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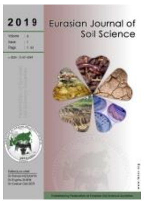

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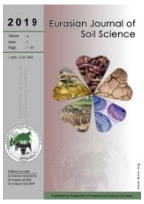

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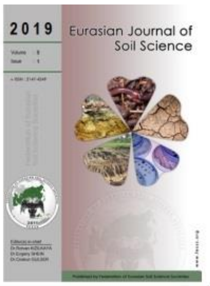

Biochar and clinoptilolite zeolite on selected chemical properties of soil cultivated with maize (Zea mays L.)

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Abstract

Increase in cost of chemical fertilizers encourages the use of soil amendments such as biochar and zeolites to improve soil fertility. In this study, biochar produced from empty fruit bunch-palm oil mill effluent (EFB-POME) and clinoptilolite zeolite were used as soil amendments to improve soil fertility. The field experiment was carried out for two planting cycles to determine the effects of different rates of EFB POME biochar (0, 10, and 20 t ha^{-1}), clinoptilolite zeolite (0, 1.25, and 2.5 t ha^{-1}), and urea (60 and 120 kg ha^{-1}) on selected soil chemical properties of Tanjung Lipat (*Typic Paleudults*). Biochar produced from EFB-POME increase soil total N, P, K, Ca, and Mg. The higher soil total N, P, K, Ca, and Mg could be related to the increase in soil pH, cation exchange capacity, and total organic carbon in soil with EFB-POME biochar but not with clinoptilolite zeolite. Thus, EFB-POME biochar was more suitable to be used in a tropical soil (*Typic Paleudults*) compared to clinoptilolite zeolite for improving the selected soil pH, CEC, TOC and available P, K, Ca and Mg.

Keywords: Biochar, clinoptilolite zeolite, EFB-POME, tropical acid soil, agriculture waste.

Introduction

Soils in the tropics are considered to be acidic, strongly weathered, low in nutrient reserves, and depend on their soil organic matter (SOM) for efficient nutrient recycling (Sanchez and Logan, 1992). Oxisols and Ultisols, which are acidic in their nature, are two major soil types in Malaysia and cover about 72% of the land (Anda et al., 2008). Generally, Oxisols and Ultisols are high Fe and Al oxides which contribute to the soil acidity (Schlesinger, 1997), low in effective cation capacity and nutrient reserves (Sanchez and Logan, 1992). In addition, these soils are degraded physically, chemically, and biologically due to human activities such as intensive farming, continuous and over usage of fertilizers and pesticides, removal of soil organic matter, as well as the topsoil layer (Scherr and Yadav, 1996). The conventional and most popular way to effectively increase soil fertility is to apply chemical fertilizers. This has led to increase in demand for fertilizers worldwide (IFA, 2014). Although chemical fertilizers are effective in increasing soil nutrient status and crop yield, their adverse effect in the long term and the harm to the environment is worth attention as fertilizers can be one of the sources of pollutants to soil and water.

For sustainable agriculture, biochar and zeolites can be used as soil amendments or conditioners to improve soil fertility. Biochar is a carbon rich organic material which originated from the *terra-preta* of Brazillian Amazon that has undergone pyrolysis process at relatively high temperature (300 – 700°C) (Lehmann and Joseph, 2009). One of biochar's unique properties is high porosity, which can be favourable for improving

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soil water holding capacity and soil structure (Karhu et al., 2011; Vaccari et al., 2011). Crop productivity is positively affected by biochar addition as the amendment can increase and retain nutrients in the soil due to its high CEC (Cornelissen et al., 2013; Liang et al., 2006). Some types of biochar also possess high pH, a property which is favourable especially in acidic soils as biochar helps to buffer soil pH, substituting the use of liming to increase soil pH, and indirectly increasing nutrient availability for crop nutrient uptake (Novak et al., 2009; van Zwieten et al., 2010; Nigussie et al., 2012). Biochar also improves soil quality by increasing soil biota as biochar is a suitable habitat for soil micro and macro organisms due to its high surface area and organic matter (Lehmann et al., 2011). In this study, biochar produced from empty fruit bunch and palm oil mill effluent (EFB-POME) was used. In 2010, Malaysia exported a total of 14.7 million tonnes of palm oil and palm oil products, contributing US$ 4500 million revenue to the country (Bazmi et al., 2011). However, the biomass left from the palm oil production is as high as 90% because the oil extraction rate is only about 10% (Basiron and Weng, 2004). Due to the abundance of EFB and POME wastes in the oil palm industry, charring of these waste materials (to produce biochar) is one of the effective ways to return the biomass into the soil.

Clinoptilolite zeolite was also used in this study in combination with EFB-POME biochar for maize cultivation. Zeolites are hydrated aluminosilicates of alkaline and alkaline-earth minerals and their structure is made up of a framework of $[SiO_4]^{-4}$ and $[AlO_4]^{-5}$ tetrahedron linked to each other's corners by sharing oxygen atoms forming a 3-dimensional framework (Akbar et al., 1999). The 3-dimensional pore structures of zeolites are interconnected and form long wide channels for easy movement of ions and molecules into and out of the structures (Polat et al., 2004). The silicate (SiO_4) tetrahedron is a compromise between electrical neutrality and packing efficiency. To be electrically neutral, stable minerals require other positively charged accessory cations. This need for electrical neutrality and accessory cations leads to the important property of cation exchange capacity. Zeolites in natural conditions are combined with cations such as Na^+, K^+, Ca^{2+} and others (Navrotsky et al., 1995). In agriculture, zeolites are used as slow release fertilizer, soil amendment for pH buffering, increase CEC and fertilizer use efficiency, serve as water reservoir in the soil due to their high porosity and water filter in aquaculture systems (Polat et al., 2004).

Maize (*Zea mays* L.) is one of the important crops in the world, which serves as livestock's feed, food, and oil source for human consumption, and raw material for many agro-based industries. In 2014, Malaysia imported 3.2 billion tonnes of maize mainly from Argentina, Brazil, and India whereas domestic production was only 56,000 tonnes (Wahab and Rittgers, 2014). This study was carried out to determine the effects of biochar from empty fruit bunches and palm oil mill effluent (EFB-POME) and clinoptilolite zeolite on selected chemical properties of soil cultivated with maize.

Material and Methods

Study site and selected soil chemical properties

The field study was conducted in Faculty of Sustainable Agriculture, Universiti Malaysia Sabah (5°55'48.1''N, 118°00'29.8''E). The soil in the research plot belongs to Tanjung Lipat series which is equivalent to *Typic Paleudults* of the USDA system of soil classification. The soil is derived from sandstone and mudstone parent materials (Acres et al., 1975). The soil texture was classified as clay loam with clay content of 35%. The soil chemical properties are presented in Table 1.

Table 1. Selected soil chemical properties of Tanjung Lipat (*Typic Paleudults*)

pH	4.50
Cation exchange capacity ($cmol^+ kg^{-1}$)	2.10
Total organic carbon (%)	3.15
Total N (%)	0.65
NH_4^+ ($mg kg^{-1}$)	1.09
NO_3^- ($mg kg^{-1}$)	0.02
Available P ($mg kg^{-1}$)	1.56
Exchangeable K ($mg kg^{-1}$)	15.20
Exchangeable Ca ($mg kg^{-1}$)	87.00
Exchangeable Mg ($mg kg^{-1}$)	132.80

Field layout and site description

The field experiment arranged in a randomized complete block design (RCBD) with three factors involved; EFB POME biochar (0, 10 and 20 t ha^{-1}), clinoptilolite zeolite (0, 1.25 and 2.5 t ha^{-1}) and urea (60 and 120 kg ha^{-1}), replicated four times. The rates of biochar and zeolite were based on preliminary study pot study done previously and the properties of biochar and zeolite used in this study is presented in Table 2. Thai Super Sweet maize was used as a test crop in the field study. Each plot was 1.5 m x 2.5 m in size with planting distance of 75 x 25 cm. The maize plants were harvested after reaching maturity, at 10 weeks after planting and planted for two cropping cycles. Fertilizers were applied in four splits. Triple Super Phosphate (TSP) and Muriate of Potash (MOP) fertilizers were applied at 60 kg ha^{-1} of P and K, respectively. Rainfall data was collected throughout the field trial from a weather station located approximately 5 m from the field trial plots (Figure 1).

Table 2. Properties of biochar and zeolite used in the study

Properties	EFB-POME biochar	Clinoptilolite zeolite
pH (KCl)	7.45	8.56
Cation exchange capacity (cmol$^+$ kg^{-1})	35.11	160.00
Total C (%)	17.98	9.51
Total N (%)	0.56	1.37
NH_4^+ (mg kg^{-1})	0.44	0.58
NO_3^- (mg kg^{-1})	173.05	0.03
Available P (%)	0.01	ND
Available K (%)	0.27	2.26
Available Ca (%)	0.08	2.56
Available Mg (%)	0.01	1.50

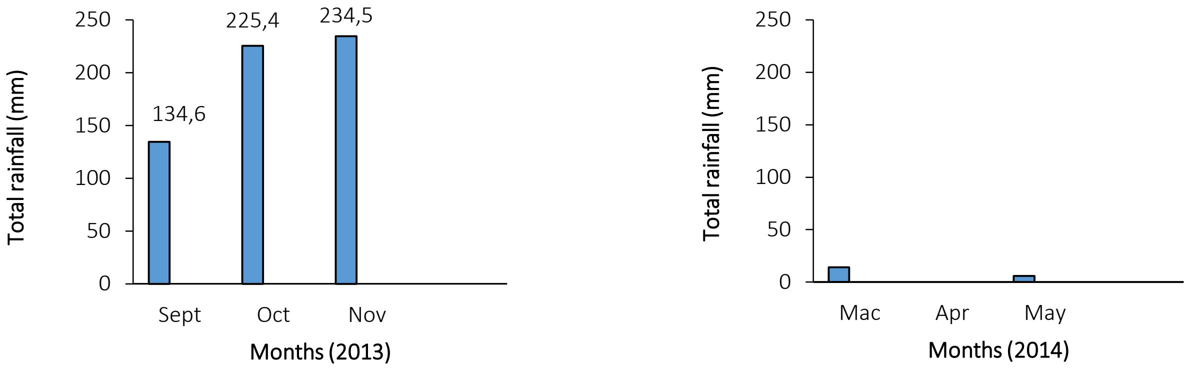

Figure 1. Monthly total rainfall distribution during the first and second cycles of maize cultivation

Soil sampling and analysis

Soil samples were randomly taken using an auger in the middle of each experimental plot up to 15 cm depth after every harvest. Soils were analyzed for total N, NH_4^+, NO_3^-, total organic C, pH, CEC, available P, exchangeable K, Ca, and Mg. The soil samples were air dried at room temperature, ground, and sieved to pass a 2 mm sieve. Soil available P was extracted using the Mehlich 1 method and the concentration was determined by colourimetry method (Pansu and Gauthevrou, 2006) using continuous flow auto analyser (SEAL Analytical AA3). Exchangeable K, Ca, and Mg were extracted using ammonium saturation method (Tan, 1995) and the concentrations determined with Inductively Coupled Plasma (Perkin Elmer ICP-OES model Optima 5300 DV).

Statistical Analysis

Analysis of variance (ANOVA) on all data at 5% significant level was done using Statistical Package for Social Science (SPSS) version 21. Least Significant Different test was used to separate the means for variables that showed significant difference between the treatments for main effects.

Results and Discussion

Soil pH, cation exchange capacity, and total organic carbon for the first and second planting cycles

The main treatment effects on soil pH, total CEC, and TOC are presented in Table 3. In the first planting cycle, there was a significant interaction effect between all the three factors on soil pH and also a significant interaction effect between biochar and clinoptilolite zeolite on soil TOC. There was no significant interaction in the second planting cycle between all the factors for all the variables. However, biochar resulted in significant main effects on all the three variables (soil pH, CEC, and TOC) (Table 3).

Table 3. The effects of biochar, clinoptilolite zeolite, and urea on soil properties for the first and second planting cycles

	First planting cycle			**Second planting cycle**		
	pH	**Total CEC ($cmol^{+}kg^{-1}$)**	**TOC (%)**	**pH**	**Total CEC ($cmol^{+}kg^{-1}$)**	**TOC (%)**
Biochar (t ha^{-1})						
0	4.02^{c}	5.16^{b}	2.09^{b}	3.77^{a}	7.43^{a}	3.32^{b}
10	4.15^{b}	5.68^{b}	2.41^{b}	3.78^{a}	9.40^{a}	4.15^{b}
20	4.26^{a}	7.85^{a}	2.95^{a}	3.98^{b}	12.36^{b}	4.81^{a}
P	<0.01	0.01	<0.01	0.02	0.02	0.05
Std. Error	± 0.03	± 0.63	± 0.13	± 0.06	± 0.92	± 0.41
Clinoptilolite zeolite (t ha^{-1})						
0	4.02^{b}	5.45^{a}	2.11^{b}	3.79^{a}	9.10^{a}	3.59^{a}
1.25	4.18^{a}	7.09^{a}	2.24^{b}	3.88^{a}	9.80^{a}	4.71^{a}
2.5	4.20^{a}	6.15^{a}	3.09^{a}	3.86^{a}	10.30^{a}	3.98^{a}
P	<0.01	0.20	<0.01	0.53	0.65	0.16
Std. Error	± 0.03	± 0.63	± 0.13	± 0.06	± 0.92	± 0.41
Urea N (kg ha^{-1})						
60	4.16^{a}	6.22^{a}	2.48^{a}	3.80^{a}	9.63^{a}	4.20^{a}
120	4.12^{a}	6.25^{a}	2.49^{a}	3.88^{a}	9.83^{a}	3.98^{a}
P	0.14	0.97	0.91	0.25	0.85	0.65
Std. Error	± 0.02	± 0.51	± 0.10	± 0.05	± 0.75	± 0.33
P (interaction)						
B*Z	0.37	0.73	0.02	0.15	0.15	0.49
B*U	0.19	0.95	0.31	0.90	0.59	0.72
Z*U	0.03	0.77	0.63	0.59	0.88	0.38
B*Z*U	0.02	0.40	0.13	0.38	0.82	0.84

Means with the same letter within the columns are not significantly different ($P<0.05$) using LSD test. P = probability value from ANOVA. B*Z = biochar and zeolite interaction. B*U = biochar and urea interaction. Z*U = zeolite and urea interaction. B*Z*U = biochar, clinoptilolite zeolite, and urea interaction

The results of the treatments interaction on soil pH in the first planting cycles are shown in Figure 2. The plots with 60 kg ha^{-1} urea and 1.25 t ha^{-1} clinoptilolite zeolite resulted in higher soil pH (4.05) compared with that of the unamended soil (3.93). However, increase in clinoptilolite zeolite rate (2.5 t ha^{-1}) did not further increase soil pH (4.05). The soil pH was 3.98 in the plots with 10 t ha^{-1} biochar and the combined 10 t ha^{-1} biochar and 1.25 t ha^{-1} clinoptilolite zeolite treatment resulted in an increase in soil pH to 4.26. However, in the plots with the same rate of biochar combined with 2.5 t ha^{-1} zeolite, soil pH was lower (4.19). For the plots with 20 t ha^{-1} biochar, soil pH showed a value of 4.07. The combination treatment of 20 t ha^{-1} biochar and 1.25 t ha^{-1} zeolite increased soil pH to 4.3 and combining the same rate of biochar with higher rate of zeolite (2.5 t ha^{-1}) resulted in the highest value of soil pH (4.55) (Figure 2).

The 120 kg ha^{-1} of urea, soil without biochar, and clinoptilolite zeolite amendments resulted in lowest soil pH (3.89) and treating the soil with 1.25 and 2.5 t ha^{-1} resulted in increased soil pH (4.07 and 4.09, respectively). Soil pH was 4.12 when treated with 10 t ha^{-1} biochar and combining the 10 t ha^{-1} biochar with 1.25 and 2.5 t ha^{-1} zeolite did not show significant changes in soil pH (4.13 and 4.12, respectively). Soil pH was 4.15 for the 20 t ha^{-1} biochar alone, but combining 20 t ha^{-1} biochar and 1.25 t ha^{-1} increased soil pH to 4.26. However, the soil pH decreased (4.19) for the combination treatment of 20 t ha^{-1} biochar and 2.5 t ha^{-1} clinoptilolite zeolite.

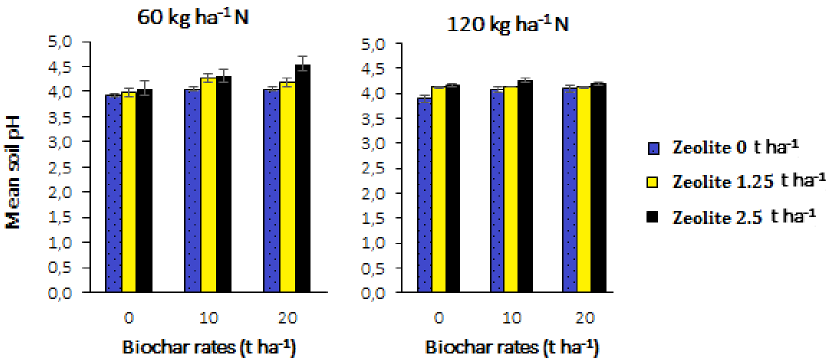

Figure 2. Soil pH for interaction between biochar, clinoptilolite zeolite, and urea in the first planting cycle. Error bars indicate standard error.

The soil pH was higher with biochar and zeolite application at low N rate. Previous studies had reported the influence of biochar and zeolite in increasing soil pH due to liming effect. According to Polat et al. (2004) zeolites are marginally alkaline and fusing them with fertilizer helps in buffering soil pH levels, thus reducing the need for liming. van Zwieten et al. (2010) reported an increase in soil pH with biochar application. In this study, N fertilizer applied to the soil was in the form of urea. Upon hydrolysis, urea is converted to NH_4^+, however, plants favour N in the form of NO_3^- and the oxidation of NH_4^+ to produce NO_3^- results in the released of H^+ which is a potential source of the increase in soil acidity (Magdoff et al., 1997). This explains the lower soil pH observed in the higher rates of urea. Muhammad Zaid et al. (2014) reported a lower soil pH in oil palm plantations due to acidifying effects of ammonium compared to non-cultivated areas. The findings of this study is congruent with that of Chan et al. (2007) who reported that 100 t ha^{-1} biochar application to Alfisols resulted in an increase in soil pH by 1.22 units in the absence of N fertilizer but the corresponding increase was only 0.61 units with the application of N fertilizer.

In the second planting cycle (Table 3), biochar main treatment effects on soil pH showed that soil applied with 20 t ha^{-1} biochar resulted in significantly higher soil pH (4.28). Adding 10 t ha^{-} biochar did not significantly increase soil pH and soil without biochar treatments resulted in the lowest soil pH (4.07).

The effects of clinoptilolite zeolite diminished in the second planting cycle as biochar main effects alone showed significant increase in soil pH. This indicates that the effects of biochar sustains longer compared with zeolite. Increase in soil pH observed in biochar treated soil may be due to the high ash content of biochar which has the ability to neutralize acidic soils (Nigussie et al., 2012). Increase in soil pH from 4-6 to 6-7 was reported by Cornelissen et al. (2013) with 5% wood biochar application in Ultisols. An increase in soil pH by 0.52 units with 12 t ha^{-1} biochar treatment in a moderately acidic Ultisols Kandiudults in Ethiopia was documented by Abewa et al. (2014). Novak et al. (2009) reported an increase in soil pH up to 64% with poultry litter biochar applied at 40 t ha^{-1} in Norfolk Typic Kandiudults. The rise in pH was attributed to the alkaline oxides or carbonates formed during biochar pyrolysis, that released into the soil and reacted with H^+ and Al^{3+}, thus reducing the exchangeable acidity.

The decrease in soil acidity when biochar is applied may also be the result of decrease in exchangeable aluminium ions in the soil. Aluminium ions (Al^{3+}) are the dominant cations in majority of soils with pH less than 5 (Coleman and Thomas, 1967). Nigussie et al. (2012) recorded an increase by 9% in soil pH with 10 t ha^{-1} maize stalk biochar amendment and the increase was attributed to the high surface area and porous characteristics of biochar that elevates cation exchange capacity thus, resulting in a possibility for Al and Fe to bind with the exchange sites of soils thus decreasing the exchangeable Al and Fe in biochar treated soil. Chan et al. (2007) reported an increase in soil pH by 1.22 units when biochar is applied and the increase in pH was accompanied by a decrease in exchangeable Al by more than 50% at 50 and 100 t ha^{-1} biochar treatments.

In the first planting cycle, higher soil total CEC was observed in soil treated with 20 t ha^{-1} biochar (7.85 cmol$^+$ kg^{-1}) (Table 3). The increase in CEC with 10 t ha^{-1} biochar was not significant (5.68 cmol$^+$ kg^{-1}) compared to that of the unamended soil. Cation exchange capacity was lowest in the unamended soil (5.16 cmol$^+$ kg^{-1}). In the second planting cycle, amending soil with 20 t ha^{-1} biochar resulted in significantly higher CEC (12.36 cmol$^+$ kg^{-1}) and untreated soil resulted in the lowest CEC (7.43 cmol$^+$ kg^{-1}). Cation exchange capacity of the soil treated with 10 t ha^{-1} biochar was 9.40 cmol$^+$ kg^{-1}.

The increase in cation exchange capacity in the biochar treated soil was possibly due to the increase of net negative charges at the surface of biochar which attracts the positive cations, thus increasing the soil CEC. Glaser et al. (2003) attributed the higher net negative charge of the anthropogenic soils rich in black carbon from Brazillian Amazon (the origin of biochar) to oxidation of the aromatic C and formation of carboxyl group at biochar surface. Lehmann et al. (2005) suggested that such formation of carboxyl groups or other functional groups with net negative charge might be from the outcome of two varied processes which were surface oxidation of the biochar particles themselves and/or adsorption of highly oxidised organic matter onto the biochar surface. Liang et al. (2006) concluded that oxidation increased from the biochar's core to the surface and non-biochar particles may be adsorbed on the surface of biochar particles creating highly oxidised surface. As a result of both oxidations, the charge density or potential CEC per unit surface area was increased.

The increase in pH in biochar treated soil may also related to the soil CEC. Soil pH influenced variable charges of soil minerals of Oxisols and Ultisols. As pH increased, the minerals became net-negatively charge which results in increase in soil CEC as the net-negative charges attract positively charged cations minerals

(Shamshuddin and Daud, 2011). The increase in CEC with the increase of pH was also reported by Shamshuddin and Ishak (2010).

Unlike in the first planting cycle, soil CEC was higher in the second planting cycle (Table 3). This could be due to heavy rain in the first planting cycle which may have leached out the cations compared to minimal rain in the second planting cycle. There is also a possibility that the higher CEC in the second planting cycle could be partly due to the aging of biochar. The CEC of biochar has been shown to increase as biochar ages (Cheng et al., 2008) because of an increase in some oxygenated functional groups on the surface of the biochar (Cheng et al., 2006). The increase in CEC in this study due to biochar application is similar to the results of previous researches such as Nigussie et al. (2012) who observed a significant increase in soil CEC by 30% with biochar application in the soil. Cornelissen et al. (2013) also reported a significant improvement in soil CEC in soil treated with biochar in maize farming sites in Zambia. Sukartono et al. (2011) documented an increase in soil CEC by 13% for the application of 15 t ha^{-1} coconut shell biochar in a sandy soil of Lombok, Indonesia. Chan et al. (2007) reported an increase in CEC by 26% with green waste biochar soil amendment.

Figure 3 represents the significant interaction effects ($P<0.05$) of biochar and clinoptilolite zeolite on soil TOC for the first planting cycle. Soil without amendment resulted in lowest soil TOC (1.76%). The 10 and 20 t ha^{-1} biochar increased TOC to 1.99 and 2.59%, respectively. Total organic C for soil treated with 1.25 t ha^{-1} zeolite was 2.23% and TOC increased to 2.23 and 2.28% when treated with a combination of 1.25 t ha^{-1} clinoptilolite zeolite with 10 and 1.25 t ha^{-1} clinoptilolite zeolite with 20 t ha^{-1} biochar, respectively. The TOC for 2.5 t ha^{-1} clinoptilolite zeolite treatment was 2.28%. A combination of 2.5 t ha^{-1} zeolite with 10 t ha^{-1} biochar increased soil TOC to 3.02% and soil TOC was the highest (3.98%) when the same rate of clinoptilolite zeolite combined with higher rate of biochar (20 t ha^{-1}). In the second planting cycle, the biochar main treatment effects on soil TOC (Table 2) showed that soil treated with 20 t ha^{-1} bicohar resulted in significantly higher TOC (4.81%) whereas, soil without biochar resulted in the lowest TOC (3.32%). The TOC for soil treated with 10 t ha^{-1} biochar was 4.15% but the result was not significantly different from no biochar treatment.

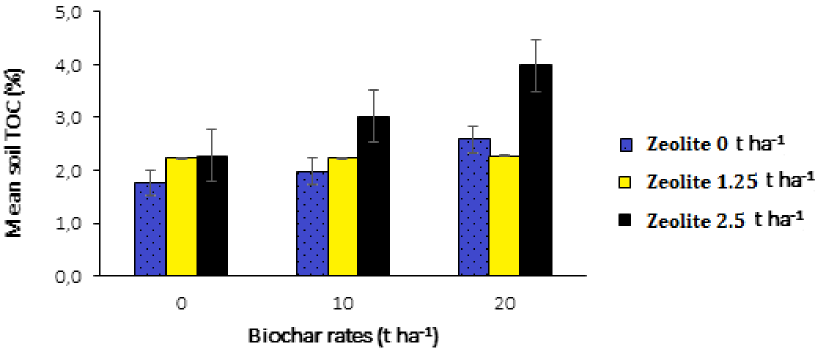

Figure 3. Interaction effect between biochar and clinoptilolite zeolite for soil total organic C for the first planting cycle. Error bars indicates standard error.

For the first planting cycle, soil TOC increased linearly with increasing rates of both biochar and clinoptilolite zeolite amendments. The increase in soil pH with biochar and clinoptilolite zeolite treatments may have influenced the increase in soil organic C by favouring microbial decomposition activities, thus resulting in increased total organic C. However, for the second planting cycle only biochar showed significant main effects on soil TOC (Table 3). This could be due to the recalcitrant effects of biochar over time compared with clinoptilolite zeolite. The organic C in the soil was also influenced by the quality and quantity of organic matter input into the soil (FAO, 2005). The higher soil TOC in plots amended with biochar could be due to the high inherent content of carbon in the biochar, as biochar itself is a term reserved for biomass derived materials contained within the black carbon (BC) continuum (Lehmann et al., 2006). Higher organic C was observed in a *Terra Preta* soil in Brazillian Amazon which is rich in black carbon or biochar compared to the adjacent soil (Liang et al., 2006). Novak et al. (2009) also reported higher soil organic C in biochar treated soils. These findings are also supported by the results of Sukartono et al. (2011) who reported an increase of soil organic C by 27% with 15 t ha^{-1} biochar treatment. Zhang et al. (2011) reported an increase of soil organic C by 25 and 42% with 20 and 40 t ha^{-1} biochar amendments compared with no biochar treatment with urea. Without urea addition, soil organic C was reported to increase by 44 and 58% with 20 and 40 t ha^{-1} biochar treatments, respectively.

Kimetu et al. (2008) also reported that the application of biochar increased the SOC by 45%. The addition of biochar increased the soil organic matter as the biochar itself is a component of soil organic matter (Kimetu et al., 2008). Sinclair et al. (1994) observed an increase in soil C by 0.5% with 10 t ha^{-1} biochar application. Soil total C was increased from 3.57% to 4.50% in Oxisols with 10 t ha^{-1} papermill waste biochar amendment in a study conducted by van Zwieten et al. (2010). An increase of soil TOC by 11% was also reported by Abewa et al., (2014) with 12 t ha^{-1} amendment in a Northwestern Ethiopia Ultisols and Prabha et al. (2013) observed an increase in soil organic C by 13% with biochar treatment under rice cultivation.

Soil available phosphorus, exchangeable potassium, calcium, and magnesium

There were no significant interaction effects between all the three factors on soil available P, K Ca and Mg irrespective of planting cycle (Table 4). In the first planting cycle, only biochar showed significant on main treatment effects for soil available P, so was exchangeable K and Mg. In the second planting cycle, soil available P and exchangeable K was affected by biochar main treatment effects whereas the biochar and zeolite main treatment effects significantly affected soil exchangeable Mg. All the treatments showed no significant effects on soil exchangeable Ca in the second planting cycle.

In the first planting cycle, soil treated with 20 t ha^{-1} biochar resulted in significantly higher soil available P (8.10 mg kg^{-1}). Soil available P was the lowest in untreated soil (1.38 mg kg^{-1}). Applying 10 t ha^{-1} biochar increased soil available P to 3.90 mg kg^{-1} but the increase was not significant compared to untreated soil. After the second crop, mean separation using LSD test resulted in no significance different in soil available P between 10 and 20 t ha^{-1} biochar treatments but both were significantly higher than the 0 t ha^{-1} biochar treatment by 135.00% and 111.67%, respectively.

For soil exchangeable K, 10 t ha^{-1} and 20 t ha^{-1} biochar treatments significantly increased the soil exchangeable K by 64.30% and 111.57 %, respectively compared with 0 t ha^{-1} biochar treatment. Soil without biochar treatment resulted in the lowest soil K (10.98 mg kg^{-1}). In the second planting cycle, soil exchangeable K was the highest in 20 t ha^{-1} biochar treatment (35.74 mg kg^{-1}) while 0 t ha^{-1} biochar treatment resulted in the lowest soil available K (23.65 mg kg^{-1}). Soil exchangeable K for 10 t ha^{-1} biochar treatment (25.24 mg kg^{-1}) was not significantly different than soil available K in 0 t ha^{-1} biochar treatment.

Soil exchangeable Mg was higher in soil treated with 10 and 20 t ha^{-1} compared with soil without biochar application. Unamended soil resulted in the lowest soil Mg (74.06 mg kg^{-1}). In the second planting cycle, biochar main treatment effects on soil exchangeable Mg showed that the 10 and 20 t ha^{-1} biochar amendments resulted in no significant difference in soil exchangeable Mg but both were significantly higher by 9.49 and 14.12%, respectively, compared to 0 t ha^{-1} biochar treatment. For clinoptilolite zeolite main treatment effects, soil exchangeable Mg in soil treated with zeolite at 1.25 and 2.5 t ha^{-1} did not show significant difference but both were significantly higher by 6.06% and 6.02%, respectively, compared with the 0 t ha^{-1} zeolite treatment.

