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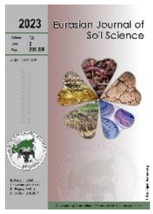

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Spatial distribution of soil organic carbon content in the agricultural land uses: Case study at the territory of the Rahoveci municipality, Kosovo

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Abstract

Due to the soil formation factors and different geographic areas of Dukagjini Plain, particularly in Rahovec municipality, the variation of soil organic carbon is high. Soil organic carbon (SOC) has a crucial role in the determination of the physical, chemical and biological behaviour of the soil. The most common land use types of this area are vineyards, table grapes, horticulture such as peppers and cabbage, and arable lands such as maize, winter wheat, alfalfa, and meadows. Considering the lack of soil information data in Kosovo, it is necessary to have soil information about this territory. The main objectives of the present study are, therefore: i) to investigate and determine the concentration of the soil organic matter (SOM), SOC, nitrogen (N) and soil pH-H_2O, using laboratory analysis, and ii) to show the spatial distribution of SOC, SOM, N and pH using the Kriging and inverse weighting interpolation methods. Spatial variability of soil chemical parameters such as SOM, SOC, N, and pH are important to be interpolated to view the changeable soil properties by kriging and inverse distance weighting method and to generate the continuous sample for site-specific management. Disturbed soil samples were collected from the top soil 0-30 cm and 30-60 cm depth, to determine selected soil chemical parameters, during June-July 2019. A large number of soil samples were collected, 2087 in the first horizon and 2065 in the second. The average of SOC of the first horizon was 0.91%, which variates from 0.07 to 4.06%, while in the second horizon was 0.0 to 2.84%, the average content of N in the first horizon was 0.09%, which variate from 0.01 to 0.60%, while in the second horizon was 0.0 to 0.39%, meanwhile, the average of soil pH-H_2O in the first horizon was 7.67, which variates from 4.25 to 9.35, while in the second horizon was 7.79, which variate from 3.25 to 9.30.

Keywords: Soil organic carbon, agriculture land, spatial interpolation, kriging, inverse weighting.

Introduction

When it comes to soil fertility soil organic matter (SOM) is a significant factor for sustainability and productivity (Johnston et al., 2009) and has great importance in any terrestrial ecosystem (Dengiz et al., 2019).

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It has numerous functions, which determine physical factors, and it is essential for the supply of plant nutrients and to regulate the water flow. It is important to manage soil organic matter, to sustain croplands, grasslands, and forests. According to (Lal, 2008) the amount of stored carbon in the soil is around 2500 GT tons, which is 3.1 times larger than the amount of what is found as (CO_2) in the atmosphere (Oelkers and Cole, 2008). The storage of carbon in SOM can also have an impact on greenhouse concentrations, and if soils increase their organic matter, CO_2 content in the atmosphere will be decreased (Cotrufo et al., 2011). The amount of SOM depends on organic materials and their breakdowns in soil, where plant communities and microorganisms are the basic sources of the process of decomposition. The amount of organic matter that is needed in the soil depends on the form of land use. It is worth notice that if there is a decrease in soil organic matter, the soils will experience loss of structure and erosion (Spain and Isbell, 1983). Soil organic matter is no doubt that is highly important but defining the nature of SOM is still challenging. However, organic matter retains nutrients, which increases plant growth and water quality content. The process that is studied is humification and humic substances which make soil humus. But no precise evidence or analytic techniques are made to observe this substance. What makes it difficult for this observation is that organic compounds are mixed with soil minerals. Its specific is dark coloration and in some soils such as arable soils, organic matter is around 5% (Lehmann and Kleber, 2015). The percentage of organic matter usually is between 2-10%. However, even if a small percentage is detected it is important because the biological activity of soil depends on it. It affects soil in numerous in every feature, and there is a need for restoring organic matter to balance the agro-ecosystem and to provide sufficient nutrients for plants (Bot and Benites, 2005).

According to Bresilla (2012), the most representative reference soil groups of Kosovo are Cambisols, Vertisols, Luvisols, Fluvisols, Leptosols, and Calcisols, and because of this wide range of these soil are characterized by the highly changed spatial distribution of the Kosovo relief materials as referring to (USDA-NRCS, 2012) .

Agricultural practices does make certain changes into the soil. In order to define these changes there is developed the soil quality index which helps to identify the effects and changes on soil parameters (Gelaw et al., 2015).

The degradation of soil and deterioration of soil fertility are considered a serious threat to human existence and the natural environment due to changing climate change, topography, soil characteristics, and the uniqueness of agriculture.

Performance indicators of healthy soil are soil colour, soil texture, organic matter, weeds, topography, and soil water holding capacity (Nimmo, 2004).

Devastation impacts of agricultural practices on soil quality include salinization, erosion, compaction, desertification, and pollution (Lal and Stewart, 2015). One of the major threats to agricultural productivity in developing countries is declining soil fertility. These factors which affect soil degradation are extensive use of farming practices, poor agronomic practices, low use of inputs, low rotation spectra, and climate change effects.

Soil information remains an issue for farmers and agricultural institutions of Kosovo. Therefore, having a unique database for the location n-based analysis is more than important for agricultural development and policies. Soil resource inventories has undergone in many countries changes from physical to digital techniques.

This municipality's soil use is distinguished by intensive plantation owners of vineyards, cereal products, and vegetable production. Crop plantation variation occurs as a consequence of land formation and climatic condition, which makes it suitable to many farming system where soil organic matter is produced; as long as there is a diverse crop production, litter from multiple sources is provided, increasing soil organic matter and sustaining cultivars.

Since this area, is agricultural intensively used in different cropping systems many agricultural practices are applied as: land cultivation, preparation, fustigation, fertiliser and manure use – as indicators on soil and crop health and to provide the ability to change soils mineral and biological activity.

The current study aims: i) to investigate and determine the concentration of the soil organic matter [SOM], soil organic carbon (SOC), nitrogen (N) and soil pH-H_2O, using laboratory analysis, and ii) to show the spatial distribution of SOC using the Kriging and inverse weighting interpolation methods. Moreover, it was relevant: i) to determine SOC, SOM, N and soil pH – H_2O in two soil depths and show their spatial variability, ii) differentiate the differences on two soil horizons in order for later to identify the effects which came to these spatial changes, and iii) classify soil sampling locations based on corine land cover classification.

Material and Methods

Study area

This study was conducted in Rahoveci Municipality, which is located in the western part of Kosovo, on the Dukagjini plain, with a surface of 275.9 km^2, and is about 2.5% of the country (Figure 1). Due to the soil formation factors and different geographic areas of Dukagjini Plain, soils of the agricultural land of Rahoveci Municipality are very diverse and are situated between the northern latitude of $42^0 29' 12.54''$ and $42^0 17' 31.43''$ and between the longitude of $20^0 40' 19.39''$ and $20^0 39' 19.49''$ east, in Drini Bardh River basin and are characterized with a great potential for agriculture development, mainly for vegetables in flat area and vineyard in sloping land and hilly sites. The most common land use types of this area are vineyards, table grapes, horticulture such as peppers and cabbage, arable lands such as maize, winter wheat, alfalfa, and meadows.

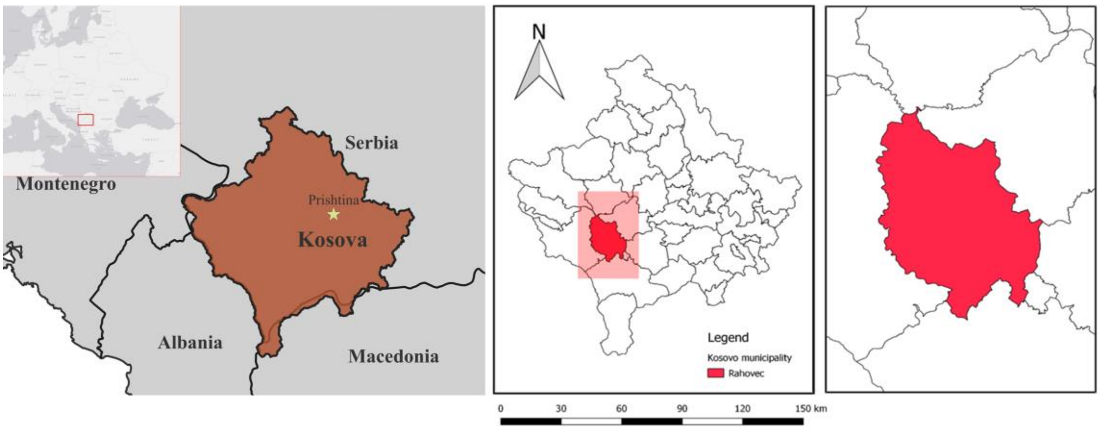

Figure 1. Study area, Rahovec

The highest peak above sea level is 920 m and is situated in the northern part of the territory and the lowest peak above sea level is 310 m and is situated in the southern part of the territory (Figure 2).

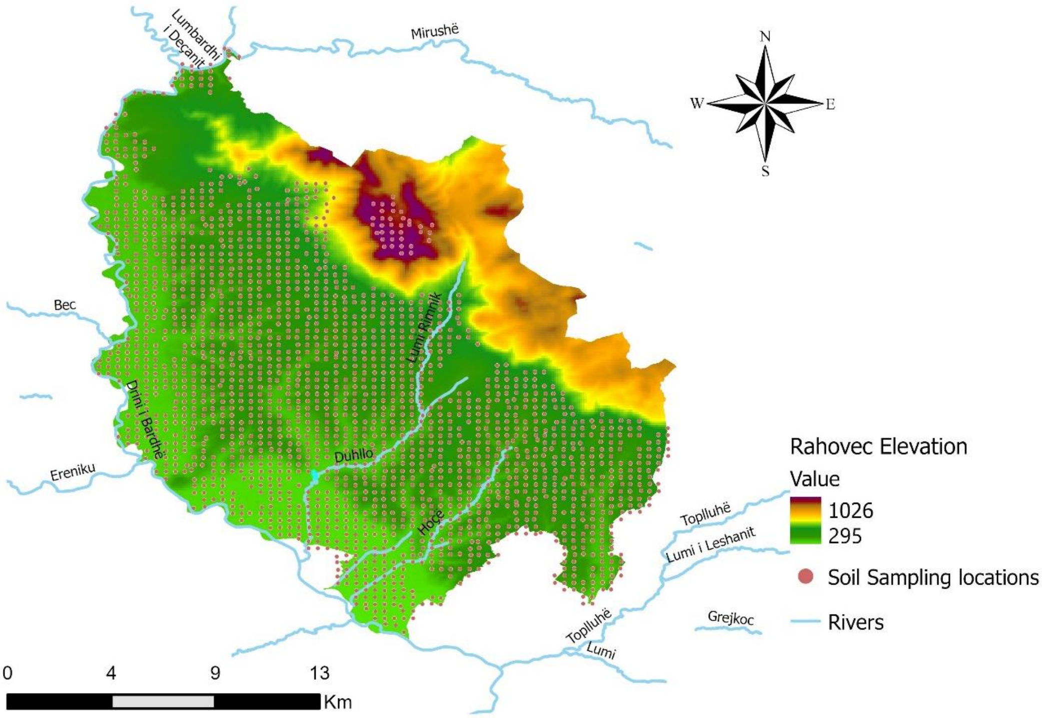

Figure 2. Soil sampling location map

Climate condition of the study area

Based on (KECA, 2008), the climate of the country is predominantly continental. The study area climate is characterized by warm to hot summers and cold winters, with an average of 700-780 mm precipitation per year, moreover, air temperatures are characterized by an average annual temperature of 12.2 ^{0}C which may range from -20 ^{0}C in the winter to +35 ^{0}C in the summer (KEPA, 2020) .

Soil sampling

The field sampling was carried out during June-July, 2019. In order to determine selected soil chemical parameters, disturbed soil sampling were collected in two depths, from the top soil horizon 0-30 cm and second soil horizon 30-60 cm. A total of 4152 soil samples were collected, 2087 soil samples belongs to the top soil horizon 0-30 cm and 2065 soil samples belong to the second soil horizon 30-60 cm. The samples were organised based on a pre prepared sampling grid of 300 x 300 m (every 9 ha) (Figure 2). The auguring samples were taken based on the sampling grid with a maximum of 49 m deviation, when it was needed. The samples that were marked based on the grid in the middle of group of the houses and had the possibility of displaced to a maximum distance of 49 m, were displaced, otherwise those that did not have this possibility were cancelled. For each disturbed soil sample were taken approximately 500 g of soil, then the samples were purified from stones, granules, leaves and roots, then were subjected for further procedure. The soil samples were dried at room temperature, crushed, homogenized, and sifted with a 2 mm sieve. The chemical parameter that were performed are pH-H_2O, soil organic carbon (SOC), soil organic matter (SOM) and nitrogen (N). Soil organic matter (SOM) and nitrogen (N) were analyzed based on the soil organic carbon (SOC).

Soil chemical analyses

The chemical parameters that have been analyzed and the methods that have been used for determination are presented in Table 1. The Walkley-Black procedure was followed for the determination of Soil Organic Carbon (SOC), 1 g of dried fine earth sample were mixed with 10 ml of potassium dichromate 0.1667 M and 20 ml of sulphuric acid 36%, and after 30 minutes 250 ml of distilled water was added and 3-4 drops of indicator solution added. The 1 M ferrous sulphate solution was used for titration (GLOSOLAN, 2019). For pH determination, the 1:5 ratio of soil and water was used, following ISO 10390:2005 method. Calcium carbonate ($CaCO_3$) was analyzed based on the volumetric methodology, using Calcimeter Bernard.

Table 1. Chemical characteristics of the soil and their representative methods and standards

Soil parameters	Unit	Methods
Chemical parameters		
Soil Organic Carbon [SOC] Soil Organic matter [SOM] Nitrogen [N]	%	Walkley and Black, FAO, 2019
pH		ISO 10390: 2005

Interpolation and statistical analysis

The geostatistical method was used to generate SOC, SOM, N and soil pH – H_2O distribution maps of the study area for the two first soil horizons (0-30 and 30-60 cm). Values of the SOC, SOM, N and soil pH – H_2O were described with classical statistics [mean, standard error, media, mode, standard deviation, sample variance, kurtosis, skewness, range, minimum, maximum, count and Confidence Level (95.0%) were generated using Excel. The IDW method was generated in QGIS 3.16 while the Kriging method was on ArcGIS Pro 2.9.

For the interpolation methods, we have decided to make the spatial distribution using the inverse weighing distance and with the kriging method. Although the spatial distribution of the measured parameters using the IDW method does not cancel any bias when displaying the data from the sample location to the surroundings from the maps which were made of out soil analysis its spatial distribution is highlighted more when displayed with the kriging method (Cressie, 1990).

$$Z(s_0) = \sum_{i=0}^{N} \Lambda_i Z(s_i)$$

Where $Z(s_i)$ is the measured value at the i location; $\Lambda_i (lambda)$ is an unknown weight for the measured value at the i location; s_0 is the prediction location; N is the number of measured values.

For the kriging method the measured values determine the unknown location Λ_i for as in our case the spherical and Gaussian methods were used in which the value of the unknown location was determined by weighting the 5 surrounding known locations whereas in the IDW interpolation is does predict or rely on spatial distribution values of other close values. IDW in this classification is considered as a mathematical method whereas the kriging method is applied as geostatistical method. For such we have considered the kriging method is more suitable since the data are spatially correlated (Virdee and Kottegoda, 1984). Reza et al. (2010) on the evaluation and comparison or ordinary kriging and inverse distance weighting methods does display the similarities of two methods although the accuracy of spatial analytical methods through cross-validation does give.

Results and Discussion

Evaluation of SOM, SOC, N and pH in different soil depths

The descriptive statistical properties of chemical analysis of the soil analysis of both depths have been summarized in Table 2.

Table 2. Descriptive statistics analysis of the SOM, SOC, N and pH – H_2O for 0 – 30 depth

	pH - H_2O		SOM %		SOC %		N %	
	0-30	30-60	0-30	30-60	0-30	30-60	0-30	30-60
Mean	7.67	7.79	1.56	0.92	0.91	0.53	0.09	0.05
Standard Error	0.02	0.02	0.02	0.01	0.01	0.01	0.00	0.00
Median	7.91	8.10	1.48	0.83	0.86	0.48	0.08	0.05
Mode	8.46	8.59	1.62	0.77	0.94	0.45	0.08	0.04
Std	0.90	0.94	0.73	0.54	0.43	0.31	0.04	0.03
Sample Variance	0.82	0.89	0.54	0.29	0.18	0.10	0.00	0.00
Skewness	-0.87	-1.07	1.78	1.68	1.78	1.68	1.76	4.80
Range	5.10	6.05	6.88	4.85	3.99	2.84	0.38	0.60
Minimum	4.25	3.25	0.12	0.00	0.07	0.00	0.01	0.00
Maximum	9.35	9.30	7.00	4.85	4.06	2.84	0.60	0.39

The results of the Table 2 showed that the mean value of SOM, SOC and N content decreases with soil depth and variates from 1.56% to 0.92%, 0.91% to 0.53% and 0.09 to 0.05% respectively, while soil pH increases with the depth and variates from 7.67 to 7.79. Moreover, the SOC was determined from 0.07% to 4.06% in the top soil horizon 0-30 cm, while in the second soil horizon 30-60 cm was determined from 0.00% to 2.84%.

The reduction or accumulation of soil organic carbon content in the top soil horizon can be influenced by shifting of land use types and land cover management in short term periods. The high variation of SOC in the studied area may be influenced by the dominance of differences of land use types are vineyards, table grapes, horticulture such as peppers and cabbage, arable land such as maize, winter wheat, alfalfa and meadows, as well as due to the undulating landscape of Dukagjini Plain, particularly in Rahovec municipality (Green Report, 2021).

Converting native pasture to cropland can lead to a decrease in SOM and soil aggregate stability (Celik, 2005). Some of the other changes, such as returning natural land into croplands, erosion was increased because it influenced soil physical properties (Li et al., 2007). One of the main attributes is also tillage practices because observation leads to the lowest SOM is founded on these cultivated lands (Haghighi et al., 2010). Moreover, natural pastures, which were not influenced by tillage or other agriculture practices showed that have better conditions in the aspect of soil properties (Bormann and Klaassen, 2008), whereas the agricultural practices in Rahoveci municipality may change from very intensive to non-intensive, due to that we have considered that using the top soil horizon 0-30 cm and second soil horizon 30-60 cm would provide accurate information for the agricultural practices and land uses in Kosovo.

The relationship between variation of land cover type and SOC content

To determine the land cover of the study area, Corine land cover classification (CLC) raster image of 2020 were used. Based on the Corine land cover classification of the Figure 3 and Table 3 the main land cover are complex cultivation patterns with 41% of the area which mainly includes crops such as winter wheat and maize and contain around 0.7 to 0.873% SOC, non-irrigates arable land with 21% of the area which mainly includes vegetables such as peppers, melons and water melons, cabbage contains 0.937 to 1.804% SOC, agriculture land (natural vegetation) which cover 18% of the studied area and dominate uncultivated land contains 0.923 to 0.936% SOC, vineyards occupy 8% of the territory and because of very intensive agriculture practices and unfavourable land management practices showed the lowest SOC content with 0.072 to 0.699% same results were observed by Martin et al. (2011), while the rest belong to broad leave forest with 0.937 to 4.05% SOC, natural grassland with 0.94 to 1.176% SOC, pastures 0.94 to 1.001%, orchards and urban representing smaller area, table 3 displays the sample distribution on each CLC category.

Land use has a great impact on carbon stock in the soil (Dengiz et al., 2019). According to Martin et al. (2011) the SOC content on the soil depends mostly on the land use and land cover type, while, the highest vales of SOC were observed under natural vegetation such as forest, grassl, and and wetland, while the lowest SOC content was observed in vineyards. Agriculture activities that enhance the decomposition of SOM as a result of land preparation activities, in most cases reduce the SOM (Six et al., 2000), meanwhile vegetation has a significant effect on the quality and quantity of SOM (Lovett et al., 1993).

Table 3. Distribution of sampling points in land uses

CLC classification	Samples	Samples (%)
112 - Discontinuous urban fabric	18	1%
211 - Non-irrigated arable land	433	21%
221 - Vineyards	166	8%
222 - Fruit trees and berry plantations	15	1%
231 - Pastures	43	2%
242 - Complex cultivation patterns	853	41%
243 - Agriculture land (natural vegetation)	382	18%
311 - Broad-leaved Forest	69	3%
321 - Natural grasslands	42	2%
324 - Transitional woodland-shrub	45	2%
331 - Beaches - dunes - sands	1	0%
333 - Sparsely vegetated areas	8	0%
	2057	100%

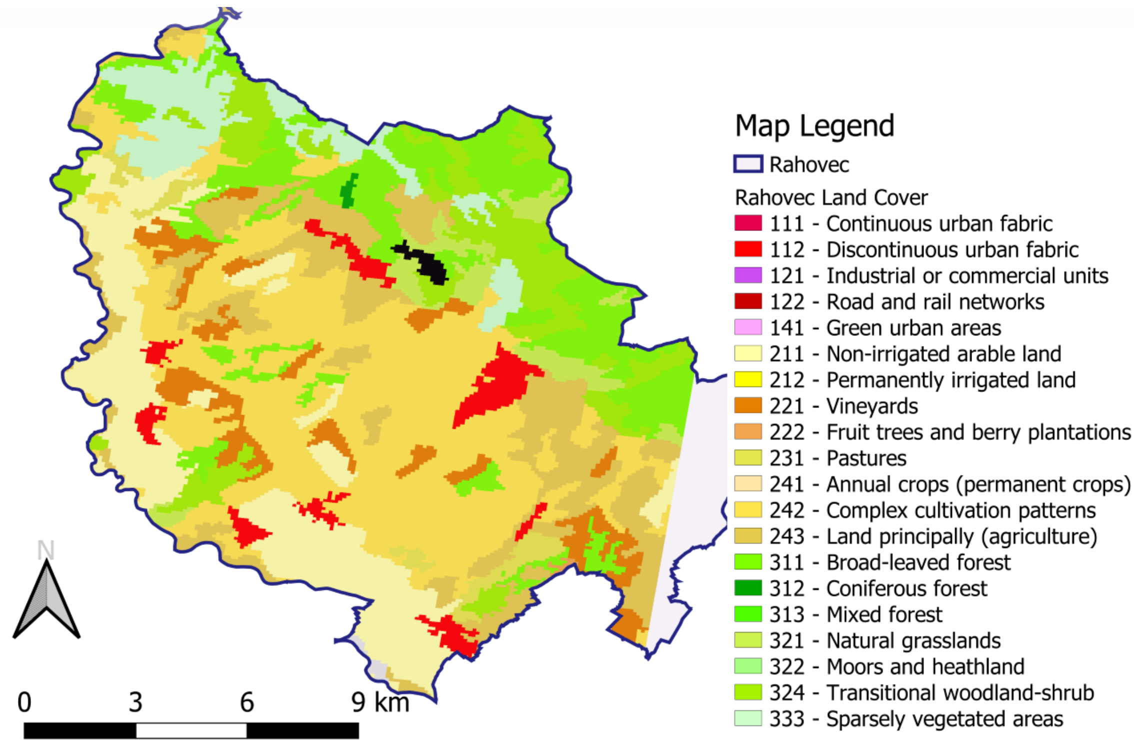

Figure 3. Land cover map of Rahoveci municipality

Estimation of interpolation maps for SOM, SOC, N and pH

Spatial analysis of the analysed parameters are shown in Figure 4, 5, 6 and 7. In two different sample selection depths, we directly interpolated the data in QGIS and ArcGIS using inverse distance weighting and the kriging model. For IDW interpolation for its analysis requires wights of neighbouring samples the spatial distribution of samples is displayed the non-continuity of soil mapping results figure 4 and 6. For SOC, SOM, and N, we have used optimized Gaussian model for Kriging interpolation, meanwhile for pH, we used the spherical model shown in Figures 5 and 7. Mapping produced an interconnected soil surveying result display importance of soil analysis.

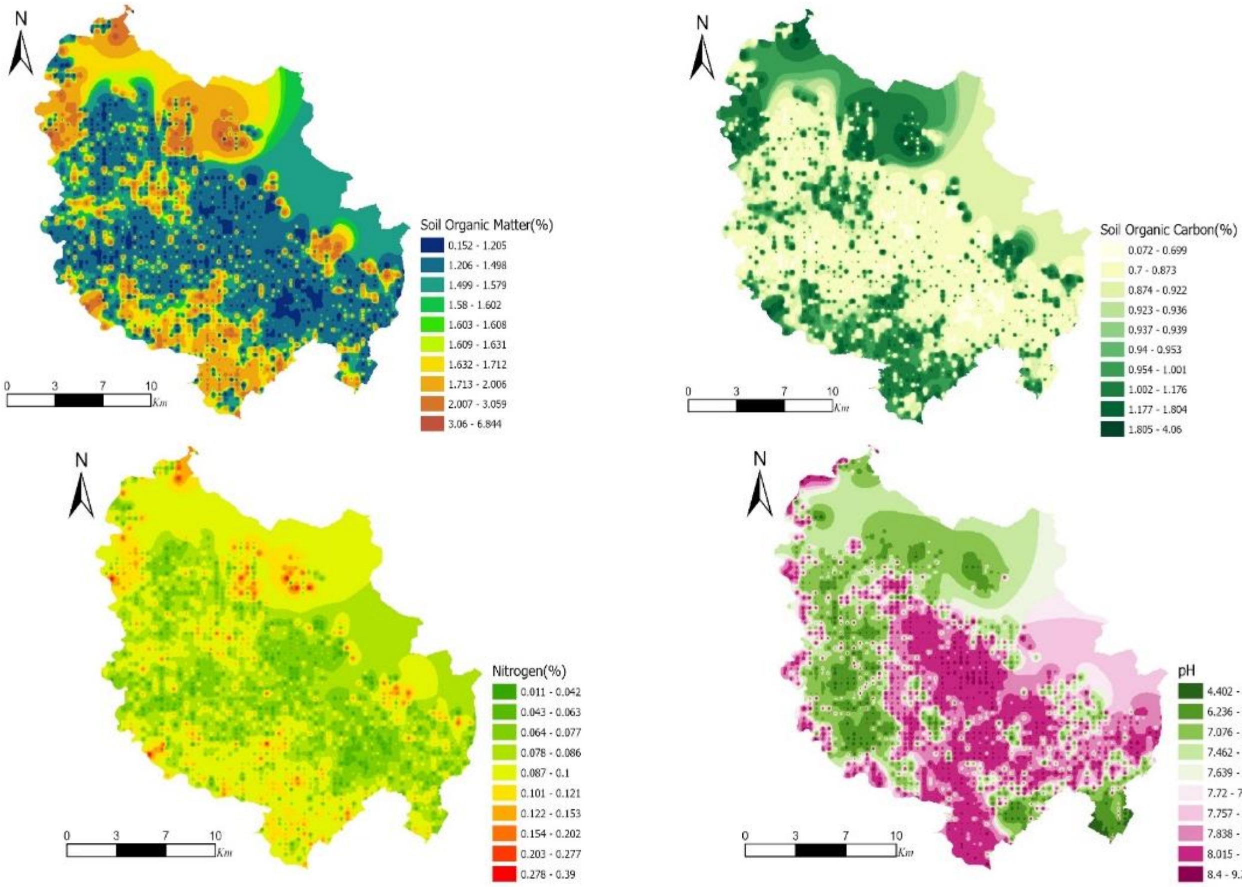

Figure 4. Inverse Distance Weighted interpolation of the results of the 0-30 cm soil samples for SOM – Soil organic matter, SOC – Soil organic carbon, N – Nitrogen and soil pH – H2O.

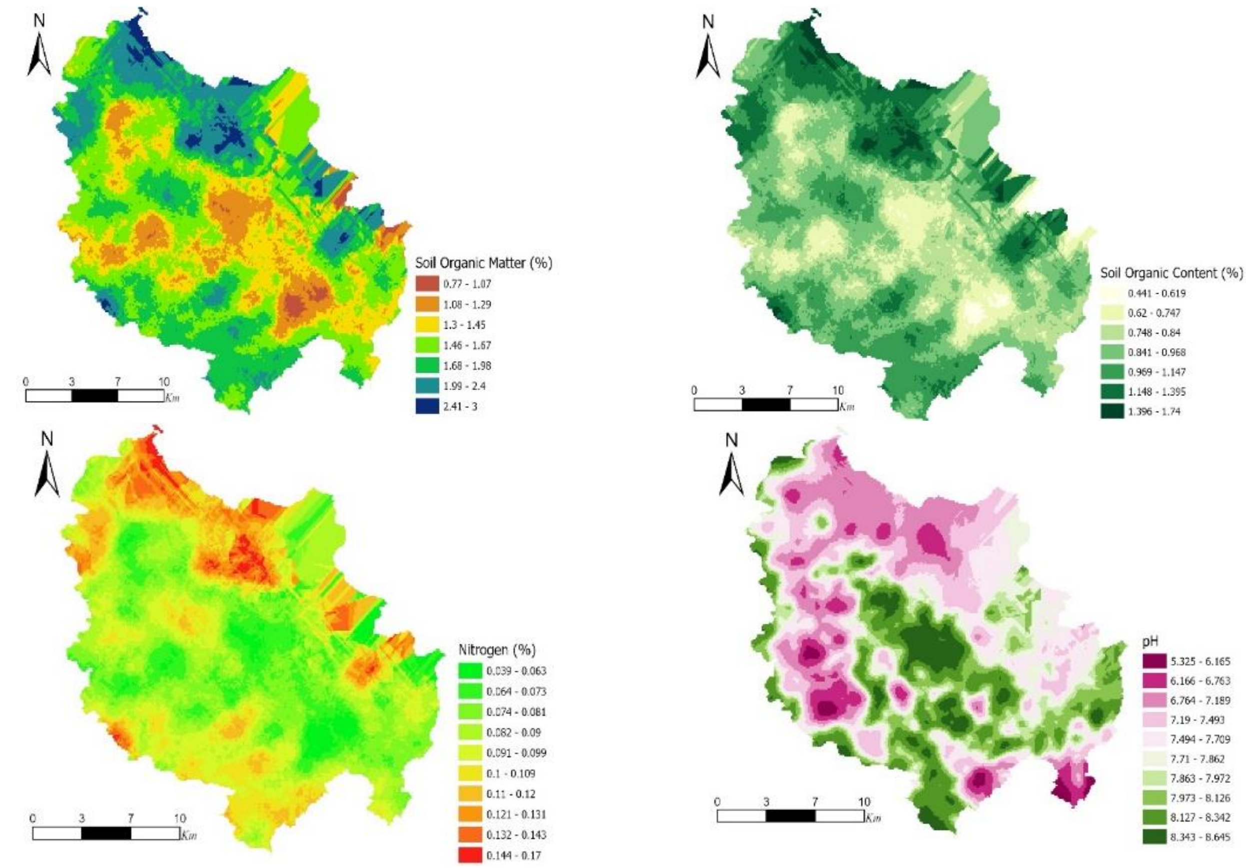

Figure 1. Kriging interpolation of the results of the 0-30 cm soil samples for SOM – Soil organic matter, SOC – Soil organic carbon, N – Nitrogen and soil pH – H_2O

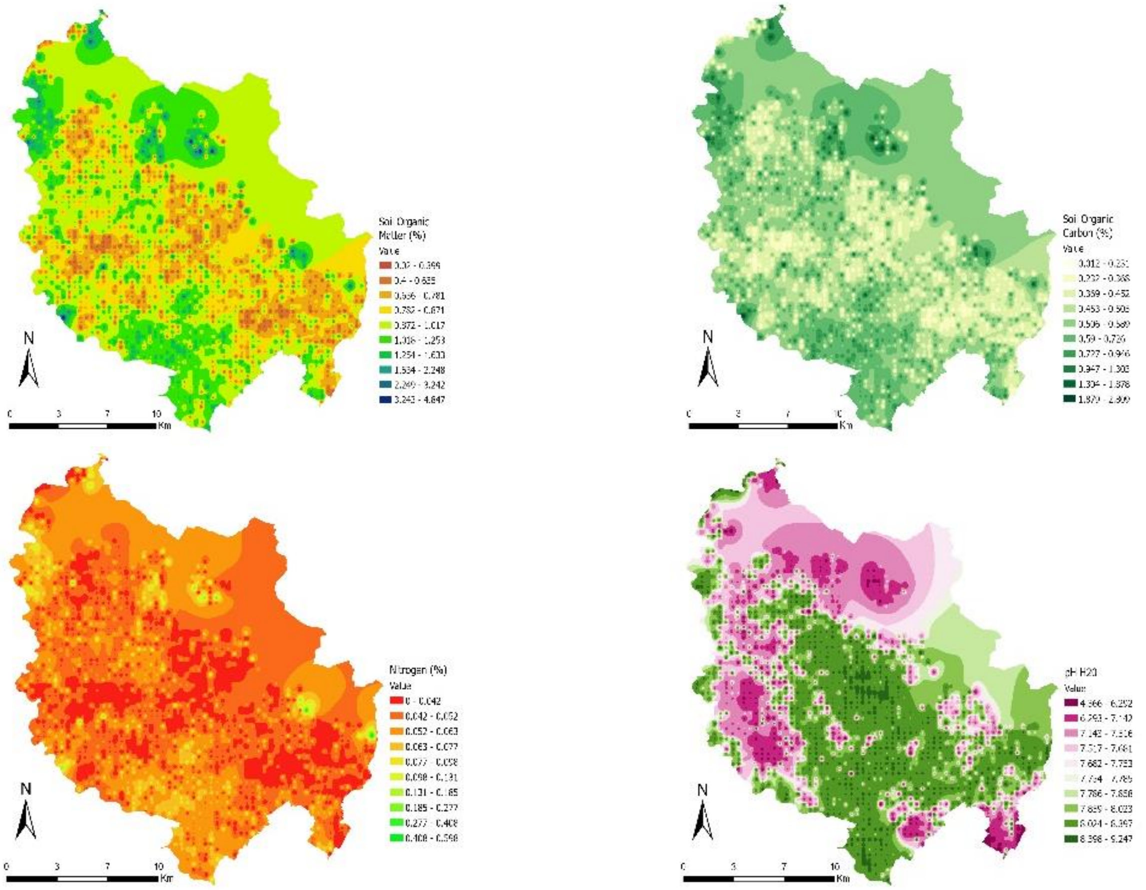

Figure 6. Inverse Distance Weighted interpolation of the results of the 30-60 cm soil samples for SOM – Soil organic matter, SOC – Soil organic carbon, N – Nitrogen and soil pH – H2O

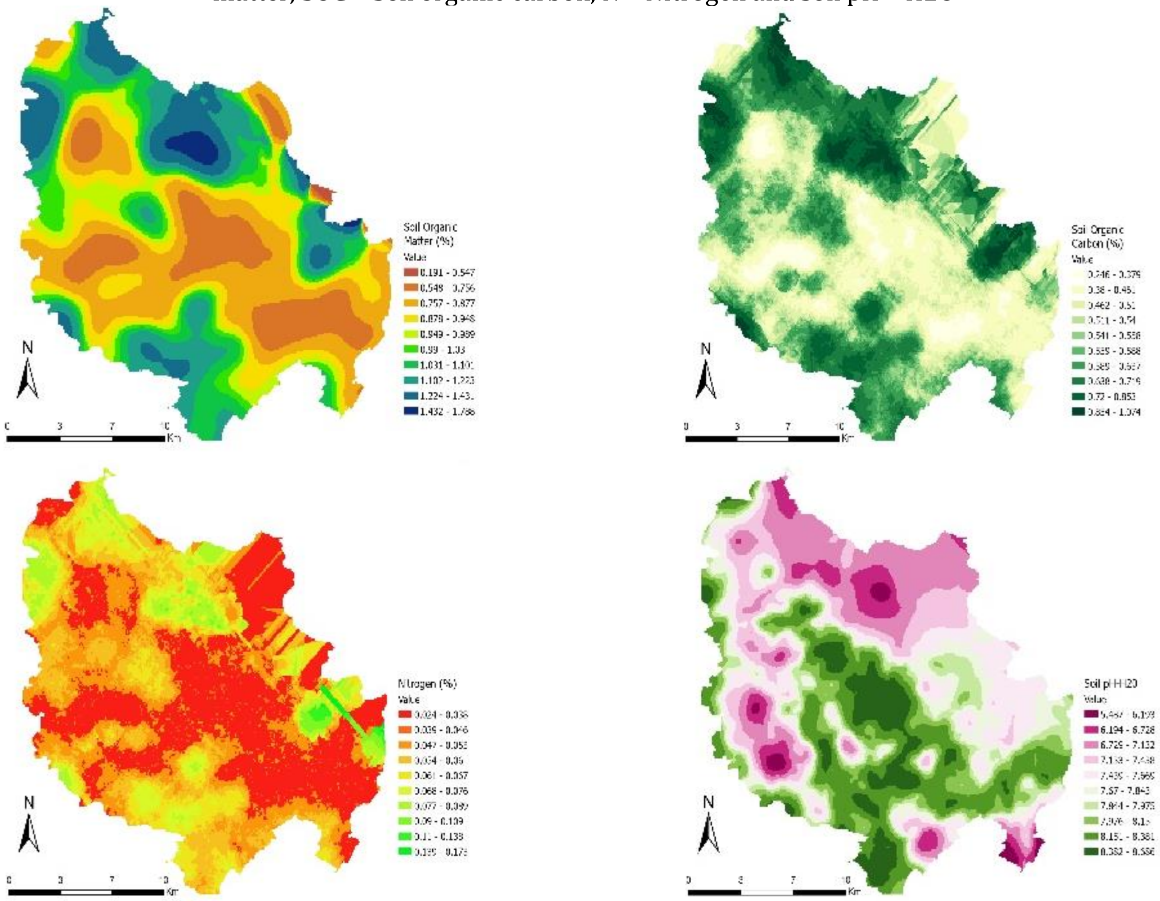

Figure 7. Kriging interpolation of the results of the 30-60 cm soil samples for SOM – Soil organic matter, SOC – Soil organic carbon, N – Nitrogen and soil pH – H2O

Conclusion

The spatial distribution of SOM, SOC, N, and pH content across the study area is shown by Inverse Distance Weighted interpolation and Kriging interpolation technique. The SOC content distribution showed higher values in the area of natural vegetation, in the forest with up to 4.05% and grassland with up to 1.17%, followed by arable land and the lowest SOC content was observed in vineyards with maximum 0.69%. In this study area, the visualization of SOC distribution can help regional farmers in the selection of crops for certain areas for better management of their lands and agricultural production. This study has explained in detail the distribution of SOC, SOM, N and pH using inverse distance weighted interpolation and Kriging interpolation technique that can be applied to different study areas with other soil components. Spatial analyses characterize the current state of the soil for the current year, but do not represent dynamic changes over time, although changes in soil measurements between two depths represent the effect of agricultural practices (human impact). Although based on the analysis we consider that the Kriging method is more spatially accurate compared to IDW as a mathematical method. Due to the unfavourable agricultural practices that are being applied by the farmers of the municipality of Rahovec, it should be taken into account that the farmers need more theoretical and practical trainings such as indoor and outdoor explanations on how to prepare the land for planting or cultivation during the vegetation period in order to protect against further degradation.

