfate soil. The introduction of ameliorants disrupts the equilibrium state of the soil's ion-salt system, which involves the salts of the solid phases of the soil and the soil absorbing complex. These solid phase components constantly interact with the soil solution and air.

The ionic composition analysis of the water extract from the soda-sulfate soil reveals that the application of phosphogypsum ($CaSO_4 \cdot 2H_2O$) increases the Ca^{2+} and sulfate ion content in the soil solution. Specifically, there is a noticeable difference between the PG2.0 variant and the control. It appears that Ca^{2+} in the soil solution interacts with the soil-absorbing complex (SAC) of the soda-sulfate soil, displacing absorbed sodium into the solution, and introducing Ca^{2+} into the SAC according to the reaction: $2(SAC - Na) + CaSO_4 \rightarrow (SAC - Ca) + 2Na_2SO_4$. This process leads to a significant increase in the displaced sodium content in the solution compared to the control (5.43 meq $100g^{-1}$), observed after 60 days of incubation with phosphogypsum (7.4 meq $100g^{-1}$). This difference is statistically significant (M=2.0). Since the reaction product is Na_2SO_4, which is readily soluble and toxic to plants, the Na^+ and SO_4^{2-} ion content decreased after leaching to 2.73, 3.55 and 3.75 meq $100g^{-1}$, and 2.95, 3.84, and 5.17 meq $100g^{-1}$, respectively, compared to the initial values before leaching. Another possible interaction of gypsum is with bicarbonates and sodium carbonates. The chemical reaction between $CaSO_4$ and Na_2CO_3 forms sparingly soluble calcium carbonates according to the equation: $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$. Despite noticeable changes, previous studies (Feofarova, 1950) suggest that the introduction of phosphogypsum reduces the initial rate of interaction with the soil on sulfate, especially in soda-alkaline soils, due to the coating of their crystal surfaces with a humus-clay-carbonate film.

The introduction of elemental sulfur powder and nanosulfur into soda-sulfate soil significantly increases the sulfate ion content. After 60 days of incubation, the sulfate ion content reaches 9.32-11.0 meq $100g^{-1}$ for elemental sulfur and 7.6 meq $100g^{-1}$ for nanosulfur, compared to 5.64 meq $100g^{-1}$ in the control. This indicates that a portion of the introduced elemental sulfur gradually transforms into its di- and trioxide forms with the involvement of sulfur-oxidizing microorganisms, following the scheme: $S° \rightarrow SO_2^{2-} \rightarrow SO_3^{2-}$. The trioxide form combines with water ($SO_3 + H_2O \rightarrow H_2SO_4$), resulting in the formation of sulfuric acid, an ideal ameliorant for alkaline soils. The reclamation process, which involves the conversion of alkaline salts (Na_2CO_3 and $NaHCO_3$) into neutral salts (Na_2SO_4, $MgSO_4$, and $CaSO_4$), occurs under mild conditions due to the gradual transformation of sulfur into sulfuric acid. The slight increase (~1.5-2 times) in the concentration of Ca^{2+} and Mg^{2+} ions can be attributed to the decomposition of carbonates during their interaction with the newly formed sulfuric acid, as described by the equation: $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$, resulting in the formation of a more soluble salt ($CaSO_4$ 0.2 g/l) from an insoluble one ($CaCO_3$ 0.02 g/l).

The application of sulfuric acid in the form of 1%, 3%, and 5% solutions induces significant changes in the ionic composition of the liquid phase of the soil. The sulfuric acid solution primarily reacts with the soil's liquid phase, instantaneously neutralizing alkaline sodium salts and converting them into neutral sodium sulfate (which is 10 times less toxic than Na_2CO_3), as shown in the reactions: $Na_2CO_3 + H_2SO_4 \leftrightarrow Na_2SO_4 + H_2O + CO_2\uparrow$ and $2NaHCO_3 + H_2SO_4 \leftrightarrow Na_2SO_4 + H_2CO_3 + H_2O + CO_2\uparrow$. This leads to a substantial decrease in the bicarbonate ion (HCO_3^-) content to 0.38-0.69 meq $100g^{-1}$, compared to 0.86 meq $100g^{-1}$ in the control (M=-0.4), thus reducing its toxicity and completely eliminating normal carbonate (CO_3^{2-}). Additionally, sulfuric acid reacts with carbonates in the solid phase of the soil, mainly calcium carbonate, converting it into a more water-soluble form, secondary subsoil gypsum, through the reaction: $CaCO_3 + H_2SO_4 \leftrightarrow CaSO_4 + H_2O + CO_2\uparrow$. This is supported by the increased sulfate ion content (M = 5.1 and M = 7.7) and calcium ion content (M = 2.6 and M = 4.4) in the solution of the SA3% and SA5% variants, respectively, compared to the control. The newly formed fine-crystalline gypsum dissolves and increases the calcium concentration in the soil solution, leading to a shift in the previously established balance between Ca^{2+} and Na^+. As a result, calcium in the solution helps displace the absorbed sodium from the SAC. Therefore, the most effective ameliorant is found to be the sulfuric acid solution, with increasing concentrations leading to faster attainment of equilibrium state between the pore solution and SAC, which occurs within less than a day. Amezketa et al. (2005) indicated that the addition of sulphuric acid was the most effective treatment in leaching and reducing salinity in comparison with gypsum amendments. However, the application of acidic amendments can lower soil pH, thus, their applications need some consideration.

Conclusion

In conclusion, the laboratory experiment conducted to assess the ameliorative efficiency of phosphogypsum, elemental sulfur, and sulfuric acid on soda-saline soils in the foothill plain of the Northern Tianshan region has provided valuable insights. Among the tested ameliorants, sulfuric acid solution demonstrated the highest effectiveness. Even at a 5% concentration, it was able to completely neutralize normal carbonates in the soil solution, effectively reducing soil alkalinity. The positive impact of sulfuric acid was observed as early as 15 days of incubation in the soda-saline soil. The introduction of sulfuric acid resulted in a significant decrease in bicarbonate and carbonate ion content after 60 days of incubation, while the sulfate ion content increased proportionally to the concentration of sulfuric acid, reaching levels of 8.12, 12.98, and 15.19 meq $100g^{-1}$. This increase in sulfate ions can be attributed to the interaction of sulfuric acid with calcium carbonates in the solid phase of the soil, leading to the formation of subsoil gypsum. The presence of subsoil gypsum facilitates the displacement of absorbed sodium from the soil-absorbing complex (SAC) by calcium ions. Similarly, the introduction of phosphogypsum also resulted in an increase in sodium ion content in the soil solution after 60 days of incubation, indicating the displacement of sodium from SAC by calcium ions.

The application of finely dispersed elemental sulfur in soda-sulfate soil significantly increased the sulfate ion content, reaching 11.0 meq $100g^{-1}$ compared to 5.64 meq $100g^{-1}$ in the control. This increase can be attributed to the oxidation of elemental sulfur to its di- and trioxide forms, with the latter combining with water to form subsoil sulfuric acid. The action of subsoil sulfuric acid is expected to be milder compared to directly introduced sulfuric acid.

The findings of this laboratory experiment contribute to a better understanding of the reclamation processes involved in the treatment of soda-saline alkaline soils. This knowledge provides a theoretical basis for the chemical reclamation of saline-sodic soils, which are prevalent in Kazakhstan and other regions worldwide.

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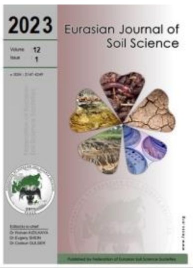

Biodiversity of symbiotic microbes in association with *Sulla aculeata* spp. from semi-arid regions of Morocco

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Abstract

Twenty-six root nodule bacteria from two native forage legumes namely *Sulla aculeolata* subsp. *aculeolata* and *Sulla aculeolata* subsp. *mauritanica* were isolated and analyzed using a polyphasic approach comprising phenotypic traits, ERIC-PCR, and 16S rRNA gene sequencing. This is the first time a study has been performed to determine the diversity of bacteria associated with *Sulla aculeolata* spp. Phenotypically, all the isolates were identified as fast-growing bacteria and shows high tolerance toward various stressed conditions, particularly those derived from *S. aculeolata* subsp. *mauritanica*. On the other hand, the genotypic characterization revealed high diversity among the isolated bacteria and clustered into 14 clusters at the similarity index of 90% based on ERIC-PCR analysis. Furthermore, the 16S rRNA gene sequencing of representatives strains indicates that all the strains share 99 to 100% identity with bacteria belonging to *Pseudomonas*, *Enterobacter*, *Serratia,* and *Paenibacillus* genera with a clear relation to their host plant. In conclusion, the findings of the present study suggested the inoculation of plants with appropriate bacteria to enhance plant growth and quality of *Sulla aculeolata* under semi-arid conditions of the Mediterranean area.

Keywords: Genotypic characterization, Root-nodule bacteria, *Sulla aculeata* spp.

Introduction

The genus *Hedysarum* spp., tribe Hedysareae, family Fabaceae is one of the most important temperate forage legumes in the Mediterranean region. The genus consists of various annual or perennial herbaceous species, recognizable by their distribution, morphology, genetic diversity (Boussaïd et al., 1995; Ben Fadhel et al., 2006), and ability to adapt to severely marginal and stress-prone environments (Gutierrez-Mas, 1983; Lupi et al., 1988; Abdelguerfi-Berrekia et al., 1991; Moore et al., 2006; Annichiarico et al., 2008) including drought stress (Lefi et al., 2023) and calcaro-saline soil (Jlassi et al., 2013; Tilaki et al., 2016; Tounsi-Hammami et al., 2016). Species such as *Sulla coronaria* L. and *Sulla flexuosa* L. have shown high quantities of green matter (Douglas and Foote, 1985; Chouaki et al., 2006), and good quality fodder (Issolah et al., 2014; Elyemlahi et al., 2019a). Therefore, they have been widely exploited as a forage crop to feed animals both in the pastoral and livestock sectors in several countries (Sulas and Ledda, 2008; Zirmi-Zembri and Kadi, 2021). The genus is also known for its ability to establish nitrogen-fixing symbiosis with soil bacteria (Kishinevsky et al., 2003; Elyemlahi et al., 2019b). However, only a few of them have been identified and characterized. In Morocco, this genus is represented by nine species (Fennane et al., 2007), including the endemic one such as *Sulla aculeolata* syn. *Hedysarum aculeolatum* (Amirahmadi et al., 2014). The plant is a diploide species, displayed an inter-population morphological polymorphism as a function of pedoclimatic variations (Kheffache and Combes, 1992). In addition, the species is known to harbor several genetically distinct bacteria in their root nodules, in relation to the geographical origin of the plants (Bezini et al., 2010). It has been stated that legume nodules in their wild status may be colonized by several endophytic bacteria (Benhizia et al., 2004; Muresu et al., 2019;

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Pang et al., 2021) from *Pseudomonas*, *Enterobacter*, and *Bacillus* genus (Peix et al., 2015), preferentially selected by legumes to cope with stressed environments (Ahemad and Kibret, 2014; Gamalero and Glick Bernard, 2015; Muresu et al., 2019). On other hand, several studies have shown that inoculation of legumes with appropriate bacteria had the advantage of improving crop yield and quality (Zhang et al., 2016; Li et al., 2022; Shome et al., 2022). In this framework, this research aimed to investigate the phenotypic and genotypic characteristics of the root nodules bacteria associated with two forage legumes namely *Sulla aculeolata* subsp. *mauritanica* and *Sulla aculeolata* subsp. *aculeolata* growing spontaneously in natural pastures located in the North of Morocco. Isolation and characterization of native bacteria populations could be a valuable biological resource when searching for biofertilizers that can help to reduce the use of chemical fertilizers while enhancing crop growth and quality.

Material and Methods

Plants sampling and bacteria isolation

The whole plant (leaves and stems) of *Sulla aculeolata* subsp. *aculeolata* and *Sulla aculeolata* subsp. *mauritanica* at the early flowering stage was assembled from two distinct sites located in the North of Morocco (Figure 1). Soil chemical and physical characteristics were showing in Table 1. The symbiotic efficiency of native rhizobia was estimated by recording the *in vivo* relative abundance of root nodules (Howieson and Dilworth, 2016), and nitrogen content using the Kjeldahl method.

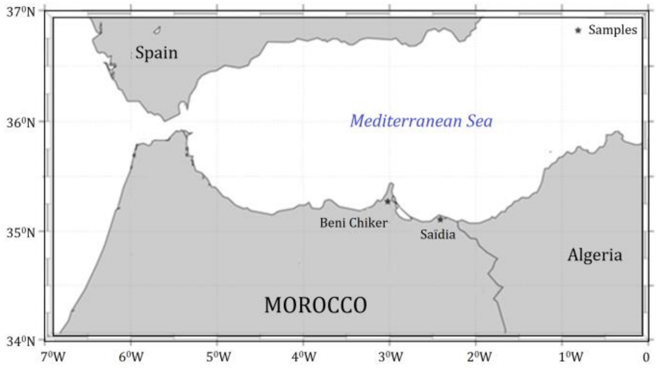

Figure 1. Location of sampling sites of *Sulla aculeolata* spp.

Table 1. Soil characteristics of the sampling site

	Beni Chiker	Saïdia
Slope	30°(NE)	0°
pH (water)	8.75	8.82
N, %	0.11	0.08
P_2O_5, ppm	5.13	6.21
K_2O, ppm	111.46	250.04
Organic Matter, %	2.00	0.60
$CaCO_3$, %	33.6	21.03
Clay, %	10.20	5.13
Fine silt, %	10.20	20.51
Coarse silt, %	4.14	17.33
Fine sand, %	27.45	35.18
Coarse sand, %	14.39	0.82

Bacteria isolation and purification

Bacteria were isolated from naturally *Sulla aculeolata* spp. root nodules as described by Ezzakkioui et al. (2015). The isolates were verified for purity by repeated streaking on YEM (Howieson and Dilworth, 2016) agar medium and Gram staining. Pure isolates were stored at -20°C using 50% glycerol until analysis.

Phenotypic characterization

Response to environmental stress conditions

The tolerance ability of different bacteria isolates to grow under stress conditions was inspected using YEM agar as a basic medium. The pH tolerance was examined by growing isolates on YEM agar medium adjusted to a pH range from 4 to 10. Heat tolerance was assessed by incubating strains at 28, 37, 40, and 42°C. Salt tolerance was tested on YEM agar medium containing different levels of NaCl (0.5%, 1% and 2%w/v). Finally, drought resistance was conducted in YEM broth using polyethylene-glycol 6000 (PEG 6000) as indicated by Busse and Bottomley (1989).

Utilization of carbon and nitrogen sources

All isolates were tested for their ability to utilize different carbon (Glucose, Sucrose, Maltose Fructose, Raffinose, and Lactose) and nitrogen (Asparagine, Histidine, NH_4NO_3, and KNO_3) sources, using modified YEM agar medium as described by Kishinevsky et al. (2003).

Intrinsic heavy metal and antibiotic resistance

Determination of intrinsic and heavy metals and antibiotic resistance were examined on a solid YEM medium containing the filter-sterilized in µl.mL^1: Spectinomycine (100), Chloramphenicol (150), Streptomycin (10), Kanamycin (10), Tetracyclin (50), Erythromycin (50), Ampicillin (100), $ZnCl_2$ (200), $CdCl_2$ (20), $CoCl_2.6H_2O$ (100), $HgCl_2$ (20), $AlCl_3.6H_2O$ (400), $CuCl_2.6H_20$ (100), and $MnCl_2.4H_2O$ (400).

Genotypic characterization

DNA extraction and ERIC-PCR fingerprinting

Total genomic DNA was extracted using the phenol/chloroform procedure as outlined by Chen and Kuo (1993). The quantity of DNA was ascertained by using a NanoDrop spectrophotometer (NanoDrop ND2000/2000c, Thermo Fisher Scientific). To assess the genotypic diversity among the isolates and to avoid any duplicates or clonality, ERIC-PCR (Enterobacterial repetitive intergenic consensus polymerase chain reaction) was performed using primers ERIC1R and ERIC2 according to Versalovic et al. (1991). Amplification was verified by horizontal gels electrophoresis (2%w/v agarose (Bioline) in Tris-acetic-EDTA buffer) at 70 V for 3 h, and finally photographed under UV light using the ENDUROTM GDS Gel Documentation System (Labnet International, Inc., US). Analyses of the ERIC-PCR profiles were carried out with GelCompar II software (version 2.5 Applied Maths, Belgium) using Dice similarity coefficient and UPGMA (Unweighted Pair Group Method with Arithmetic Averages) clustering method.

16S rDNA gene sequence and phylogenetic analysis

PCR amplification of 16S rRNA was performed using two universal primers fD1 and rD1 (Weisburg et al., 1991). Amplification products were firstly cheek by horizontal electrophoresis in 1% (w/v) agarose (Bioline) gels at 70V for 1 h, then purified using the purification system of Qiagen and finally subjected to cycle sequencing using the same primers as for PCR amplification. The sequences obtained were compared with those from the GenBank database, then corrected manually using MEGA 7 software (Kumar et al., 2016).

Results

Twenty-four strains were recovered from root nodules of *Sulla aculeolata* spp. and characterized as phenotypic and genotypic features. All strains were fast-growers and failed to absorb Congo red (RC) when incubated in YEM-RC agar plates. Some phenotypic properties are presented in Table 2 and 3.

Table 2. Nodulation and efficiency of *Sulla aculeata* spp. evaluated at different sites in Morocco.

	Infectivity[1]	Nodule color	Nodule size	Aerial dry matter (%)	Nitrogen content (%)
Sulla aculeolata subsp. *aculeolata*	Ample	Brown	Small	18.25±0.48	2.23±0.23
Sulla aculeolata subsp. *mauritanica*	Extremely abundant	Pink to brown	Big	36.28±1.13	2.20±0.25

[1] using the chart proposed by (Howieson and Dilworth, 2016).

Physiologically, all the isolates were capable to grow at 37°C, or when incubated in presence of 0.5% of NaCl (Table 3). Most of them grow at a pH range from 4.00 to 9.00 independently of their origin-soil pH (Table 1). By contrast, most of them were sensitive to high temperatures, where three isolates from *Sulla aculeolata* subsp. *mauritanica* were able to grow at 42°C, and only those from the same species were capable to tolerate high salinity level (up to 2%w/v). Furthermore, the evaluation of intrinsic resistance to heavy metals showed that all of the isolates were more endurable and exhibited the highest tolerance to manganese (up to 400 µl.mL^{-1}), and most of them tolerate cadmium and zinc (Table 3). However, only those from *Sulla aculeolata* subsp. *mauritanica* resisted copper and five isolates from the same plant grown in presence of cobalt. Finally, all the isolates appear sensitive toward aluminum and mercury, except one isolate from *Sulla aculeolata* subsp. *aculeolata* (Table 3). In compliance with these results, the evaluation of antibiotic sensibility showed that the majority of the isolates from *Sulla aculeolata* subsp. *mauritanica* were resistant to the tested antibiotic, while those from *Sulla aculeolata* subsp. *aculeolata* were highly sensitive to most antibiotics except for Streptomycin and Ampicillin (Table 3). By the same token, drought resistance shows that 27% of the isolates from *Sulla aculeolata* subsp. *aculeolata* were highly tolerant and able to grow at a water potential of – 0.25 MPa, while, more than 78% of the isolates from *Sulla aculeolata* subsp. *mauritanica* survived at the same water potential. However, only 14% of isolates from *Sulla aculeolata* subsp. *mauritanica* were capable to grow at – 0.5 MPa and none of the isolates tolerate PEG-induced drought stress set to -1 MPa (Figure 2).

Table 3. Phenotypic characterization of root-nodule bacteria of Sulla aculeata spp.

	Sulla aculeolata subsp. *aculeolata*	*Sulla aculeolata* subsp. *mauritanica*
Strain	(n=12)	(n=14)
Growth at temperature		
37°C	+	+
40°C	1	+
42°C	-	3
Growth at pH		
4	+	+
5	+	+
8	+	+
9	10	+
NaCl tolerance		
0,5 %	+	+
1 %	1	+
2 %	-	+
Carbohydrate assimilation, 1%		
Sucrose	+	3
Fructose	5	3
Maltose	7	13
Glucose	7	-
Lactose	-	12
Raffinose	+	4
Utilization of nitrogen sources, 0.1%		
Histidine	2	4
Asparagine	-	1
KNO_3	1	+
NH_4Cl	2	+
Antibiotic sensibility, µl.mL^{-1}		
Chloramphenicol (150)	-	11
Spectinomycin (100)	-	9
Streptomycin (10)	+	9
Tetracyclin (50)	-	9
Erythromycin (50)	-	+
Ampicillin (100)	8	13
Kanamycin (10)		
Heavy metal resistance, µl.mL^{-1}		
Zinc (200)	11	12
Cadmium (20)	8	12
Cobalt (100)	-	5
Mercury (20)	1	-
Aluminum (400)	-	-
Copper (100)	-	12
Manganese (400)	+	+

(+): positive growth; (-): no growth and numbers indicate the number of positive strains

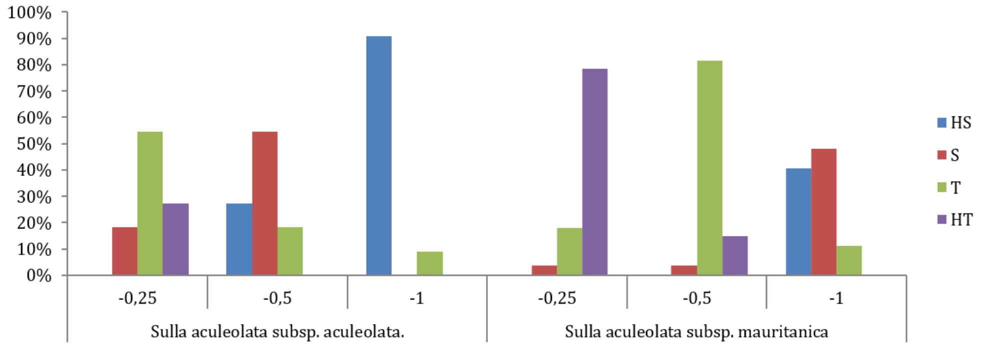

Figure 2. Effect of different water potential levels (-0.25; -0.5 and -1MPa) on growth percent of root nodule bacteria of *Sulla aculeolata* spp. HS: highly sensitive (DO<0.5); S: sensitive (DO=0.3-0.4); T: tolerant (DO=0.4-0.5); TT: highly tolerant (DO>0.5).

Finally, the metabolic properties (Table 3) of *Sulla aculeolata* spp. root-nodule isolates disclose great variations among the strains. In this regard, the majority of the strains from *Sulla aculeolata* subsp. *aculeolata* appear able to use a large range of carbohydrates as the sole carbon source for growth, except lactose, preferentially Sucrose and Raffinose. While the isolates from *Sulla aculeolata* subsp. *mauritanica* were unable to grow in a Glucose-based medium, and only 3 and 4 (out of 14) isolates used Sucrose and Raffinose respectively. In addition, all the isolates were greatly inhibited in presence of Asparagine and Histidine as nitrogen sources, and only isolates from *Sulla aculeolata* subsp. *mauritanica,* except for 2 and 1 isolates from *Sulla aculeolata* subsp. *aculeolata,* were able to use respectively NH_4Cl and KNO_3 for growth.