Soil available P was increased with biochar application after both crops. Given the low pH of the field, increase in soil P availability may also be the result of increasing pH in biochar treated soil. At low soil pH, Al concentration in soil solution is higher which may lead to the formation of Al phosphate that can be precipitated or strongly adsorbed in the soil causing a reduction in P availability (von Uexkull, 1986). Shamshuddin and Ishak (2010) reported a decrease in exchangeable Al with increasing soil pH. The increase in pH may reduce the activity of Al, thus contributing to increase in P availability (Shamshuddin et al., 2011).

In a related study, Widowati et al. (2012) reported an increase in soil available P by 28% with biochar treatment in maize field trials. Liang et al. (2006) observed a higher P concentration at all four sites of carbon-rich Anthrosols of the Brazillian Amazon compared to non carbon-rich adjacent soils. Nigussie et al. (2012) reported an increase in P availability with the application of 10 t ha^{-1} maize stalk biochar in soil planted with lettuce. Fellet et al. (2011) reported an increase in soil P concentration in main tailing soil from 81.8 mg kg^{-1} to 445 mg kg^{-1} with 10% biochar addition to the soil and remarkably higher P concentration by 179-208% in biochar treated soil was observed by Widowati and Asnah (2014).

In the second planting cycle biochar treatments resulted in significant effects on soil available K and Mg. Available K and Mg occur in the form of cations (K^+ and Mg^{2+}) in the soil solution. The increase of both cations can be explained by the increase of pH and CEC with biochar application. As pH increases, the net negative charge of variable clay in Oxisols and Ultisols increase (Sanchez and Logan, 1992; Shamshuddin and Daud, 2011). This in turn will increase the soil CEC and adsorption of cations. Biochar also possess the ability to adsorb cations due to its high net negative surface charge and adsorption affinity of cations (Liang et al., 2006). This will result in cations flush on the surface of biochar thus increasing the availability of cationic species in biochar treated soil.

Table 4. Soil available nutrients as affected by biochar, clinoptilolite zeolite, and urea in the first and second planting cycles

	First Planting Cycle				**Second Planting Cycle**			
	Avail. P	**Exch. K (mg kg^{-1})**	**Exch. Ca**	**Exch. Mg**	**Avail. P**	**Exch. K**	**Exch. Ca (mg kg^{-1})**	**Exch. Mg**
Biochar (t ha^{-1})								
0	1.38^{b}	10.98^{b}	181.12^{a}	74.06^{c}	1.80^{a}	23.65^{b}	199.44^{a}	81.68^{b}
10	3.90^{b}	18.04^{a}	157.44^{a}	86.39^{b}	4.23^{b}	25.24^{b}	206.44^{a}	89.43^{a}
20	8.10^{a}	23.23^{a}	192.73^{a}	95.61^{a}	3.81^{b}	35.74^{a}	217.31^{a}	93.22^{a}
P	<0.01	<0.01	0.65	<0.01	0.02	0.02	0.16	<0.01
Std. Error	± 1.34	± 2.30	± 27.38	± 2.87	± 0.60	± 3.22	± 6.43	± 1.44
Zeolite (t ha^{-1})								
0	5.10^{a}	19.58^{a}	164.53^{a}	80.94^{a}	3.41^{a}	28.48^{a}	205.13^{a}	84.70^{b}
1.25	4.31^{a}	18.32^{a}	142.37^{a}	90.12^{a}	3.72^{a}	27.33^{a}	213.71^{a}	89.83^{a}
2.5	3.98^{a}	14.35^{a}	224.39^{a}	84.99^{a}	2.71^{a}	28.81^{a}	204.36^{a}	89.80^{a}
P	0.83	0.26	0.11	0.09	0.48	0.94	0.53	0.02
Std. Error	± 1.34	± 2.30	± 27.38	± 2.87	± 0.60	± 3.22	± 6.43	± 1.44
Urea (kg ha^{-1})								
60	4.83^{a}	15.97^{a}	172.92^{a}	84.74^{a}	3.01^{a}	27.16^{a}	205.16^{a}	88.89^{a}
120	4.09^{a}	18.86^{a}	181.28^{a}	85.96^{a}	3.55^{a}	29.26^{a}	210.31^{a}	87.33^{a}
P	0.64	0.28	0.79	0.71	0.45	0.58	0.49	0.35
Std. Error	± 1.09	± 1.88	. ± 22.35	± 2.34	± 0.49	± 2.63	± 5.23	± 1.18

Means with the same letter within the columns are not significantly different (P<0.05) using LSD test. *P* = probability value from ANOVA.

Increase in soil K by up to 189% with biochar treatment was reported by Widowati et al. (2012) and in a study by Widowati and Asnah (2014), soil available K was observed to be higher (69-89%) as a result of biochar treatment. Soil K was observed to be higher by up to 14% with biochar treatment in an experiment conducted by Nigussie et al. (2012). In an experiment conducted by Sukartono et al. (2011), 15 t ha^{-1} biochar treatment increased soil K by 11% and an increase in soil K with biochar application in Colombian Savanna Oxisols was observed by Major et al. (2010). Fellet et al. (2011) also observed an increase in soil K from 38.2 mg kg^{-1} in nutrient poor mine tailing soil to 2398 mg kg^{-1} K with 10% biochar addition. Prabha et al. (2013) recorded a higher soil available K by 29% with biochar application under rice cultivation.

Major et al. (2010) reported an increment of soil Mg by 64 to 217% in a Colombian Savanna Oxisols with 20 t ha^{-1} biochar treatment compared to soil without biochar treatment. Nigussie et al. (2012) however reported a lower percentage of soil Mg increment (by 8%) with 10 t ha^{-1} biochar in a Southwest Ethiopia Ultisols. An increase by 17% of soil Mg was documented by Sukartono et al. (2011) with 15 t ha^{-1} coconut shell biochar application. After the second crop, zeolite showed significant main effects on soil Mg. Zeolite is manufactured made from alkaline earth mineral possessing net negative surface charge, high cation exchange capacity and high cations adsorption ability (Sand and Mumpton, 1978). Zeolite also has the ability to trap small cations and inhibiting the cations from being leached out. The increase in exchangeable Mg in the soil with zeolite application may be the result of these features of zeolite. This result is supported by the finding of Rădulescu (2013) who also reported an increase of soil mg by up to 72.8% with zeolite application under oat cultivation.

Conclusion

Biochar produced from EFB-POME increased soil total N, P, K, Ca and Mg contents compared with clinoptilolite zeolite. The higher of soil total N, P, K, Ca and Mg could be related to the increase in soil pH, cation exchange capacity, and total organic carbon in biochar treated soil. EFB-POME biochar was more suitable to be used in a tropical soil (Typic Paleudults) compared with clinoptilolite zeolite for improving the selected soil chemical properties. Over time, only biochar treatments showing improvement on soil properties as it can be seen in the results of second cycle planting where contrary to biochar, soil treated with zeolite did not show any significant different on soil properties.

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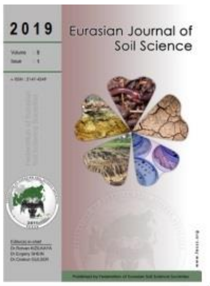

Study on pH in water and potassium chloride for Bulgarian soils

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Abstract

Soil pH is commonly measured in water pH(H_2O) or pH(KCl). The relationship between pH(H_2O) and pH(KCl) across all Bulgarian soils were investigated and results examining the effect of soil type on the relationship were presented. Several functions were used to estimate dependence between the two measures. For all soils and depths, a linear regression accounted for 95.32% of the variation, which predicts pH(KCl) very well. From the analysis of data follows that they were differentiated into three clusters.

Keywords: Soil pH, soil database, cluster analysis.

Introduction

Study on pH measured by different methods are in progress in different countries such as: Romania (Gavriloaei, 2012), Australia (Ahem et al. 1995; Minasny et al., 2011), Poland (Kabała et al., 2016). Unfortunately, there are several measures of soil reaction used worldwide. The most common extracts are distilled water (H_2O), 1 mol L^{-1} KCl (KCl), and 0.01 mol L^{-1} $CaCl_2$ ($CaCl_2$). Different measurement methods lead, however, to incompatibility of data from various countries and disturb data integration in the international soil databases.

In this article the relationship between pH(H_2O) and pH(KCl) across all Bulgarian soils were investigated and results examining the effect of soil type on this relationship were presented. For all soils and depths, several regression equations were calculated, which predicts pH(KCl) in dependence of pH(H_2O). The study was intended to help scientists and practitioners in using both methods of pH when dealing with problems of liming of acidic soils.

Material and Methods

Since 1956 the data from the large-scale soil survey have been used to compile soil maps of Bulgarian geographical regions at different scale. Thematic maps of the whole of Bulgaria have been prepared also to facilitate the soil agro-ecological partition at a scale of 1:600,000 (Yolevski et al., 1980), land evaluation for crop production at 1:1,000,000 scale (Kabakchiev et al., 1985). Until that time the so-called agro-ecological grouping of soils was adopted for the needs of agriculture. In Table 1 the total areas and arable areas are presented.

The materials of the study are the values of pH(H_2O) and pH(KCl) given in Reference database for soils in Bulgaria (Teoharov et al., 2009). This valuable source contains 306 data from different soils, namely: Chernozems (64), Gray Forest soils (33), Pseudopodzolic Forest soils (54), Cinnamonic Forest soils (33), Zheltozem soils (30), Leached Smolnitsa (15), Brown Forest soils (11), Mountainous Meadow soils (3), Alluvial Meadow soils (21), Peat-gley soils (11), Rankers (21), Regosols (9), Rendzinas (2), and Technogenic soils (17).

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Table 1. Agro-ecological groups of the total and arable area (Yolevski, 1986).

Code	Agro-ecological groups	Total area		Arable area	
		1000 ha	(%)	1000 ha	(%)
01	Calcareous and typical chernozems	1047.25	9.435	444.04	16.332
02	Leached chernozems	967.29	8.714	410.13	13.965
03	Podzolic chernozems and dark gray forest soils	538.62	4.852	228.37	5.598
04	Gray forest soils	1158.31	10.435	491.12	11.657
05	Light gray pseudopodzolic forest soils	577.49	5.203	244.86	3.742
06	Smolnitsa soils	659.67	5.943	279.70	8.698
07	Cinnamonic forest soils	2037.87	18.359	864.06	14.617
08	Cinnamonic podzolic forest soils	928.42	8.364	393.65	4.374
09	Brown forest soils	1910.16	17.209	809.91	2.909
10	Meadow soils	999.50	9.005	423.79	16.653
11	Rendzinas (humus-carbonate soils)	275.42	2.481	116.78	1.455
	Sum	11100.00	100.00	4706.40	100.00

Preliminary check of the data shows that three points were erroneous (Chernozem profile No. 32/3/C1k and C2k; Gray Forest profile No. 8 B2t) and were excluded from the analysis. The Technogenic soils also have been excluded. So we had 304 pairs for analysis. First step was performing descriptive statistical analysis. Results are given in Table 2 and 3.

Table 2. Statistical characteristics of different soils.

Soil	Variable	Valid N	Mean	Median	Std.Dev.	Minimum	Maximum	Skewness	Kurtosis
Chernozems	H_2O	62	7.4403	7.75	0.7221	6.00	8.30	-0.686	-0.945
	KCl	62	6.6226	7.10	0.9510	4.60	7.80	-0.725	-0.897
Gray Forest	H_2O	32	6.2531	5.50	1.2324	4.30	8.20	0.541	-1.307
	KCl	32	5.2922	4.70	1.2422	3.40	7.40	0.524	-1.333
Pseudopozolic Forest	H_2O	54	5.3796	4.85	1.1690	4.00	8.40	1.209	0.269
	KCl	54	4.3287	3.85	1.2783	2.90	7.20	1.174	0.044
Cinnamonic Forest	H_2O	32	7.0500	7.70	1.1188	4.70	8.20	-1.049	-0.249
	KCl	32	6.1016	6.80	1.2652	3.40	7.40	-1.048	-0.219
Zheltozem	H_2O	30	4.9300	4.90	0.2818	4.40	5.90	1.322	4.224
	KCl	30	3.8017	3.75	0.3865	3.20	4.95	1.489	2.905
Leached Smolnitsa	H_2O	15	6.9867	7.10	0.7130	6.10	8.20	0.332	-1.095
	KCl	15	5.9933	5.90	0.7363	5.10	7.20	0.377	-1.329
Brown Forest	H_2O	11	5.4864	5.40	1.1845	4.00	7.20	0.074	-1.640
	KCl	11	4.4055	4.40	1.0340	3.10	5.90	0.067	-1.667
Alluvial Meadow	H_2O	21	7.6810	8.10	0.6853	5.80	8.30	-1.236	1.135
	KCl	21	7.0714	7.50	0.8113	5.40	7.80	-1.104	-0.246
Peat-gley	H_2O	11	7.5727	7.70	0.4052	6.80	8.00	-0.839	-0.493
	KCl	11	7.0727	7.10	0.2687	6.50	7.40	-0.818	0.757
Rankers	H_2O	21	4.9643	4.95	0.5730	4.10	6.20	0.035	-0.418
	KCl	21	4.2333	4.20	0.6187	3.10	5.50	0.217	-0.500
Regosols	H_2O	9	7.9333	8.00	0.5745	6.70	8.60	-1.275	1.873
	KCl	9	6.8556	6.90	0.6002	5.60	7.50	-1.139	1.301

Table 3. Descriptive statistics from combined analysis of pH(H_2O) and pH(KCl).

pH	N	Mean	Median	Std.Dev.	Min	Max	Skewness	Kurtosis
H_2O	304	6.4158	6.45	1.3879	4.00	8.60	-0.095	-1.519
KCl	304	5.4976	5.50	1.5262	2.90	7.80	-0.047	-1.528

There is another collection of data with the properties of soils in Bulgaria (Ninov et al., 1975). Unfortunately, it is too limited and not all pH analyzes by both methods are included simultaneously for different soils.

Next step was performing regression analysis to describe the link between pH(H_2O) and pH(KCl). The aim was to find the most appropriate function, which accurately describes the relationship between the values of both pH analyzes. It was also interesting to investigate the distribution of pH and its differentiation across the different soil groups. For this purpose cluster analysis was applied.

We are looking for a regression of the type

$$y = f(x),$$

where y = pH(KCl), x = pH(H_2O) and f is a selected regression model.

We consider the following types of equations:

(a) $y = a + bx,$ Linear function

(b) $y = a + bx + cx^2,$ Quadratic function

(c) $y = \frac{1}{a + bx + cx^2},$ Reciprocal Quadratic function

(d) $y = ab^x x^c,$ Hoerl function

Selected function have no more than three parameters to be estimated. The principle of Ocam is followed: "Of two competing theories, the simpler explanation of an entity is to be preferred" (Duignan, 2017). If you have a few hypotheses that could explain an observation, it is usually best to start with the simplest one.

Results and Discussion

The United States Department of Agriculture, formerly Soil Conservation Service (Soil Survey Staff, 1993) classifies soil pH in water ranges as follows in Table 4. FAO classification applicable in Bulgaria is given in (Gyurov and Artinova, 2015).

Table 4. pH classification by USA and FAO (applicable in Bulgaria).

USA accepted classification		FAO accepted classification	
Denomination	pH range	pH(H_2O)	Reaction
Ultra acid	< 3.5	< 3.0	Extremely acid
Extremely acid	3.5–4.4	3.0-4.0	Very strongly acid
Very strongly acid	4.5–5.0	4.1-5.0	Strongly acid
Strongly acid	5.1–5.5	5.1-6.0	Moderately acid
Moderately acid	5.6–6.0	6.1-6.9	Slightly acid
Slightly acid	6.1–6.5	7.0	Neutral
Neutral	6.6–7.3	7.1-7.5	Very slightly alkaline
Slightly alkaline	7.4–7.8	7.6-8.1	Slightly alkaline
Moderately alkaline	7.9–8.4	8.2-8.6	Moderately alkaline
Strongly alkaline	8.5–9.0	8.7-8.9	Alkaline
Very strongly alkaline	> 9.0	9.0-10.0	Strongly alkaline
		10.1-11.0	Very strongly alkaline

First, for each of the soils all models (a), (b), (c) and (d) are calculated. Results of corresponding correlation coefficients R^2 are presented in Table 5. Because of their small numbers of data Mountainous Meadow soils and Rendzinas are excluded from separate consideration, but they are included in the combined analysis.

Table 5. Values of correlation coefficients R^2 of models for different soils.

Soils	N	Models			
		(a)	(b)	(c)	(d)
Chernozems	62	0.9078	0.9174	0.9206	0.9183
Gray Forest soils	32	0.9291	0.9291	0.9299	0.9292
Pseudopodzolic Forest soils	54	0.9623	0.9636	0.9660	0.9634
Cinnamonic Forest soils	33	0.9786	0.9786	0.9791	0.9786
Zheltozem soils	30	0.9152	0.9161	0.9176	0.9161
Leached Smolnitsa	15	0.9060	0.9080	0.9082	0.9081
Brown Forest soils	11	0.9884	0.9884	0.9893	0.9884
Alluvial Meadow soils	21	0.9298	0.9328	0.9328	0.9323
Peat-gley soils	11	0.8008	0.8597	0.8600	0.8596
Rankers	21	0.8438	0.8439	0.8424	0.8438
Regosols	9	0.9945	0.9943	0.9949	0.9948

Types of models: (a) Linear function, (b) Quadratic function, (c) Reciprocal Quadratic function, (d) Hoerl function.

It is evident that the highest values of R^2 are for the model (c) Reciprocal Quadratic function in almost all soils. But let's not rush to the conclusions about the most suitable function before looking at combined data and applying Ocam's principle.

In the analysis of all 304 value pairs, the following regressions are obtained,

where y = pH(KCl) and x = pH(H_2O):

(a)	$y = a + bx,$	$a = -1.39116$	$b = 1.07371$		$R^2 = 0.9533$
(b)	$y = a + bx + cx^2,$	$a = -0.38044$	$b = 0.73943$	$c = 0.02632$	$R^2 = 0.9766$
(c)	$y = \dfrac{1}{a + bx + cx^2},$	$a = 0.72916$	$b = -0.13037$	$c = 0.0006526$	$R^2 = 0.9776$
(d)	$y = ab^x x^c,$	$a = 0.49694$	$b = 0.99356$	$c = 1.31154$	$R^2 = 0.9767$

If you follow the Ocam's principle, it is natural to accept the linear regression, which has only two coefficients:

$$\text{pH(KCl)} = -1.39116 + 1.07371 \times \text{pH}(H_2O) \text{ with } R^2 = 0.9533.$$

The R-Squared statistic indicates that the model as fitted explains 95.33% of the variability in pH(KCl). The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 95.32%. The standard error of the estimate shows the standard deviation of the residuals to be 0.33029. This value can be used to construct prediction limits for new observations.

If available data for pH are analyzed with KCl, it can be used the reverse analysis, where y = pH(H_2O), x = pH(KCl) and gives the equation:

$$\text{pH}(H_2O) = 1.53466 + 0.88787 \times \text{pH(KCl)} \text{ with } R^2 = 0.9533.$$

It should not be forgotten that the analyzes of both methods - in water and potassium chloride, produce results with a certain error. It is logical to use the orthogonal regression method (Total least squares), which is appropriate in such case. That gives the equation:

$$\text{pH(KCl)} = -0.076319 + 0.86878 \times \text{pH}(H_2O) \text{ with } R^2 = 0.9536.$$

It should be noted that this method gives the same average value of the dataset, but with a smaller standard error equal to 1.2057. Figure 1 shows the straight lines of linear and orthogonal regression.

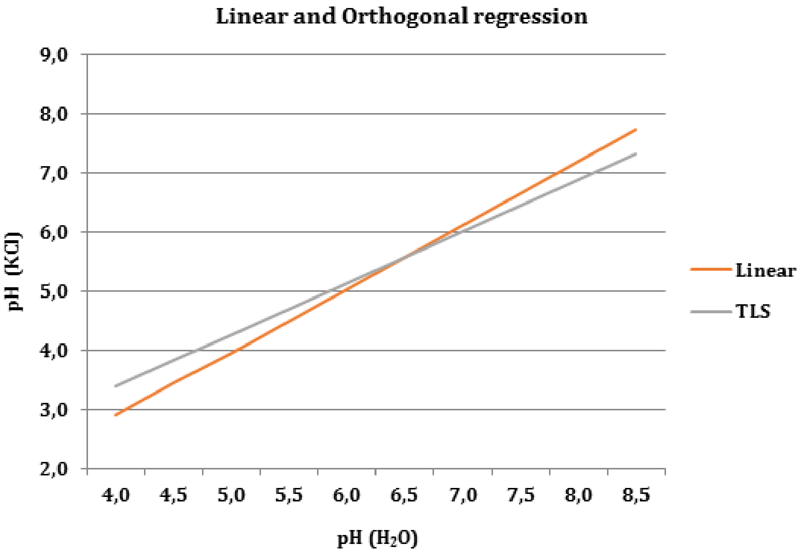

Figure 1. Both regression lines.

It is interesting to see the histograms of the distributions of the two variables.

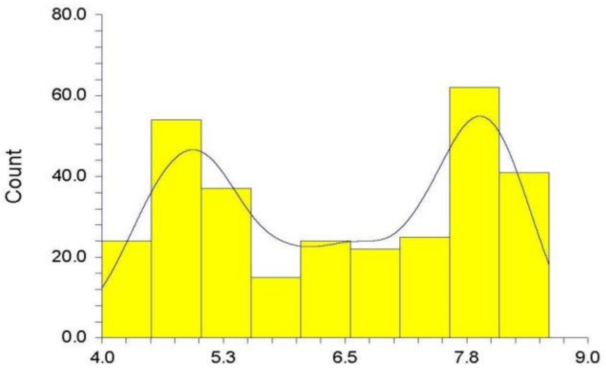

Figure 2. Histogram of pH(H_2O)

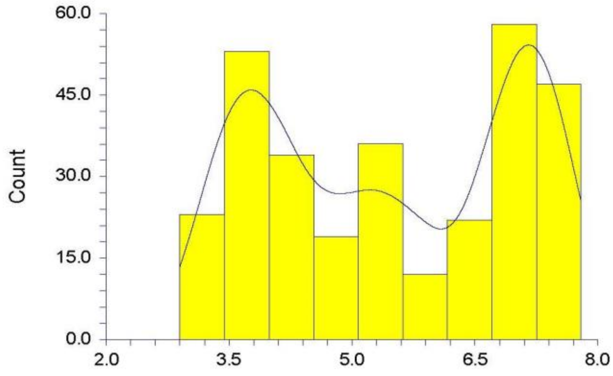

Figure 3. Histogram of pH(KCl)

Obviously, it differs significantly from Normal (Gaussian) distribution and is a mixture of two or more different distributions. This justifies the use of cluster analysis to identify the groups that determine the differences in analyses. As a result of this analysis, three clusters were obtained, the statistical characteristics of which are given in Table 6.

Table 6. Statistical characteristics of three Clusters.

	pH	N	Mean	Median	St. Dev.	Min	Max	Skewness	Kurtosis
Cluster 1	H_2O	123	7.8728	7.90	0.3343	6.80	8.60	-0.470	0.208
	KCl	123	7.1305	7.20	0.3612	6.30	7.80	-0.311	-0.447
Cluster 2	H_2O	62	6.4565	6.40	0.4344	5.40	7.20	-0.095	-0.741
	KCl	62	5.4387	5.45	0.4112	4.60	6.30	0.100	-0.264
Cluster 3	H_2O	119	4.8887	4.90	0.4090	4.00	5.60	-0.171	-0.620
	KCl	119	3.8404	3.80	0.4563	2.90	4.90	0.294	-0.562

Closer examination of the data shows the following:

- Members of Cluster 1 are predominantly data from Alluvial Meadow soils, Chernozems and Gray Forest soils. Hypothesis for Normal distribution can't be confirmed.

- Members of Cluster 2 are data from Chernozems, Brown Forest soils and Leached Smolnitsa. Hypothesis for Normal distribution can't be rejected.

- Members of Cluster 3 are data from Pseudopodzolic Forest soils, Rankers and Zheltozem soils. Hypothesis for Normal distribution can't be rejected.

Figure 4 shows a distinct differentiation between the three clusters.

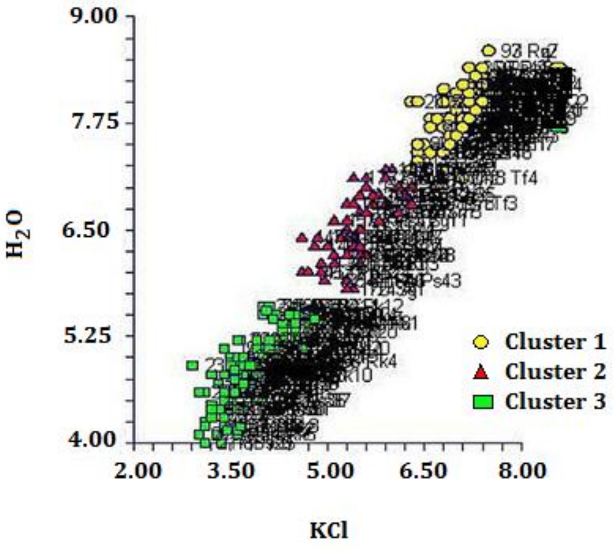

Figure 4. Cluster analysis

The presence of objects from the same soil group as members of different clusters can be explained by the large soil diversity in Bulgaria and some inaccuracies in the identification of soil profiles.

The simple linear model equation (a) seems to perform very well and is almost accurate as the nonlinear models equations (b, c, d) across all the datasets. As a result, values of pH in KCl can be predict as a function of pH in water and vice versa. From a purely statistical point of view, it is advisable to use orthogonal linear regression, which takes into account the fact that in both methods the results are obtained with a certain error.

Conclusion

The analysis of 304 pairs results from soil samples is the basis for reliable conclusions. The results of this study allow soil reaction data obtained from different methods - with distilled water (H_2O) and 1 mol L^{-1} KCl (KCl), to be converted and integrate into national and international soil databases. The difference between pH in water and pH in KCl is that the first refers to the acidity of the soil solution, while the pH in KCl refers to the acidity of the soil solution plus the reserve acidity in the colloids and therefore it is always more acid than pH in water. Regression between pH(H_2O) and pH(KCl) is important because it gives the possibility for soil scientists to directly compare own values with the data already existing in literature from other country.

Monitoring pH changes over time is an important management tool. By comparing past and present soil tests, it is possible to see if the soil acidity is increasing over time and, if it is, to alter management methods to prevent this trend from continuing. Analysis of the results from the soil survey in Bulgaria shows that almost half of the soil resources are vulnerable to anthropogenic acidification. Special attention must be paid to genetically acid soils under cultivation. Their additional acid loading has to be controlled to avoid anthropogenic soil degradation.

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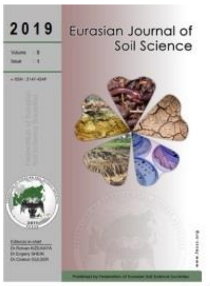

Interactive effect of phosphorus and boron on plant growth, nutrient accumulation and grain yield of wheat grown on calcareous soil

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Abstract

Most of the arable soils in Pakistan are deficient in plant available phosphorus (P) and boron (B) primarily due to alkaline and calcareous nature along with low organic matter. A combined deficiency of these nutrients may intensify the plant growth suppression by reducing their efficient utilization. A pot experiment was conducted to investigate the interactive effect of P and B on growth, nutrient accumulation and grain yield of wheat grown on calcareous soil. Wheat crop was grown at three P levels (45, 90 and 135 kg P ha^{-1}) in combination with five B levels (0, 0.5, 1.0, 1.5 and 2.0 kg B ha^{-1}) following completely randomized design. The results revealed that yield and yield related attributes increased linearly with the addition of B at each P level. Nonetheless, the significant interactive effect of both nutrients was most pronounced in the treatment having 90 kg P ha^{-1} and 1.5 kg B ha^{-1}. Applied B rates resulted in relatively higher P concentration in grains and straw at P level of 90 kg ha^{-1} contrarily to 45 and 135 kg P ha^{-1}. The B concentration in grains and straw increased with corresponding addition of B at each P level but at variable rate, with the maximum response at higher P level. Grain and straw yield illustrated positive correlation with total P uptake (R^2 = 0.96 and 0.81) and total B uptake (R^2 = 0.95 and 0.70) respectively. Likewise, positive correlation (R^2 = 0.94) between total P uptake and total B uptake under combined application of P and B indicated their synergistic relationship. Overall, the treatment combination of 90 kg P ha^{-1} with 1.5 kg B ha^{-1} was found as the most suitable dose for better plant growth, nutrient accumulation and grain yield of wheat.

Keywords: Boron nutrition, grain yield, nutrient interaction, synergism, wheat.

Article Info

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Introduction

Phosphorus (P) is the second essential macronutrient after nitrogen required for normal plant growth and development (Brady and Weil, 2008). It is the key constituent of nucleic acids, phospholipids and ATPs and play role in array of plant cellular processes such as cell division, energy storage and transfer, respiration, photosynthesis and enzymatic regulation (Watanabe et al., 2006; Lambers and Plaxton, 2015). It is involved in seedling development, growing of early roots, early heading formation and accelerates maturity of crops (Alinajoati et al., 2011). Boron (B) is also an essential micronutrient having crucial role in multiple physiological and biochemical processes within plant body such as cell division and enlargement, cell wall formation, sugar translocation, carbohydrate metabolism, nitrogen metabolism and water relations (Oyinola, 2007; Marschner, 2012). On plant level, the key role of B includes floral organs development, flower male fertility and pollen tube growth (Gupta and Solanki, 2013).