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Impact of different organic fertilizers on soil available nutrient contents, potato yield, tuber nitrate contents

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Abstract

In this study, field experiment was conducted to assess the effect of different organic fertilizer and mineral fertilizer on mineral and different organic fertilizer treatments effect on available N, P, K contents, the yield of potato (*Solanum tubevosum* L.), cultivar Astana, nitrate contents of tuber under dark chestnut soil conditions in southeast of Kazakhstan during the spring and summer of 2022. The experiment was carried out in the field and laid out as complete randomized block design with four replicates. Thirteen treatments that are, control without fertilizer treatment, mineral fertilizer with recommended dose ($N_{150}P_{90}K_{120}$) and eleven different organic fertilizers treatment were used. The results showed that available nutrient (N, P and K) contents of the post-harvest soil were affected by mineral and different organic fertilizers compared to the control. And, the available N, P and K contents in the soils taken from the biohumus (10 t ha^{-1}) and cattle manure (40 t ha^{-1}) treated plots were found to be higher than all of the other treatments and control. Similarly, plots treated recommended mineral fertilizer and different organic fertilizers had a significantly higher yield of potato tuber compared with control. When all applications were compared with each other, it was determined that the treatments that increased the potato yield the highest was the treatment of Biohumus (10 t ha^{-1}) + BioZZ (5 L ha^{-1}, 3 times). The highest nitrate content of tubers was obtained in mineral fertilizer with recommended dose ($N_{150}P_{90}K_{120}$). Hence, these results suggest that organic production of potato (Biohumus, 10 t ha^{-1} + BioZZ 5 L ha^{-1}, 3 times) could be an alternative to conventional production in Kazakhstan without reduction in yield, and with low nitrate content of tuber and high available nutrient contents in soil.

Keywords: Potato, organic fertilizer, biohumus, soil, nutrient, tuber nitrate.

Introduction

Potato (*Solanum tubevosum* L.) is one of the world's major staple crops after wheat, maize and rice to the world's food security (Waqas et al., 2021). Also, potatoes are an important crop in the Central Asian Republics (Loebenstein and Manadilova, 2003). They are the second most important crop in Kazakhstan, after wheat, grown on about 205.000 ha and its yields average 19.5 t ha^{-1} (Alimkhanov et al., 2021).

Potato adapts to many environmental conditions and is of short life cycle when compared with other tropical tuber crops (Horton, 1988, Esan et al., 2021). The importance of potato is increasing in Kazakhstan's farming and food systems because it is easy to plant, matures easily and has enormous industrial and economic potentials. Potato planting is done using conventional methods using chemical fertilizers, organic potato production is not done today in Kazakhstan. Organically grown food is attractive to both scientific and non-scientific communities (Hajšlová et al., 2005). Considering Kazakhstan's agricultural land capacity, farmer habits and increases in potato consumption in Kazakhstan and other countries, organic potato production

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could be important for Kazakhstan and make Kazakhstan a brand for organic potato production. Because, health benefits associated with organic food remains a focal point for research and production (Holden, 2001).

Several research results indicated that potatoes produced with organic practices are healthier than potatoes produced using conventional methods (Michaelidou and Hassan, 2008; Baudry et al., 2017). Potatoes produced with organic agricultural inputs contain less nitrate than potatoes produced with conventional methods using chemical fertilizers (Erhart et al., 2005; Lairon, 2009; Kazimierczak et al., 2019). Likewise, increases in dry matter, vitamin C, total amino acids, total protein, total sugars, and mineral plant nutrients were noted for potatoes produced with organic inputs when compared to potatoes produced by conventional methods (Wszelaki et al., 2005; Hajšlová et al., 2005; Rembialkowska, 2007; El-Sayed et al., 2015; Djaman et al., 2021; Esan et al., 2021; Li et al., 2022). And also, in principle, organic fertilizers are more environmental friendly and less expensive than mineral fertilizers.

It is well known that organic fertilizers improved the soil physical, chemical and biological properties and this consequently encourage the plant to have a good growth (Kızılkaya and Hepşen, 2007; Courtney and Mullen, 2008; Kızılkaya et al., 2012; Gülser et al., 2015; Bayadilova et al., 2022). Moreover, the slow released nutrients contained in organic fertilizers permit the plants to beneficial of it. All these reasons resulted in improve plant growth. The value of organic fertilizers as a source of nutrients for potato plants has been revived by several investigators (Hamouz et al., 2005; Singh and Kushwah, 2006; Maggio et al., 2008; Blecharczyk et al., 2023).

Mineral fertilizers are usually applied below the recommended rate ($N_{150}P_{90}K_{12}$) for potato production in Southern Kazakhstan. However, the effects of organic fertilizers on yield of potato on dark chestnut is unknown in Kazakhstan. For potato cropping, nutrients' primary source is the mineral fertilizer. Therefore, this study was aimed to determine different organic fertilizers and mineral fertilizer with recommended dose treatments effect on available N, P, K contents, the yield of potato, nitrate contents of tuber under dark chestnut soil conditions in South-east Kazakhstan.

Material and Methods

Study site and Soil Properties

During the spring and summer of 2022, the current research was conducted at the Regional Branch "Kainar" of the LLP "Kazakh Research Institute of Fruit and Vegetable Growing", foothill zone of the southeast of Kazakhstan (1050-1100m above sea level) on a dark chestnut soil. The commercial potato (*Solanum tuberosum* L.) cultivar Astana which are generally planted in April and harvested in September was used.

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 (-32,-35^{0}C), and maximum values in July (37-43^{0}C). The warm period lasts 240-275 days, the frost-free period is 140-170 days and an annual amount of precipitation is 250 – 600 mm.

A soil sample was collected from the experimental field at the beginning of the experiment. Physical and chemical properties of the experimental soil were determined Kazakh National Agrarian Research University according to the Rowell (1996). The soil belongs to the general soil type of dark chestnut. The land was medium high with loamy. The soil was characteristically slightly alkaline (pH 7.3-7.4), soil organic matter 2.9-3.0% (moderate), total N 0.18-0.20% (high), available P_2O_5 35-40 mg kg^{-1} (moderate), available K_2O 360-390 mg kg^{-1} (low), cation exchange capacity 20-21 meq 100g^{-1} soil, bulk density 1.1-1.2 gr cm^{3}, field capacity 26.6%.

Soil Preparation, Experimental design and Cultivation

As per standard commercial cultural practice for chestnut soil. The field was plowed using a chisel plow. Thereafter, the experimental field was divided into 180 cm wide strips. For each fertilizer treatment described below, two 1.80 m strips were divided into 50 m long sections. Total plot area was 180 m^{2} (3.6 m by 50 m) to which organic and mineral fertilizers. Organic and mineral fertilizers were then incorporated into the soil using a rotavator. Fertilizer treatments were arranged in a complete randomized block design with four replicates.

Potato (*Solanum tuberosum* L.) cultivar Astana seeds were cut (approximately 35 g pieces) and left for a week for curing before planting. Potato tubers were mechanically planted on 28 April 2022, using a four-row-planter leaving 25 cm between hills and 90 cm between rows in all plots. Therefore, each plot was 50 m by 3.6 m with four rows of 0.90 m.

Treatments, Fertilizer application and Harvest

The experiment consisted of thirteen treatments as follows:

T1	Control (without fertilizer)
T2	Mineral fertilizer ($N_{150}P_{90}K_{120}$)
T3	Biohumus (10 t ha^{-1})
T4	Biohumus (10 t ha^{-1})+BioZZ (5 L ha^{-1}, 3 times)
T5	Cattle manure (40 t ha^{-1})
T6	Bird manure (30 t ha^{-1})
T7	Bird manure (10 t ha^{-1}) + Terra Sorb Foliar (3 L ha^{-1}, 3 times)
T8	Wheat straw (3 t ha^{-1}) + Megavit, (5 L ha^{-1}, 3 times)
T9	Baraebong Organic Fertilizer (10 t ha^{-1})
T10	Megavit, (5 L ha^{-1}, 3 times)
T11	WORMic, (5 L ha^{-1}, 3 times)
T12	BioEkoGum, (3 L ha^{-1}, 3 times)
T13	ZhGU (3 L ha^{-1}, 3 times)

Mineral fertilizers were applied at a rate of $N_{150}P_{90}K_{120}$. All amounts of phosphorus and potassium were applied manually during soil preparation in the form of double superphosphate (46%P_2O_5) and potassium sulfate (56% K_2O), while nitrogen was divided into two equal portions, and applied during soil preparation and 6 weeks after planting in the form of ammonium nitrate (34.5% N). Biohumus (in many countries of the former Soviet Union such as Azerbaijan, Kazakhstan and Russian Federation, vermicompost is called biohumus) consisted of 40% organic matter, 3% N, 5% P_2O_5, 1.2% K_2O, 5% Ca, 5% Mg, Cattle manure (0.6% N, 0.3% P_2O_5, 0.7% K_2O, 0.7% Ca, 0.15% Mg, 0.1% S), Bird manure (1.5% N, 1.8% P_2O_5, 1.0% K_2O), Wheat straw (0.5% N, 0.25% P_2O_5, 0.8% K_2O) and Baraebong Organic Fertilizer (3.5 % organic matter, 2.50 % N, 2.05% P_2O_5, 1.56 % K_2O) were applied during the planting. On the other hand, Terra Sorb Foliar (20% Organic matter, 6% Total N, 1% Organic N and 6% free amino acid), Megavit (contains amber, oxalic, citric, orthophosphoric acids, extract from biohumus, extract from unripe coals, nano-carbon, N,P,K,B, Ca, S, enriched with chelated form of 3 g Mg L^{-1}, 2 g B L^{-1}, 2 g Fe L^{-1}, 1 g Zn L^{-1}, 1 g Cu L^{-1}, 1 g Mn L^{-1}), WORMic (contains N, P, Ca, S, Zn, Cu, Mn, Zam-Zam water, phytohormones, amino acids, fulvates, gibberellins, auxins, peptides, humins, soil bactericides), BioEkoGum (contents: 189 N mg mL^{-1}, 31 mg P mL^{-1}, 310 mg K mL^{-1}, 1.2 g total C L^{-1}, 2.1 g humic acid L^{-1}, 0.28 g fulvic acid L^{-1}, 0.14 mg Cu mL^{-1}, 135.2 mg Zn mL^{-1}, 170, 4 mg Mn mL^{-1}, 748.5 mg Mo mL^{-1}, 11.2 mg Fe mL^{-1}, 4.4 mg B mL^{-1}), and ZhGU (liquid humic fertilizer contains all components of biohumus in dissolved state: humic acids, fulvic acids, vitamins, natural phytohormones, micro- and macroelements in the form of bioavailable organic compounds; 1500 mg N $100g^{-1}$, 1600 mg P $100g^{-1}$, 2500 mg K $100g^{-1}$), were applied just after planting, and 3, 6, and 9 weeks after planting. These foliar fertilizers were applied in the form of liquid using knapsack pesticide sprayer.

Harvesting of the crop was done treatment-wise on 30 September 2022. Firstly one border row from both sides and two plants from both ends were harvested to eliminate the border effect from each plot. Harvesting was done by digging of plants with the help of sickle axe.

Data collection

Soil Sampling and Analyses

After harvest, the soil samples collected from depth of 20 cm were naturally air-dried, milled and passed through 2.0 mm sieve. Available nitrogen (NH_4+NO_3) by the modified Kjeldahl method, available Phosphorus was determined by the 0.5M $NaHCO_3$ extraction method, available Potassium content were determined by the 1N NH_4OAc extraction method according to the Rowell (1996) and Jones (2001)

Plant Sampling and Analyses

After harvesting, tubers were separated according to the treatment and weighed on double pan balance for each treatment separately. After this, total tuber yield was calculated as the sum of the weights of marketable and unmarketable tubers from the net plot area and transformed to ton per hectare.

Procedure for Nitrate Determination

Immediately after the harvest, potato tuber samples were placed in a storeroom at a temperature of 10^{0}C and RH of 80%. After three days of storage, the part of potato tubers were washed. Raw tubers were cut into 1 x 1 x 1 cm cubes and frozen in liquid nitrogen. Frozen potato samples were stored at a temperature of -18^{0}C. The samples were then lyophilised and ground (particle size of 0.3–0.5 mm) using a laboratory mill Ultra-Centrifuge. The ground samples were stored in the dark in tightly sealed bags in a desiccator until laboratory testing. In this way, the nitrates and nitrites content were determined in the prepared material. Two grams of freeze-dried potatoes were mixed with 50 mL of 1% $KAl(SO_4)_2$ solution and well extracted. The extraction was carried out for 1 h using a shaker. The samples were filtered through Whatman No. 4 filter paper. Ten millilitres of 60% $Al_2(SO_4)_3$ solution was added to the filtrate and mixed immediately before the assay. The nitrate content was determined based on the KNO_3 standard curves. At each stage of the analytical testing, deionised water was used. Nitrate concentration in samples determined by the ion-selective potentiometric method according to Baker and Thompson (1992).

Results and Discussion

Nutrient contents of post-harvest soil

The effect of mineral and different organic fertilizers on available nutrient contents of post-harvest soil are presented in Figure 1. The soils from every plot after harvest of potato (*Solanum tuberosum* L.) cultivar Astana were analyzed for available nitrogen, phosphorus and potassium contents. The result from this study indicated that the available nutrient contents of the soil were affected by mineral and different organic fertilizers compared to the control. Available nitrogen content in soil was the highest (67.60 mg kg^{-1}) in T3 treated plot which was similar to the all treatments i.e. T5, T6, T7, T8, T2 and T9 treatments with the values of 64.4, 60.4, 58.3, 53.2, 50.4 and 47.6 mg kg^{-1}, respectively. Available phosphorus contents in soil had increased in all treated soils including control plot. The T5 treatment showed the highest value (134 mg kg^{-1}) which was different from all other treatments. Next to T3, the other three treatments (T6, T9 and T7) were differ. But, other treatments were identical. All treatments except T8 treatment increased the available potassium content of soils compared the control, the values being 300-520 mg kg^{-1}. The highest K content was noted with the T3 treatment which was significantly higher over all other treatments. The T3 treatment (Biohumus, 10 t ha^{-1}) showed the best positive effect on available soil nutrients (N, K and P) which was presumably due to higher mineralization. Thus, it is likely that the residual effects of organic amendment would have positive contribution to the next crop(s).). Sultana et al. (2021) stated that organic and inorganic integrated treatment gave the higher values for soil N, P and K contents whereas the inorganic treatment gave significantly lower values for those nutrients. Thomas et al. (2019) reported that application of anaerobic digestate (AD), compost, farmyard manure (FYM), straw, and mixes of amendment + straw applications can increase available N, P and K contents in the soil. Previous studies (Whalen and Chang, 2002; Diacono et al., 2010. Sürücü et al., 2014; Gülser et al., 2015) have reported that organic fertilizers were able to effectively improve the content of these nutrient elements in newly reclaimed land. Similarly, the results from this study indicated that the effect of organic fertilizers was dependent on the kind of organic fertilizers as well as the nutrient elements compared the mineral fertilizer.

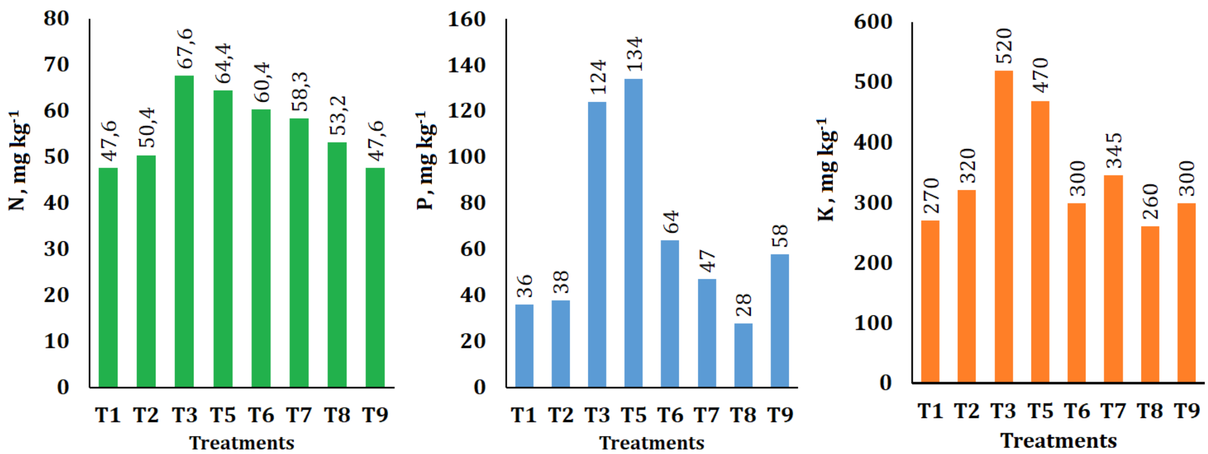

Figure 1. Effect of mineral and different organic fertilizer treatments on available N, P and K content in dark chestnut soil T1: Control (without fertilizer), T2: Mineral fertilizer ($N_{150}P_{90}K_{120}$), T3: Biohumus (10 t ha^{-1}), T5: Cattle manure (40 t ha^{-1}), T6: Bird manure (30 t ha^{-1}), T7: Bird manure (10 t ha^{-1}) + Terra Sorb Foliar (3 L ha^{-1}, 3 times), T8: Wheat straw (3 t ha^{-1}) + Megavit, (5 L ha^{-1}, 3 times), T9: Baraebong Organic Fertilizer (10 t ha^{-1}).

Potato yield

The effect of mineral and different organic fertilizers on total yield of potato tuber is presented in Figure 2. Plots treated recommended mineral fertilizer rate ($N_{150}P_{90}K_{120}$) in conventional systems and plots treated with different organic fertilizers had a significantly higher yield of potato tuber compared with control plots. In this study, the yield of potato tuber in the control treatment (T1) without NPK was determined as 18.4 t ha^{-1}, while the potato yield in the recommended treatment of mineral fertilizers (T2) was determined as 26.9 t ha^{-1}. The result from this study indicated that Potato yield was significantly affected by fertilizer treatments, and mineral/organic fertilizers exhibited a significant increase (17.4% in T13 treatment–87.5% in T4 treatment) in yield of potato tuber compared to the control. T4 increased potato yield by 87.5%, followed by T3 which increased by 72.3%.

Some of the organic fertilizers used in this experiment were applied to the plant only as foliar spraying (T10, T11, T12 and T13), some of them were applied only from the soil (T3, T5, T6 and T9) and some of them were applied both from the soil and from the leaves (T4, T7 and T8). According to the results, it was determined that the application of organic fertilizer applied to the potato with only foliar spraying in 3 times increased the yield of potato tuber compared to the control, but this increase was lower than the mineral fertilizer. However, it was determined that only the application of organic fertilizer from the soil increased the yield of potato tuber compared to the control. It was determined that the increase in T3, T5 and T9 treatments were higher than the mineral fertilizer application. However, the increase in T6 treatment was found to be lower than the application of mineral fertilizers. It was determined that the effect of both soil and foliar spraying treatments (T4, T7 and T8) on yield of potato tuber, the increase in all applications was higher than both control and mineral fertilizer application. These treatments, T4 treatments (Biohumus, 10 t ha^{-1} + BioZZ, 5 L ha^{-1}, 3 times) were highest in yield of potato tuber compared with the all of other treatments. It was determined that the effects of organic fertilizers on yield of potato tuber were also different. The various effects of organic fertilizers on yield of potato tuber may be mainly attributed to the difference in their composition. In agreement with the result of this study, some previous studies (Butler and Muir, 2006; Zhao et al., 2020; Li et al., 2022) have also reported the use of organic fertilizers in the yield of potato tuber. For example, Liu et al. (2014) reported the effects of biochar treatments on rapeseed and potato yields and water stable aggregate in upland red soil.

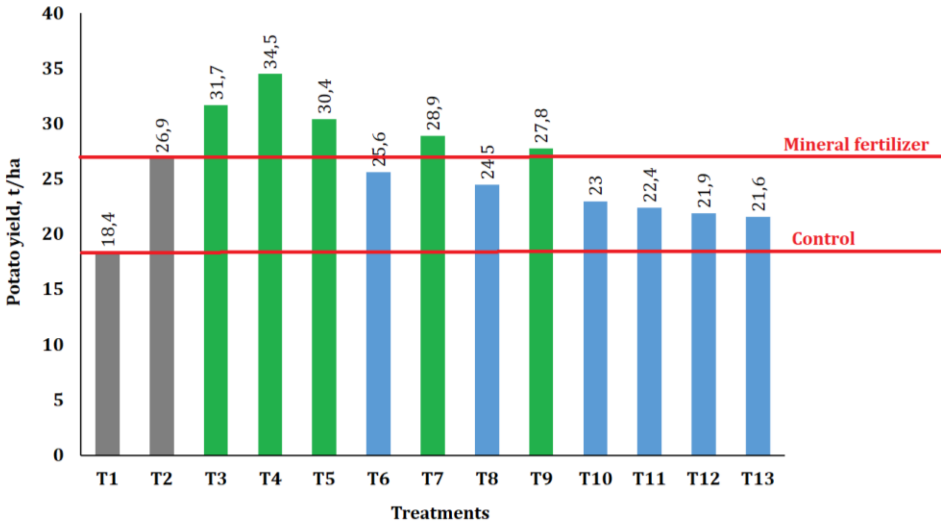

Figure 2. Effect of mineral and different organic fertilizer treatments on yield of potato tuber in dark chestnut soil. T1: Control (without fertilizer), T2: Mineral fertilizer ($N_{150}P_{90}K_{120}$), T3: Biohumus (10 t ha^{-1}), T4: Biohumus (10 t ha^{-1})+BioZZ (5 L ha^{-1}, 3 times), T5: Cattle manure (40 t ha^{-1}), T6: Bird manure (30 t ha^{-1}), T7: Bird manure (10 t ha^{-1}) + Terra Sorb Foliar (3 L ha^{-1}, 3 times), T8: Wheat straw (3 t ha^{-1}) + Megavit, (5 L ha^{-1}, 3 times), T9: Baraebong Organic Fertilizer (10 t ha^{-1}),T10: Megavit, (5 L ha^{-1}, 3 times), T11: WORMic, (5 L ha^{-1}, 3 times), T12: BioEkoGum, (3 L ha^{-1}, 3 times), T13: ZhGU (3 L ha^{-1}, 3 times).

Nitrate contents of potato tuber

In this research, the results indicate a higher nitrate contents in potato tubers produced under mineral fertilizer treatment, as compared to an organic fertilizer treatments. This results from the treatment of recommended mineral fertilizer rate ($N_{150}P_{90}K_{120}$) in conventional systems (Figure 3). This was also confirmed by other researches (Tamme et al., 2006; Wierzbowska et al., 2018; Kazimierczak et al., 2019). In addition, nitrate contents of potato tuber increased in response to mineral fertilizer (T2) and some organic fertilizer treatments (T3, T4, T5, T6, T7, T9, T12, T13) relative to the control (T1) treatment. The nitrates content in the potato tubers, determined immediately after the harvest, ranged from 65 to 223 mg kg^{-1}. Similarly, Wszelaczyńska et al., (2022) reported that the nitrates content in potato tubes ranging from 77.0 to 259.9 mg kg^{-1}. According to Commission Regulation (EC) No. 1822/2005 of 8 November 2005, the nitrates content of potato tubers should not exceed 200 mg kg^{-1}. The higher nitrate contents of potato tuber for the T2 (mineral fertilizer) and T6 (Bird manure, 30 t ha^{-1}) treatments than for any of the other rates of treatments and control (T1). These differences between T6 and other organic fertilizer treatments in these nitrate contents of potato tuber were probably related associated with high application doses and high nitrogen contents of bird manure.

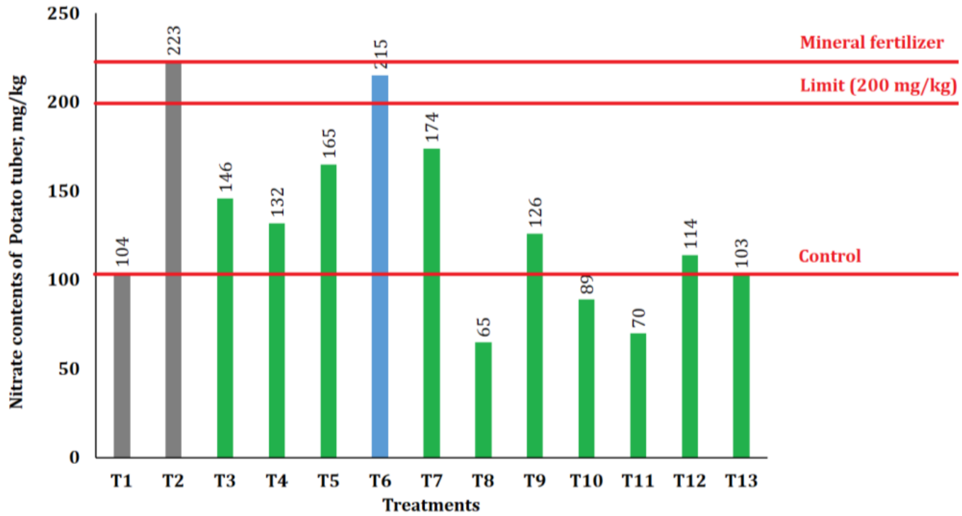

Figure 3. Effect of mineral and different organic fertilizer treatments on nitrate contents of potato tuber in dark chestnut soil. T1: Control (without fertilizer), T2: Mineral fertilizer ($N_{150}P_{90}K_{120}$), T3: Biohumus (10 t ha^{-1}), T4: Biohumus (10 t ha^{-1})+BioZZ (5 L ha^{-1}, 3 times), T5: Cattle manure (40 t ha^{-1}), T6: Bird manure (30 t ha^{-1}), T7: Bird manure (10 t ha^{-1}) + Terra Sorb Foliar (3 L ha^{-1}, 3 times), T8: Wheat straw (3 t ha^{-1}) + Megavit, (5 L ha^{-1}, 3 times), T9: Baraebong Organic Fertilizer (10 t ha^{-1}),T10: Megavit, (5 L ha^{-1}, 3 times), T11: WORMic, (5 L ha^{-1}, 3 times), T12: BioEkoGum, (3 L ha^{-1}, 3 times), T13: ZhGU (3 L ha^{-1}, 3 times).

Conclusion

It can be concluded that integrated use of organic manure and recommended dose of mineral fertilizer and different organic fertilizer resulted in significant improvement in the yield of potato (*Solanum tubevosum* L.), cultivar Astana and available nutrient (N, P and K) contents of the post-harvest soil. Hence, these results suggest that organic production of potato (at the level of 10 t ha^{-1} Biohumus, + BioZZ 5 L ha^{-1}, 3 times) could be an alternative to conventional production (mineral fertilization at a rate of $N_{150}P_{90}K_{120}$) without reduction in potato yield, and with low nitrate content of tuber and soil available nitrogen, phosphorus and potassium contents under dark chestnut soil conditions in South-east Kazakhstan. Therefore, treatment of organic fertilizers that are locally available, eco-friendly, improve soil nutrients can substantially improve potato yield and good returns under better management practices. Thus, we recommend that organic fertilizers should be incorporated into agronomic practices for potatoes which should substitute chemical fertilizers to improve potato productivity. Lastly, the study further recommends additional research to replicate the study in a wider spatial and temporal aspects.

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Reducing nitrogen fertilizer combined with biochar amendment improves soil quality and increases grain yield in the intensive rice cultivation system

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Abstract

Intensive rice cultivation for a long time resulted in increasing soil degradation and less yield. This study aimed to evaluate effects of the combining reducing nitrogen fertilizer (N) with biochar amendment on soil chemical properties, rice growth parameters, and grain yield in the rice cultivation system in the Mekong Delta region, Vietnam (VMD). Field experiment was designed in the split-plot design with two factors, including N fertilizer (main plot) and biochar (sub-plot). Two N fertilizer rates were: (N_{50})—50 kg N ha^{-1} and (N_{100})—100 kg N ha^{-1}, which is the farmer's practice. Biochar was amended with three rates: no applied biochar (B_0), 5 t ha^{-1} (B_5), and 10 t ha^{-1} (B_{10}). The results indicated that reducing N fertilizer by 50% combined 5–10 t biochar ha−1 resulted in maintaining soil pH, soil electrical conductivity, soil organic carbon, cation exchange capacity, and rice biomass. Applying biochar at a rate of 5–10 t ha^{-1} significantly increased the available N, available P, and rice height compared to the treatment with no applied biochar (B_0). Rice yield in the treatments applied with 5–10 t ha^{-1} was significantly higher than the treatment without the use of biochar by 11.6–14.7%. The findings of this study confirmed that reducing 50% N fertilizer combined with 5 t ha^{-1} or 10 t ha^{-1} of biochar could improve soil available N, available P, rice growth, and grain yield in intensive rice cultivation systems in the VMD region.

Keywords: Biochar, nitrogen, Oryza sativa L., paddy soil, phosphorus, soil fertility.

Introduction

In the intensive rice production system in the Vietnamese Mekong Delta (VMD) region, farmers often use a large amount of N fertilizer to gain a high yield (Dung et al., 2021). However, this application could increase fertilizer costs and high-risk environmental pollution. In addition, rice plant often takes up only 40–50% of N fertilizer applied, and the remaining N fertilizer will be lost through NH_3 and N_2O volatilization, or runoff to the water environment (Wulf et al., 2002; Choudhury and Khanif, 2004; Weil and Brady, 2017).

Soil degradation, which is the loss of soil functions capacity to reduce soil fertility and soil biodiversity, is the most serious problem in the world (Brusseau et al., 2019). It causes industrial, commercial pollution, and especially in agricultural production because of the rapidly increasing demand for food and fiber (Kopittke et al., 2019). Over the years, soil degradation leads to reduce rice growth and loss of grain yield. The intensification of rice production is already resulting in acidification, salinization, loss of organic matter, decline of nutrients availability, and increase greenhouse gas emission (Scharlemann et al., 2014; Shcherbak et al., 2014; Kopittke et al., 2017; Dung et al., 2022).

Biochar has been known as a biomaterial that can improve soil characteristics such as water content, soil pH, cation exchange capacity (CEC), and soil organic carbon (SOC) (Jaafar et al., 2015; Bass et al., 2016; Bera et al., 2016). Its effect is dependent on some factors such as soil types (Anthrosols, Ferrasols, or Acrisols) and the amount used (5, 10, 15, or 20 tons of biochar ha^{-1}) (Agegnehu et al., 2017). The application of biochar results

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in reducing soil compaction, increasing field capacity (Chan et al., 2008; Abel et al., 2013), soil pH, organic matter, nutrients availability, and cations exchangeable (Glaser et al., 2002; Laird et al., 2010; Thies et al., 2015), and microorganisms biomass (Chan et al., 2008; Shah et al., 2021). Besides, the increase of plant growth and yield as affected by biochar amendment was reported in some previous studies. A number of studies reported that the application resulted in increased maize yield by 98–150% (Uzoma et al., 2011), wheat (Solaiman et al., 2010), peanut (Agegnehu et al., 2015), and rice (Asai et al., 2009; Bakar et al., 2015; Ali et al., 2021). The crop yield increased in the treatment applied biochar due to increasing soil pH, available soil nutrients, and nutrient uptake capacity (Agegnehu et al., 2017). However, the information about reducing N fertilizer combined with biochar in the paddy rice system in the VMD region was limited.

We hypothesized that the application of biochar could enhance some soil chemical properties and macro-nutrients such as N, P, and K without rice yield loss under reducing N fertilizer conditions. Therefore, this study aimed to determine the effects of N fertilization combined biochar amendment on (i) some soil chemical characteristics such as pH, EC, SOC, and CEC; (ii) availability of macronutrients including N, P, and K; and (iii) growth, rice biomass, and grain yield of paddy rice.

Material and Methods

Soil and biochar properties

The field experiment was conducted at the intensive rice (3 crops per year) area in Giuc Tuong commune, Chau Thanh district, Kien Giang province, which is located in the Vietnamese Mekong Delta (VMD) region (9°57'43.0" N, 105°11'18.1" E). The soil in the experimental area was classified as Dystric Gleysols (IUSS Working Group WRB, 2015). At the depth of 0–20 cm, the soil is acidic (pH 4.90), and soil EC is 0.50 mS cm^{-1}. Soil organic carbon (6.47 %C) ranged in high level for paddy rice (Metson, 1961). Soil texture was silty clay, with the clay contents around 54.45%. Biochar used in this study was a commercial product of Mai Anh Co., Dong Thap province, Vietnam, which was made from rice husk, have a total porosity of 92.3%, according to Phuong et al. (2020a). The characteristics of experimental soil and biochar are presented in Table 1.

Table 1. Experimental soil (0–20 cm) and biochar properties in this study

Characteristics	Soil	Biochar
Sand (%)	1.84	-
Silt (%)	43.71	-
Clay (%)	54.45	-
pH	4.90	7.70
EC (mS cm^{-1})	0.50	4.10
Organic carbon (%C)	6.47	47.1
Total N (%)	0.27	0.47
Available N (mg kg^{-1})	39.90	nd
Total P (% P_2O_5)	0.18	nd
Available P (mg kg^{-1})	3.89	800.00
CEC (cmol$_{(+)}$ kg^{-1})	17.10	6.50
Exchangeable K (cmol$_{(+)}$ kg^{-1})	0.38	12.90

EC: electrical conductivity; CEC: cation exchange capacity; nd: not detected

Experimental design, treatments, and management

The field experiment was conducted in a split-plot design with 3 replicates, while N fertilizer rate was the main factor and biochar amendment was the sub-factor. Two N fertilizer rates were 50 kg N ha^{-1} (N_{50}) and 100 kg N ha^{-1} (N_{100}) as the farmer's practices. Three biochar amendments included no applied biochar (B_0), applied biochar with a rate of 5 t ha^{-1} (B_5), and 10 t ha^{-1} (B_{10}).