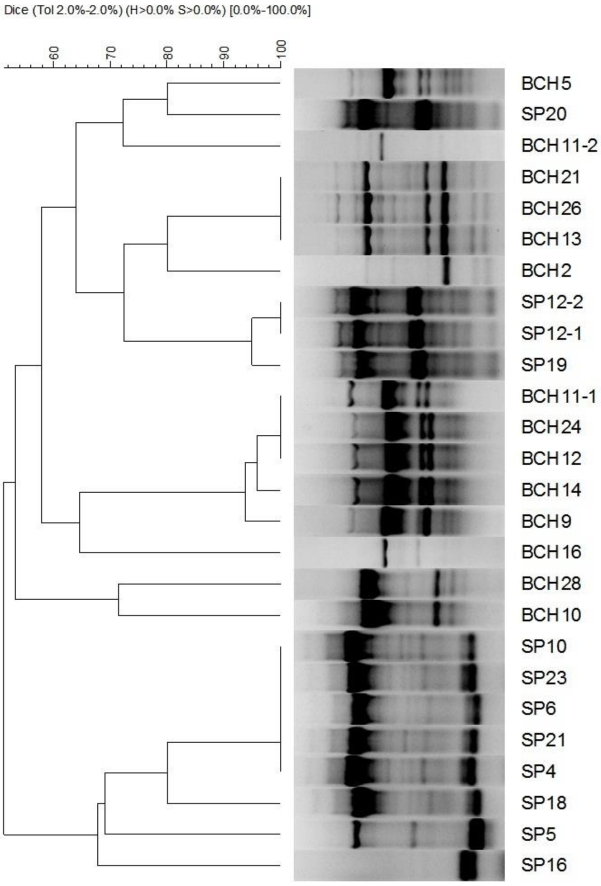

Figure 3. Dendrogram generated by UPGMA clustering from ERIC-PCR fingerprinting of 26 bacterial strains isolated from *Sulla aculeolata* spp. BCH: *Sulla aculeolata* subsp. *mauritanica* and SP: *Sulla aculeolata* subsp. *aculeolata*.

From a genetic perspective, the 26 indigenous bacteria isolated from root nodules of *Sulla aculeata* spp. were first examined for their genetic diversity using ERIC-PCR analysis. Results revealed a high level of genetic divergence among studied strains and form 14 distinct groups at 90% of similarity according to their host plant (Figure 3). Furthermore, analysis of the 16S rRNA gene sequence from the representative isolates originated from each ERIC-PCR pattern and their comparison with the sequences retained in the GenBank database showed that the majority of strains belonged to *Pseudomonas, Enterobacter,* and *Paenibacillus* genera, depending on their host plant (Table 4).

Table 4. Molecular identification of representative root nodules bacteria associated with *Sulla aculeata* spp. based on 16S rDNA sequence analysis.

Host plant	Strain	Closest related bacteria[1]	Sequence Similarity (%)
Sulla aculeolata subsp. *mauritanica*	BCH16	*Pseudomonas* sp. BT1	100
	BCH10	*Serratia plymuthica* strain IHB B 12183	99.80
	BCH5	*Pseudomonas* sp. BSP24	100
	BCH24	*Pseudomonas moraviensis* strain SP9	99.80
	BCH2	*Enterobacter* sp. BSP12	99.93
	BCH13	*Enterobacter hormaechei* strain AUH-ENM30	99.87
Sulla aculeolata subsp. *aculeolata*	SP6	*Pseudomonas frederiksbergensis* strain DSM 13022	99.61
	SP4	*Pseudomonas frederiksbergensis* strain DSM 13022	99.74
	SP12-1	*Pseudomonas thivervalensis* strain SBK26	99.58
	SP5	*Paenibacillus polymyxa* strain DSM 36	99.87

[1] determined using the BLAST algorithm (http://blast.ncbi.nlm.nih.gov/Blast.cgi/).

Discussion

In the Mediterranean basin, *Hedysarum* spp., widely Known as Sulla (Choi and Ohashi, 2003), are an important component in many ruminant diets. Those groups of forage legumes establish symbiosis with indigenous soil microorganisms such as mycorrhizal fungi (M'Saouar et al., 2020), reputable for their mineral absorption enhancement under several environmentally stressed conditions (Labidi et al., 2012; 2015), and rhizobial bacteria with high Plant Growth Promoting Rhizobacteria (PGPR) activity (Achkouk et al., 2018; Hamane et al., 2020). Within this framework, two Sulla species, namely *Sulla aculeolata* subsp. *aculeolata* and *Sulla aculeolata* subsp. *mauritanica* (native to Morocco), located in northern Morocco, were harvested and analyzed for symbiotic diversity of native soil bacteria that colonized their root nodules. Primary results (Table 1) show the occurrence of *Sulla aculeolata* spp. on calcareous silty soil, rich in potassium and total limestone and poor in nitrogen and phosphoros. Similar findings were reported by Ionesco and Stéfanesco (1967); Abdelguerfi-Berrekia et al. (1991); Hannachi-Salhi et al. (2002) who indicated the occurrence of *Sulla aculeolata* spp. in a very limited distribution area in scrub and pasture zones at low altitudes, on sloping sandy-clayey to clayey soils moderately watered, under the sub-humid and semi-arid climates of Morocco and Algeria.

From a symbiotic point of view, the on-field survey (Table 2) of examined leguminous species showed great productivity (up to 36.28% of dry matter in the case of *S. aculeolata subsp. mauritanica*) and high nitrogen content (in mean: 2.21%), comparable with others species evaluated under field conditions within the genus *Hedysarum* (Fitouri et al., 2012; Elyemlahi et al., 2017). A particular result was linked to the capacity of the species to establish a specific nitrogen-fixing symbiosis with soil bacteria known as rhizobia.

In this study, the phenotypic analysis of the 24 sampled isolates of both *Sulla aculeolata* spp. subspecies revealed a high degree of variation toward a large set of stressful treatments such as salinity, drought, and heavy metals, in concordance with previously reported root nodules isolates of *Sulla spinosissuma* L. (Oubohssaine et al., 2022), and *Sulla pallida* Desf. (Hamane et al., 2020) from the mining sites of the northeast region of Morocco and *Sulla aculeolata* spp. growing wild in Algerian soils (Bezini et al., 2010). Such results indicate a possible adaptation of those isolates to prevailing growth conditions and allow the selection of strains with ecological important traits. Indeed, molecular characterization of representative isolates, shows they belong to different bacterial genera (Table 4), however, no clue of the occurrence of rhizobia species. Similar findings were advanced by Benhizia et al. (2004), who reported no evidence of any rhizobial-like strains isolated from root-nodules of wild *Hedysarum* species, which could be related to the putative oxidative stress caused during bacteria isolation (Muresu et al., 2013).

Some of those strains such as *Enterobacter hormaechei*, *Serratia plymuthica*, *Pseudomonas frederiksbergensis,* and *Paenibacillus polymyxa* have been previously isolated from the root-nodules of different legume species such as *Hedysarum carnosum* Desf. (Muresu et al., 2008), *Sphaerophysa salsula* Pall. (Deng et al., 2011), *Glycine max* L. (Annapurna et al., 2013), *Phaseolus vulgaris* L. (Kawaka et al., 2018), and *Lupinus* (Ferchichi et al., 2019), usually regarded as plant growth promoter rhizobacteria (PGPR) (Hamane et al., 2020). Therefore, they were preferentially selected by the host plants as they can promote not only plant growth and health but also nodulation and N availability in sustainable agriculture systems under stress conditions including drought stress (Benhizia et al., 2004; Muresu et al., 2019; Hanaka et al., 2021).

On the other hand, it was reported that inoculation by some of those root nodule non-rhizobial endophytic bacteria such as *Pseudomonas frederiksbergensis* isolated from root nodules of *Sulla aculeolata* subsp. *aculeolata*, has been proven to be an effective inoculant for enhancing plant abiotic stress tolerance (Subramanian et al., 2015; Chatterjee et al., 2017). Bacteria like *Pseudomonas* sp. BT1 isolated from root nodules of *Sulla aculeolata* subsp. *mauritanica*, was identified as a barophilic bacterium (up to 60MPa), can be used for plant inoculation under drought-stress environments (Kaneko et al., 2000). While, other bacteria such as *Paenibacillus polymyxa* are demonstrated in their ability to increase organic dry matter digestibility and forage quality (Zayed et al., 2020).

Conclusion

The present study provides the first characterization of root nodules bacteria associated with two forage legumes i.e. *Sulla aculeolata* subsp. *aculeolata* and *Sulla aculeolata* subsp. *mauritanica* growing wild in natural pastures located North of Morocco. From an applied point of view, the leguminous species chosen for this survey are appropriate for revegetation and soil-restoration of degraded pasturelands. Furthermore, the inoculation of *Sulla aculeolata* spp. with appropriate bacteria resistant to water stress would ensure root nodulation and improve plant performance under semi-arid conditions of the Mediterranean area. However, further study should be conducted, under a controlled environment, to determine the main microsymbiot of *Sulla aculeolata* spp.

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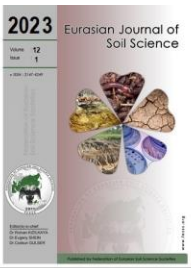

Morphologic and chemical characterizations of some salep orchids

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Abstract

Salep orchids have been used as a food for centuries without cultivating but, mainly harvesting from nature. After powdering, their tubers are utilized as hot beverage and in ice-cream industry as a stabilizer. Due to their importance in food industry, it is important to characterize the morphology and chemistry of salep orchids. In this study, it was aimed to determine some morphological (fresh weight, dry weight and dry matter ratio of tubers and the number of tubers required for 1 kg salep powder) and chemical (glucomannan, starch, protein, moisture, ash, nitrogen, phosphorus, calcium, magnesium, potassium, iron, copper, manganese and zinc contents and glucomannan/starch ratio of tubers) properties of 10 salep orchid species from 6 genus namely, *Anacamptis pyramidalis*, *Dactylorhiza romana*, *Himantoglossum caprinum*, *Himantoglossum comperianum*, *Ophrys apifera*, *Ophrys mammosa*, *Orchis coriophora*, *Orchis morio*, *Orchis tridendata*, *Serapias vomeracea* grown in nature of Black Sea Region of Türkiye. Such a kinds of data is the first and can be beneficial in utilizing the researched species in food industry.

Keywords: Mineral contents, Orchidacea, sahlep, terrestrial orchids, tuber.

Introduction

The Orchidacea family is the second one that has the highest number of species, naturally grown in many diversified habitats of the world. This family consists of terrestrial, tropical, epiphytic and lithophilic species and is one of the most biologically complex taxon of the plant kingdom (Swarts and Dixon, 2009). Terrestrial orchids are naturally distributed in temperate climatic regions and many species of this group form a tuber under the ground. Tubers of those orchids have been used as food, healing agents and aphrodisiac for centuries. Tuberous orchids, which are widely used in India, Nepal, China, Turkey, the Middle East, Europe and other temperate regions of the world, are called salep orchids (Farazi et al., 2013; Bozdoğan and Yaşar, 2016; Tığlı and Fakir, 2017). Some species are widespread throughout the world, while others adapted to the climate and soil structure of each region and altitude differences and therefore spread in certain areas. In other words, the areas where salep orchids grow are different due to their ecological demands on a species basis.

Today, Salep is largely collected in Asia Minor, Germany, Greece, Iran, Afghanistan and India (Turgay and Cinar, 2017). It is not possible to mention the total collected amount of tubers as they are not domesticated and are mainly obtained by wild-crafters. Many species from 10 different genera are used in the production of salep in Turkey. The number of salep orchids in Turkish flora is indicated as 38 to 60 (Sezik, 2002; Tamer et al., 2006; Kreutz, 2009).

Salep, which has been consumed fondly for centuries as a hot beverage due to its medicinal properties, is also an indispensable raw material in the production of Maraş type ice cream (Kasparek and Grim, 1999; Kurt and Kahyaoglu, 2017). The history of salep goes back thousands of years. In Historia Plantarum, Theophrastus (372-286 BC) attributed medicinal properties to orchid species, and in De Materia Medica Dioscorides (50-70

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AD) ascribed healing properties were ascribed to two terrestrial orchids based on the resemblance of their tubers to testicles (Kreziou et al., 2015). In traditional medicine, salep has been prescribed for dressing and treating glottal inflammations and intestine disorders, tuberculosis, diarrhea, parkinson, cancer, fever, and is especially used to strengthen the sexual activity, erectile dysfunction therapy, physical strength enhancement and increase vigorousness (Thakur et al. 2009; Tekinşen and Güner, 2010; Farazi et al., 2013; Pourahmad et al., 2015; Atashpour et al., 2017; Tatiya et al., 2018).

The main components of salep tubers are glucomannan and starch both of which are carbohydrate derivative (Farhoosh and Riazi, 2007). Besides, salep contains different compounds such as nitrogenous substances, protein, particularly calcium, potassium, iron, chlorides and phosphates, and some trace levels of volatile oils, ferulic acid, quercetin, daucosterol, cirsilineol and steroids. The most important factor that affects chemical composition and quality is the species of orchids from which salep powder is produced. Ecological conditions of plant habitat also affect the chemistry and quality of salep (Hossain, 2011; Lalika et al., 2013). Glucomannan is a polysaccharide formed by the binding of β-D-glucose and α-D-mannose molecules with β-1,4 bonds (Yaşar et al., 2009). One gram of glucomannan is capable of absorbing 200 ml of water. Doi (1995) reported glucomannan can absorb up to 50 times its weight in water, making it one of the most viscous dietary fibers known. With this feature, glucomannan gives consistency to salep drink, which is a hot beverage. It gives hardness and late melting properties to Maraş type ice cream and also delays the melting time of ice cream.

Salep orchids are taken under protection around the world due to the fact that they are collected from nature without cultivation (Dixon et al., 2003). The international trade of naturally grown plants in the world is regulated by the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES), which was put into practice for the first time in 1976. This convention has been signed by 183 countries. The European Union (EU), on the other hand, put into practice the conditions required by the CITES contract with the Council Regulation No. 3626/82, which entered into force in 1984 (Jenkings and Oldfield, 1992). Annex I of this regulation defines the endangered orchid species whose trade is prohibited. All salep species, except those in Annex-I, are included in the CITES Annex-II list (Yaman, 2013).

Despite all the prohibitions, the collection of salep tubers from the natural flora continues today. It is not known exactly how much salep is collected, as it is the product that is collected from nature without cultivating. However, it is estimated that around 500 tons of salep tubers are collected annually throughout Turkey, 80-100 tons of salep flour is obtained by drying and grinding them, used in ice cream production and consumed as a beverage (Caliskan et al., 2019, 2020).

In the present study, it was aimed to determine the morphological features and chemical properties of the tubers of some salep orchids (*Anacamptis pyramidalis* (L.) Rich., *Dactylorhiza romana* (Sebast.) Soo, *Himantoglossum caprinum* (M.Bieb.) Spreng., *Himantoglossum comperianum* (Steven) P.Delforge, *Ophrys apifera* (Huds.), *Ophrys mammosa* (Desf.), *Orchis coriophora* (L.), *Orchis morio* (L.), *Orchis tridendata* (Scop.) and *Serapias vomeracea* (Burm.f.) Briq.) grown wildly in the nature of Central Black Sea Region, Türkiye. This study could be the first report on tuber morphology, mineral element composition and chemical content of the tested species.

Material and Methods

The research was carried out in the Central Black Sea region, within the borders of Samsun province. The total area of studied region is 1055 km^2 and the altitude of sampling sites varies from 0-1500 m causing high diversity in salep flora. The districts, altitudes and coordinates for plant-growing sites are shown in Table 1. In this region, which has a rich flora in terms of the diversity of salep orchids, field trips were made in March-June and samplings were done.

Table 1. Geographical data for sampling sites where the tested salep orchids were collected

Species	District *	Altitude (m)	Latitude (N)	Longitude (E)
Anacamptis pyramidalis (L.) Rich.	Yakakent	132	41° 62′ N	35°51′ E
Dactylorhiza romana (Sebast.) Soo.	Bafra	192	41° 47′ N	35° 91′ E
Himantoglossum caprinum (M.Bieb.) Spreng.	Bafra	1011	41° 37′ N	35° 54′ E
Himantoglossum comperianum (Steven) P.Delforge	Bafra	1005	41° 39′ N	35° 58′ E
Ophrys apifera (Huds.)	Çarşamba	248	41° 09′ N	36° 64′ E
Ophrys mammosa (Desf.)	Bafra	8	41° 64′ N	35° 92′ E
Orchis coriophora (L.)	Ondokuzmayıs	1	41° 66′ N	36° 05′ E
Orchis morio (L.)	Ladik	740	41° 55′ N	36° 07′ E
Orchis tridendata (Scop.)	Ondokuzmayıs	208	41° 45′ N	36° 03′ E
Serapias vomeracea (Burm.f.) Briq	Çarşamba	49	41° 23′ N	36° 05′ E

*Samsun province in Turkey.

Required legal tuber collection permission was obtained before the study. The number of species in the region is more than twenty, but rare species were ignored. With this purpose the common wild-growing species namely, *Anacamptis pyramidalis* (L.) Rich., *Dactylorhiza romana* (Sebast.) Soo, *Himantoglossum caprinum* (M.Bieb.) Spreng., *Himantoglossum comperianum* (Steven) P.Delforge, *Ophrys apifera* (Huds.), *Ophrys mammosa* (Desf.), *Orchis coriophora* (L.), *Orchis morio* (L.), *Orchis tridendata* (Scop.) and *Serapias vomeracea* (Burm.f.) Briq were sampled to obtain 10 gram of dry sample for each species.

The fresh weights of tubers collected from natural flora were determined after washing and cleaning. The tubers were boiled in hot water at 110-120°C for 6-8 minutes and left to dry. By dividing the fresh and dry weights by the number of tubers, the average single tuber weight and the number of tubers required to obtain one kilogram of dry salep were calculated. Thus, data for tuber size and morphology were obtained. The dried and powdered samples were objected to chemical analyses to determine their macro and micro nutrients contents as detailed below.

Total moisture, protein and ash contents

The gravimetric method was used to determine moisture the content at 105°C. Dried plant samples were ground to powder size before analysis. Ash contents of plant samples were determined in a muffle furnace at 550°C for 24 h. Protein content was determined according to the Kjeldahl method based on the nitrogen conversion factor of 5.7. For P contents by spectrophotometric method, for K, Ca, Mg, Fe, Mn, Zn, and Cu contents using atomic absorption spectrophotometer (AOAC, 2000; Kacar and Inal, 2008).

Glucomannan and starch contents

Glucomannan (1) (K-GLUM 12/19) and starch (2) (K-TSTA 11/20) assay kit purchased from Megazyme International Ireland Ltd. was used to determine glucomannan and starch content of salep samples. Absorbance values of prepared blank and sample solutions were measured to determine the glucomannan and starch contents of the samples using a UV-Vis Spectrophotometer at 340 nm for glucomannan and 510 nm for starch. The following formulas were used to calculate the contents (Megazyme, 2004a,b):

$$\Delta \mathrm{Aglucomannan} = (\mathrm{A3} - \mathrm{A1})\mathrm{sample} - (\mathrm{A3} - \mathrm{A1})\mathrm{blank} \times 36.8\ [\mathrm{g}/100\mathrm{g}] \quad (1)$$

where A1 and A3 were the measured absorbance values of prepared blank and sample solutions for glucomannan at the end of reaction approximately after 3 min and 20 min, respectively.

$$\mathrm{Starch} = \Delta \mathrm{A} \times \mathrm{F}/\mathrm{W} \times 9.18\ [\mathrm{g}/100\mathrm{g}] \quad (2)$$

where

ΔA = absorbance value of sample solution against reagent blank after 50°C for 20 min incubation
W = the weight of the sample
F = (100 (μg of glucose control)) / (Absorbance value of glucose control (1.111))

Data analysis

Data for morphological and chemical tuber characters for each species tested were objected to one-way analysis of variance (ANOVA) and significant differences among mean values were tested with the Duncan Multiple Range Test (P<0.01) by using the statistical software package XLSTAT2010 Trial Version.

Results and Discussion

Morphological characters

The tubers of salep orchids are divided into two groups in terms of morphological appearance. The *Dactylorhiza* genus, which has palmate tuber shape and is called footed or fingered, is in one group, while other oval-shaped genera are in the other group. As shown in Figure 1, *D. romana* which is one of the tested species is always recognized with two bulges, formed on lower part of its tuber. Tuber shape is oval, close to round or narrow oval for the other tested genera. Variations in tuber shape have been attributed to genetic factors, varied with species (Aybeke, 2012; Kurt, 2020). Fresh and dry tuber weights of the tested species are shown in Table 2. The number of tubers, required to obtain 1 kg dry salep was calculated based on tuber dry weights.

As shown in Table 2, *Himantoglossum comperianum* produced the highest values for fresh and dry tuber weights (9.09 and 0.32 g, respectively), while *Orchis morio* tubers had the lowest dry and fresh weights (2.35 and 0.32 g, respectively). Interestingly, mean values of tuber fresh weight were lower than 3 g for *Dactylorhiza romana* and *Ophrys mammosa* together with *Orchis morio*, thus these species can be characterized as small tuberous ones. As for dry matter ratio of tubers, mean values varied from 13.6-22.3% depending on species. As in the cases of fresh and dry tuber weights, *Orchis morio* produced the lowest tuber dry matter ratio, but this character reached its highest levels in *D. romana* (22.1%), *O. coriophora* (22.3%) and *S. vomeracea* (22.2%). It is noteworthy to note that *H. caprinum* and *H. comperianum* which have large tubers also produced lower dry matter ratio when compared to the other tested species. Based on the data, presented in Table 2, it can be concluded that about 7 kg of the fresh tuber is required approximately to obtain 1 kg of dry salep.