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Deficiencies of P and B are among the leading soil fertility problems in Pakistan where most of the cultivated soils are alkaline and calcareous nature characterized by low organic matter and high base saturation (Niaz et al., 2016). Although many soils have large reserves of total P, but the bio-available fraction is often 100-times less than the total P (Hinsinger et al., 2011). Added P may form secondary minerals of calcium and magnesium or bound to surfaces of $CaCO_3$ and clay minerals in alkaline calcareous soils thereby reducing its availability to plants (Akhtar et al., 2008, Irfan et al., 2016; Abbas et al., 2018a). Phosphorus deficiency reduces cell division, carbohydrate metabolism, soluble protein contents and dry matter accumulation (Lambers and Plaxton, 2015). Boron is the second most deficient micronutrient in Pakistan after zinc and is reported to influence the growth of major filed crops like wheat, cotton, maize, rice, sugarcane, potato, rapeseed and mustard (Rashid, 2006). Its deficiency impaired the biomass production by manipulating relative concentration of individual element as well as the balance among certain nutrient elements within plants (Tariq and Mott, 2007).

Various soil factors influence the availability of B to plants i.e., soil pH, native soil B contents, organic matter, carbonates, clay mineralogy, soil moisture, temperature and soil texture (Matula, 2009). The rapid fixation of applied B on calcareous soils is a serious problem to maintain adequate B concentration in soil solution (Majidi et al., 2010). Interaction of B with other nutrients could be antagonistic or synergistic depending upon soil type, crop species, growth stages, plant tissues and environmental conditions (Tariq and Mott, 2007). Type of B interaction with other nutrients results in shifting of internal physiological balance between certain elements causing secondary alterations in the absorption and accumulation of other ions (Bonilla et al., 2004). Huang et al. (2012) have reported the increase in P uptake by plants under B application indicating their synergistic relationship. Positive interaction of adequate P and B levels has been found in *brassica* resulting in enhanced biomass production (Lei et al., 2009).

Wheat (*Triticum aestivum* L.) is an important cereal crop having a central significance in agriculture sector of Pakistan. During 2016-17, area under wheat cultivation in Pakistan was 9.05 million hectares with total production of 25.75 million tonnes. It contributed 9.6% in value addition of agriculture and 1.9% in GDP of Pakistan (GOP, 2017). Cereal crops are relatively tolerant to B deficiency during vegetative growth phase. Nonetheless, during reproductive phase, B deficiency may cause severe yield losses through sterility (Uraguchi and Fujiwara, 2011). The yield losses in wheat by sterility can be retrieved by ensuring adequate B supply to plants during reproductive phase. Several earlier investigations revealed that combined application of P and B significantly enhanced the growth, yield and quality of various field crops (Huang et al., 2012; Kabir et al., 2013; Chowdhury et al., 2015; Muhlbachova et al., 2017). The current study was therefore conducted to investigate the interactive effect of P and B on growth, nutrient accumulation and grain yield of wheat grown on calcareous soil.

Material and Methods

Plant material and site description

Healthy and uniform seeds of wheat genotype TD-1 were kindly provided by wheat section of Agriculture Research Institute, Tandojam – Pakistan. The study was carried out during Rabi, 2016-17 under natural conditions in a net-house at Nuclear Institute of Agriculture (NIA), Tandojam – Pakistan (Latitude 25º 25' 19.8" North and Longitude 68º 32' 27.8" East). The climate of the research area is arid with mean annual precipitation of 136 mm. During the study period, the average daily maximum and minimum temperatures were 27 and 9.8 ^{o}C respectively, while average evaporation was 2.7 mm day^{-1}, average sunshine was 8.0 hours day^{-1}, and average relative humidity was 54.9 %. The maximum total rainfall (3.0 mm) was recorded in the month of January, 2017 (NAMC, 2017). Bulk soil (15 cm surface layer) was collected from experimental farm area of NIA, Tandojam. Then a composite sample of the selected soil was air dried and grinded to pass through 2 mm sieve and analyzed for basic soil physico-chemical properties (Table 1). In brief, the respective soil was silt loam in texture characterized by alkaline in reaction, low in organic matter, nitrogen, available phosphorus and boron while high in available potassium and calcium carbonate ($CaCO_3$) contents.

Pot experiment

Plastic pots (19 cm diameter, 30 cm depth) inner lined with polythene sheet were filled with seven kilograms of thoroughly mixed soil. Experiment was conducted according to completely randomized design with factorial arrangements having three replications. Canal water was used in each pot prior to sowing of seeds for attaining appropriate moisture for seed germination. In each pot, five seeds were sown manually while three plants were maintained after seedling emergence and allowed to grow till maturity. Fifteen treatment combinations were formulated using three P levels (i.e. 45, 90 and 135 kg P ha^{-1}) and five B levels (i.e. 0, 0.5, 1.0, 1.5, and 2.0 kg B ha^{-1}). Each treatment was also fertilized with nitrogen (N) and potassium (K) at the rate of 120 kg N ha^{-1} and 60 kg K ha^{-1} respectively. Description of treatments detail is presented in Table 2. The required quantities of P and B according to treatment plan and potassium were applied at the time of wheat sowing while, N was applied in three equal splits viz; at sowing, two, and five weeks after sowing. Urea (46% N), triple super phosphate (TSP, 46% P_2O_5) and sulphate of potash (SOP, 50% K_2O) were used as the source of N, P and K, respectively. All pots were irrigated during the entire crop period according to plant requirements. Plants were harvested at maturity, threshed manually to separate grains from straw. After recording yield and yield related attributes, samples were dried at 70°C for 72 hours in a forced air-driven oven till further analysis.

Table 1. Basic physico-chemical properties of collected soil used in experiment (0-15 cm surface soil)

Soil properties	Unit	Value	Method/ Reference
Physical properties			
Sand	%	22.22	Bouyoucos (1962)
Silt	%	55.83	~
Clay	%	21.95	~
Textural class	-	Silt loam	~
Chemical properties			
pH $_{(1:2.5)}$	-	8.10	Mclean (1982)
EC $_{(1:2.5)}$	dS m^{-1}	0.56	Richards (1954)
Total calcium carbonate	%	6.25	Estefan et al. (2013)
Organic matter	%	0.83	Nelson and Sommers (1982)
Oxidizable organic carbon	%	0.36	~
Total organic carbon	%	0.48	~
Kjeldahl nitrogen	%	0.04	Jackson (1962)
Available phosphorus	mg kg^{-1}	2.23	Soltanpour and Workman (1979)
Available potassium	mg kg^{-1}	250	~
Available zinc	mg kg^{-1}	0.99	~
Available iron	mg kg^{-1}	40.24	~
Available boron	mg kg^{-1}	0.65	Estefan et al. (2013)

Table 2. Detail of treatments used in experiment

Treatment	Treatment abbreviation	Phosphorus applied		Boron applied	
		kg P ha^{-1}	mg P kg^{-1} soil	kg B ha^{-1}	mg B kg^{-1} soil
T_1	$P_{45} - B_{0.0}$	45	22.5	0.0	0.00
T_2	$P_{45} - B_{0.5}$	45	22.5	0.5	0.25
T_3	$P_{45} - B_{1.0}$	45	22.5	1.0	0.50
T_4	$P_{45} - B_{1.5}$	45	22.5	1.5	0.75
T_5	$P_{45} - B_{2.0}$	45	22.5	2.0	1.00
T_6	$P_{90} - B_{0.0}$	90	45.0	0.0	0.00
T_7	$P_{90} - B_{0.5}$	90	45.0	0.5	0.25
T_8	$P_{90} - B_{1.0}$	90	45.0	1.0	0.50
T_9	$P_{90} - B_{1.5}$	90	45.0	1.5	0.75
T_{10}	$P_{90} - B_{2.0}$	90	45.0	2.0	1.00
T_{11}	$P_{135} - B_{0.0}$	135	67.5	0.0	0.00
T_{12}	$P_{135} - B_{0.5}$	135	67.5	0.5	0.25
T_{13}	$P_{135} - B_{1.0}$	135	67.5	1.0	0.50
T_{14}	$P_{135} - B_{1.5}$	135	67.5	1.5	0.75
T_{15}	$P_{135} - B_{2.0}$	135	67.5	2.0	1.00

Each treatment was also fertilized with nitrogen and potassium at the rate of 120 kg N and 60 kg K ha^{-1}. The 120 kg N, 90 kg P and 60 kg K ha^{-1} are the general recommended rates of N, P and K for wheat crop in the region

Phosphorus and boron assay

Oven dried samples (grains and straw) were grinded using Wiley's mill (3383L10, Thomas Scientific, USA) fitted with stainless steel blades to pass through a 0.42 mm screen. Total P concentration was determined following yellow color method as described by Chapman and Pratt (1961). Briefly, the plant material (0.2 g each) was wet digested using 10 mL of di-acid mixture [nitric acid: perchloric acid (5:1, *v/v*)] in a conical flask, kept overnight and then placed on a hot plate until a clear solution was obtained. After digestion, volume was made upto 100 mL with distilled water and then filtered. The 10 mL of clear filtrate and 10 mL of ammonium-vanadomolybdate reagent was used to develop yellow color. For B determination, samples (grains and straw) were ashed at 550°C for six hours and subsequently ash was treated with 10 mL of 0.36 N H_2SO_4 on a steam bath for 20 minutes. Azomethine-H was used for developing color for B determination by taking 1 mL sample aliquot into 10 mL polypropylene tube (Bingham, 1982). Total P and B concentration in the samples was determined by reading light absorption at 470 nm wavelength using spectrophotometer (U-2900UV/VIS, Hitachi, Japan). Phosphorus and boron uptake by grains and straw of wheat plants was calculated as described by Irfan et al. (2017).

$$\text{Phosphorus uptake (mg plant}^{-1}) = \text{Phosphorus concentration (mg g}^{-1}) \times \text{Dry matter (g plant}^{-1})$$

$$\text{Boron uptake (µg plant}^{-1}) = \text{Boron concentration (µg g}^{-1}) \times \text{Dry matter (g plant}^{-1})$$

Statistical analysis

The data regarding plant growth, yield and related attributes, and nutrient uptake by wheat plants under combined P and B fertilization was statistically analyzed using computer software STATISTIX 8.1 (Analytical Software, Inc., Tallahassee, FL, USA) following the methods of Steel et al. (1997). Correlations among various parameters were carried out using Microsoft Excel (Redmond, WA, USA). A two factorial completely randomized design was employed for analysis of variance while least significant difference test at $p \leq 0.05$ was used to determine the differences among treatment means.

Results

Yield and yield related attributes

The data regarding yield and yield related attributes (i.e. plant height, number of tillers per plant (NTP), number of grains per spike (NGS) and 100-grain weight) of wheat crop is presented in Table 3.

Table 3. Interactive effect of phosphorus and boron on yield and yield attributes of wheat grown on calcareous soil

Treatments	Plant height (cm)	No. of tillers plant^{-1}	No. of grains spike^{-1}	100-grain weight (g)	Grain yield (g plant^{-1})	Straw yield (g plant^{-1})
$P_{45} - B_{0.0}$	65.1 g	4.0 d	37.0 e	2.57 d	3.58 e	6.34 i
$P_{45} - B_{0.5}$	66.4 fg	4.0 d	38.7 e	2.64 d	3.72 e	6.77 hi
$P_{45} - B_{1.0}$	66.9 fg	4.2 cd	40.0 de	3.78 c	3.94 e	6.80 hi
$P_{45} - B_{1.5}$	67.7 e-g	4.3 b-d	41.3 c-e	3.89 bc	4.07 e	7.23 g-i
$P_{45} - B_{2.0}$	68.4 d-g	4.4 b-d	43.3 b-e	3.96 bc	4.13 e	7.45 g-i
$P_{90} - B_{0.0}$	70.4 c-g	5.1 ab	49.0 a-d	4.26 a-c	5.83 b-d	8.61 f-h
$P_{90} - B_{0.5}$	70.6 c-f	5.2 a	49.7 a-d	4.53 ab	5.39 d	9.17 fg
$P_{90} - B_{1.0}$	71.8 b-f	5.1 ab	50.7 a-c	4.61 ab	5.68 cd	10.19 ef
$P_{90} - B_{1.5}$	73.0 a-e	5.3 a	53.7 a	4.77 a	6.13 a-c	12.14 de
$P_{90} - B_{2.0}$	73.8 a-d	5.7 a	53.7 a	4.87 a	6.14 a-c	13.24 cd
$P_{135} - B_{0.0}$	75.6 a-c	5.0 a-c	51.0 a-c	4.78 a	5.81 b-d	14.60 bc
$P_{135} - B_{0.5}$	76.6 ab	5.1 ab	51.7 ab	4.88 a	6.38 ab	16.36 ab
$P_{135} - B_{1.0}$	77.3 ab	5.1 ab	53.3 a	4.79 a	5.76 b-d	16.58 ab
$P_{135} - B_{1.5}$	77.7 a	5.7 a	53.7 a	4.87 a	6.61 a	16.64 a
$P_{135} - B_{2.0}$	76.2 ab	5.6 a	52.3 ab	4.81 a	5.92 b-d	16.79 a
LSD $_{0.05}$ (P)	2.45	0.36	4.42	0.33	0.30	0.90
LSD $_{0.05}$ (B)	3.17	0.46	5.70	0.43	0.39	1.16
LSD $_{0.05}$ (P × B)	5.48	0.80	9.87	0.74	0.68	2.01

Treatment explanations are in Table 2. P = phosphorus levels; B = boron levels; P × B = interaction between P and B levels. Treatment means not sharing similar letter(s) in the same column differ significantly from each other (LSD test, $p \leq 0.05$). Values are means of three replications (n = 3)

The P and B levels influenced significantly ($p \leq 0.05$) the plant height, NTP and NGS. Nonetheless, the interaction between P and B levels was non-significant. Plant height increased linearly with corresponding increase in B levels at each P level. Maximum plant height (77.7 cm) was recorded in treatment $P_{135} - B_{1.5}$ which was statistically at par to treatment $P_{90} - B_{1.5}$ and onward all other treatments. The effect of B levels was most pronounced for NTP at lower P level as compared to medium and higher P levels. Minimum NTP (4.0) were observed in treatment $P_{45} - B_{0.0}$ while maximum NTP (5.7) were recorded in treatments $P_{90} - B_{2.0}$

and $P_{135} - B_{1.5}$. The NGS showed increasing trend to applied B rates with relatively higher response at lower P level (i.e. 45 kg P ha^{-1}) than at higher P levels (i.e. 90 and 135 kg P ha^{-1}). The maximum NGS (53.7) were counted in treatment $P_{135} - B_{1.5}$, while the treatment $P_{45} - B_{0.0}$ produced minimum NGS (37.0). Phosphorus and B interaction had significant ($p \leq 0.05$) effects on 100-grain weight, grain yield and straw yield (Table 3). The treatment $P_{135} - B_{0.5}$ produced highest 100-grain weight of 4.88 g among all treatments. The treatment $P_{135} - B_{1.5}$ produced maximum grain yield (6.61 g plant^{-1}) which was at par to grain yield at $P_{135} - B_{0.5}$ (6.38 g plant^{-1}), $P_{90} - B_{2.0}$ (6.14 g plant^{-1}) and $P_{90} - B_{1.5}$ (6.13 g plant^{-1}). Straw yield illustrated increasing trend in relation to B addition at each P level. Boron application at the rate of 2.0 kg ha^{-1} showed maximum response for straw yield at all P levels. The treatment $P_{135} - B_{2.0}$ produced maximum straw yield of 16.79 g plant^{-1} while minimum grain yield of 6.3 g plant^{-1} was noticed in $P_{45} - B_{0.0}$ treatment.

Phosphorus accumulation

Phosphorus concentration [P] in grains of wheat plants was increased significantly ($p \leq 0.05$) in response to combined application of increasing P and B levels (Table 4). The maximum grain [P] was estimated in treatment $P_{135} - B_{2.0}$ while minimum was determined in treatment $P_{45} - B_{0.0}$ (4.17 vs. 2.70 mg g^{-1}). Significant main effects of P and B levels were observed for straw [P] of wheat plants. The straw [P] enhanced linearly in relation to increasing P and B levels with maximum value of 1.43 mg g^{-1} in $P_{135} - B_{2.0}$ treatment. Phosphorus uptake by grain, straw and total (grain + straw) was increased significantly with the additional inputs of P and B fertilizers (Table 4). Overall, the response of higher P level was most pronounced in terms P uptake by grains and straw as compared to lower levels. The treatment $P_{90} - B_{1.5}$ exhibited grain P uptake of 22.59 mg plant^{-1}, which was statistically at par to all other subsequent treatments. Nonetheless, maximum grain P uptake (24.63 mg plant^{-1}) was recorded in $P_{135} - B_{2.0}$ treatment. Likewise, highest straw P uptake was noticed in treatment $P_{135} - B_{2.0}$ while minimum was observed in treatment $P_{45} - B_{0.0}$ (5.40 vs. 24.12 mg plant^{-1}). The maximum total P uptake (50.11 mg plant^{-1}) by wheat plants was recorded in pots with treatment $P_{135} - B_{1.5}$ showing statistically similarity to treatments $P_{135} - B_{2.0}$ (48.75 mg plant^{-1}), $P_{135} - B_{0.5}$ (46.84 mg plant^{-1}), and $P_{135} - B_{1.0}$ (45.63 mg plant^{-1}).

Table 4. Interactive effect of phosphorus and boron on phosphorus concentration and uptake by grains and straw of wheat plants grown on calcareous soil

Treatments	P concentration (mg g^{-1})		P uptake (mg plant^{-1})		
	Grain	Straw	Grain	Straw	Total
$P_{45} - B_{0.0}$	2.70 d	0.84 g	9.69 e	5.40 i	15.10 f
$P_{45} - B_{0.5}$	2.93 cd	0.95 fg	11.03 e	6.45 hi	17.48 f
$P_{45} - B_{1.0}$	3.03 cd	1.01 e-g	12.30 e	6.85 hi	19.15 f
$P_{45} - B_{1.5}$	3.11 cd	1.03 d-g	12.62 e	7.42 hi	20.04 f
$P_{45} - B_{2.0}$	3.12 cd	1.08 c-g	12.89 e	8.00 g-i	20.89 f
$P_{90} - B_{0.0}$	3.28 b-d	1.11 b-f	19.09 cd	9.62 g-i	28.71 e
$P_{90} - B_{0.5}$	3.33 b-d	1.19 a-f	17.87 d	10.87 f-h	28.74 e
$P_{90} - B_{1.0}$	3.62 a-c	1.25 a-e	20.53 b-d	12.81 e-g	33.34 de
$P_{90} - B_{1.5}$	3.68 a-c	1.32 ab	22.59 a-c	15.91 d-f	38.50 cd
$P_{90} - B_{2.0}$	3.94 ab	1.24 a-e	24.24 ab	16.45 c-e	40.69 bc
$P_{135} - B_{0.0}$	3.98 ab	1.26 a-d	23.08 a-c	18.46 b-d	41.54 bc
$P_{135} - B_{0.5}$	4.00 ab	1.29 a-c	25.53 a	21.32 a-c	46.84 ab
$P_{135} - B_{1.0}$	4.01 ab	1.36 a	23.08 a-c	22.54 ab	45.63 ab
$P_{135} - B_{1.5}$	4.03 ab	1.39 a	26.70 a	23.41 ab	50.11 a
$P_{135} - B_{2.0}$	4.17 a	1.43 a	24.63 ab	24.12 a	48.75 a
LSD $_{0.05}$ (P)	0.35	0.11	2.10	2.32	3.11
LSD $_{0.05}$ (B)	0.45	0.14	2.72	2.99	4.02
LSD $_{0.05}$ (P × B)	0.78	0.24	4.71	5.19	6.96

Treatment explanations are in Table 2. P = phosphorus levels; B = boron levels; P × B = interaction between P and B levels. Treatment means not sharing similar letter(s) in the same column differ significantly from each other (LSD test, $p \leq 0.05$). Values are means of three replications (n = 3)

Boron accumulation

The data pertaining to boron concentration [B] and B uptake by grains and straw of wheat plants is presented in Table 5. Phosphorus and B levels had significant ($p \leq 0.05$) effects on [B] in both grains and straw. At each P level, increase in B levels resulted in enhanced [B] of aboveground plant parts. The minimum grain [B] of 9.20 µg g^{-1} was determined in $P_{45} - B_{0.0}$ treatment while maximum (19.57 µg g^{-1}) was recorded in $P_{135} - B_{2.0}$ which was at par to 18.98 µg g^{-1} under $P_{135} - B_{1.5}$. Overall, the magnitude of straw [B] was comparatively higher than grain [B]. The highest straw [B] of 29.40 µg g^{-1} was observed in treatment $P_{135} - B_{2.0}$ followed by 25.80 µg g^{-1} ($P_{135} - B_{1.5}$). Significant ($p \leq 0.05$) main and interactive effects of P and B levels were observed for grain B uptake, straw B uptake and total (grain + straw) B uptake (Table 5). The average straw B uptake of wheat plants was about three fold higher than grain B uptake under each P level. The maximum and minimum grain B uptake was recorded in treatments $P_{135} - B_{1.5}$ and $P_{45} - B_{0.0}$ respectively (125.81 vs. 32.88 µg plant^{-1}). Numerically, the highest value of straw B uptake (492.90 µg plant^{-1}) was recorded in treatment $P_{135} - B_{2.0}$ which was statistically identical to 433.35 µg plant^{-1} ($P_{135} - B_{1.5}$) and 416.92 µg plant^{-1} ($P_{135} - B_{1.0}$). Increasing B rates at each P level resulted in enhanced total B uptake by wheat plants and exhibited maximum value of 608.74 µg plant^{-1} in treatment $P_{135} - B_{2.0}$ followed by 559.16 µg plant^{-1} ($P_{135} - B_{1.5}$) and 516.66 µg plant^{-1} ($P_{135} - B_{1.0}$), while minimum (117.87 µg plant^{-1}) was recorded in $P_{45} - B_{0.0}$ treatment.

Table 5. Interactive effect of phosphorus and boron on boron concentration and uptake by grains and straw of wheat plants grown on calcareous soil

Treatments	B concentration (µg g^{-1})		B uptake (µg plant^{-1})		
	Grain	Straw	Grain	Straw	Total
$P_{45} - B_{0.0}$	9.20 h	13.62 e	32.88 h	84.99 g	117.87 i
$P_{45} - B_{0.5}$	9.83 gh	15.14 de	36.69 h	102.75 g	139.43 hi
$P_{45} - B_{1.0}$	10.40 gh	16.03 de	41.59 gh	108.74 g	150.33 hi
$P_{45} - B_{1.5}$	11.97 fg	17.48 de	48.73 gh	126.51 fg	175.25 hi
$P_{45} - B_{2.0}$	13.05 ef	19.48 cd	54.00 g	145.21 fg	199.21 g-i
$P_{90} - B_{0.0}$	12.94 ef	15.84 de	75.32 f	135.43 fg	210.75 g-i
$P_{90} - B_{0.5}$	14.45 de	16.77 de	78.19 f	152.13 fg	230.32 gh
$P_{90} - B_{1.0}$	14.57 de	20.23 b-d	82.81 ef	205.22 ef	288.03 fg
$P_{90} - B_{1.5}$	15.88 cd	25.45 ab	97.19 c-e	308.83 cd	406.02 de
$P_{90} - B_{2.0}$	17.12 bc	26.24 a	105.04 bc	350.43 b-d	455.46 c-e
$P_{135} - B_{0.0}$	14.66 de	19.20 cd	84.91 d-f	282.84 de	367.75 ef
$P_{135} - B_{0.5}$	16.33 cd	24.01 a-c	103.73 bc	393.48 bc	497.21 b-d
$P_{135} - B_{1.0}$	17.28 bc	25.24 ab	99.74 cd	416.92 ab	516.66 a-c
$P_{135} - B_{1.5}$	18.98 ab	25.80 a	125.81 a	433.35 ab	559.16 ab
$P_{135} - B_{2.0}$	19.57 a	29.40 a	115.84 ab	492.90 a	608.74 a
LSD $_{0.05}$ (P)	0.97	2.46	7.09	41.75	42.58
LSD $_{0.05}$ (B)	1.25	3.17	9.16	53.89	54.97
LSD $_{0.05}$ (P × B)	2.17	5.49	15.86	93.35	95.20

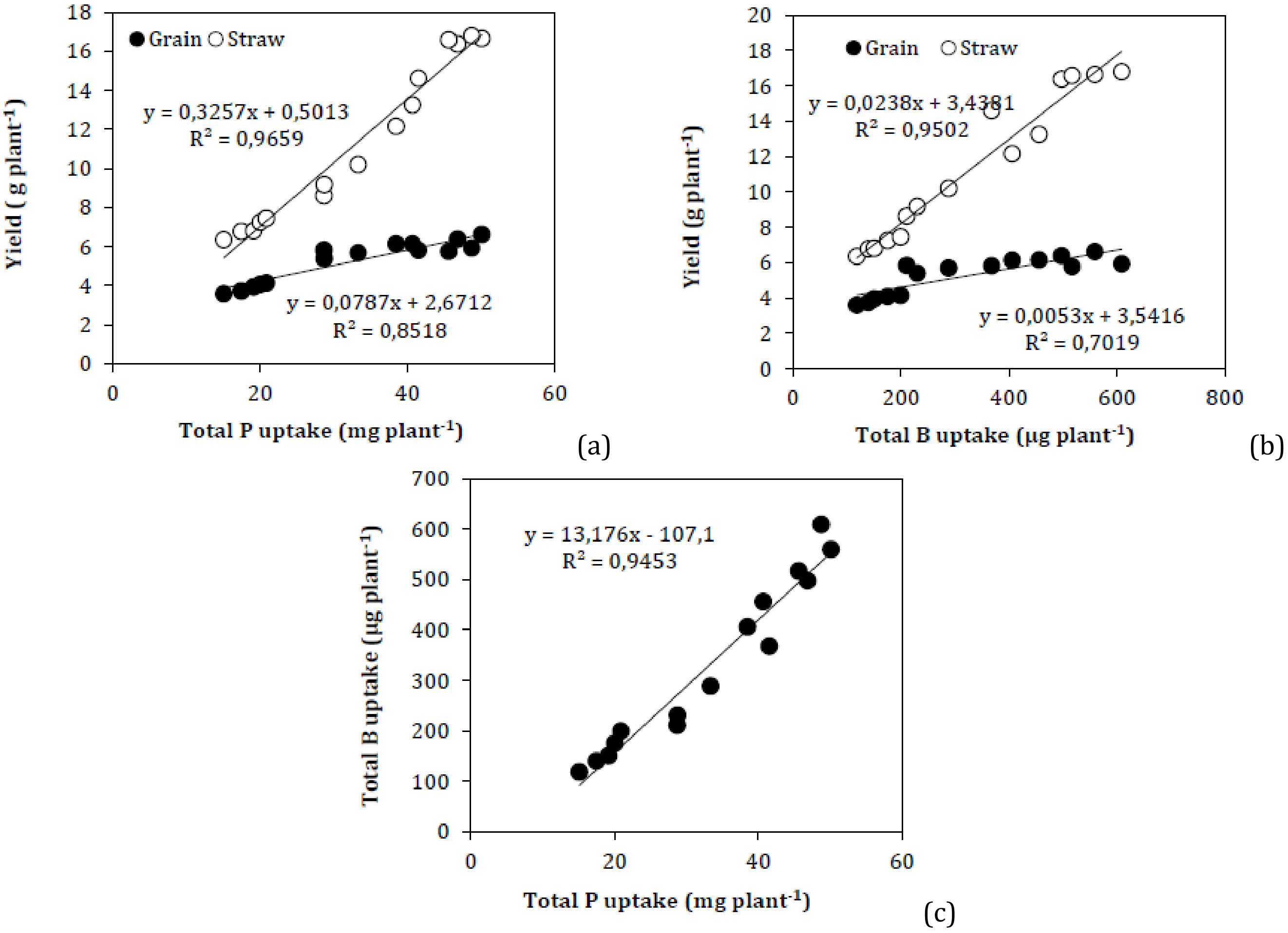
Treatment explanations are in Table 2. P = phosphorus levels; B = boron levels; P × B = interaction between P and B levels. Treatment means not sharing similar letter(s) in the same column differ significantly from each other (LSD test, $p \leq 0.05$). Values are means of three replications (n = 3)

Discussion

Most of the cultivated soils in Pakistan have moderate to severe deficiencies of macronutrient P (Irfan et al., 2018) and micronutrient B mainly due to alkaline and calcareous nature of soils accompanied with low organic matter (Niaz et al., 2016). The rapid fixation and low availability of applied P and B fertilizers on such soils is a serious problem to maintain their adequate concentration in soil solution (Abbas et al., 2018b). Interaction among nutrients might be synergistic or antagonistic which causes a shift in the internal physiological balance between certain elements resulting in secondary alterations in the absorption and accumulation of other ions (Bonilla et al., 2004). Hence, the prime objective of the present study was to investigate the interactive effect of P and B on plant growth, nutrient accumulation and yield of wheat grown on calcareous soil.

In current study, significant effect of increasing P and B rates were observed regarding plant height, number of tillers per plant, spike length and number of grains per spike. Nonetheless, the effect of B was most prominent at lower P level as compared to medium and higher P levels. Similarly, Kabir et al. (2013) have reported that application of P in combination with B significantly increased the plant height and number of branches per plant in groundnut. The increase in plant height by P might be due to enhanced photosynthetic rate thereby encouraging the vegetative growth (El-Habbasha et al., 2007). Furthermore, B is essential for cell division and cell elongation resulting in enhanced plant growth and plant height (Camacho-Cristóbal et al., 2015). Boron has positive role in transporting carbohydrates from source to sink while its deficiency retards the synthesis of nucleic acids, carbohydrates metabolism and ultimately reduce biomass (Rashid et al., 2004). According to Han et al. (2008), B deficiency influence plant growth by reducing enzymatic activities and lowering stomatal conductance and CO_2 assimilation in plant leaves. On the other hand improved B nutrition lowers the sterility in bread wheat from 42.6 – 4.5% thereby increasing grain yield (Subedi et al., 1997). Combined deficiencies of P and B generate a chain reaction to inhibit protein synthesis leading to impaired growth and dry weight (Hewitt, 1983). Alam et al. (2010) have observed the increase in 1000-grain weight of summer mungbean under the combined fertilization of P and B. Positive interaction of adequate P and B levels has been found in *brassica* to enhance biomass yield (Lei et al., 2009).