Dai Thom 8 rice variety, which was the local variety has a growth duration of 90–95 days, was used for this experiment. Each treatment plot was covered in an area of 25 m^2 (5 m × 5 m), separated by 0.3 m height of soil bund. A plastic was installed between plots to minimize hydrological connectivity between each plot. The rate of P and K fertilizers was 60 P_2O_5-30K_2O (kg ha^{-1}cr^{-1}) in all plots. Phosphorus fertilizer was applied all before sowing, and urea fertilizer was topdressed at 10, 20, and 45 days after sowing (DAS) while potassium fertilizer at 20 and 40 DAS.

Soil sampling and analyses

At the prior to experiment and harvest stage, soil samples were collected to determine the soil characteristics. Its were taken at the depth of 0–20 cm in the field. The pipette method was used to analyze the contents of clay, silt, and sand (Kroetsch and Wang, 2008). Soil pH and EC were determined in 1:2.5 (w:v) filtered soil:water suspensions, measured using pH meter and EC meter, respectively. Soil organic carbon (%C) was determined by the Walkley and Black method (Walkley and Black, 1934). Available soil P was determined as Olsen-P by extracting the soil with 0.5*M* $NaHCO_3$ (Olsen and Sommers, 1982). Soil total P concentration was measured by molybdate colorimetric method (Murphy and Riley, 1962). Total N was analyzed by Kjeldahl digestion, and available soil N was analyzed by extracting soils with KCl 2M at 1:10 ratio, measured by the Spectrophotometer in 650 nm. Cation exchange capacity and exchangeable K were determined by the NH_4OAc extraction method.

Rice growth parameters and grain yield collection

Rice height was collected at active tillering (20 DAS), panicle initiation (45 DAS), heading (60 DAS), and flowering (75 DAS) stages. Biomass was calculated from samples in an area of 0.25 m^2 (0.5 × 0.5 m) at the harvest stage. Grain yield was collected in an area of 5 m^2 of each plot. Grains were separated, treated, air-dried, and then weighed. Grain moisture was also determined at weighing or by grain moisture tester. The final grain yield at 14% of the moisture was then calculated based on the weight and the determined moisture

Statistical analysis

The effect of N fertilizer (N) and biochar rates (B) and their interaction on soil properties and rice parameters were determined by analysis of variance using R (V4.0.5) statistical software. Only treatments with significant differences were submitted to the Tukey comparison test (LSD < 0.05).

Results

Soil chemical properties

Table 2 showed the effects of combining N fertilizer with biochar amendment on soil characteristics. The results showed that reducing N fertilizer by 50% did not significantly affect soil pH, EC, SOC, and CEC compared to the treatments applied 100 kg N ha^{-1}. Similarly, there were no significant difference in pH, EC, SOC, and CEC in the treatments applied 5–10 t biochar ha^{-1} (B_5 and B_{10}) compared to the treatments without received biochar amendment (B_0). This study confirmed that reducing N fertilizer by 50% combined with 5–10 t biochar ha^{-1} amended did not significantly affect soil chemical properties.

Table 2. Effects of nitrogen fertilizer and biochar on soil properties

Treatments	pH	EC, mS cm^{-1}	SOC (%C)	CEC ($cmol_{(+)}kg^{-1}$)
N_{50}	4.51±0.08 [a]	0.55±0.09 [a]	8.05±0.79 [a]	15.2±0.54 [a]
N_{100}	4.50±0.06 [a]	0.51±0.10 [a]	8.41±0.79 [a]	15.3±0.61 [a]
B_0	4.50±0.07 [a]	0.55±0.11 [a]	7.84±0.99 [a]	15.4±0.77 [a]
B_5	4.49±0.04 [a]	0.54±0.08 [a]	8.19±0.64 [a]	15.2±0.54 [a]
B_{10}	4.53±0.09 [a]	0.50±0.09 [a]	8.66±0.55 [a]	15.1±0.38 [a]
F test (N)	ns	ns	ns	ns
F test (B)	ns	ns	ns	ns
F test (N×B)	ns	ns	ns	ns
LSD	0.08	0.16	1.31	1.08
CV(%)	0.95	16.4	8.47	3.78

The value after ± showed the standard deviation of the mean of three replications; means in a column for each factor followed by the same letter are not significantly different; ns mean P > 0.05; N and B treatments are explained in the text.

Marco nutrients availability

The results indicated that the soil N, P, and K availability in the treatment that applied 50 kg N ha^{-1} were not significantly different compared to the treatment received 100 kg N ha^{-1} (Table 3). However, available N in the B_{10} treatment was varied in 15.5 mg kg^{-1}, significantly higher than the B_0 and B_5 treatments (11.4 and 12.4 mg kg^{-1}, respectively). Besides, applying biochar at a rate from 5 to 10 t ha^{-1} significantly increased available P compared to the treatment with no applied biochar ($P < 0.05$). This study also indicated that applying 5–10 t biochar ha^{-1} did not significantly change soil exchangeable K compared to treatment without biochar amended (Table 3). The finding of this study demonstrated that reducing N fertilizer by 50% combined with 5–10 t biochar ha^{-1} could significantly increase available N and available P while exchangeable K is maintained.

Table 3. Effects of nitrogen fertilizer and biochar on macro nutrients

Treatments	Available N (mg kg^{-1})	Available P (mg P kg^{-1})	Exchangeable K (cmol$_{(+)}$kg^{-1})
N_{50}	11.6±2.71 ^{a}	13.0±2.30 ^{a}	0.16±0.04 ^{a}
N_{100}	14.6±2.22 ^{a}	13.6±3.53 ^{a}	0.14±0.03 ^{a}
B_0	11.4±1.87 ^{b}	10.1±1.61 ^{b}	0.13±0.01 ^{a}
B_5	12.4±1.20 ^{b}	14.1±1.20 ^{a}	0.14±0.01 ^{a}
B_{10}	15.5±2.12 ^{a}	15.8±2.02 ^{a}	0.18±0.05 ^{a}
F test (N)	ns	ns	ns
F test (B)	*	***	ns
F test (N×B)	*	**	ns
LSD	3.56	2.63	0.07
CV(%)	14.4	10.5	24.8

The value after ± showed the standard deviation of the mean of three replications; means in a column for each factor followed by the same letter are not significantly different; means in a column for each factor followed by the different letters are not significantly different; ns means P >0.05; * means P <0.05; ** means P <0.01; *** means P <0.001; N and B treatments are explained in the text.

Rice growth

The results showed no significantly different in rice height between the two N fertilization treatments at the various growth stages (Table 4). However, rice height in the treatments applied 5–10 t biochar ha^{-1} (B_5 and B_{10}) were significantly greater than the treatment no received biochar in 40 DAS, 60 DAS, and 75 DAS ($P < 0.05$). In general, this study indicated that reducing 50 kg N ha^{-1} combined with 5–10 t biochar ha^{-1} could significantly increase plant height compared to the treatments with no received biochar (B_0) or 100 kg N ha^{-1}.

Table 4. Effects of nitrogen fertilizer and biochar on rice height at the various growing stages

Treatments	Active tillering (25 DAS)	Panicle initiation (40 DAS)	Heading (60 DAS)	Flowering (75 DAS)
N_{50}	42.6±2.56 ^{a}	66.4±5.96 ^{a}	85.9±5.07 ^{a}	108±4.65 ^{a}
N_{100}	42.0±2.60 ^{a}	68.8±4.78 ^{a}	87.6±3.16 ^{a}	107±5.84 ^{a}
B_0	41.8±3.21 ^{a}	64.3±7.73 ^{b}	84.0±5.75 ^{b}	102±3.49 ^{b}
B_5	42.8±2.93 ^{a}	70.4±3.63 ^{a}	88.2±3.11 ^{a}	112±1.76 ^{a}
B_{10}	42.3±1.49 ^{a}	68.1±1.73 ^{ab}	88.0±1.91 ^{a}	110±3.31 ^{a}
F test (N)	ns	ns	ns	ns
F test (B)	ns	*	*	***
F test (N×B)	ns	*	*	*
LSD	6.01	7.84	5.55	4.24
CV(%)	7.55	6.16	3.40	2.10

The value after ± showed the standard deviation of the mean of three replications; means in a column for each factor followed by the same letter are not significantly different; means in a column for each factor followed by the different letters are not significantly different; ns means P >0.05; * means P <0.05; *** means P <0.001; N and B treatments are explained in the text.

Rice straw biomass and yield

The effects of N and biochar amendment on biomass and grain yield are shown in Table 5. The rice biomass ranged from 17.0 to 17.9 t ha^{-1} in the treatments applied 50–100 kg N ha^{-1} and varied between 14.5 and 19.5 t ha^{-1} in the biochar amended treatments. In the harvest stage, rice biomass in the treatments applied with 50 and 100 kg N ha^{-1} did not differ significantly, neither among the treatments applied with 0, 5, and 10 t biochar ha^{-1}.

Table 5. Effects of nitrogen fertilizer and biochar on rice height at the various growing stages

Treatments	Rice biomass (t ha^{-1})	Grain yield (t ha^{-1})
N_{50}	17.0±3.03	5.96±0.63 ^{a}
N_{100}	17.9±4.75	6.03±0.41 ^{a}
B_0	14.5±2.40	5.52±0.53 ^{b}
B_5	19.5±4.51	6.32±0.36 ^{a}
B_{10}	18.3±3.04	6.15±0.27 ^{a}
F test (N)	ns	ns
F test (B)	ns	**
F test (N×B)	ns	*
LSD	7.42	0.65
CV(%)	22.6	5.79

The value after ± showed the standard deviation of the mean of three replications; means in a column for each factor followed by the same letter are not significantly different; means in a column for each factor followed by the different letters are not significantly different; ns means P >0.05; * means P <0.05; ** means P <0.01; * means P <0.001; N and B treatments are explained in the text.

Similarly, the results showed that rice yield in the treatment reduced N fertilizer by 50% varied around 5.96 t ha^{-1}, and was not a significant difference compared with treatment received 100 kg N ha^{-1} as the farmer's practice (6.03 t ha^{-1}). However, rice yield in the treatments applied 5–10 t biochar ha^{-1} ranged from 6.15–6.32 t ha^{-1}, significantly higher than the treatment no received biochar (5.52 t ha^{-1}). The results indicated that the biochar application at a rate of 5–10 t ha^{-1} could significantly increase grain yield compared to no applied biochar by 11.4–14.5%. The findings of this study demonstrated that the combination of 50 kg N ha^{-1} with 5–10 t biochar ha^{-1} could reduce the N fertilizer amount and increase rice yield compared to traditional rice cultivation.

Discussion

In this study, experimental soil has the C:N varied around 24.0 (organic carbon and N contents were 6.27 %C and 0.27 %N, respectively). In this C:N level, available soil N may be released into soil solution throughout the processes of decomposition rice straw residues or mineralization (Weil and Brady, 2017; Kopittke et al., 2020; Dung et al., 2022). It explained why the organic carbon and available N contents in the treatment that applied 50 kg N ha^{-1} did not differ significantly compared to the treatment that applied 100 kg N ha^{-1}. This results were in agreement with Dung et al. (2021) studied the effects of reduced N fertilizer on two rice varieties in the VMD region. Dung et al. (2021) reported that applying 50 kg N ha^{-1} could maintain the number of tillers, rice height, and grain yield of OM5451 and OM6976 compared to the traditional cultivation applied 100 kg N ha^{-1}.

pH is the most important factor in the soil has directly affected the availability of soil nutrients (Weil and Brady, 2017). The change in soil pH is most dependent on the pH of biochar and soil pH. Previous studies reported that applying biochar in the low soil pH such as Ferrasols or Acrisols could significantly increase soil pH (Glaser et al., 2002; Lehmann et al., 2003; Chan et al., 2007; Li et al., 2015; Thies et al., 2015), but did not differ significantly in the near-neutral soil (Lashari et al., 2013). Besides, the application of biochar at a rate of 5–10 t ha^{-1} resulted in no differ significantly different in soil EC, SOC, exchangeable K, and CEC compared to the treatment with no received biochar may be due to the low biochar application rates (Lashari et al., 2013). Agegnehu et al. (2017) reported that the rate of biochar application higher than 39 t ha^{-1} resulted in significantly increased soil pH in the neutral soil. Similarly, some previous studies have also shown that applying the biochar at a rate of 50 t ha^{-1} could improve the soil pH, EC, exchangeable K, SOC, and CEC (Van Zwieten et al., 2010; Rajkovich et al., 2012; Schulz and Glaser, 2012; Abel et al., 2013; Biederman and Harpole, 2013; Abiven et al., 2015; Sánchez-García et al., 2016). The other reasonable explanation for did not change in these soil characteristics is closely correlated to the short time of biochar application. According to Griffin et al. (2017), applying biochar was not significantly affect exchangeable soil K in the first two years. However, the amount of K in treatments applied biochar was significantly higher than the treatment with no applied biochar after three years (Griffin et al., 2017).

Our study indicated that the application of biochar from 5 to 10 t ha^{-1} resulted in significantly higher available N and available P contents than the treatment without biochar. This study is in line with some previous studies which have reported that N available content significantly increased in the treatment applied biochar at a rate of 15 t ha^{-1} or higher (Vaccari et al., 2015; Bera et al., 2016; Cao et al., 2018; Ullah et al., 2018; Ali et al., 2021). Applying biochar in the soil could be enhanced the mineralization process of the soil because of the high C content in biochar (Weil and Brady, 2017). According to Phuong et al. (2020b), the availability of P was significantly higher in the treatments applied biochar at a rate of 5–10 t ha^{-1} due to the mineralization of soil organic P to inorganic P, increasing P availability. The findings of this study agree Ullah et al. (2018) and Ali et al. (2021), who reported that biochar amendment enhances soil available P compared to the soil without biochar. Nitrogen and phosphorus, which are the macronutrient of plant, helps enhance plant growth in all soil types (Weil and Brady, 2017). According to Ali et al. (2021), the increase in rice yield was highly positively correlated with the soil chemical properties such as N and P available contents. This study showed that applied biochar in a rate of 5–10 t ha^{-1} resulted in significantly higher N and P available contents, and it explained why the significantly higher rice height and grain yield compared to the treatment without biochar. Similarly, the positive effect of biochar on rice yield was reported by previous studies (Dong et al., 2015; Ali et al., 2021). The findings of this study indicated that reducing N fertilizer by 50% combined biochar at a rate of 5–10 t ha^{-1} could improve soil quality and increase rice yield compared to the no applied biochar.

Conclusion

This study indicated that reducing N fertilizer by 50% did not significantly affect soil properties, rice growth, and yield. Applying biochar in a rate of 5–10 t ha^{-1} resulted in significantly higher N and P availability, rice height, and grain yield than without biochar admended. The combining of 50 kg N ha^{-1} with biochar in a rate of 5–10 t ha^{-1} may be recommended in the same paddy rice soil conditions. Further research is required to evaluate the effects of biochar as soil amendment combined N fertilizer on soil quality, C sequenstration, greenhouse gases emissions on the rice cultivation system in the VMD region.

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Understanding relationship between physical quality indicators and organic carbon in soils affected by long-time continuous cultivation under sub-humid ecosystem

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Abstract

The objectives of this present study were to analyses soils and find out some soil quality properties and check relationship between soil compaction, crust formation and erodibility - K of the soils with the soil organic carbon (SOC) amount in the surface (0-20 cm) and subsurface (20-40 cm) soils affected by long-time continuous cultivation under sub-humid environmental condition. The research out comes showed that soil compaction, crust formation, erodibility K is highly significantly ($P < 0.001$) related to organic carbon, organic carbon stock, organic matter and between each other. The research also identifies that the study area generally, has clay texture, neutral pH, low amount of the CaCO3, high amount of OC and OM in top layer (0-20 cm) and moderate amount in bottom layer (20-40 cm). It was not identified significant differences between the soil properties in surface and subsurface soil layers.

Keywords: Soil organic carbon, compaction, crust formation, erodibility- K.

Introduction

In recent times the importance of soils organic carbon in the carbon cycle has been increasingly acknowledged as the CO_2 concentrations rising in the atmosphere and the increasing global warming (Rumpel et al., 2020). Soils organic carbon topic is researched in the scientific community not only for its imports for global warming butalso for its effect on soil quality and sustainable food production. The soil organic carbon (SOC) is one of the most crucial natural resource that is highly important to securing the soil quality. In addition to that, one of the essential non-renewable natural resources that all living things require is also soil (Schoonover and Crim, 2015). Therefore, one of the most major questions for scientist currently is finally to found efficient ways how increase SOC in soil and how to stop decrease CO_2 emission to the atmosphere.

The soil quality is much more complex when description of water quality and air quality (Bünemann et al., 2018). The easiest definition to define soil quality is "the capacity (of soil) to function". Soil quality must contain three main parts sustained biological productivity, plant and animal health and environmental quality. All these three parts mustfully function and be balanced between each other (Karlen et al., 1997). Here are no one definition who would define soil quality, because here no common agreement on it by scientific community. In addition, here are no one set of soil quality indicators recognized internationally by the scientists. However, here is common sense that the soil quality index must be made from the multiple physical, biological, and chemical attributes (Karlen et al., 2003).

The main goal of the present investigation is to determine relationship between some soil physical quality properties and soil organic carbon. The study area' soils have been cultivated for a long time period. Therefore, the motivation in the current research is to find out and understand some soil physical quality properties such as compaction, crust formation and soil erodibility-K factor of the study area' soils and check its relationship with the SOC amount in the soil.

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Material and Methods

Description of the study area

The study area is located at the 40th km on the Samsun-Bafra highway and is between 249000-254000 East and 4599200-4602400 North (WGS-84, Zone 37, UTM-m) coordinates (Figure 1). Total land asset is 923.9 ha. Bünyan Mountain in the south, and the Bafra Plain in the west and north, is adjacent to the western shore of Balık Lake in the Kızılırmak Delta.

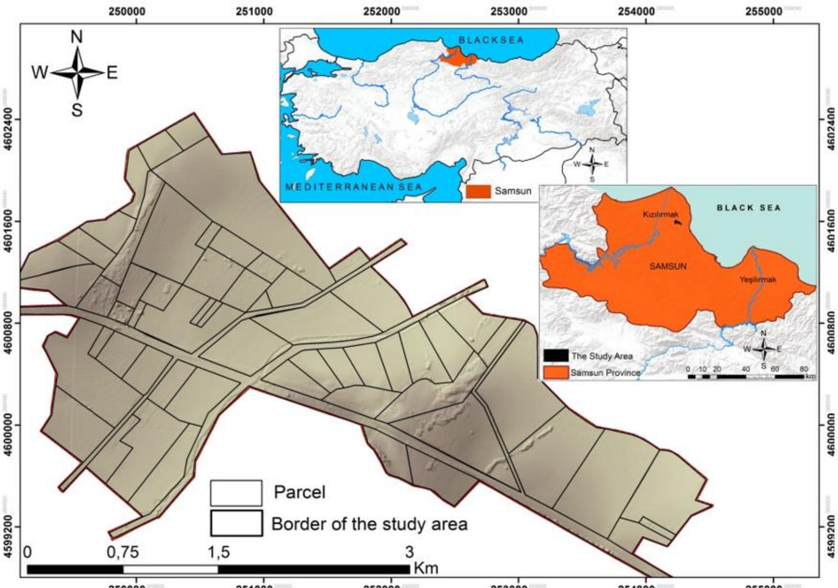

Figure 1. Location map of the study area

While the north-west and south-east parts of the land are areas where moderately steep and steep slopes are distributed in terms of slope, generally the middle and northwest parts of the land constitute areas with 0-4%, nearly flat and gently slopes (Figure. 2).

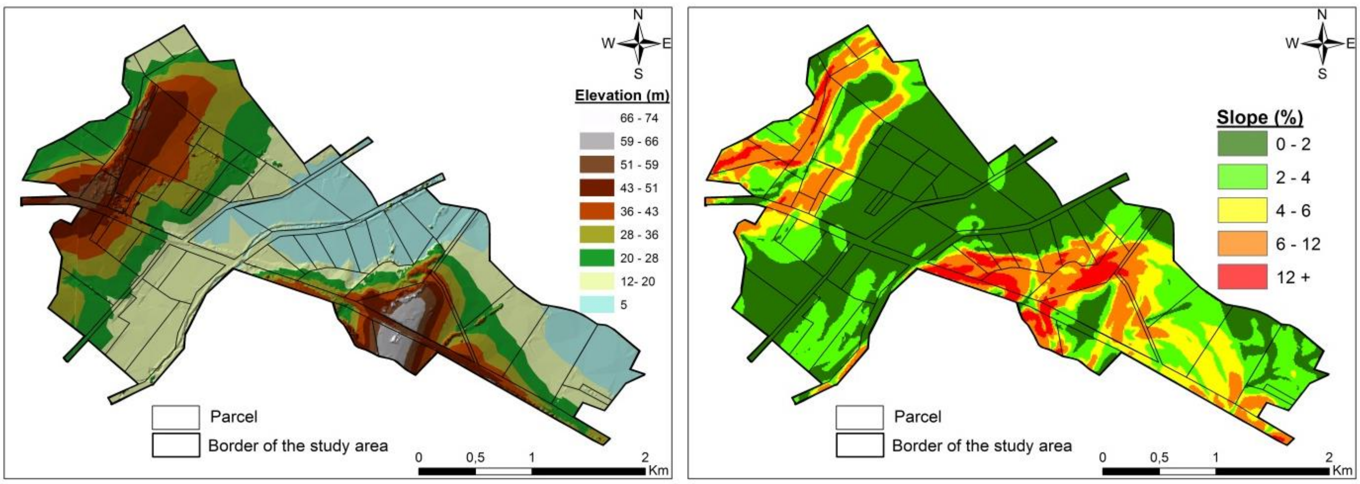

Figure 2. Elevation and slope map of the study area

The Black Sea climate, which is rainy in all seasons, cool in summers and warm in winters, is active on the coastline of the Black Sea Region. The annual average temperature of the study area was 14.3˚C, the highest average air temperature was 18˚C and the lowest average temperature was 10.7˚C. The average annual rainfall of the study area is around 710.0 mm. In addition, according to the Newhall model, soil temperature and moisture regimes (van Wambeke, 2000) were determined as mesic and ustic (wet tempustic in sub-class) (Turan et al., 2018).

Soil sampling and analysis

The grid-based soil sampling system was conducted with 89 sampling points located 300 m from each other (Figure 3). From each sample point was taken 2 soil samples; one from depth 0 to 20 cm and another from 20 to 40 cm. In totally 178 soil samples were collected from the study area. The collection of samples was done in 2021. After collection all samples were air dry and passed on a 2 mm sieve.

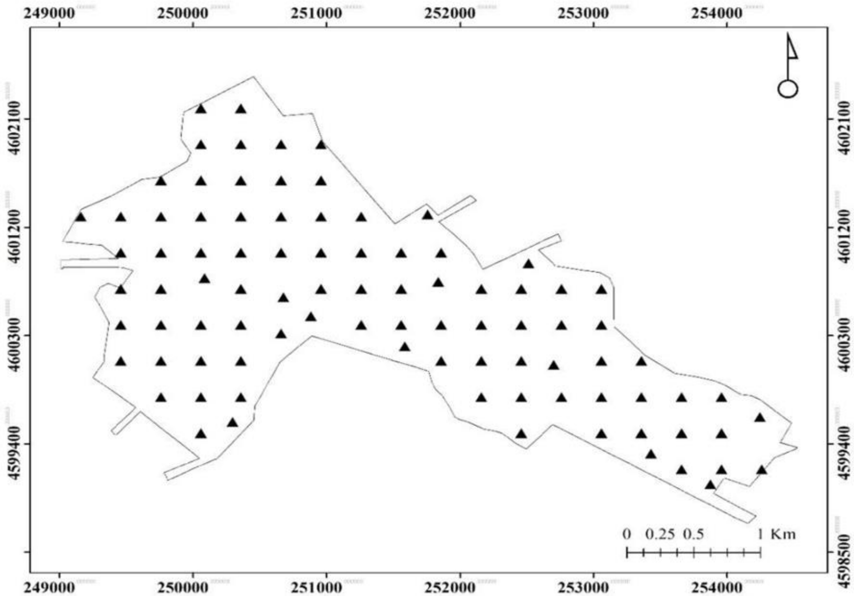

Figure 3. Soil sampling pattern

By using the Bouyoucos hydrometer method, the mechanical analysis of the soil (% sand, silt, and clay) was determined (Bouyoucos, 1962) and in a 1:1 soil-water suspension, electrical conductivity (EC) and soil reaction (pH) values were measured (Soil Survey Staff, 2014; Kacar, 2016). CaCO3 content was determined by volumetric calcimeter, and organic matter content was defined by considering the modified Walkley-Black method (Soil Survey Staff, 2014).

Determination of SOC stock

The SOC_{stock} of the surface layers (0–20 cm and 20-40 cm), described in kgm^{-2}, was estimated by the following equation (1) (IPCC, 2003):

$$SOCstock = SOC * BD * H * \frac{(100-SK)}{100} \quad (1)$$

SOC: soil organic carbon content (%), BD: bulk density (g cm^{-3}), SK: skeleton content (% by weight), H: soil depth (2 dm)

Soil compaction susceptibility

For calculating the soil compaction susceptibility was used Vignozzi et al. (2007) index. This index is associated with the algorithm of Smith et al. (1997) with the equation for calculating the ρ100kPa Pellegrini et al. (2018). Soil compaction susceptibility index (CI) calculated based on the following equation (2):

$$\rho100kPa = 1.04231 + \exp(-0.486474 - 0.464448186 * SOC) \quad (2)$$
$$CI = -0.09266 + 0.01576 * (Si + Cl) - 0.00012 * (Si + Cl)^2 + \rho100kPa$$

SOC: soil organic carbon (%), Si: silt (2–50 μm) (%), Cl: clay (< 2 μm) (%)

Soil crusting susceptibility

For calculating soil crusting susceptibility, the FAO (1979) crust formation index (Ic, dimensionless) was used (Pellegrini et al., 2018). The soil crusting susceptibility estimated according to the following equation (3):

$$I_c = \frac{1.5*(Sif)+0.75*(Sic)}{Cl+5.8*SOC} \quad (3)$$

Sif: fine silt (2–20 μm) (%), Sic: coarse silt (20–50 μm) (%), SOC: soil organic carbon (%)

Cl: clay (< 2 μm) (%)

Soil erodibility K factor

The soil erodibility K-value based on the basic soil properties analyses results was indicated in calculation by Wischmeier and Simith (1978). The soil erodibility was calculated with formula wish is below (4):

$$K\text{-factor} = \{0.00021 \times M^{1.14} \times (12\text{-}OM) + 3.25 \times (SSC\text{-}2) + 2.5 \times (PSHCC\text{-}3)\}/100 \quad (4)$$

OM: organic matter (%), SSC: soil structure code (1= very fine granular, 2 = fine granular, 3 = medium or coarse granular, or 4 = blocky, platy, or massive), PSHCC: profile saturated hydraulic conductivity code (1, 2, 3, 4, 5, or 6), M: textural factor, M = (silt 0.002-0.05mm (%) + fine sand 0.05-0.1mm (%)) × (100 - clay <0.002mm (%))

Geostatistical and statistical analysis

In the current study, Inverse Distance Weighting (IDW) method, the most common method used in geostatistical studies, was selected (Alaboz et al., 2021). The IDW approach predicts the values at the unsampled points using the linear combination of the values at the sampled points using the inverse distance functions of the distances. According to logic in IDW, the similarities get smaller the more away the target point is from the point where the assumption value is known (Li and Heap, 2008). The IDW can be calculated as follow (Equation 5):

$$Z = [\sum_{i=1}^{n}(Zi/di^{m}) \ / \sum_{i=1}^{n}(1/di^{m})] \quad (5)$$

Z: estimated value, *Zi*: the value at the known point (observed value), di: the distance between point i and the point whose value will be estimated, n: the number of observations, m: weighting power parameter (generally it can be used between 1 and 5 (Keshavarzi and Sarmadian, 2012; Dengiz, 2020). The weighting powers (1., 2., and 3.) commonly used in the estimation of IDW was considered in this study.

Results and Discussion

Descriptive statistics of soil physical and chemical properties

The descriptive statistic values of analysed soil physical and chemical properties for 0–20 cm and 20–40 cm depths in the study area is presented in the Table 1. In the present study, soils were in the fine and medium-fine texture group, and their texture classes were determined as C, CL, SiC and soil particle content is around 50 %, silt around 30 % and in sand around 20 % for both layers. The estimate bulk density in the farm is estimated around 1.3 g cm^3 in both layers. The pH values of the soil samples ranged between 5.68 - 7.98 at top 20 cm and 6.05 – 8.11 in down 20 cm while the mean of both layers is around 7.0 which indicate neutral soil reaction. The electrical conductivity has big range from 124. 2 µS m^{-1} to 1873 µS m^{-1} at 0-20 cm and 139.8 – 1094 µS m^{-1} in the 20 and 40 cm layer, while the average for both layers is around 400 µS m^{-1}. $CaCO_3$ mean is a little above 3 % in both layers. Therefore, the $CaCO_3$ content of the study area soils was classified as 'limey' and 'low limey', OM content varied from 'low' to 'high', soil reaction was also categorized as 'slightly acid and slightly alkaline', and the EC was 'non-saline', as per the methodologies of Doran and Jones (1996), Kacar (2016) and Hazelton and Murphy (2016). OC and OM are higher in top layer with mean 2.0 % and 3.45 % respectively and in down layer OC is 1.48 % and OM 2.55 %.

Table 1. Descriptive statistics of soil properties in soils

Parameters	Mean	SD	CV	Variance	Min.	Max.	Skewness	Kurtosis
Surface (0–20 cm depth)								
pH	7.21	0.52	7.27	0.27	5.68	7.96	-0.83	0.20
EC	433.71	304.87	70.29	92946.80	124.20	1873.00	2.39	6.51
CaCO3	3.22	2.91	90.43	8.48	0.38	18.87	3.08	12.28
OM	3.45	1.43	41.38	2.04	1.02	7.96	0.60	0.22
Sand	20.29	7.58	37.37	57.52	8.25	55.41	2.06	7.40
Silt	31.78	4.84	15.23	23.42	16.70	44.61	-0.23	1.39
Clay	47.93	7.00	14.61	49.04	27.90	68.90	-0.44	1.19
BD	1.28	0.05	4.27	0.00	1.17	1.50	1.09	2.38
SOC_{stock}	5.10	1.99	39.12	3.98	1.60	10.81	0.43	-0.12
Compaction	1.70	0.09	5.22	0.01	1.52	1.92	0.23	-0.55
CF	0.49	0.17	34.56	0.03	0.04	1.11	0.93	3.07
Ero.-K	0.19	0.04	21.54	0.00	0.13	0.37	1.67	3.74
Sub-surface (20–40 cm depth)								
pH	7.28	0.50	6.81	0.25	6.05	8.11	-0.54	-0.45
EC	413.00	210.60	51.00	44377.90	139.80	1094.00	1.31	1.51
CaCO3	3.46	4.52	130.57	20.41	0.37	37.07	5.34	35.97
OM	2.55	1.11	43.67	1.24	0.23	4.92	-0.02	-0.60
Sand	20.31	9.76	48.08	95.32	7.36	74.56	3.23	13.69
Silt	30.72	6.19	20.14	38.26	8.10	43.75	-0.90	1.70
Clay	48.98	7.62	15.55	58.00	17.34	62.01	-1.40	3.19
BD	1.30	0.07	5.43	0.005	1.19	1.58	1.74	3.66
SOC_{stock}	3.81	1.60	42.00	2.56	0.37	7.11	-0.08	-0.58
Compaction	1.76	0.10	5.57	0.01	1.59	2.02	0.54	-0.11
CF	0.50	0.20	39.25	0.04	0.17	1.45	1.67	5.70
Ero.-K	0.20	0.06	31.04	0.00	0.13	0.59	3.54	18.22

SD: standard deviation, Min: minimum, Max: maximum, CV: coefficient of variation, BD: Bulk Density, OM, Organic matter, SOC: Soil organic carbon, EC: Electrical conductivity, Ero.-K: Erodibility K factor, CF: Crust formation

The organic carbon stock is higher in top layer where the mean is 5.10 kg m^{-2} when down layer has mean of 3.81 kg m^{-2}. The compaction is mostly the same in both layers with mean around 1.70 and the range around 1.5-2.0. The crust formation in both layers is generally same with a mean around 0.5. In addition, the erodibility-K is also most same in both layers with a mean of 0.19 in top and 0.20 in bottom. According to Table 1, mostly all soil parameters were found in unsymmetrical position called as skewness. It can be noted that the analysed soil properties generally exhibit moderate to high variations when the changes in physical and chemical soil properties in both soil depths of the research area are examined in terms of coefficient of variation (CV). The CV can be classified in 3 groups accordingto Wilding (1985): low (<15%), medium (15% and 35%) and high (>35%). In comparison to dynamic soil parameters like water content, hydraulic conductivity, bulk density, compaction and organic matter, static soil characteristics including mineralogy, soil texture and soil thickness have a lower amount of variation, according to Salam et al. (2015). In the current study, the pH, bulk density and compaction of soils were classified as 'low' CV, the silt, clay and erodibility-K at top layer amounts were medium, and the values for the other properties were 'high' CV.

Spatial Distribution of the physical soil quality parameters

The surface soil later has more organic carbon stock when compared to bottom layer. Previous study done in Ethiopia also states that SOC stock was significantly higher in the top layer (0 to 15 cm) compared with bottom layer (15 to 30 cm) (Mohammed et al., 2017). The distribution in the field is identical in both layers. The study area can be separated in 2 parts northwest and southeast (Figure 4). The highest concentration of soil organic carbon is in the northwest part and the lowest in the southeast part.

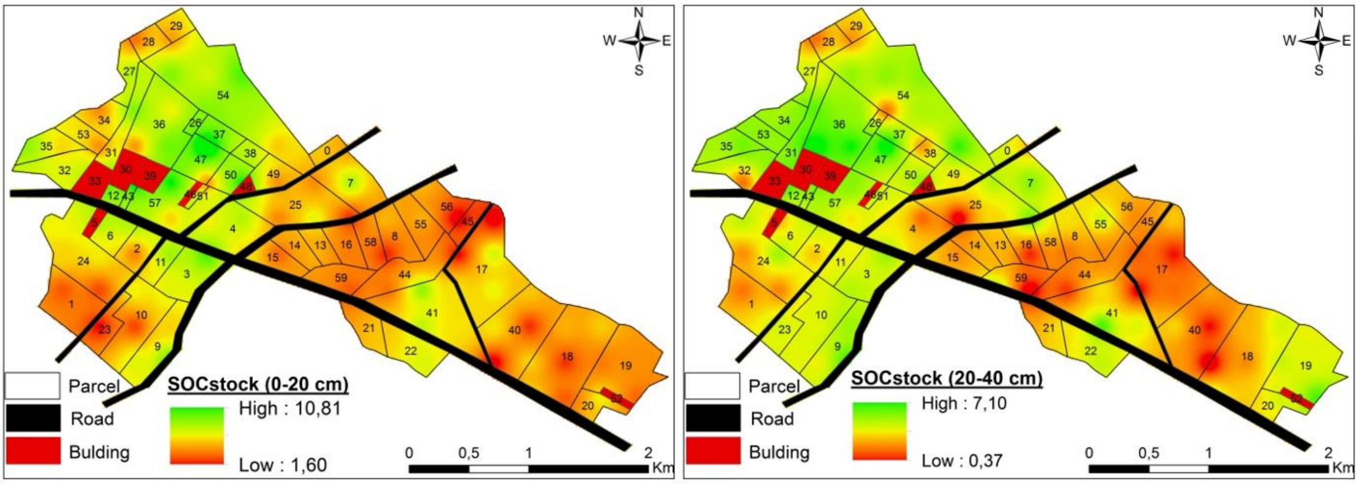

Figure 4. Soil Organic Carbon Stock (kg m^{-2}) maps

It is possible to characterize soil compaction as a densification procedure where porosity is reduced, leading to major changes in the soil's structural characteristics, behaviour, and temperature and moisture regimes. In the study area, the soil compaction is higher in the bottom layer. However, the effected locations are mostly identical between both layers. Moreover, Stone and Lorson (1980) indicated that compressibility, which is the ease with which a soil experiences a reduction in volume when subjected to pressure, determines a soil's susceptibility to compaction. The most compacted area is the centre place of the research area where is pasture, forest, and some rice fields (parcels no: 13-17, 44, 45, 55, 56, 58, 59). Also, the most compacted place has lower amount of soil organic carbon, higher bulk density and the highest amount of sand and clay particles in the soil (Figure 5). On the other hand, the other cultivated areas are compacted less.