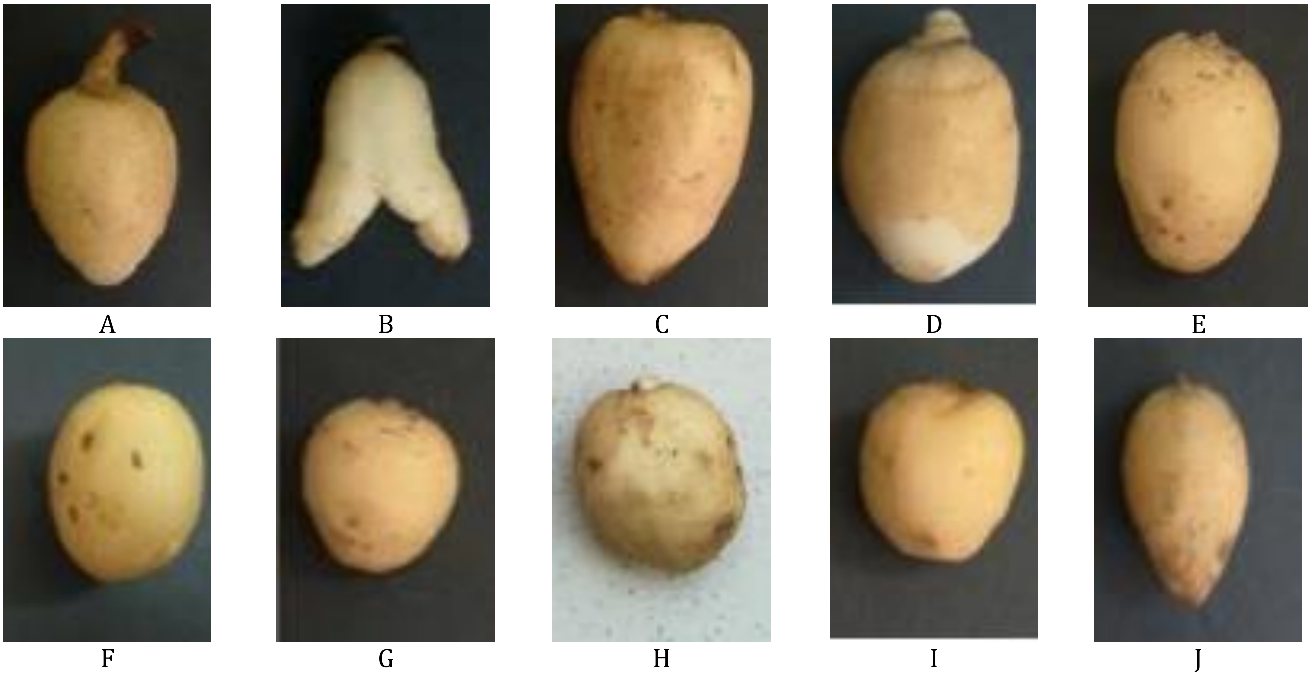

Figure 1. Views from tubers of the studied orchid species. A; *Anacamptis pyramidalis* (L.) Rich., B; *Dactylorhiza romana* (Sebast.) Soo, C; *Himantoglossum caprinum* (M.Bieb.) Spreng., D; *Himantoglossum comperianum* (Steven) P.Delforge, E; *Ophrys apifera* (Huds.), F; *Ophrys mammosa* (Desf.), G; *Orchis coriophora* (L.), H; *Orchis morio* (L.), I; *Orchis tridendata* (Scop.) and J; *Serapias vomeracea* (Burm.f.) Briq.

Table 2. Some morphologic characters of the tubers of salep orchids tested

Species	Fresh tuber weight (g /tuber)	Dry tuber weight (g /tuber)	Dry matter ratio (%)	The number of tuber required to obtain one kg salep powder
Anacamptis pyramidalis (L.) Rich.	5.88	1.16	19.8	859
Dactylorhiza romana (Sebast.) Soo.	2.99	0.66	22.1	1516
Himantoglossum caprinum (M.Bieb.) Spreng.	6.00	0.88	14.7	1134
Himantoglossum comperianum (Steven) P.Delforge	9.09	1.32	14.5	757
Ophrys apifera (Huds.)	3.20	0.64	20.0	1565
Ophrys mammosa (Desf.)	2.55	0.40	15.8	2488
Orchis coriophora (L.)	3.11	0.69	22.3	1445
Orchis morio (L.)	2.35	0.32	13.6	3139
Orchis tridendata (Scop.)	4.18	0.83	19.9	1201
Serapias vomeracea (Burm.f.) Briq	2.40	0.53	22.2	1877

Ghorbani et al. (2014) reported that 1 kg of salep is produced from 4-8 kg of fresh tubers, depending on plant age, species and harvest time. They also reported that the number salep tubers, required to obtain one kg dry salep is 605±219 for *Dactylorhiza* genus and 1117±236 for other species. Here we observed that one kg dry salep could be produced from 1516 salep tubers for *D. romana*. The fresh weight of single tuber in *Anacamptis sancta* was 4.9 g (Parlak, 2016). In a previous study, conducted out on Bucak district of Burdur province, fresh tuber weight was reported to be 1.17 g for *Orchis mammosa*, 1.04 g for *Orchis anatolica,* 16.8 g for *H. comperianum*, 1.7 g for *Ophrys rein* subsp. *leucotaenia*, 1.57 g for *Ophrys amanensis* subsp. *antalyensis* and 1.65 g for *Orchis palustris* (Tığlı and Fakir, 2017). As in our case, *O. mammossa* was characterized as small tuberous, but *H. comperianum* as large tuberous one in this previous report. Quantitative differences, however, between the present and previous results could be ascribed the evidently different ecological conditions of plant habitats as the two sampling areas are separated by a distance of 850 km and Bucak district of Burdur province has higher temperature and precipitation values.

The number of tubers to be used to obtain ready-to-eat salep flour is a reflection of the wet tuber weight and dry matter ratios. We observed a great variation for the number of tuber required to obtain 1 kg salep powder varying with 757-3139 depending of the species tested. While producing salep powder by using dry tubers, a loss of 3% occurs. Considering this loss, it appears that the number of tuber required to obtain 1 kg salep powder, in fact, is higher than that of our detection for many of species. This number was reported to be 1000-4000 (Sezik, 2002) and 1000-4350 (Lande, 1998) without indicating the orchid species used. Here, it is the first time we have reported the number of tuber required to obtain 1 kg salep powder for each species which has practical meaning in evaluating the tested species in food industry and protecting the wild plant populations.

Chemical characters

In the present study conducted out on a total of 10 species from 6 genera, we also observed a great variation in the chemical characters of tubers as in the case of morphologic ones (Table 3). Especially, starch, protein and glucomannan contents of tubers varied significantly with species. We detected a twofold difference between the lowest and highest starch contents (21.09% for *S. vomeracea* and 42.16% for *H. comperianum* % 42.16) and a more than threefold difference between the lowest and highest glucomannan contents (9.68% for *O. mammossa* and 32.54% for *A. piramidalis*) of tubers. Our current data are not in accordance with the previous ones in literature. Starch and glucomannan contents of tubers were reported to be 5.44-38.7% and 17.7-54.6% respectively, depending on species (Tekinşen and Güner, 2010). Sen et al. (2019) reported starch and glucomannan contents of six salep orchids to be 12.24-40.21% and 7.84-43.67%, respectively. Glucomannan content of five salep orchids from south eastern part of Anatolia was reported to vary with 29.47-59.63% namely, 30.13% for *O. lutea*, 59.63% for *S. vomeracea*, 28.60% for *O. mammosa*, 30.17% for *O. umbilicata* and 29.47% for *O. sancta* (Ertaş et al., 2019). The general opinion is that genetic factors are the main factor determining the chemical content of salep species. In addition, environmental factors of plant growing habitat are also indicated to affect the chemical content of orchid tubers (Sen et al,. 2019). Arabacı et al. (2017), for example, reported that starch and glucomannan contents of *Serapias vomeracea* tubers varied significantly with plant developmental stages. In our case, plants were sampled at the end of flowering period.

Table 3. Starch, glucomannan, protein and moisture contents and glucomannan / starch ratio of the tubers of salep orchids tested

Species	Starch (%)	Glucomannan (%)	Glucomannan / starch ratio (%)	Protein (%)	Moisture (%)
Anacamptis pyramidalis (L.) Rich.	21.34 d	32.54 a	1.52	3.25 de	10.93 a
Dactylorhiza romana (Sebast.) Soo.	28.09 c	21.20 c	0.75	4.82 b	8.65 de
Himantoglossum caprinum (M.Bieb.) Spreng.	29.04 c	15.64 d	0.53	3.15 e	8.41 e
Himantoglossum comperianum (Steven) P.Delforge	42.16 a	10.32 e	0.24	7.83 a	9.06 cde
Ophrys apifera (Huds.)	39.66 b	11.74 e	0.30	4.58 bc	9.22 b-e
Ophrys mammosa (Desf.)	41.24 ab	9.68 e	0.23	4.87 b	9.75 a-d
Orchis coriophora (L.)	22.69 d	26.95 ab	1.18	3.99 cd	10.53 ab
Orchis morio (L.)	21.75 d	23.79 bc	1.09	3.97 cd	9.98 abc
Orchis tridendata (Scop.)	40.93 ab	13.48 e	0.32	5.19 b	10.25 abc
Serapias vomeracea (Burm.f.) Briq	21.09 d	30.52 a	1.45	2.43 e	9.71 a-d
CV (%)	2.12	8.54	-	7.37	5.24

Results from the limited number of previous studies revealed a negative relationship between starch and glucomannan contents of salep orchids' tubers as confirmed by our present results. The most important quality character of salep tubers is their glucomannan content which is crucial for hot beverage and ice-cream production and a high ratio is desirable. Thus, glucomannan/starch ratio was supplied for each species tested and presented in Table 3. Such kind of data could be useful for further evaluating the tested species in food industry.

Protein contents of the tested species varied from 2.43-7.83% and we observed 2-3-fold differences among mean values. The protein content of tubers was reported to be 3.17-4.95% (Tekinşen and Güner, 2010) and 2.70-11.93% (Sen et al. 2018) for other salep orchids. The protein content of orchid tubers has been affected by several factors such species, soil characteristics and climatic peculiarities. For example, protein content of *Serapias vomeracea* tubers which is one the most prevalent and studied species was reported to be 4.83% (Tekinşen and Güner, 2010), 2.70% (Sen et al., 2019), 12.9% (Arabacı et al., 2017) and 11.2% (Kurt and Kahyaoglu, 2017).

Our present results are within the scope of literature data together with some insignificant differences. For example, protein content of *Orchis tridendata* tubers was reported as 4.94% by (Tekinşen and Güner, 2010) while we detected it as 5.95%. The same authors also reported this value to be 4.95% for *Orchis morio*, but we found it to be 3.97%. Glucomannan contents of the tested orchids exhibited a greater variation when compared to results of the previous studies on the same species. Tekinşen and Güner (2010) reported glucomannan content of *O. mammosa* tubers as 17.7%, but we detected as 9.68%. There is indeed a big difference between these data but it should be noted that the lowest glucomannan content was produced by the same species, *O. mammosa,* among the tested salep orchids in both studies. Based on the present and previous results, it can be concluded that chemical content of salep orchids are affected not only by soil and climatic factors but also genetic ones. Harvesting time, of course, is another factor affecting chemical content of tuber. Likewise, Arabacı et al. (2017) reported that starch content of *Serapias vomeracea* was 14.01% at the beginning of blooming but 21.41% at full blooming in two consecutive years. We detected starch content of the same species as 21.09%.

Ash ratio is regarded as a quality character for salep orchids and this criterion varied significantly with species in the present study. *Himantoglossum caprinum* (2.86%) and *Himantoglossum comperianum* (2.67%) produced the highest ash content while the lowest value for this criteria was supplied by *Orchis tridendata* (0.93%) (Table 4). Türkmen (2019) reported ash ratio of *Anacamptis. pyramidalis, Orchis. mascula, Ophrys apifera, Dactylorhiza majalis, Serapias lingua, Platanthera. grandiflora, Himantoglossum hircinum, Ophrys sphegodes, Habenaria repens, Platanthera chlorantha* tubers to be 1.42-3.37%. As for the nitrogen content of tuber, we detected no significant difference among the tested species and it is noteworthy to note that this criterion does not affect the on quality of salep powder. On the contrary, the moisture and ash contents are important in terms of storage and detecting the adulteration. To store the salep tubers for a long time, the amount of moisture should be less than 10%, and the amount of ash should be less than 5% in order to obtain white salep flour (Sezik, 2002; Karaman et al., 2012).

Table 4. Mineral contents of the tubers of salep orchids tested

Species*	Ash (%)	N (%)	P (%)	Ca (%)	Mg (%)	K (%)	Fe (ppm)	Cu (ppm)	Mn (ppm)	Zn (ppm)
A	1.90 c	0.95 b	0.120 de	0.125 d	0.058 bcd	0.495 de	66.55 f	39.13 d	6.99 e	38.06 b
B	1.28 d	1.05 b	0.118 de	0.071 f	0.047 d	0.374 fg	115.89 d	109.89 a	12.40 cd	106.13 a
C	2.86 a	1.03 b	0.134 de	0.097 e	0.065 b	0.526 cd	190.32 a	44.34 d	23.85 b	46.30 b
D	2.69 a	1.56 a	0.210 b	0.152 c	0.100 a	0.662 a	64.81 f	97.82 ab	10.74 de	111.31 a
E	2.37 b	0.99 b	0.170 c	0.193 b	0.106 a	0.584 bc	202.64 a	50.95 cd	12.20 cd	42.38 b
F	1.88 c	1.53 a	0.240 a	0.099 e	0.064 cb	0.619 ab	169.45 b	46.35 d	13.50 cd	49.05 b
G	2.32 b	0.72 c	0.171 c	0.334 a	0.097 a	0.473 de	86.22 e	24.95 e	10.67 de	25.40 b
H	1.79 c	0.98 b	0.109 e	0.099 e	0.045 d	0.440 ef	60.95 f	60.46 c	16.11 c	63.65 ab
I	0.93 e	0.95 b	0.119 de	0.160 c	0.069 b	0.573 bc	138.31 c	92.00 b	11.40 cde	74.35 ab
J	1.25 d	0.88 bc	0.138 d	0.188 b	0.051 cd	0.319 g	112.28 d	48.03 d	61.30 a	39.59 b
CV (%)	6.89	9.63	8.85	5.67	10.79	8.57	9.28	12.44	14.81	5.88

*A; *Anacamptis pyramidalis* (L.) Rich., B; *Dactylorhiza romana* (Sebast.) Soo, C; *Himantoglossum caprinum* (M.Bieb.) Spreng., D; *Himantoglossum comperianum* (Steven) P.Delforge, E; *Ophrys apifera* (Huds.), F; *Ophrys mammosa* (Desf.), G; *Orchis coriophora* (L.), H; *Orchis morio* (L.), I; *Orchis tridendata* (Scop.) and J; *Serapias vomeracea* (Burm.f.) Briq.

To the best of our knowledge, no study has been done on mineral content of salep orchids, except for *Dactylorhiza romana* P, Ca, K and Mg contents of which were reported to be 0.170, 0.152, 0.734 and 0.066% respectively. Fe, Mn, Cu and Zn contents of the same species were detected to be 117.62, 12.91, 4.05 and 13.85 ppm, respectively (Palaz et al., 2018). We also determined similar Fe and Mn contents but somewhat different contents of the rest minerals in the present study for *D. romana*. Mean values for mineral contents of the tested salep orchids are shown in Table 4. Mineral contents varied significantly by species and were doubled between the lowest and highest N, P and K contents; we observed a four-fold difference for the Zn content and a nine-fold difference for the Mn content. These evident differences in the mineral contents of tubers could be attributed mainly to soil characters and genetic factors because results from the studies on plant nutrition and soil productivity indicated that mineral contents of plant species depend greatly on the presence of available mineral matter contents in soils. Considering the size of sampling area (1055 m^2), soil characters of plant habitats are greatly different, and the type and amount of minerals, taken from the same soil are significantly different and depend greatly on plant species and genotypes. Mineral contents of the tested species here are reported for the first time.

Conclusion

Salep orchids, which are widely distributed in the temperate zone, have a rich diversity with tens of genera and hundreds of species. Salep orchid species have always been important medicinal plants from historical times to the present. For this reason, they have been illegally collected from the natural flora and offered to the market for hundreds of years. A large number of tissue culture studies are carried out on species around the world and production possibilities are tried to be improved. However, the morphological and chemical characteristics of the species are not known enough. For example, how many salep tubers need to be collected to produce one kg of salep flour is presented here for the first time on a species basis. According to the tuber size and dry matter ratio of the species, this number varied between 757-3139. The mineral content of salep tubers was revealed for the first time in this study. *Himantoglossum caprinum* (M.Bieb.) Spreng. and *Himantoglossum comperianum* (Steven) P.Delforge have the highest ash content. The most important component in salep orchids is glucomannan. It is understood that the glucomannan ratio varies greatly according to the species. *Ophrys mammosa* (Desf.) had the lowest glucomannan ratio (9.68%). The highest glucomannan ratio is in *Anacamptis pyramidalis* and *Serapias vomeracea* (Burm.f.) Briq species (32.54-30.52 %). There is more than a threefold difference in glucomannan content between the species considered. A similar situation is observed when few sources are examined on the chemical content of salep species. A large number of tissue culture studies are carried out on species around the world and production possibilities are tried to be improved. In future studies, tuber chemical content should be taken into account for the food industry, and it will be important to concentrate the research on species with high glucomannan and protein content.

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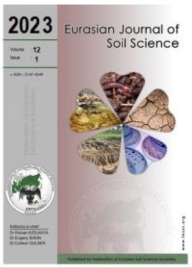

Evaluation of thermal properties of soils amended with microplastics, vermicompost and zeolite using experimental and modeling data

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Abstract

The thermal properties of soils can be influenced by additives of different origins (non-organic, organic and mineral) and roles in soil quality. This study aims to evaluate the effects of microplastics, vermicompost, and zeolite on the thermal properties of two soil types using a combination of experimental data and modeling approaches. Laboratory experiments were conducted using surface layer samples of a clay soil (Vertic Phaeozem) and a loam soil (Haplic Cambisol). Each additive was applied at a mass ratio of 10% to the soil samples. The thermal conductivity (λ), thermal diffusivity (D) and volumetric heat capacity (C_v) were measured with the SH1 sensor of a KD2Pro device during the drainage process of the soil samples at different matric potentials. The relationships between λ, C_v, D, gravimetric water content, and matric suction (h) were analyzed using linear and polynomial regression models (for C_v and D) and a closed-form equation (for λ). The fitted models exhibited small errors, such as a root mean square error (RMSE) of 0.03-0.06 W m^{-1} K^{-1}, and high coefficient of determination R^2>0.9. The effects of the different additives on water retention, λ, C_v and D were found to be specific to each soil type and depended on the properties of both the soil and the additives. These findings highlight the significance of additives in modifying soil thermal properties and emphasize the importance of considering the interactions between soil characteristics and additive properties. The combination of experimental data and modeling approaches provides valuable insights into understanding the complex dynamics of soil thermal properties and the potential impacts of additives on soil functionality and quality.

Keywords: Microplastics, thermal conductivity, thermal diffusivity, vermicompost, volumetric heat capacity, zeolite.

Introduction

The additives in soils can be purposely applied for improvement of soil quality or casually disposed which can cause soil contamination and deterioration of soil properties. Most popular soil ameliorants which are used in agricultural practice are the vermicompost, biochar, zeolites, etc. Unlike the ameliorants, the microplastics (MPs) (plastic fragments <5 mm) are principally non-degradable, inactive pollutants.The MPs can occur in soil due to improper storage of packages and other plastic materials during the agricultural operations. The distribution and migration of the MPs in soils, their extraction from soils, and the ecological effects of the microplastic pollution were subject of an increased scientific interest (Rubio et al., 2016; Qi et al., 2020 etc.; He et al., 2018). The heat transfer in semicrystalline and amorphous polycarbonate (PC) polymers was studied by direct measurement with a KD2Pro device (Rubio et al., 2016; Rubio and Rodríguez, 2017; Wiśniewska and

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Rubio, 2020). The obtained results (Rubio et al., 2016) indicated that the semicrystalline polymers transferred the heat flow better than the amorphous polymers. The addition of the polymer (Moplen polypropylene homopolymers with filler of Scott pine shavings) into a Fluvisol provoked a decrease of its thermal conductivity (λ) (Doneva and Rubio, 2015).

The zeolites and vermicompost are applied in soil as conditioners. The application of zeolites to the soil acts as slow release fertilizers, heavy metal removers, soil conditioners, and leads to increasing of the nutrient and water use efficiency and crop yield (Jakkula and Wani, 2018). Dilkova et al. (1982) found that the natural zeolite had significant quantity of micropores of size less than <0.2 μm and the effect of 10% and 20% applications on plant available water capacity (PAWC) of a silty clay loam soil (Kastanozem) depended on the size of the zeolite fractions. The fragments with sizes less than 0.5 mm had a positive effect on PAWC, while the larger fragments (0.5-5 mm) provoked a reduction in PAWC and an increase of the aeration pores. Such effect of increased air-filled large pores was observed when applying a single fraction of biochar, especially of large (>5 mm) fraction of biochar, while the mix of different size fractions had higher bulk density, λ and D (Usowicz et al., 2016). Katsarova (2021) reported a positive effect of 10% zeolite concentration on the plant available water holding capacity of a loam soil (Fluvisol).

Goswami et al. (2017) reported that the vermicompost amendment shifted the soil pH toward neutrality and the presence of organic matter increased the soil total porosity. The organic matter eventually increased the water holding capacity and aggregation of soil particles (Song et al., 2015). The results (Shein and Mady, 2016) showed that the lowest values of λ and D were at the highest value of organic matter, because organic matter leads to increase of macro pores volume and soil total porosity.

The additives can change the soil bulk density and water retained at different suctions and correspondingly can influence the soil thermal properties. Usowicz et al. (2016) studied the effect of biochar derived from wood off cuts on the soil bulk density and soil thermal properties. They found that the increase in λ and D with the soil water content was greater in soil with higher rather than lower bulk density. Shein and Mady (2016) also found that the largest values of λ and D were corresponding to the largest values of soil bulk density.

The dependence of thermal properties on the varying volumes of soil constituents can be described by experimental data and models (de Vries, 1963; Campbell et al., 1994; Ochsner et al., 2001a; Usowicz, 1992; Lu et al., 2019). According to Lu et al. (2019) the use of soil matric suction rather than volumetric water content (θ) enables more robust and transferable comparisons across soils of different textures. Some models allowed to derive an inverse information on the soil bulk density by the measured data of the volumetric heat capacity or thermal conductivity and water content (Ochsner et al., 2001b; Lu et al., 2016). The soil thermal diffusivity at different water content was estimated from easily available data on soil texture, bulk density, and organic matter content (Mady and Shein, 2018). It was concluded that the best results for D were received when was taken into account the percentage of sand, silt, and clay (soil texture). Wessolek et al (2023) validated ten well established pedo-transfer functions for predicting λ by using easily available soil information such as soil texture, bulk density, and water content. The authors compared measured vs. predicted results and concluded that reliable pedo-transfer models are the de Vries model, and the Brakelmann approach.

The aim of this study was to assess the impact of additives of varying origins (non-organic, organic, and mineral), characteristics, and purposes on the thermal properties of clay and loam soils. This was achieved by comparing experimental data obtained at different matric suctions with model outputs. Additionally, the study aimed to investigate the changes in thermal properties of soils following the addition of microplastics, vermicompost, and zeolite.