Grain and straw yield of wheat plants exhibited increasing trend to B addition under each P level. A highly positive correlation of grain and straw yield was also observed with total P uptake (R^2 = 0.96 and 0.81) and total B uptake (R^2= 0.95 and 0.70). Likewise, positive correlation (R^2 = 0.94) between total P uptake and total B uptake under combined application of P and B indicating their synergistic relationship (Figure 1). The enhanced B contents in wheat plants in relation to increasing P levels also suggested the improvement of metabolic functioning of plants. Muhlbachova et al. (2017) have found positive correlation between dry matter yield and B contents in Barley (R^2 = 0.3273, $p \leq 0.001$) under P fertilization. In contrast (Kaya et al., 2009) reported that B toxicity in tomato plants could be mitigated by the supplemental P fertilizer. But the soils in Pakistan are deficient in available B contents so it is possible to assume that increased B contents in wheat was induced by increasing P levels. However, a possible competition between B and P cannot be excluded as both nutrients are available to plants as anions i.e., $B(OH)_4^-$ and $H_2PO_4^-$ (Matula, 2009).



(a) (b) (c)

Figure 1. Correlation between yield and total P uptake (a), yield and total B uptake (b), and total P uptake and total B uptake (c) of wheat plants grown on calcareous soil

Phosphorus and B accumulation in grains and straw of wheat plants enhanced considerably at each P level in relation to increasing B levels. Ali et al. (2015) have reported the positive effect of B addition on the P concentration in tobacco leaves. In barley, increased B, N, P, K and Na contents and decreased Ca and Mg contents under B application have been observed by Singh and Singh (1983). In contrast, lower concentrations of P, K and Ca has been observed in healthy plants in comparison to severally B deficient plants which is perhaps due to the dilution effect occurred in healthy plants. According to Pollard et al. (1977), B deficiency reduces the capacity for the absorption of phosphate due to the reduced ATPase activity, which could be rapidly restored by the B addition. The evidences regarding the function of B in the regulating plant membranes and ATPase as a component of transport process are well documented. The possible mechanism behind this control is the elevation of endogenous levels of auxins and the interaction of B with polyhydroxyl components of the membranes.

The synergistic effect of P and B was found for most of the growth and yield parameters of wheat crop in present study. Plant growth suppression was relatively more under the combined deficiency of both nutrients which might be due to the retardation of their efficient utilization. As P is the integral part of nucleic acids and B is also required for the synthesis of some components of nucleic acids, so their deficiency induces degradation of nucleic acids (Rashid et al., 2004). Boron deficiency during grain filling results in poor anther and pollen development, causing significant reduction in grain yield (Uraguchi and Fujiwara, 2011). Combined deficiencies of P and B may intensify these responses in plants. Plant biomass production can be predicted by the available P and B contents, as stated by Davies et al. (2011). Several earlier investigations revealed that combined application of P and B significantly enhanced the growth, yield and quality of various field crops (Huang et al., 2012; Kabir et al., 2013; Chowdhury et al., 2015; Muhlbachova et al., 2017). Therefore, an adequate and consistent supply of P and B is necessary to achieve better nutrient balances and more biomass production.

Conclusion

Phosphorus and Boron have crucial roles in array of physiological, biochemical and metabolic functions within plant body. As most of the cultivated soils in Pakistan are deficient in both nutrients, so the combined deficiency of these nutrients may adversely affect plant growth and their utilization efficiency. A synergistic effect of combined application of P and B was found for most of the growth and yield attributes in present study. However, the significant interactive effect of both nutrients was most pronounced in the P_{90} – $B_{1.5}$ treatment. Thus the treatment combination of 90 kg P ha^{-1} with 1.5 kg B ha^{-1} was the most suitable dose for better plant growth, nutrient accumulation and grain yield of wheat. However, further verification of results is warranted under field conditions in relation to crop species, growth stages, analyzed plant organs and soil type.

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Assessment of the potential mobility of copper in contaminated soil samples by column leaching test

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Abstract

Column leaching tests become methodology important for assessing the risk of release of pollutants from soil into groundwater. In this present study column leaching test were applied on soil samples taken directly in the vicinity of Kenadsa coking plant (Algeria) in order to evaluate the mobility of copper and their potential environmental risks. These samples have been lixiviated in laboratory column in water-saturated condition at room temperature. All leachates have been collected by fraction and analyzed from copper and dissolved organic carbon. The percentages leached in column with water are very low (< 1%). The concentrations of copper in the resulting leachates do not present a toxicological hazard. The effect of dissolved organic carbon on copper leaching was also investigated in this study; the results of column leaching showed that the mobility of copper in these contaminated soil samples is associated with the mobility of dissolved organic carbon.

Keywords: Contaminated soil, copper, column experiment, dissolved organic carbon.

Introduction

Mining and associated activities have a negative impact on the environment both during the mining operations and for years after mine closure. The soils in the vicinity of this mining may contain high levels of organic pollutants particularly polycyclic aromatic hydrocarbons (PAHs) and heavy metals. It is essential to predict their mobility and fate and to evaluate the risk of transfer to sensitive targets, such as water resources, ecosystems and human health.

In the commune of Kenadsa (south-west of Algeria), since 1962, the date of the stop of the exploitation of coals in the Kenadsa mine, the problem of the environment is still talked about, where hills of waste pollute this site. A study conducted by Kadari et al. (2015) put the action on the pollution of the soil samples collected on this site by the polycyclic aromatic hydrocarbons (PAHs). In addition, the preliminary analysis of soil samples taken in the vicinity of this aged coking plant showed that such soil samples were polluted by heavy metals and especially by copper.

The behavior of Copper in the soil depends on many factors: the pH of the soil, its redox potential, its capacity of cationic exchange, the type and the distribution of organic matter, the presence of oxides, the speed of decomposition of the organic matter, the proportions of clays, silts and sands, the climate and the type of vegetation present (Adriano, 1986; Dameron and Howe, 1998; Picard et al., 2005).

The best-known method for studying the transport and mobility of Heavy metals in polluted soils is the leaching test, which extracts the elements of interest in order to quantify the potential risk of their mobility.

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Column leaching test are widely used to predict the mobility of heavy metals (Temminghoff et al., 1997; Voegelin et al. 2003; Xu et al.2005; Kalbe et al., 2008; Cappuyns and Swennen, 2008; Mouni et al., 2016). The principle of the experiments in column consists in placing a quantity of soil in a column and subjecting it to a leaching solution by ascending/descending percolation, then the measurement of the quantity of the pollutants in the leachates thus obtained. Column tests give a better simulation of field conditions than batch tests (e.g. more realistic L/S ratio, laminar instead of turbulent flow) (Cappuyns and Swennen, 2008). In addition; the percolation of water through materials in column tests is so far to the closest simulation to natural conditions in comparison with any other leaching tests and at the same time provides the most reliable results (Kalbe et al., 2008).

The aim of this study is to evaluate the contamination of soil samples taken directly in the vicinity of Kenadsa coking plant and the potential release as well as the mobility of copper. The potential release and mobility of copper was estimated by column leaching tests. Moreover, copper is famous for its affinity with the organic matter of the soil, therefore it is interesting at the time of studying the risk to be able to determine a correlation between the mobility of copper and dissolved organic carbon (DOC) in kenadsa soil samples.

Material and Methods

Origin and preparation of studied soils

Kenadsa soil samples been collected in the vicinity of abandoned coking plant, located in the commune of Kenadsa (South-west of Algeria), with geographic location, Latitude N 31° 33' 32'' and Longitude W 2° 25' 24''. A study conducted by Kadari et al (2015) shown that the soil samples collected on this site were contaminated by polycyclic aromatic hydrocarbons (PAH_S). For our study, Approximately 15 kg of a soil samples were prepared by collecting 1–2 kg of soil samples with a small stainless at depth of 0–20 cm at 11 points. This quantity was homogenized by quartering, screened at 4 cm and air dried at 20 °C. A 5-kg sub-sample was taken and sieved at 2 mm; the fraction (<2 mm) was used in this work, prior to laboratory analysis and column leaching testes. The sample thus prepared was stored in plastic bags and kept refrigerator at + 4°C until use.

Since, there is no information available on the local background values for Algerian soils in this area of study. Control soil obtained about 4 kilometers southern from the studied area, which assumed to have background concentration of analyzed elements. The procedure of sampling and preparing the soil control were the same of sampling and preparing of kenadsa soil samples.

Characterization physicochemical of studied soils

The solutions used were prepared with demineralized water. All the reagents used were of trace pure grade (Merck, Sigma-Aldritch). All the equipment (glassware, polyethylene bottles, etc.) were systematically decontaminated using HNO_3 (10%, v/v).In addition, reagent blanks were analyzed to verify the absence of contamination and precision of the analysis. For each test, three tests were carried out, but only the mean of the results obtained is presented.

Percentages of sand (2–0.05 mm), silt (0.05–0.002 mm), and clay (<0.002 mm) were determined by wet sieving method and the hydrometer method. The moisture content was determined by measuring the mass loss of the soil following its drying at 105 ºC for 24 h. Soil pH in water was determined with a pH meter using 5:1 (v/ v) water/soil suspensions. The total organic carbon was determined according to the Anne modified method (Mathieu and Pieltain, 2003). Cation exchange capacity (CEC) was determined by the 0.05N cobalthexamine method according to the standard (ISO 23470).

The Chemical compositions in major elements (Fe, Al, Mg, Ca, Si, S, K, P, and Na) were determined by X-ray Fluorescence Spectrometer (PW 2400 –Philips -in Alicante University - Spain). Pseudo total concentration of Heavy metals (Cu, Ni, Cr, Zn) were measured using flame atomic absorption spectrometry (FAAS, Thermofisher model 651074), after Wet digstion by aqua regia (proportion in volume of 2/3 of HCl at 37% and a 1/3 of HNO_3 at 65%) according to the standard (ISO 11466). The calibration was performed using standard SCP Science.

Column experiments

Column leaching tests were carried to simulate the release of pollutants following rainwater infiltration. The principal of Column leaching tests was inspired in the work of Benhabib (Benhabib et al., 2017). The experimental set-up was composed of a borosilicate glass column (XK 26/20) from (GE Healthcare, Sweden) with an inner diameter of 2.6 cm. This column was powered by a peristaltic pump (Heidolph model 5206, Germany) capable of ensuring a constant flow rate of 2 to 3900 ml/min. All these elements (column, pump, tanks) are connected by Teflon capillary tubes with an inner diameter of 0.8 mm. Column was filled with about 83 gr (dry mass) of Kenadsa soil (< 2 mm) for a 12.5 cm height, The bulk density was approximately 1.25 (gr cm^{-1}). Leaching experiments and tracing were carried out successively without replacing the soil sample at room temperature (20 ± 2 ºC). The column filled with soil was previously saturated from bottom to top with demineralized water at a flow rate of 2 mL min^{-1}. The experiment started at the end of the column saturation at a constant flow rate of 2 mL min^{-1}. It consists in continuously sweeping the column with demineralized water to reach a liquid-to-solid ratio (L/S = 10 mL gr^{-1}) of dry soil corresponding to 830 mL leached (This report is used to compare our results with other standardized batch or column tests). During the leaching, 50 mL fractions were continuously collected. The pH, conductivity of the leachates was measured. Then, the leachates were then filtered at 0.45 µm and the concentrations of copper and DOC was measured in the filtrates. Concentrations of copper were measured using graphite furnace atomic absorption spectroscopy (GF-AAS, THERMOFISHER model 651074), the limit of Detection for copper was 0.06µg L^{-1}. The DOC was measured by a TOC meter (SieversInnovOx; Version 3.01).

A tracing experiment was run on column at the end of the leaching experiment, non-reactive tracer (sodium nitrate) tests were conducted to characterize the hydrodynamic properties of soil column and verify reproducibility of experiments. The column was fed by a 2×10^{-3} mol L^{-1} $NaNO_3$ solution until conductivity at the outlet reached conductivity of the feed solution. A step-wise injection of a 10^{-2} mol L^{-1} $NaNO_3$solution was then done until conductivity stabilization, followed by a step-wise injection of the 2×10^{-3} mol L^{-1} $NaNO_3$ solution.

Results and Discussion

Physicochemical properties of studied soils

The main physico-chemical properties of studied soils are presented in Table 1. By deferring the percentages of sand, silt and clay in the texture triangle proposed by the United States Department of Agriculture (USDA), the Kenadsa soil has a sandy texture; Its pH is slightly alkaline, the pH of this soil is in a range indicating a priori a propensity of this soil to fix the heavy metals (generally between 6.5 and 8.5). The organic carbon content is high (12.6%) as well as organic matter (MO) (21.8%); this is due to the presence of a large amount of aromatic hydrocarbon in this coking plant soil (Kadari et al., 2015). The CEC of kenadsa soil is low; characteristic of a sandy soil poor in the limestone, despite the presence of a large amount of organic matter. Concentrations of major elements (mean of three replicates) in Kenadsa soil samples (% in mass) determined by X-ray spectrofluorometer were: SiO_2: 54.12, Fe_2O_3: 4.81; Na_2O: 0.45; MgO: 1.51; Al_2O_3: 10.52; CaO: 8.78, K_2O: 1.90; SO_3: 11.97; P_2O_5 : 0.48; others: 0.83.

Table 1. physico-chemical characteristics of studied soils (mean of three replicates) and mean concentrations of heavy metals in studied soils and Canadian Soil Quality Guidelines (CCME, 2007) for analysed elements expressed in (mg kg^{-1})

Parameter	Kenadsa soil	Control soil	Canadian Soil Quality Guidelines (CCME, 2007)	
			Residential/Parkland soil	Agricultural soil
Sand (%)	91.18	ND	-	-
Silt (%)	7.99	ND	-	-
Clay (%)	0.82	ND	-	-
Moisture(%)	2.20	2.5	-	-
pH (H_2O)	7.50	7.88	-	-
CEC (cmol kg^{-1})	12.60	3.30	-	-
TOC (%)	12.60	0.50	-	-
OM^{a}(%)	21.80	0.86	-	-
Heavy metyals (mg kg^{-1})				
Cu	106.6	2.80	63	63
Ni	16.00	1.30	50	50
Cr	22.00	2.60	64	64
Zn	75.00	250	200	200

^{a} organic matter (OM) = TOC × 1.72 (Duchaufour ,1997) ND: not determined

Concentrations of Heavy metals in studied soils

In the absence of Algerian standards for soil quality, Concentrations of Heavy metals in studied soils were compared with Canadian Soil Quality Guidelines (CCME, 2007). They are defined as the concentrations recommended providing a healthy, functioning ecosystem capable of sustaining the existing and likely future uses of the site by ecological receptors and humans (Mileusnić et al., 2014). Canadian soil quality guidelines can be used as the basis for soil contamination assessment of four types of land uses: agricultural, residential/parkland, commercial, and industrial. Heavy metals concentrations in studied soils were compared with agricultural land use and residential/parkland use.

The mean values of Heavy metal contents in the kenadsa soil samples are 106.6 mg kg^{-1}for Cu, 16 mg kg^{-1} for Ni, 22 mg kg^{-1} for Cr and 75 mg kg^{-1} for Zn (Table 1). Control soil data represent Locale background values of analyzed elements in kenadsa soil.

For Copper; comparing to background value, kenadsa soil contains elevated concentration of copper (approximately 38 time higher the background value in control soil). In addition; Concentration of copper in kenadsa soil exceeds the Canadian soil quality guidelines for agricultural and residential/parkland use (CCME, 2007). Guideline values of 63 mg kg^{-1} for copper are exceeded by up to 1.63 times. For Ni, Cr and Zn; the results show that the mean concentrations of this element in kenadsa soil exceed the mean concentrations in control soil by a factor of 12, 8, and 3, respectively. While these concentrations do not exceed Canadian soil quality guidelines for agricultural and residential/parkland use (Table 1). It is worthy to note, however, that, heavy metal concentrations never exceed the Canadian soil quality guidelines for agricultural and residential/parkland use in the control soil (1.3 mg kg^{-1} for Ni, 2.6 mg kg^{-1} for Cr and 25mg kg^{-1} for Zn).

The results prove the anthropogenic impact on Cu, Ni, Cr and Zn concentrations in the kenadsa soil. The location of this studied soil in the vicinity of coking plant increased the accumulation of analyzed heavy metals. But the only analyzed element which exceeded Canadian soil quality guidelines for agricultural and residential/parkland use if the copper. If for that it chose this element for the leaching in column.

Results of Column experiments

The results of column experiments are presented as a function of the relative volume V/Vp; where V denotes the volume of the cumulative leachates and Vp the pore volume of the column. We first present the results of the tracing experiments, and then discuss the results of column leaching under saturated conditions.

Column hydrodynamics

The Figure1 shows an example of tracer breakthrough curves (BTC) for a positive step injection and a negative step. The two curves (Figure 1) have a symmetry with respect to the point ($V/V_p = 1$; $C/C_0 = 0.5$), and they are symmetrical with respect to the vertical $V/V_p = 1$. The moments of order one and two of the RTD (Residence time distribution) are determined numerically by the trapezoid method, which made it possible to deduce the pore volume and the porosity. The average residence time of the fluid in the column is 13.3 min at the flow rate 2 ml min^{-1}, which corresponds to a porous volume V_P of 26.6 ml and a total porosity of 0.4.

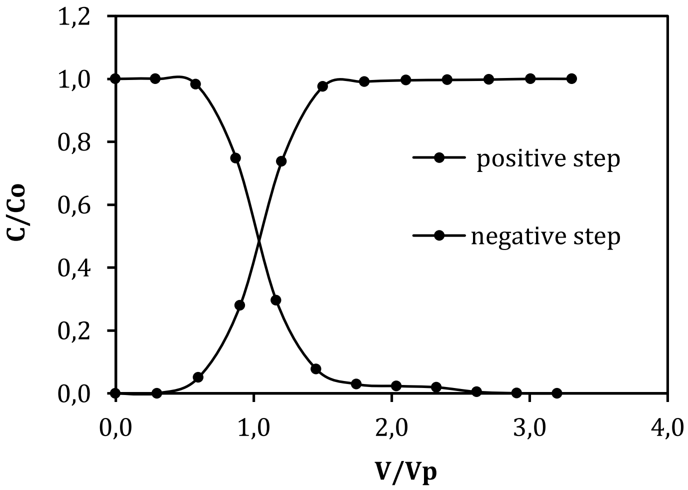

Figure 1.Response of the column to a positive step ($NaNO_3$ solution at 10^{-2} M) and a negative step ($NaNO_3$ solution at 2×10^{-3} M), with a flow rate of 2 ml/min.

In addition, the differences between the volumes of water obtained by weighing the column before and after saturation and by RTD are very small (between 2 and 3%). This shows that during the column experiments, the entire volume of water participated in the flow, indicates the absence of preferential paths or dead zones.

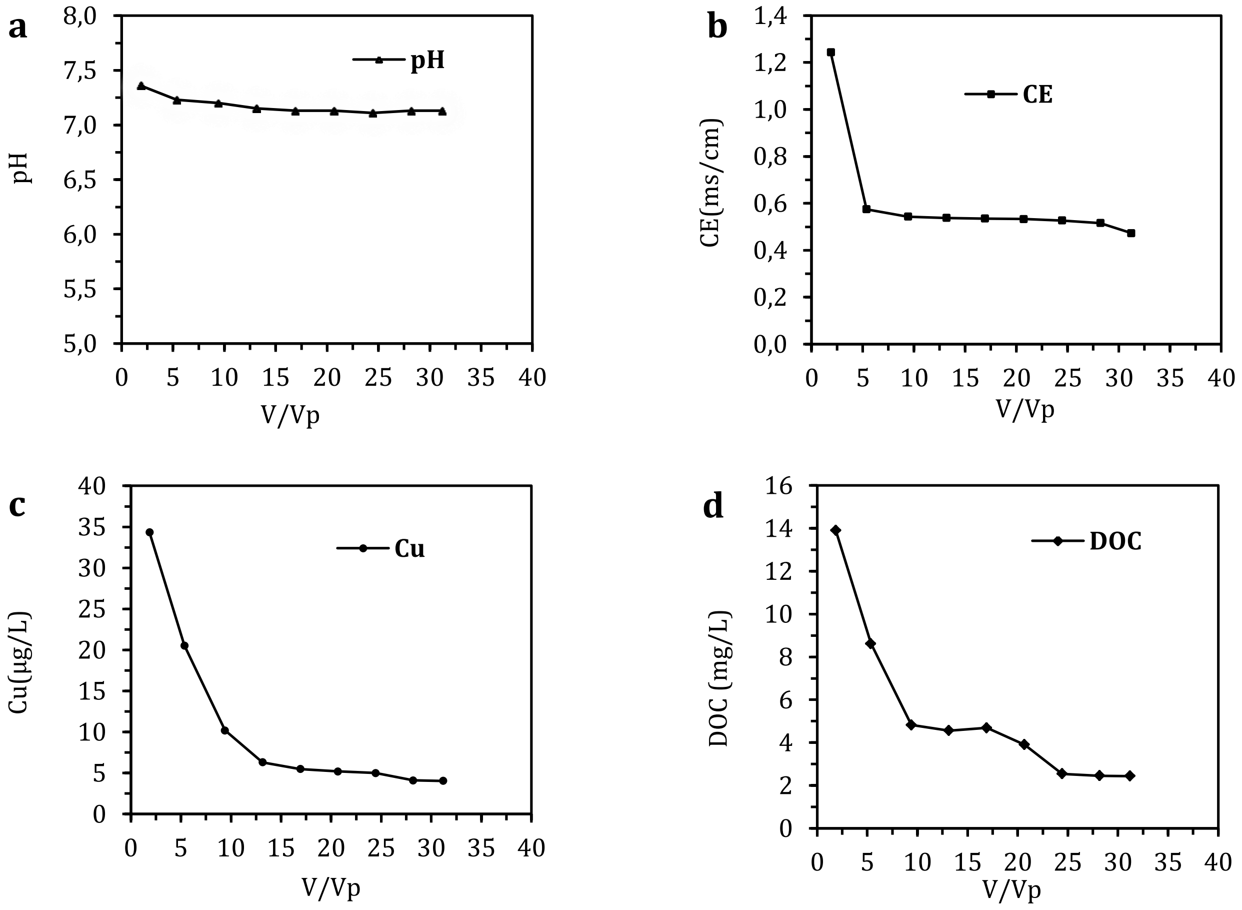

Figure 2. Result of Continuous Leaching.
a: pH, b:conductivity, c: Copper concentrations, d: DOC concentrations; in the leachates as a function of V/V_p.

Results of continuous leaching tests

Evolution of the pH and conductivity

The curves of Figure 2a, 2b give the evolution of the pH and the electrical conductivity (CE) in the leachates as a function of V/V_P. The pH evolves very little; it remains in the vicinity of 7.2. This pH is lower than that of soil in water (7.5) due to a release of organic matter during the experiment (Totsche et al., 2006). The conductivity drops sharply during the first five V_P, and then it reaches a plateau and decreases much more slowly until the end of the experiment. The conductivity measurement shows a decrease in the concentration of the elements in solution.

Evolution of concentrations of Copper and DOC

The breakthrough curve Figure2c, 2d shows the evolution of copper and DOC concentrations in the leachates as a function of V/V_P. Generally speaking, leaching is always accompanied by relatively high concentrations of Cu and DOC, which decrease very rapidly when percolation continues, until you reach a plateau. The effluents of the first pore volumes are coloured in yellow because of dissolved organic carbon (DOC) (Benhabib et al., 2017).

The breakthrough curves of copper (Figure 2c) have two parts. First, for about $10V_P$, the copper concentration at the column outlet decreases rapidly and then reaches a plateau and decreases much more slowly until the end of the experiment. The relatively high concentrations of the beginning of leaching (34.3 µg L^{-1}) are due to the solubilisation of the poorly fixed elements in the macropores of the soil. These concentrations are in fact lower than the guideline values for drinking water: Cu = 2 mg L^{-1} (WHO, 2008).The equivalent of at least 20 V_P was collected before the Cu contents stabilized at values around 4 µg L^{-1}. This behavior has also been observed by (Xu et al., 2005) during leaching experiments on a polluted soil column at the laboratory with deionized water (DIW) at a flow rate of 1.0 ml min^{-1}, The copper concentrations are of the same order of magnitude as those observed here, namely around 35 µg L^{-1}. This observation confirms the fact that copper has a very strong affinity for the solid matrix. Moreover, Copper is more soluble and more mobile at pH values below 5, beyond pH = 7 (which is the case here) copper is practically no longer mobile (Adriano, 1986). Several authors (Adriano, 1986; Dameron and Howe, 1998) suggest that Copper migrates slightly in depth, except in particular conditions of drainage or in a very acid medium, the copper remains strongly adsorbed in the few upper centimeters of the soil, especially on the organic matter present. In addition, the aging of the contamination is another very important factor that influences the mobility of copper; Sequestration is favored by the age of the pollution (McBride et al., 1997; Jalali and Khanlari, 2008). This is clearer when the cumulative releases of Cu (Table 2), does not exceed 1%.

Table 2. Evaluation of the yields of copper and DOC extractions by water in column

dry soil (gr)	Water (mL)	L/S (mg mL^{-1})	Cu^a (mg kg^{-1})	Cu^b (%)	DOC^a (mg kg^{-1})	DOC^b (%)
83	830	10	0.29	0.29	173.82	0.14

^{a} The cumulative release of Cu and DOC (mg kg^{-1} dry soil) are calculated by the relationship:

$$Qp = \sum^{n} Qpi = \sum^{n} Cpi \times (L/S)i$$

Q_P: cumulative release of Cu or DOC in mg kg^{-1}.
Q_{pi}: cumulative release of Cu or DOC during the extraction i expressed in mg kg^{-1}.
C_{pi}: concentration of Cu or DOC in the leachates resulting from the extraction i.
$(L/S)_i$: Liquid / Solid ratio of extraction i expressed in l kg^{-1}.
^{b} % of Cu and DOC was based on pseudo total Cu and on total DOC, content in dry soil.

The same observation for DOC (Figure 2d), The DOC breakthrough curve also has two parts. First, for about 10V$_P$, the DOC concentration at the column outlet decreases rapidly and then reaches a plateau and decreases much more slowly until the end of the experiment. Several authors have also postponed that a DOC exit in two stages (Münch et al., 2002; Totsche et al., 2006; De Jonge et al., 2008). The high initial concentration of DOC is due to the large amount of dissolved organic carbon mobilized during the saturation of the columns (Münch et al., 2002). In addition; Temminghoff et al. (1997) found that when DOC was added to the feed solution, the solid organic matter became larger in the first two sampled layers of the columns due to coagulation.

Data in Figure 2c and 2d indicate that the leaching of copper and DOC follow the same pattern. Moreover; there is a strong correlation between eluted copper and soil organic carbon with a regression coefficient of 0.967 (Figure 3). The formation of copper-organic compounds increases at pH values above 7, due to the higher solubility of soil organic matter at high pH (Adriano, 1986; Di Palma et al., 2007), especially in the pH range characterizing the studied soils (pH = 7.5); Conversely, Copper may be complexed with DOC in the soil so that the mobility decreased (Xu et al., 2005). The relationship between DOC and copper is clear in this study. Each increase/decrease in DOC concentration is associated with a corresponding increase or decrease in Cu concentrations. Given the results obtained, we can suggest that the leaching of Cu is due to the release of Cu complexed with DOC; this hypothesis is consistent with the hypothesis of Zhao et al. (2007) that the DOC governed the mobilization of Cu.

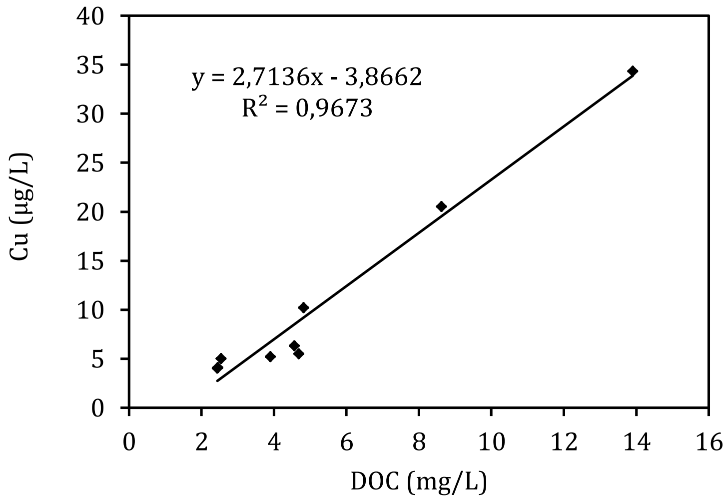

Figure 3. Evolution of Cu concentrations as a function of DOC concentrations during Continuous Leaching

Conclusion

The results of analysis indicated that the kenadsa soil samples taken in the vicinity of kenadsa coking plant were contaminated by heavy metals and especially by copper. The mean concentrations of copper exceeding largely the local background value (factor of 38) and exceeded by up to 1.63 times guideline values of 63 mg/kg for agricultural and residential/parkland use (CCME, 2007). These results prove the anthropogenic impact on Cu, Ni, Cr and Zn concentrations in the kenadsa soil. The location of this studied soil in the vicinity of coking plant increased the accumulation of analyzed heavy metals.

The results of column leaching testes show that, in the presence of a high organic matter content and slightly alkaline pH, the mobility of copper is very low, the percentages leached of copper does not exceed 1 % content in the soil samples.In addition, the results of column leaching testes in this study showed that the mobility of copper in Kenadsa soil is associated with the mobility of DOC. Therefore; we can conclude that under the conditions of our experimentation; potential toxicity of copper is not significant, despite its relatively high pseudo total concentration.

Acknowledgement

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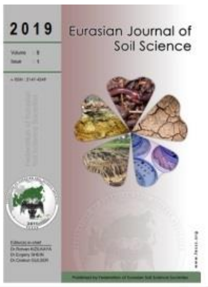

Spatial variability of soil organic carbon density under different land covers and soil types in a sub-humid terrestrial ecosystem

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Abstract

The main objectives of the current study are i) to estimate SOC in different soil depths and to generate their spatial distribution maps, ii) to assess relationship between variation of different soil types and SOC density, iii) to determine effects of land cover types on SOC in Inebolu Watershed located in sub-humid terrestrial ecosystem. In order to determine land cover types of the study area, aster satellite image was used and five main land cover types that are bare land, sparsely vegetated area, broadleaved forest area, mixed forest area and needleleaved forest area were classified. Results indicated that soil types and land cover were two crucial influencing factors for spatial variation of SOC density. It was determined that SOC density of soil types, Vertic Haplustept (12.93 kg.m^{-2}) was significantly higher than other soil subgroups. In this case, it can be said that main reasons of this result are indicated as soil profile depth and pedological development. In addition, when comparing the two main factors, land cover explained more of the SOC density variability and was the main controlling factor in the surface; in the subsurface, not only land cover types but also some properties of soil types such as texture, genetic horizons, soil depth have an important role on SOC density. On the other hand, it can be conclude that the combination of the soil type and land cover was a dramatically better predictor of SOC density.