As for crust formation, between the most frequent physical deterioration processes of cultivated soils are surface sealing and crusting, which involve the mechanical degradation of surface aggregates by the impact of raindrops and the subsequent drying process. The crust formation of the study area is much more visual in the surface soil layer of the research area. Demirağ Turan and Dengiz (2021) stated that surface sealing or crusting, which include the mechanical destruction of top soil structure by the effect of raindrops and the subsequent drying process, are two of the most frequent physical deterioration processes of cultivated soils. In the top layer most, vulnerable location is in the centre location where is high amount of silt and sand, the lowest amount of soil organic carbon (parcels no 4, 25, 14, 15) and sub soil layer crusting is disperse in some regional parts in the parcels; 8, 40, 41 and 58 (Figure 6).

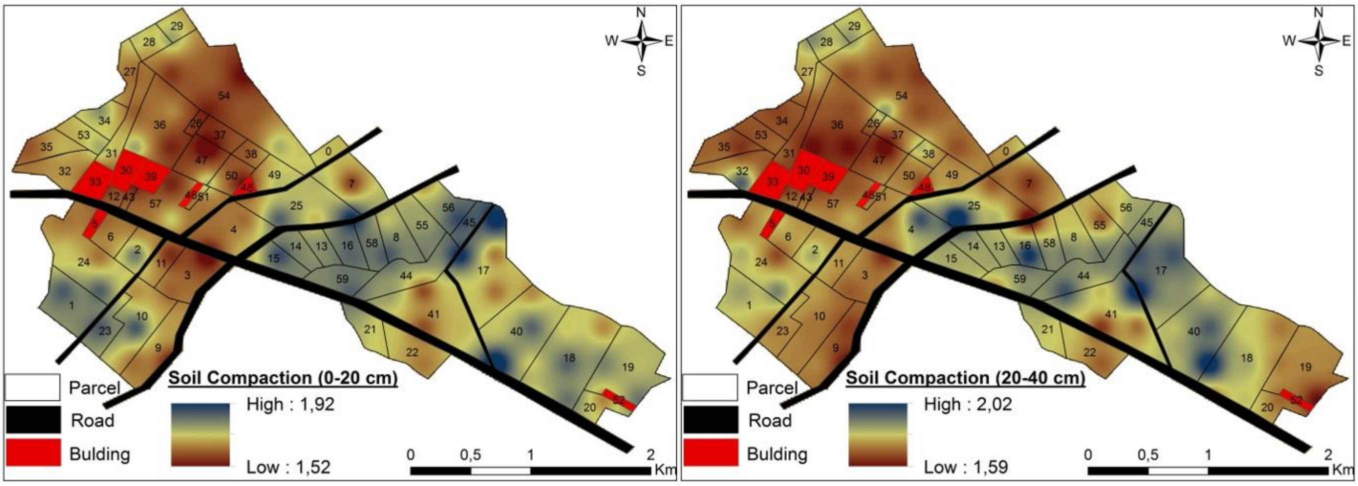

Figure 5. Soil compaction maps

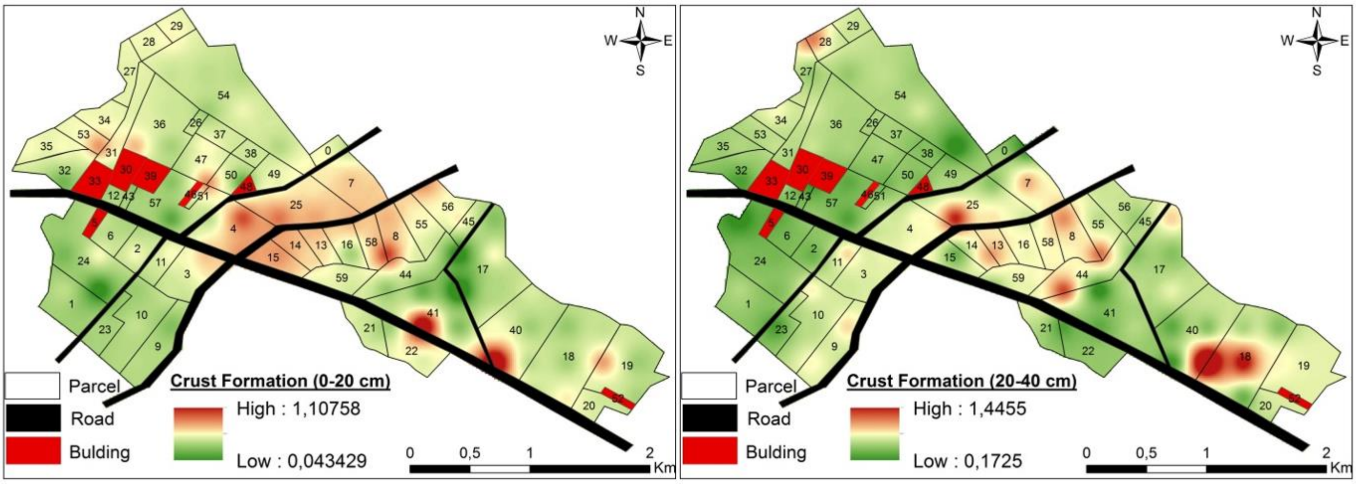

Figure 6. Soil crusting formation maps

The soil erodibility maps of the top and bottom layers of the study area's soils are mostly identical. The most areas at risk for soil erosion is the centre location of the study area with the lowest soil organic carbon amount, the highest amount sand and silt particles in the soil (parcels no: 4, 13- 16, 25, 44, 58, 59), the other territory where high amount of clay particles is in soil is less vulnerable for soil erosion risk (Figure 7). The land use for most vulnerable location is pasture area which was chosen as prevention against erosion. It is well known that cover crops prevent soil erosion and improve soil condition (Ruiz-Colmenero et al., 2013). Moreover, vegetation coverage has a big effect on erosion prevention and reducing loss ratio of nutrients and fine particles fine particles (Yan et al., 2013).

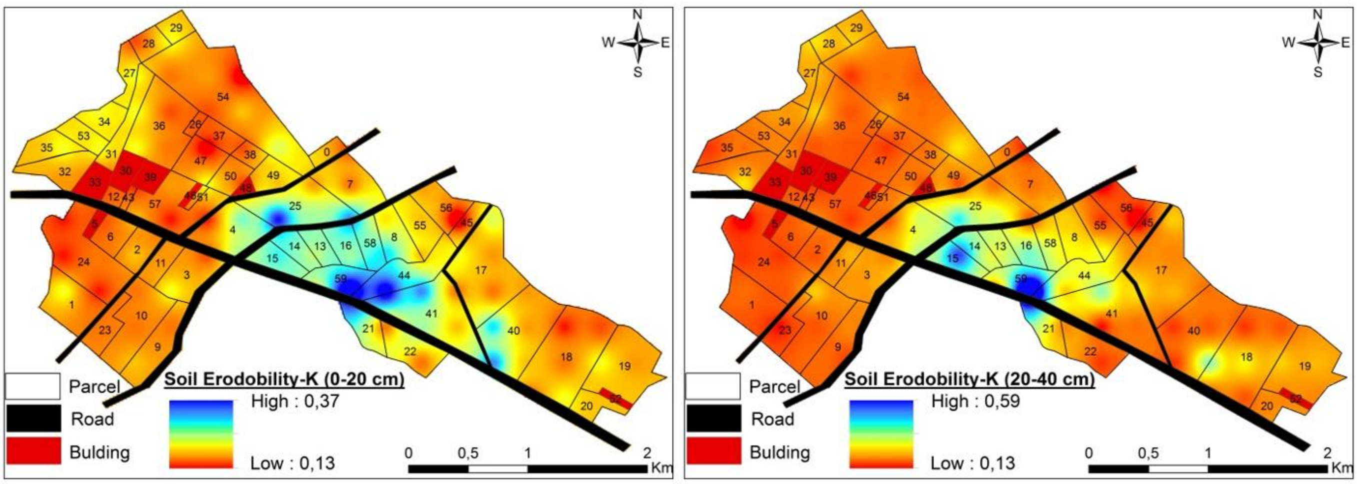

Figure 7. Soil erodibility Factor (K) maps

Correlation between soil characteristics and physical quality parameters

Correlations between soil properties and physical soil quality parameters are given in Table 2. The soil properties were examined for checking statistically significant relationships between soil organic carbon and soil physical properties such as soil compaction, crust formation, erodibility K. The correlation analysis showed that erodibility-K is highly significantly (P<0.001) related to soil organic carbon, soil organic carbon stock, organic matter and between each other. Moreover, the erodibility-K factor has relationship (P<0.001) with pH, sand, clay, bulk density. Many previous studies of soil erosion confirmed that erodibility is strongly related to soil organic matter, soil texture and structure (Wang et al., 2013). Dikinya's study results have shown that erodibility K factor significantly correlates with organic matter amount, clay fractions percentage, slope length, bulk density, structural properties, and soil porosity (Dikinya, 2013). In addition, the Radziuk study says that decrease in soil organic carbon increases the erodibility (Radziuk and Switoniak, 2021).

The compaction has a relationship (P<0.001) with to organic carbon, organic carbon stock, organic matter, clay, bulk density, and lesser relationship (P<0.005) with sand. The previous studies confirm the findings. For example, Kumar reported that compaction of soil highly related with its texture (Kumar et al., 2009). Also, many other scientists' studies confirmed the significant relationship between organic matter and soil compaction and stated that an increase in soil organic matter reduces the compactability (Kumar et al., 2009; Shahgholi and Jnatkhah, 2018).

The crust formation has a relationship (P<0.001) with soil organic carbon, SOC stock, organic matter, silt, and clay. It is well known in previous studies that the soil crusting not only depends on the external factors but also on soil factors such as organic matter content, soil texture, clay mineralogy, exchangeable cations, sesquioxide content, soil water content (Pagliai et al., 2004). Maïga-Yaleu et al. (2013) pointed out that there is a significant relationship between soils crusting and SOC. In addition, Négyesi et al. (2021) states that the surface crusts differentiate depending on the soil texture and silty loamy soils resulted in harder and more solid crusts in comparison with other textures. Also in the current study, soil compaction, crust formation and erodibility K have strong relationships (P<0.001) between each other.

The soil quality parameters that, on the whole, indicate small differences, both in soil layers, are erodibility-K and susceptibility to compaction and crusting. On the other hand, since erodibility-K can change by a rate of up to about six times, it must be taken into account that even small differences in erodibility-K might have an impact on the eventual erosion rate from a specific storm (0.13 to 0.59, Murphy, 2014).

Table 2. Pearson correlation between soil properties and physical quality parameters

Parameters	SOC_{stock}	Compaction	CF	Erodibility-K
pH	-0.348**	0.355**	0.101	0.338**
EC	0.109	-0.180	0.187	-0.132
CaCO3	-0.067	0.099	0.195	0.064
OM	0.996**	-0.961**	-0.290**	-0.495**
Sand	-0.212*	0.262*	-0.136	0.767**
Silt	0.060	-0.034	0.682**	-0.110
Clay	0.223*	-0.309**	-0.379**	-0.893**
BD	-0.469**	0.569**	0.201	0.852**
SOC_{stock}	-	-0.951**	-0.300**	-0.465**
Compaction		-	0.324**	0.455**
CF			-	0.369**
Ero.-K				-

BD: Bulk Density, OM, Organic matter, SOC: Soil organic carbon, EC: Electrical conductivity, Ero.-K: Erodobility K factor, CF: Crust formation, **. Correlation is significant at the 0.01 level, *. Correlation is significant at the 0.05 level.

Conclusion

The most vulnerable farmlands for soil compaction, erodibility and crust formation are the centre part of the study area where were the lowest amount of organic carbon and clay, highest bulk density, silt and sand concentration.

Soil compaction and susceptibility to erodibility (K) and crusting are the soil quality parameters that, on the whole, show minor changings, both in layers. Comparing the farmland use maps for 2020-2021 with the soil properties maps, we can see that for the most vulnerable location for soil erodibility-K, crust formation and compaction the prevention agriculture techniques such as land cover by grass are already used. The land cover should be continued use in the risky territory for preventing erosion. The correlation analysis showed that soil compaction, crust formation, erodibility K is highly significantly (P<0.001) related to organic carbon, organic carbon stock, organic matter and between each other. Here was a not identified significant difference between the soil properties in top and bottom layers. The study showed importance of the soil quality assessment for tracking the soil degradation and making policies for improving soil quality.

Finally, the soil sensitivity indicators based on chemical and biological characteristics and attributes may be a topic for future investigation. Also, similar methods considered cropping systems on certain types of soil could be used to explore variations in critical soil managements and soil fertility factors such as manure application, nutrient availability, soil reaction and so on.

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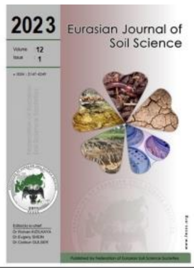

Tillage system and cover crop effects on organic carbon and available nutrient contents in light chestnut soil

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Abstract

Optimal use of management systems including tillage and cover crops are recommended to improve available nutrient contents in soils and sustain agricultural production. The effects on organic carbon and available nutrient contents of three tillage methods (conventional tillage, minimum tillage and no-tillage) and different cover crops such as flaxseed oil, buckwheat, soybean, pea, corn, sorghum, spring oilseed rape and sugar beet were evaluated in a short-term experiment on a light chestnut soil in Kazakhstan. Organic carbon and available nutrient contents were measured in the autumn of 2021. The field measurements included the yield of cover crops and input of organic matter into soils with root and other residues of cover crops. In the laboratory, total organic carbon, labile organic carbon, easily hydrolyzable nitrogen (NH_4-N), NO_3-N, available P and exchangeable K were measured. The results showed that one season of cover crop growth was not enough to find detectable changes in soil organic matter and available nutrient status in light chestnut soils. On the other hand, even in a short-term field experiment period of 3 months, the most labile organic carbon in soil organic carbon was obtained in conventional tillage. Overall, the results show that at least in the short term and under lower drip irrigation rate in summer for the study area, reduced tillage methods (no-tillage and minimum tillage) is suitable in the study area for soybean, corn and sugar beet production after intensive tillage in the previous year.

Keywords: Cover crops, tillage, no-tillage, available nutrient, organic matter.

Introduction

The need for sustainable management strategies to maintain and improve soil health & quality, reducing problems such as land degradation & desertification and enhance agricultural production has been stressed by many studies in the light of an increasing world population and climate change (Komatsuzaki and Ohta, 2007; Lal, 2009; Abdollahi and Munkholm, 2014). In recent years, the concept of conservation agriculture has been promoted as an integrated management tool to meet the challenges of the future. The conservation agriculture concept includes increase soil organic matter, minimize tillage, rotate crops, plant and animal residue management, and cover crops as key elements (Farooq and Siddique, 2015; Jayaraman et al., 2021).

Currently, about 75% of the territories of Kazakhstan are subject to an increased risk of desertification, more than 30.5 million hectares are subject to soil erosion by wind and water, and 54% of these territories are located in the southern part of Kazakhstan (Turebayeva et al., 2022). In recent years, systemic measures have been taken in agriculture field in the Kazakhstan to apply highly efficient resource conserving technologies. No-tillage or reduced tillage were introduced in Kazakhstan as a system for soil protection which contributed to slow down soil erosion processes and increased the yield of crops (FAO, 2013: Saparov, 2014). Moreover, in different agricultural zones of the Kazakhstan, the basic principles of conservation agriculture has been

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developed by applying plant residues or animal wastes and No-tillage or Reduced tillage. Thus, no-tillage or reduced tillage are contributing to enhanced agricultural sustainability of dryland crops in semiarid areas by reducing erosion, and improving soil health & quality and soil ecosystem services (Suleimenova et al., 2019). Also, many studies have assessed the impact of the different conservation agriculture elements on soil health and quality, soil available nutrient contents, plant productivity individually in different ecological zone of Kazakhstan (Kurishbayev, 2003; Wall et al., 2007; Nurbekov et al., 2016), but no scientific studies have quantified the effect of different tillage practices combined with cover crops.

Cover crops are traditionally defined as crops grown to cover the ground to protect the soil from erosion and from loss of plant nutrients through leaching and runoff (Reeves, 1994) and these crops have been referred to as crops planted primarily to manage soil and water health, increase of biodiversity, limitation of pests, diseases, weeds, etc. (Lu et al., 2000; Scavo et al., 2022). Most cover crops are not grown solely for economic benefits, but for the ecosystem benefits they provide. Yunusa and Newton (2003) referred to cover crops as 'primer plants'; crops grown to condition the soil for the subsequent crops. Growing cover crops has been a popular practice in crop production throughout history (Reeves, 1994). They were originally grown as green manures, serving as a mulch and soil amendment, and were later incorporated into soil to improve fertility (Kasper and Singer, 2011) Also, cover crops can enhance soil health and quality through addition of organic matter when incorporated into the soil, helping to reduce compaction and increase infiltration; thus increasing available nutrient contents of soil and yield of plant (Dabney et al., 2001). We hypothesize that tillage and cover crop may significantly affect soil organic matter and available nutrient contents in the short term. The specific objective of this study was to assess the influence of different tillage practices combined with cover crops on total and labil organic matter, available nitrogen, phosphorus.

Material and Methods

Study Area

The experiment was performed at Agropark Kaskelen experimental-demonstration field of the Zailiyskiy Alatau, Kazakhstan (43°17'43.70 "N76°41'46.60 "E). This region is characterized by a semi-arid climate. The locations of the evaluations were characterized by the sharply continental climate (low cloud cover and a small amount of atmospheric precipitation, which fall mainly in the warm season), the air temperature reaches minimum values in January (-41^{0}C), and maximum values in July (+42^{0}C), the average annual temperature is +7.6 ^{0}C and an annual amount of precipitation is 414 mm.

Soil

A soil sample was collected from the experimental field at the beginning of the experiment. Physical and chemical properties of the experimental soil were determined Kazakh National Agrarian Research University according to the Rowell (1996) and Jones (2001). The main soil type is piedmont light chestnut soils. The soil had been developed from ormed on loess-like loams has a clearly pronounced fertile profile and contained 50% clay, 35% silt and 15% sand. The soil was characteristically slightly alkaline (pH 7.3-7.4), soil organic matter 2.02% (moderate), total N 0.12-0.14% (high), available phosphorus 23-25 mg kg^{-1} (low), exchangeable potassium 245-255 mg kg^{-1} (moderate).

Experimental design

In September 2020, winter wheat seeds (200 kg ha^{-1}) were planted on the 5 ha experimental land. With the sowing of the seeds, 100 kg ha^{-1} of ammonium phosphate (ammophos) fertilizer (11%N, 46%P_2O_5) was added to the soil. On 12 July 2021, the harvest of winter wheat in the field was carried out. At the end of the harvest, the wheat yield was determined as 5.66 t ha^{-1}. After the wheat harvest in the field, the land was divided into parcels and the experiment was established. The two factors (treatments) were three methods of tillage (no-tillage (NT), minimum tillage (MT) and conventional tillage (CT)) and eight types of cover crop (Flaxseed oil (FO), Buckwheat (BW), Soybean (SB), Pea (PE), Corn (CN), Sorghum (SM), Spring Oilseed Rape (OR) and Sugar beet (SB)). The field experiment field was a randomized complete block design on a 5 ha field arranged in a 3-factor factorial design with three replicates (a total of forty-eight plots). Each of the plots measured 34,5 m x 20 m (691 m^2). The experiment consisted of 72 parcels in total. The planting and harvesting dates of the rotation crops in the experiment and the agricultural practices are shown in the Table 1. All plants in the plots were harvested and yield and input of organic matter into soils with root and other residues of cover crops were converted to t ha^{-1}.

Table 1. The sowing and harvesting dates of the rotation crops in the experiment and the agricultural practices

Cover crops	Sowing date	Seed rate	Harvesting date	Drip irrigation rate
Flaxseed oil (FO)	12/07/2021	25 kg ha^{-1}	18/10/2021	400 m^3 ha^{-1}
Buckwheat (BW)	12/07/2021	32 kg ha^{-1}	18/10/2021	400 m^3 ha^{-1}
Soybean (SB)	12/07/2021	120 kg ha^{-1}	18/10/2021	600 m^3 ha^{-1}
Pea (PE)	12/07/2021	100 kg ha^{-1}	05/10/2021	600 m^3 ha^{-1}
Corn (CN)	14/07/2021	45 kg ha^{-1}	12/10/2021	800 m^3 ha^{-1}
Sorghum (SM)	12/07/2021	25 kg ha^{-1}	05/10/2021	600 m^3 ha^{-1}
Spring Oilseed Rape (OR)	12/07/2021	25 kg ha^{-1}	05/10/2021	400 m^3 ha^{-1}
Sugar beet (SB)	15/07/2021	2 kg ha^{-1}	18/10/2021	1000 m^3 ha^{-1}

100 kg Ammophos fertilizer (11%N, 46%P_2O_5) applied at sowing for all cover crops based on the recommendations of Kazakh Research Institute of Farming and Crop Production.

Soil Sampling and Analyses

After harvest, the soil samples collected from depth of 20 cm were naturally air-dried, milled and passed through 2.0 mm sieve. Total (TOC) and labile organic carbon (LOC) content by the titrimetric method using the biochromatic oxidation procedure by Tyurin-Kononova, Ammonia (easily hydrolyzable nitrogen) by the modified Kjeldahl method, nitrate by potantiometrically, available phosphorus was determined by Machigin method, exchangeable potassium content were determined by the 1N NH_4OAc extraction method according to the Tyurin, (1965), Rowell (1996) and Jones (2001).

Results and Discussion

The effects of different tillage methods on the yield of cover crops are given Table 2. It has been determined that different tillage methods have a significant effect on the yields of the cover crop. According to the results obtained; While the highest yield results were obtained in FO, BW, PE, SM, OR cultivation with CT, it was determined that the highest yield was obtained in CN and SB cultivation with MT, and in SB cultivation with NT. In this experiment, as in the short-term effects, it is thought that the absence of plant residue on the soil surface in the cultivation of cover crops, NT and MT conditions cause poor plant growth compared to CT. Therefore, it has been determined that NT and MT are not suitable for many plants (FO, BW, PE, SM and OR) in conditions where there is no cover layer consisting of plant residues on the soil surface, considering only the crop yield. Because the benefits of NT or MT are due to this cover (mulch) layer formed on the soil. Compared to the CT system, the advantage of the NT and MT systems are not the fact that the soil is not cultivated, but the presence of plant residues on the soil surface.

Table 2. The effect of different tillage methods on the yield of cover crops (t ha^{-1})

Cover Crops	Tillage methods		
	Conventional tillage (CT)	Minimum tillage (MT)	No-tillage (NT)
Flaxseed oil (FO)	1,01 ± 0,04	0,99 ± 0,03	0,89 ± 0,03
Buckwheat (BW)	1,53 ± 0,06	1,33 ± 0,04	1,12 ± 0,04
Soybean (SB) †	14,58 ± 0,50	13,32 ± 0,56	16,76 ± 1,09
Pea (PE) †	9,90 ± 0,44	8,52 ± 0,43	7,26 ± 0,37
Corn (CN) †	19,44 ± 0,91	19,99 ± 0,84	15,90 ± 0,76
Sorghum (SM) †	23,06 ± 1,06	17,33 ± 0,74	12,20 ± 0,68
Spring Oilseed Rape (OR) †	23,34 ± 0,82	13,85 ± 0,58	5,44 ± 0,17
Sugar beet (SB)	7,88 ± 0,35	10,60 ± 0,55	6,98 ± 0,36

† Green mass of cover crop

Input of organic matter into soils with root and other residues of cover crops with different methods of tillage are given Table 3. Contrary to the yield results of the cover crops, it was determined that the amount of organic matter (mulch) added to the soil by the cover crops differed according to the tillage methods. In the case of CN and SB plants grown as cover crops, the highest organic matter input was determined in CT, while the maximum in FO, BW, SB, OR cultivation was determined in MT, and in NT in PE, SM cultivation. With CT, the development of weeds in the soil is limited. In the experiment, weed control was not done with the weeds formed in the plots with cover crops by using any chemicals (herbicides). Therefore, the reason for the increase in the amount of organic matter added to the soil under MT and NT conditions in the experiment may have been caused by weeds that were not controlled.

Table 3. Input of organic matter into light chestnut soils with root and other residues of cover crops with different tillage methods (t ha^{-1})

Cover Crops	Tillage methods		
	Conventional tillage (CT)	Minimum tillage (MT)	No-tillage (NT)
Flaxseed oil (FO)	1,52	2,00	1,27
Buckwheat (BW)	1,25	0,40	0,82
Soybean (SB)	1,90	2,12	1,60
Pea (PE)	0,66	0,52	0,67
Corn (CN)	7,97	7,62	7,80
Sorghum (SM)	2,40	2,52	2,95
Spring Oilseed Rape (OR)	3,50	3,72	3,12
Sugar beet (SB)	0,60	0,27	0,25

The total organic carbon (TOC) and labile organic carbon (LOC) contents of the light chestnut soil samples taken at the end of the harvest from the plots where different cover crops were grown are given in Table 4. According to the results obtained, it was determined that different tillage methods affected the TOC and LOC contents of the soils of the plots where different cover crops were grown at different rates. LOC is a component of TOC. While LOC constitutes 11.05% of the TOC as the average of all plots in CT, this rate is determined as 9.54% in MT and 7.86% in NT. In CT methods, the mineralization rate of organic matter, the amount of LOC and the amount of CO_2 production as a result of mineralization of organic C increase as the soil is cultivated frequently and the aeration capacity of the soil increases. Soils that have been degraded through excessive tillage tend to have less SOM due to an increased amount of exposed surface area, which facilitates aerobic decomposition (DeBusk et al., 2001). Carbon makes up more than half the mass of SOM (Montgomery et al., 2000), and it has been shown that cultivating the land influences the dynamics of SOC and, in turn, the amount of C emitted from the soil as CO_2 due to the oxidation or decomposition of SOM (Paustian et al, 1995; Reicosky et al., 1995).

Table 4. Changes in the total organic carbon (TOC) and labile organic carbon (LOC) contents of light chestnut soils with different tillage methods and cover crops.

Cover Crops	Tillage methods					
	Conventional tillage (CT)		Minimum tillage (MT)		No-tillage (NT)	
	TOC, %	LOC, mg kg^{-1}	TOC, %	LOC, mg kg^{-1}	TOC, %	LOC, mg kg^{-1}
Flaxseed oil (FO)	0,78	940	0,83	920	1,03	690
Buckwheat (BW)	0,88	1190	1,03	820	0,94	780
Soybean (SB)	1,05	1070	0,88	820	0,94	800
Pea (PE)	1,01	1070	0,83	690	1,03	820
Corn (CN)	1,00	1070	1,05	940	0,91	570
Sorghum (SM)	1,12	1070	0,94	920	0,85	690
Spring Oilseed Rape (OR)	0,88	940	0,88	840	0,88	780
Sugar beet (SB)	1,03	1190	1,05	1190	0,83	680

In order to determine the effects of different tillage methods and cover crops on the available amounts of nitrogen, phosphorus and potassium in the soil, the results obtained from the light chestnut samples taken at the end of the harvest in this experiment are given in Table 5. According to the results obtained from the experiment, it was determined that there were significant differences in the amount of available nutrients according to the type of cover crops and tillage methods. Considering the average data of the plots where different cover crops were grown, it was determined that CT increased the most NH_4-N and exchangeable potassium content in the soil, while MT increased the NO_3-N content of the soil and NT increased the available phosphorus content. The reason for the high NH_4-N content in CT is probably related to soil organic matter and its mineralization. Soil organic matter is made up of approximately 5% N, which is mineralized into ammonium (NH_4^+) during the decomposition process. Mineralized N is susceptible to removal from or translocation within the soil after nitrification through the leaching of nitrate (NO_3^-) and through gaseous losses during denitrification (Havlin et al., 2013).

This study did not reveal very significant results on the effects of different cover crops and tillage methods on the available nutrient content of light chestnut soils. In addition, it is very difficult to say that any tillage method or cover crop comes to the fore with the results obtained. Possible reasons could be: 1) the field experiment in this study is that only 3 months have passed between the sowing and harvesting dates of the cover crops; 2) the organic matter entry into the soil from the cover crops has not yet been achieved. Similarly, Chan and

Heenan (1996) and Jokela et al. (2009) suggested that soil quality indicators like the ones used in this study might only be detectable after more than four years of continuous cover crop growth.

Table 5. Changes in mineral N (NH_4-N and NO_3-N), available P and exchangeable K contents of light chestnut soils with different tillage methods and cover crops.

Cover Crops	NH_4-N, mg kg^{-1}			NO_3-N, mg kg^{-1}			Available P, mg kg^{-1}			Exchangeable K, mg kg^{-1}		
	CT	MT	NT	CT	MT	NT	CT	MT	NT	CT	MT	NT
Flaxseed oil (FO)	56	47	56	61	45	60	19	35	60	230	200	294
Buckwheat (BW)	81	56	81	38	44	44	19	56	40	230	283	373
Soybean (SB)	63	60	60	40	42	39	25	46	57	456	210	327
Pea (PE)	63	49	77	36	43	45	35	28	57	408	262	230
Corn (CN)	61	85	56	40	57	46	24	28	19	350	339	272
Sorghum (SM)	71	70	61	39	91	45	24	61	29	373	361	241
Spring Oilseed Rape (OR)	106	96	51	51	46	51	51	31	47	350	272	251
Sugar beet (SB)	79	51	65	42	53	51	30	30	37	350	283	230

Conclusion

This short-term field experiment shows that one season of cover crop growth was not enough to find detectable changes in soil organic matter and available nutrient status in light chestnut soils. On the other hand, even in a short-term field experiment period of 3 months, the most labile organic carbon in soil total organic carbon was obtained in conventional tillage. This is a clear evidence that as a result of conventional tillage, organic matter will be rapidly broken down and its amount in the soil will decrease. Overall, the results show that at least in the short term and under lower drip irrigation rate in summer (for the study area), No-tillage and minimum tillage is suitable in the study area for soybean, corn and sugar beet production after intensive tillage in the previous year. Moreover, there is no doubt that a significant amount of organic matter will enter the soil as a result of the cover crop harvest. Therefore, the long-term effects of cover crops and different tillage methods need to be determined by field experiment.

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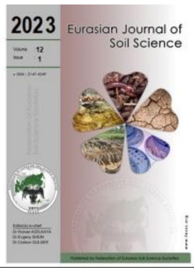

Development of Hungarian spectral library: Prediction of soil properties and applications

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Abstract

Updating soil information systems (SIS) requires advanced technologies to support the time and cost-effective and environment-friendly soil data. The use of mid-infrared (MIR) Spectroscopy as alternative to wet chemistry has been tested. The MIR spectral library is a useful technique for predicting soil attributes with high accuracy, efficiency, and low cost. The Hungarian MIR spectral library contained data on 2200 soil samples from 10 counties representing the first Soil Information and Mentoring System (SIMS) survey. Archived soil samples were prepared and scanned based on Diffuse Reflectance Infrared spectroscopy (DRIFT) technique and spectra data were saved in the fourier transform infrared (FTIR) spectrometer OPUS software. Preprocessed filtering methods, outlier detection methods and calibration sample selection methods were applied for spectral library. MIR calibration models were built for soil attributes using Partial Least Square Regression (PLSR) method. Coefficient determination (R2), The Root Mean Squared Error (RMSE) and Ratio of Performance to Deviation (RPD) were used to assess the goodness of calibration and validation models. MIR spectral library had the ability to significantly estimate soil properties such as SOC, CaCO3, sand, clay and silt through various scale models (national, county and soil type). The findings showed that our spectral library soil estimations are precise enough to provide information on national, county and soil type levels enabling a wide range of soil applications that demand huge amounts of data such as soil survey, precision agriculture and digital soil mapping.

Keywords: Fourier-transform infrared spectroscopy, mid-infrared spectroscopy, partial least square regression, soil information system.

Introduction

Soil is a finite natural resource with diverse environmental functions: storing nutrients, and organic carbon, functioning as buffer and filter, biodiversity conservation, cultural and living space for humans. It is crucial for ensuring food security and coping with climate change (Grunwald et al., 2011). Soil quality and its fertility are deemed vital for soil scientists, decision-makers, farmers, etc. Furthermore, soils cultivated with crops and forests has gained scientific, social, and political attention. Thus, it is critical to recognize, monitor, and store soil physical and chemical attributes using innovative approaches. Demands of soil-related information have risen substantially (Pásztor et al., 2015), and there is ample evidence that soil information systems are required to satisfy the growing need for soil data (Bullock and Montanarella, 1987). Globally and continentally, the properly organized soil information databases represent a comprehensive scientific basis of the various plans of action for sustainable land use and soil management. A significant quantity of soil data has been accumulated during long-term activities of land observations and soil surveys in Hungary and arranged in different spatial soil information systems. For instance, the Hungarian Soil Information Conservation and Monitoring System (SIMS) is an independent soil subsystem, consists of integrating environmental data and a

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monitoring database. Soil information systems must rely on accurate, reliable, good quality and updated soil information. Updating soil information systems has to include alternative laboratory technologies to support the time, cost-effective and environment-friendliness of soil data analysis. Many new soil analysis techniques have recently been developed, in particular, diffuse reflectance spectroscopy. Although soil wet chemistry techniques are widely regarded as accurate methods for characterizing soil attributes, they sometimes have been viewed as impractical due to their, time-consuming, and occasional imprecision (Demattê et al., 2019). When numerous measurements are required for soil taxonomy and mapping, wet chemistry frequently necessitates a large amount of sample preparation and sophisticated apparatus, which is usually insufficient (Viscarra Rossel et al., 2016). Also, traditional wet chemistry has disadvantages such as physical damage to the soil system's nature (Waruru et al., 2014) and generation of toxic wastes (environmentally harmful) that must be disposed off properly (Sila et al., 2017).

Soil infrared techniques are promising and have demonstrated several advantages over wet chemistry methods, making it more extensively used in the soil research community, notably in soil analysis. It permits rapid acquiring of soil data and attributes prediction (Seybold et al., 2019), e.g., soil samples preparation and spectral scanning carry out within a few minutes, allowing for a high throughput of samples per day. This approach is cheap, utilized tiny subsamples and have the advantage that a single spectrum of soil sample integrates many attributes with highly precise (Raphael, 2011; Waruru et al., 2015). Besides, the prior mentioned advantages, these methods do not require the use of chemical extracts that might harm the environment (Viscarra Rossel et al., 2006), allowing for the scanning diverse of soil types without samples dilution (Siebielec et al., 2004). The IR spectroscopy is a repeatable and reproducible analytical approach for predicting soil properties (Soriano-Disla et al., 2014). Fundamentally, soil infrared spectroscopy relies on the interplay of electromagnetic energy with matter to characterize samples' physical and biochemical composition. The given soil spectrum represents a unique fingerprint of a specific compound in the tested system (Tinti et al., 2015). 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 spectroscopy spectrum contains a high reflectivity, useful spectral features and gives greater information on soil attributes (Shepherd and Walsh, 2007; Stenberg et al., 2010); it has been confirmed to show better results and high predictions for several soil properties across soil types in comparison to near-infrared spectroscopy (Minasny and McBratney, 2008; Pirie et al., 2005). This is due to the fact that MIR range results are based on fundamental molecular vibrations, 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 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). 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. Soil mid-infrared spectroscopy data has the ability to store in databases known as spectral libraries. These soil spectral libraries are frequently required as reference patterns, making spectral data useful to the soil specialists community (Demattê et al., 2019). Additionally, it also applied for applications of soil remote sensing, spectral variations across sample sites (Deng et al., 2013), and building statistical models used in predictions of soil properties (Terra et al., 2015). Many publications showed soil attributes have been efficiently estimated based on the mid-infrared spectral library with high accuracy. It has been usefully applied to predict various soil physical properties, including soil texture (Shepherd and Walsh, 2005), and some properties of clay-like plasticity (Kasprzhitskii et al., 2018). In addition, it is been used to investigate and predict several biological and chemical soil properties like soil organic carbon fraction (Knox et al., 2015), organic carbon, calcium carbonates, soluble salts, cation exchange capacity, and soil pH (Reeves and Smith, 2009; D'Acqui et al., 2010). Since the soil properties can vary greatly, it is difficult to build accurate models for soil samples that are not present in spectral libraries. As a result, extensive spectral libraries are required to give robust models over broad areas with a lot of soil diversity (Nocita et al., 2015) to ensure models include soil samples identical to those predicted (Guerrero et al., 2016). Soil mid-infrared spectral libraries are ranging from large (regional, national and global) to local databases, including the field level (Wijewardane et al., 2016). For example, the LUCAS spectral library in Europe has approximately 20000 soil samples from the surface; the spectral library of the Australian continent represents 4000 soil samples, and the ICRAF-ISRIC soil spectral library contains 785 profiles (Demattê et al., 2019). On other hand, traditional soil surveys and fresh soil sampling campaigns are costly and time-consuming. Soil archives in agriculture associations, universities, and research centers might allow building of soil spectral libraries (Nocita et al., 2015). The majority of large soil spectral databases are built from archived historical soil samples (Rossel and Webster, 2012). Even soil samples obtained decades ago may have an abundance of spectral information that can be utilized to improve the calibration models of the mid-infrared spectral library. Analyzing soil mid-infrared spectral data using multivariate statistical techniques has given a powerful approach for soil component discrimination. Several multivariate regression approaches have been developed, such as Partial Least Square Regression (PLSR) that relates both response and predictor variables. 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).