Material and Methods

The soil samples were taken in May 2020 from the surface 0-20 cm horizon of - a Vertic Phaeozem (S1), under grassland from the experimental field Gorni Lozen (42.63°N, 23.46°E, 585 m a.s.l) and - a Haplic Cambisol (S2), arable land, from the experimental station of potatoes in Samokov (42.34°N, 23.54°, 945 m a.s.l.). After the bulk soil samples were air-dried, grounded and sieved through 2 mm openings, these soil samples were used for the basic soil analyses and for preparing the studied variants. The soil particle-size distribution was determined by sieving and the pipette method (ISO 11277: 2009). The texture classes and soil names were determined according to IUSS Working Group WRB (2022). The total soil organic carbon content (SOC, %) was determined by the modified Tjurin's method (Kononova, 1963; Filcheva and Tsadilas, 2002). The estimate of soil organic matter (SOM) content was done by multiplying of SOC with the Van Bemmelen's conventional factor of 1.724. The acidity of soil was measured by a pH meter in a 1:2.5 soil-water suspension. The mineralogical composition of the soil fractions >63 μm and <63 μm were determined after organic matter removal by X-ray diffraction analysis (XRD) by D2 PHASER (Bruker).

The investigation of soil thermal properties at different matric water suctions was conducted on the intact soil cores in metal rings of 100 cm^3 taken from the fields and on the artificially repacked in laboratory conditions soils and mixtures. The mixtures were maintained for 6 months at 75% of Field Capacity (FC) by periodically wetting of the samples in order to facilitate the aggregates formation between the soil particles and the additives. Then the repacking of the air-dried samples (soil and mixtures) in metal rings of 100 cm^3 volume (d=5.1 cm, h=4.9 cm) was done with 1.2 cm increments and compacting in order to achieve uniform bulk density. The mass of the samples was estimated to achieve a desired soil bulk density (ρ_b) taking into account the bulk densities of the intact soil cores sampled under grassland for S1 (1.47 g cm^{-3}) and in the arable soil layer for S2 (1.15 g cm^{-3}). The laboratory experiment comprised four variants for soils S1 and S2 each performed in two replicates: controls (repacked soil, no additive), mixtures of soil plus 10% by mass of: Polycarbonate (PC) polymer, product Makrolon 2407 produced by Bayer Material Science; Polymethyl methacrylate (PMMA) polymer, product PLEXIGLAS 8N produced by Evonik Industries; vermicompost (V), produced by "Biotor" Ltd; and zeolite (Z), produced by "Bentonite" JSC, respectively. The particle size of PC and PMMA was about 2 mm and for the zeolite it was between 0.8-2.5 mm. The natural zeolite was obtained from the Beli plast deposit, Kardjali region. The density values were 1.20 and 1.19 g cm^{-3} for PC and PMMA, respectively. The measured particle density (ρ_s) of vermicompost was 1.98 g cm^{-3} and of zeolite 2.37 g cm^{-3}.

The particle densities of additives and soils were measured in pycnometers filled with water. The total porosity (*Pt*, %) was calculated using the measured ρ_b and ρ_s ($Pt=[(\rho_s-\rho_b)/\rho_s]\times 100$).

The samples in the 100 cm^3 rings were preliminary capillary wetted at suction 0.25 kPa (pF0.4) on a sand bath during more than 20 days. The gravimetric water content (W) at suctions less than 33 kPa (pF 2.5) was determined during drainage of the wetted samples using a suction type apparatus (Shot filters G5 with diameters of pores 1.0-1.6 μm) connected with a hanging column for suctions 1, 5, 10 kPa and with a vacuum chamber for 33kPa. The method is similar to the methods described in ISO 11274: 1998. Equilibrium for each suction was established for 5–7 days. Then the samples were left for air-drying by natural evaporation at room temperature and periodically weighed for determining the soil wetness reduction and corresponding soil thermal properties measurements. At the end of the analyses the soil cores were oven dried at 105°C in order to estimate the mass of dry samples and calculate W and ρ_b. A similar procedure was applied in other studies (Usowicz et al., 2013; Markert et al., 2017; Lu et al., 2019). The gravimetric water content at suction 1500 kPa (pF 4.2 – Wilting Point, WP) and the hygroscopic soil water content (Wh), corresponding to pF 5.6 were determined on fine earth samples in three replicates using correspondingly the pressure membrane apparatus (ISO 11274:1998) and the vapour-pressure method in desiccators containing saturated solution of NaCl for maintaining 75% relative air humidity. The measurements of thermal properties of the studied samples were conducted with the SH-1 sensor of a KD2Pro device (Decagon Devices Inc., Pullman, USA). The sensor was placed vertically in the center of the metal cylinders and after 15 minutes interval for achieving equilibrium the thermal properties were measured. The thermal conductivity (λ), volumetric heat capacity (C_v), and thermal diffusivity (D) were measured at each suction pF (pF=$\log_{10}$(|-cm H_2O|) with parallel gravimetric measuring of the soil water content. The conducted measurements were 7 to 12 for each sample.

The water retention experimental data at different suctions were approximated by the closed-form equation of van Genuchten (1980) in order to assess the water potentials corresponding to the water contents measured during the air-drying stage of the experiment:

$$W=(W_{sat}-W_{res})\times[1+(\alpha\times h)^{n}]^{-(1-1/n)}+W_{res} \quad (1)$$

where W is the gravimetric water content (kg kg^{-1}), h is the suction (hPa), W_{sat} is the water content at saturation, W_{res} is the residual water content (h→∞), α (hPa^{-1}), and n are the fitted parameters.

Unlike Lu and Dong (2015) who used the closed-form equation for approximating the relationship λ-θ, we used this type of equation to describe λ-h relationship:

$$\lambda=(\lambda_{sat}-\lambda_{dry})\times[1+(\alpha^{*}\times h)^{n^{*}}]^{-(1-1/n^{*})}+\lambda_{dry} \quad (2)$$

where λ is the thermal conductivity (W m^{-1} K^{-1}), h is the suction (hPa), λ_{sat} is λ at saturation, λ_{dry} is the dry soil thermal conductivity (h→∞), α^* (hPa^{-1}), and n^* are the fitted parameters.

The parameters of the closed form equations W_{sat}, W_{res}, α, n, λ_{sat}, α^*, and n^* (Eqs. 1, 2) were fitted with statistical non-linear regression analysis method of the OriginPro 6.1. Stable results for the parameters were obtained when the parameter W_{res} in Eq. 1 was fixed to zero in cases with estimated negative values. The parameter λ_{dry} in Eq. 2 was calculated by a linear relationship proposed by (Lu et al., 2007) between dry soil thermal conductivity (λ_{dry}) and soil total porosity (Pt).

$$\lambda_{dry} = -0.56 \times Pt + 0.51 \tag{3}$$

The volumetric heat capacity (C_v) was modeled by the additive model of de Vries (1963):

$$C_v = C_s \times \rho_b/\rho_s + 4.18 \times \theta/100 \tag{4}$$

where ρ_b and ρ_s are the soil bulk and particle densities; θ is the volumetric water content $\theta = W \times \rho_b$; W – gravimetric water content, C_s – volumetric heat capacity of the solids. C_s was calculated according to de Vries (1963) taking into account the proportions of solid constituents (minerals, soil organic matter, and additives), their specific heat capacity c_s and the soil particle density.

The variability of soil bulk density due to the effect of expansion and shrinkage at different water contents was estimated based on the heat capacity approach (Ochsner et al., 2001b):

$$\rho_{b\ calc} = C_{ve}/(C_s/\rho_s + 4.18 \text{ x } W/100) \tag{5}$$

The measured thermal diffusivity ($D = \lambda/C_v$) is compared with the ratio of modeled λ and C_v.

The performance of the models was estimated by the coefficient of determination R^2 and the root mean square error (RMSE):

$$\text{RMSE} = (\Sigma(x_e - x_m)^2/\text{N})^{1/2} \tag{6}$$

where N is the number of data points, x_e and x_m are the estimated and measured values, respectively.

Results and Discussion

The studied soils differed with respect to their soil texture. Nearly half of the particles of the Vertic Phaeozem (S1) had the size of clay (<0.002 μm) while the Haplic Cambisol (S2) was dominated by the sand fraction (>0.063 mm) (Table 1).

Table 1. Soil texture fractions, soil organic carbon content (SOC) and hygroscopic water content (Wh)

Soil variety	Sand (2-0.063 mm), %	Silt (0.063-0.002 mm), %	Clay (<0.002 mm), %	Texture class	SOC, %	Wh,%
Vertic Phaeozem (S1)	12	40	48	clay	0.92	6.63±0.03
Haplic Cambisol (S2)	46	32	22	loam	1.10	2.81±0.03

The finer texture of S1 explained the higher hygroscopic water content (Wh at pF5.6) compared to S2. The soil organic carbon content (SOC) was 0.92% and 1.10%, respectively for S1 and S2 (Table 1), which corresponded to 1.6% and 1.9% soil organic matter content. The main minerals determined by XRD are presented in Table 2.

Table 2. XRD mineralogical composition (%) of sand (>0.063 mm) and silt+clay (<0.063 mm) fractions and volumetric heat capacity of the minerals (C_v) after de Vries (1963)

Minerals	S1		S2		C_v,
	>0.063 mm	<0.063 mm	>0.063 mm	<0.063 mm	MJ m^{-3} K^{-1}
Quarz (SiO_2)	18.0	24.6	29.2	13.2	2.13
Plagioclase [$(Na,Ca)(Si,Al)_4O_8$]	29.5	29.9	32.7	26.8	2.64
K-feldspar ($KAlSi_3O_8$)	22.6	14.7	13.2	16.9	2.08
Muscovite {$KAl_2[AlSi_3O_{10}](OH)_2$}	23.2	20.4	19.2	31.7	2.52
Amphibol {$Ca_2[Mg_4(Al,Fe)]Si_7AlO_{22}(OH)_2$}	6.8	4.9	1.4	5.2	2.61

The content of quartz was differently distributed among the particles' fractions in S1 and S2. Taking into account the proportions of the sand in the bulk soil, it can be estimated that S1 and S2 contained correspondingly 2% and 13% quartz in the sand-sized particles. As the XRD analyses were not performed separately on the clay fraction, the quartz content in the fraction below 0.063 mm for S1 may be overestimated, but the presence of this mineral in all particle size fractions has to be taken into consideration.

The clay soil (S1) was slightly acidic while the loam soil (S2) was strongly acidic. The vermicompost had very slightly alkaline reaction (pH 7.42) and zeolite had slightly alkaline reaction (pH 7.79) which explained the increase of pH of the mixtures (Table 3).

The soil particle densities (ρ_s) are typical for the mineral soils with low organic matter content (Table 3). The particle densities of the vermicompost (1.98 g cm^{-3}) and zeolite (2.37 g cm^{-3}) caused decrease of ρ_s of the mixtures. The target bulk density (ρ_b) of the repacked soils was close to the intact soil cores taken from the field, which was 1.47 g cm^{-3} under grassland for S1 and 1.15 g cm^{-3} in the arable soil layer for S2. This resulted in about 10% higher Pt of S2 than of S1 at the time of repacking of the air dried soil samples (Table 3).

Table 3. Characteristics of the studied variants at repacking: clay soil (S1), loam soil (S2) and mixtures with additives: microplastics (PC and PMMA), zeolite (Z) and vermicompost (V)

Parameter	S1	S1+PC	S1+PMMA	S1+V	S1+Z	S2	S2+PC	S2+V	S2+Z
Bulk density (ρ_b, g cm^{-3})	1.46	1.43	1.43	1.47	1.51	1.15	1.16	1.19	1.21
W at repacking, %	4.90	4.40	4.70	6.70	5.20	2.30	2.00	3.50	2.60
Particle density (ρ_s, g cm^{-3})	2.71	2.56	2.56	2.64	2.68	2.69	2.50	2.58	2.62
Total porosity (*Pt*, %vol.)	46.10	44.00	44.10	44.10	43.40	56.50	53.80	54.00	53.90
pH in H_2O	6.38	6.43	6.41	6.68	6.64	4.49	4.50	5.92	4.77

The approximated by Eq. 1 soil water retention curves of the intact soil cores as taken from the field and on the repacked control samples are presented in Figure 1.

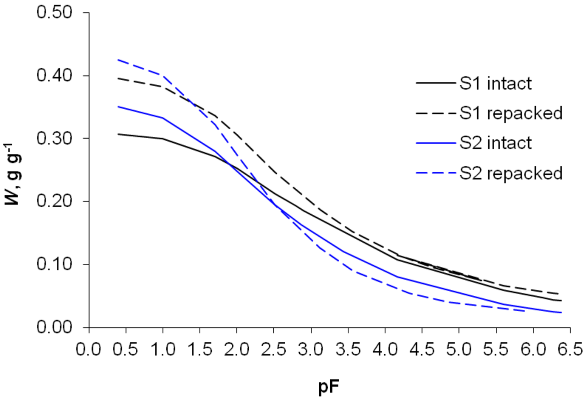

Figure 1. Approximated by Eq. 1 soil water retention curves (SWRC) of the intact soil cores taken from the field and of the repacked soils used as control variants in the laboratory experiment

The water held in micropores was similar for the intact and repacked soil samples, while the water held in the mesopores at suctions less than pF 2.5 depended on the aggregates arrangement and compactness and differed significantly between the intact and repacked samples. The finer textured S1 was characterized with a higher content of capillary pores (pF>2.5) than the medium textured S2. The fitted parameters of the van Genuchten equation (Eq. 1) for the repacked controls and mixtures are presented in Table 4 and the SWRCs are drawn in Figure 2.

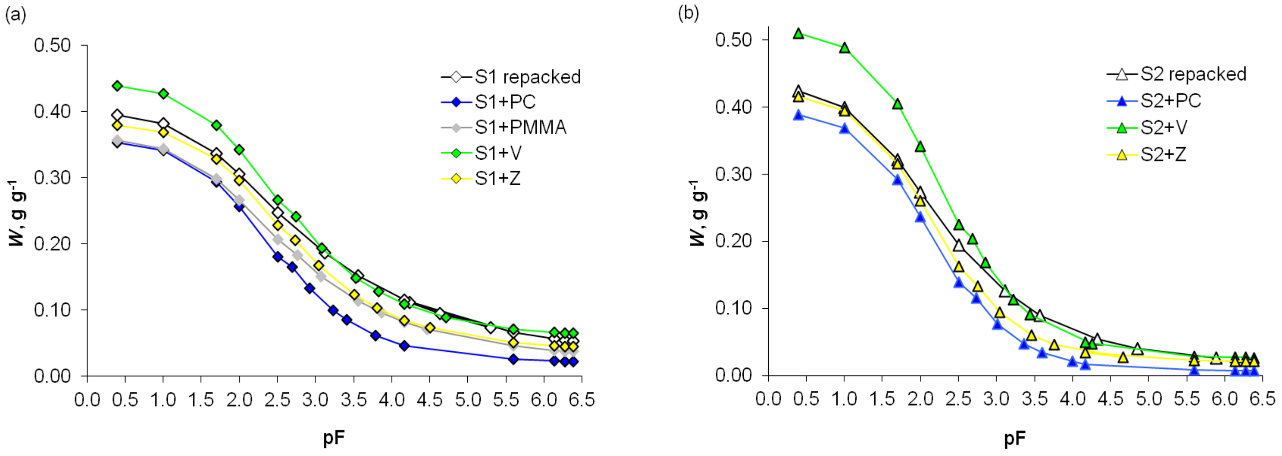

Figure 2. Soil water retention curves (SWRC) approximated by van Genuchten model (Eq. 1) for the studied repacked variants of Vertic Phaeozem, S1 (a) and Haplic Cambisol, S2 (b)

The addition of the microplastics (PC, PMMA) to the studied soils decreased *W* values throughout the whole range of suctions (Figure 2). At the wet end (pF<2.5) the relative decrease of W was better pronounced for S1+PC and S1+PMMA (from 8% to 14%) than for S2+PC (from 2% to 8%). The zeolite addition did not change significantly the water retained at pF<2.5 for both soils. The largest increase of *W* was observed in the variants with vermicompost. At field capacity (pF 2.5) the relative increase of *W* was 27% for S1+V and 44% for S2+V. These results corresponded to Khosravi Shakib et al. (2019) who concluded that the addition of vermicompost to the substrate improved the water retention capacity.

The calculated volumetric heat capacity of soils solids *Cs* for S1 and S2 (Table 5) were close to the often cited value of 2.4 MJ m^{-3} K^{-1} (Campbell and Norman, 1998).

Table 4. Fitted parameters of Eq. 1, RMSE - root mean square error

Parameter	S1	S1+PC	S1+PMMA	S1+V	S1+Z	S2	S2+PC	S2+V	S2+Z
W_{sat} (g g^{-1})	0.400	0.357	0.361	0.443	0.383	0.434	0.396	0.519	0.425
W_{res} (g g^{-1})	0.030	0.021	0.027	0.058	0.039	0.017	0.007	0.026	0.021
α (hPa^{-1})	0.022	0.010	0.018	0.011	0.01	0.024	0.011	0.011	0.012
n	1.255	1.511	1.324	1.394	1.396	1.387	1.713	1.595	1.657
RMSE (g g^{-1})	0.021	0.021	0.010	0.017	0.014	0.019	0.035	0.036	0.033

Table 5. Calculated volumetric heat capacity of solids (C_s, MJ m^{-3} K^{-1})

Variant	Vertic Phaeozem (S1)	Haplic Cambisol (S2)
S	2.361	2.345
S+10% PC	2.258	2.245
S+10% PMMA	2.275	
S+10% vermicompost	2.508	2.491
S+10% zeolite	2.338	2.324

The addition of both types of microplastics (PC, PMMA) decreased this value by 0.1 MJ m^{-3} K^{-1}, the vermicompost increased it by 0.15 MJ m^{-3} K^{-1}, while the zeolite almost did not influence it. The C_v at given soil moisture content differed between the studied soils due to the difference in the initial soil bulk density observed under the grassland in case of S1 and of the arable soil (S2). The estimated bias between S1 and S2 of the predicted C_v (Eq. 4) was 0.23 MJ m^{-3} K^{-1} (Figure 3).

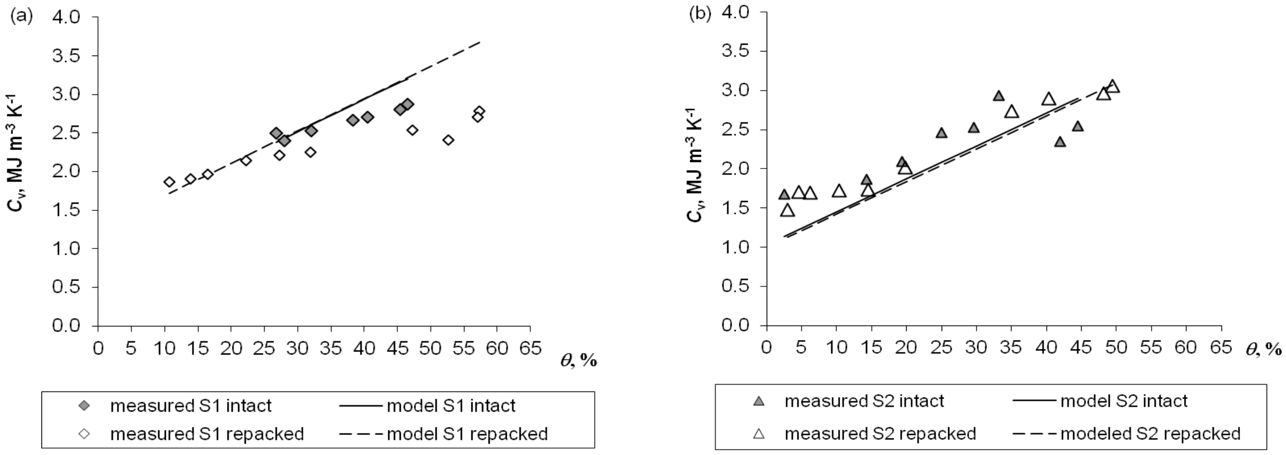

Figure 3. Measured and estimated (Eq. 4) volumetric heat capacity (C_v, MJ m^{-3} K^{-1}) versus volumetric fraction of water content (θ, % vol.) for S1 (a) and S2 (b)

The experimental data obtained on the intact and repacked samples scattered around the model predictions in a different manner for both soils (Figure 3). In the clay soil (S1) the measured C_v values were lower than predictions at soil water content above 22%vol. for the repacked samples and above 32%vol. for the intact samples. The experimental data for S2 were higher than predicted values except at near saturation. Kodešová et al. (2013) reported variable line slopes of the linear regressions between the measured C_v and θ. The authors obtained mostly higher slopes for this relationship than the value of 4.18 MJ m^{-3} K^{-1} (heat capacity of water, Eq.4) for the representative soils of the Czech Republic. In our experiment this can be explained with changes of soil bulk density of the samples during the wetting and air drying processes. This hypothesis was tested by the reverse calculation of ρ_b, so-called the C-approach (Ochsner et al., 2001b) using the measured C_v (Eq. 5) and C_s of solids as determined by the solid constituents (Table 5). The calculated ρ_{bcalc} are presented in Figure 4.

The decreasing of calculated ρ_{bcalc} with increasing of the soil water content in S1 was less pronounced on the intact samples and most evident in the mixture with PMMA (Figure 4a). The other mixtures and the control (repacked soil) were between these cases. Due to the unstable structure, the medium textured arable soil S2 showed a tendency for slaking as shown by the increased bulk density (Figure 4b). The exception was the variant with the vermicompost which prevented such slaking (Figure 4b). A lot of studies pointed out that the soil bulk density has significant influence on the volumetric heat capacity (Abu-Hamdeh, 2003; Usowicz at al., 2016; Tong et al., 2020). The varying ρ_b (Figure 4) and some uncertainties of the parameters C_s hindered the use of Eq. 4 for describing the relationship between C_v and the volumetric water content. We applied a simple linear regression between the measured C_v and the gravimetric water content W (g g^{-1}) (Figure 5).