Keywords: Land use effect on soil, soil organic carbon, soil classification, soil mapping.

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Introduction

Soil organic carbon (SOC) stock has a great importance component in any terrestrial ecosystem, and is any variation in its abundance and composition has important effects on many of the processes that occur within this system (Vasconcelos et al., 2014; İmamoğlu and Dengiz, 2016). The magnitude of organic matter and soil organic carbon (SOC) stock result from an equilibrium between the inputs (mostly from biomass detritus) and outputs to the system (mostly decomposition and transport), which are driven by various parameters of natural or human origins (Schlesinger and Palmer Winkler, 2000; Amundson, 2001; Khan and Kar, 2017). The decrease of organic matter in top soils can have dramatic negative effects on water holding capacity of the soil, on structure stability and compactness, nutrient storage and supply and on soil biological life (Sombroek et al., 1993). These cause mainly a combination of unfavorable natural biophysical conditions and negative human impacts. The negative human impacts are mainly the result of inappropriate land use, including deforestation, overgrazing and inappropriate agricultural practices that lead to soil erosion, salinization and vegetation degradation, which are strongly linked to harmful changes in hydrological processes that affect the soil water and carbon balance.

The SOC stock in terrestrial ecosystems is almost thrice as large as the carbon storage in the plant biomass of such environments and approximately twice as large as carbon storage in the atmosphere (Batjes and

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Sombroek, 1997; Grimm et al., 2008; Sevgi et al., 2011). The carbon balance of terrestrial ecosystems can be changed markedly by the direct impact of human activities. Land use change is responsible for 20% of the global anthropogenic CO_2 emissions during the 1990s (Anonymous, 2007). The type of land use system is an important factor that controls SOC levels particularly in the top soils. Changes of land use and management practices influence the amount and rate of SOC losses (Guggenberger et al., 1995). The clearing of forests or woodlands and their conversion into farmland in the terrestrial ecosystem reduces the soil organic carbon content, mainly through reduced production of detritus, increased erosion rates and decomposition of soil organic matter by oxidation. Many researchers agree and their results have confirmed that soil organic carbon associated with different land uses varies dramatically at the regional or catchment scale (David White II et al., 2009; Zhang et al., 2011; Jaiarree et al., 2011). Based on 1407 soil profiles in Laos, Chaplot et al. (2009) found that median SOC density under forestland (112.0 $Mg.ha^{-1}$) is significantly higher than continuous cultivation (108.8 $Mg.ha^{-1}$) management at 0-30 cm depth. Chiti et al. (2011) found that mean SOC density under rice field soils (63.3 $Mg.ha^{-1}$) is significantly greater than arable land soils (53.1 $Mg.ha^{-1}$) at 0-30 cm depth in Italy, using a database created from the national project and regional map reports. Land use can reflect differences in regional scale SOC spatial distribution, expressing its dominant influence at the hillside and catchment level (Fang et al., 2012). In addition, conversion of forests to pasture did not change soil carbon (Guo and Gifford, 2002) or may actually increase the soil organic matter content (Sombroek et al., 1993). Changes in soil carbon under shifting cultivation were half as large (Detwiler, 1986). Commercial logging and tree harvesting did not result in long-term decreases in soil organic matter (Knoepp and Swank, 1997; Houghton et al., 2001; Yanai et al., 2003). Changes in the amount of soil organic matter following conversion of natural forests to other land uses depend on several factors such as the type of forest ecosystem undergoing change (Rhoades et al., 2000), the post conversion land management, the climate (Pastor and Post, 1986) and the soil type and texture (Schjønning et al., 1999).

The main objectives of the current study are i) to estimate SOC in different soil depths and to generate their spatial distribution maps, ii) to assess relationship between variation of different soil types and SOC density, iii) to determine effects of land cover types on SOC in İnebolu Basin.

Material and Methods

Field Description of the Study Area

The study area, Inebolu Basin, found in border of Kastamonu province geographically located in west part of the Black Sea region of Turkey is coordinated at 4636000-4648000 N and 557000-569000 E (UTM-m) and the total area is approximately 114 km^2 (Figure 1).

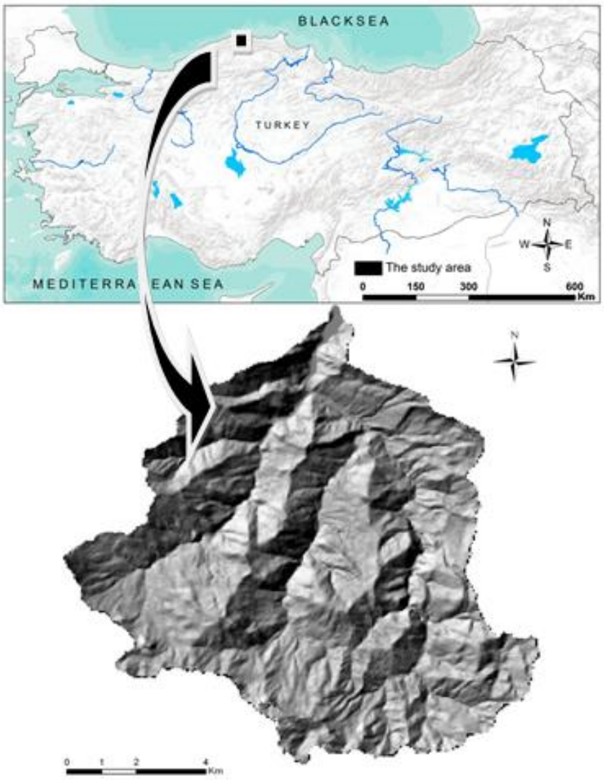

Figure 1. Location map of the study area

Mean sea level altitude of the Basin is 621 m. The study area is representativeness of semiarid catchments and the mean annual temperature, rainfall, average relative moisture and evaporation are 1033 mm, 13 ^{o}C, 75% and 680.58 respectively. According to Soil Survey Staff (Anonymous, 1999), soil temperature and moisture regime are mesic and ustic. The study area consists of various topographic features (flat, hilly, rolling etc.) particularly includes mountainous highland areas and slope varies between 2% and 45%. The underlying bedrocks within the study area consist of quartzit-quartz schist, andesine, sand stone-mud stone, and lime stone. Land use and vegetation of the study area are generally, covered by forest, arable land and pasture.

Methods

Soil sampling

Two kinds of soil sampling methods which are surface and profile were used to determine soil organic carbon density in the Basin. Soil samples were obtained from surface in random system (Figure 2).

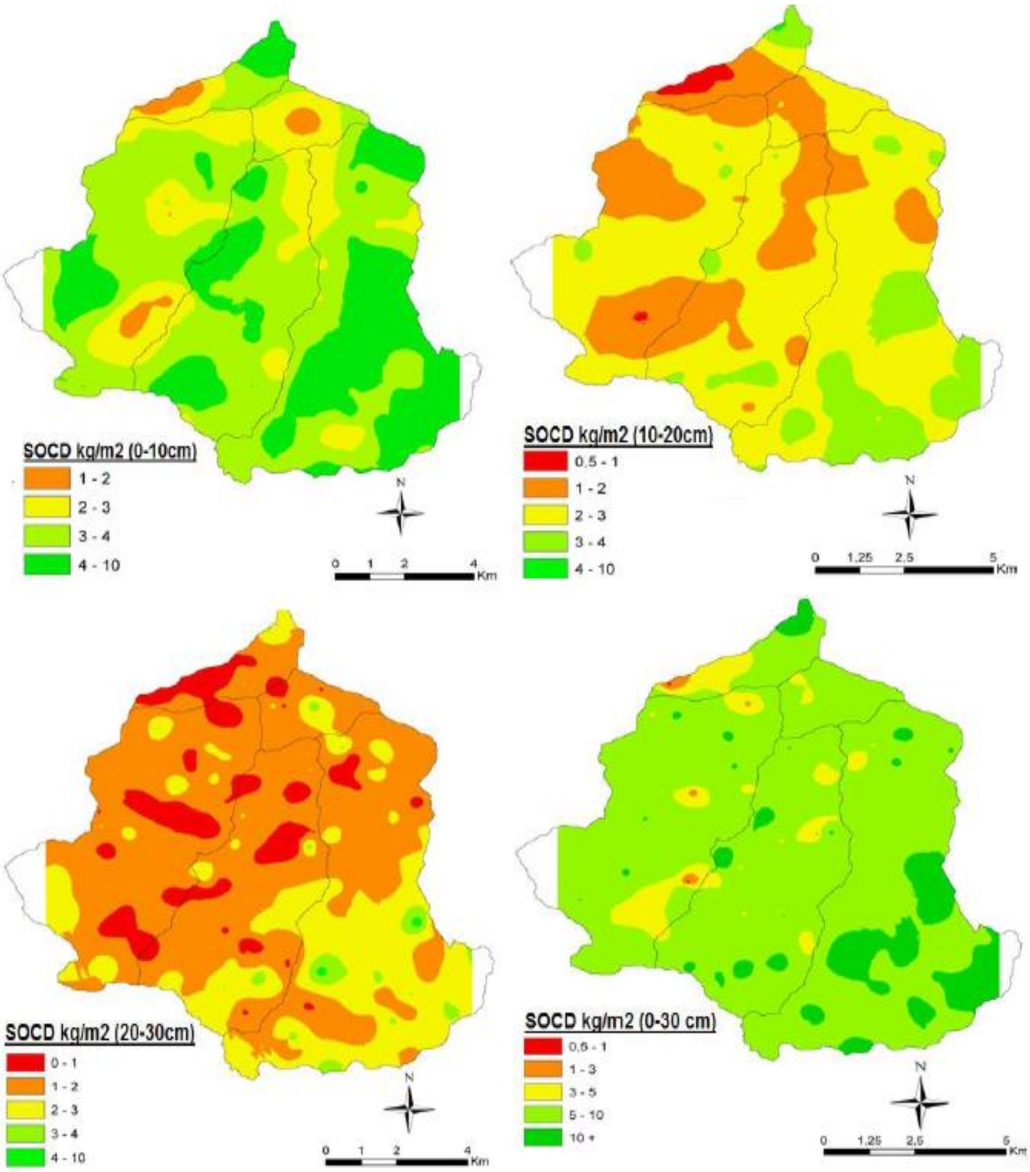

Figure 2. Spatial distribution maps of the SOCD for each depth

Total 230 soil samples were collected from surface (0-20 cm) for each land use and land cover. In addition, 32 soil profiles were investigated and described. 61 soil samples were taken from each horizon of profiles. The samples were transported to the laboratory. The soil samples were crumbled gently by hand without root material. These samples were used to determine some physico-chemical properties such as bulk density and organic matter. Selected soil properties were determined by the following methods: Bulk density (Blacke and Hartge, 1986) and organic matter was determined in air-dry samples using the Walkley-Black wet digestion method (Nelson and Sommers, 1982).

Soil organic carbon density estimation

For each profile, SOC density (SOCD) was estimated in the soil layer of profile (0-100 cm) with the following equation:

$$\mathrm{SOCD_D} = \sum_{i=1}^{n} \frac{(1-\delta i\%)\,\mathrm{x}\,\rho i\;x\;\mathrm{C}i\;x\;\mathrm{T}i}{100}$$

For each soil depths, SOC density was estimated with the following equation:

$$\mathrm{SOCD_D} = \frac{(1-\delta i\%)\,x\,\rho i\;x\;\mathrm{C}i\;x\;\mathrm{T}i}{100}$$

Where; SOCD$_D$ represents the SOC density of a soil profile with a depth D (cm); n is the number of pedogenic horizons in the soil survey, δi % represents the volumetric percentage of the fraction > 2 mm (rock fragments), ρi is the bulk density (g.cm^{-3}), C*i* is the SOC content (g.kg^{-1}), and T*i* represents the thickness (cm) of the layer *i.* The SOC was estimated to a maximum depth of 100 cm.

Interpolation and statistical analysis

Geostatistical method was used to generate SOC distribution map of the study area for surface and subsurface soils for both depth, values of SOC were described with classical statistics (mean, standard deviation, maximum and minimum mean, and coefficient of variation, Skewness, Kurtosis). In addition, range, nugget and sill variance values were determined using semi-variograms. The degree of spatial dependence of a random variable Z(xi) over a certain distance can be described by the following semivariogram function:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{n} \left(Z_{(x_i)} - Z_{(x_i+h)}\right)^2$$

Where $\gamma(h)$ is the semivariance for the interval distance class h, N(h) is the number of pairs of the lag interval, Z(x_i) is the measured sample value at point i, and Z(x_i+h) is the measured sample value at position (i+h). To determine spatial variability of SFI variables, the isotropic semivariogram models as Exponential and Gaussian were used.

The isotropic exponential model:

$$\gamma(h) = C_0 + C\left[1 - \exp\left(\frac{-h}{a}\right)\right]$$

The isotropic spherical model:

$$\gamma(h) = \begin{cases} C_0 + C\left[\dfrac{3h}{2a} - \dfrac{1}{2}\left(\dfrac{h}{a}\right)^3\right] & 0 \le h \le a \\ C_0 + C & h > a \end{cases}$$

Where; Co is the nugget variance ≥0, C is the structural variance ≥ Co, (Co+C) is the sill variance, and is the range of spatial correlation.

Geostatistical software (GS$^+$ 7.0, 2007) was used to construct semivariograms and spatial structure analysis for variables. In addition, maps of SOC variables for each depth (surface and subsurface soils) were produced by kriging technique (Isaaks and Srivastava, 1989) using ArcGIS 9.3v geography information system program.

Results and Discussion

Estimation of SOCD in different soil depths and interpolation maps

Accumulation or reduction soil organic carbon content can be markedly noticed in surface soil due to shifting land use types and land cover in short term. Various reviews agree this case that the loss amounts to 20 to 50% of the original carbon in the topsoil, but deeper layers would be little affected, if at all (Murty et al., 2002; Guo and Gifford, 2002). On the other hand, conversion of forests to pasture did not change soil carbon (Guo and Gifford, 2002) or may actually increase the soil organic matter content (Sombroek et al., 1993). The descriptive statistics properties of SOCD for different depths are presented in Table 1.

Table 1. Descriptive statistics of the SOCD for each depth

	Depths of SOCD			
Properties	0-10 cm	10-20 cm	20-30 cm	0-30 cm/total
Mean	3.56	2.35	1.69	7.59
Standard Deviation	1.31	0.99	0.88	2.71
Sample Variance	1.72	0.997	0.77	7.37
Minimum	0.21	0.18	0.06	0.44
Maximum	7.27	4.91	4.85	15.39
Skewness	-0.01	0.26	0.65	0.25
Kurtosis	-0.2	-0.39	0.37	0.13
Samples (n)	230	230	230	230

According to Table 1, it can be seen that mean value of SOCD decreases with increasing soil depth and varies between about 3.6 kg.m^{-2} and 1.7 kg.m^{-2}. In addition to that, it was determined SOCD level between 0.44 and 15.39 kg.m^{-2} in 0-30 cm for each soil samples.

Geostatistics provides a set of statistical tools for incorporating spatial coordinates of observations in data processing (Loganathan et al., 2007). It also provides a tool to optimise sampling design and interpolate to unsampled locations, taking into account the spatial correlation of adjacent pixels based on the semi-variance. This procedure is optimal in that estimates are unbiased and the estimation variance is minimal (Di et al., 1989). This technique has been widely applied by soil scientists (Leenaers et al., 1990; Kravchenko and Bullock, 1999; Başkan and Dengiz, 2008). The isotropic exponential and model provided the best fit value for the computed semi-variance points for SOCD in this study. The experiment semivariogram depicts the variance of the sample values at various separation distances (Hani et al., 2010). The ratio of nugget to sill (nugget/sill) can be used to express the extent of spatial autocorrelations of environmental factors. If the ratio is low (<25%), the variable has strong spatial autocorrelations at a regional scale. A high ratio of the nugget effect (>75%) indicates spatial heterogeneity of soil properties. In this study, low ratio of nugget to sill (less than 25%) was found for each depth of SOCD indicated the existence of a strong spatial auto-correlation (Table 2).

Table 2. Parameters of isotropic models for best fitted semi-variogram models of SOCD for each depth.

Depth (cm)	Model	Nugget	Sill	Range	RSS	R^2	Nugget/Sill ratio (%)
SOCD (0-10)	Spherical	0.247	1.340	2916	0.0148	0.975	18.43
SOCD (10-20)	Spherical	0.141	0.638	2954	7.024×10^{-3}	0.943	22.10
SOCD (20-30)	Exponential	0.001	0.407	2028	1.801×10^{-3}	0.942	0.25
SOCD (0-30)	Exponential	0.100	4.309	2202	0.223	0.969	2.32

Assessment of relationship between variation of different soil types and SOCD

The parameters of the spherical and exponential models were used for kriging to produce the spatial distribution maps of SOCD for each depth in soils in the study area. These maps are shown in Figure 2 and SOCD were classified at four and five levels in Table 3.

Table 3. Distribution of SOCD for each depth

Class	Description (kg.m^{-2})	Area (ha)	Ratio (%)	Class	Description (kg.m^{-2})	Area (ha)	Ratio (%)
SOCD (0-10 cm)				SOCD (20-30 cm)			
1	1-2	244.0	2.19	1	0-1	11056.0	9.9
2	2-3	2007.3	18.00	2	1-2	6785.5	60.8
3	3-4	5517.6	49.47	3	2-3	3048.4	27.3
4	4+	3384.4	30.34	4	3-4	200.6	1.8
SOCD (10-20 cm)				5	4+	12.7	0.11
1	0.5-1	110.4	0.99	SOCD (0-30 cm)			
2	1-2	2830.0	25.37	1	0.5-1	1.08	0.01
3	2-3	656.1	58.83	2	1-3	38.8	0.3
4	3-4	1646.1	14.76	3	3-5	704.4	6.3
5	4+	5.4	0.05	4	5-10	9257.8	83.0
				5	10 +	1151.1	10.3

As it can be seen from the Table 3, the highest SOC density coded as forth class for 10 cm soil depth located at south east parts of the study area generally covered by natural forest and pasture whereas, SOC density was determined the lowest level found on north parts of the Basin where generally used for rainfed agriculture. Besides, SOC density is dramatically decreasing with increasing soil depth which trend can be also observe in this study. As for SOCD 10-20 cm and 20-30 cm, more than 4 kg.m^{-2} SOCD value of lands was found in south east part of the study area and they cover about 0.05 and 0.11% of the total area, respectively.

Soil organic carbon is the largest terrestrial carbon pool (Janzen, 2004), and plays an important role in the global carbon cycle. Assessments of SOC density within and among soil types are important in understanding causes and effects of climate or land use changes on the ecosystem CO_2 balance. According to Soil Survey Staff (Anonymous, 1999), major soil groups of the study area were classified as in subgroup level and determined to assess relationship between variation of different soil types and SOC stock (Table 4).

Table 4. Amount of SOCD for each soil types classified by taking into consideration of soil survey staff (Anonymous, 1999)

Order	Suborder	Great Group	Subgroup	SOCD (kg.m^{-2})
ENTISOL	Fluvent	Ustifluvent	Vertic Ustifluvent	2.46
	Orthent	Ustorthent	Lithic Ustorthent	0.87
		Ustorthent	Typic Ustorthent	6.50
INCEPTISOL	Ustept	Haplustept	Lithic Haplustept	6.05
		Haplustept	Typic Haplustept	7.31
		Haplustept	Vertic Haplustept	12.93

The horizon succession of Entisol was defined as A/C or A/R. This means that this soil order had no diagnostic subsurface horizons and low pedogenetic development. Therefore, Entisol can be defined as a young soil formed on sediment alluvial deposit or rock. There are three subgroups which are Lithic Ustorthent, Vertic Ustifluvent and Typic Ustorthent were defined (Figure 3) and it was found their SOC density significantly different mainly stemmed from land cover, soil depth and texture. The highest SOCD value (6.5 kg.m^{-2}) was determined in Typic Ustorthent covered by natural forest and pasture whereas, Lithic Ustorthent located on hillslope position includes the lowest SOCD value due to soil erosion process. In addition, Vertic Ustifluvent which includes high clay content in surface layer has 2.46 kg.m^{-2} SOC. The horizon succession of Inceptisol was defined as A/B/C.

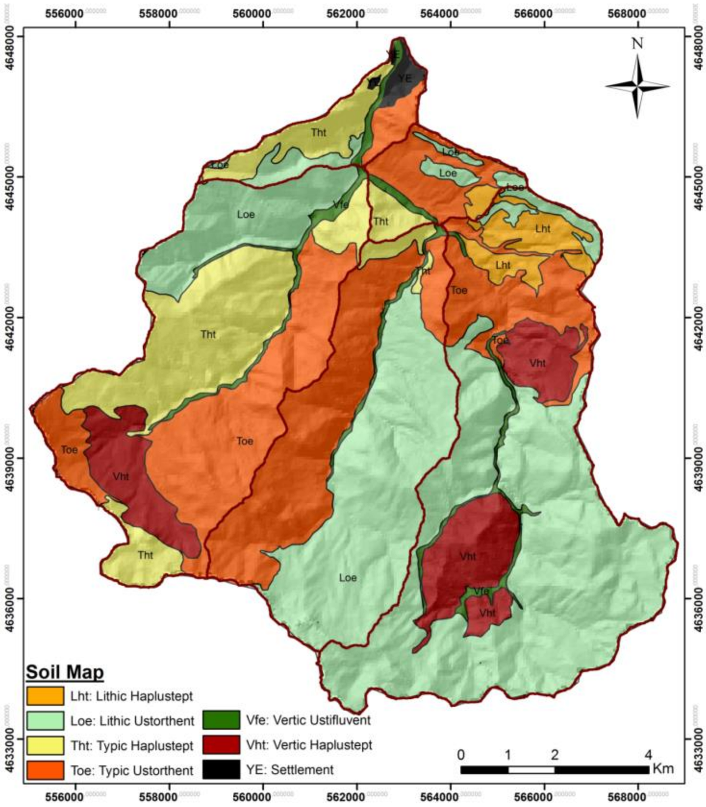

Figure 3. Soil map of the study area

Main subsurface diagnostic horizon for this order is cambic horizon developed as a result of structural formation in soil profile. This order has also three subgroups which are Lithic Haplustept, Typic Haplustept and Vertic Haplustept. Vertic Haplustept has the highest SOC content in the Inceptisol, followed by Typic Haplustept (7.31 kg.m^{-2}), Lithic Haplustept (6.05 kg.m^{-2}). Moreover, when compared at these two order soil, it can be seen there is a significantly difference between two soil orders. Inceptisol has more SOC content than that of Entisol because of more pedogenic process, soil depth, and fine texture.

Dengiz at el. (2015) also estimated the same results in their study carried out in Madendere Basin. According to their result, Haplustept (37.58 kg.m^2) was significantly higher than other soil great groups, flowed by Dystrustept (10.20 kg.m^2), Calciustept (5.69 kg.m^2), and Ustorthent (3.78 kg.m^2). They reported for this result that there were two important cases affected on SOC density in soil types. One of them is mainly pedological development and soil layers' depth and secondly is land use and land covers.

Effect of land cover types on SOCD

Land cover can have a huge impact on soil carbon stocks. Kızılkaya and Dengiz (2010) in a study according to land cover changes in natural forest of Cankiri-Uludere Basin indicated that deforestation and subsequent tillage practices resulted in significant decrease in organic matter and total nitrogen. To determine land cover of the study area, aster satellite image that has 15m x 15m spatial resolution and dated 2013 was used. According to remote sensing analysis, primary land covers are bare land, sparsely vegetated area, broadleaved forest area, mixed forest area and needleleaved forest area (Figure 4). Sparsely vegetated area is the highest land cover in the study area and has about 33.01 % of the total area, followed by broadleaved forest area (27.37%), bare land (14.94%), mixed forest area (14.01%) and needleleaved forest area (10.66%).

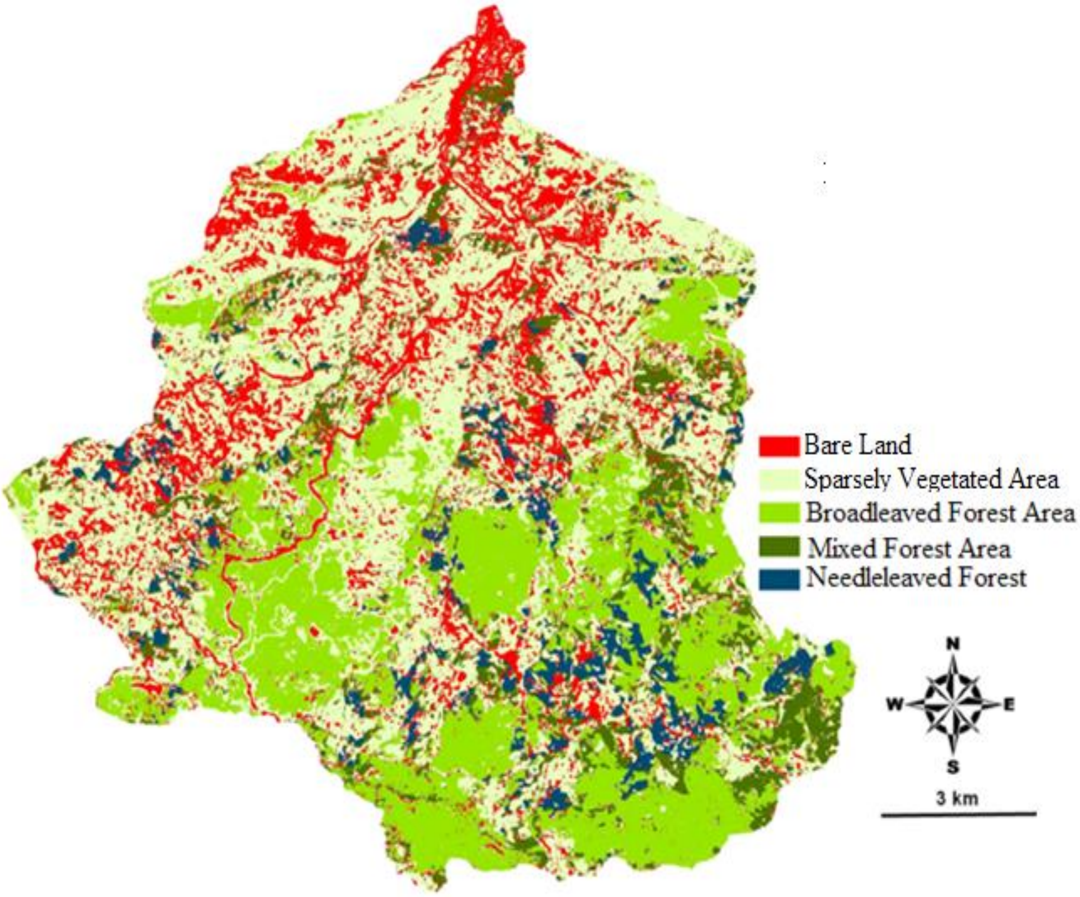

Figure 4. Land Cover maps of the study area

Distribution of SOCD classes under different land cover types for each soil depth was given in Table 5. Result of SOCD distribution for 10 cm soil depth in the Table 5 showed that the highest soil organic carbon density coded as 4. class was found under mixed forest area covering about 1029.5 ha whereas, it was determined that the area of SOC density between 1 and 2 kg.m^{-2} under all land cover types has the lowest distribution in the Basin. As for depth of between 10-20 cm, third class of SOCD has common distribution in the study area.

The highest distribution area for this class was determined under sparsely vegetate cover whereas, 687.6 ha of the total area that includes between 2 and 3 kg.m^{-2} SOC content was detected under needleleaved forest cover. It was also observed that general trend of organic carbon concentration decreases with increasing soil depth under all land cover types. This case can be said for soil depth of between 20-30 cm. The highest SOC density class coded as five was found as the lowest distribution area for each land cover type in the study area. On the other hand, very low and low SOC density classes have common distribution area in the Basin.

Conclusion

In this study it was investigated the relationship between soil type and land cover, with SOC density spatial distribution in the İnebolu Basin. Relative to the subsurface layer, soil type and land cover have a greater impact on SOC density in the surface layer. Comparing the two main factors, land cover explained more of the SOC density variability and was the main controlling factor in the surface; in the subsurface, not only land cover types but also some properties of soil types such as texture, genetic horizons, and soil depth have an important role on SOC density. On the other hand, it can be said that the combination of the soil type and land cover was a dramatically better predictor of SOC density. In addition, the results showed that at the catchment scale, soil type and land cover should be combined SOC spatial distribution and estimate SOC density with the land use and land management priorities

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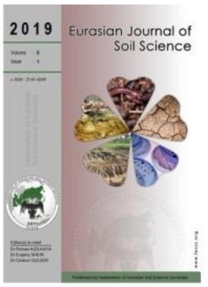

Soil organic carbon mapping and prediction based on depth intervals using kriging technique: A case of study in alluvial soil from Sudan

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Abstract

Soil organic carbon plays a vital role in the arid and semiarid regions. This study aimed to predict and map soil organic carbon content at soil depth intervals of 0-0.3 m, 0.3-0.6 m, 0.6-0.9 m, and 0.9-1.2 m in alluvium soils along Blue Nile and River Nile, Sudan. Ordinary kriging (OK) technique was used as a geostatistical tool and applied to model the spatial variability of soil organic carbon in the study area. A total of 38 soil profiles were excavated in the study area and 152 samples from the four depths intervals were collected for determining organic carbon content. Results revealed that, the spatial autocorrelation for the different soil layers was moderate to weak with a nugget to sill ratios ranging from 0.21 to 0.86 suggesting their controlled by both intrinsic and extrinsic factors. The root mean square error standardized (RMSE) of the predictions ranging from 0.79 to 0.83 indicating that the model which generated by ordinary kriging was correctly estimating the variability of soil organic carbon in the study area.