The reflectance spectroscopy approach is being used for soil analysis in Hungary. There is no evidence for the existence of national spectral libraries that include a wide diversity of soils. There are only scattered studies using mid-infrared soil applications which represent small areas. Such lack of information opens up additional opportunities for study and research to take advantage of its applications, such as soil properties prediction. The study objectives are: 1)developing the first Hungarian mid-infrared spectral library 2) build a multivariate statistical models using PLSR and 3) test the predictive capacity of the developed spectral library in the spectral based estimation of key physical and chemical soil properties (SOC, $CaCO_3$, sand, silt and clay).

Material and Methods

Resources of data and the MIR spectral library

The MIR spectral library was built at the Hungarian University of Agriculture and Life Sciences, Szent István Campus. The soil samples of spectral database belong to the first SIMS project survey, 1992. This system provides yearly data regarding the condition of the Hungarian soils. The SIMS contains 1235 observation points based on physiographical-soil-ecological units. All points have geographic coordinates and approximately correspond to a 1:100.000 scale map. The soil profile sites have been distributed mainly among agricultural (arable) land, forests, and environmentally threatened (hot spot) regions. A total of 2200 soil samples, corresponding to horizons of 543 points were collected from the laboratory bank archives of SIMS, representing 10 Hungarian counties which are: Baranya, Fejer, Komarom_Esztergom, Nograd, Pest, Tolna, Bacs-Kiskun, Bekes, Csongrad and Jasz-Nagykun-Szolnok (Figure 1).

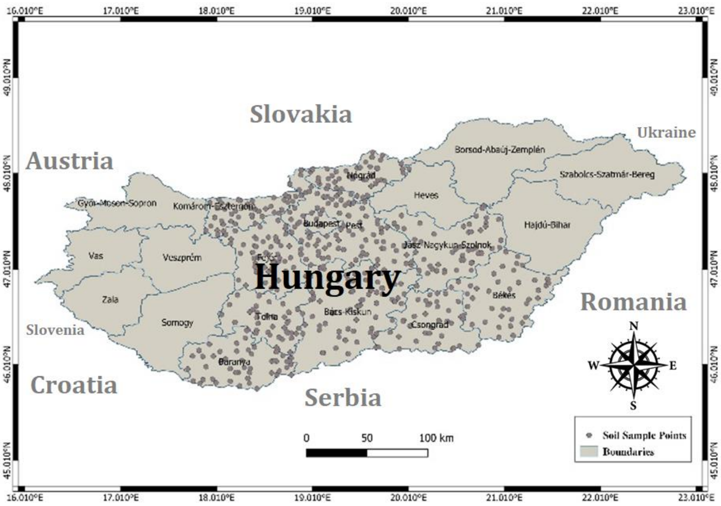

Figure 1. Spread of sampling points according to counties in Hungary

Preparation and scanning of soil samples

Previously, all soil samples have been dried, mashed, and filtered via a two-millimetre sieve, with the remaining part stored in SIMS archives in plastic containers at room temperature. 300 g from each sample were packaged in plastic sacs and shipped out to the Department of Soil Science, Gödöllő. Coning and quartering were used to obtain 20 g of soil subsamples, which were then grinded to less than 0.5 um (fine powdered particle size between 20 and 53um) by hand using an agate pestle and mortar. Samples were not mixed with alkali halides to avoid interferences that may cause ion exchange between KBr powder and soil sample (Janik et al., 1998). 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.

Mid Infrared Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT)

Nguyen et al. (1991) and Janik et al. (1995) introduced the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) approach for determining soil composition, which is a result of electromagnetic radiation interaction with matter. 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 uses as a reference material in mid-infrared spectroscopy methods since it does not absorb infrared light (Nash, 1986). While it could also be used to absorb other reflections throughout the IR spectrum. 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 Ateku, 2014). The collected information of all spectra was saved with the FTIR spectrometer OPUS software.

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) gives detail 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 preprocessing and transformations

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). Both techniques are used to reduce and remove noise that represents random fluctuations around the signal. This noise may originate from the instrument or environmental laboratory conditions.

Chemometric analyses

It might be challenging to estimate soil properties from big spectral data, resulting in increased prediction errors (Stevens et al., 2013). Chemometrics procedures can deal with the complexity of spectral data (Ramirez-Lopez et al., 2013) through statistical tools and mathematical methods (Varmuza and Filzmoser, 2016). 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. Two outlier detection methods were carried out on principal component scores of spectral data: Mahalanobis distance (Figure 2) and H distance.

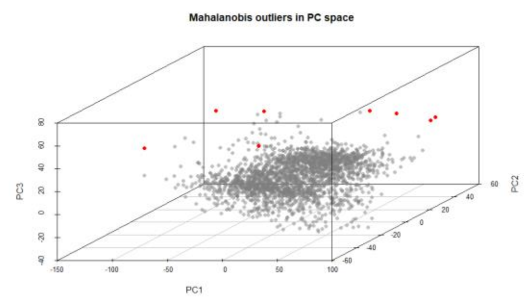

Figure 2. Location of outliers detected from PCs

The purpose of these methods is 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, while outlier samples were excluded using H distance values greater than 3.

Calibration sample selection

Kennard-Stone Sampling (Kennard and Stone, 1969), k-means cluster sampling (Næs, 1987), and Conditioned Latin Hypercube sampling (Minasny and McBratney, 2006) were applied to the spectral library data to define how many observations (samples) should be listed in calibration dataset in order to develop the best mid-infrared spectral models. According to representativity plots, the optimal calibration sample sets were selected by using the Kennard-Stone sampling (KSS) method (Figure 3), where the curve „flattens out". The remaining samples were retained for the validation set.

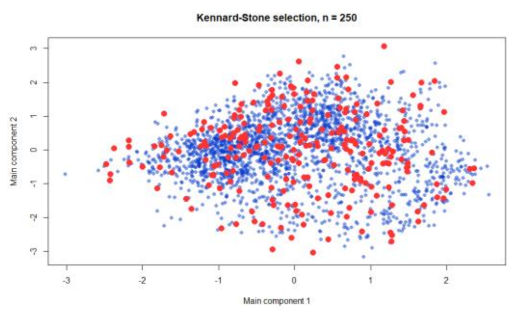

Figure 3. Kennard-stone sampling distributions

Build of soil properties prediction models

Prior to building the models, 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 a 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.

PLSR was introduced by (Lorber et al., 1987), which is the widely used approach (Burns and Ciurczak, 2007) for estimating physical and chemical soil characteristics (Johnson et al., 2019). Its purpose is to estimate a collection of dependent variables (soil attributes) by choosing a subset of 'orthogonal' components from the spectra (or latent variables). The following are the equations of PLSR:

$$X = TP^T + E$$

$$Y = UQ^T + F$$

Where: X is predictor variables, while Y is response variables, T and U are score matrices, P and Q are loading matrices, E is the matrix of residuals for X, and F is the matrix of residuals for Y.

In this research, statistical the 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). The number of PCA was determined by plotting the RMSEP of predication models and RMSEP of bias-adjusted. The components amount with the lowest RMSE were selected. 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. Five soil properties in the frame of this study were predicted, including, organic carbon (OC), percentages of clay, silt, and sand content and calcium carbonate ($CaCO_3$). Rsoftware (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 assessment

Soil attribute model performance was assessed by comparing predicted (MIR spectral library) and observed (reference soil database) values using different metrics. 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. Prediction reliability based on coefficient determination and ratio performance to deviation values classified the regression models into three categories: RPD > 2: “good” models that predicted with an acceptable or high level of accuracy; RPD ranging from 1.4 to 2: “satisfactory” models that had a medium level of prediction and might be improved and RPD lower than 1.4: “unreliable” or poor models with no predictive abilities. While the smaller the RMSE value, the reliability the accuracy of the models. RPD is widely used to determine the consistency and correlation of observed and predicted values (not of accuracy).

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

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

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

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

Building the Hungarian Mid-Infrared spectral library

The legacy soil samples of SIMS project represent a huge part of Hungary soils. These soils were formed on relatively young rock, with a small part covered by soils formed on older parent material and can be classified into four main categories: forest, grassland, meadow formations, and salt affected soils. The Hungarian MIR spectral library of the typical soil profile's at various depths reveals absorption signatures that were consistent with the criteria in Figure 4. The spectral curves of minimum and maximum absorption values recorded from the many sites showed wide variation in absorption intensities. Differences in physical and chemical soil properties impact the shape of the spectrum curves. Despite, the presence of spectral library overlapping bands, several absorption bands linked to certain functional groupings were identified (Figure 4). The hydroxyl stretching vibrations of kaolinite, smectite, and illite are thought to be responsible for the absorption bands amongst 3800 and 3600 (1/cm). More specifically, the absorption peak at 3620 (1/cm) might be due to clay minerals, similar result was obtained by (Nguyen et al., 1991). The wide band around 3400 (1/cm) may be caused by hydroxyl stretching vibrations of water molecules in 2:1 mineral. The presence of carbonate in soil was detected by diagnostic absorption bands. Bands around 2592, 2515 and 720 (1/cm) which were attributed to calcite while the peaks at 2510, 1479-1408 and 887-866 (1/cm) were assigned to carbonates. The existence of quartz was recognized by absorption bands at about 2000, 1870 and 1790 (1/cm) respectively which is consistent with the result by (Janik et al., 2007; Rossel et al., 2008). Quartz mixtures were confirmed by a band at 798 and near 779 (1/cm). Even though soil organic matter spectra include vast and overlapping regions, our spectra showed some bands of SOM function groups in Figure 4. The absorption bands at 2930 and 2850 (1/cm) attributable to alkyl material are especially, effective for detecting organic materials in soils. The spectra also displayed absorption bands due to C=O stretch of carbonyl C (1720-1700 1/cm), proteins (1640 and 1530 1/cm), aromatic amines (1342-1307 1/cm), carbohydrates (near 1100–1050 1/cm) and Lignin (835 1/cm) in soil organic matter. Some studies have the same finding (Skjemstad and Dalal, 1987; Kaiser et al., 2011; Tinti et al., 2015).

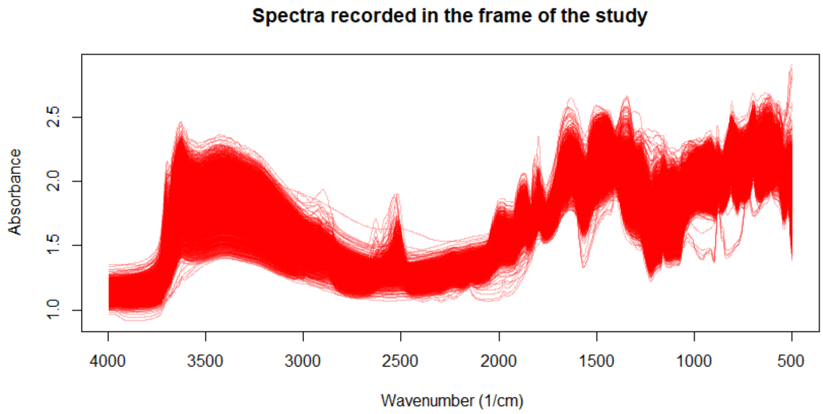

Figure 4. Absorbance mid-infrared spectral library data

Summary statistics of spectral library soil attributes

Descriptive statistics tables (1-5) clarify the summary statistics of training and testing sets for soil types, counties and national levels that were used in the modelling of the five soil attributes. The soil attributes of the spectral library dataset showed wide-ranging distributions. This factor was expected in this database, due to 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 activity. Calibration and validation datasets contained comparable mean values demonstrating the partition of data was somewhat balanced with some narrower differences ranges for some soil attributes. This is a positive indication that the selected validation points were within the calibration space's threshold which may led to increased prediction reliability and effective models assessment.

Principle component analysis

Figure 3 show scores plots of the overall structure data and Mahalanobis outlier samples respectively. The first three PCs accounted for 63 % of the variance in the whole spectral library data, as seen in Figure 3. In soil types levels, the PC1 was accounted for most of the variability in the spectral data and it ranged between 33 - 34 % while, the other successive components (PC2 and PC3) explain a smaller percentage of the remaining variability in the data and it ranged between 11 - 21%. While for the counties scale, the amount of variance in PC1 ranged from 32 - 36% and the remaining PC1 and PC2 together were ranging between 10 to 19 %. These few components with lower dimensions explained the variation in the spectral data and showed also different spectral distribution patterns in the counties. Figure 3 indicates, eight samples were observed as outliers (wmahald > 1) at the national level, scattered randomly. Among spectral data from 10 Hungarian counties, only two sample outliers were detected in Pest County, in addition to one outlier in Fejer and Tolna counties respectively. Also, one sample was detected as an outlier in Meadow soils and skeletal soils in terms of soil types. Detected outlier samples were filtered away from the mid-infrared spectral library data set at different levels of the scenarios then further investigation and calibration were performed on the remaining samples.

Prediction of soil properties for national, counties and soil types models

Soil organic cabon content

Table 1 represents the descriptive statistics and model results of organic carbon content. The models' performance assessment of SOC showed a high level of prediction accuracies for most of the calibration and validation datasets scenarios. The national organic carbon content (1.35 and 1.21 %) produced a good models in both the calibration set (R2 of 0.80, RPD of 2.23 and RMSE of 0.5) and validation set (R2: 0.81, RPD: 2.28 and RMSE: 0.46). For soil types, the soil organic carbon content was accurately predicted with R2 ranging from 0.99 to 0.76 and RMSE from 0.09 - 0.55 in the calibration model while R2 and RMSE varied from 0.88 – 0.68 and 0.35 to 0.50, repectively, in the validation model. Salt-affected, Brown forest, alluvial and colluvial soils presented the best modeled, whereas Skeletal soils presented the lower result, which may be due to the high sand and gravel content in these soils. These results were expected since the majority of Hungarian soils have high organic carbon. The only unexpected result was from Chernozem soils. For county scenarios, soil organic carbon content prediction within 10 counties showed that six counties had R2 ≥ 0.90, while only two counties had R2 < 0.75 in the calibration set, while in validation set six counties had R2 ≥ 0.75. The county with the highest prediction model in calibration set was Komarom_Esztergom with R2 of 1, RMSE is 0.01 and RPD of 125.8. Variation in results were due to the variety of soil types and different land management practices in these counties. Moreover, the existence of carbonates in soil could affect the predictions of soil organic carbon (Reeves and Smith, 2009). Similar results with a high prediction model for SOC were found in some spectral libraries studies by (Rossel et al., 2008; Baumann et al., 2021). In addition (Ng et al., 2022) through numerous studies observed excellent predictions of soil organic carbon with R2 ranging between 1.0 and 0.80.

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

		Calibration set							Validation set						
	SOC %	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	0.02	6.72	1.35	0.80	0.57	2.23	1959	0.01	6.56	1.21	0.81	0.46	2.28
Counties	Pest	98	0.05	5.34	1.18	0.93	0.33	3.70	294	0.01	5.07	1.16	0.85	0.40	2.55
	Baranya	70	0.04	5.14	1.06	0.92	0.31	3.65	141	0.10	3.78	0.88	0.81	0.33	2.33
	Fejer	49	0.02	6.26	1.59	0.90	0.49	3.28	186	0.03	4.65	1.38	0.68	0.60	1.76
	Komarom-Esztergom	35	0.01	4.30	0.93	1.00	0.01	125.80	125	0.01	4.48	0.89	0.52	0.67	1.45
	Nograd	55	0.11	4.07	1.11	0.81	0.41	2.35	88	0.14	4.01	1.26	0.71	0.47	1.86
	Tolna	39	0.12	6.72	1.67	0.99	0.16	10.23	153	0.13	4.50	1.27	0.77	0.43	2.08
	Bacs-Kiskun	98	0.07	5.20	1.02	0.74	0.49	1.98	186	0.07	2.97	0.69	0.79	0.30	2.20
	Bekes	70	0.14	5.76	1.54	0.96	0.24	5.29	132	0.23	3.69	1.57	0.85	0.39	2.56
	Csongrad	50	0.11	5.74	1.12	0.67	0.66	1.77	116	0.10	5.00	1.29	0.61	0.70	1.61
	Jasz-Nagykun-Szolnok	40	0.50	3.57	1.75	0.75	0.56	2.03	179	0.23	4.04	2.01	0.84	0.47	2.52
Soil types	Chernozem	149	0.01	3.86	1.19	0.76	0.49	2.06	530	0.01	4.03	1.53	0.79	0.47	2.19
	Brown forest	99	0.04	4.510	0.88	0.94	0.24	3.97	395	0.02	4.48	0.945	0.71	0.43	1.87
	Alluvial & colluvial	55	0.04	3.98	1.45	0.90	0.35	3.16	153	0.08	4.50	1.15	0.68	0.50	1.76
	Meadow	149	0.04	6.72	1.64	0.89	0.49	3.08	261	0.08	5.00	1.55	0.88	0.39	2.92
	Skeletal	99	0.01	5.15	0.93	0.76	0.55	2.03	200	0.02	5.07	0.59	0.70	0.35	1.83
	Salt-affected	27	0.13	5.76	1.15	0.99	0.09	13.56	64	0.15	4.77	1.07	0.77	0.43	2.10

Calcium carbonate

Predictions of calcium carbonate for spectral library had wide-ranging results (Table 2). $CaCO_3$ at the national level (16.57 and 15.01 %) was well modeled with R2 of 0.84, RPD of 2.54 and RMSE of 5.96 in the calibration set and R2 of 0.77, RPD of 2.08 and RMSE of 5.96 in the validation set. These high results may be due to the fact that about 49 % of Hungarian soils are calcareous having $CaCO_3$ content ranging from 1-25 % (TIM, 1995). From all the Hungarian counties, only Csongrad county had a low prediction level of $CaCO_3$ in the training set (R2 of 0.60 and RMSE of 8.11) and testing set (R2 of 0.51 and RMSE of 7.09). $CaCO_3$ in Pest county was predicted slightly better with R2 of 0.76 and RMSE of 6.61 in the training set and R2 is 0.67 in validation set. Performance model results of the other 8 counties were well modeled at a high level of accuracy with R2 of 0.94 to 0.83 and RPD from 4.0 to 2.44 in calibration sets (Table 2). Four counties had R2 < 0.75 in validation sets, while the remaining six counties had R2 ≥ 0.75. The $CaCO_3$ assessment statistics for soil types prediction showed that a good calibration model was obtained for salt-affected soils (R2 of 0.91, RPD of 3.41, RMSE = 4.4) with corresponding high validation results (R2 0.81). This can partly be explained by the fact that of Hungarian soils were moderately or highly alkaline and were basically all salt-affected. Modest predictions were obtained by Chernozem soils and Skeletal soils in the calibration set (R2 = 0.73 to 0.56) performing slightly better in the validation sets (R2 = 0.78 to 0.76). Other remaining soil types produced R2 values from 0.89 to 0.79 and RMSE from 3.59 to 6.33 in the calibration sets while RMSE ranged from 4.51 - 5.21 and R2 from 0.85 - 0.79 in the validation sets (Table 2). Viscarra Rossel et al. (2016) obtained R2 values of 0.77 and RMSE of 3.96 for the calcium carbonate predictions, while Knox et al. (2015) and Seybold et al. (2019) showed good calcium carbonate predictions models with R2 of 0.92 and RMSE of 0.30 and R2 of 0.99 and RMSE of 1.2, respectively. Generally, the high prediction model of SOC and calcium carbonate was attributed to the specific strong absorption bands associated with chemical bonds of carbon-containing compounds in soil (Rossel and Behrens, 2010; Wijewardane et al., 2018).

Table 2. PLSR model values, descriptive statistics and results of calibration and validation prediction models of $CaCO_3$

		Calibration set							Validation set						
	$CaCO_3$ %	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	0.10	96.0	16.57	0.84	5.96	2.54	1959	0.10	86.0	15.01	0.77	5.96	2.08
Counties	Pest	98	0.10	65.0	16.41	0.76	6.61	2.07	294	0.10	67.0	17.12	0.67	7.41	1.75
	Baranya	70	0.10	51.0	14.57	0.93	3.11	3.70	141	0.10	52.0	13.24	0.92	3.19	3.50
	Fejer	49	0.20	96.0	26.62	0.94	5.92	4.00	186	0.50	56.0	21.94	0.78	5.75	2.13
	Komarom-Esztergom	35	0.10	43.0	14.66	0.83	5.47	2.44	125	0.30	38.0	13.70	0.72	5.68	1.90
	Nograd	55	0.10	26.0	7.32	0.88	1.99	2.86	88	0.10	17.0	4.88	0.84	1.58	2.50
	Tolna	39	0.90	38.0	20.08	0.86	4.94	2.75	153	0.70	41.0	18.81	0.84	4.89	2.53
	Bacs-Kiskun	98	0.10	47.0	17.14	0.91	3.74	3.42	186	0.10	49.0	14.61	0.89	3.38	2.96
	Bekes	70	0.50	45.0	11.41	0.85	4.03	2.63	132	0.10	30.0	10.87	0.84	3.50	2.51
	Csongrad	50	0.10	64.0	13.12	0.60	8.11	1.59	116	0.10	66.0	11.15	0.51	7.09	1.44
	Jasz-Nagykun-Szolnok	40	0.70	40.0	10.71	0.93	2.70	3.70	179	0.10	32.0	7.57	0.73	3.50	1.92
Soil types	Chernozem	149	0.50	53.0	16.27	0.56	7.54	1.51	530	0.10	45.0	17.33	0.76	5.37	2.06
	Brown forest	99	0.10	65.0	15.77	0.79	6.33	2.21	395	0.10	52.0	10.25	0.81	4.51	2.28
	Alluvial & colluvial	55	0.10	49.0	14.43	0.89	3.59	3.03	153	0.50	47.0	16.23	0.79	4.97	2.19
	Meadow	149	0.60	85.0	19.99	0.89	5.43	3.04	261	0.10	67.0	14.78	0.85	5.21	2.56
	Skeletal	99	0.10	50.0	11.44	0.73	5.03	1.94	200	0.10	50.0	9.95	0.78	3.89	2.11
	Salt-affected	27	0.50	47.0	20.63	0.91	4.40	3.41	64	0.10	49.0	16.35	0.81	5.71	2.31

Sand

Amongst all soil properties in this study, soil texture, especially, sand content (39.81 - 40.32 %) showed the highest prediction model at the national level in the calibration set (R2 of 0.89) and validation set (R2 of 0.85) (Table 3). All calibration models had coefficient determination higher than 0.81 at counties scenario and 6 counties had coefficient determination ≥ 0.90, while in validation models five counties had coefficient determination higher than 0.8 and ratio performance to deviation higher than 2 (Table 3). All soil types' levels had highest calibration models with R2 greater than 0.83 and RPD higher than 2.53, as well as R2 greater than 0.74 and RPD near 2 in validation models. Meadow soils and salt-affected soils had R2 greater than 0.90 and RPD higher than 3.36 in the calibration sets and R2 greater than 0.83 and RPD higher than 2.48 in the validation model sets (Table 3). Based on TIM (1995), the sand content in Hungary represents (16 %) which may partly explain high prediction of sand and also partly by robust interaction between Mid-infrared radiation and minerals of sandy soils. The high accuracy performance models of sand content agreed with the results of some other mid-infrared spectral libraries reported by some authors (Wijewardane et al., 2018; Demattê et al., 2019).

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

		Calibration set							Validation set						
	Sand %	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	2.23	99.02	39.81	0.89	9.35	2.96	1959	0.70	99.02	40.32	0.85	10.97	2.57
Counties	Pest	98	2.40	96.20	52.01	0.82	11.1	2.39	294	6.70	96.50	48.15	0.85	10.76	2.62
	Baranya	70	2.50	95.00	34.30	0.85	9.64	2.62	141	1.60	96.30	25.89	0.62	12.32	1.62
	Fejer	49	7.40	95.20	46.86	0.93	6.39	3.90	186	2.23	86.80	38.74	0.68	10.85	1.73
	Komarom-Esztergom	35	2.00	94.50	47.82	0.90	8.54	3.19	125	9.10	92.10	48.58	0.63	13.38	1.66
	Nograd	55	1.3	94.60	36.90	0.83	11.51	2.48	88	1.80	91.90	33.23	0.68	12.26	1.79
	Tolna	39	0.70	94.50	36.55	0.91	8.32	3.41	153	0.90	93.50	33.59	0.70	11.44	1.82
	Bacs-Kiskun	98	8.15	98.55	59.43	0.96	5.84	5.09	186	8.62	99.02	69.34	0.92	7.45	3.61
	Bekes	70	3.20	76.82	19.84	0.94	4.06	4.28	132	2.92	65.46	19.16	0.85	5.72	2.61
	Csongrad	50	3.65	95.65	50.01	0.84	14.5	2.52	116	2.52	96.02	36.35	0.87	11.45	2.76
	Jasz-Nagykun-Szolnok	40	3.83	91.82	32.57	1.00	0.11	249.8	179	1.53	92.88	22.94	0.82	8.03	2.36
Soil types	Chernozem	149	0.70	98.55	45.65	0.84	10.16	2.54	530	1.80	92.10	31.07	0.74	9.56	1.96
	Brown forest	99	1.60	92.20	43.11	0.87	9.20	2.82	395	1.30	94.60	36.22	0.75	11.64	2.02
	Alluvial & colluvial	55	0.90	96.46	43.92	0.85	9.97	2.59	153	0.90	98.06	39.90	0.74	13.28	1.96
	Meadow	149	1.53	95.10	34.30	0.91	7.84	3.37	261	2.47	93.60	24.78	0.84	8.70	2.49
	Skeletal	99	12.9	98.70	70.39	0.85	10.23	2.61	200	8.90	99.02	81.22	0.79	11.1	2.18
	Salt-affected	27	3.65	82.06	26.59	0.96	4.3	5.33	64	4.24	95.78	29.05	0.88	8.42	2.92

Clay

The clay content at the national scale (22.88 and 22.86 %) showed high results in the calibration set with R2 of 0.80 and RMSE of 5.94 and in the validation set with R2 is 0.80 and RMSE is 6.59 (Table 4). At the counties level, clay content within 8 counties was well with R2 ranging from 0.97 to 0.80 in calibration set and 5 counties had R2 ranging from 0.73 to 0.80 in validation model sets. Nograd County showed the worst result in the calibration set with R2 of 0.34 and RMSE of 15.92 while Tolna county had (R2 of 0.74, RMSE = 5.30 and RPD of 2.00) but still had a medium level of prediction (Table 4). At soil types scenario, salt-affected soils showed the best performing calibration model with R2 of 0.92 and RMSE of 4.30, whereas R2 was 0.80 in the validation sets. In three soil types, the coefficient determination was higher than 0.84 and only Brown forest soils and Skeletal soils had R2 of 0.76 and 0.64, respectively in the calibration models. Validation sets showed four soil types had R2 higher than 0.78 and RPD higher than 2.14 (Table 4). Since clay minerals are spectrally active molecules (Ng et al., 2022), this may be the reason why the clay content was predicted accurately, furthermore, clay has fundamental vibrations. Therefore, the low and medium coefficient determination and variation of clay predictions results may associate either with the low total clay or the variability of clay content in the soil. Some studies have justified the low clay predictions with presence of high carbonate content in the soil samples (Seybold et al., 2019).

Table 4. PLSR model values, descriptive statistics and results of calibration and validation prediction models of Clay

		Calibration set							Validation set						
	Clay %	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	2.23	99.02	39.81	0.89	9.35	2.96	1959	0.70	99.02	40.32	0.85	10.97	2.57
Counties	Pest	98	1.90	62.60	17.12	0.92	3.19	3.47	294	0.10	45.60	18.89	0.77	5.16	2.07
	Baranya	70	1.40	53.00	23.69	0.85	4.48	2.60	141	1.20	44.40	24.08	0.78	4.21	2.13
	Fejer	49	1.40	50.80	19.60	0.92	3.25	3.66	186	0.40	46.10	19.26	0.28	6.22	1.18
	Komarom-Esztergom	35	2.20	48.30	17.83	0.80	5.36	2.27	125	1.50	41.20	15.26	0.30	6.45	1.20
	Nograd	55	0.90	82.70	24.59	0.34	15.92	1.24	88	1.80	56.90	26.13	0.45	10.08	1.36
	Tolna	39	0.30	39.60	19.83	0.74	5.30	2.00	153	0.10	42.30	19.89	0.49	6.23	1.40
	Bacs-Kiskun	98	0.16	56.32	14.06	0.97	2.04	6.08	186	0.16	31.68	7.874	0.80	3.02	2.24
	Bekes	70	9.02	67.04	38.30	0.96	2.77	4.86	132	2.24	64.88	38.55	0.73	6.34	1.95
	Csongrad	50	2.88	62.55	24.02	0.81	7.84	2.34	116	0.24	61.92	29.87	0.48	12.89	1.40
	Jasz-Nagykun-Szolnok	40	6.81	64.01	33.54	0.94	3.78	4.07	179	4.81	64.89	38.47	0.83	4.90	2.45
Soil types	Chernozem	149	1.28	51.72	19.47	0.85	4.34	2.58	530	0.30	54.46	23.81	0.68	6.10	1.77
	Brown forest	99	1.70	56.90	21.54	0.76	6.72	2.03	395	0.80	82.70	23.06	0.53	8.29	1.46
	Alluvial & colluvial	55	0.10	62.60	19.14	0.87	4.63	2.80	153	0.10	45.75	19.22	0.86	4.12	2.65
	Meadow	149	1.92	67.04	29.06	0.88	5.55	2.93	261	2.40	64.89	36.38	0.83	6.43	2.44
	Skeletal	99	0.24	40.37	10.01	0.64	4.62	1.68	200	0.16	44.77	7.11	0.78	3.84	2.14
	Salt-affected	27	4.80	54.40	34.35	0.92	4.30	3.56	64	2.88	57.90	31.52	0.80	7.11	2.23

Silt

Silt content had similar prediction results as clay content in most of the levels, but with some lower values, particularly in the validation sets. For the national scenario, silt content (37.75 and 37.92 %) had a medium level with R2 of 0.64 and 0.69 in calibration and validation sets, respectively (Table 5). From 10 counties with silt calibration prediction, six counties had R2 ≥ 0.83, three counties had R2 ≥ 0.70 and one county had R2 of 0.53 (Table 4). Predictive modeling of silt at soil types scale showed all calibration sets had R2 ≥ 0.70, except the Chernozem soils type which had R2 of 0.69. Salt-affected soils had R2 of 0.94 and RMSE of 3.85 (Table 5). Four soil types had R2 ranging from 0.55 to 0.81 in the validation sets.

Generally, our prediction results for clay was similar to those found in other studies (e.g., Terhoeven-Urselmans et al., 2010; Baumann et al., 2021) which focused mostly on legacy soil samples. For the same studies, the authors had lower prediction results of silt content (R2 range from 0.55 - 0.51). Ng et al. (2022) reported that the prediction accuracies of sand, clay and silt and had R2 values of 0.80, 0.84 and 0.70, respectively which generally had higher accuracy predictions of particle size distribution compared to our national-level results.

Generally, from all soil properties predicted in Hungarian MIR spectral library, Fejer county showed poorest result with R2 of 0.28 in the validation datasets (Tables 4). While sand showed highest results with R2 of 0.89 in calibration set and 0.85 in validation set.

At the national scale, silt presented lower predictive model in validation set with R2 of 0.69 (Table 5). Komarom_Esztergom and Jasz-Nagykun-Szolnok counties showed best prediction models with R2 of 1 (Tables 1 and 3) in calibration sets. While Baranya and Bacs-Kiskun showed best prediction models with R2 of 0.92 (Tables 2 and 3) in validation sets. A similar high result with R2 of 1 was obtained by (Sanderman et al., 2020) for organic carbon. At soil type scal Salt-affected soils presented best performing model with a R2 of 0.99 (Table 1) in calibration sets while in validation sets, Meadow and Salt-affected soils presented best performing model with a R2 of 0.88 (Table 1 and 3).The descriptive statistics tables showed some soil attributes had small datasets that may have affected the predictions accuracies.

Table 5. PLSR model values, descriptive statistics and results of calibration and validation prediction models of Silt

		Calibration set							Validation set						
	Silt %	n	Min	Max	Mean	R2	RMSE	RPD	n	Min	Max	Mean	R2	RMSE	RPD
National		241	2.19	94.40	37.75	0.64	11.5	1.68	1959	0.61	102.4	37.92	0.69	10.79	1.79
Counties	Pest	98	1.50	70.70	30.98	0.86	7.15	2.65	294	1.10	71.30	32.94	0.82	8.34	2.35
	Baranya	70	3.30	71.10	42.01	0.75	8.97	2.01	141	2.60	76.50	50.30	0.38	11.86	1.27
	Fejer	49	3.60	69.64	32.24	0.83	7.38	2.42	186	6.11	102.4	42.32	0.53	11.85	1.47
	Komarom-Esztergom	35	1.80	76.80	34.36	0.92	5.33	3.63	125	4.60	83.50	36.20	0.66	10.76	1.71
	Nograd	55	2.80	98.70	38.58	0.53	16.59	1.48	88	5.30	96.20	40.82	0.30	14.31	1.21
	Tolna	39	2.10	85.60	43.72	0.74	11.6	1.99	153	2.50	81.40	46.67	0.46	12.82	1.37
	Bacs-Kiskun	98	1.09	73.74	29.78	0.93	5.83	3.78	186	0.61	74.38	30.01	0.91	6.61	3.27
	Bekes	70	14.1	57.80	41.83	0.90	3.09	3.18	132	18.7	56.00	42.27	0.42	6.53	1.31
	Csongrad	50	1.20	66.45	25.97	0.70	10.9	1.85	116	1.06	71.10	33.78	0.33	16.24	1.23
	Jasz-Nagykun-Szolnok	40	1.37	64.52	33.74	0.93	3.98	3.91	179	2.19	58.57	38.63	0.68	5.87	1.76
Soil types	Chernozem	149	1.42	74.10	35.26	0.69	10.3	1.79	530	2.86	102.4	45.20	0.40	11.65	1.30
	Brown forest	99	5.30	94.40	35.59	0.72	9.88	1.90	395	2.60	98.70	40.85	0.55	12.64	1.50
	Alluvial & colluvial	55	1.50	79.30	37.58	0.81	8.01	2.29	153	1.59	81.40	41.18	0.56	12.5	1.51
	Meadow	149	2.30	76.38	36.64	0.70	8.84	1.84	261	2.55	72.14	38.85	0.54	8.84	1.48
	Skeletal	99	1.10	70.70	21.33	0.77	9.66	2.08	200	0.61	66.70	14.29	0.81	6.67	2.32
	Salt-affected	27	5.80	64.29	39.05	0.94	3.85	4.13	64	1.06	73.74	40.03	0.80	6.38	2.27

Despite, we used a large number of samples (n = 2200), we assume completion of the Hungarian spectral library with missing soil samples (9 counties) may expand and enhance the use of the spectral library. Hungary's soils were formed mainly on the relatively young rock bed and old parent material as well as on eolic, alluvial and colluvial deposits (TIM, 1995). In addition to climatic conditions and natural vegetation, human activities like intensive land use, soil improvement and cultural techniques have significant effect on soil information processes in Hungary. Results of these diverse interactions between soil formation factors may produced great variability in performance of models for soil types and Counties. Reeves and Smith (2009) found that dataset diversity, parent materials, land uses, and climate can lead to poor model prediction results.