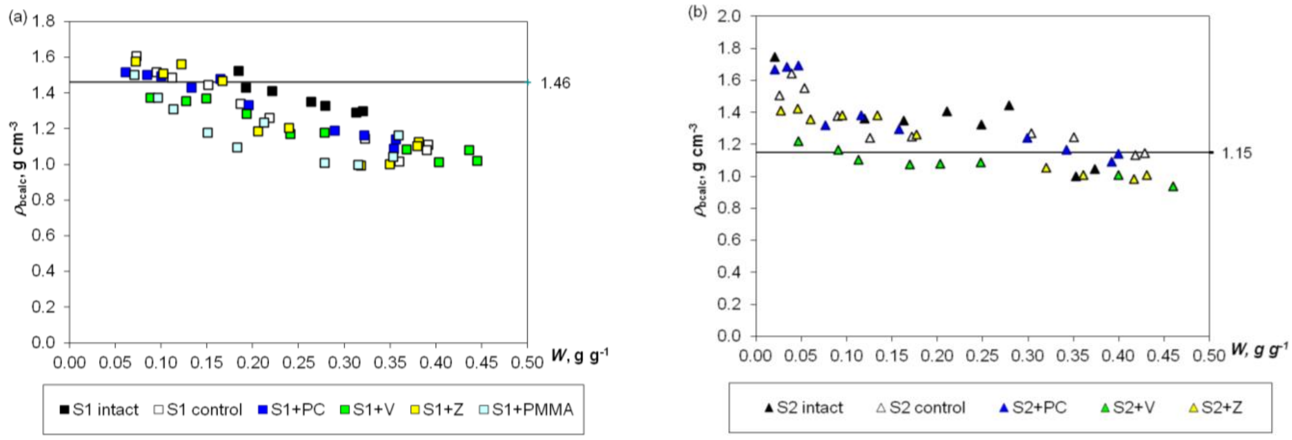

Figure 4. Calculated soil bulk density (ρ_{bcalc}, g cm^{-3}) (Eq. 5) versus gravimetric water content (W, g g^{-1}) for S1 variants (a) and for S2 variants (b)

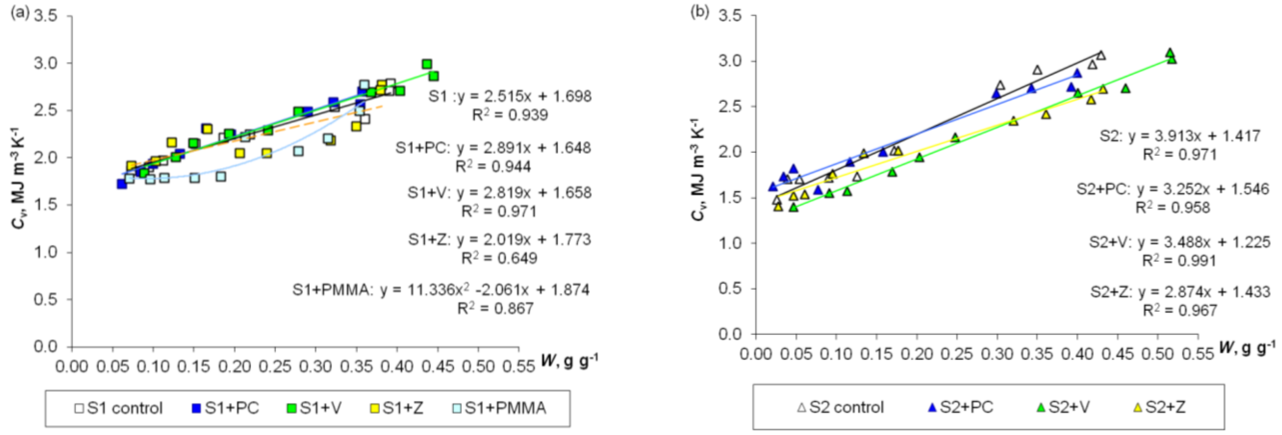

Figure 5. Regression relationships between measured volumetric heat capacity (C_v, MJ m^{-3} K^{-1}) and gravimetric water content (W, g g^{-1}) for variants with S1 (a) and S2 (b)

In most cases the coefficients of determination were very high (R^2=0.93÷0.99). The exceptions were S1+Z (R^2=0.649) and S1+PMMA where a better fit was achieved by a second order polynomial (R^2=0.867), which can be due to the non-linear relations of ρ_b and W in these cases.

The intercepts of the obtained linear regression models confirmed the higher volumetric heat capacity of the clay soil S1 than of the loam soil S2 at dry conditions (Figure 5). While the addition of PC almost did not influence C_v in both soils, the addition of vermicompost decrease C_v in S2 (Figure 5b) by preventing of slaking (Figure 4b) and did not affect C_v of S1 (Figure 4a). The zeolite also decreased C_v at the higher W more pronouncedly in S2 than in S1. We tested PMMA only in the clay S1 and obtained a decrease of C_v at the intermediate W. The models which are most cited for describing the relationship between λ and h (McCumber and Pielke, 1981; Lu et al., 2019) did not fit well our data as it is shown in Figure 6.

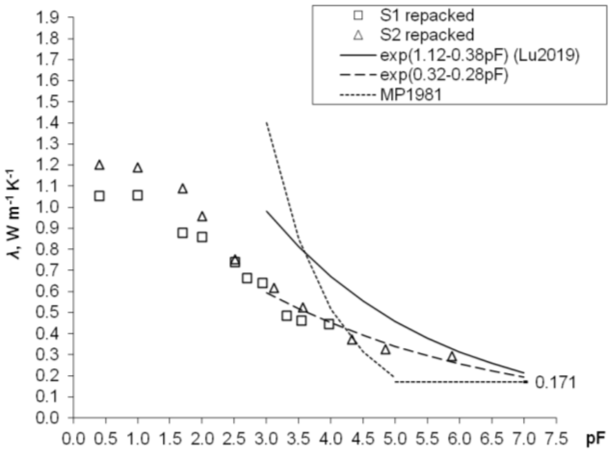

Figure 6. Relationships between λ and pF for the repacked controls of S1 and S2. Symbols – measured data; lines - models: MP model of McCumber and Pielke (1981); Lu et al. (2019) for dry end (pF>3); fitted exponential equation to the current experimental data

The thermal conductivity at not-wet region (pF>3) is considered less dependent on the soil texture and ρ_b and Lu et al. (2019) proposed a universal exponential equation for describing λ-pF relation. We compared the predicted with the measured data for the repacked S2 and obtained RMSE of 0.224 W m^{-1} K^{-1}. A better result (RMSE=0.032 W m^{-1} K^{-1}) was obtained when the exponential equation was fitted with the measured data. Both exponential models tended to the value λ=1.171 W m^{-1} K^{-1} which was fixed by McCumber and Pielke (1981) for pF>5.1. Another option, also used by Tong et al. (2020), was the empirical equation found by Lu et al. (2007) for estimation of λ_{dry} by the *Pt* data (Eq. 3). We estimated λ_{dry} and then performed the non-linear regression analyses for fitting the rest of the parameters of the closed-form equation (Eq. 2). The obtained values of the parameters are shown in Table 6 and the simulated λ-pF curves are drawn in Figure 7.

Table 6. Parameters of the closed-form equation $\lambda(h)$ (Eq. 2), RMSE – root mean square error

Parameter	S1	S1+PC	S1+PMMA	S1+V	S1+Z	S2	S2+PC	S2+V	S2+Z
λ_{sat} (W m^{-1} K^{-1})	1.063	0.990	0.875	1.064	1.060	1.216	1.124	1.078	1.232
λ_{dry} (Eq.3), W m^{-1} K^{-1}	0.252	0.263	0.263	0.262	0.266	0.189	0.210	0.208	0.209
$\alpha*$ (hPa^{-1})	0.025	0.004	0.014	0.009	0.054	0.022	0.011	0.012	0.006
$n*$	1.267	1.659	1.344	1.607	1.238	1.270	1.492	1.454	1.492
RMSE (W m^{-1} K^{-1})	0.031	0.049	0.035	0.063	0.042	0.026	0.050	0.056	0.053

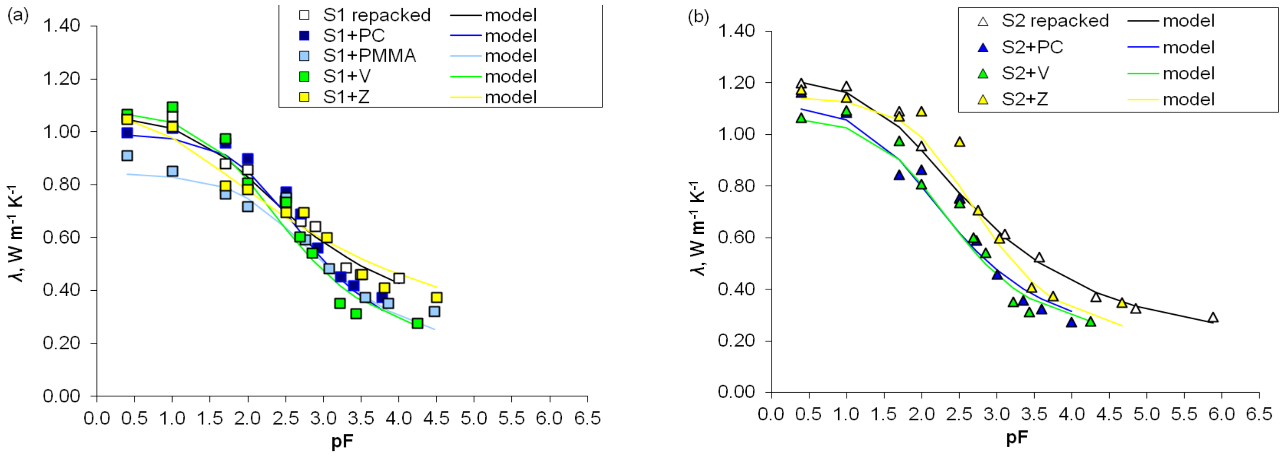

Figure 7. Relationships between measured λ and pF for variants with repacked soils (S1) (a) and S2 (b). Model (Eq. 2)

The RMSE of the predicted λ by Eq. 2 were in the range 0.023÷0.063 W m^{-1} K^{-1} and were lower than the most of the reported RMSE for the dry-end approximation of Lu et al. (2019). We did not found a statistical relationship between the parameters of van Genuchten equation for describing SWRC (n and α) and that of λ (h) ($n*$ and $\alpha*$).

The estimated higher λ_{sat} of S2 than of S1 can be explained with higher content of sand (46%) and respectively of quartz as discussed above which has higher λ (8.8 W m^{-1} K^{-1}) in comparison with that of clay minerals (2.9 W m^{-1} K^{-1}) (de Vries, 1963). The λ_{sat} of the mixtures with microplastics decreased at water saturation by 7% in S1+PC, 8% in S2+PC and 18% in PMMA+S1 due to the lower λ of the polymers (Table 6).

The decrease of λ in the mixtures with the studied microplastics was observed almost throughout the whole range of suctions (Figure 8), except at pF2.5, and pF2.0 for S1+PC, where λ were close to the control values.

The addition of vermicompost decreased λ_{sat} by 11% in S2+V and also throughout the whole range of suctions, while the decreased of λ in S1+V commenced at pF>3. The addition of zeolite to S2 increased λ values in the whole suction range and more pronouncedly at pF>2.5. In case of S1+Z there was a slight negative effect on λ (-1% to -10%).

The dependence of thermal diffusivity (*D*) on gravimetric water content was described with 2nd order polynomials with high coefficients of determination R^2 (Figure 8). The curvature was better pronounced in all variants of the coarser textured S2 and in the variant S1+PMMA. The thermal diffusivity was higher in S2 and in variants with non-organic additives. The addition of vermicompost decreased *D* at given soil moisture content. The latter corresponded to the results received by Usowicz et al. (2014) who revealed that addition of different organic amendments (biochar, peat, compost) into the soil caused considerable reduction of the λ and *D*. When *D* is presented as a function of matric suctions the variants with clay textured S1 were grouped more closely to the control (Figure 9a), while the increase of *D* in S2+Z at a given suction was well distinguished (Figure 9b).

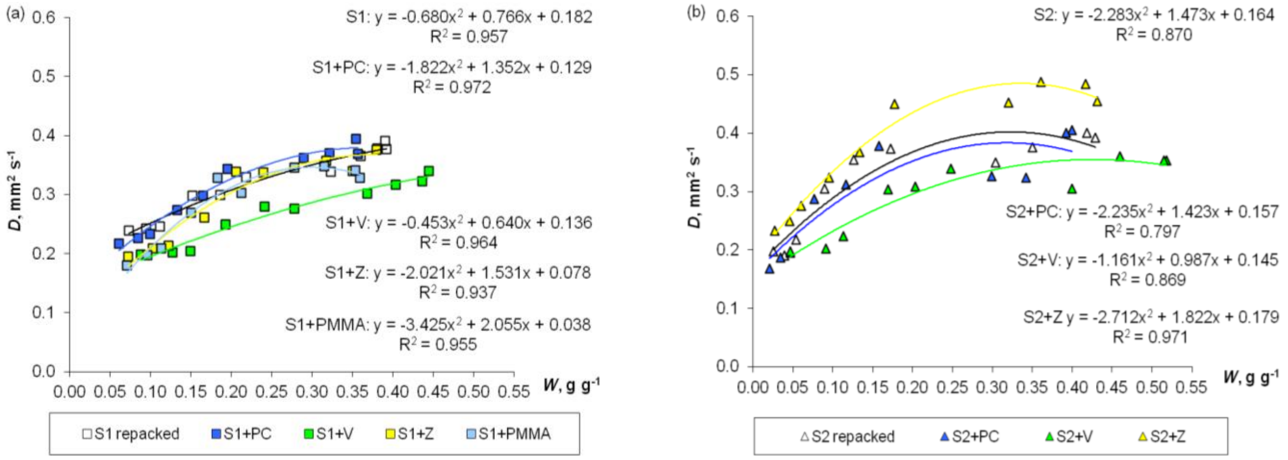

Figure 8. Regression relationships between soil thermal diffusivity (D, mm^2 s^{-1}) and gravimetric water content (W, g g^{-1}) for variants with S1 (a) and S2 (b)

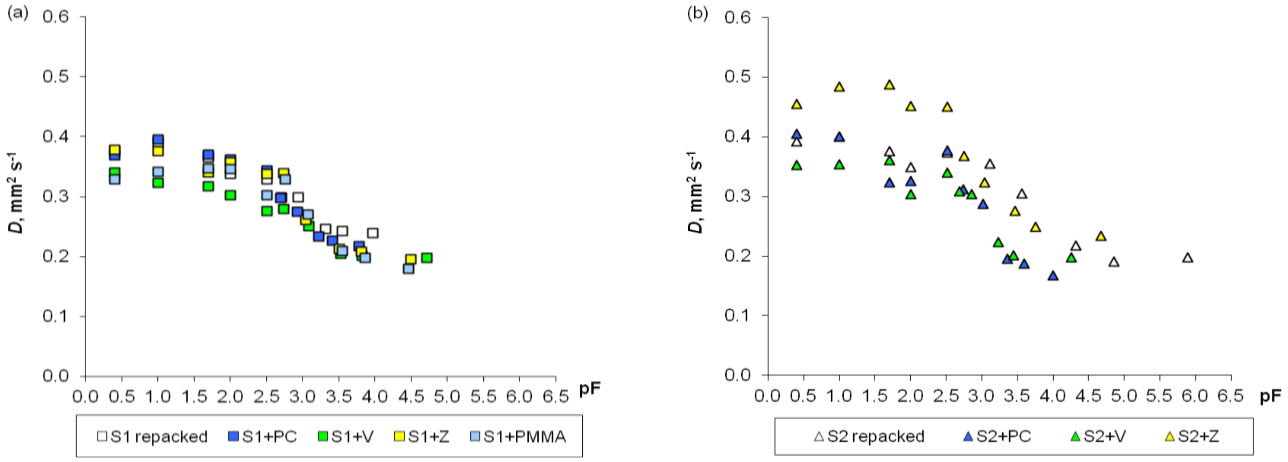

Figure 9. Soil thermal diffusivity (D, mm^2 s^{-1}) versus matric suction (pF) for variants with S1 (a) and S2 (b)

Conclusion

The effects of microplastics (PC, PMMA), vermicompost, and zeolite on soil water retention and thermal properties of clay (S1) and loam (S2) soils were evaluated by comparing experimental data with models' outputs. The main conclusions drawn from this study are as follows:

1. The use of gravimetric water content is recommended over volumetric water content when direct measurements are taken and when the repacked soil cores are susceptible to expansion or slaking during wetting-drainage cycles.

2. Closed-form equations, such as the van Genuchten equation (1980), were successfully applied to describe the soil water retention characteristics (SWRC) (as well as the relationship between thermal conductivity (λ) and water suction (h), yielding satisfactory results with a root mean square error (RMSE) ranging from 0.03 to 0.06 W m^{-1} K^{-1}.

3. The addition of microplastics (PC, PMMA) led to a decrease in water retention capacity across the entire range of suctions. The reduction in soil thermal properties was more pronounced for PMMA compared to PC in S1. The addition of PC had minimal influence on volumetric heat capacity (C_v) in both soils. The decrease in thermal conductivity (λ) and thermal diffusivity (D) was more significant in S2 due to decreased pore space and the lower λ of the polymers.

4. Vermicompost increased water retention capacity, C_s and λ_{dry} in both soils by preventing slaking of water saturated soils it caused a reducing of soil thermal properties, especially in S2.

5. Zeolite exhibited a more pronounced decrease in C_v at higher water content levels in S2 compared to S1. The effects on λ were opposite in both soils, with an increase in λ observed at pF>2.5 in S2 and a slight decrease in S1. The increase in thermal diffusivity (D) in S2+Z was distinct from the other variants at a given suction.

These findings provide valuable insights into the effects of microplastics, vermicompost, and zeolite on soil water retention and thermal properties, contributing to our understanding of their potential impacts on soil functionality and environmental sustainability.

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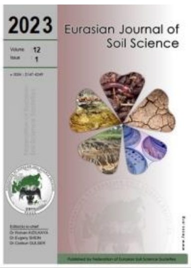

Effects of different fertilization practices on CH_4 and N_2O emissions in various crop cultivation systems: A case study in Kazakhstan

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Abstract

The present study investigates the effects of different fertilization practices, including chemical and organic fertilizers, on CH_4 and N_2O emissions in various crop cultivation systems in Kazakhstan. The research focuses on three staple crops: wheat, barley, and corn, which are commonly grown in the region. A randomized complete block design field trial was conducted with three replications for each crop, totaling 27 plots. Gas sampling was carried out five times between June and September 2021, with cylindrical gas sampling chambers inserted into the soil at a depth of 10 cm. The concentrations of CH_4 and N_2O were analyzed using GS-MS. Results reveal that all three crops exhibited moderate to high CH_4 and N_2O emissions, with corn consistently displaying the highest emissions. Both chemical and organic fertilizers led to increased emissions of CH_4 and N_2O compared to control plots. The organic fertilizer treatment occasionally showed slightly higher emissions compared to chemical fertilizer treatment. However, the differences in CH_4 and N_2O concentrations between fertilized and unfertilized plots were not drastically significant. Notably, environmental factors, such as soil moisture and temperature, played a more prominent role in influencing CH_4 and N_2O production than the type of fertilizer applied. These findings underscore the significance of optimizing fertilization practices to minimize greenhouse gas emissions while maintaining crop productivity and promoting sustainable agriculture in Kazakhstan.

Keywords: Greenhouse gas emissions, fertilization practices, crop cultivation, Kazakhstan.

Introduction

The rapid increase in global population over the past century has posed significant challenges to agricultural practices, leading to a surge in food demand (Hemathilake and Gunathilake, 2022). In response, modern agriculture has heavily relied on the use of chemical fertilizers to enhance crop yields and meet the growing food requirements of the world's population (Umesha et al., 2018). Crop cultivation plays a pivotal role in providing essential agricultural products such as wheat, barley, and maize. However, widespread adoption of conventional agricultural practices has resulted in adverse effects on soil health. Also, this intensified use of chemical fertilizers, while capable of enhancing crop yields, has brought about several environmental implications, including to water pollution, soil degradation, nutrient imbalance, and contribute to greenhouse gas (GHG) emissions (Tellez-Rio et al., 2017; Malyan et al., 2021). In recent years, there has been a growing emphasis on eco-friendly agricultural practices, and organic fertilizers have emerged as a notable alternative. Compared with chemical fertilizer, organic fertilizers have many positive effects on soil fertility and quality including increasing soil carbon and nitrogen, improving the soil physical structure, and enhancing crop yield and quality (Dillon et al., 2012; Zhao et al., 2014; 2020). Organic fertilizers comprise natural components such as animal manure, compost, and green manure. Utilizing organic fertilizers can improve soil productivity and

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health, and nutrient release, while reducing potential environmental impacts. Organic matter stimulates respiration and growth of microorganisms and provides carbon for denitrification. The growth of microorganisms increases oxygen consumption and anaerobic conditions for denitrification, which produces nitrous oxide (N_2O) (Jena et al., 2013). Food and Agriculture Organization (FAO) introduced organic agriculture to reduce the contribution of GHGs in agricultural sector and climate change adaptation (FAO, 2002; 2009). However, organic fertilizers can affect the production of methane (CH_4) and N_2O from soil (Anshori et al., 2020).

Carbon dioxide (CO_2), CH_4, and N_2O are prominent GHGs that contribute to the greenhouse effect, trapping heat in the Earth's atmosphere and causing global warming. Among these gases, CH_4 is of particular concern, being the second most important contributor to radiative forcing after CO_2 (Cassia et al., 2018). It possesses a significantly higher global warming potential, with a 100-year warming potential approximately 28 times that of CO_2 (Dlamini et al., 2022). Agricultural practices, especially in rice paddies, have been identified as substantial sources of CH_4 and N_2O emissions. The flooded conditions of rice fields create anaerobic environments, promoting CH_4 production through the decomposition of organic matter by methanogenic bacteria. Moreover, N_2O emissions often arise from nitrogen-based fertilizers due to nitrification and denitrification processes in the soil (Datta et al., 2014).

The situation is particularly relevant for Kazakhstan, where agriculture plays a crucial role in ensuring food security and supporting the economy. As a country with diverse climatic and soil conditions, Kazakhstan faces unique challenges in managing GHG emissions from agricultural activities. To address these challenges, sustainable and environmentally friendly agricultural practices are of utmost importance. In this context, the present study aims to investigate the effects of different fertilization practices, including chemical and organic fertilizers, on CH_4 and N_2O emissions in various crop cultivation systems, focusing on three staple crops in the region: barley, wheat, and corn. By conducting a field trial under the specific conditions of Kazakhstan, this research endeavors to quantify GHG emissions and study the impact of different fertilizers on soil fertility, nitrogen management, and the overall sustainability of agricultural practices (Kussainova et al., 2023).

Furthermore, this study represents the first scientific endeavor conducted in Kazakhstan to comprehensively assess the effects of fertilization on GHG emissions. As such, it holds significant importance for guiding future agricultural practices and policy decisions in the region. By providing unique insights into the specific challenges and opportunities faced by Kazakhstan, the research aims to contribute to the country's efforts in mitigating the environmental impact of agricultural activities while ensuring food security and sustainable development. Ultimately, the findings of this study are expected to contribute to the scientific understanding of GHG emissions in Kazakhstani agricultural systems. By identifying best practices for minimizing GHG emissions and maximizing crop productivity, the research can pave the way for the adoption of sustainable agricultural approaches tailored to the unique conditions of Kazakhstan. This can help enhance the resilience of the agricultural sector, support economic growth, and promote environmental conservation in the face of global climate change challenges.