Keywords: Alluvial soil, spatial autocorrelation, semivariogram, soil organic carbon, Cokriging, soil depth intervals.

Introduction

It is well known that soil is the major pool of organic carbon in the terrestrial biosphere, storing more carbon than that in the plants and atmosphere together (Scharlemann et al., 2014). Soil organic carbon (SOC) plays an important role in agricultural productivity (Acín-Carrera et al., 2013), therefore SOC could be a useful indicator for soil health and quality for soil fertility and climate regulation (Beguería et al., 2015; Chen et al., 2017).

Level of SOC mainly revert to soil properties such as aggregate stability, soil structure, porosity or nitrogen content (Cotching et al., 2014; Bienes et al., 2016, Sulieman et al., 2018) and resultant soil processes related to land degradation like soil erosion (García-Díaz et al., 2016; Jin et al., 2009). Thus, nature-based solutions should be applied in order to conserve the soil carbon stocks in some specific degraded environments such as forests, agricultural fields or alluvial areas (Keesstra et al., 2018, Sulieman et al., 2016).

In this way alluvial areas over the world are highly demanded for intensive agricultural production, and this is mostly attributed to their high quality of the soils and water as well (Parker, 1995; Bertalan et al., 2016). In the South-east Anatolia region of Turkey, Dengiz (2010) studied the morphology, physico-chemical properties and classified the soils developed on terraces of the Tigris River. He concluded that, the soils developed on floodplain were characterized by weak pedogenesis, however, development of the B horizon (Bw, Bt, Bss) and carbonate

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accumulation were the main pedogenic processes in terraces soils, and the main soil order were Entisols, Inceptisols, Alfisols and Vertisols. Specifically, in North African regions, non-suitable land use managements are affecting the soil properties and microbial diversity and only well-planned decisions by farmers and policy makers could be revert this dramatically situation (Bounouara et al., 2017; Camilli et al., 2016, Mlih et al., 2016). More specifically, in Sudan, the most irrigated intensive crop farming areas for vegetables and fruits are largely situated within the alluvium plains of the Blue Nile, White Nile, and River Nile terraces. In these alluvial terraces, research on soil properties and their relationships among them that condition their geographical distribution is not highly conducted (Elfaki et al., 2015; Sulieman et al., 2015a,b, 2016).

The distribution of SOC and other soil properties change across the landscape and it also varies by depth (Bogunovic et al., 2017, Sulieman et al., 2018). Dengiz et al. (2015) studied the effects of soil types and land use - land cover on SOC density at Madendere watershed, they concluded that, the two factors had great influence on SOC density spatial variation at the different land use systems. In most natural soils, SOC is higher in the surface horizons and it decreases with depth, however, in agricultural areas the spatial variability can be very high (Lado et al., 2004). Such depth-wise variability is mostly continuous in forest or mountainous soils (Bishop et al., 1999; Hartemink and Minasny, 2014) except in soils with a strong human impact like some soils in the Netherlands (Kempen et al., 2011) or after the abandonment (Rodrigo-Comino et al., 2017). Therefore, soil human impacts can be considered as a driving factor of SOC changes (Gómez et al., 2009; Johannes et al., 2017). Despite the most SOC studies and inventories are confined to 30 cm soil depth, the amount of SOC stored below 30 cm is also relevant in many ecosystems (IPCC, 2003; Smith et al., 2005). Sudan is a poorly mapped country in terms of soil data (Sulieman et al., 2018). Likewise, the spatial variability of SOC is not yet understanding all over the country and, most specifically, in alluvial areas.

Geographic Information Systems can contribute as a useful tool for soil mapping (Pereira et al., 2018). The creation of soil maps that show the distribution of soil properties along the landscape is considered a powerful tool to organize the territory suitably (Behrens et al., 2010; Grunwald, 2009). To achieve this goal in semiarid environments, different methods have been applied such as modelling (Keshavarzi et al., 2018; Shiri et al., 2017), pedotranfers (Nasri et al., 2015) or geospatial analysis (Zeraatpisheh et al., 2017).

In this current study, it was pretend to fill lack of information by applying digital soil mapping techniques to quantify the SOC content and distribution. Therefore, the main objective of this research is to applied ordinary kriging (OK) geostatistical method to predict and map the spatial distribution of SOC at soil depth intervals of 0-30 cm, 30-60 cm, 60-90 cm, and 90-120 cm in selected alluvium soils along the Blue Nile and River Nile terraces in Sudan.

Material and Methods

Study Area

The studied samples representing soils from across the upper, middle, and lower Nile River terraces and the upper and lower Blue Nile terraces (10º00" to 15º 45" N, 30º00" to 35º00" E) in Sudan were collected and analyzed (Figure 1). According to the updated map of climatic classification (Peel et al., 2007), the climate of the study area varies from arid to semiarid zone, characterized by hot dry in most periods of the year to relatively heavy rains during short period in summers. The mean annual temperature varies from 28.3 to 29.6 °C and mean annual precipitation varies from 163 mm to more than 700 mm (Van der Kevie, 1976).

Geologically, the alluvium soils along Nile River belong to the Cretaceous Period which comprises continental clastic sediments including sandstones, siltstones, mudstones and conglomerates and locally known as Nubian Sandstone Formation. Whereas, the soils from Blue Nile terraces belong to the Tertiary Period (Gezira Formation), which comprises unconsolidated fine materials and gravels, and Quaternary Periods comprises unconsolidated sands with some gravels, and shales locally known as Umm-Ruwaba Formation (Figure 2) (Whiteman, 1971; Ministry of Energy and Mines, 1981). Topographically, the study area is mostly gently undulating. The soil moisture and temperature regimes are aridic to ustic and thermic to hyperthermic, respectively, and the soils are classified as fluvents suborder according to USDA soil Taxonomy (Soil Survey Staff, 2014). The main form of land use in the study area is intensive irrigated agriculture for vegetables and fruits. Ecologically, the area lies within the desert to semi desert ecological zone (Harrison and Jackson, 1958), consists of a wide variety of natural plant species, notably Fagonia cretica, Indigofera oblongifolia, Aerva javonica, Acacia toritllis and Maerua crassifolia.

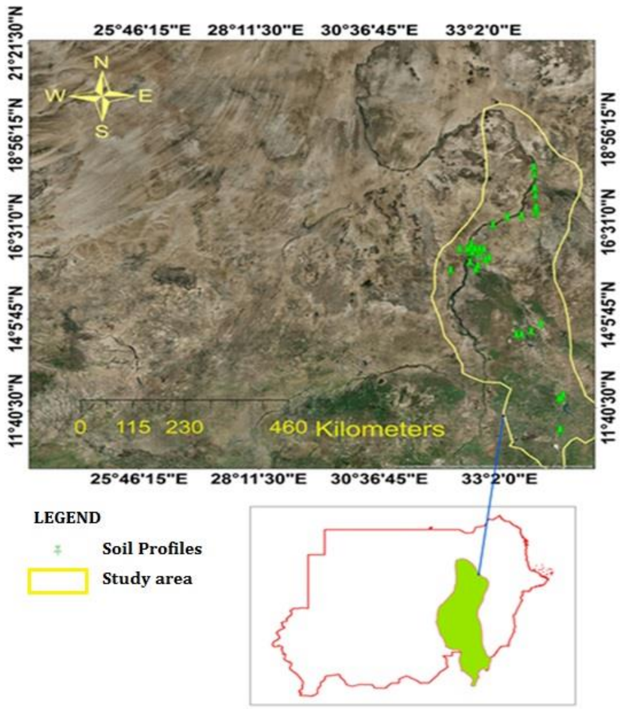

Figure 1. Study area represent some of selected profile's locations along the Nile River and Blue Nile terraces

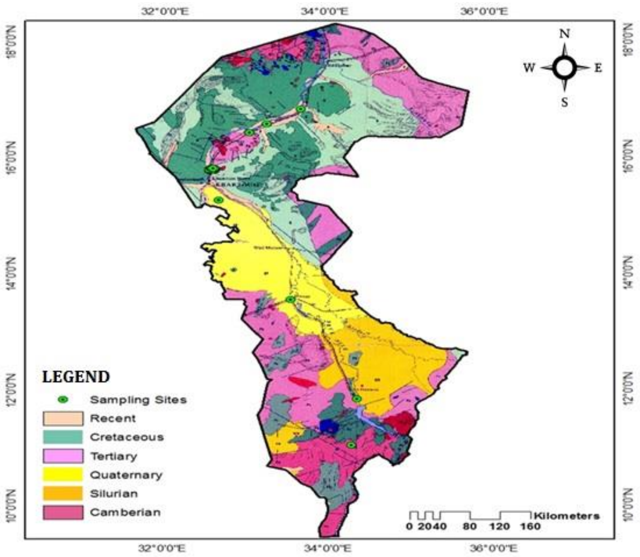

Figure 2. Selected profiles locations inside the subset of geological map of Sudan

Soil sampling and analysis

A total of 38 soil profiles were excavated along the study area, fully described following the field books of Schoeneberger (2012), classified according to USDA soil taxonomy (Soil Survey Staff, 2014). Based on the genetic horizons, a total of 152 soil samples were collected from four depth intervals of 0 to 120 cm within each profile as follows; 0-30 cm, 30-60 cm, 60-90 cm, and 90-120 cm. In laboratory, soil samples were first air-dried, ground, and then passed through a 2 mm sieve to obtain the fine fraction. The soil organic carbon was measured by wet oxidation with chromic acid and back titrated with ferrous ammonium sulfate following the standard Walkey and Black method (Nelson and Sommers, 1996). A histogram tool in Arc GIS software version 10.4 was used to identify the outliers of SOC, where a more isolated bar from the main group of bars in the histogram was taken to represent a possible outlier (Chabala et al., 2017). Therefore, in case if outliers observed, the laboratory analyses were repeated and any outliers recorded one more were removed from the samples set.

Statistical analyses

General basic statistics parameters such as minimum and maximum values, mean, median, standard deviations, first quartile, third quartile, Skewness, and Kurtosis were calculated for both tested and validated samples to provide a basic understanding of the characteristics of data using Statistix software version 8.1 (Steel and Torrie, 1980).

Predicting spatial distribution of SOC

In this study, the spatial variability of SOC at four depths intervals was studied using ordinary kriging (OK) method. OK is a geostatistical models that use a set of statistical tools to predict the value of a given soil property (in this case SOC) at a location that was not sampled (Goovaerts, 1998; Regalado and Ritter, 2006; Johnston et al., 2001). Based on OK, the predicted SOC at an unsampled location ($pred(x_0)$), using measured values $obs(xi)$ is given as:

$$pred(x_0) = \sum_{i=1}^{n} w_i(x_0) * obs(x_i) \tag{1}$$

Where $w_i(x_0)$ is the kriging weight.

In order to model the spatial variability of SOC with OK, further data evaluation was performed to check whether the SOC data conformed to the necessary assumptions required for OK include that data are required to be normally distributed with no trend. The histogram and normal quantile-quantile (Q Q) plots tools in

ArcGIS were used to evaluate the distribution of the data. The trend analysis tool was also applied to check for trend in the SOC data set. The data check revealed that the data set had no trend. The central tool of geostatistical procedures such as OK is the semivariance, which is half the expected squared difference between the SOC values at two locations. The semivariance quantified the spatial variability of SOC for all possible pairing of SOC data. The plot of the semivariance as a function of distance is referred to as a semivariogram (Chahouki et al., 2011). The semivariogram described how SOC varied with distance among the sampling locations. Positive definite models were applied to fit the semivariogram using ordinary least squares to capture spatial features of the SOC. An automated fitting procedure was followed when fitting the semivariogram of SOC using the exponential model. All data processing and analysis for OK were done in ArcGIS software package version 10.4 with the variogram redrawn in Microsoft excel.

Data validation

The prediction accuracy of SOC at the unsampled locations was evaluated using the leave-out-one cross validation (LOCV) techniques (Reza et al., 2010; Liu et al., 2013; Martín et al., 2016). The indices used during LOCV were root mean square error (RMSE), average standard error (ASE), and standardized RMSE (RMSSE). Thus, for each of the sampled locations, there was a measured value for SOC (*obs(xi)*) and a predicted value (*pred(xi)*), with standard values being $obs1(xi)$ and $obs2(xi)$, respectively. The ASE, RMSE, and RMSSE were calculated according to Yang et al. (2009) as follows:

$$ASE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left[pred_{(xi)} - \left(\frac{\sum_{i=1}^{n} pred_{(xi)}}{n}\right)\right]^2} \tag{2}$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left[obs_{(xi)} - pred_{(xi)}\right]^2} \tag{3}$$

$$RMSSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left[obs1_{(xi)} - obs2_{(xi)}\right]^2} \tag{4}$$

Where *n* is the number of validation points.

The RMSSE varies between 0 and 1, with a value of 1 indicating a perfect model and 0 indicating a poor model. In addition, a cross plot of measured and predicted SOC values was drawn in a scatter plot and associated summary statistics of predicted SOC values were compared with those of measured values (Leuangthong et al., 2004) using the Sample *t*-test (Paired *t*-test).

Results and Discussion

Summary of basic statistics

The summary of descriptive statistics for the measured and predicted SOC data are presented in Table 1. Results show that the SOC showed a decreasing trend with increasing soil depth. Mean SOC for both measured and predicted was 0.75, 0.64, and 0.50 g kg^{-1} for soil layers 0-30 cm, 30-60 cm, and 90-120 cm, respectively, while the mean for measured and predicted SOC at layer 60-90 cm was 0.56 and 0.59 g kg^{-1}, respectively. This indicates that the model was reliable for SOC prediction in this depth compared to the other three depths, meanwhile, it can be taken into account. The standard deviation (±SD) in the measured SOC was 0.53, 0.52, 0.46, and 0.43 g kg^{-1} for layers 0-30 cm, 30-60 cm, 60-90 cm, and 90-120 cm, respectively compared to 0.29, 0.29, 0.28, and 0.26 g kg^{-1}, respectively for the same layers in the predicted SOC. The coefficients of variation (CV) of SOC for both measured data for all layers ranged from 71.56 to 86.72 % with gradually increased from the surface to the bottom layers in the soil profile. This could be due to the complex textural layers. This result is in line with previous studies of He et al. (2009) and Chen et al. (2015). A coefficient of variation (CV) value of 10% indicates low variability and values ranging from 10–90% indicate a moderate variability; CV values > 90% indicate high variability (Fang et al., 2012). Therefore, measured SOC in our study indicated a moderate variability. The coefficients of skewness at four depths were 0.53, 0.61, 71, and 1.23 in the measured SOC, respectively and 0.49 and 0.20, 0.23, and 0.53 in the predicted SOC, respectively. This indicated that the measured and predicted SOC followed similar pattern distribution. Further, the skewness (<0.5) and kurtosis

(<3) of SOC indicated the approximate normal distributions of data (Rosemary et al., 2017). The first and third quartiles at the four depths were (0.51, 0.91), (0.34, 0.90), (0.40, 0.78), and (0.30, 0.61) g kg−1, respectively in the predicted values, which were comparable to the recorded values in the measured data. Overall, the summary statistics in the measured and predicted SOC indicated that the model was well fitted for the prediction of SOC at the different soil layers.

Table 1. Summary basic statistics of the measured and predicted SOC at four different layers.

Depth (cm)	SOC	Mean	Minimum	Maximum	Median	±SD^{a}	CV (%)	1st Qu	3rd Qu	Skewness	Kurtosis
		g kg^{-1}									
0-30	Measured	0.75	0.10	1.84	0.59	0.53	71.56	0.24	1.28	0.53	−0.93
	Predicted	0.75	0.13	1.19	0.77	0.29	40.45	0.51	0.99	−0.49	−0.84
30-60	Measured	0.64	0.04	1.92	0.46	0.52	81.26	0.19	1.16	0.64	−0.75
	Predicted	0.64	0.13	1.16	0.66	0.29	45.97	0.34	0.90	−0.20	−1.13
60-90	Measured	0.56	0.04	1.76	0.53	0.46	79.86	0.16	0.96	0.71	−0.51
	Predicted	0.59	0.09	1.24	0.61	0.28	47.56	0.40	0.78	0.23	−0.45
90-120	Measured	0.50	0.04	1.68	0.44	0.43	86.72	0.13	0.67	1.23	1.06
	Predicted	0.50	0.08	1.08	0.49	0.26	53.61	0.30	0.61	0.58	−0.41

±SD = standard deviation; CV = coefficient of variance; 1st Qu = 25%; 3rd Qu = 75%.

Variography and kriging interpolated of SOC at different depth intervals

Figures 3 shows the fitted semivariogram and the associated variograhpic parameters for the different depth intervals. Depending on the criteria suggested by Cambardella et al. (1994), the spatial dependence or autocorrelation was judged to be strong if the nugget to sill ratio was less than 0.25, to be moderate if between 0.25 and 0.75, and to be weak if higher than 0.75. In this study, the spatial autocorrelation (SAC) at depth intervals of 0-30 cm, 30-60 cm, and 60-90 cm has a nugget to sill ratios of 0.42, 0.28, 21 respectively, and at layer 90-120 cm was 0.86 (Fig. 3a,b,c,d), demonstrating a moderate to weak spatial dependence of SOC for the different soil layers which was controlled by both intrinsic and extrinsic factors.

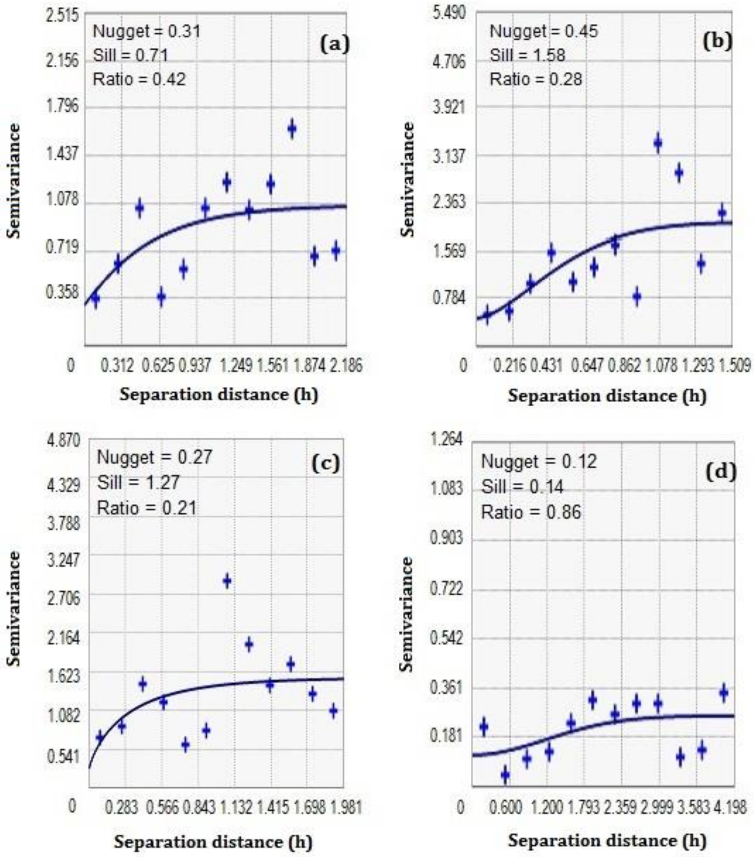

Figure 3. Experimental semivariograms and spatial models for SOC in the vertical direction at depths (a) 0-30 cm, (b) 30-60 cm, (c) 60-90 cm, (d) 90-120 cm

This was evidenced by local, intensive agricultural management, such as tillage and fertilization, widely used in the study area to improve the fruit and vegetables productivity (Sulieman et al., 2016). The maps of SOC spatial distribution generated depending on the measured SOC values and fitted variogram is shown in Figure 4. However the standard error maps of SOC spatial prediction is shown in Figure 5. According to Wang et al. (2009) and Fu et al. (2014), a strong spatial dependence of soil properties is attributed to soil intrinsic properties, such as soil parent materials, soil texture, topography and vegetation. Whereas, a weak spatial dependence of soil properties indicates that the spatial variability is mainly regulated by extrinsic variations, such as soil fertilization and cultivation practices, and moderate spatial dependence is controlled by both intrinsic and extrinsic factors (Kılıç et al., 2004; Wang et al., 2009). The exponential nature of the fitted semivariogram may indicate that SOC at the site had a gradual transition or that several patterns interfered. This variation in SOC levels can be attributed to the vertical illuviation of mineral and organic material from surface layers downward the soil profiles (Brodsky et al., 2013).

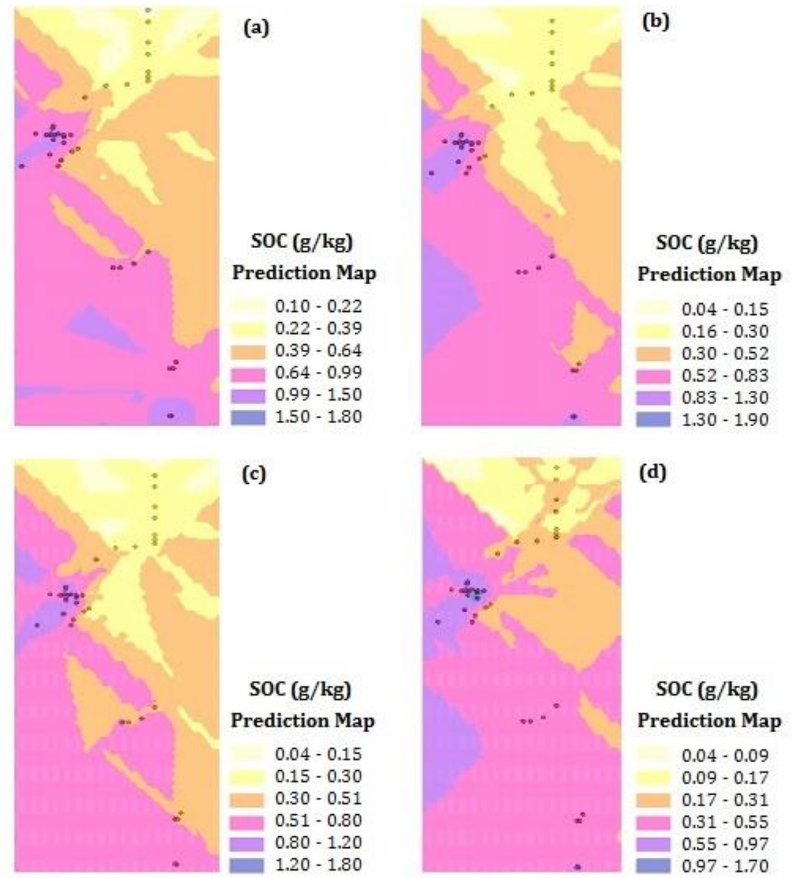

Figure 4. Maps of soil organic carbon spatial distribution, generated based on measured data and fitted variogram at soil depths (a) 0-30 cm, (b) 30-60 cm, (c) 60-90 cm, (d) 90-120 cm

Modeling validation

The indices generated during the leave-out-one cross validation (LOCV) of OK model at four different depths are presented in Table 2. It was observed that goodness of fit between observed and predicted values was higher in surface soil layers than sublayers. The average standard error was 0.58 at depth 0-30 cm (RMSE = 0.47), 0.57 at depth 30-60 cm (RMSE = 0.43), 0.51 at depth 60-90 cm (RMSE = 0.39), and 0.48 at depth 90-120 cm with the RMSE of 0.35. The standardized RMSE was 0.83, 0.79, 0.80, and 0.79 for the same depths grades, respectively. The RMSSE with a value closed to 1 indicating a perfect model (Tang et al., 2017). Overall, the RMSSE values in our study indicating that the model was correctly estimating the variability of SOC at the unsampled locations at the four different layers, and the best model was observed at the surface layer (0-30 cm). Chabala et al. (2017) studied the spatial distribution of SOC at depth 0-20 cm in soils of a selected part of Zambia by using OK technique, they conclude that the model generated by OK was reliable in predict SOC and produce a RMSSE of 1.02. Figure 6 shows the predicted versus measured SOC, and the cross plot clearly indicated a weak to medium positive correlations. Further, there were no significant differences (P >0.05) between the measured and predicted SOC in all soil layers when compared by the Sample t-test (Paired t-test).

Table 2. Indices used for leave-out-one cross validation (LOCV) of ordinary kriging model for SOC prediction at different soil depths.

Depth (cm)	Mean	MS[a]	ASE[b]	RMSE[c]	RMSSE[d]
0-30	−0.006	−0.015	0.58	0.47	0.83
30-60	−0.005	−0.01	0.57	0.43	0.79
60-90	0.003	0.00001	0.51	0.39	0.80
90-120	−0.003	−0.001	0.48	0.35	0.79

[a] Mean standardized; [b] average standard error; [c] root mean standard error; d root mean square error standardized.

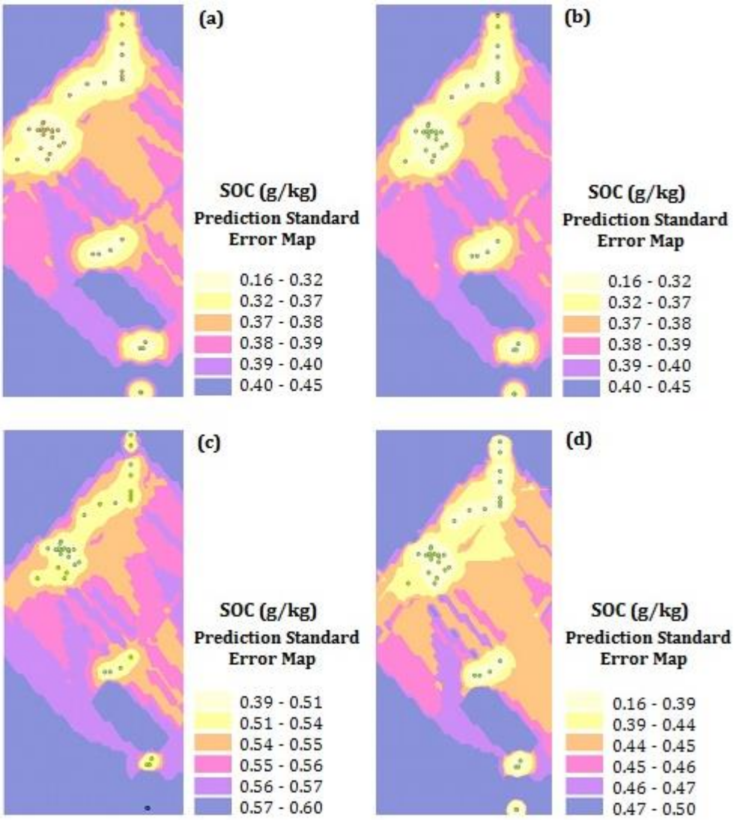

Figure 5. Standard error maps of SOC spatial prediction at soil depths (a) 0-30 cm, (b) 30-60 cm, (c) 60-90 cm, (d) 90-120 cm

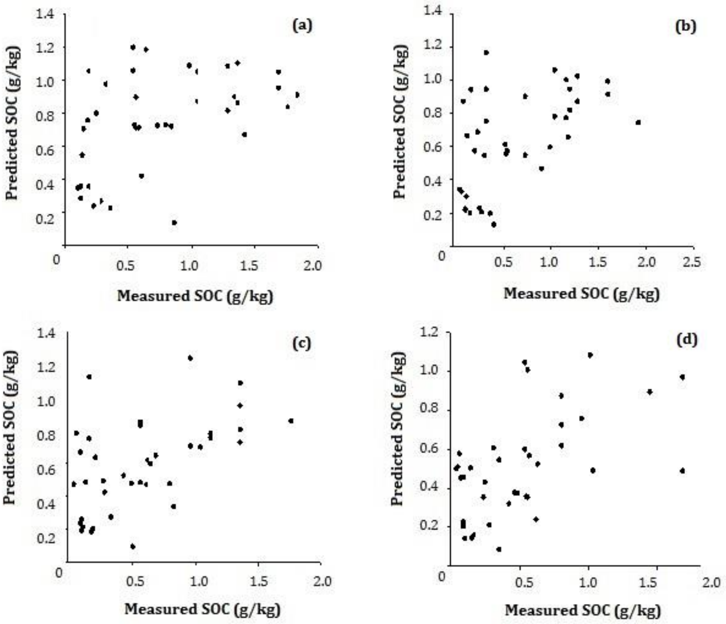

Figure 6. Cross-validation of OK interpolation for SOC at soil depths (a) 0-30 cm (b) 30-60cm (c) 60-90 cm (d) 90-120 cm.

Conclusion

In this study, OK was applied to study the spatial interpolation of SOC at 0–30 cm, 30–60 cm, 60-90 cm and 90–120 cm using the measured data from 152 samples in alluvium soils along Blue Nile and River Nile in Sudan. The results indicated that the short-range spatial dependence was moderate to weak with a nugget shifted from zero. Spherical model was selected to describe the spatial pattern of SOC in the study area. A moderate to weak spatial dependence of SOC was observed, indicating that SOC was controlled by both intrinsic factors (e.g. soil parent materials and soil texture) and extrinsic factors (e.g. application of fertilizers and tillage treatment).

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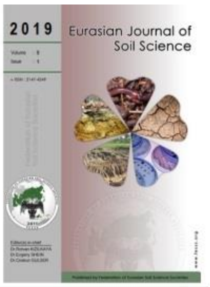

Does anthropogenic phosphorus input reduce soil microbial resource allocation to acquire nitrogen relative to carbon?

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Abstract

We aimed to test if anthropogenic P input into ecosystems reduces microbial resource allocation to acquire N (and alleviate N shortage if any) because microbes no longer produce N-rich phosphatase for P acquisition. Literatures reporting the effect of P fertilization on C-acquiring (β-1,4-glucosidase, BG) and N-acquiring (β-1,4-N-acetylglucosaminidase, NAG, which also acquires C) enzymes were collected and synthesized. We predicted that P addition elevates BG:NAG especially in P-poor ecosystems because P addition alleviates N shortage and reduces the microbial resource allocation to acquire N relative to C. The synthesized data demonstrated that P fertilization occasionally reduced BG:NAG, which is inconsistent with the prediction. However, this might not mean that the initial hypothesis was rejected. Stimulated microbial activity and turnover by P fertilization could have caused microbes depend the C sources more on chitin (and peptidoglycan) compared with on cellulose because chitin (and peptidoglycan) is a main component of microbial body and re-provided through microbial turnover. The changes in C resources accompanied by the altered P availability may have largely influenced BG:NAG, masking the role of BG:NAG for indicating microbial resource allocation to C and N acquisitions.