Conclusion

We report the first soil MIR spectral library with 2200 soil samples for Hungary based on legacy soil samples of the SIMS project as well as, predicting an array of five soil attributes in the Hungary SIMS system. 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. Hungarian MIR spectral library is valuable for estimating soil properties such as SOC, $CaCO_3$ and physical soil texture with variable results between national, county and soil type models scenarios. The results were logical for spectrally active elements that include: soil organic carbon, $CaCO_3$, sand and clay as well as for silt which are not spectrally active but correlated with other active elements. The results showed that legacy soil samples can be used to generate a spectral library with good quality information. The developed first Hungarian Mid-infrared spectral library provides rapid soil estimates with low cost-effectiveness, which is the basis for updating soil information and monitoring systems. Furthermore, it can be used in soil survey, DSM and soil classification. We expect to improve this spectral library by adding new soil samples, in addition to the remaining soil samples from the SIMS survey. We also hope that its soil information will be available to soil scientists, land managers, conservationists and other stakeholders.

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Mapping the sensitivity of land degradation in the Ouergha catchment (Morocco) using the MEDALUS approach

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Abstract

Soil degradation is a global phenomenon affecting the productivity of agricultural land. Due to the low vegetation cover and the aggressive climate, Morocco presents a significant case of soil degradation through erosion and desertification. The Ouergha catchment is highly vulnerable to this scourge. The objective of this study was to assess the sensitivity of land to degradation in the Ouergha catchment area. The MEDALUS approach, widely used in the Mediterranean region, was used to assess the sensitivity of soils to degradation/desertification. This approach integrates four indicators that strongly influence this phenomenon (climate, soil, vegetation and human pressure). The results show that more than half of the study area has a medium sensitivity of land to degradation. The critical areas represent 16.2% and correspond to bare land characterized by steep slopes and absence of vegetation. Low sensitivity areas occupy a limited proportion of 21.9% and correspond to wet summits and conserved forest areas. Climate change could lead to a further increase in areas susceptible to degradation.

Keywords: Land degradation, MEDALUS approach, GIS, Ouergha catchment, Morocco.

Introduction

Soil degradation is a global phenomenon that hinders the productivity of agricultural land (Contador et al., 2009). Several processes such as water and wind erosion, salinity and especially desertification cause this degradation. The United Nations Convention of to Combat Desertification (Paris, 1994), defined desertification as « the degradation of land in arid, semi-arid and dry sub-humid areas as a result of various factors, including the climate variations and human activities. This phenomenon is the result of the interaction of environmental factors (topography, climate, soil and vegetation) and anthropogenic factors such as deforestation, overgrazing and inappropriate management practices (Bouabid et al., 2010; Salvati et al., 2016). The consequences of desertification are often dramatic for poor people in developing countries. It leads to a loss of land productivity (Sepehr et al., 2007), affecting about 40% of the world's land surface. The economic losses of this phenomenon are estimated at 42.3 billion dollars per year (Mokhtari, 2016).

In Morocco, desertification affects approximately 90% of the national territory (Ghanam, 2003). This phenomenon could be aggravated by climate change, characterized by a decreasing trend in precipitation and an increasing trend in temperature (Driouech et al., 2021; Balhane et al., 2022), which leads to a displacement in arid bioclimates, semi-arid and sub-humid towards sub-humid or even humid zones, thus increasing the phenomenon of land degradation. In addition, incompatible human practices implemented locally, such as deforestation and overgrazing, increase the vulnerability of land degradation (Zaher et al., 2021; El Mazi et al., 2022). The Ouergha catchment, largely dominated by semi-arid and sub-humid bioclimates, is more sensitive to land degradation and desertification (Boutallaka, 2019).

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To deal with this scourge, the scientific community has developed several approaches and methods to assess the sensitivity of land to degradation (Lahlaoi et al., 2017; Prăvălie et al., 2017; Lamqadem et al., 2018; Rabah and Aida, 2019). Some of these approaches are based on the integration of environmental indicators that influence this phenomenon and others combine anthropogenic indicators (Lamqadem et al., 2018). The MEDALUS approach (Mediterranean Desertification and Land Use) is widely deployed to assess the sensitivity of land to degradation/desertification. This approach integrates into the GIS, biophysical and environmental indicators such as soil quality, vegetation cover, climate quality and human indicators. Several studies have applied this method to assess the sensitivity of land to degradation (Sepehr et al., 2007; Contador et al., 2009; Prăvălie et al., 2017; Rabah and Aida, 2019). In Morocco, this approach has been tested in particular to map the sensitivity of soils to desertification in regions characterized by hyperarid, arid and subhumid climates (Bouabid et al., 2010; Lahlaoi et al., 2017; Lamqadem et al., 2018). In northern Morocco, this method has been tested in the Moulouya watershed (Mokhtari, 2016), and in the Upper Ouergha dominated by a subhumid climate (El Ouazani Ech-chahdi et al., 2020).This work aims to assess the sensitivity of land to degradation in the Ouergha catchment, by applying the MEDALUS approach. It also aims to spatialize the degree of severity in order to help decision makers take the necessary measures to maintain the sustainability of natural systems.

Material and Methods

Study area

The present study concerns the Ouergha catchment in northern Morocco, part of the Sebou watershed located in the Central Rif, and covering an area of 6150 km^2. The altitudes vary from 200 m in its downstream part to more than 2400 m in mountainous ridges. The geological context is dominated by fragile lithological formations composed mainly of marls and shales of the Ktama Unit (Maurer, 1968). The dominant climate is the Mediterranean type (Janati Idrissi, 2010) with rainfall varying between 350 mm the low altitudes to more than 800 mm in the wet slopes. It is characterized by a bioclimatic gradient ranging from semi-arid to humid and cold winter. This catchment has four dams and is considered a water reservoir since it has more than 13% of the surface water of Morocco. It is characterized by a high population density, essentially rural (more than 120 inhabitants/km^2). Economic activities are based on agriculture. The principal land uses are cereal crops, tree crops, forest cover and uncultivated land. The population exerts strong pressure on natural resources, in particularly on the forest, the soil and the water, to meet its needs.

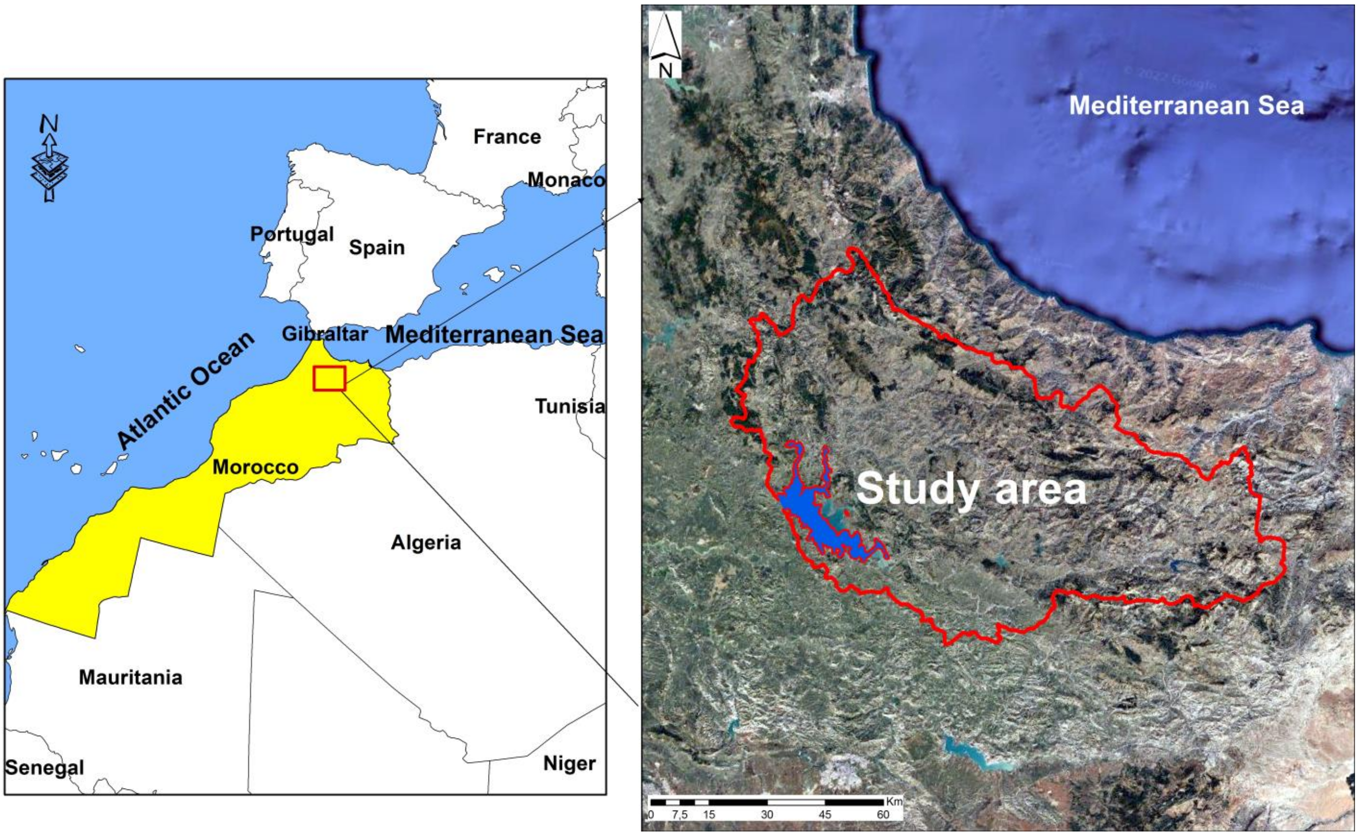

Figure 1. Study area

Data used

The data used to produce the map of land sensibility to degradation are:

- The geological map of the Rif at 1:500,000 was used to extract parent materials;
- The soil map at 1:200,000 and soil analyzes carried out as part of the agricultural development studies (department of agriculture) were used to extract texture and depth from soils;
- Series of rainfall data (1980-2015) were collected from the Sebou ccatchment Agency to characterize the quality of the climate;
- The Landsat OLI 8 image (15 September 2017) was collected from the USGS Earth Explorer database ("http://earthexplorer.usgs.gov/"), then processed and analyzed to extract the types of land use. Thus, the 2014 forest inventory map was used to determine the characteristics of forest formations (type, rate of cover, sensitivity to fire);
- The ASTER Global Digital Elevation Model (GDEM) is downloaded from the Earth Explorer website (earthexplorer.usgs.gov), and used to obtain the physiographic aspects of the study area (slopes, slope exposures).
- Demographic data from the 2014 National Population and Habitat Census were acquired from Morocco's High planning Commission. These data are available on the website https://www.hcp.ma.

Methodological approach

In this study, the MEDALUS approach was used to assess the sensitivity of land to degradation. This approach is based on the integration of the main biophysical, climatic and anthropogenic indicators influencing this phenomenon (Bouhata and Kalla, 2014; Lamqadem et al., 2018), according to the following formula (Eq.1).

$$SDI = (CQI \times SQI \times VQI \times MQI)^{1/4} \quad (1)$$

Where SDI is the soil degradation index, CQI is the climatic quality index, SQI is the soil quality index, VQI relates to the vegetation quality index, and MQI is the management quality index. These indicators were combined in the GIS to extract the weighted geometric mean of each indicator (Figure 2).

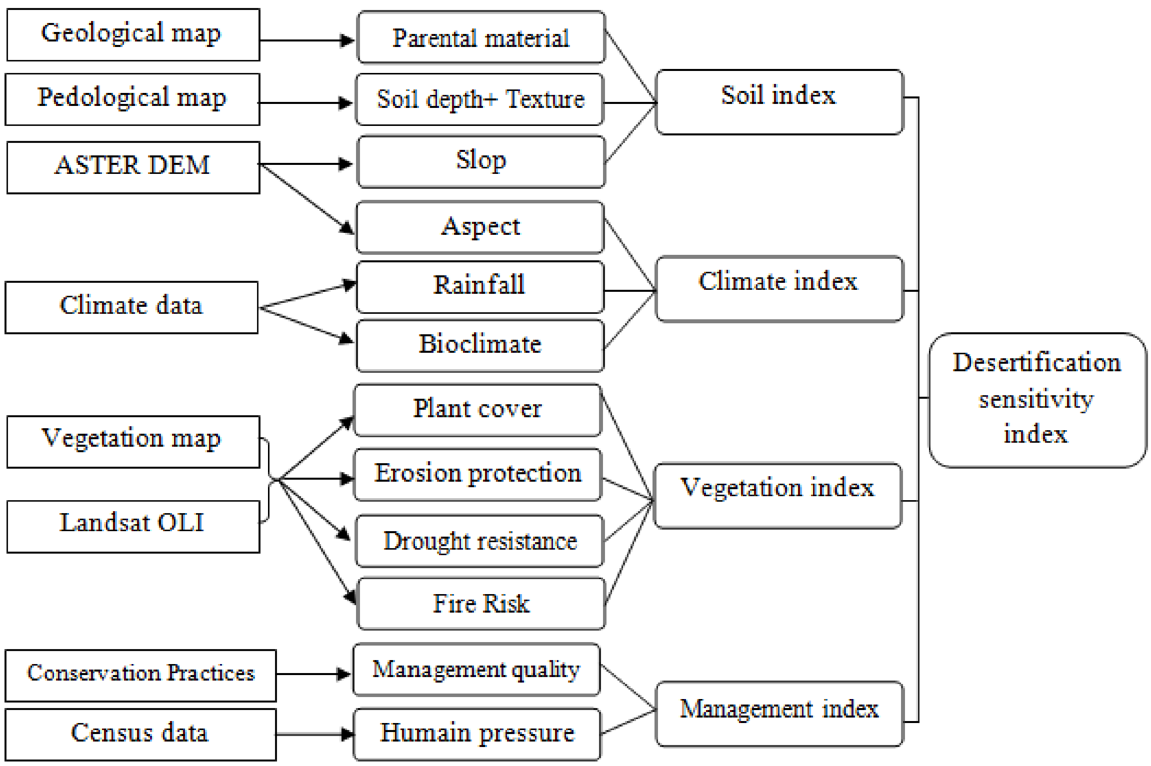

Figure 2. Methodological flowchart

Climate Quality Index (CQI)

Climate is an important parameter in the land degradation process (Bouabid et al., 2010). Indeed, rainfall variability, prolonged drought accompanied by extreme climatic events such as heat waves and intense rains can make vegetation cover and land vulnerable to desertification (Lahlaoi et al., 2017). The calculation of the quality of the climate according to the MEDALUS approach is based on three parameters: namely the aridity index, the annual precipitation and the topographical aspect. This index is calculated using the Eq. 2:

$$CQI = (P \times AI \times A)^{1/3} \quad (2)$$

Where P is precipitation, AI is the aridity index, A is the topographical aspect.

The aridity index was developed from the Emberger and Martonne indices, which are widely used to characterize climate aridity in the Mediterranean region (Mokhtari et al., 2013). The precipitation map was prepared based on the spatialization of climate data provided by measuring stations located in the study area and its borders using the IDW technique in Arcmap. The topographical aspect is an important parameter that influences the quality of the climate and the humidity of the soil from based on its sunshine and its location in relation to humid disturbances. The topographical aspect was obtained from Aster GDEM with a resolution of 30m.

Soil Quality Index

The Soil factor is a key element in the desertification process (Trotta et al., 2015). The susceptibility of soils to degradation is determined by the cohesion between soil particles, water retention capacity, horizontal depth of soil, soil texture, structure and organic matter content (Lahlaoi et al., 2017). The algebraic expression reflecting the effect of the soil factor is indicated by Eq. 3:

$$SQI = (Pm \times Dp \times T \times S)^{1/4} \quad (3)$$

Where Pm is parent material, Dp is the soil thickness, T is the soil texture, S is the topographical slope.

The geological map of the Rif at 1/500.000 was used to determine the lithological types and classified according to their degree of resistance to water erosion to obtain the parental material. Data relating to soil texture, thickness and organic matter content were extracted from the 1/20.000 soil map and from physico-chemical analyses carried out as part of the Ouergha catchment management study in 1994. The slopes were established from the analysis of an Aster GDEM.

Vegetation Quality Index (VQI)

Vegetation cover plays an important role in the process of land degradation. It provides significant protection of the soil against erosion. This protection depends on the type of vegetation and the rate of vegetation cover. Well-maintained forests enrich the soil with organic matter and act as a barrier to precipitation, and reduce land loss. Indicators of land degradation related to vegetation are: fire risk, erosion protection, drought resistance, and vegetation cover (Trotta et al., 2015) . The VQI was determined using Eq. 4.

$$VQI = (Fr \times Dr \times Ep \times Vc)^{1/4} \quad (4)$$

Where Fr is the Fire risk, Dr is the Drought resistance, Ep is the Erosion protection and Vc is the Vegetation cover.

The fire risk index (Fr) is obtained from the study established by Benabid (2007) and the forest inventory map of 2014. The results are validated by our experiences in the field. The sensibility of forest formations to fire depends on the types of vegetation, the density of the strata, mainly the lower strata which play an important role in the spread of flames from the lower strata to tree strata. Soil protection against plant erosion is determined by the types of land use, coverage rates and studies conducted in the region. A classification with the maximum likelihood algorithm of the Landsat OLI images (Thakkar et al., 2017) was used to classify land cover types. The coverage rate is established using the NDVI index of these images (Tucker, 1979).

Management Quality Index (MQI)

The anthropogenic factor can be both destructive and positive in the soil degradation process (Boutallaka, 2019). Human pressure on its natural environment and incompatible practices such as deforestation, overgrazing and successive tillage can aggravate the sensitivity of the soil to degradation (El Mazi et al., 2022). On the other hand, soil conservation practices such as reforestation, construction of terraces and residue management are considered as solutions to mitigate the process of land degradation (Laouina, 2013; Eekhout and de Vente, 2022).

In this study, the MQI was calculated from two sub-parameters: namely the human pressure and the quality of the management practices (Eq. 5). The human pressure index is obtained from the population density in each administrative community. The Quality of Development Practices Index was obtained from our field observations and studies carried out on the evaluation of the effectiveness of development interventions.

$$MQI = (\text{Human pressure} \times \text{management quality})^{1/2} \quad (5)$$

Results and Discussion

The use of the MEDALUS approach permitted to evaluate the sensitivity of soils to degradation and to assess the degree of sensitivity in the Ouergha catchment. The results are presented in maps illustrating the weighting of the indices influencing the land degradation process (climate, vegetation, soil and human factor).

Climate Quality Index

Climate is a crucial parameter influencing the susceptibility of soils to degradation (Tribak, 2020). This parameter is conditioned by two essential elements (temperature and precipitation). The spatial distribution of bioclimate in the region is characterized by a very high spatial variability due to orographic factors (Boutallaka, 2019). The CQI was obtained by combining three sub-indicators (aspect, precipitation and aridity index). The results were ranked according to the values in the table and spatialized in the map. The Table 1 gives the scores of the different classes of each sub-index. The semi-arid and sub-humid bioclimates are the most dominant. The SW and SE aspects, are the most extensive (51.5%), which are the sunniest and sheltered from humid Atlantic disturbances (Janati Idrissi, 2010). The evaluation of the climate factor based on three sub-indices shows an index oscillating between 1.00 and 2 with an average of 1.38 (Figure 3). The low and very low classes are the most dominant, representing 43.66% of the total area. These zones are dominated by the semi-arid bioclimatic stages with a rainfall less than 400 mm and sub-humid (between 400-660 mm), which extend in the southern and eastern part of the catchment. They also correspond to the SE/SW oriented slopes, which are sunnier, less watered and more exposed to erosion (Tribak et al., 2021). While the good CQI only represents a limited area (13.76%). These are slopes with a humid bioclimate located at high altitude and exposed to humid perturbations that receive a significant amount of precipitation (>660 mm).

Table 1. The climate quality index

Index	Class	Score	Surface (%)	Description
Precipitation (mm)	>600	1	30,1	High
	400-600	1,5	31,5	Moderate
	<400 mm	2	38,4	Low
Aspect	NW/ NE	1	46,98	Wet
	SE/SW	2	51,5	Dry
	Unclassified	-	1,52	-
Aridity index	Semi-arid	2	38,4	High
	Sub-humid	1,5	30,4	Moderate
	Humid	1,3	31,2	Low

Soil Quality Index

The soil quality index is obtained by combining four sub-parameters (Bouabid et al., 2010). The result of this index is presented in Table 2 and the Figure 4. They show that the study area is characterized by medium to low soil quality, representing respectively 21.2% and 40,81% of the total area. They correspond to areas dominated by friable lithological formations (Schist, Flysch and marl), Stony soils poor in organic matter, and by high topographic slopes which lead a progressive stripping of the arable surface layers (Al Karkouri, 2017). However, the slopes with high soil quality occupy 37.99% of the total area. These correspond to areas of sediment accumulation and lithological formations that are more resistant to erosion (limestone, sandstone, etc.), especially on the gentle slopes. In these areas, the soil thickness is deep and can provide water reserves and optimal conditions for the development and growth of vegetation (Lahlaoi et al., 2017).

Table 2. The soil quality index

Index	Class	score	Surface (%)	Description
Parent material	Coherent	1	17,5	Limestone, dolomite, sandstone
	Moderately	1,5	55,2	Marl-limestone, shale, Flysch
	Soft	2	27,3	Marl, clay, alluvium and colluvium
Soil thickness (cm)	> 80	1	8,1	Low
	50-80	1,3	18,4	Moderate
	25-50	1,6	59,2	High
	<25	2	12,3	Very High
Soil Texture	Balanced	1	38,5	Low
	Fine at mean	1,3	30,1	Moderate
	Fine	1,6	29,6	High
	Rude	2	1,8	Very High
Slopes (degree)	<6	1	12,7	Low
	6-18	1,3	48,4	Moderate
	18-35	1,6	35,3	High
	>35	2	3,6	Very High

Vegetation Quality Index

The results of the Vegetation Quality Index (VQI) are presented in the Table 3 and in the Figure 5. They show that the Ouergha catchment area is dominated by the high and moderate VQI, representing respectively 34.66% and 36.8% of the total area. The moderate quality vegetation corresponds to the fruit plantations. The high quality vegetation is located in the northern part of the basin and corresponds to natural forests developed in the sub-humid and humid bioclimate and irrigated crops in the alluvial terraces. The climax forest is composed of oak, cedar and pine forests that belong to the Mediterranean ecosystem characterized by a high resilience to drought (FAO, 2022). Furthermore, this ecosystem is highly susceptible to forest fires (Mharzi Alaoui et al., 2017), but it is also characterized by a high capacity for regeneration after a fire. The rapid regeneration of vegetation has contributed to the protection of soils from erosion (Laouina et al., 2013; Francos et al., 2019). In addition, areas with low and critical VQI represent 22.16% and 6.37% of the total area respectively. These areas are located in the southern and eastern part of the study area and correspond to bare soil and agricultural land. These occupations are often considered vulnerable to degradation and have low soil protection against erosion and low sensitivity to fire risk.

Table 3. The vegetation quality index

Index	Class	Score	Surface (%)	Description
Fire risk	Low	1	40.4	Agricultural land, bare land
	Moderate	1.6	41.3	Sub-dense natural forests
	High	2	18.3	Reforestation (pine forest) and secondary training
Erosion protection	Low	1	11.8	Agricultural land, bare land
	Moderate	1.6	36.3	Maquis and matorral
	High	2	51.9	Natural and artificial forests, lawns
Drought resistance	High	1	6.0	Natural and artificial forests
	Moderate	1.6	65.1	Arboricultures, formations secondary
	Low	2	28.9	Agricultural land, Bare land
Vegetation cover (%)	>40	1	4.9	High coverage
	10-40	1.5	76.5	Low coverage
	<10	2	18.6	Very low coverage

Management Quality Index

The Management System Quality Index (MQI) is an indicator of human pressure on the natural environment. In this study, the MQI was calculated by combining two parameters (human pressure and management effectiveness), and has been classified and illustrated in Table 4. These results show that 52.3% of the Ouergha catchment is exposed to high human pressure on the natural environment, and corresponds to heavily populated areas (>160 hab./km^2) in the northern part. The areas of moderate human pressure occupy 28.9%, while the areas of low to very low overexploitation, where the population density is less than to 80 hab./km^2, are very limited and concern the sparsely populated communes in the southern part of the study region.

The land management systems quality index (Figure 6) shows that the areas of average and good management quality are the most dominant, accounting for 46.2% and 38.4% of the total area respectively. These include dense natural forests and reforestation, as well as erosion control techniques (terraces, dry stone walls). These practices can provide additional ecosystem services, including soil enrichment of organic matter that contributes to the mitigation of degradation (Eekhout and de Vente, 2022). Areas of low management quality occupy 15.4% and correspond to land that has not benefited from management interventions and to cleared land put under cultivation.

Table 4. Management System Quality index

Index	Class	Score	Surface (%)	Description
Human pressure	Very low	1	7,2	< 80 hab./Km^2
	Low	1,3	11,6	80-120 hab./km^2
	Moderate	1,6	28,9	120-160 hab./km^2
	High	2	52,3	>160 hab/km^2
Management quality	High	1	38,1	Reforestation, terraces, managed forest
	Moderate	1,5	46,2	Cultures and forests, agricultural land.
	Low	2	15,7	Abandoned land, cleared land

Index of soil sensitivity to degradation

The use of the MEDALUS approach allowed us to assess the sensitivity of land to degradation in the Ouergha catchment. It was developed by combining four indicators (climate, soil, vegetation and human factor) in the GIS using Eq. 1. The results obtained illustrated in the Table 5 and Figure 7. The sensitivity of land to degradation in the Ouergha catchment is classified according to severity, from low to highly critical. Four classes were established according to similar studies (Sepehr et al., 2007; Bouabid et al., 2010; Mokhtari, 2016). Low sensitivity to degradation, (SDI<1.2), medium sensitivity (SDI between 0.2 and 1.4), highly fragile areas (SDI between 1.4 and 1.6) and finally critical areas (SDI between 1.6 and 2).

The low sensitivity areas cover an area of 21.9% of the total area. They cover the northern and north-western part of the basin, and correspond to the humid and sub-humid climatic zones that receive a significant amount of precipitation (Jbel Ouedka, Senhaja Srair, Jbel Tidghin and Jbel khezana, Bab Bard and Bab Taza). As well as the areas protected by high vegetation cover which protects the soil against water erosion (Arrebei et al., 2020; El Mazi et al., 2021). They also correspond to the deep soils in the alluvial terraces which contributed to the supply of a significant proportion of water resources and offer optimal conditions for the development of vegetation. In the south of the basin, there are extensive areas along the valleys and alluvial plains, these lands have a fertile and deep soil. These areas are characterized by low slopes and agricultural activities dependent on irrigation, due to its proximity to valleys. This category is of high quality and has a great capacity to protect the soil against degradation, in particular water erosion.

Table 5. Class areas of each sub-indicator

Index	Classes	Intensity	Proportion (%)
VQI	1.00-1.2	High	34,66
	1.2-1.4	Moderate	36,80
	1.4- 1.6	Low	22,16
	1.6-2	Very low	6,37
SQI	1-1.3	High	37,99
	1.3-1.6	Moderate	21,20
	1.6-2	Low	40,81
CQI	<1	High	13,76
	1-1.2	Moderate	42,58
	1.2-1.6	Low	24,97
	1.6-2	Very low	18,69
MQI	1-1.3	High	34,87
	1.3-1.6	Moderate	46,93
	1.6-2	Low	18,20

The areas moderately sensitive to degradation (SDI between 1.2 and 1.4) cover 27.9% of the total area. They are spread out along the edge of valleys and alluvial plains, as well as the slopes with medium to low slopes, and moderately protected by secondary vegetation. Fragile areas with high sensitivity to degradation (SDI between 1.4 and 1.6) occupy 31.7% of the area of the basin studied. They are located in the southern and eastern part. This sensitivity is linked to natural factors such as poor climate quality, soft and low permeability rocks, but also intense land use and poor soil quality, which increase the risk of land degradation (Bouabid et al., 2010). This underlines the urgency of conservation of these areas and integrated planning to reduce the sensitivity of soils to degradation. The slope factor has contributed to the rapidity of rainwater drainage and the strong concentrated runoff, due to the regression of vegetation areas which is characterized by low cover, increasing surface degradation and evolution of water erosion activity especially on bare slopes (Tribak et al., 2021). Areas highly susceptible to degradation (SDI between 1.6 and 2) cover about 16.2% of the total basin area, according to the results of other similar studies. They concern areas characterized by an arid climate or rainfall of less than 500 mm, steep slopes and lack of vegetation, leading to severe soil degradation by water erosion. In addition, anthropogenic action on the environment and incompatible practices implemented locally such as deforestation followed by cultivation and successive tillage increase land degradation (El Mazi et al., 2021). These areas require urgent intervention to minimize the damage.

Conclusion

The present study focuses on the assessment of land sensitivity to degradation in the Ouergha catchment using the MEDALUS approach. This approach is flexible because it allows the sub-indicators to be modified. Four main parameters, each comprising several sub-indicators, were combined and represented in a GIS to produce a hierarchical map of the degree of sensitivity to degradation. The results revealed that the high and medium degradation sensitivity index prevailed in 59.6% of the total area, and mainly affected the eastern, southern and south-western parts of the basin. The occurrence and amplification of this phenomenon is often the result of a combination of natural and anthropogenic factors.

This sensitivity is expected to increase in the future due to the effects of current climate change (decreasing in precipitation, increasing in temperature), which is leading to a northward shift of the most sensitive dry areas, as well as the concentration of a high-density poor population exerting strong pressure on the natural environment. This underlines the urgency of natural ecosystem conservation and integrated planning to reduce the sensitivity of land to degradation. The study also demonstrates that soil conservation practices, reforestation and terracing are effective measures to mitigate environmental fragility.

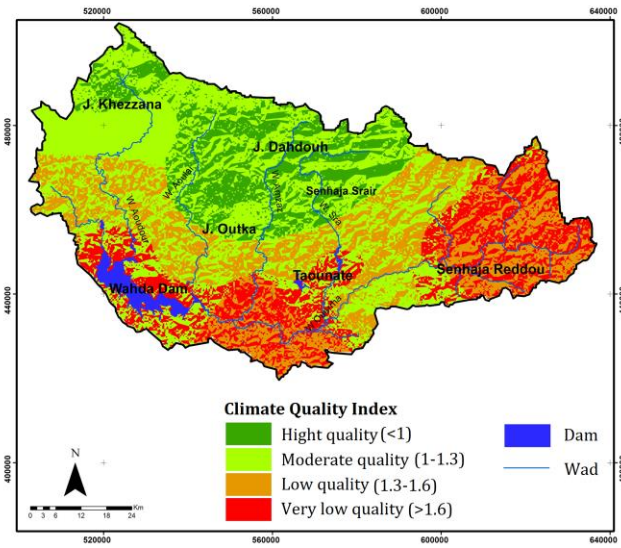

Figure 3. The climate quality Index

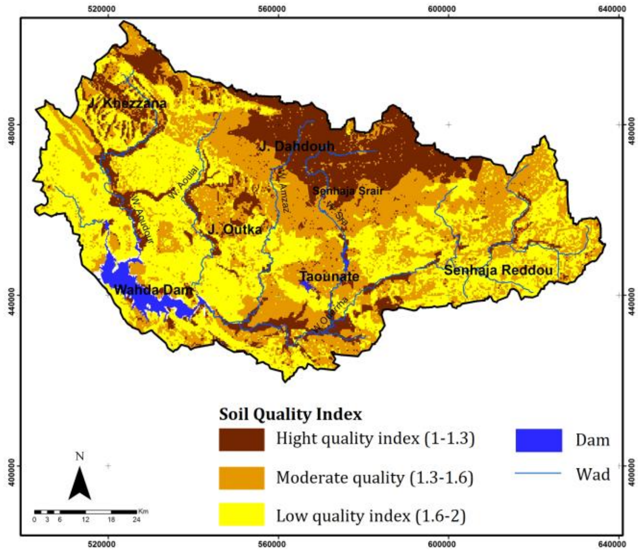

Figure 4. The soil quality Index

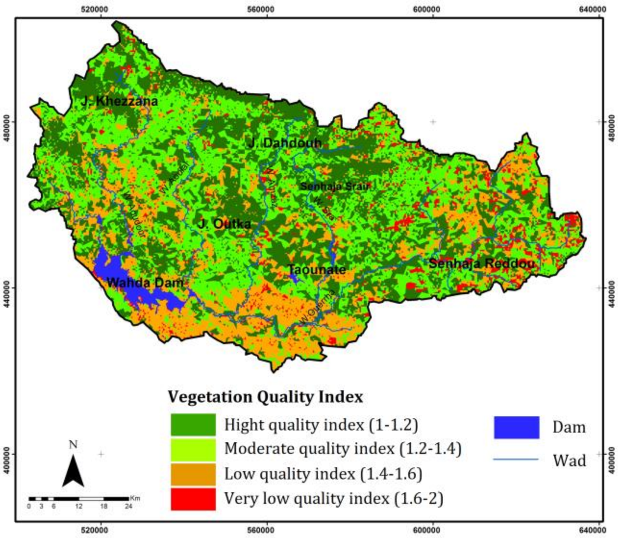

Figure 5. The vegetation quality Index

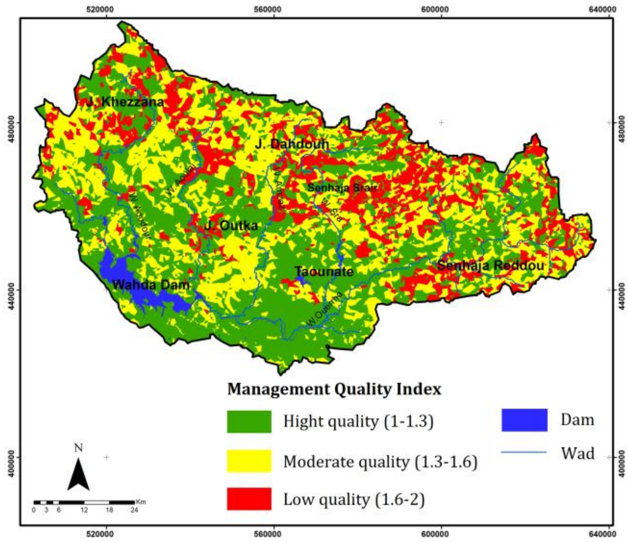

Figure 6. Management Quality Index

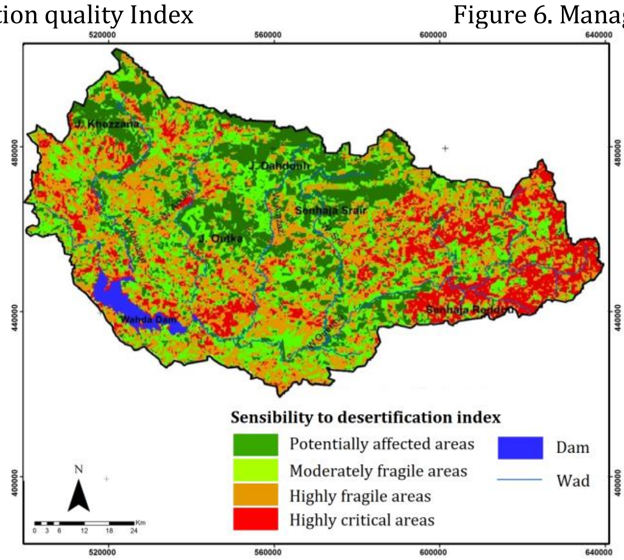

Figure 7. Index of soil sensitivity to degradation in the Ouergha catchment

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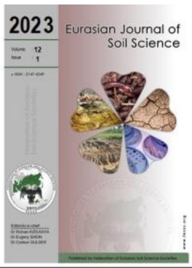

Simulation of irrigation in southern Ukraine incorporating soil moisture state in evapotranspiration assessments

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Abstract

The paper studies the accuracy of modeling moisture transport under the conditions of sprinkler irrigation using evapotranspiration assessment methods that take into account the soil moisture conditions. Appropriate modifications of the Penman-Monteith and the Priestley-Taylor models are considered. Moisture transport modeling is performed using the Richards equation in its integer- and fractional-order forms. Parameters identification is performed by the particle swarm optimization algorithm based on the readings of suction pressure sensors. Results for the two periods of 11 and 50 days demonstrate the possibility of up to ~20% increase in the simulation accuracy by using a modified Priestley-Taylor model when the maintained range of moisture content in the root layer is 70%-100% of field capacity. When irrigation maintained the range of 80%-100% of field capacity, moisture content consideration within evapotranspiration assessment models did not enhance simulation accuracy. This confirms the independence of evapotranspiration from soil moisture content at its levels above 80% of field capacity as in this case actual evapotranspiration reaches a level close to the potential one. Scenario modeling of the entire growing season with the subsequent estimation of crop (maize) yield showed that irrigation regimes generated using evapotranspiration models, which take into account soil moisture data, potentially provide higher yields at lower water supply.