Material and Methods

Experimental Site and Climatic Conditions

Experimental site is in “Baibulak” training and experimental farm of KazNARU located in the foothills of the dry network of Ile Alatau, Almaty oblast, Talgar district (N $43^0 28.99'$; E $43^0 28.99'$) (Figure 1). The locations of the evaluations were characterized by the continental climate (large daily and annual fluctuations in air temperature, characterized by cold winters and long hot summers), the air temperature reaches minimum values in January (-11, -13 ^{0}C), and maximum values in July (25 ^{0}C). The average number of days with a maximum air temperature equal to or above 25°C is 108.2 days, 30°C is 44.5 days, and 34°C is 9.4 days. The mean duration of periods with temperatures not exceeding 0°C is 105 days with an average temperature of -2.9°C. For temperatures not exceeding 8°C, the duration is 164 days with an average temperature of 0.4°C, and for temperatures not exceeding 10°C, the duration is 179 days with an average temperature of 0.8°C. Throughout the year, precipitation exhibits two peaks. The first peak occurs in the months of March or April, and the second peak occurs in October or November. The annual precipitation ranges from 148 to 509 mm. In some years, significant fluctuations in the amount of precipitation are observed, ranging from complete absence to abundant rainfall.

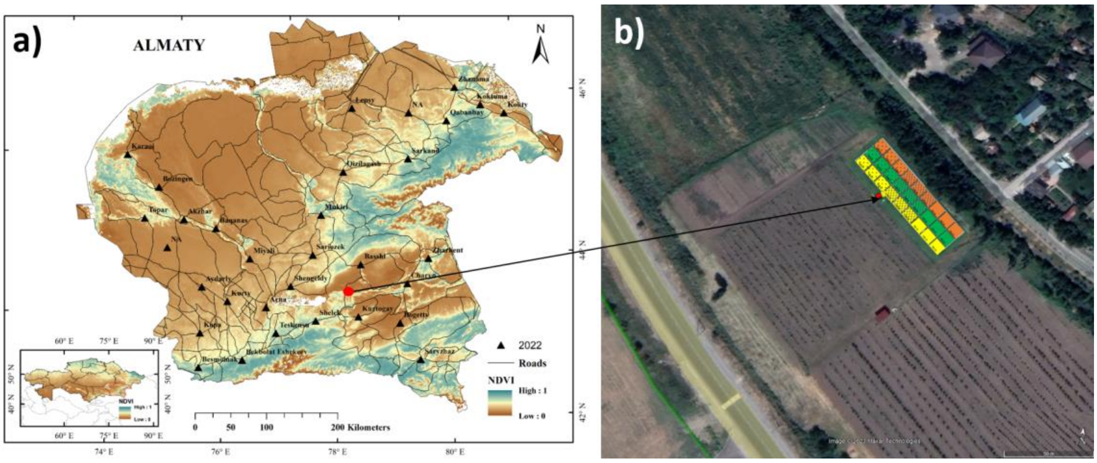

Figure 1. Location of the research site in Almaty oblast, Kazakhstan a) Elevation map of Kazakhstan and Almaty oblast b) Research site

Soil Properties of the Experimental Site

The soil type of the experimental field is "Haplic Kastanozems." In order to determine some soil characteristics of the experimental field, soil samples were taken from depths of 0-5 cm, 5-25 cm, 25-35 cm, and 35-65 cm. Particle size distribution of the collected soil samples was determined by the hydrometer method (Bouyoucos, 1962). Total organic matter was determined by the Walkley-Black method (Walkley and Black, 1934). Soil reaction was measured using a pH meter in a 1:1 soil-to-distilled water solution (Bower and Wilcox, 1965). Mineral Nitrogen was determined by Kjeldahl distillation in a 1 N KCl extract (Bremner, 1965). Available phosphorus was determined in a 0.5M $NaHCO_3$ extraction (Olsen and Dean, 1965). Available potassium was determined in a 1 N NH_4OAc extraction (Pratt, 1965).

Experimental Design

The experiment was set up in a total area of 1500 m^2 (100m x 15m) following a randomized complete block design in 2021, with three replications, totaling 27 plots (Figure 2). The study utilized Kazakhstan 435 CB variety of corn, Susyn variety of spring barley, and Zhenis variety of spring wheat, which are commonly grown in Kazakhstan, as the plant materials. The aim of the experiment was to determine the GHG emissions (CH_4 and N_2O) released from the soil under different plant cultivation practices and fertilizer applications. The chemical fertilizer Ammophos (11% N, 49% P_2O_5) and organic cattle manure (21% organic matter, 0.5% N, 0.25% $P_2O_5$and 0.6% K_2O) were used for the respective treatments, while plots without any fertilizer application were considered as controls. In the experiment, the planting of crops in the plots was carried out on May 18, 2021. Then, on June 3, 2021, the fertilizer applications (180 kg Ammophos ha^{-1} and 230 kg organic fertilizer ha^{-1}) were applied to the respective plots. The harvest of the wheat crop in the trial was on August 18th, the harvest of the barley crop was on August 23rd, and the harvest of the corn crop was done on September 22nd. The wheat trial lasted for 89 days, the barley trial for 95 days, and the corn trial lasted a total of 125 days.

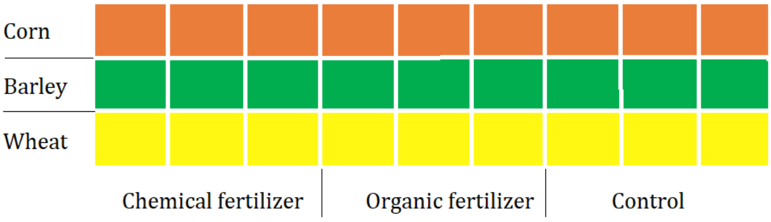

Figure 2. Experimental design

Gas Sampling and Analysis

Gas sampling was carried out five times from each plot, resulting in a total of 135 samples collected between the months of June and September 2021. Cylindrical gas sampling chambers were inserted into the soil at a depth of 10 cm between 09:00 and 11:00 in the morning. After 24 hours, the gas sampling chambers were utilized to determine the concentrations of CH_4 and N2O emitted from the soil. Gas samples were extracted from each chamber using a medical syringe through a rubber stopper and then injected into a vacuum container. CH_4 and N_2O fluxes in the gas samples were analyzed using a triple quadrupole gas chromatograph/mass spectrometer, specifically the Thermo Scientific TSQ 8000 EVO triple quadrupole mass spectrometer (MS) with a capillary column (Trace 1310 GC/TSQ 8000 Evo, Thermo Fisher Scientific). Sample separation was performed using a Supel-Q PLOT column (30m x 0.32 mm). Helium (class A) was used as the gas carrier, and 10 µl of sample was injected at a flow rate of 1 mL/min. Calibration was achieved using certified reference gas mixtures. The retention times for CH_4 and N_2O were 1.15 and 1.45 minutes, respectively. To allow sufficient time for equilibration, sample collection, injection, and data collection (IAEA, 1992), the total time per sample was set at 5 minutes.

Results

The physical and chemical properties of the soils from the experimental site with the soil type "Haplic Kastanozems" are given in Table 1 and 2. According to the obtained results, the soils of the experimental site have a loamy texture. It has been observed that as we go from the surface (0-5 cm) to the subsoil horizons, the amounts of organic matter and available N, P, and K in the soil decrease, while the soil pH increases.

Table 1. Granulometric composition of the experimental field soils

Soil depth, cm	Fraction size, mm					
	Sand		Silt			Clay
	1-0,25	0,25-0,05	0,05-0,01	0,01-0,005	0,005-0,001	<0.001
0-5	10,886	35,912	19,644	10,231	10,231	13,096
5-25	18,615	25,173	24,033	10,591	7,332	14,257
25-35	18,801	25,102	28,049	4,065	10,569	13,415
35-65	26,655	17,110	27,603	7,307	12,178	10,148

Table 2. Chemical composition of the experimental field soils

Soil depth, cm	Total Organic matter, %	Available nutrients, mg kg^{-1}			pH
		Nitrogen	Phosphorus	Potassium	
0-5	3,93	36,4	100,0	680	8,19
5-25	3,24	28,0	32,0	240	8,21
25-35	1,57	25,2	8,0	220	8,19
35-65	1,18	14,0	6,0	170	8,44

The results of the study on CH_4 and N_2O emissions from soil samples in different crop cultivation systems with various fertilization practices are presented in Figure 3 and 4.

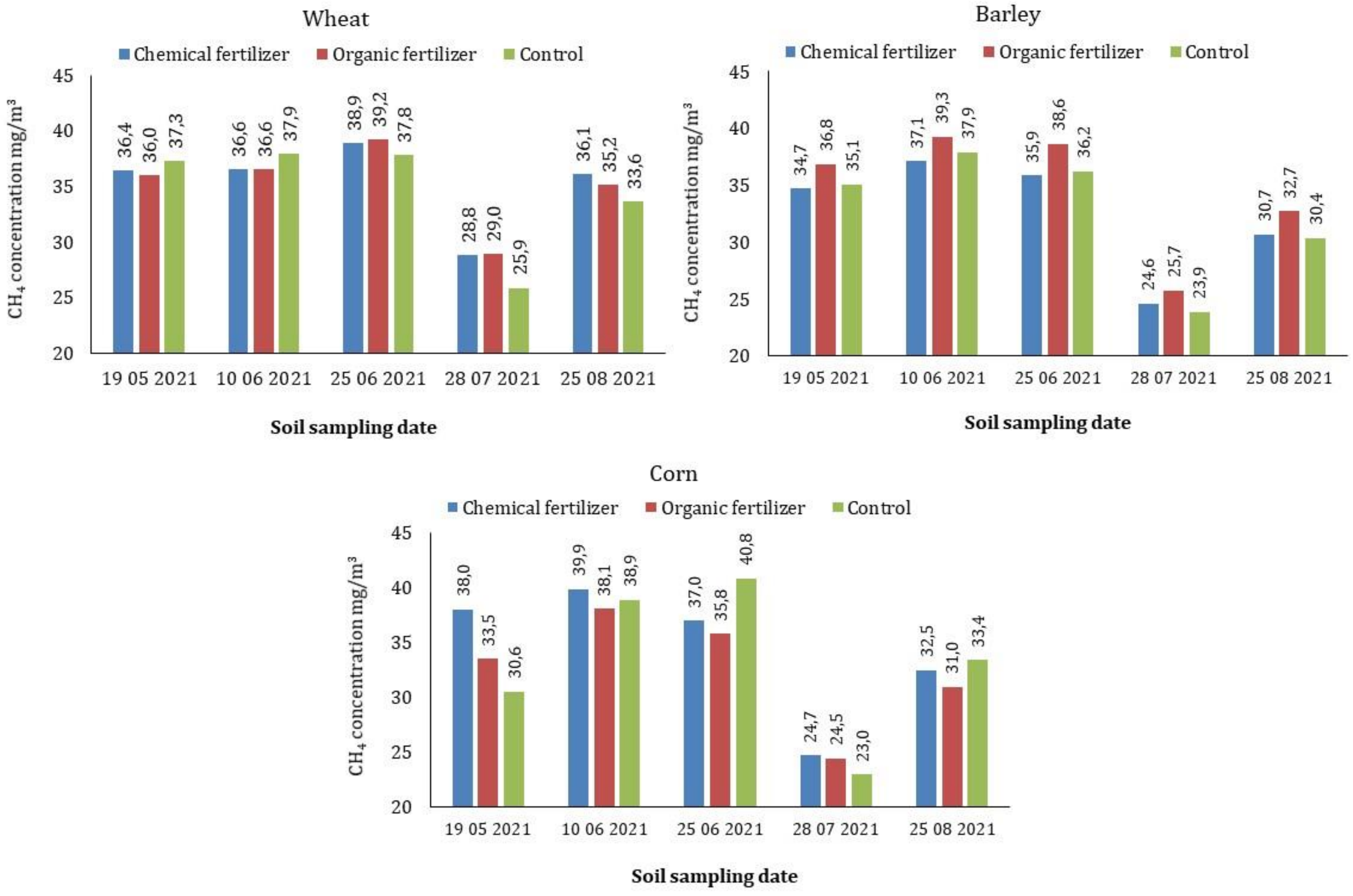

Figure 3. CH_4 concentration of soil samples from wheat growing plots at different sampling times

The measurements were taken at different sampling times between May and August 2021 for wheat, barley, and corn plots treated with chemical fertilizer, organic fertilizer, and a control group without any fertilizer application. In Figure 3, which display the CH_4 concentration of soil samples from wheat, barley, and corn growing plots, respectively, it can be observed that the CH_4 concentrations varied over time and across different fertilization treatments. For all three crops, the chemical fertilizer and organic fertilizer treatments generally exhibited higher CH_4 concentrations compared to the control plots. Notably, the organic fertilizer treatment showed slightly higher CH_4 emissions than the chemical fertilizer treatment in some cases. Regarding N_2O concentrations, Figure 4 illustrate the results for wheat, barley, and corn plots, respectively. Similar to CH_4 emissions, both chemical and organic fertilizer treatments led to elevated N_2O concentrations compared to the control plots for all three crops. The organic fertilizer treatment, in some instances, demonstrated higher N_2O emissions than the chemical fertilizer treatment.

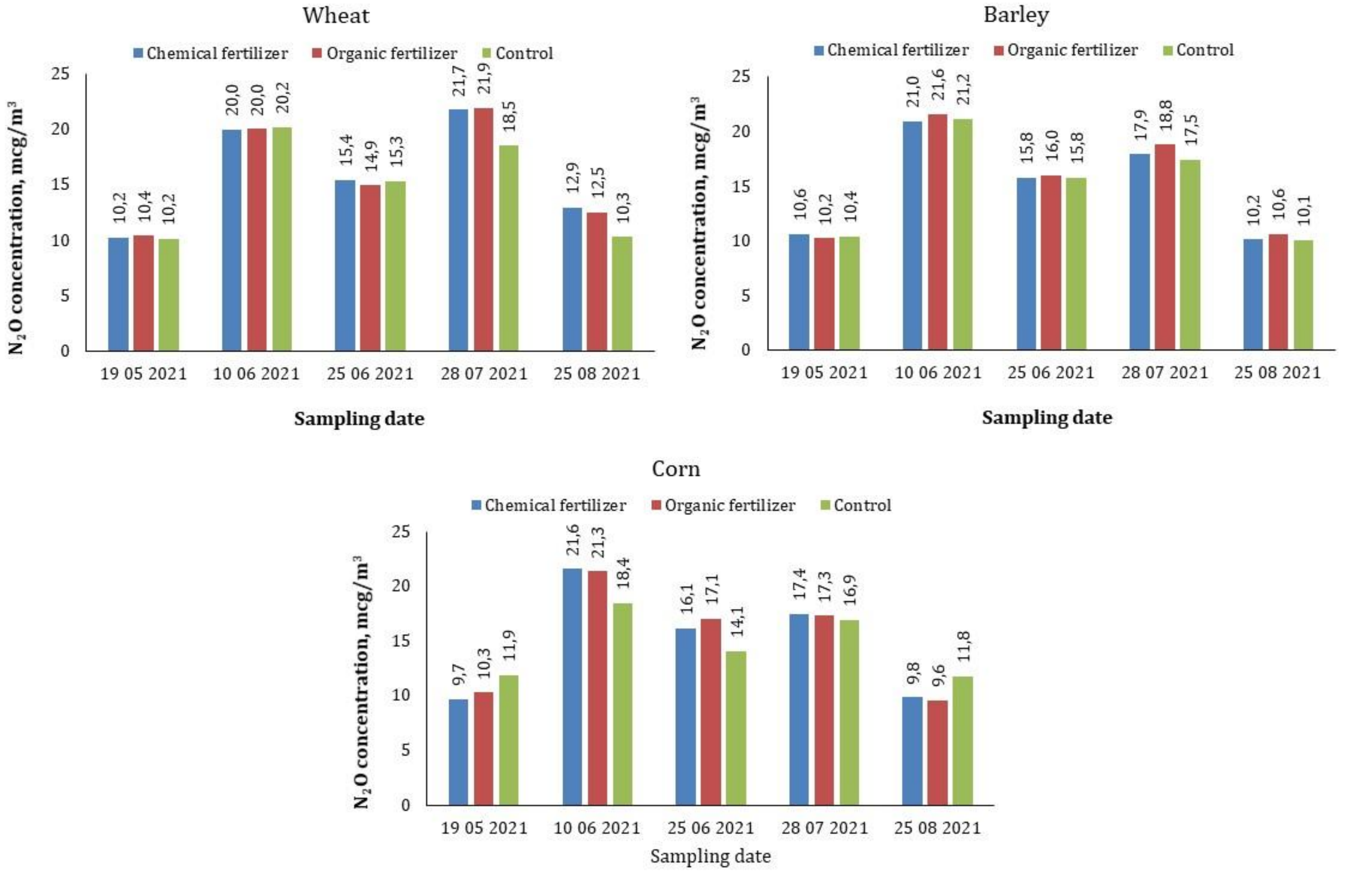

Figure 4. N_2O concentration of soil samples from wheat growing plots at different sampling times

Discussion

The present study aimed to investigate the effects of different fertilization practices on CH_4 and N_2O emissions in various crop cultivation systems of Kazakhstan, focusing on three staple crops: barley, wheat, and corn. The comparison of these crops based on the observed CH_4 and N_2O emissions provides valuable insights into the greenhouse gas dynamics and responses of each crop to varied fertilization treatments, shedding light on potential implications for soil fertility, nitrogen management, and overall agricultural sustainability.

Wheat, barley, and corn all exhibited moderate to high CH_4 emissions during the study period, consistent with the prevalence of anaerobic microbial processes in agricultural soils associated with these staple crops. Among the crops, corn consistently displayed the highest CH_4 emissions. This may be attributed to factors such as its longer growing season, higher root biomass, and potentially greater inputs of organic matter from crop residues, which create favorable conditions for methanogenic microbes. Wheat and barley showed similar CH_4 emissions, with both crops exhibiting relatively lower emissions compared to corn, likely due to their shorter growing seasons and lower root biomass. In the experiment, the lowest CH_4 emissions were determined both in plots where both chemical and organic fertilizers were applied and in control plots without any fertilizer application, during July and August. This is undoubtedly related to the region where the experiment field is located experiencing hot and low rainfall conditions during July and August, resulting in low soil moisture. CH_4 production and consumption are reported to be strongly controlled by soil moisture (van den Pol-van Dasselaar et al. 1998). Mosier et al. (1996) determined that as soil moisture content decreased in the Colorado shortgrass steppe, CH4 emissions from the soil also decreased.

Corn consistently showed the highest N_2O emissions compared to wheat and barley. The higher N_2O production in corn plots can be attributed to its higher nitrogen demand and uptake, leading to increased nitrogen availability in the soil, stimulating nitrification and denitrification processes, and subsequently resulting in higher N_2O emissions. Both wheat and barley exhibited similar N_2O emissions, with both crops showing relatively lower emissions compared to corn. The lower nitrogen demands of wheat and barley likely resulted in reduced nitrogen availability in the soil, leading to lower rates of nitrification and denitrification and subsequently reduced N_2O emissions. In the experiment, significant differences were observed in the N_2O content of the samples taken from both plots where both chemical and organic fertilizers were applied to all plants and control plots without any fertilizer application, depending on the sampling times. This indicates that environmental conditions have a more significant effect on N_2O production from soil. Increased temperature promotes nitrification and denitrification rates, and also enhances N_2O production (Granli and Bøckman 1994). Background N_2O emissions have spatial and/or inter-annual variation due to the variations in soil and climate (Lu et al., 2006; Gu et al., 2007, 2009). Gu et al. (2007) reported that background N_2O emissions from cultivated mineral soils across various soil and climatic regions were controlled by soil total N and C contents.

Overall, the application of both chemical and organic fertilizers led to elevated CH_4 and N_2O emissions compared to the control plots for all three crops. This finding emphasizes the importance of efficient and targeted nutrient management practices to minimize greenhouse gas contributions while ensuring optimal crop productivity. The organic fertilizer treatment, with its higher organic matter content, occasionally showed slightly higher CH_4 and N_2O emissions compared to the chemical fertilizer treatment. While organic fertilizers can enhance soil organic carbon content and overall soil health, they may also promote microbial activity and subsequent GHG production when applied in excessive amounts. However, the differences in CH4 and N2O concentrations between samples taken from both plots where both chemical and organic fertilizers were applied and control plots without any fertilizer application do not show a dramatic distinction. The variations in CH_4 and N_2O production in the soil are more pronounced at different sampling times. This indicates that the influence of environmental factors on CH_4 and N_2O production from the soil is more significant than the impact of fertilization activities. Similarly, in Shimizu et al. (2013), a study conducted on grasslands in Japan to investigate CH_4 and N_2O production in soils with chemical fertilizer and manure application, they found that climatic factors have a more substantial effect on CH_4 and N_2O emissions from the soil than the fertilizers applied to the soil.

Conclusion

This study aimed to investigate the effects of different fertilization practices on CH_4 and N_2O emissions in various crop cultivation systems in Kazakhstan, with a focus on three staple crops: barley, wheat, and corn. The comparison of these crops based on the observed greenhouse gas (GHG) emissions provides valuable insights into their unique responses to fertilization treatments and their implications for soil fertility, nitrogen management, and overall agricultural sustainability. The study explored the effects of varied fertilization practices on CH_4 and N_2O emissions in different crop cultivation systems of Kazakhstan, focusing on barley, wheat, and corn. Corn exhibited consistently higher CH_4 and N_2O emissions compared to wheat and barley due to its longer growing season and higher nitrogen demand. Both chemical and organic fertilizers led to increased CH_4 and N_2O emissions in all three crops, emphasizing the importance of efficient nutrient management. However, the differences in CH_4 and N_2O concentrations between fertilized and unfertilized plots were not highly pronounced, suggesting that environmental factors have a more substantial impact on gas production than the type of fertilizer used. Environmental conditions, such as soil moisture and temperature, were found to influence CH_4 and N_2O emissions significantly.

In conclusion, this study provides valuable data for developing sustainable agricultural practices to mitigate greenhouse gas emissions while ensuring optimal crop productivity in the region. Future research should further explore the interplay of environmental factors and fertilization practices on greenhouse gas dynamics for more comprehensive mitigation strategies.

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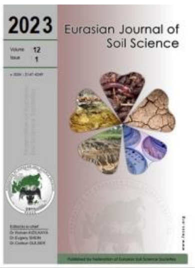

Impact of varied NPK fertilizer application rates and seed quantities on barley yield and soil nutrient availability in chestnut soil of Azerbaijan

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Abstract

In the Gobustan district of Azerbaijan, the cultivation of barley is influenced by a complex interplay of soil properties, climate change effects, and agricultural practices. This study explores the impact of varying NPK fertilizer application rates and seed quantities, under natural climatic conditions, on barley yield and soil nutrient availability within Chestnut soils. The district's unique Chestnut soils, combined with evolving precipitation patterns due to climate change and the role of agricultural irrigation, create intricate challenges for successful barley farming. The experiment, conducted from 2016 to 2019, utilized a randomized complete block design with four replications to investigate the "Celilabad-19" barley variety. The results reveal a significant positive correlation between nitrogen application and grain yield. Notably, treatment 140-N60P45K45 (140 kg seed rate, 60 kg N/ha, 45 kg P/ha and 45 kg K/ha) demonstrated the highest average grain yield of 5.14 t/ha. The years 2017-2018 exhibited higher yields, possibly due to favorable climate conditions. Soil analyses indicated that higher NPK application rates led to elevated soil nutrient levels. However, nutrient content declined as plants progressed through growth stages, emphasizing the dynamic nutrient exchange between plants and soil. This study underscores the importance of adaptive agricultural strategies that consider climate variability and changing environmental conditions. The findings offer insights into sustainable cultivation practices essential for food security and crop production in the evolving climate of the Gobustan district.