Keywords: β-1,4-glucosidase (BG), β-1,4-N-acetylglucosaminidase (NAG), ecoenzymatic stoichiometry, phosphatase, phosphorus fertilization.

Article Info

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Introduction

Marklein and Houlton (2012) proposed in their meta-analysis that anthropogenic nitrogen (N) elevation can compensate phosphorus (P) shortage of biota through elevating phosphatase production, because N-rich phosphatase (C:N ratio of protein is generally up to 4) synthesis requires a large amount of N (Olander and Vitousek; 2000; Treseder and Vitousek, 2001; Houlton et al., 2008). From their hypothesis, it can be indicated that P shortage elevates microbial N requirement in order to produce the N-rich phosphatase and accelerates N shortage (if any). Accordingly, anthropogenic P inputs into ecosystems can reduce microbial resource allocation to acquire N (relative to C) and alleviate N shortage because microbes reduce the production of the N-rich phosphatase in P-rich conditions.

Many previous studies assumed that the resource allocation of microbes to acquire nutrients and energy could be expressed as ecoenzymatic stoichiometry, i.e., ratios of extracellular enzymes targeting C, N and P (Sinsabaugh et al., 2008, 2009; Waring et al., 2014). Among a variety of extracellular enzymes targeting C, N, and P, β-1,4-glucosidase (BG, catalyzing the terminal reaction in cellulose degradation), β-1,4-N-acetylglucosaminidase (NAG, catalyzing the terminal reaction in chitin degradation), and acid (or alkaline) phosphatase (AP, hydrolyzing organic phosphorus) has been measured most widely (Olander and Vitousek,

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2000; Allison and Vitousek, 2005; Sinsabaugh et al., 2009; Turner and Wright, 2014; Waring et al., 2014; Jian et al., 2016). Thus the ratio of BG and NAG (BG:NAG), and of BG and AP (BG:AP) are often used as indicators of microbial resource allocation to the acquisition of N and P relative to C, respectively (Sinsabaugh et al., 2008, 2009; Turner and Wright, 2014; Waring et al., 2014; Moorhead et al., 2016; Zhou et al., 2017; Rosinger et al., 2018; Tatariw et al., 2018), although few studies recently suggested that the BG:NAG may not always indicate the microbial resource allocation to the acquisition of N relative to C because NAG can be also produced for acquiring C as well as N (Mori et al., 2018a, b; Wang et al., 2018).

Based on the above hypothesis and assumption, it is predicted that P addition would elevate BG:NAG because P addition reduces the microbial resource allocation to acquire N relative to C through reducing the N requirement to synthesize phosphatase (note that P addition does not necessarily reduce the absolute resource investment on N acquisition). The response ratio of BG:NAG to P addition would be larger in P-poor ecosystems where BG:AP is smaller (Figure 1). We also need to consider P-poor but N-rich conditions (such as areas with extremely high N deposition or fertilized with N), where the reduced requirement of N in relation to P addition would not affect BG:NAG because NAG is probably produced targeting C acquisition rather than N (Mori et al. 2018a,b; Wang et al. 2018) (note that chitin contains both N and C) (Figure 2). In such conditions, P addition would not elevate BG:NAG (Figure 1). Overall, the relationship between BG:AP and the response ratio of BG:NAG to P addition is predicted as follows: (i) the response ratio of BG:NAG to P fertilization would be higher than 1 and become larger as BG:AP decreases; or (ii) BG:NAG does not change in response to P addition if the soil is rich in N (response ratio is around 1) (Figure 1).

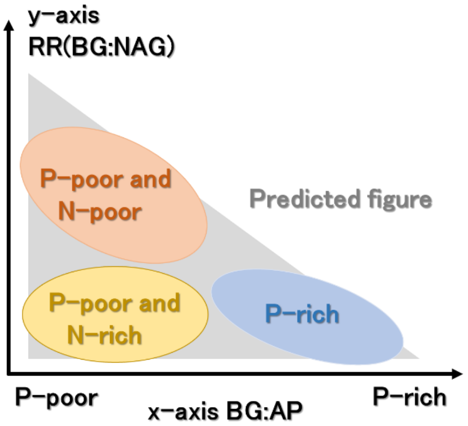

Figure 1. The predicted relationship between BG:AP and the response ratio of BG:NAG to P addition. RR(BG:NAG) represents the response ratio of BG:NAG to P addition.

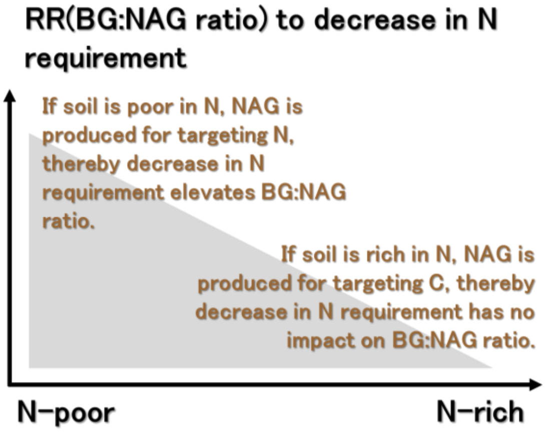

Figure 2. Predicted response of BG:NAG to a decrease in N requirement. RR(BG:NAG) represents the response ratio of BG:NAG to a decrease in N requirement. If soil is poor in N, NAG is produced for targeting organic N. In such a case, a decrease in N requirement reduces microbial allocation on N-acquiring enzyme (NAG) and as a result BG:NAG will be elevated. Meanwhile, if soil is rich in N, NAG is produced for targeting C, thereby a decrease in N requirement has no impact on BG:NAG.

In this study, we aimed to test if anthropogenic P input into ecosystems reduces microbial resource allocation to acquire N (and alleviate N shortage if any) by collecting the literatures reporting the effect of P fertilization on the activities of extracellular enzymes including BG, NAG, and AP.

Material and Methods

We collected the literatures reporting the effects of P addition on the activities of NAG and BG. We used the search engine Web of Science to collect published literatures with the following combinations of key words for searching; ("phosph* add*" OR "P add*" OR "phosph* elevat*" OR "P elevat*" OR "phosph* fertiliz*" OR "P fertiliz*" OR "phosph* appl*" OR "P appl*"OR "phosph* enrich*" OR "P enrich*") AND (glucosidase OR β-glucosidase OR "β glucosidase" OR BG OR βG) AND (NAG OR chitinase OR β-1,4-N-acetyl-β-glucosaminidase OR "N-acetyl β-glucosaminidase" OR glucosaminidase). All papers collected in the above procedure reported AP activity as well as BG and NAG activities, which enabled us to evaluate the relationship between BG:AP and the response ratio of BG:NAG to P addition. We compensated the literature list by using other search engines, Google and Google Scholar, because several papers were not collected by the procedure. Since only a few number of papers were available for our research purpose, the data taken in the same site but with different types of nutrient addition (e.g., comparison between data in N-added and NP-added site) or different soil layer were counted as different data points (Table 1).

Results and Discussion

We found 29 data points from 9 literatures (Table 1). At the first glance, the relationship between BG:AP and the response ratio of BG:NAG to P fertilization (Figure 3) seems consistent with the predicted pattern (Figure 1): As BG:AP increased up to 0.5, the response ratio of BG:NAG to P fertilization declined (Figure 3). However, there were critical differences between the result and the prediction. We observed that response ratios of BG:NAG to P addition were lower than 1 in several cases (i.e., P addition reduced BG:NAG). Originally, we assumed that (i) the response ratio of BG:NAG to P fertilization should be higher than 1 if P fertilization reduces microbial N requirement, or (ii) BG:NAG does not change in response to P addition if the soil is rich in N (response ratio is around 1). The lower response ratio than 1 may indicate that the P addition increased N requirement relative to C requirement by biota. Although we cannot completely deny the possibility, it is less likely because P fertilization reduces N-rich phosphatase production (Marklein and Houlton, 2012). Thus the present analysis failed to testify the hypothesis: anthropogenic P input into ecosystems reduces microbial resource allocation to acquire N.

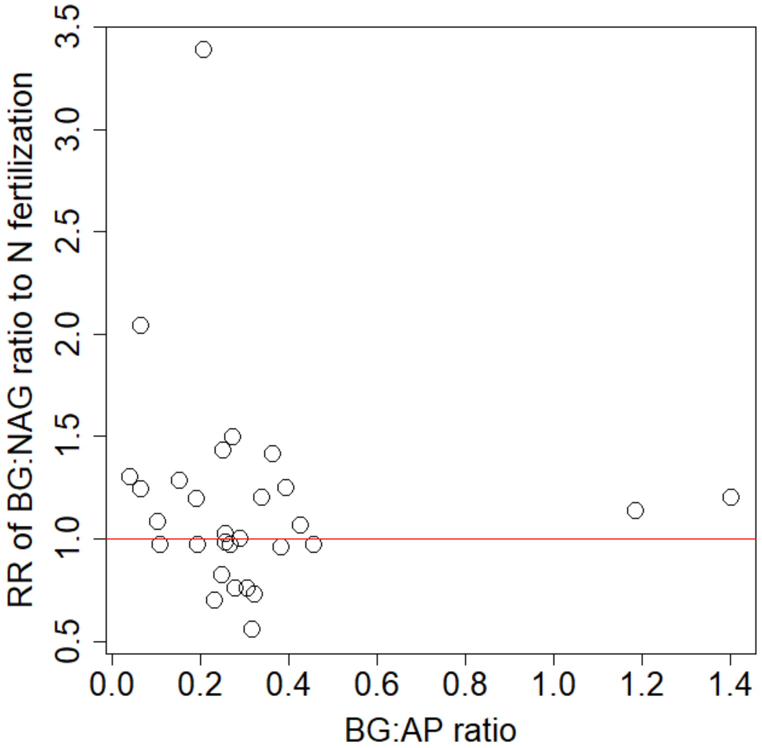

Figure 3. The relationship between BG:AP and the response ratio of BG:NAG to P addition in no P controls. This figure was drawn using data taken from literatures. RR(BG:NAG) represents the response ratio of BG:NAG to P addition. 1:1 line was drawn in the figure.

Table 1. Reference information

No	Comments	Location	MAT (°C)	Annual precipitation (mm)	Reference
1	Tropical lowland forest	Barro Colorado, Panama	26.0	2600	Turner and Wright (2014)
2	O-layer without N fertilization in stream	The Bear Brook Watershed in Marine	5.1	1320	Mineau et al. (2014)
3	O-layer with N fertilization in stream	The Bear Brook Watershed in Marine	5.1	1320	Mineau et al. (2014)
4	B-layer without N fertilization in stream	The Bear Brook Watershed in Marine	5.1	1320	Mineau et al. (2014)
5	B-layer with N fertilization in stream	The Bear Brook Watershed in Marine	5.1	1320	Mineau et al. (2014)
6	Chinese fir plantation (without N addition)	Qianyanzhou Forest Experimental Site, China	17.9	1471.2	Dong et al. (2015)
7	Chinese fir plantation (50 kg N per ha was added)	Qianyanzhou Forest Experimental Site, China	17.9	1471.2	Dong et al. (2015)
8	Chinese fir plantation (100 kg N per ha was added)	Qianyanzhou Forest Experimental Site, China	17.9	1471.2	Dong et al. (2015)
9	Rice cropping system (N and K was added simultanously)	Jiangxi, China	18.0	1470	Zhang et al. (2015b)
10	Cropland (N was added simultanously)	South Lake station, China	>10.0	1300	Zhang et al. (2015a)
11	Shortgrass prairie	Cedar point, Nebraska, USA	9.3	454	Riggs and Hobbie (2016)
12	Shortgrass prairie (N was added simultanously)	Cedar point, Nebraska, USA	9.3	454	Riggs and Hobbie (2016)
13	Shortgrass prairie (K was added simultanously)	Cedar point, Nebraska, USA	9.3	454	Riggs and Hobbie (2016)
14	Shortgrass prairie (N and K were added simultanously)	Cedar point, Nebraska, USA	9.3	454	Riggs and Hobbie (2016)
15	Tallgrass prairie	Konza Prairie, Kansas, USA	12.0	872	Riggs and Hobbie (2016)
16	Tallgrass prairie (N was added simultanously)	Konza Prairie, Kansas, USA	12.0	872	Riggs and Hobbie (2016)
17	Tallgrass prairie (K was added simultanously)	Konza Prairie, Kansas, USA	12.0	872	Riggs and Hobbie (2016)
18	Tallgrass prairie (N and K were added simultanously)	Konza Prairie, Kansas, USA	12.0	872	Riggs and Hobbie (2016)
19	Shortgrass prairie	Shortgrass Steppe, Colorado, USA	8.4	364	Riggs and Hobbie (2016)
20	Shortgrass prairie (N was added simultanously)	Shortgrass Steppe, Colorado, USA	8.4	364	Riggs and Hobbie (2016)
21	Shortgrass prairie (K was added simultanously)	Shortgrass Steppe, Colorado, USA	8.4	364	Riggs and Hobbie (2016)
22	Shortgrass prairie (N and K were added simultanously)	Shortgrass Steppe, Colorado, USA	8.4	364	Riggs and Hobbie (2016)
23	Glaciated mixed hardwood forest	Ohio, USA	8.1	1200	Carrino-Kyker et al. (2016)
24	Glaciated mixed hardwood forest (elevated pH)	Ohio, USA	8.1	1200	Carrino-Kyker et al. (2016)
25	Unglaciated mixed hardwood forest	Ohio, USA	10.7	1000	Carrino-Kyker et al. (2016)
26	Unglaciated mixed hardwood forest (elevated pH)	Ohio, USA	10.7	1000	Carrino-Kyker et al. (2016)
27	Broadleaf forest	Maoershan Forest Ecosystem Research Station, China	−18.5 to 22.0	629	Zhou et al. (2017)
28	Pine forest	Maoershan Forest Ecosystem Research Station, China	−18.5 to 22.0	629	Zhou et al. (2017)
29	Watershed	Lead Mountain in Maine, USA	-	-	Tatariw et al. (2018)

The discrepancy between our predictions and the result could be explained by an altered C resource composition. It was reported that cellulose decomposition was stimulated by P fertilization (Kaspari et al., 2008; Fanin et al., 2015), which leads a decrease in BG-targeting C in soils (i.e., cellulose). Although the stimulated cellulose decomposition is associated with elevated BG activity, the BG:NAG ratio could not be altered if decomposition of chitin and peptidoglycan (NAG is involved in the degradation of peptidoglycan, as well as chitin) is equally stimulated by P fertilization (which needs to be tested). Instead, the cellulose:chitin (and peptidoglycan) ratio could be lowered because chitin and peptidoglycan is re-provided in soils through microbial turnover as as chitin and peptidoglycan are main components of microbial body. By contrast, cellulose is basically not provided from the microbial body. Accordingly, microbial activity could be more chitin (and peptidoglycan)-dependent under P-added conditions, leading to a larger NAG activity relative to BG (lower BG:NAG) because microbes shift enzyme activity for targeting more-abundant substrates. If this is true, at least in some cases, changes in BG:NAG represent the progress of decomposition stage or the strength of microbial activity rather than a microbial allocation on C and N acquisition, which challenges the idea suggested in previous studies (e.g., Waring et al., 2014). Although this new hypothesis still lacks definitive evidences, it potentially explains the synthesized pattern. Monitoring the BG:NAG ratios as well as decomposition ratios of cellulose and chitin both in manipulated N-shortage and N-rich conditions in a laboratory experiment may provide a chance to examine what actually controls the pattern of BG:NAG.

The present analysis failed to demonstrate the reduced N requirement by P fertilization, but this might not mean that the initial hypothesis was rejected. As discussed above, changes in C resources accompanied by the altered P availability may have largely influenced BG:NAG, masking the role of BG:NAG for indicating microbial resource allocation to C and N acquisitions. Another indicator to access microbial N acquisition, which is not affected by the changes in C resources, is necessary for testing if P input into ecosystems reduces microbial resource allocation to acquire N and alleviate N shortage.

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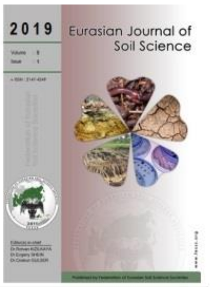

Chemical weathering indices applied to soils developed on old lake sediments in a semi-arid region of Turkey

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Abstract

Climate is a major influence on weathering processes affecting soil parent materials. Important contributors to soil formation in arid and semi-arid climatic zones are the diurnal cycles of solar heating and cooling that cause mechanical or physical disintegration of rock or parent materials, and wind-blown sands that score and abrade exposed rock surfaces. By using the Soil Taxonomy classification system, the initial aim of this study was to carry out a pedological evaluation for four soil profiles, classified as Xeric Haplocalcid and Xeric Haplocambid, formed on different parent materials (limestone, marl and old alluvial deposits) under the same conditions, including topography and vegetation, in a semiarid region. The second stage was the exploration of the similarities and differences in the classifications resulting from either the pedogenic processes, or from other factors, by determining the degree of soil weathering using geochemical data. To achieve this, soil samples were collected from the horizons to investigate their mineralogical, geochemical and physiochemical properties. The study also considered other features, such as the pedogenic evolution of soils, through the use of weathering indices, namely the Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW), Base/R2O3 Ratio, Weathering Index of Parker (WIP) and Plagioclase Index of Alteration (PIA). The results clearly showed that soil development at the Altınova State Farm at Konya in the Central Anatolia region of Turkey is due to slow progressive weathering. For this case, the main indicators are secondary calcium carbonate illuviation and weak structural development with a weathering ratio of silicon to aluminium greater than two in all profiles.

Keywords: Alteration index, geochemical evolution, soil formation, dry region.

Article Info

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Introduction

To a pedologist or soil geographer, soil means a natural, three-dimensional body that has formed at the Earth's surface through the interactions of five soil-forming factors, namely climate, biota, relief, parent materials and time (Schaetzl and Anderson, 2005), and a field mapper is often able to explain and predict soil variation as a function of these five factors (Jenny, 1946; Johnson and Hole, 1994).

Soil formation is a dynamic rather than a static process, with soil developing where there is a dynamic interaction between the air, water, parent material and organisms. Wherever one or more of these major factors changes, the soil will be different. Significant differences in soil chemical, physical and morphological properties, particularly in a small area, are known to be related to the dynamic interaction between

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microclimate, topography and parent material (Lark, 1999; Dengiz et al., 2006), whereas the regional processes, macroclimate and vegetation, are important at the continental scale (Lark, 1999).

Weathering can be described as the physical and chemical alteration of rocks and minerals on or near the Earth's surface (Pope et al., 2002). In physical weathering, also known as mechanical weathering or disintegration, physical stresses combine to break rocks into smaller pieces. In contrast, water and oxygen are important to many chemical weathering reactions. Chemical weathering indices estimate the intensity of soil chemical weathering by comparing changes in major and trace metal concentrations as ratios of mobile to immobile elements in soil and rock or parent material. (Duzgoren-Aydin et al., 2002; Price and Velbel, 2003). These indices also provide a measure of the weathered state of the saprolite underlying the mobile soil column. This weathered condition is likely to play a critical role in governing how physical processes disrupt the saprolite, and is therefore an important parameter in determining resistance to alteration and erosion. Weathering indices are conventionally calculated using the molecular proportions of the oxides of major elements. Stoichiometrical changes during weathering are reflected in the index value. The molecular proportion of each oxide is easily calculated from the percentage of the oxide based on weight. Vogt (1927) proposed a geochemical method for assessing the maturity of residual sediments: the Vogt's Residual Index. The Chemical Index of Alteration (CIA) was proposed by Nesbitt and Young (1982) to quantitatively evaluate the weathering history recorded in sediments and sedimentary rocks. The CIA has been used to evaluate chemical weathering in specific drainage basins (McLennan, 1993; Yang et al., 2004). As the transformation of feldspar to clay minerals and the coincident mobility of the main cations are belong to a major chemical process, Parker (1970) proposed a more useful index known as the Weathering Index (WIP), which can evaluate minor changes in Na^+, K^+, Ca^{2+} and Mg^{2+}. The Chemical Index of Weathering (CIW) was initially proposed by Harnois (1988). This index is similar to the CIA, except that it eliminates K_2O from the equation. The Plagioclase Index of Alteration (PIA) was proposed by Fedo et al. (1995) as an alternative to the CIW. Because plagioclase is abundant in silicate and dissolves quickly, the PIA may be used when plagioclase weathering needs to be monitored.

The differences in soils are due to differences in variables such as parent material, topographical position, slope steepness, distribution of moisture, vegetation, and age of the associated landscape (Birkeland, 1999; Dengiz and Usul, 2018). Particularly, parent materials changes can affect many soil properties in local condition due to their minerological and textural variation.

By considering weathering indices, geochemical and mineralogical data, the present study was a pedological evaluation that aimed at identifying individual mineralogical and geochemical characteristics of aridisols with different parent materials but located in a similar topographical position, with similar climatic conditions, land use and vegetation. In addition, the second aim of the study was to determine how different parent materials located on old lake sediments affect the morphology, minerology and physicochemical properties of soils under similar conditions of topography and vegetation in a semi-arid region.

Material and Methods

The study site description

This study was carried out on an area of approximately 29608.6 ha in the Altınova State Farm, located between eastern longitudes 421239–4535249 m and northern latitudes 488389–4272469 m (Universal Transverse Mercator-UTM, WGS 84, 915 m) (Figure 1) in the middle of central Anatolia, Turkey. The farm is located approximately 189 km from Ankara and about 126 km from Konya in the Great Konya Basin.

The pedological and geological properties of the soils and sediments, and the formation and diagenesis of carbonates under the lacustrine environment in the Great Konya Basin, have been investigated (de Ridder, 1965; Driessen and de Meester, 1969; Driessen, 1970; Vergouwen, 1981). A geological map of the study area is provided in Figure 2. The Great Konya Basin is predominantly occupied by Quaternary alluvial sediments (de Meester, 1971). According to their reports, during some periods of the Late Pleistocene epoch, most of the Great Konya Basin was covered by a shallow lake with a fairly constant water level of 12 to 20 m, which left a number of sandy beach ridges and sand plains located roughly at the 1010 m contour. On top of the soft-lime lake bottom, a large variety of other sediments were deposited, resulting in various physiographic units, which divided the Great Konya Basin plain into uplands, colluvial slopes, piedmont plains, bajadas, terraces, alluvial plains and lacustrine plains. The terraces of the flat Neogene limestone formation are located along the fringes of the Great Konya Basin. The alluvial plains and fans comprise the sediments of some rivers debouching into the southern part of the basin. In addition, Özaytekin et al. (2012a) reported that the alluvial fans or inland deltas consist of sediments ranging from coarse sand to a heavy clay texture while the lacustrine plains are flat and contain carbonates. Deposited under water, the lacustrine plains cover vast areas in the centre of the Great Konya Basin. These ridges and shores were formed from the continual washing of the former Pleistocene lake (Roberts et al., 1979).

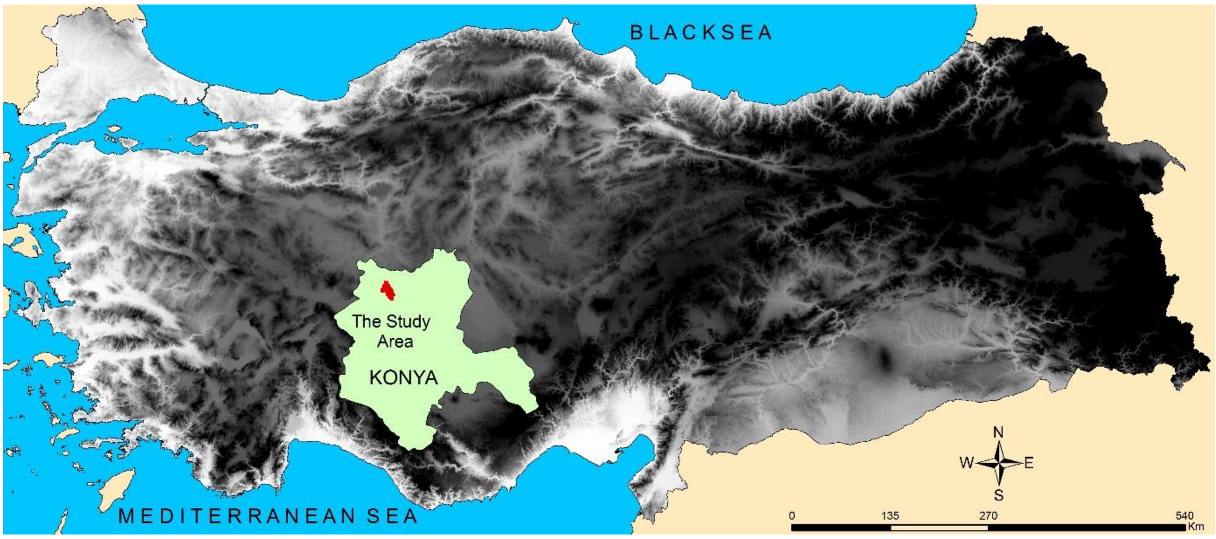

Figure 1. The study area

Over the long term (1999–2011), according to data from the State Farm's meteorological station, the mean annual precipitation is 302.3 mm, the total evapotranspiration is 1296.1 mm, and the mean annual temperature is 12.8 °C. Soil temperature and soil moisture regimes at the study site were classified according to the Soil Survey Staff as mesic and aridic (Soil Survey Staff, 1999), respectively. All farm land has been used as dry farming.

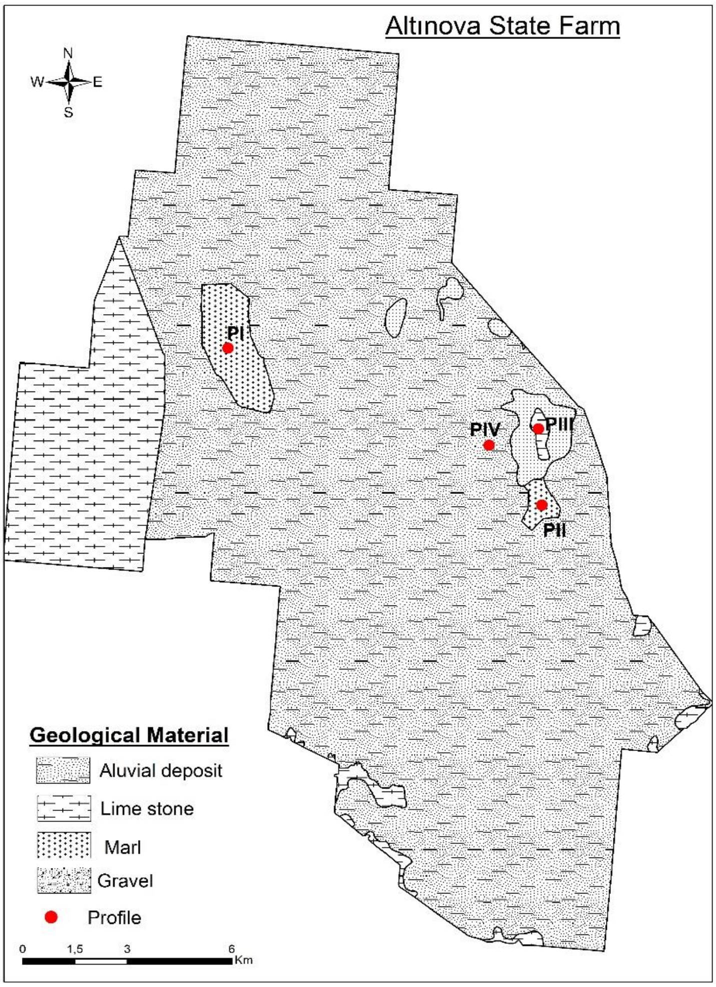

Figure 2. Geological map of the study area

Soil sampling

Soil samples were collected from four representative profiles in the State Farm. In geological terms, profiles I and III were formed from hollow clay filler on Neogen old lake terraces and profiles II and IV were formed from subcreek alluvion material on Neogen old lake terraces. The morphological properties of these four profiles were described and sampled according to genetic horizons and then classified according to the Soil Survey Manual (1993) and Soil Survey Staff (1999). A total of nineteen disturbed soil samples in total were collected to investigate their physical, chemical and mineralogical properties in the laboratory. Soil samples were air-dried and passed through a 2 mm sieve to prepare them for laboratory analysis.

Physical, chemical and mineralogical analysis

After the soil samples taken from four soil profiles were air-dried and passed through a 2 mm sieve. Particle size distribution was determined with the hydrometer method (Bouyoucos, 1962). Organic matter was removed with 30 per cent H_2O_2, sulphate was removed by leaching salts with distilled water, and carbonates were removed with 1 M NaOAc at pH= 5 with dispersion, by agitating the sample in 10 ml of 40 per cent sodium hexametaphosphate (Calgon) (Gee and Bauder, 1982). Bulk density was determined by using undisturbed samples (Black, 1965). Soil organic matter was measured by Fe_2SO_4 titration of an acid-dichromate digestion (Walkley and Black, 1934). The methods of the Soil Survey Laboratory (2004) were used to determine the pH and EC (electrical conductivity) values of the saturated soil samples. $CaCO_3$ content was measured with a Scheibler calsimeter (Soil Survey Manual, 1993), and exchangeable cations and cation exchange capacity (CEC) were measured with the 1 N NH_4OAc (pH 7) method (Soil Survey Laboratory Manuals, 2004).