Keywords: Evapotranspiration, Richards equation, soil moisture, corn productivity.

Introduction

The accuracy of evapotranspiration estimates is one of the determining factors for performing forecasts of soil moisture state in the irrigation management process (Wanniarachchi and Sarukkalige, 2022). In the areas of agricultural production, evapotranspiration can be considered as consisting of three components: evaporation of intercepted moisture, transpiration, and evaporation from the soil surface (Savenije, 2004).

Changes in the corresponding fluxes are mutually influenced by fluctuations in meteorological parameters, vegetation dynamics, and soil moisture (Rodriguez-Iturbe, 2000; Shao et al., 2017). Thus, to quantify the intensity of evapotranspiration for more accurate modeling of moisture transport in the “soil-plant-atmosphere” system, integrated models that consider soil and atmospheric physics along with plant physiology are needed (Overgaard et al., 2006).

A widely used evapotranspiration model based on the Penman–Monteith equation (Monteith, 1965) successfully estimates it in the case of closed vegetation for various weather and soil conditions (see, e.g., Shao et al., 2022). In it, the processes of transpiration and evaporation from the bare soil, which are different intrinsically, are not considered separately. One of the first models in which the description of these processes was separated was the Shuttleworth-Wallace model (Shuttleworth and Wallace, 1985). Among the disadvantages of this model, the need to determine the values of numerous parameters that limits its

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application can be singled out (Gharsallah et al., 2013). The compromise between the model's complexity and prediction accuracy is provided, in particular, by the Priestley-Taylor energy balance model (Priestley and Taylor, 1972). The modified Priestley–Taylor model can also effectively evaluate evaporation and transpiration separately using the data on the downward energy flux (Qiu et al., 2019), which can be considered as the main factor determining the intensity of crops evapotranspiration (Gong et al., 2021).

In the studies of irrigated crops' growing processes, the best strategy according to Faybishenko (2007) is to choose the methods that take into account the highest number of input parameters. At the same time, the problem of determining the accuracy of evapotranspiration estimates remains urgent in each specific situation and such approaches as the usage of different methods' linear combination with fittable coefficients (Romashchenko et al., 2020) or machine-learning-related approaches (Elbeltagi et al., 2023) are used. The need for scenario modeling here stems from the fact that under irrigation the maintained ranges of moisture content in soil's root layer significantly influence the availability of moisture for plants. Hence, the processes that have a decisive influence on evapotranspiration and the parameters that quantify their intensity may change.

In this paper, evapotranspiration estimates are used as input to the models of moisture transport based on the Richards differential equation. The study of their accuracy is carried out by assessing the compliance of the simulated dynamics with sensor readings. The model parameters were identified using the readings in the initial part of the growing season. Then, to assess the accuracy, we perform extrapolation modeling over longer time ranges including the entire growing season.

Material and Methods

We investigate two models for evapotranspiration assessment - the Priestley-Taylor and Penman-Monteith methods - along with their modifications that consider the current state of soil moisture.

The Penman-Monteith method

Having a weather station equipped with sensors of temperature and relative humidity of air along with solar radiation and wind speed, estimation of potential evapotranspiration by the Penman-Monteith method can be performed the following way (Cannata, 2006). The soil component of evapotranspiration is calculated as (Cannata, 2006)

$$ET_{rad} = \frac{\Delta}{\Delta+\gamma^*}\frac{R_n - G}{\lambda}$$

where $\Delta = \frac{4098 e_a}{(237.3+T)^2}$, $e_a = 0.61078 e^{\frac{17.27T}{T+237.3}}$ is the coefficient of the dependency between the saturated vapor pressure and temperature T (*kPa K-1*); $\lambda = 2.501 - 0.002361T$ is the heat of water evaporation (*J kg-1*); $\gamma = 0.001\frac{c_p P}{\varepsilon\lambda}$ is the psychrometric constant (*kPa K-1*), $P = P_0\left(\frac{T_{ko} - \eta(Z - A_0)}{T_{ko}}\right)^{\frac{g}{\eta R}}$ is the atmospheric pressure (in the absence of an appropriate sensor), $c_p = 1.013$ (*kJ kg-1 °C*) is the specific heat of air, $\varepsilon = 0.622$ is the ratio of molecular weight of water and dry air, $T_{ko} = 293.16$ *K* is the temperature at the sea level, $P_0 = 101.3$ *kPa* is the atmospheric pressure at the sea level, $A_0 = 0$ *m* is the altitude at the sea level, $\eta = 0.0065$ *K m-1* is the constant vertical temperature gradient, $g = 9.81$ *m s-2* is the acceleration of gravity, $R = 287$ is the universal gas constant; $d = \frac{2}{3}h_c, Z_{om} = 0.123 h_c, Z_{oh} = 0.1 Z_{om}$, h_c is the height of plants (*m*); $u_{10} = u_2 \log(67.8*10 - 5.42)/4.87$ is the assessment of wind speed (*m s-1*) at the height of 10 m, u_2 is the wind speed at the height of 2 m; $\gamma^* = \gamma(1+\frac{r_s}{r_a})$ is the modified psychrometric constant, $r_s = \frac{100}{12h_c}$,

$r_a = \begin{cases} \dfrac{\log\dfrac{Z_w - d}{Z_{om}}\log\dfrac{Z_h - d}{Z_{oh}}}{k^2 u_2}, h_c < 2 \\ 94 / u_{10}, h_c \geq 2 \end{cases}$, $Z_w = 2$ m is the height of wind speed measurement, $Z_h = 2$ m is the height of air humidity measurement, $k = 0.41$ is the von Karmann's constant.

Soil heat flux G is set to be linearly dependent on the flux of solar radiation R_n ($mJ\ m^{-2} s^{-1}$).

The atmospheric component of evapotranspiration is calculated as (Cannata, 2006)

$$ET_{aero} = \frac{3.6}{\lambda(\Delta + \gamma^*)} \frac{\rho c_p (e_a - e_d)}{r_a},$$

$$\rho = \frac{100P}{T_{kv} R},\ T_{kv} = \frac{T + 273.15}{1 - 0.378 e_d / P},\ e_d = R_h e_a / 100.$$

Total potential evapotranspiration is then obtained in the form

$$ET_0 = ET_{rad} + ET_{aero}.$$

Soil surface resistance r_s can be estimated based on the so-called "relative soil moisture index" R_{sm2} (Sellers et al., 1992; Kustas et al, 1998), which is defined as the ratio between the volumetric moisture content on the soil surface (SM_2, $m^3 m^{-3}$) and the saturation moisture content (S_p, $m^3 m^{-3}$) in the form

$$r_s = e^{a - bR_{sm2}},\ R_{sm2} = SM_2 / S_p \tag{1}$$

where a and b are empirical constants.

The Priestley-Taylor method

The Priestly-Taylor method can be considered as a simplified form of the Penman-Monteith method (Priestly and Taylor, 1972; Gong et al., 2021) and its computation formula is

$$\lambda ET = a_e \frac{\Delta}{\Delta + \gamma}(R_n - G)$$

where λET is the heat flux ($W\ m^{-2}$), α_e is the volume coefficient.

The heat flux λET can be divided into λE_s (evaporation in the form of energy flux) and λT_r (transpiration in the form of energy flux), which are calculated as (Gong et al., 2021)

$$\lambda E_s = a_s \frac{\Delta}{\Delta + \gamma}(R_{ns} - G),\ \lambda T_r = a_c \frac{\Delta}{\Delta + \gamma} R_{nc}$$

where R_{ns} and R_{nc} are the energy ($W\ m^{-2}$) received by soil and vegetation surfaces; α_s and α_c are the coefficients for λE_s and λT_r. R_{ns}, R_{nc}, α_s, and α_c can be defined as (Gong et al., 2021)

$$R_{ns} = R_n \tau, R_{nc} = R_n - R_{ns}, \tau = e^{-kLAI},\ a_s = f_{sw} a_{s0}, a_c = (1 - f_s) f_t a_{c0}$$

where τ is the fraction of radiation that reaches the surface of soil; LAI is the Leaf Area Index; α_{s0} and α_{c0} are the coefficients for soil and vegetation defined as (Gong et al., 2021)

$$a_{s0} = \begin{cases} 1.0, \tau \leq \tau_c, \\ a_0 - \dfrac{(a_0 - 1)(1 - \tau)}{1 - \tau_c}, \tau > \tau_c, \end{cases}\quad a_{c0} = \frac{a_0 - a_{s0}\tau}{1 - \tau}$$

where α_0 is the reference coefficient (*1.26*), τ_c is the critical value of τ when the closure of vegetation is maximal.

Leaf aging coefficient f_s can be determined as (Gong et al., 2021) $f_s = 0.05 e^{\frac{CDC}{0.98} t - 1}$ where t is the time from the beginning of leaf aging and CDC is the aging factor. The limiting factor f_t for plant temperature is defined as (Ershadi et al., 2014) $f_t = e^{-\left(\frac{T_a}{T_{opt}} - 1\right)^2}$ where T_{opt} is the optimal temperature for crop growth (°C).

The soil moisture stress index f_{sw} is used to combine the data on soil and atmospheric conditions and can be determined according to the model presented in Deardorff (1978) as (Gong et al., 2021):

$$f_{sw} = \begin{cases} 1.0, S_e \geq 0.75, \\ S_e, S_e < 0.75 \end{cases}$$

where $S_e = (\theta - \theta_w)/(\theta_s - \theta_w)$ is the effective moisture saturation in the upper soil layer with the depth of *0.1 m*; θ, θ_s, and θ_w are the actual volumetric moisture content, saturated moisture content, and wilting point, correspondingly.

To finally obtain the expression for α_e, G is described as a function of R_{ns} (Choudhury et al., 1987) in the form $G = f_G R_{ns}$ where f_G is the fraction of G in R_{ns}. Combining all the above mentioned, for α_e we have (Gong et al., 2021)

$$a_e = \frac{f_{sw} a_{s0}(1 - f_G)\mathrm{e}^{-kLAI} + (1 - f_s) f_t a_{c0}(1 - \mathrm{e}^{-kLAI})}{1 - \mathrm{e}^{-kLAI} f_G}.$$

The method described by Venturini and co-authors in Venturini et al. (2008) modifies the Priestley-Taylor method representing, in particular, Δ as $F\Delta$ where

$$F = \frac{SM}{SM_c} \tag{2}$$

SM is the volumetric moisture content in the soil, and SM_c is the field capacity.

Methods for modeling moisture transport

The main aim of our study is to experimentally test the effectiveness of the combined use of the above-mentioned evapotranspiration models and differential moisture transport models while simulating changes in moisture content in irrigated soil. For this purpose, considering the Penman-Monteith method, we determine the values of r_s according to (1) with *a=8.2*, *b=5.9* according to Kustas et al. (1998). The value of Δ is multiplied by F calculated according to (2).

As an alternative, we use the Priestley-Taylor model with similar modifications.

To model moisture content dynamics, we consider the classical integer-order one-dimensional head-based Richards equation according to the method described in Romashchenko et al. (2020). The corresponding equation has the form

$$\frac{\partial}{\partial t} H = C^{-1}(h)\left[\frac{\partial}{\partial z}(k(H)\frac{\partial H}{\partial z}) - S\right], 0 \leq z \leq L,\ t \geq 0 \tag{3}$$

where $h(z,t) = \frac{P(z,t)}{\rho g}$ is the water head (*m*), $H(z,t) = \frac{P(z,t)}{\rho g} + z$ is the full moisture potential (*m*), $P(z,t)$ is the suction pressure (*Pa*), ρ is the water density ($kg\ m^{-3}$), g is the acceleration of gravity ($m\ s^{-2}$), $C(h) = \frac{\partial \theta}{\partial h}$, $\theta(x,z,t)$ is the volumetric soil moisture content (%), $k(H)$ is the hydraulic conductivity ($m\ s^{-1}$).

In (3) the function S describes water uptake by root systems.

To the water head function H at the lower boundary $z = L$ of the simulation domain in the case of confining bed presence we set the condition $\frac{\partial H}{\partial z} = 0$. In the case of groundwater presence, the condition $H = H_L$ where H_L is the given function is set.

At the upper boundary $z = 0$, in the case when the soil is saturated, the Dirichlet boundary condition is set (van Dam and Feddes, 2020). In other cases the Neumann boundary condition is set in the form $k\frac{\partial H}{\partial z} = Q_e - Q_p - Q_i$ where Q_e, Q_p, Q_i are the flows ($m\ s^{-1}$), caused by evaporation, precipitation, and irrigation.

The function S that models water uptake by plant roots has the form (Molz and Remson, 1970) $S = \frac{TL(z)}{\int_0^v L(z)dz}$, where v is the depth of the root layer, $L(z)$ is the function of root length distribution density, T is the transpiration.

With the known value of actual evapotranspiration ET, it is subdivided on the components Q_e and T according to Gigante et al. (2009) the following way: $Q_e = e^{-\mu \cdot LAI} ET$, $T = (1 - e^{-\mu \cdot LAI}) \cdot ET$ where LAI is the leaf area index, μ is a given constant.

The finite difference method (Samarskii, 2001) is used to numerically solve the initial-boundary value problem for Equation 3 as described in Romashchenko et al. (2020).

Additionally, we consider the one-dimensional space-time-fractional equation of moisture transport in the form (Romashchenko et al., 2021)

$$D_t^{(\beta)} H = C^{-1}(h) \left[D_z^{(\alpha)} (k(H) \frac{\partial H}{\partial z}) - S \right], 0 \le z \le L,\ t \ge 0$$

where $D_t^{(\beta)}, D_z^{(\alpha)}$ are the Caputo derivatives of fractional order subject to time *t* and depth *z* (Podlubny, 1999). The numerical technique for the fractional-differential model is described in Romashchenko et al. (2021).

In computational experiments, soil's water retention curves are determined by selecting the parameters of the van Genuchten model (van Genuchten, 1980) considered to have the form $\theta(h) = \theta_0 + \frac{\theta_1 - \theta_0}{\left[1 + \left(10\alpha |h|\right)^n\right]^m}$ (θ_0, θ_1, α, n, $m=1-1/n$ are the model parameters) the way to make the model best describe the laboratory analysis data on the dependency of soil moisture content on suction pressure. Hydraulic conductivity is represented in the form (Averianov, 1982) $k(H) = k_f \left(\frac{\theta(H-z) - \theta_0}{\theta_1 - \theta_0} \right)^\beta$ where k_f is the saturated hydraulic conductivity (filtration coefficient), $\beta = 3.5$ is the fixed power.

To compensate for the errors in the measurement of irrigation water flow, precipitation flow, and evapotranspiration estimates, the corresponding flows were multiplied by coefficients, the values of which are, similarly to the described in Romashchenko et al. (2020), fitted by the particle swarm optimization (PSO) algorithm (Zhang et al., 2015). These coefficients are fitted in a way to minimize the total sum of squares deviations of the simulated water head dynamics from the measured one. To compensate for the errors in laboratory determination of the saturated hydraulic conductivity, as well as errors arising from soil heterogeneity, the value of the saturated hydraulic conductivity was also determined by the PSO algorithm.

An approach for assessing the impact of evapotranspiration models' accuracy on the effectiveness of irrigation management

The use of the considered technique in irrigation management involves estimating the time and rate of subsequent watering by predictive modeling with evapotranspiration estimated using forecast weather data.

To estimate the seasonal irrigation rate and the volume of actual evapotranspiration the irrigation simulation is performed for the entire growing season with watering assigned to maintain in the given range the average water head in the root layer.

The seasonal effectiveness of irrigation can be assessed using the so-called relative yield function (Kovalchuk and Matiash, 2006), which simulates the decrease of yield due to not-optimal irrigation. In particular, according to Kovalchuk and Matiash (2006), for maize grown in southern Ukraine, such a function has the form

$$f(u,w,p) = -0.444 + 2.02\left(\frac{u+p}{w+p}\right) - 0.556\left(\frac{u+p}{w+p}\right)^2 \tag{4}$$

where u is the actual seasonal irrigation rate (*mm*), w is the biologically optimal irrigation rate (*mm*) defined as an irrigation rate for a regime, in which evapotranspiration is maintained at the level close to the potential one, p is the precipitation (*mm*).

Given the close relationship between w and evapotranspiration, we transform (4) into

$$f(W, ET) = -0.444 + 2.02\frac{W}{ET} - 0.556\left(\frac{W}{ET}\right)^2 \quad (5)$$

where W is the actual seasonal water supply (*mm*), ET is the total potential evapotranspiration (*mm*).

After conducting a scenario modeling of irrigation assignments throughout the growing season and obtaining simulated values of W and ET, the effectiveness of the method of evapotranspiration assessment for irrigation management can be estimated by the value of $f(W, ET)$.

Input data

Two sets of the time series of monitoring data obtained during the 2018 and 2021 growing seasons were used for simulation.

The first data set was collected while growing soybeans under sprinkler irrigation in the fields of State Enterprise "Experimental Farm "Brylivske" (Privitne village, Kherson region, Ukraine) in 2018. The data set covers the time range from May 21 to August 22, 2018. Suction pressure measurements were performed using Irrometer 200SS-5 Watermark Soil Moisture Sensor using the Imetos® Pessl Instruments Internet Weather Station. The sensors were installed at the depths of 0.1 m, 0.25 m, 0.4 m, 0.55 m, 0.7 m, and 0.85 m.

A detailed description of the data set obtained in 2018 is given in Romashchenko et al. (2020). The values of the van Genuchten model's coefficients for the three-layer soil model are given in Romashchenko et al. (2020), Table 1.

The second data set was collected in 2021 in production conditions with pivot sprinkler irrigation in the fields of the LLC "Agrotechnology" (Bratske village, Kherson region, Ukraine). In the 2021, the "Tesla" variety of maize (UIPVE, 2019) was grown there. Data were collected using the same equipment as in 2018 located at 46°47'56.4"N 34°06'15.2"E. The sensors were installed at the depths of 0.2 m, 0.4 m, and 0.6 m. The actual yield was 13.8 *t/ha* with the total water supply equal to 439 *mm* for the active vegetation season from 19.05.2021 to 01.09.2021.

Data collected from 26.07.2021 to 14.09.2021 were used to model the dynamics of moisture content. The height of plants for the whole period was assumed to be equal to 1 *m*, and the depth of the root system was assumed to be 0.5 *m*.

In the scenario modeling of the entire growing season using the data collected in 2021, irrigation was applied when the average relative volumetric moisture content in the root layer of the soil decreased below 70% of field capacity that corresponds to the moisture content level of 24.8%. Irrigation was simulated until the corresponding level rises above 100% of field capacity (35.4%). The simulation was performed using the data acquired during the period of intensive irrigation from 25.07.2021 to 01.09.2021. In the period from 19.05.2021 to 25.07.2021 water supply to plants was provided mainly by precipitation. To test the sensitivity of computational procedures to inaccuracies in forecast meteorological data, modeling was also performed using the data on temperature, humidity, and wind speed, from the weather station located (46°51'N, 34°24'E) at a certain distance from the field. In the absence of predicted data on solar radiation, it was assumed that accurate measurements are performed once per 5 days, and then a constant value is used in the simulation.

The soil at the experimental sites corresponds to the southern low-humus heavy loam chernozem on loess. A single-layer soil model with the following values of the van Genuchten model's parameters was used for the data collected in 2021: θ_0=0.094, θ_1=0.5059, α=0.00919, n=1.475, m=0.3223. Parameters' values were obtained using Rosetta software based on soil particle size distribution data.

The actual irrigation regime, according to the data obtained in 2021, allowed the decrease of moisture content down to 68% of field capacity compared to the maximum reduction to 78% of field capacity according to the data collected in 2018. The minimum recorded value of suction pressure was *-132 kPa* compared to *-40 kPa* according to the data collected in 2018.

To identify the parameters of the models in the case of the data collected in 2018, a time interval of 11 days from the initial moment was used. For the data collected in 2021, we used a 7 days interval. For both cases, one watering was carried out within these intervals. An interval of 50 days was used to test the influence of different evapotranspiration assessment methods' usage on modeling accuracy.

The population size of the PSO algorithm was 20 particles, 20 iterations were performed with the following values of the parameters: $\omega=\varphi_r=\varphi_p=0.8$.

The smallest errors for the data set collected in 2018 were achieved when modeling a domain with the depth of *3 m* with the Dirichlet condition *H=-3.8 m* at its lower boundary on the finite-difference grid with 50 nodes. In the case of data collected in 2021, a *1 m* deep domain was used with the Neumann condition at the lower boundary on the finite-difference grid with 20 nodes.

Results and Discussion

The root-mean-squared error (RMSE) and average relative error ($\varepsilon_{rel}=\frac{1}{N}\sum_{i=1}^{N}\left|\frac{H_i-\bar{H}_i}{H_i}\right|$ where $H_i, \bar{H}_i, i=1,\ldots,N$ are the measured and the modeled water head values, N is the number of measurements) for the intervals of 11 and 50 days are given in Tables 1 and 2. The results show that for 2018 the differences between the modeling errors using different algorithms for estimating evapotranspiration are insignificant. Given the maintained high level of soil moisture content, its consideration has no significant impact on the obtained dynamics of evapotranspiration. Regarding the use of the model that contains the derivatives of fractional order, the results confirm the conclusions given in Romashchenko et al. (2021). Thus, the accuracy of the parameters' identification for the fractional-order model is ~10% higher, but when modeling for longer intervals it decreases faster than in the case of the classical model.

Table 1. Modeling errors for the model (3)

	Interval of 11 days		Interval of 50 days	
Data collected in 2018	RMSE, *kPa*	Average relative error, *%*	RMSE, *kPa*	Average relative error, *%*
Penman-Monteith method	1.750	30.66%	1.756	50.35%
Modified Penman-Monteith method	1.759	30.96%	1.783	52.75%
Priestley-Taylor method	1.751	30.67%	1.775	50.56%
Modified Priestley-Taylor method	1.747	30.38%	1.860	51.47%
Data collected in 2021				
Penman-Monteith method	11.086	41.07%	8.272	49.63%
Modified Penman-Monteith method	10.548	39.23%	7.894	47.57%
Priestley-Taylor method	10.474	39.22%	7.917	47.97%
Modified Priestley-Taylor method	10.528	38.08%	7.560	40.40%

Performing simulation based on the data collected in 2021 we observed up to ~10% reduction in RMSE using the modifications of the Penman-Monteith and the Priestley-Taylor methods that take the data on soil moisture content into account. This decrease can be explained by a larger range of water head changes than in the case of the data collected in 2018. Accuracy when using the Priestley-Taylor model was higher here and an additional increase in accuracy when using the fractional-differential model was observed for both considered intervals.

Table 2. Modeling errors for the fractional-differential model

	Interval of 11 days		Interval of 50 days	
Data collected in 2018	RMSE, *kPa*	Average relative error, *%*	RMSE, *kPa*	Average relative error, *%*
Penman-Monteith method	1.636	21.96%	2.729	60.56%
Modified Penman-Monteith method	1.635	21.96%	2.728	60.55%
Priestley-Taylor method	1.636	21.96%	2.731	60.59%
Modified Priestley-Taylor method	1.635	21.96%	2.728	60.54%
Data collected in 2021				
Penman-Monteith method	11.037	39.23%	8.313	50.99%
Modified Penman-Monteith method	10.360	38.54%	7.656	44.99%
Priestley-Taylor method	8.387	35.32%	6.292	35.04%
Modified Priestley-Taylor method	10.448	37.50%	7.389	38.41%

Thus, in regard of RMSE and average relative errors when modeling one or several irrigation cycles in two cases of different average moisture content and corresponding pressures we confirmed that, even when input data are collected in production condition, the incorporation of soil moisture assessments into the considered evapotranspiration models allows obtaining the increase in simulation accuracy in accordance with experimental results (see, e.g. Ding et al., 2013; Gong et al., 2021) on the importance of soil moisture factor.

Some of the obtained results on the dynamics of water heads are shown in Figure 1, 3 and 4. The dynamics of average volumetric moisture content in the 0.5 *m* layer of the soil is given in Figure 2 and 5. The results show that taking into account soil moisture in the Penman-Monteith method leads to an overall increase in the simulated moisture content level compared to the basic version of the method (Figure 2 and 5). When using the Priestley-Taylor model, the opposite trend was observed. The reasons for the latter could be the error accumulation in the performed long-range simulations that, in turn, could be caused by lower accuracy of the Priestley-Taylor model in water stress condition as reported in Shao et al. (2022).

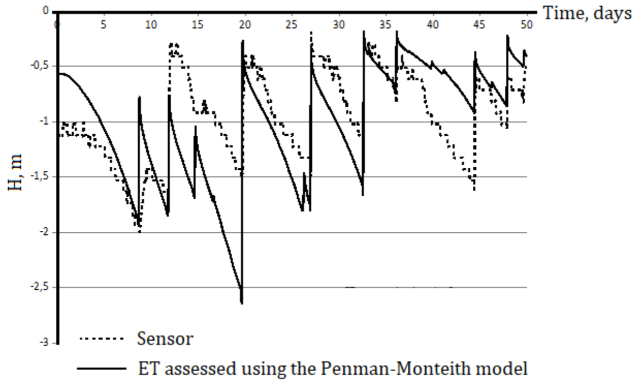

Figure 1. Dynamics of water head at the depth of 0.25 m for the data collected in 2018

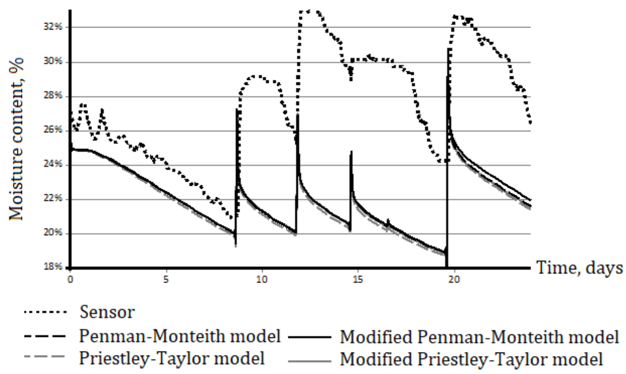

Figure 2. Average moisture content in the 0.5 m layer for the data collected in 2018

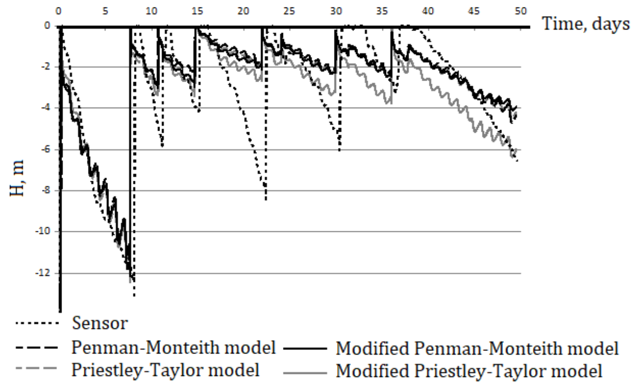

Figure 3. Dynamics of water head at the depth of 0.2 m for the data collected in 2021

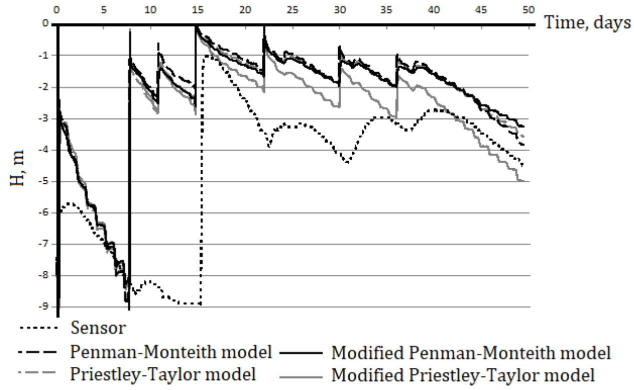

Figure 4. Dynamics of water head at the depth of 0.4 m for the data collected in 2021

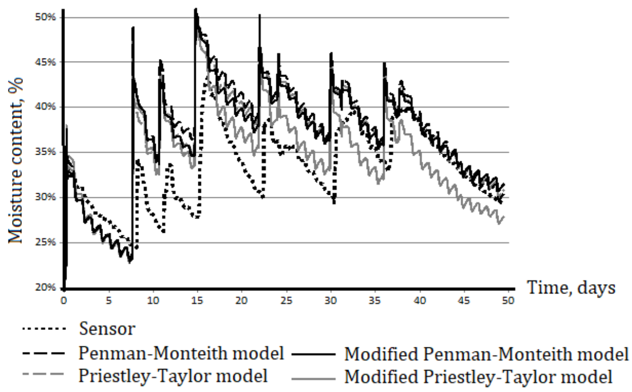

Figure 5. Average moisture content in the 0.5 m layer for the data collected in 2021

In the case of the data collected in 2018, there was an overestimation of water intake according to the data of the two upper sensors located at depths of 0.1 m and 0.25 m (Figure 1). Another reason for significant errors in predictive modeling here is the delayed or elongated in-time response of sensors to irrigation. RMSE values when modeling the data collected in 2018 were significantly lower compared to the RMSE values for the year 2021 which can be explained by the fact that average values of water heads in 2018 were to the same level lower when compared to 2021. It is confirmed by the same order of relative errors for the data collected in 2018 and 2021.

In the case of the data collected in 2021, there was an underestimation of water intake in computational experiments while performing predictive modeling. This is the main reason for the greater efficiency in this case of the modified Priestley-Taylor model. As can be seen from Figure 4, the reason for the high modeling errors is the lack of response of the sensor located at the depth of 0.4 *m* to the second and third irrigation. A similar trend was observed for the sensor located at the depth of 0.6 *m*. The simulation results were consistent with the data of the sensor located at the depth of 0.2 *m* (Figure 3) and with subsequent dynamics of water head changes according to the other two sensors. Thus, the used modeling procedure has stable response to inaccuracies in input data subject to the change of evapotranspiration assessment method similarly to the reported about other factors in Bohaienko et al. (2022).

Influence of evapotranspiration models' accuracy on the efficiency of irrigation management

The values of total water supply, total actual evapotranspiration, and the relative crop yield function (5) in the scenario modeling of the 2021 growing season are given in Table 3.

Table 3. Total water inflow W (*mm*), actual evapotranspiration ET (*mm*), and the relative crop yield $f(W,ET)$ in the scenario modeling of the 2021 growing season

Evapotranspiration assessment method	Actual meteorological data			Forecast meteorological data		
	W	ET	$f(W,ET)$	W	ET	$f(W,ET)$
Penman-Monteith	395	465	0.87	405	482	0.86
Modified Penman-Monteith	382	315	1.18	348	202	1.38
Priestley-Taylor	399	420	0.97	391	383	1.04
Modified Priestley-Taylor	457	367	1.21	364	188	1.38

At the maximum maize yield equal to 14.5 t/ha (UIPVE, 2019); total evapotranspiration, calculated from the actual meteorological data according to the Penman-Monteith equation; and the actual measured water supply, the expected yield according to Equation (5) differs from the actual one by 1.5%, which confirms its applicability in the considered case. The simulation technique's sensitivity to the meteorological data when using the Penman-Monteith method was low (not more than 4% deviation in the seasonal parameters between the cases of actual and forecast meteorological data). When using the Priestley-Taylor method, it increases (deviation <9%). The use of the considered modifications of evapotranspiration assessment methods leads to seasonally simulated scenarios with lower levels of both water supply and evapotranspiration compared to the usage of original methods. This decrease is more significant when using forecast meteorological data, to which the modified formulas are more sensitive (average deviations of parameter values equal to ~14%). The values of the relative crop yield function when using modified methods are 24-61% higher.

Conclusion

The results of water head dynamics modeling under sprinkler irrigation according to the two data sets collected growing different crops in different meteorological conditions demonstrate the possibility to increase modeling accuracy by ~20% using the Priestley-Taylor method modified to take into account the data on soil moisture content when compared with the classical Penman-Monteith method. The efficiency of this scheme increases with the increase of the range in which moisture content changes. For the data set collected under the irrigation regime aimed at maintaining moisture content in the root layer in the range of 80%-100% of field capacity, modified methods did not improve the accuracy of modeling. These results confirm the well-known conclusion that using such irrigation regimes, moisture content level is optimal for the grown crops, and evapotranspiration is maintained at the level close to the potential one. The results of scenario modeling for the entire growing season and the estimation of yield under the formed water regime showed that, according to the used yield model, the application of evapotranspiration estimates that incorporate moisture content data generates irrigation regimes with lower water supply.

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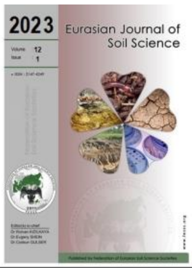

The effects of clinoptilolite type of zeolite and synthesised zeolite-enriched fertilizer on yield parameters of Cucumber (*Cucumis sativus*) plant and some chemical properties in dark chestnut soil

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Abstract

Zeolites have been used in agriculture since the 1960s, due to the effectiveness of these crystalline microporous solids as soil amendments for plant growth, their cation exchange capacity (CEC) and slow-release fertilizer properties. Most work on slow-release fertilizers has focused on natural Clinoptilolite, Phillipsite and Chabazite. The aim of this study was to synthesize clinoptilolite type of zeolite-enriched fertilizer study their effectiveness as soil amendments. Greenhouse experiments were performed to study the effects of clinoptilolite type of zeolite, synthesised zeolite-enriched ammophos fertilizer and ammophos fertilizer (12% N, 52% P_2O_5) on yield parameters of Cucumber (Cucumis sativus) plant and some chemical properties in dark chestnut soil. According to greenhouse experiment results, there were significant differences among the treatments in relation to yield parameters (weight of one cucumber, shoot length, number of leaves, area of 10 leaves, number of fruits and fruit weight per plant) of cucumber and available nutrient contents of soil. It was determined that the yield parameters of cucumber plant, available nutrient contents (N, P and K) and cation exchange capacity were increased the most by synthesised zeolite-enriched fertilizer application.

Keywords: Zeolite, clinoptilolite, synthesis of zeolite enriched fertilizer, cucumber, nutrient,

Introduction

Zeolites are hydrated aluminosilicates with an infinite three dimensional crystal structure, containing cations of alkaline elements and alkaline soil elements or, less frequently, other cations (Jarosz et al., 2022). Zeolites are important materials with very broad applications in agriculture and environmental engineering. One of the most important applications of zeolites in agriculture is the slow/controlled-release fertilizer aspect. Slow release is a term that is interchangeable with delayed-release, controlled-release, controlled-availability, slow acting and metered-release (Ming and Allen, 2001). Some of the natural zeolites that have been studied for slow-release fertilizer aspects are Clinoptilolite, Chabazite, Phillipsite and Mordenite. The widespread abundance of these zeolites in nature and their selectivity for certain cations (i.e. NH_4^+ and K^+) makes them suitable for this purpose. Zeolite incorporation in soil was found to increase crop yields and to promote nutrient use efficiency. Other possible uses being investigated include applications as a carrier of slow-release fertilizers, insecticides, fungicides, and herbicides, and as a trap for heavy metals in soils (Ramesh and Reddy, 2011).