Keywords: Barley cultivation, NPK fertilizer, seed rates, climate change, soil nutrient dynamics.

Introduction

Barley is the fourth most-produced cereal worldwide behind wheat, rice and maize (Oliveira et al., 2019). Also, Barley, a vital cereal crop in arid and semi-arid regions, assumes particular significance in Azerbaijan. As demonstrated by Cammarano et al. (2019) in the Mediterranean context, the cultivation of barley stands as a linchpin for food security. It is cultivated from the equator to the Arctic Circle and at different elevations (Friedt et al., 2010; Dawson et al., 2015). In Azerbaijan, this cereal is subject to an intricate interplay of factors, including unique soil properties, evolving climate patterns, and agricultural practices. In the Gobustan district of Azerbaijan, a distinctive intersection of factors profoundly influences the cultivation of barley. The region's Chestnut soils, providing an essential substrate for agricultural activities, play a pivotal role in sustaining plant growth and nutrient retention. However, the complex interplay between these soil properties, evolving precipitation patterns resulting from climate change, and the significant role of agricultural irrigation intensifies the impact of these elements on barley farming in the area. However, little attention has been focused on the effects of varied NPK fertilizer application rates and seed quantities on barley yield and soil nutrient availability in chestnut soil of Gobustan district, Azerbaijan.

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Azerbaijan's diverse topography encompasses a variety of soil compositions, with Chestnut soils standing out prominently within the Gobustan district. These soils, characterized by moderate drainage and fertility levels, offer a versatile foundation for diverse agricultural practices (Aliyev, 2021). Notably, in the context of barley cultivation, the attributes of Chestnut soils wield a direct influence over crop yield and quality.

The ever-evolving patterns of temperature and precipitation associated with climate change present a spectrum of challenges and opportunities for agricultural activities (Malhi et al., 2021; Abbass et al., 2022). Variations in temperature and shifting rainfall trends have far-reaching effects on planting schedules, water availability, and pest dynamics, all of which are crucial determinants of successful barley cultivation (Ullah et al., 2021; Skendžić et al., 2021). The Gobustan district, facing modifications in its traditional climate dynamics, must swiftly adapt its agricultural approaches to align with these changing conditions.

Of equal significance is the role of agricultural irrigation, emerging as a linchpin in upholding barley farming within the Gobustan district. As climate change renders precipitation patterns less predictable, the role of irrigation becomes even more pronounced in ensuring a consistent water supply for crops. Implementing efficient irrigation methodologies can ameliorate the repercussions of water scarcity and bolster crop resilience amid the shifting climatic backdrop.

In essence, the intricate interrelationship between Azerbaijan's distinctive topography, the inherent attributes of Chestnut soils, the ongoing ramifications of climate change, and the strategic deployment of agricultural irrigation collectively emphasize the paramount importance of these factors in barley cultivation within the Gobustan district. A comprehensive grasp and adept management of these intertwined elements stand as imperatives for upholding successful and sustainable barley farming practices in this region. Consequently, this study seeks to explore the influence of varying NPK fertilizer application rates and seed quantities, under distinct irrigation-absent conditions, on barley yield and the available forms of nitrogen, phosphorous, and potassium within Chestnut soils over a three-year period.

Material and Methods

Experimental Site

The field experiments were conducted from 2016 to 2019 in the Mereze area of the Gobustan Experimental Station, which is part of the Azerbaijan Research Institute of Crop Husbandry (40^{0}31’07.6372”N, 48^{0}53’50.8362”E). The experiments were carried out under rainfed conditions in the open dry chestnut soils of the Gobustan district, located in the Mountainous Shirvan region of Azerbaijan (Figure 1).

Figure 1. Experimental field

The Gobustan district, situated in the Mountainous Shirvan region of Azerbaijan, exhibits distinct long-term climate characteristics. The region experiences a semi-arid warm temperate desert climate in the southern part and a semi-arid warm temperate steppe climate in the northern part. The average annual temperatures range from 6 to 14°C, with the coldest months experiencing temperatures of 2 to 4°C, while the warmest period sees temperatures ranging from 15 to 25°C. The temperature remains relatively stable despite variations. The annual precipitation ranges from 360.3 mm to 542.9 mm, with an average of 412 mm. Notably, the distribution of rainfall during the crop vegetation period varies across years, impacting agricultural practices and water management strategies. These climate features play a crucial role in shaping agricultural sustainability and the livelihoods of the local population.

A chestnut soil sample was collected from the experimental field at the outset of the experiment. Some chemical properties of the soil were determined using methods outlined by Rowell (1996) and Jones (2001).

Experimental Design

The experimental design employed the "Celilabad-19" barley variety, known for its resilience to drought and rust diseases, and extensively cultivated in the region. The field trial was conducted between 2016 and 2019 using a randomized complete block design with four replications, resulting in a total of 48 plots. Each plot measured 50 m^2 (25 m x 2 m), with a spacing of 0.30 m between adjacent plots. During the three-year field trial, barley seeds were sown 5 cm below the soil surface using agricultural mechanization tools in the second week of October each year. Plant harvesting was performed in June, aligning with the climatic conditions of the region. The preceding crop in the rotation was a leguminous plant, which was mixed with the soil.

Different seed rates and NPK fertilizer doses were selected as experimental factors. The varying seed rates used in the trial were 2.67 million/ha (120 kg/ha), 3.11 million/ha (140 kg/ha), and 3.55 million/ha (160 kg/ha). The different NPK fertilizer treatments consisted of application doses of 30, 45, and 60 kg/ha (Table 1). Ammonium Nitrate (34% N) was used as the nitrogen fertilizer, Superphosphate (20.5% P_2O_5) as the phosphorus fertilizer, and Potassium Sulfate (46% K_2O) as the potassium fertilizer. For phosphorus and potassium fertilizers, the entire dose, along with 30% of the nitrogen fertilizer, was applied at seeding. The remaining 70% of the nitrogen fertilizer was applied during the tillering stage of barley plants in March.

Table 1. Experimental design

Treatments	Seed Rate (kg/ha)	Nitrogen fertilizer rate (kg/ha)	Phosphorus fertilizer rate (kg/ha)	Potassium fertilizer rate (kg/ha)
120-$N_0P_0K_0$	120	0	0	0
120-$N_{30}P_{30}K_{30}$	120	30	30	30
120-$N_{45}P_{45}K_{45}$	120	45	45	45
120-$N_{60}P_{45}K_{45}$	120	60	45	45
140-$N_0P_0K_0$	140	0	0	0
140-$N_{30}P_{30}K_{30}$	140	30	30	30
140-$N_{45}P_{45}K_{45}$	140	45	45	45
140-$N_{60}P_{45}K_{45}$	140	60	45	45
160-$N_0P_0K_0$	160	0	0	0
160-$N_{30}P_{30}K_{30}$	160	30	30	30
160-$N_{45}P_{45}K_{45}$	160	45	45	45
160-$N_{60}P_{45}K_{45}$	160	60	45	45

Throughout the trial period, no artificial irrigation was applied, and no plant protection chemicals were used. The trial design aimed to investigate the effects of different seed rates and NPK fertilizer doses on the growth, development, and yield of the "Celilabad-19" barley variety under the natural climatic and soil conditions of the Gobustan district. The experiment's focus on these factors aims to provide insights into sustainable cultivation practices for barley in the region.

Plant and Soil Sampling and Analyses

During the three-year field trial conducted from 2016 to 2019, mature barley plants were harvested to determine grain yields. Additionally, soil samples were collected at a depth of 25 cm during different developmental stages of the barley plant, including tillering, heading, and full maturity. These samples underwent various analyses to assess the dynamics of plant-available nitrogen, phosphorus, and potassium in response to different NPK fertilizer applications and varying levels of barley planting.

Following the methods outlined by Rowell (1996) and Jones (2001), mineral nitrogen (NH_4 and NO_3), available phosphorus, and exchangeable potassium contents were determined through 1 N KCl extraction and 1% $(NH_4)_2CO_3$ extraction from the soil samples. These analyses facilitated the assessment of the impacts of different NPK fertilizer dosages and varying levels of barley planting on the soil's capacity to supply plant-available nitrogen, phosphorus, and potassium. These insights contribute to a comprehensive understanding of how different soil nutrient dynamics interact with barley growth and development during various growth stages, thereby enriching the interpretation of the experiment's outcomes.

Data Analysis

Statistical analysis of the research results was conducted using the SPSS26 program.

Results and Discussion

The results obtained from soil samples taken at depths of 0-25 cm, 25-50 cm, and 50-70 cm, with the aim of determining the soil properties of the trial area with Chestnut soil type, are presented in Table 2. According to the acquired outcomes, it is observed that as the subsoil depth increases, the soil's calcium carbonate ($CaCO_3$)

content increases, consequently leading to an elevation in soil pH. In contrast, within the uppermost 0-20 cm soil layer, higher levels of organic matter, total nitrogen (N), mineral nitrogen forms (NH_4-N and NO_3-N), available P_2O_5, and exchangeable K_2O contents were detected. As the subsoil depth increases, these components were found to decrease.

Table 2. Characteristics of Chestnut soil type in the experimental area

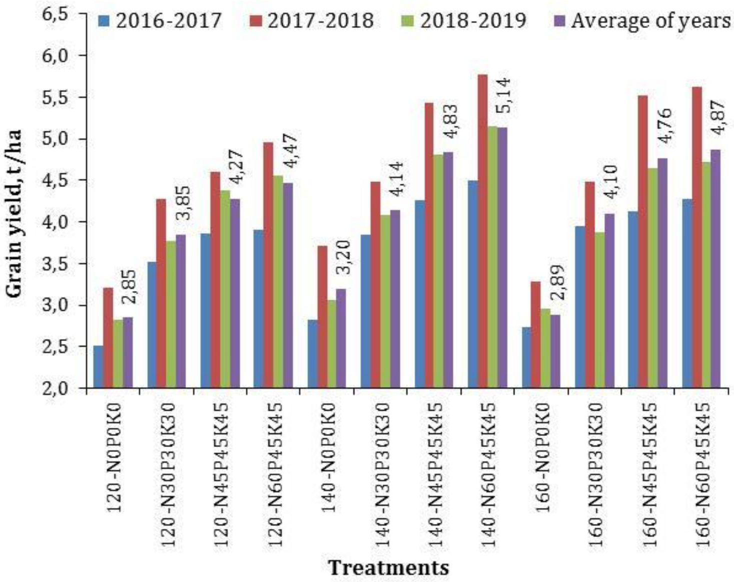
Soil Dept, cm	pH	$CaCO_3$, %	Organic Matter, %	Total N, %	NH_4-N, mg/kg	NO_3-N, mg/kg	Available P_2O_5, mg/kg	Exchangeable K_2O, mg/kg
0-25	8,25	4,34	2,23	0,165	18,2	14,0	30,45	292
25-50	8,45	5,90	1,37	0,099	12,8	8,5	12,60	167
50-70	8,60	7,70	0,73	0,056	8,2	5,2	5,75	112

Changes in Grain Yield

The experimental design encompassed a comprehensive investigation into the effects of varying seed rates and different levels of NPK fertilizers on barley grain yield within the Chestnut soil type of the Gobustan district. The data collected over three consecutive years, spanning from 2016 to 2019, along with their averages, shed light on the dynamic relationship between the applied treatments and the resultant grain yields. Across the examined years, it becomes evident that the treatment combinations had a significant impact on barley yield. Among the treatments, those involving N application exhibited an observable trend of enhancing grain yield. For instance, treatment 140-N60P45K45 consistently demonstrated the highest average grain yield of 5.14 t/ha across the three years, indicating the substantial positive effect of nitrogen fertilization on yield improvement (Figure 2). Similarly, in a field experiment conducted by Mengie et al. (2021) under Ethiopian conditions, aiming to investigate the impact of varying seed rates (5, 7.5, 10, 12.5, and 15 kg/ha) on the growth, yield, and yield components of Tef, it was observed that different seed rates significantly influenced the yield and yield components of the Tef plant. The maximum yield of 2.301 kg/ha was achieved with a seed rate of 5 kg/ha, demonstrating the importance of appropriate seed rate selection. This finding aligns with the outcomes of the current study, where varying seed quantities and sowing methods were found to interactively affect barley yield and its related parameters. Therefore, the significance of optimizing seed rates for enhanced crop productivity is further highlighted by both studies. Kiria's (2022) study in Kenya reinforces our findings, emphasizing the vital role of seeding rates. Optimal outcomes were observed at 10 kg/ha seeding rate for highest grain yield and biomass production in teff cultivation, aligning with our results. After a 3-year field experiment, it was determined that increasing doses of NPK application significantly increased barley yield in the soils. Similarly, other studies have also demonstrated that increasing fertilizer application doses enhance crop yields (Shah et al., 2009; Nogalska et al., 2009; Wilczewski et al., 2013; Agegnehu et al., 2016).

Analyzing the results, it becomes evident that higher crop yields were achieved during the 2017-2018 period in comparison to both the preceding 2016-2017 and succeeding 2018-2019 periods. This observation is noteworthy, particularly considering that the 2017-2018 period experienced the lowest levels of precipitation. To provide specific figures, there was 704.4 mm of rainfall during the 2016-2017 period, 435.4 mm during the 2017-2018 period, and 692 mm during the 2018-2019 period (Figure 3). Interestingly, this situation contradicts the common assumption in the literature that increased rainfall positively influences barley yield. The higher yield during the 2017-2018 period may plausibly be attributed to the cultivation of leguminous plants in the preceding year, which were incorporated into the soil before the trial. This practice likely contributed to soil improvement, potentially explaining the yield increase observed during that specific period. The studies (Freidenreich et al., 2022; Gou et al., 2023) have shown that incorporating leguminous plants into the soil as cover crops increases crop production. Prior to setting up the experiment, leguminous plants, which were used as cover crops in the field, were mixed with the soil just before the experiment, followed by barley planting. The higher barley yield in the second year (2017-2018) of the experiment, compared to the first (2016-2017) and third years (2018-2019), is primarily attributed to the incorporation of leguminous plants into the soil. It is believed that immediately after incorporation, the effect of the legume residue becomes more pronounced in the following year due to its slow mineralization, while in the third year, it has completely decomposed and lost its impact on the soil. Furthermore, when comparing the three annual periods, it is clear that variations exist in grain yield performance. Notably, the years 2017-2018 recorded consistently higher yields compared to the preceding and succeeding years. This discrepancy could potentially be attributed to climate fluctuations specific to the Gobustan region during those years. The relatively milder conditions and possibly favorable precipitation patterns during the 2017-2018 period might have significantly contributed to the enhanced barley yields observed during that time frame. Conversely, the dip in yields during the 2018-2019 period suggests the potential influence of less conducive climate conditions or other environmental factors. These disparities underscore the intricate relationship between agricultural outcomes and the broader climatic context, emphasizing the need for adaptable strategies to accommodate such variations and maintain sustainable yields.

In conclusion, the results of this study highlight the dynamic interplay between seed rates, NPK fertilizer application, and climate dynamics on barley grain yield within the Chestnut soil type of the Gobustan district. The observed variations in yield across the three years further emphasize the importance of considering climate variability and its potential implications for agricultural outcomes. Going forward, the insights derived from this study can contribute significantly to the development of targeted and adaptable agricultural strategies, which are essential for ensuring sustainable crop production in the face of the region's changing climate scenario. This conclusion aligns with the findings of Clark (1974), who, in his study on barley, suggested that the variation in barley yields over successive years may be attributed to climate fluctuations. Similarly, Cammarano (2019) conducted research on the influence of climate change on barley yield in the Mediterranean and projected a negative impact due to drier and hotter conditions. The study explored various climate scenarios, indicating potential yield reductions of up to 27% under dry conditions, while wetter projections saw an 8% increase. The study also emphasized the role of interactions between soil type, rainfall, and temperature in influencing water-stress dynamics and yield variations, reinforcing the necessity of location-specific adaptation strategies in response to changing climate conditions.



	F-value	
Experimental period (Year)	775,968	***
Seed rate	197,842	***
Fertilizer doses	1718,069	***

Figure 2. Changes in grain yield across treatments during the experimental periods

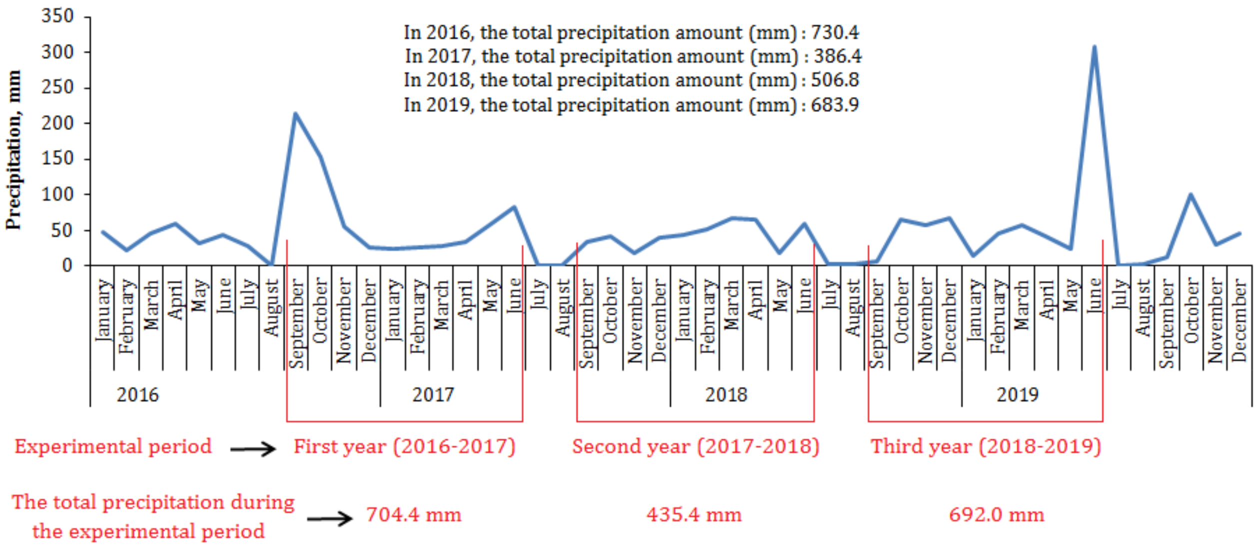
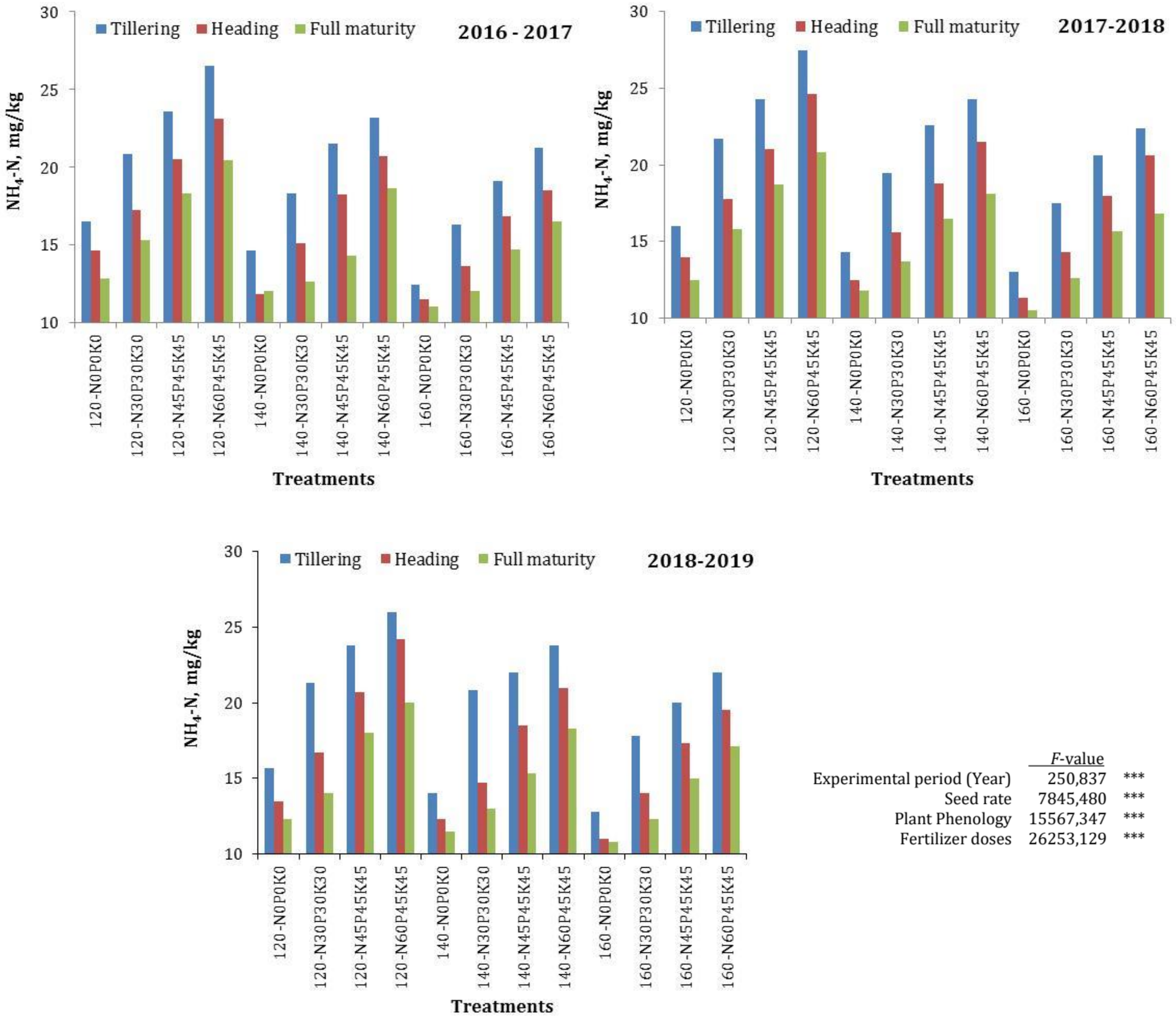


Figure 3. The precipitation amounts in the location where the trial site is located during the experimental periods

Changes in Soil Ammonium Content

Figure 3 illustrates the dynamics of soil NH_4^+ content across different growth stages and treatments over the three-year experimental period (2016-2019). The data provides insights into how varying NPK fertilizer applications and different barley seed quantities influence NH_4^+ levels. The investigation into the variations in soil NH_4^+ content across different treatments and growth stages offers crucial insights into the complex interactions between fertilizer applications, barley growth, and nutrient dynamics. As the barley plant progresses from the tillering to the full maturity stage, it is observed that the soil NH_4^+ content tends to decrease. This decline can be attributed to the plant's uptake of NH_4^+-N from the soil as it transitions through its phenological development.

NPK fertilization had a significant impact on the NH_4^+ content of the soil (Figure 4). With the increase in the dose of NPK fertilizer, the content of NH_4^+-N increased. Similarly, Rutkowski and Łysiak (2023) found that increasing doses of nitrogen fertilizer application (0 kg, 60 kg, and 120 kg N/ha) in soils where cherries are cultivated resulted in an increase in the ammonium content of the soil. Throughout the experimental years (2016-2019), the results consistently indicate that as the plant advances through its growth stages, the soil's NH_4^+ content decreases. This decline in NH_4^+ levels is consistent with the notion that the growing barley plants actively absorb NH_4^+-N from the soil to fulfill their nutritional requirements. Consequently, the reduced availability of NH_4^+ in the soil is a direct consequence of the plant's NH_4^+ uptake. The significant impact of plant uptake on NH_4^+ levels highlights the dynamic nature of nutrient exchange between the soil and the plants. The observed differences in NH_4^+ content among the various treatments and years emphasize the interplay between fertilizer application, nutrient availability, and plant demand. Treatments with higher NPK fertilizer application rates generally exhibited elevated NH_4^+ levels, reaffirming the positive relationship between fertilization and NH_4^+ content. However, as the plant progresses from the tillering to the full maturity stage, the nutrient requirements change, leading to increased ammonium uptake and subsequent reduction in NH_4^+ content.



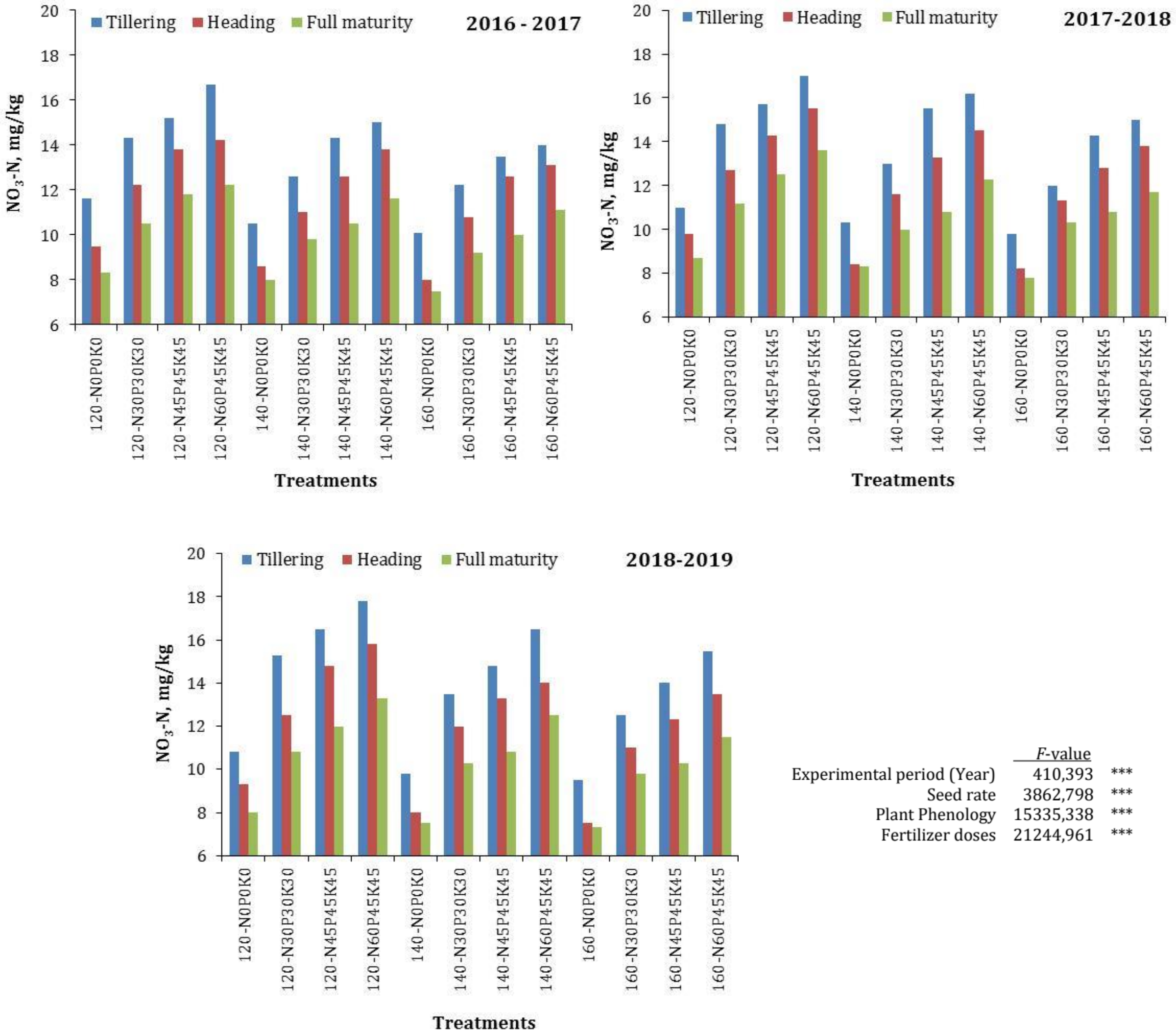
	F-value	
Experimental period (Year)	250,837	***
Seed rate	7845,480	***
Plant Phenology	15567,347	***
Fertilizer doses	26253,129	***

Figure 4. Changes in soil ammonium (NH_4-N) content across growth stages and treatments

Changes in Soil Nitrate Content

Figure 5 reveals the alterations in soil NO_3^- levels in response to varying NPK fertilizer applications and different seed quantities. Throughout the experimental years (2016-2019), consistent patterns emerged with regard to soil nitrate content in relation to different growth stages and treatments. While no significant variations were observed among the years, notable differences existed among the treatments in terms of their impact on soil NO_3^- levels. As the barley plant advanced from the tillering to the full maturity stage, a distinct trend in soil nitrate content became evident (Carillo and Rouphael, 2022). The observed trend of decreasing soil nitrate content as the plant progressed through its growth stages can be attributed to the plant's active uptake of NO_3^--N from the soil. This phenomenon is consistent with the concept that growing barley plants utilize nitrate nitrogen as a crucial nutrient to support their development and growth (Tischner, 2000; Nacry et al., 2013).

The findings suggest that the varying treatments, including different seed rates and NPK fertilizer doses, played a significant role in influencing soil NO_3^- content. Treatments with higher NPK fertilizer application rates generally led to elevated soil NO_3^- levels. This outcome is in line with the positive correlation between fertilizer application and soil nitrogen content. However, the observed decline in soil NO_3^- content from tillering to full maturity underscores the dynamic relationship between plant uptake and nutrient availability in the soil. Similarly, studies conducted by Chen et al. (2004), Petropoulos et al. (2008) and Liu et al. (2014) have found that the application of N-based chemical fertilizers at increasing levels to the soil increases the nitrogen conten of both the soil and the plant. Depending on the growth stage of the plant, they have determined that NO_3^- is transported from the soil to the plant through plant roots, leading to a decrease in soil concentration. It is noteworthy that the absence of significant year-to-year variations in soil NO_3^- content points to the stability of the results over the experimental period. This stability implies that the observed trends are consistent and can be reliably attributed to the experimental treatments.



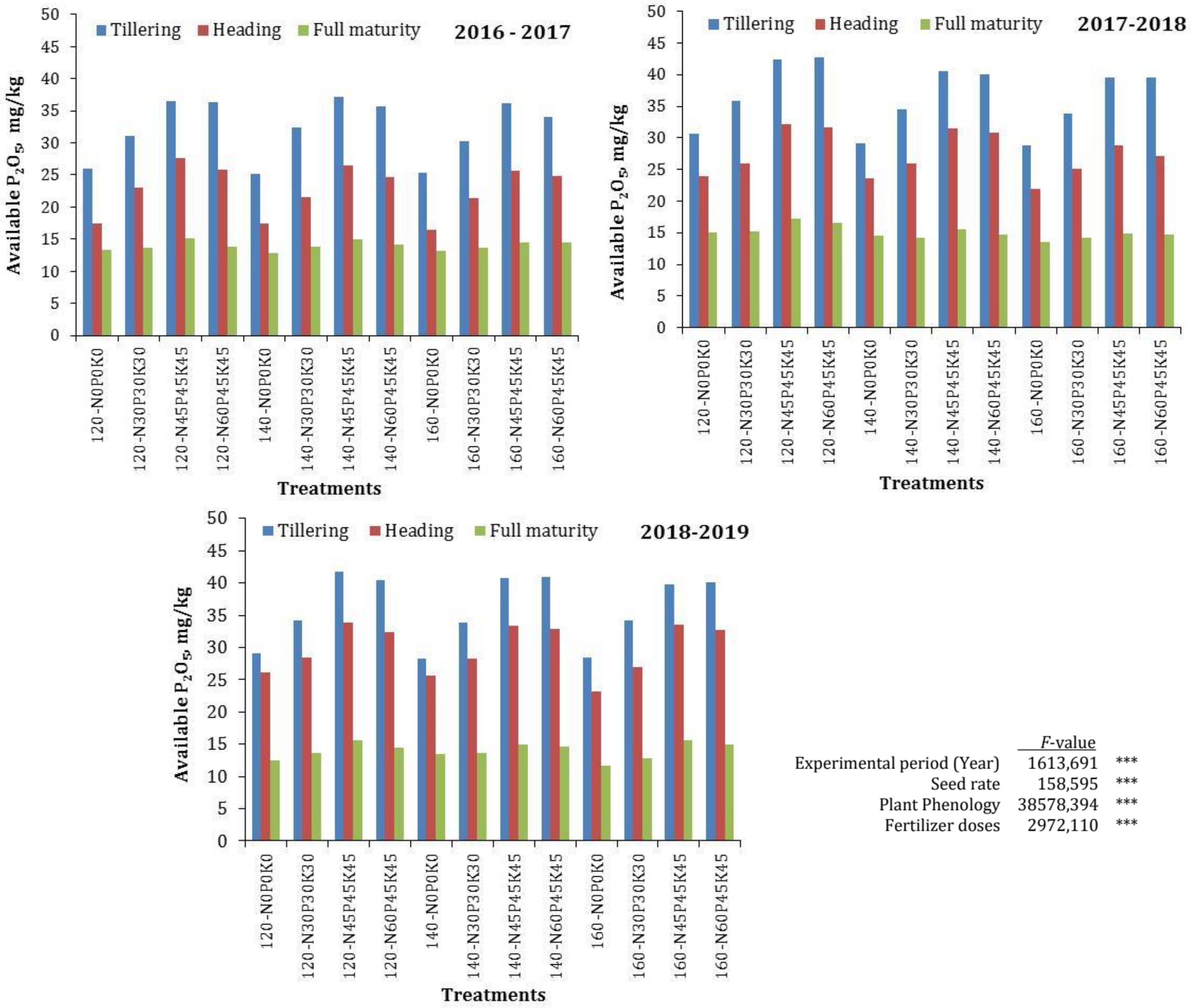
	F-value	
Experimental period (Year)	410,393	***
Seed rate	3862,798	***
Plant Phenology	15335,338	***
Fertilizer doses	21244,961	***

Figure 5. Changes in soil nitrate (NO_3-N) content across growth stages and treatments

Changes in Soil Available Phosphorus Content

The alterations in soil available P_2O_5 content were examined across different treatments and growth stages over the three-year experimental period (2016-2019). The data from the soil samples collected during the tillering, heading, and full maturity stages were analyzed to understand the impact of varying NPK fertilizer applications and different seed quantities on soil phosphorus levels (Figure 6).

The trends observed in the changes of soil available P_2O_5 content were consistent with the experimental design factors. The results indicated distinct patterns in phosphorus availability influenced by both the applied treatments and the developmental stages of the barley plants. As the plant progressed from tillering to full maturity, a general trend of decreasing soil available P_2O_5 content was evident. Similarly, studies conducted by Medinski et al. (1998), Wu et al. (2020) and Wang et al. (2022) have determined that increasing application rates of NPK chemical fertilizers to the soil result in both increased crop yields and improved phosphorus content in the soil. The observed decrease in soil available phosphorus content aligns with the understanding that growing plants actively uptake phosphorus from the soil to support their growth and development. This dynamic exchange between plants and soil nutrients contributes to the observed trend of declining soil P_2O_5 levels as the plant advances through its phenological stages. Among the different treatments, those with higher NPK fertilizer application rates tended to exhibit elevated soil available P_2O_5 content. This relationship between fertilization and soil nutrient content emphasizes the influence of applied nutrients on soil properties. However, the decline in soil P_2O_5 availability over the growth stages underscores the importance of considering plant nutrient requirements and uptake dynamics in designing effective fertilization strategies. It's worth noting that while the variations in soil available P_2O_5 content were evident among different treatments and growth stages, there were no significant year-to-year differences.



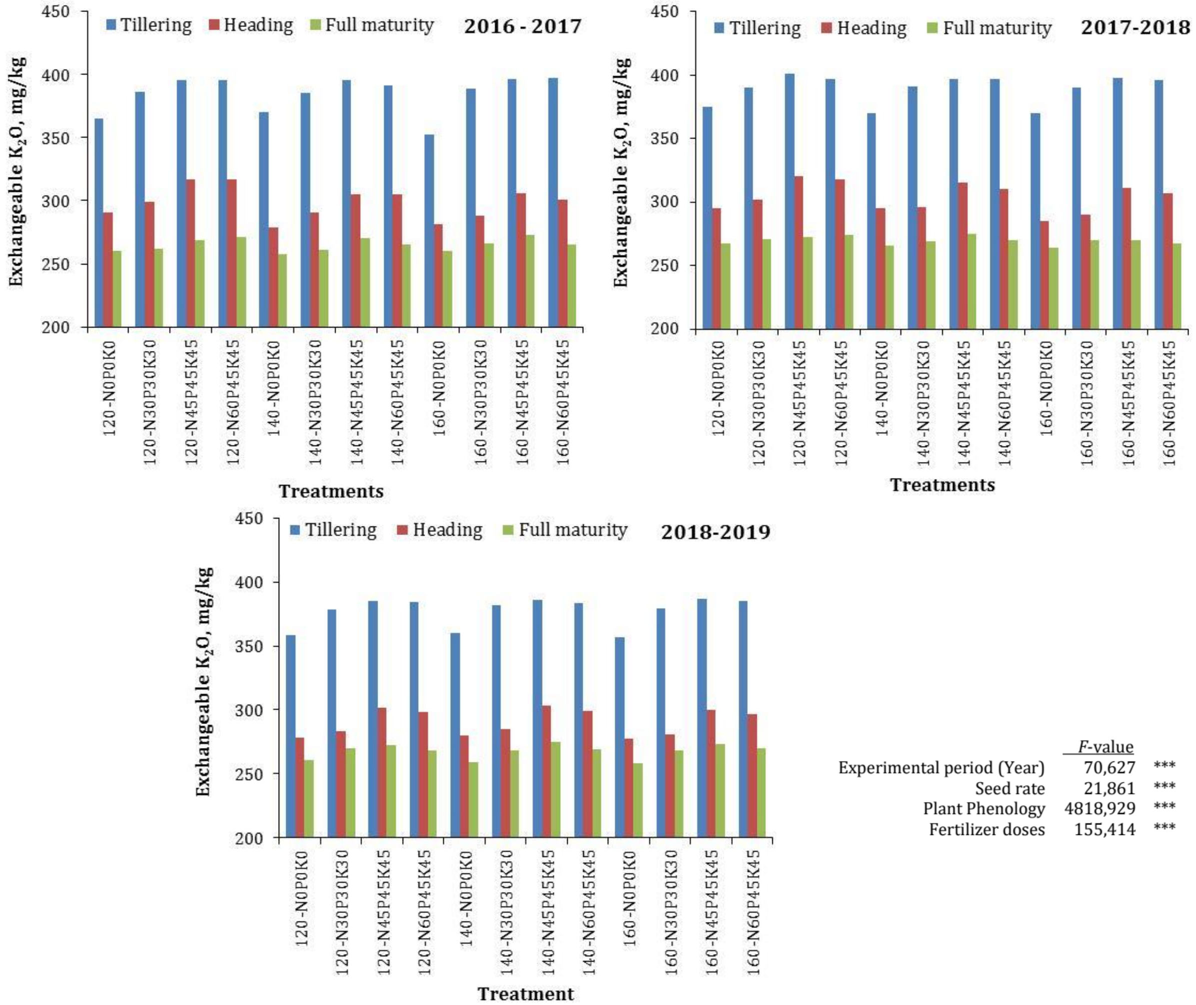
	F-value	
Experimental period (Year)	1613,691	***
Seed rate	158,595	***
Plant Phenology	38578,394	***
Fertilizer doses	2972,110	***

Figure 6. Changes in soil available phosphorus (P_2O_5) content across growth stages and treatments

Changes in Soil Exchangeable Potassium Content

The variation in soil exchangeable potassium content was investigated across different treatments and growth stages over the three-year experimental period (2016-2019). Soil samples collected during the tillering, heading, and full maturity stages were analyzed to understand the impact of diverse NPK fertilizer applications and different seed quantities on soil potassium levels. Figure 7 present the changes in soil exchangeable potassium content for each treatment and growth stage across the three experimental years. These tables reveal the dynamic nature of soil potassium availability and its response to varying experimental factors. While no significant year-to-year differences were observed, notable variations emerged among the treatments in terms of their influence on soil potassium levels.

Throughout the experimental period, the results consistently indicate trends in soil exchangeable potassium content that align with the applied treatments and barley growth stages. Higher NPK fertilizer application rates generally led to elevated soil potassium levels. This outcome reflects the positive correlation between fertilization and soil nutrient content. However, as the barley plant progressed from the tillering to the full maturity stage, a noticeable reduction in soil exchangeable potassium content was observed. The observed decrease in soil exchangeable potassium content as the barley plant advanced through its phenological development can be attributed to the plant's active uptake of potassium from the soil. This trend suggests that as the plant matures, its demand for potassium increases, leading to enhanced potassium uptake and subsequent depletion of soil potassium content.



	F-value	
Experimental period (Year)	70,627	***
Seed rate	21,861	***
Plant Phenology	4818,929	***
Fertilizer doses	155,414	***

Figure 7. Changes in soil exchangeable potassium (K_2O) content across growth stages and treatments

It was determined that changes in soil exchangeable potassium content, it is noteworthy that the dynamics of soil potassium availability mirror the growth and developmental stages of the barley plant. This alignment suggests a close relationship between the plant's potassium requirements and its phenological progression. As the plant transitions from the tillering stage, characterized by early vegetative growth, to the full maturity stage, marked by reproductive and grain-filling processes, its demand for potassium increases. This intensified potassium uptake is attributed to the plant's metabolic activities, which peak during the reproductive phase. Similarly, studies conducted by Song et al. (2020) and Setu (2022) have determined that increasing levels of NPK chemical fertilizers applied to the soil, depending on the increasing application rates, both increase crop yield and enhance the available potassium content. In the field trial, the effect of increasing NPK doses on the available potassium content of the soil, while showing a similar effect to mineral nitrogen and available phosphorus content, is not as pronounced between application doses, unlike N and P. This situation is undoubtedly related to the behavior of nutrients in the soil. In a study conducted by Wihardjaka et al. (2022), it was found that potassium added to the soil is continuously taken up by plants from germination to harvest, and the remaining amount in the soil continuously decreases, with the difference being reduced at high K doses. The decrease in soil exchangeable potassium content can be attributed to the plant's ability to absorb potassium from the soil to fulfill its physiological needs. This observation aligns with the widely recognized phenomenon that plants actively extract nutrients from the soil to support their growth and reproduction. In the case of potassium, the plant's demand is particularly pronounced during the latter stages of development, when it allocates resources for grain production. Furthermore, the variations among different treatments in terms of their impact on soil exchangeable potassium content indicate that fertilization strategies play a significant role in influencing soil nutrient dynamics. Treatments with higher NPK fertilizer application rates led to elevated soil potassium levels, reinforcing the positive relationship between fertilization and soil nutrient availability. However, the plant's dynamic potassium requirements during different growth stages resulted in the decline of soil potassium content as the plant progressed towards full maturity.

Conclusion

In this study, we conducted field experiments over a three-year period to assess the effects of different seed rates and NPK fertilizer doses on the growth, development, and yield of the "Celilabad-19" barley variety in the Chestnut soil type of the Gobustan district. The results obtained from this investigation shed light on the dynamic interplay between agricultural practices, soil properties, and climate dynamics, contributing valuable insights to sustainable barley cultivation strategies in the region. The findings from the experimental site characterization emphasized the significance of the Gobustan district's unique climate characteristics, which encompass a semi-arid warm temperate desert climate in the southern part and a semi-arid warm temperate steppe climate in the northern part. These distinct climatic conditions, characterized by variations in temperature and precipitation, significantly influence agricultural practices and water management strategies. The variations in climate conditions across the experimental years highlighted the need for adaptable strategies to ensure consistent and sustainable yields.

The experimental design encompassed a comprehensive investigation into the effects of varying seed rates and NPK fertilizer applications on barley grain yield. The results demonstrated that nitrogen (N) application had a significant positive impact on grain yield, with treatment 140-N60P45K45 consistently yielding the highest grain yield. However, the study also revealed year-to-year variations in grain yield performance, indicating the influence of climate fluctuations on agricultural outcomes. Analyzing soil nutrient dynamics, we observed trends in soil ammonium, nitrate, available phosphorus, and exchangeable potassium content across different treatments and growth stages. The results highlighted the intricate relationships between fertilizer applications, plant uptake, and soil nutrient availability. Treatments with higher NPK fertilizer application rates generally led to elevated soil nutrient levels. Nonetheless, the decline in soil nutrient content as the barley plant progressed from tillering to full maturity underscored the dynamic nature of nutrient exchange between plants and soil.

In conclusion, this study provides valuable insights into the complex interactions between seed rates, NPK fertilizer applications, soil properties, and climate dynamics on barley growth, development, and yield. The observed variations in yield and soil nutrient content across the experimental years underscore the need for adaptive agricultural strategies that account for climate variability and changing environmental conditions. The knowledge gained from this study can guide the development of targeted and sustainable cultivation practices, crucial for ensuring food security and crop production in the Gobustan district's changing climate scenario. Additionally, the insights gleaned from this research can serve as a foundation for further studies on optimizing nutrient management and enhancing agricultural resilience in similar agroecological contexts.

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