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Kazakhstan has significant deposits of clinoptilolite, which is a natural zeolite with a high cation exchange capacity and a wide range of applications. Karatau, Kounrad, Kokshetau, Terekty and Shankanai deposits are the the main clinoptilolite deposits in Kazakhstan. Clinoptilolite from Kazakhstan is used in a variety of applications, including agriculture, animal feed, water filtration, and soil remediation. The high-quality and abundance of clinoptilolite in Kazakhstan make it an important source of this valuable mineral (Sadenova et al., 2016; Sultanbayeva et al., 2022). Natural clinoptilolite type of zeolite deposits in Kazakhstan have been used in agriculture without any enrichment with fertilizers until today.

Dark chestnut soil is an important soil type in Kazakhstan (Saparov, 2014; Maxotova et al., 2021; Nasiyev et al., 2021) , as it covers a significant portion of the country's agricultural land and it's an important resource such as fertile soil for agriculture, supports food security, economic importance and biodiversity in Kazakhstan. The aim of this study was to determine if synthesised zeolite-enriched fertilizer are better than natural clinoptilolite type of zeolite at increasing yield and yield parameters of cucumber *(Cucumis sativus)* plant and available nutrient status in dark chestnut soil.

Material and Methods

Experimental Materials

The surface dark chestnut soil (0-20 cm) used in this experiment. Soil texture can accordingly be classified as loamy. The pH in water was 7.25, the humus content was 2.15%, the total N was 0.098%, available P was 40 mg kg^{-1}, available potassium was 280 mg kg^{-1} and the soil C:N ratio was 21,94. The soil was bulked, all tones, visible roots and fauna removed, sieved to less than 2 mm and stored at room temperature until used. Cucumber variety, "F1 Gerasim", was selected as the experiment material.

Synthesis of zeolite enriched fertilizer

In this study, clinoptilolite, which is a natural zeolite with a high cation exchange capacity from Shankanai deposits of Kazakhstan and Ammophos fertilizer which is a complex mineral fertilizer (12%N, 52%P_2O_5) were used for the synthesis of zeolite-enriched fertilizer. The procedure applied for the synthesis of zeolite and fertilizer is given below in general terms.

- Clinoptilolite and Ammophos fertilizer are preliminarily colloidally ground to a fraction with sizes less than 300 nm in a planetary ball mill, thereby having sufficient energy for mechanical alloying
- Weigh out the desired amount of clinoptilolite and Ammophos fertilizer according to the desired ratio.
- Mix the clinoptilolite and fertilizer together in a beaker or flask, and add enough deionized water to create a slurry.
- Stir the slurry for several hours at room temperature to allow for ion exchange to occur between the clinoptilolite and fertilizer.
- Filter the slurry through a filter paper to separate the solid clinoptilolite-fertilizer complex from the liquid solution.
- Rinse the complex with deionized water to remove any residual impurities.
- Dry the complex at 60°C for 12 hours, and then crush it into a granular form suitable for use as a fertilizer.

X-ray diffractometer (Rigaku MiniFlex 600) in a scanning electron microscope was used to determine the elemental composition of zeolite, Synthesis of zeolite-enriched fertilizer and ammophos fertilizer (van Koningsveld and Bennett, 1999). Energy dispersive spectroscopy of all samples was carried out at shooting parameters with an accelerating voltage of 15 keV and a working distance of 15 mm.

Experimental procedure

A pot experiment was carried out in the greenhouse of the Kazakh National Agricultural Research University with the cucumber variety "F1 Gerasim" in order to investigate the effects of clinoptilolite type of zeolite (ZEO), synthesised zeolite-enriched ammophos fertilizer (SZF) and ammophos fertilizer (AMF) on yield parameters of cucumber and some soil chemical properties. The experiment consisted of 4 treatments and three replications, and the pots were distributed in completely randomized design. There were ZEO (2 gr/kg soil), AMF (0,4 gr/kg soil), SZF (4 gr/kg soil) and a control treatment without zeolite and fertilizer application. Dark chestnut soil was filled in 5L pots. One cucumber seedling was planted in each pot. The pots were regularly irrigated to maintain a proper moisture level. Plants in pots were harvested 48 days after planting.

Data collection

After the harvest, the cucumber plants evaluated individually to determine the weight of one cucumber (WEC), shoot length (SLE), number of leaves (NUL), area of 10 leaves (ALE), number of fruits (NUF), fruit weight per plant (FWP). Soil samples were taken from each pots at the end of the harvest and the soil samples were air dried and passed through a sieve with 2 mm size opening, some soil characteristics were determined as follows; total soil organic matter contents (SOM), total carbonates contents ($CaCO_3$), soil reaction (pH), mineral-N, available phosphorus and available potassium as described by GOST 26213-2021, ISO 10693:1995, GOST 26423-85, GOST R 53219-2008 and GOST 26205-91.

Results and Discussion

The chemical composition of ZEO is the most important indicator of its quality. Thus, their ion-exchange properties, thermal and acid resistance, and other technological characteristics depend on the ratio of Si to Al and the cationic composition of zeolites. Zeolites with a high content of K give the greatest effect in crop production (Jarosz et al., 2022). According to XRD data, the main phase of the original ZEO from the Shankanai deposit is clinoptilolite, the SiO_2/Al_2O_3 ratio is 3.8. Na^+, K^+, Ca^{2+}, Mg^{2+} and Fe^{3+} were found in the composition of exchange cations, with large amounts of Ca^{2+}. Clinoptilolite /$KNa_2Ca_2(Si_{29}Al_7)O_{72}.32H_2O$/ has a monoclinic lattice with parameters: a=17.64 Ǻ; c=17.88 Ǻ; c=7.40 Ǻ; β=116.300. Other constituents are plagioclase, quartz, hematite, talc and muscovite. According to the results of studies of the elemental composition of the samples (Figure 1), it can be noted that the SZF did not lose its nutritional properties after chemical and thermal treatments. Clinoptilolite was a powerful reserve for the replenishment of potassium and silicon. It was determined that the weight and atomic content of the main nutrients like N and P have been preserved in SZF (Figure 1b).

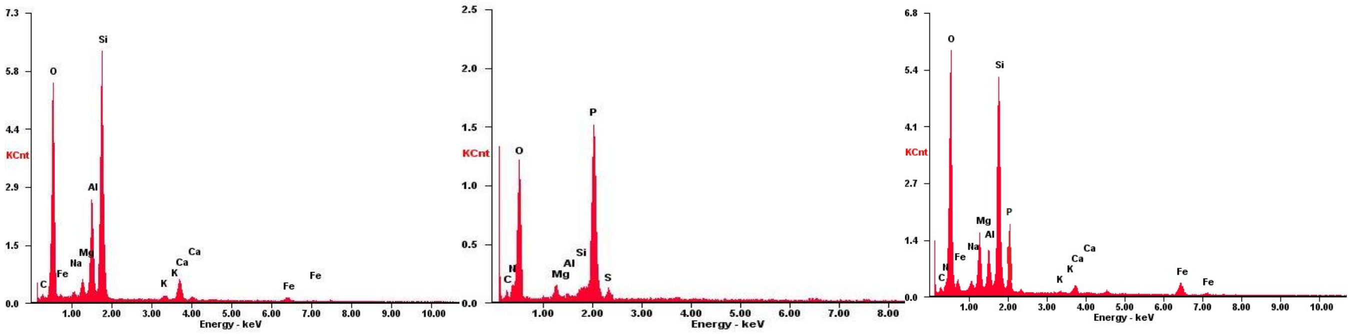

Figure 1. The elemental composition of zeolite (A), ammophos fertilizer (B) and synthesised zeolite-enriched (C)

The changes in some of the chemical properties of the dark chestnut soil in the soil samples taken at the end of the harvest of the cucumber plant are given in Table 1. According to the results, it was determined that ZEO, AMF and SZF applications made to the soils compared to the control application did not cause a change in the SOM, soil pH and $CaCO_3$ of the soil. On the other hand, it was determined that the treatments had a significant effect on the cation exchange capacity (CEC), mineral nitrogen (min.N), available phosphorus (Av.P_2O_5) and available potassium (Av.K_2O) content of the soil. In this study, it was determined that the min.N, Av.P_2O_5, Av.K_2O contents and CEC of the soils were increased the most by SZF application. Because zeolites have high CEC, ion selectivity, unique physical characteristics and chemical stability they may be effective as soil conditioners. As reported by Soca and Daza-Torres (2016), the application of zeolite significantly increased the contents of available nutrients and increased soil pH. An increase in soil pH and exchangeable potassium content was observed by Filcheva and Tsadilas (2002), who conducted an experiment to evaluate the effect of clinoptilolite on soil properties. On the other hand, the results of de Campos Bernardi et al. (2013) indicated that application of concentrated natural zeolite, stilbite, enriched with nitrogen, phosphorus, and potassium on sandy soil reduced ammonia volatilisation, increased available phosphorus contents.

Table 1. The changes in some of the chemical properties of the dark chestnut soil

Treatments	SOM, %	pH	$CaCO_3$, %	Min. N, mg kg^{-1}	Av. P_2O_5, mg kg^{-1}	Av.K_2O, mg kg^{-1}	CEC, meq 100 g^{-1}
Control	2.27	8.36	1.23	56.6	32	240	13.8
ZEO	2.27	8.42	1.28	61.9	41	320	17.8
AMF	2.27	8.39	1.30	64.4	68	238	14.1
SZF	2.27	8.40	1.28	69.4	88	380	18.1

The effects of ZEO, AMF and SZF added to dark chestnut soil on the yield parameters of the cucumber plant are given in Table 2. According to the results obtained from the experiment, it was determined that ZEO, AMF and SZF applications increased the yield parameters (WEC, SLE, NUl, ALE, NUF, FWP) of the cucumber plant. In addition, it was determined that the WEC, SLE, NUl, ALE, NUF and FWP were increased the most by SZF application. Plant growth and plant yield parameters might be directly influenced by the amount of nutrients present in soil and available for the plants to complete its life cycle. Plant growth and plant yield parameters results had to be related to available soil nutrient results uptake by cucumber plants for their metabolism. In this study, it was determined that ZEO, AMF and SZF added to the soil also increased the yield parameters of the cucumber plant due to the increase in the min.N, Av.P_2O_5, Av.K_2O and CEC of the soil.

The effects of natural zeolites and enriched zeolites with fertilizer amendment on cucumber (*Cucumis sativus*) seed germination, plant growth, and development were examined. Researchers have reported that germination was faster with ammonium sulfate, diamonium phosphate, and superphosphate (18% P_2O_5) amendment than with enriched zeolites with these fertilizer amendments. Although fertilizers suddenly affect media at initial irrigation after the sowing, zeolites work slowly due to slowly released N from their colloidal sites (Yılmaz et al., 2014). Similarly, a field experiment to investigate the effect of zeolite in the form of clinoptilolite as a supplement to mineral fertilization was conducted by Tsintskaladze et al. (2017), who used maize as a test crop. As per the results, the application of ammonium nitrate alone allowed to obtain a maize grain yield of 7.4 t ha^{-1}, while for the variant combining zeolite and ammonium nitrate, the obtained maize grain yield was 8.8 t ha^{-1}, constituting an 18.9% increase.

Table 2. The changes in yield parameters of cucumber plant

Treatments	WEC, g	SLE, cm	NUL, pcs	ALE, cm^2	NUF, pcs	FWP, g
Control	28,5	138	35	294,0	2	101
ZEO	47,4	159	34	305,3	2	144
AMF	45,3	143	22	309,0	4	183
SZF	71,7	227	36	314,3	4	184

Conclusion

In this study, greenhouse experiment on pot grown cucumber plants demonstrated that zeolitic soil amendments (clinoptilolite type of zeolite from the Shankanai deposit, Kazakhstan and synthesised zeolite-enriched ammophos fertilizer) could be effective alternatives to conventional ammophos fertilizer, providing cucumber plants with both improving soil chemical properties and plant yield parameters. Comparisons of plant growth with controls showed synthesised zeolite-enriched fertilizer amended soils at lower loadings, to be a potential source of providing plants with all the essential nutrients during all stages of growth cycle, thereby increasing plant yield parameters. In soils amended with higher cation exchange capacity of both synthesised zeolite-enriched fertilizer and natural clinoptilolite type of zeolite, plant growth was significantly increased. Higher available N, P and K in the soil may cause plant yield parameters. This study covered a broad range of issues, many of which merit further investigation. Listed below are some recommendations for further investigation.

(i) As the greenhouse experiment was carried out under controlled greenhouse conditions on pot-grown plants, it would be beneficial to compare the effects of zeolite and zeolite-enriched fertilizer addition to different type of soil under field conditions to evaluate the effectiveness of different plant growth.

(ii) The major hurdle in using synthetic zeolites as fertilizer amendments is their cost. Calculating the cost for producing zeolites on a laboratory scale it was valued to be three times an expensive product than its natural counterpart. However, based on the effectiveness of synthesised clinoptilolite type of zeolite-enriched ammophos fertilizer from the Shankanai deposit, Kazakhstan, in particular as a controlled release soil amendment, it would be worth exploring the possibilities of manufacturing zeolites on a large commercial scale under pilot conditions.

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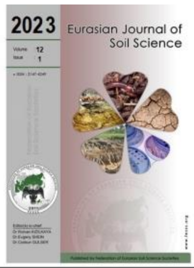

Main factors in polycyclic aromatic hydrocarbons accumulations in the long-term technogenic contaminated soil

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Abstract
The PAHs transformation in the soils of the coal mining enterprises impact zones and thermal power plants remains poorly studied. In turn, coal mining can be considered as a primary cycle in the production of electricity. One of the main sources of negative environmental impact is the coal mining industry located on the territory of the upland in the south of the East European Plain. The features of PAHs accumulation in the soils of fuel and energy enterprises have been studied on the example of mines impact zones with different service life and the current coal-fired power plant. It was established that, regardless of the period and intensity of the emission source, as well as its current status, the polycyclic aromatic hydrocarbons (PAHs) content in the soils of the impact zones was significantly higher than in the soils of the background territory. The content of low molecular and high molecular weight PAHs in the impact zones soils differed depending on the land use type, as well as the period and intensity of an industrial effect type. The pollutants content of in the soils of all considered impact zones significantly exceeded the background values and according to the low molecular weight PAHs content in the soils, they formed the following decreasing series: Mayskiy ≥ Ayutinsky > Novoshahtinsk > Power station > Background. According the high molecular weight PAHs content, the series changed to: Novoshahtinsk >Mayskiy ≥ Ayutinsky > Power station > Background. Soil pollution markers for enterprises of the fuel and energy complex were identified as pyrene and chrysene, which are part of coal, formed from the hydrocarbon sources. The influence of the power plant was accompanied by the benzo(g,h,i)perylene concentration increase.

Keywords: Priority PAHs, thermal power station, coal mining, anthracite, soil pollution.

Introduction
Industrial production is a key link in techno genesis for the whole environment and for individual components of the landscape. Diverse in intensity, duration and direction, anthropogenic impacts transform the initial parameters of the functioning of natural landscapes and create conditions for the ecological situation formation. The soil cover is a product of the natural and technogenic factors interaction, and, as the most stable component of the natural environment, reflects the level of long-term technogenic impact. The result of this impacts complex is manifested in a decrease of the soils quality up to their complete degradation, including those caused by chemical pollution. PAHs are considered as priority pollutants with carcinogenic activity (ATSDR, 1995; Adriano, 2001; Antoniadis et al., 2019). Soil pollution with PAHs is not only a direct environmental hazard for living organisms, adjacent components of natural and technogenic landscapes, but also acts as a risk factor for human's health (Asante-Duah, 2017; US EPA, 2020; Bezberdaya et al., 2022).

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Conventionally, all PAHs are classified into low molecular weight, which include 2- and 3-ringed compounds, and high-molecular, which include 4, 5, 6 or more ringed compounds. With an increase in the number of benzene rings in the PAH molecule, the stability of the pollutant in the medium increases, its lipophilicity increases, as well as its toxicity (ATSDR, 1995; Rengarajan et al., 2015; Abdel-Shafy and Mansour, 2016; IARC, 2020). At the same time, pollutants are amenable to microbiological and photochemical destruction, which allows the soil to self-purify over time (Haritash and Kaushik, 2009; Premnath et al., 2021).

Among the key anthropogenic sources of soil pollution in industrialized regions, FAO identifies mining, manufacturing, energy production, construction and transport (FAO and UNEP, 2021). Pyrolytic processes are an integral part of various branches of industrial production, which poses a threat to the continuous supply of PAHs to soils. The main sources of pollutants are emissions from thermal power plants and coal mining (Tsibart and Gennadiev, 2013; Sushkova et al., 2020).

There is not enough information about the PAHs transformation in the soils of the coal mining enterprises impact zones and thermal power plants. The coal mining industry can be considered as a primary sourse in the production of electricity. Therefore, the purpose of this study was to determine the main factors in polycyclic aromatic hydrocarbons accumulations in the long-term technogenic contaminated soil of the fuel and energy complex enterprises.

Material and Methods

The coal mining industry located on the territory of the East European Plain is one of the priority sources of negative environmental impact in the south of the above-mentioned area. Coal reserves in the south of the East European Plain amount up to 9.6 billion tons, while 7.2 billion tons of them are reserves of especially valuable anthracite, one of the best in the world in terms of calorific value and properties. Coal production volume reaches 2.3 million tons and is carried out at 7 mines (State Report, 2001). In the mining areas of the old development, significant areas are occupied by disturbed lands, quarries, dumps, mines. On this territory the special technogenic landscape-geochemical systems have been formed in the type of the mining landscapes (Perel'man, 2013). Mines not only occupy productive lands but serve as a secondary source of suspended particles and various pollutants due to dusting and combustion.

Coal reserves in the south of the East European Plain is mainly used by local industry, almost half is consumed by thermal power plants, one of which is Novocherkassk Power Station (NPS), with an installed electric capacity of 2258 MW. Annually, about 2.5 million tons of coal are consumed to produce the electricity at the station (Annual Report 2021, 2022). NPS is one of the five largest coal-fired power plants on the European territory, and the only one using anthracite pebbles. As a result of the station operation, more than 250 thousand tons of pollutants enter the atmosphere, including nitrogen oxides, carbon dioxide, sulfur oxides, greenhouse gases, PAHs, heavy metals, etc. (Korotkova et al., 2017; Sushkova et al., 2017).

The object of the study was the soils associated with mines of the coal mining industry and the impact zone of the NPS. Mines located in the western part of the region, near the rural settlements of Ayutinskaya and Mayskiy, as well as within the boundaries of the Novoshakhtinsk city. For mines located near Ayutinskaya and Mayskiy, the operation life was 58 and 48 years, and their closure took place in 2007 and 2002, respectively. The spoil mines, located on the territory of the Novoshakhtinsk city, ceased to function in 2002 after 71 years of its operation. The projected production capacity of the mines also varies. Thus, mines located near Ayutinskaya and Mayskiy are composed of coal mining waste from mines with a projected capacity of 400-600 thousand tons per year. The spoil mines, located directly within the boundaries of the Novoshakhtinsk city, was formed from an enterprise with a projected capacity of 1,500 thousand tons per year. Soils located far from industrial zones, including territories with a special protected status, were used as reference soil. The soil cover of the study area is predominantly represented by Haplic Chernozems, Gleyic Chernozems and Fluvisols (Table 1, Figure 1).

Soil sampling was carried out from each monitoring site to a depth of 0-20 cm in accordance with GOST 17.4.4.02-2017 (GOST 17.4.4.02-2017, 2019). Extraction of PAHs from soil samples was carried out with n-hexane. The pre-interfering lipid fraction was removed by saponification of 1 g of soil with a 2% KOH alkali solution. The PAHs in the extract were quantified by high performance liquid chromatography using HPLC Agilent 1260 (ISO 13877-2005, 2005). The content of individual PAHs in the analyzed samples was calculated using the external standard method.

Table 1. Soil properties of industrial and natural areas

Object type	Nearest city/village	Soil properties	Statistical parameters			
			Mean	Standart deviation	Minimum	Maximum
Power station	Novocherkassk	OM, %	2,0	0,5	1,2	2,9
		pH	7,5	0,5	6,2	8,5
		< 0,001,%	22,0	10,7	7,2	36,8
		< 0,01, %	45,4	12,8	22,4	64,4
Waste heap	Ayutinsky village	OM, %	2,6	1,2	0,3	3,5
		pH	7,6	0,3	7,3	7,9
		< 0,001,%	24,1	7,5	14,8	32,8
		< 0,01, %	47,3	11,7	33,6	58,8
	Novoshakhtinsk	OM, %	2,7	1,0	1,5	4,1
		pH	7,2	0,8	5,8	7,9
		< 0,001,%	8,3	6,5	2,2	20,4
		< 0,01, %	27,5	9,6	11,2	38,1
	Mayskiy village	OM, %	1,4	0,3	1,2	1,9
		pH	7,9	0,4	7,3	8,4
		< 0,001,%	23,9	9,3	8,0	34,0
		< 0,01, %	45,7	16,3	14,4	63,2
Background		OM, %	1,9	1,0	0,9	3,7
		pH	7,8	0,4	7,3	8,3
		< 0,001,%	21,7	11,6	1,6	31,7
		< 0,01, %	38,7	20,1	2,8	58,0

* OM - organic matter; < 0,001,% - soil particles less 0,001 mm, < 0,01,% - soil particles less 0,01 mm

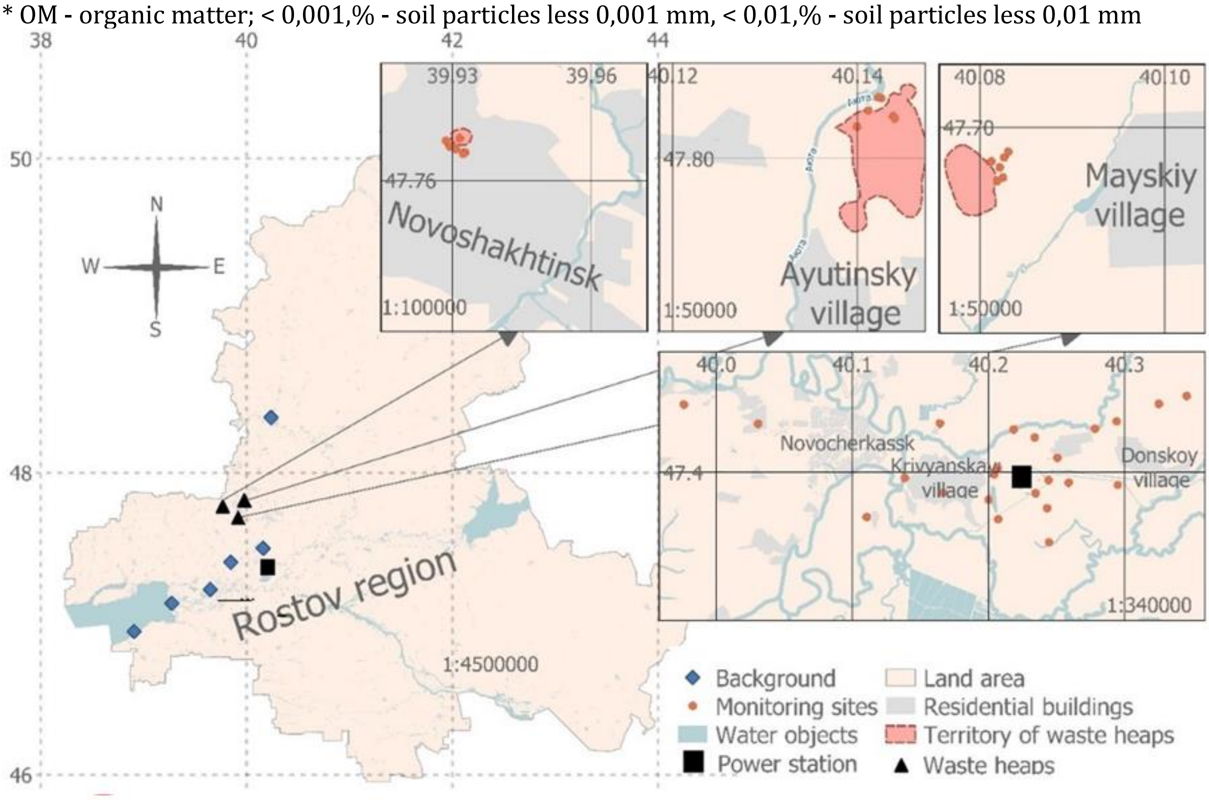

Figure 1. Soil sampling sites

During laboratory experiments, the concentrations of 15 priority PAHs were determined: low molecular weight: naphthalene, phenanthrene, anthracene, acenaphthene, acenaphthylene, fluorene; high molecular weight: pyrene, chrysene, benzo(a)anthracene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene (US EPA, 2020). All laboratory analyzes were performed in 3-fold analytical replication.

Statistical analysis of the obtained results was performed using STATISTICA 7 and OriginPro 2018 software. The significance of differences between samples was assessed using one-way analysis of variance followed by Tukey's post hoc test for unequal samples.

Results and Discussion

The content of PAHs in the soils of the background territory didn't exceed the norms established for agricultural territories (Maliszewska-Kordybach, 1996), average level of pollutants in soils of temperate latitudes and generally corresponds to the soils of natural areas (Wilcke, 2000; Sosa et al., 2017; Pikovskii et al., 2019; Hong et al,. 2020).

The content of low molecular weight (at F=67 and $p<0.0001$) and high molecular weight (at F=47 and $p<0.0001$) PAHs in the impact zones soils differed depending on the type of land use, the period and intensity of an industrial facility operation. At the same time, the content of pollutants in the soils of all considered impact zones significantly exceeds the background values. On average, in terms of the concentration of low molecular weight PAHs in the soils, they formed the following decreasing series: Mayskiy ≥ Ayutinsky > Novoshahtinsk > Power station > Background (Figure 2). For high molecular weight PAHs, the series changed to: Novoshahtinsk >Mayskiy ≥ Ayutinsky > Power station > Background. The higher values of low molecular weight PAHs in the soils of mines with a shorter service life (Mayskiy Ayutinsky), compared with the mine located within the Novoshahtinsk city, indicated ongoing processes of PAHs transformation from more nuclear compounds to less nuclear ones (Figure 2).

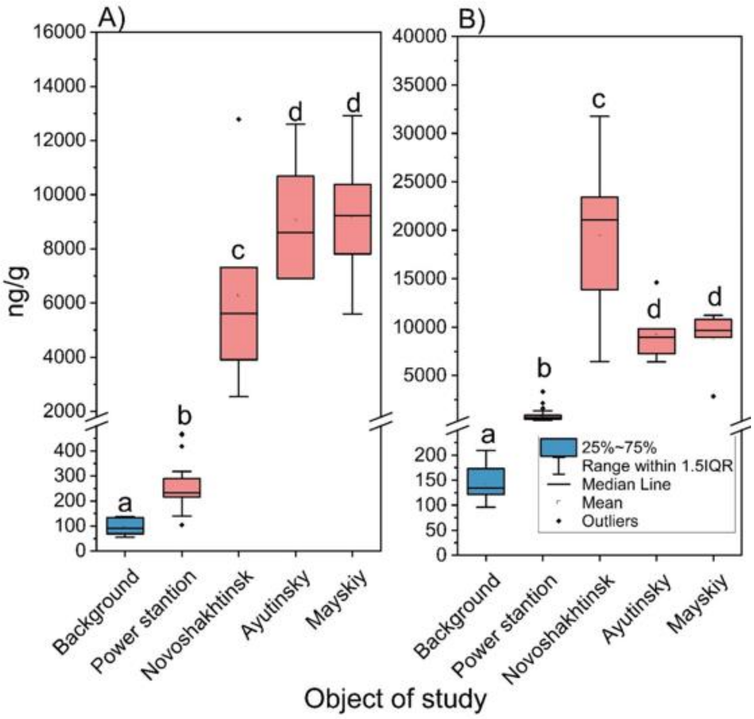

Figure 2. The content of low molecular weight (A) and high molecular weight (B) PAHs in soils of industrial and natural areas. Different letters indicate significant differences ($p < 0.05$) resulting from the post hoc Tukey's—honestly significant difference for unequal number test

The obtained values significantly exceeded the average pollution level in the soils of the coal mining enterprises and NPS impact zones. Often, the total content of PAHs in soils near coal mines does not exceed 6000 ng g, while in soils in the impact zones of power plants it reaches up to 3000 ng g (Wang et al., 2010; Kumar et al., 2014; Mukhopadhyay et al., 2017; Yakovleva et al., 2017, 2021; Amster and Lew levy, 2019; Gupta and Kumar, 2020). This may be due to the high affinity of the studied Haplic Chernozem for carbonaceous particles carriers of pollutants, as well as directly to PAHs themselves due to the high content of organic matter and finely dispersed fraction (Guo et al., 2010; Sushkova et al., 2019). On the one hand, this helps to fix pollutants and limit their migration into the tissues of living organisms (Guo et al., 2010; Cachada et al., 2014). On the other hand, the strong sorption of pollutants by the organic mineral part of the soil reduces the potential of the soil for self-purification through the microbiological destruction of PAHs due to their inaccessibility to microorganisms (Figure 2) (Liste and Alexander, 2002; Luo et al., 2012).

It is shown that the relative content of low- and high-molecular pollutants in soils of the background territory had the similar tendencies. Phenanthrene predominated (52%) in the composition of low molecular weight compounds while other PAHs had approximately equal shares. High molecular weight pollutants are characterized by an unexpressed dominance of the 4-ring association represented by fluoranthene, pyrene, and chrysene (14–16%), as well as benzo[b]fluoranthene (Figure 3).

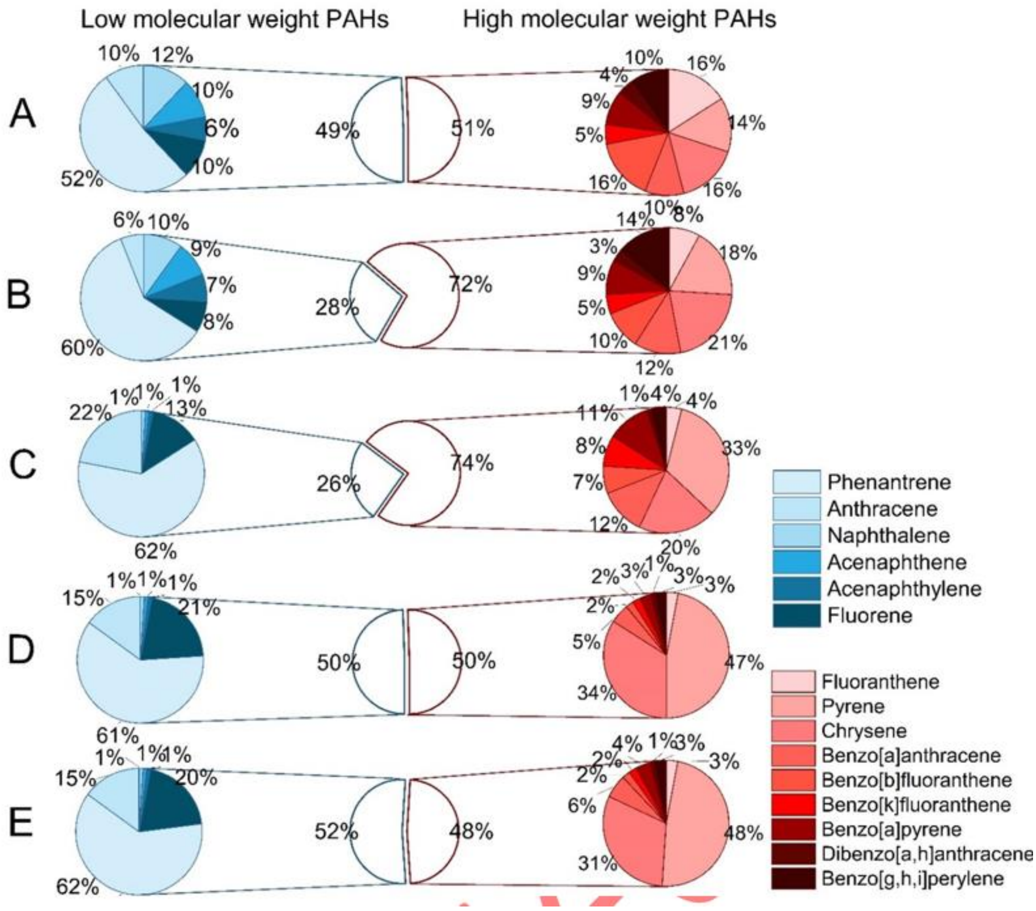

Figure 3. Relative content of individual PAH compounds in the composition of low and high molecular weight PAHs in the soils of the background area (A), the impact zone of the power plant (B), mines located near settlements Novoshahtinsk city (C), and on the territory Mayskiy (D) and Ayutinsky (E) mines

The main factors of the relative content of individual PAH compounds accumulation in the studied territories soils were established depending on the intensity and duration of an industrial facility operation and its current status (Figure 3). Under intense pressure from the power plant, there was a sharp shift in the relative content of pollutants towards the dominance of high molecular weight PAHs compounds, which indicates the lack of balance between the accumulation and destruction of pollutants in the soil. This kind of changes occurred mainly due to an increase in the pyrene, chrysene, and benzo(g,h,i)perylene proportion. Elevated concentrations of these compounds compared to other priority PAHs are markers of a pyrogenic-coal source, since pyrene, chrysene, and benzo(g,h,i)perylene are often found in soils of areas affected by fuel and energy complex enterprises and coal mining (Khaustov et al., 2021; Khaustov and Redina, 2022). At the same time, the proportion of individual low molecular weight compounds in this group is almost identical to the background territory.

In the soils of the impact zone of the mine located in the Novoshakhtinsk city, the proportion of low and high molecular weight PAHs was similar to the soils of the impact zone of the NPS. This indicates a strong fixation of 4-6 annular compounds by the organo-mineral part of the soil and the almost complete absence of pollutant transformation. However, differences were found in the dominant composition of the PAHs groups. The sum of low molecular weight compounds consists of 97% phenanthrene, anthracene, and fluoranthene, which is not typical for the soils of the NPS impact zone and indicates the presence of a large amount of these compounds in the composition of mined anthracites. Compared to the soils of the NPS impact zone, only pyrene and chrysene dominate in the composition of high molecular weight compounds. The share of pyrene (33%) is 1.5 times higher than the share of chrysene (20%). This indicates that the accumulation of pyrene in the soils of the impact zones under consideration is directly related to its presence in the composition of coal. The content of chrysene in soils is due not only to its presence in the composition of the fossil, but also to the formation of a pollutant, as in the process of coal pyrolysis at a thermal power plant.

In the technogenically disturbed soils of the impact zones of mines located near the settlements of Mayskiy and Ayutinsky, about half of the total content of pollutants falls on low molecular weight compounds, which is similar to the soil of the background site and indicates the stability of the ecosystem (Khaustov et al., 2021;

Khaustov and Redina, 2022). The composition of low molecular weight compounds is dominated by the same substances as in the soils of the more impact zone of the mines confined to the Novoshakhtinsk city (phenanthrene, anthracene, fluorene). In turn, with the PAHs active transformation in the soils of the impact zones of mines (Mayskiy and Ayutinsky), a decrease in the proportion of 5- and 6-ringed soils was observed due to an increase in 4-ringed soils. More than 70% of the total high molecular weight PAHs were pyrene and chrysene. This fact indicates that the transformation of 5- and 6-ringed pollutants proceeds with the formation of intermediate compounds of pyrene and chrysene, followed by the destruction of the PAH molecule to simple compounds. For example, pyrene in the process of microbiological or chemical oxidation according to the Fenton reaction type (Luo et al., 2014; Qin et al., 2017; Yan et al., 2017; Wang et al., 2018; Mazarji et al., 2021, 2022).

Conclusion

The study showed that in the soils of the impact zones of the largest thermal power plants in Russia, as well as mines located near the settlements of Mayskiy, Ayutinsky and Novoshahtinsk, the content of PAHs significantly exceeded the background levels, the average level for temperate latitudes, and the norms for agricultural soils. The content of pollutants in the soils of the impact zones varies depending on the type of land use, the period and intensity of operation of an industrial facility. In the soils of mines with a total service life of 48-58 years with a relatively low amount of coal mined per year (up to 600 thousand tons per year), the proportion of low-molecular and high-molecular PAHs is equalized, which is close to the values obtained for the soil of the background plots and is a consequence of the transformation of PAHs.

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