The clay fraction (< 2 µm) was obtained from the soil after the organic matter was removed with dilute, Na-acetate-buffered H_2O_2 (pH 5), followed by dispersal using calgon and sedimentation in water. Oriented specimens on glass slides were analyzed with X-ray diffraction, using Cu Kα radiation from 2° to 15° 2θ, with steps of 0.02° 2θ at two seconds per step. The following treatments were performed: Mg saturation, ethylene glycol solvation (EG) and K saturation, followed by heating for two hours at 550°C. Minerals were identified and their relative abundance was determined by their diagnostic X-ray diffraction (XRD) spacing and evaluated by their XRD relative peak intensities in the XRD (Whittig and Allardice, 1986). Identification of selected major, trace and rare earth elements was done with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Samples were taken into solution by alkaline fusion, using a mixture of 0.25 g soil or powdered sediment and 0.75 g of flux (lithium tetra- and metaborate) in 0.2 N HNO_3 solution diluted to 1:1000. An aliquot of the sample solution was analyzed for trace elements and the rare earth elements (REE) on a combination simultaneous/sequential ICP-MS. Detection limits were 0.1 to 1.0 ppm for all major and trace elements and 0.1 to 0.5 ppm for REE. The instrument was calibrated by using certified standard reference materials (OREAS24P and G1). To better evaluate the nature of soils and sediments and the effect of weathering and possible recycling of trace and rare earth elements in sediments under semi-arid conditions, a reference sediment was used for comparison; a North American Shale Composite (NASC) (Taylor and McLennan, 1985) was chosen for that purpose. All procedures were replicated three times for each soil sample, and the mean values were reported (Chao and Sanzolone, 1992).

Calculation of weathering indices

Numerous indices, including those of Nesbitt and Young (1982) and Harnois (1988), have been developed to characterize chemical weathering in soils. Those indices are similar in that they are based on the ratio of the base cations (Ca, Mg, K and Na) to Al and Si. Weathering indices used to quantify chemical weathering intensity in the current study included the Chemical Index of Alternation (CIA) (Nesbitt and Young, 1982), Chemical Index of Weathering (CIW) (Harnois, 1988), Weathering Index of Parker (WIP), (Parker, 1970), Bases/R_2O_3 Ratio (Birkeland, 1999), Plagioclase Index of Alteration (Fedo et al., 1995) and Product Index (P) (Reiche, 1950). CaO* represents the CaO contained only in the silicate fraction and is corrected for carbonate and apatite content. It is based on the assumption for CaO* that the molar CaO/Na_2O ratio of silicates is not higher than one. As the molar CaO content (corrected for apatite) was less than the molar Na_2O content, the value was taken as CaO*. On the other occasions, the CaO content of silicates was supposed to be equivalent to the molar Na_2O content (McLennan, 1993).

Results and Discussion

Morphological properties and classification

A description of the study site and four representative soil profiles are provided in Table 1. All profiles were from flat land, with profiles I and II formed on marl parent material, profile III formed on limestone, and profile IV formed on an alluvial deposit (Figure 2).

Table 1. Selected site characteristics of pedons

Pedon	Coordinates		Parent	Elevation	Slope	Slope	Land cover
No	East	North	Material	(m)	Position	(%)	Land Use
I	420723	4287966	Marl	989	Flat	0-0.5	Dryfarming
II	420025	4291459	Marl	988	Flat	0-1	Dryfarming
III	419884	4292524	Limestone	985	Flat	0-2	Dryfarming
IV	418202	4290775	Aluvial deposit	975	Flat	0-1	Dryfarming

Soils in the study area display variations in terms of particle size distribution, color and surface horizon depth. Differences in the soils represent the effects of parent material because they developed under similar climate, topographical position and land use-vegetation conditions. Profiles I and II developed on the marl, while profile III developed on the limestone, as a result of decomposition and fragmentation of the calcareous parent material. Secondary carbonate nodules were formed following the calcification process, which provides evidence for carbonate leaching and accumulation in profiles I, III and IV, but not in profile II. A cambic B horizon was initially found in each profile according to weak soil structure development and light soil color. This result is consistent with previous research which found that a cambic horizon developed along with a calcic horizon in soils of arid and semi-arid regions (Buringh, 1979; Boul et al., 1980; Dinc et al., 1987). This effect and result was seen in profiles I, III and IV.

Soil color was closely related to the parent materials, namely marl and alluvial deposits, with a hue of 10YR in profiles I, II and IV, and 7.5 YR in profile III. For all profiles, the soil had a weak or moderately developed A horizon with a granular, angular, blocky structure; a weak or moderately developed B horizon with a granular, sub-angular or angular blocky structure; and a C horizon with a massive structure (Table 2). Soil Survey Staff (1999) classification system was used in this study. Profile I, formed on marl parent material on the old Neogen lake terraces was classified as Xeric Haplocambid. The main diagnostic horizon in profile I was the subsurface cambic horizon, resulting from structural development, observed especially at depths between 21 and 72 cm. Common secondary carbonate nodules and micelles were observed at depths between 72 to 107 cm. Profile II, on marl parent material on the old Neogen lake terraces, was classified as Xeric Haplocambid. The main diagnostic horizon in profile II was the subsurface cambic horizon, resulting from structural development, observed especially at depths between 41 and 75 cm. However, there was no evidence of calcification and the calcic horizon evident in profile I. This finding indicates that profiles can form different soil genetic horizons from similar parent materials. Profile III, which formed on limestone and was classified as Xeric Haplocalcid, also showed a subsurface density diagnostic horizon, Ad, at depths between 14 and 26 cm, due to intensive field traffic, and a subsurface cambic diagnostic horizon, Bw, at depths between 75 and 96 cm. In addition, profile III showed the presence of secondary $CaCO_3$ nodules and mycelia at depths between 96 to 127 cm. Profile IV, which was formed on alluvial parent material, was classified as Xeric Haplocambid. The main diagnostic horizons in profile IV were subsurface the cambic horizons development observed at depths between 68 and 86 cm, and common carbonate nodules and micelles at depths between 86 and 104 cm (Table 2). Therefore, the genetic order of profile IV is similar to profiles I and III, although their parent materials were not the same.

Physical and chemical characteristics

The major physical and chemical properties of the soils in each profile in the study area are presented in Table 3. Properties in the different profiles varied as a result of a dynamic interaction between climate and parent material (Dengiz, 2010; Kibar et al., 2012). Solum depth ranged from 20 to 127 cm, depending upon the degree of weathering and the stage of the soil formation process. All profiles had a moderately alkaline soil (pH value range from 7.81 to 8.25) and a slightly soluble salt content, with no substantial differences among them. The main reasons for particle size distribution differences between the soil profiles were the differences in chemical and minerological composition in their parent materials, including rocks. The dominant soil texture for profiles I, II and III was clay or clay loam, with the highest clay content in the Xeric

Haplocalcid (profile III) developed on limestone parent material, and the highest sand content ranged from 60.16 to 66.39 % in profile IV which was formed on alluvial parent material.

Table 2. Morphological properties and classification (Soil Taxonomy) of pedons

Horizon	Depth (cm)	Color (dry)	Color (moisture)	Structure	Boundry	Special features
Pedon I (Xeric Haplocambid)						
Ap	0-21	10 YR 5 /2	10 YR 4/2	1mgr	as	-
Bw1	21-45	10 YR 5/3	10 YR 4/3	1msbk	gw	structure development
Bw2	45-72	10 YR 5/6	10 YR 4/6	1msbk	ga	structure development
Ck	72-107	10 YR 8/3	10 YR 7/3	mas	ga	common carbonate nodules and micelles
C2	107-152	10 YR 8/4	10YR 7/4	mas	-	-
Pedon II (Xeric Haplocambid)						
Ap	0-21	10 YR 5/3	10 YR 4/3	1fgr	cs	-
A2	21-41	10 YR 5/3	10 YR 4/3	1fgr	cs	-
Bw	41-75	7.5 YR 6/6	7.5 YR 5/6	1fgr	cs	structure development
C1	75-101	7.5 YR 7/6	7.5 YR 6/6	mas	-	-
C2	101-130	7.5 YR 7/6	7.5 YR 6/6	mas	-	-
Pedon III (Xeric Haplocalcid)						
Ap	0-14	7.5 YR 4/3	7.5 YR 3/3	2fgr	as	-
Ad	14-26	7.5 YR 4/3	7.5 YR 3/3	mas	gw	-
A3	26-75	7.5 YR 5/3	7.5 YR 4/3	1cabk	gw	-
Bw	75-96	7.5 YR 5/6	7.5 YR 4/6	1mabk	gw	structure development
Bk	96-127	7.5 YR 6/6	7.5 YR 5/6	2mabk	gw	carbonate micelles
C	127-165	7.5 YR 6/6	7.5 YR 5/6	mas	-	-
Pedon IV (Xeric Haplocambid)						
Ap	0-24	10 YR 4/2	10 YR 4/1	2mgr/ 1mabk	gs	-
A2	24-67	10 YR 4/3	10 YR 4/2	3mabk	cw	-
Bw	67-86	10 YR 5/4	10 YR 4/4	2mabk	cw	structure development
Bk	86-104	10 YR 4/6	10 YR 4/4	1msbk	ga	common carbonate nodules and micelles
C	104-150	10 YR 5/6	10 YR 4/6	mas	-	-

Abreviations: Boundary: a = abrupt; c = clear; g = gradual; d = diffuse; s = smooth; w = wavy; i = irregular. Structure: 1 = weak; 2 = moderate; 3 = strong; sg = single grain; mas = massive; vf = very fine; f = fine; m = medium; c = coarse; gr = granular; pr = prismatic; abk = angular blocky; sbk = subangular blocky

Soil Cation Exchange Capacity (CEC) varied from 14.3 to 56.8 cmolc kg^{-1}, with the highest CEC in the Xeric Haplocambid (profile II), in which smectite was the predominant clay type, indicating the presence of stratified aluminosilicates with high load intensity. The lowest CEC value was found in soil classified as Xeric Haplocambid (profile I). Ca and Mg were the dominant exchangeable cations in all profiles, with a base saturation value of 100%. As there is little deposition and accumulation of organic litter in arid and semi-arid zones, the organic matter content of the soils was low. When these soils are cultivated, the limited organic matter content is quickly decomposed (Da Costa et al., 2015). For all profiles in the study area, the organic matter content was highest (1.0 to 1.6 %) in the surface horizon and lowest in the subsurface horizons (0.4 to 1.4 %), with an abrupt decrease in the subsurface horizon. The low levels of organic matter in the subsoil can be attributed to the rapid decomposition and mineralization of organic matter.

Soil bulk density values ranged from 1.33 to 1.70 g cm^{-3}, with values generally higher in the surface horizons, especially Ap horizons, than in subsurface horizons, as a result of compaction by the relatively intensive field traffic associated with agricultural activities. Profiles I and II were formed on the same parent material (marl) but the $CaCO_3$ content of these profiles was different; profile I had the highest $CaCO_3$ content of 57.7%, and calcium carbonate accumulation in the calcic horizon. Profile IV developed on alluvial parent material and had the lowest $CaCO_3$ content of all profiles.

Table 3. Some physical and chemical properties of soils

Horizon	Depth (cm)	$pH_{(H_2O)}$ (1/2.5)	EC ($dS.m^{-1}$)	$CaCO_3$ (%)	OM (%)	Exchangeable Cations ($cmolc \cdot kg^{-1}$)			CEC ($c\ mol \cdot kg^{-1}$)	BD (gr,cm^{-3})	PSD (%)			
						Na	K	Ca+Mg			C	Si	S	Class
Pedon I (Xeric Haplocambid)														
Ap	0-21	8.12	0.43	12.40	1.20	0.60	1.70	40.30	42.80	1.42	30.80	29.10	40.20	CL
Bw1	21-45	8.14	0.41	31.50	1.10	0.60	0.50	38.20	39.60	1.35	35.10	24.90	40.00	CL
Bw2	45-72	7.81	0.45	41.50	1.10	0.70	0.70	31.20	32.60	1.34	34.90	24.80	40.40	CL
Ck	72-107	7.93	0.51	57.70	1.00	0.70	0.50	23.30	24.90	1.41	11.70	49.40	38.90	L
C2	107-152	8.01	1.23	41.40	0.70	1.40	0.40	13.70	14.30	1.47	11.80	18.50	69.80	SL
Pedon II (Xeric Haplocambid)														
Ap	0-21	8.25	0.43	4.20	1.00	1.20	1.70	53.20	56.40	1.33	35.45	29.06	35.49	CL
A2	21-41	8.06	0.37	10.70	0.80	1.00	1.20	54.80	56.80	1.44	46.49	25.01	28.50	C
Bw	41-75	8.02	0.33	19.90	0.40	0.80	1.00	52.20	54.20	1.38	52.81	22.80	24.39	C
Pedon III (Xeric Haplocalcid)														
Ap	0-14	8.22	0.47	12.10	1.60	0.70	2.70	48.20	51.60	1.41	31.10	33.23	35.67	CL
Ad	14-26	7.91	0.58	10.40	1.40	0.70	2.10	48.00	51.10	1.46	39.88	29.18	30.94	CL
A3	26-75	7.98	0.47	15.90	0.90	0.80	1.30	50.30	53.50	1.41	47.52	21.60	30.89	C
Bw	75-96	7.85	0.32	22.90	0.50	0.90	1.20	47.00	49.20	1.39	59.39	20.71	19.89	C
Bk	96-127	7.96	0.34	27.80	0.40	1.20	1.20	46.00	50.20	1.38	61.66	20.75	17.58	C
C	127-165	8.01	0.57	16.30	0.40	1.60	1.20	52.10	55.30	1.37	40.34	23.03	36.63	C
Pedon IV (Xeric Haplocambid)														
Ap	0-24	7.92	0.44	1.20	1.40	0.60	1.60	33.10	35.50	1.48	21.59	12.01	66.39	SCL
A2	24-67	8.00	0.36	1.30	1.20	0.60	1.00	31.20	33.10	1.64	26.04	9.03	64.94	SCL
Bw	67-86	7.85	0.34	4.20	0.90	0.60	0.80	27.30	29.70	1.58	22.66	11.00	66.34	SCL
Bk	86-104	7.94	0.34	9.20	1.30	0.60	0.70	26.30	27.60	1.64	21.60	12.02	66.38	SCL
C	104-150	8.01	0.31	9.60	1.10	0.60	0.70	25.20	27.60	1.70	21.62	18.23	60.16	SCL

Abreviations: EC: Electrical Conductivity, OM: Organic Matter, CEC: Cation Exchange Capacity, BD: Bulk Density,
PSD: Particle Size Distribution, C: Clay, Si: Silt, S: Sand L: Loamy, CL: Clay Loamy, SCL: Sandy Clay Loamy

Weathering indices and clay mineralogy

Chemical weathering indices are commonly used to quantitatively evaluate changes caused by chemical weathering in different materials (Birkeland, 1999; Darmody et al., 2005; Vogt, 1927; Ruxton, 1968; Harnois, 1988). The indices are based on the principle that the ratio between concentrations of mobile (e.g. SiO_2, CaO, MgO and Na_2O) and immobile (e.g. Al_2O_3, Fe_2O_3 and TiO_2) elements will decrease over time as leaching progresses. However, the weathering of heterogeneous metamorphic rocks confounds the understanding of the relationship between the weathering index and depth (Dengiz et al., 2013).

Weathering indices calculated from elemental oxide concentrations in molecular proportions are also used to evaluate the vertical changes in a weathering profile. In addition, generally, weathering indices change systematically for soil profiles formed from homogeneous parent rocks with depth. In the current study, six previously defined chemical weathering indices were used to evaluate four profiles under similar climatic and topographic conditions. Major and minor element concentrations in the studied profiles, some weathering rates obtained from the geochemical features of the soils, and some genetic rates, are provided in Tables 4 and 5.

According to total element analyses showed that the SiO_2 content in all profiles decreased with depth (range of 52.32 to 25.40%) and that Al_2O_3 values varied from 4.99 to 13.11%. SiO_2 strongly resists weathering because it is mainly contained in quartz minerals. In contrast, Al_2O_3 is mainly is less resistant to weathering because it is contained in the clay minerals; a high content of Al_2O_3 indicates a high content of clay minerals (Shan et al., 2010). The highest amount of Fe_2O_3 (5.72%) was in profile II. These results are supported by XRD analysis. In regions where the parent materials are mostly marl and limestone, elevated concentrations of CaO and MgO are seen in the soils. Generally, the CaO content in these soils range from 1 to 11%, but in some cases the CaO content increases to between 11 and 24%, or even higher (Alumaa et al., 2001).

The CIA index was proposed by Nesbitt and Young (1982) in the reconstruction of the paleoclimate from Early Proterozoic sediments of the Huronian Supergroup, north of Huron Lake. The CIA is based on the progressive removal of soluble cations (e.g. Ca, Na, and K) from minerals during chemical weathering, and it reflects the proportion of primary and secondary minerals in the bulk sample (Nesbitt and Young, 1982). Generally, rocks from the upper crust and unweathered igneous rocks have CIA values of ~ 50, whereas the soils and sediments derived from intensely weathered rocks, and containing residual clay minerals such as kaolinite and/or gibbsite, have CIA values approaching 100 (Fedo et al., 1995; Ao et al., 2010; Özaytekin et al., 2012b). The value ranges from 70 to 75 for shale rock.

In the profiles examined in the current study, the CIA values varied from 6.60 to 66.88. The highest and lowest CIA values were in the A and C horizons of the Xeric Haplocambid (profil IV and profile I), respectively. The CIA values decreased with depth in all profiles. In other words, the parent materials of all profiles had the lowest CIA values of all layers. Nesbitt and Young (1982) classified the CIA values as very slightly weathered (50 to 60), slightly weathered (60 to 70), moderately weathered (70 to 80), highly weathered (80 to 90), and extremely weathered (90 to100).

Table 4. Some major and minor element concentrations of the studied pedons

Pedon	Major Elements (%)									Minor Elements (ppm)							
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Ba	Zn	Cu	Pb	Ni	Nb	Rb	Sr
Pedon I (Xeric Haplocambid)																	
Ap	46.52	11.80	5.30	2.54	7.72	0.07	2.07	0.61	0.13	973.7	64.7	21.9	25.5	63.1	19.1	85.3	737.1
Bw1	41.84	10.19	4.60	2.50	17.69	0.07	1.70	0.55	0.14	843.4	51.2	18.2	24.4	55.2	12.7	69.1	828.4
Bw2	38.15	9.06	3.99	2.22	25.13	0.08	1.47	0.49	0.12	714.7	43.4	11.8	19.9	43.1	13.3	58.8	933.7
Ck	25.40	4.99	2.64	2.09	38.22	0.08	0.81	0.33	0.06	477.8	26.5	6.7	14.1	29.3	9.2	35.1	1093.0
C2	35.08	7.41	3.62	2.63	24.94	0.07	1.22	0.43	0.09	1126.0	39.1	11.7	18.1	43.4	10.8	52.3	1408.0
Pedon II (Xeric Haplocambid)																	
Ap	50.43	13.4	5.43	2.61	4.23	0.06	2.10	0.64	0.13	1002	72.7	26.8	28.7	70.8	24.1	97.3	689.5
A2	45.82	12.56	5.72	2.25	8.06	0.07	1.99	0.64	0.09	952.8	68.9	23.6	26.6	64.4	23.8	91.6	640.1
Bw	41.71	11.54	5.33	2.06	13.76	0.07	1.76	0.60	0.11	909.2	61.7	23.5	25.2	62.6	16.7	85.3	706.9
C1	34.47	7.26	3.84	1.96	16.74	0.07	1.33	0.42	0.08	789.5	49.7	21.2	18.3	46.2	14.4	62.8	828.0
C2	38.03	8.51	4.59	1.86	18.05	0.07	1.58	0.49	0.09	644.9	51.4	18.1	19.2	48.1	18.8	70.7	599.5
Pedon III (Xeric Haplocalcid)																	
Ap	50.55	12.61	5.28	3.02	9.03	0.07	2.09	0.62	0.17	968.1	65.9	23.3	29.4	66.8	23.3	87.2	824.7
Ad	48.58	12.41	5.24	2.92	7.55	0.06	2.03	0.61	0.13	885.8	68.1	23.2	28.3	69.1	19.5	89.2	696.9
A3	44.99	11.68	5.43	2.88	11.43	0.07	1.91	0.62	0.12	809.1	64.1	23.9	26.2	68.4	21.3	85.7	646.9
Bw	38.42	9.90	4.75	2.58	17.78	0.07	1.54	0.53	0.10	758.9	58.3	18.1	23.8	62.7	16.6	71.5	766.3
Bk	38.38	9.84	4.77	2.73	17.26	0.07	1.53	0.53	0.10	683.8	56.9	21.9	23.9	56.2	20.8	73.5	745.8
C	41.03	10.63	5.05	2.89	13.94	0.06	1.64	0.57	0.07	966.6	65.7	24.3	28.3	71.1	18.5	83.1	804.5
Pedon IV (Xeric Haplocambid)																	
Ap	52.32	12.70	5.13	1.80	1.75	0.21	2.56	0.60	0.12	1885.0	56.8	21.0	28.9	51.0	18.8	89.8	1381.0
A2	51.26	13.11	5.58	2.66	5.13	0.07	2.27	0.66	0.17	922.8	70.6	24.0	28.8	68.7	21.9	95.5	598.9
Bw	47.83	12.91	5.62	2.00	5.53	0.07	2.46	0.59	0.09	1827.0	50.5	19.1	27.6	50.9	22.9	82.0	1330.0
Bk	49.62	12.22	4.83	2.00	8.89	0.07	240	0.52	0.15	2050.0	47.7	14.1	29.2	40.5	19.5	77.7	1740.0
C	49.51	12.87	5.12	2.33	8.60	0.10	2.38	0.57	0.12	1729.0	48.2	16.6	28.5	47.0	18.1	81.2	1471.0

When the CIA classification was applied in the current study, the surface horizons of all profiles, except for profile IV, were classified as very slightly weathered. On the other hand, all subsurface horizons were in the same class (very slightly weathered). In addition, there was no obvious trend towards progressively higher alteration values for soils developed on different parent materials. Harnois (1988) proposed the Chemical Index of Weathering (CIW) which modified CIA by excluding K_2O from assessments. Because the CIW does not account for the aluminium associated with K-feldspar, it may generate very high values for K-feldspar-rich rocks, whether they are chemically weathered or not (Fedo et al.,1995).

Table 5. Weathering rate indices and some genetic ratios using rare earth elements (REE) of studied soils

Horizon	Depth	CIA	CIW	WIP	PIA	P	Baz/R_2O_3	V	Th/U	Ba/Nb	Zr/Rb	(Rb+Zr)/Sr
Pedon I *(Xeric Haplocambid)*												
Ap	0-21	41.81	45.43	45.02	33.83	83.03	1.41	0.68	1.56	50.98	3.00	0.46
Bw1	21-45	22.96	23.96	67.24	18.79	83.54	2.89	0.31	1.41	66.41	3.43	0.37
Bw2	45-72	16.02	16.48	83.47	13.19	83.94	4.28	0.20	0.92	53.74	3.09	0.26
Ck	72-107	6.60	6.68	110.95	5.43	85.68	10.52	0.07	0.85	51.93	4.01	0.16
C2	107-152	13.66	14.00	81.98	11.22	85.12	5.14	0.16	0.99	104.26	2.96	0.15
Pedon II (Xeric Haplocambid)												
Ap	0-21	57.06	63.21	36.51	47.32	82.73	0.93	1.08	1.96	41.58	2.99	0.56
A2	21-41	42.55	45.92	44.42	35.21	81.87	1.31	0.71	2.09	40.03	3.21	0.60
Bw	41-75	29.88	31.44	56.47	24.92	81.67	2.03	0.44	2.23	54.44	3.26	0.51
C1	75-101	18.41	19.18	60.10	14.79	84.94	3.56	0.24	1.36	54.82	3.43	0.33
C2	101-130	19.69	20.51	65.36	15.71	84.08	3.22	0.27	1.75	34.30	3.18	0.49
Pedon III *(Xeric Haplocalcid)*												
Ap	0-14	40.11	43.23	49.86	32.88	83.49	1.56	0.61	1.99	41.55	2.93	0.42
Ad	14-26	43.58	47.24	45.26	35.83	83.15	1.40	0.68	2.42	45.43	2.98	0.51
A3	26-75	33.68	35.82	54.04	27.70	82.57	1.88	0.48	2.08	37.99	2.82	0.51
Bw	75-96	22.46	23.35	66.25	18.66	82.58	2.95	0.29	1.91	45.72	2.84	0.36
Bk	96-127	22.85	23.77	65.30	18.98	82.61	2.92	0.29	2.18	32.88	2.69	0.36
C	127-165	28.04	29.43	58.19	23.33	82.51	2.34	0.37	1.89	52.25	2.93	0.41
Pedon IV *(Xeric Haplocambid)*												
Ap	0-24	66.88	78.37	33.05	52.21	84.00	0.64	1.91	1.89	100.27	3.10	0.27
A2	24-67	52.38	58.09	40.38	42.54	83.09	1.05	0.95	2.16	42.14	3.10	0.65
Bw	67-86	50.07	55.87	41.31	39.70	82.32	1.02	1.01	1.80	79.78	3.96	0.31
Bk	86-104	39.23	42.82	49.38	30.85	83.93	1.48	0.69	1.60	105.13	3.56	0.20
C	104-150	41.14	44.85	49.61	32.85	83.14	1.42	0.70	2.18	95.52	3.16	0.23

In the present study, the CIW values ranged between 6.68 and 78.37 and tended to decrease with depth in all profiles. The value of CIW increased with weathering. If the classification for CIA is performed for CIW as well, it is evident that all the profiles developed on different parent material are in similar classes in terms of CIW values. This result indicates that the CIW and CIA indices display similar behaviour for the different parent material.

The base/R_2O_3 values of all profiles ranged from 0.64 to 10.52. Parker's Weathering Index (WIP) is used to evaluate the intensity of the weathering of silicate rocks, based upon the proportion of alkali and alkaline earth elements in the products of weathering. The WIP also takes into account some individual mobilities, namely sodium, potassium, magnesium and calcium, on the basis of their bond strengths with oxygen (Parker, 1970). According to the definition of WIP, smaller WIP values indicate stronger chemical weathering, which is opposite to the manner in which CIA values are generated. This index has been suggested to be most appropriate for application to weathering profiles on heterogeneous parent rocks and is most likely not applicable to highly weathered mantles, because the assessment only includes highly mobile alkali and alkaline elements (Hamdan and Burnham, 1996; Duzgoren-Aydin et al., 2002; Price and Vebel, 2003). in In the present study, the WIP values of the soils formed on marl, limestone and alluvial-deposit parent rocks were between 36.51 and 110.95, 45.26 and 66.25, 33.05 and 49.61, respectively, and decreased with increasing weathering. The lowest WIP values were 33.05 in profile IV and 36.51 in profile II. These profiles were determined to be Xeric Haplocambid, whereas the C horizon of profile I, which developed on marl parent material, had the highest WIP value (110.95) and was deemed to be Xeric Haplocalcid.

There are two explanations for this phenomenon. Firstly, it means that the weathering process is more intense in Xeric Haplocambid profiles than in Xeric Haplocalcid profiles. Secondly, with time, the soil derived from the parent material diverges progressively from that of the parent material under the influence of the pedogenic process. In terms of parent material, the profile that developed on alluvial parent material showed the highest weathering, with the P index varying between 81.67 and 84.94 and tending to fluctuate slightly with depth in all profiles.

Fedo et al. (1995), proposed the Plagioclase Index of Alteration (PIA) as an alternative to the CIW. Because plagioclase is abundant in silicate and dissolves relatively rapidly, the PIA may be used when plagioclase weathering needs to be monitored (Fedo et al., 1995). In the present study, the PIA values tended to decrease with the depth in all profiles, with the Vogt's index value varying between 0.07 and 1.91. CIW values also decreased with depth.

Another way to study the degree of chemical weathering of the soil profiles investigated was to calculate the relative change in REE (Rare Earth Element) concentration. The abundance of trace elements and REEs in sediments has been employed to provide clues as to both sources and changes in sediments from weathering and sedimentary processes, as in Taylor and McLennan (1985). Some ratios of geochemical elements are used to quantify the degree of weathering of studied profiles. The trace elements and REEs of the studied soils are normalized to chondrite (Wood et al., 1979). Normalized REE patterns can indicate the degree of weathering of materials and this also applies, to a lesser extent, to the light rare earth element fraction. In many studies of weathering profiles, "immobile" elements such as Ti, Zr, Y and Nb, are used as internal references to evaluate the mobility of other elements (Nesbitt, 1979; Moore, 1998; Hill et al., 2000). The geochemical methods include also the determination of Th/U values. In the current study, the Th/U values ranged between 0.85 and 2.42 in all profiles. The lowest value was seen in the genetic horizon Bw2 of the Xeric Haplocambid. In addition, the Ba/Nb ratio ranged from 32.88 to 105.13. There was irregular change in profiles with depth, and the highest weathering was in the Bk horizon of the Xeric Haplocalcid. There was a degree of substitution of Sr for Ca in $CaCO_3$, and the variation in (Rb+Zr)/Sr was between 0.15 and 0.65. There was a large variation of $CaCO_3$ content in the profiles. Ti and Zr are often considered to be almost immobile; immobile index elements such as Ti and Zr are often used to identify enrichment or depletion of elements due to weathering and to calculate the mass balance relative mobility of other elements and soil discontinuities. They supplement the elemental concentration ratios of saprolite and parent bedrock to compensate for potential volume change during soil formation (Kabata-Pendias and Pendias, 1992; White, 1995). In the profiles studied, some weathering rates were quantified by using Zr. The values obtained when using Zr were homogenous, with Zr/Rb ranging between 2.69 and 4.01 in each profile.

X-ray diffractograms of selected samples are shown in Figure 3. According to these diffractograms, phyllosilicates of varying amounts and degrees of crystallization, including kaolinite at 1:1 and various minerals at 2:1, were formed in all four profiles. Peaks for most clay minerals were strong and indicated good crystallization. Mg-saturated clay exhibited three intensity peaks, at 1.44 to 1.40 nm, 0.95 to 1.00 nm, and 0.71 to 0.72 nm. The reflection at 0.72 nm disappeared at 550°C. The 1.4 to 1.5 nm peak was partially expanded from 1.6 to 1.5 nm by glycolation and it contracted to between 1.43 and 1.20 nm after K saturation at 20°C. An ill-defined diffraction band was observed between 1.0 and 1.1 nm at 550°C, indicating the presence of smectite (Sm), illite (I) and kaolinite (K). Illite was the most abundant clay mineral in profiles I, II and IV, whereas smectite was the most abundant clay mineral in profile III. XRD findings showed that the distribution of clay mineral types in surface horizons varied somewhat by profile, as follows: profile I, illite > smectite > kaolinite; profile II, illite > smectite > kaolinite; profile III, smectite > illite > kaolinite; and profile IV, illite > kaolinite > smectite.

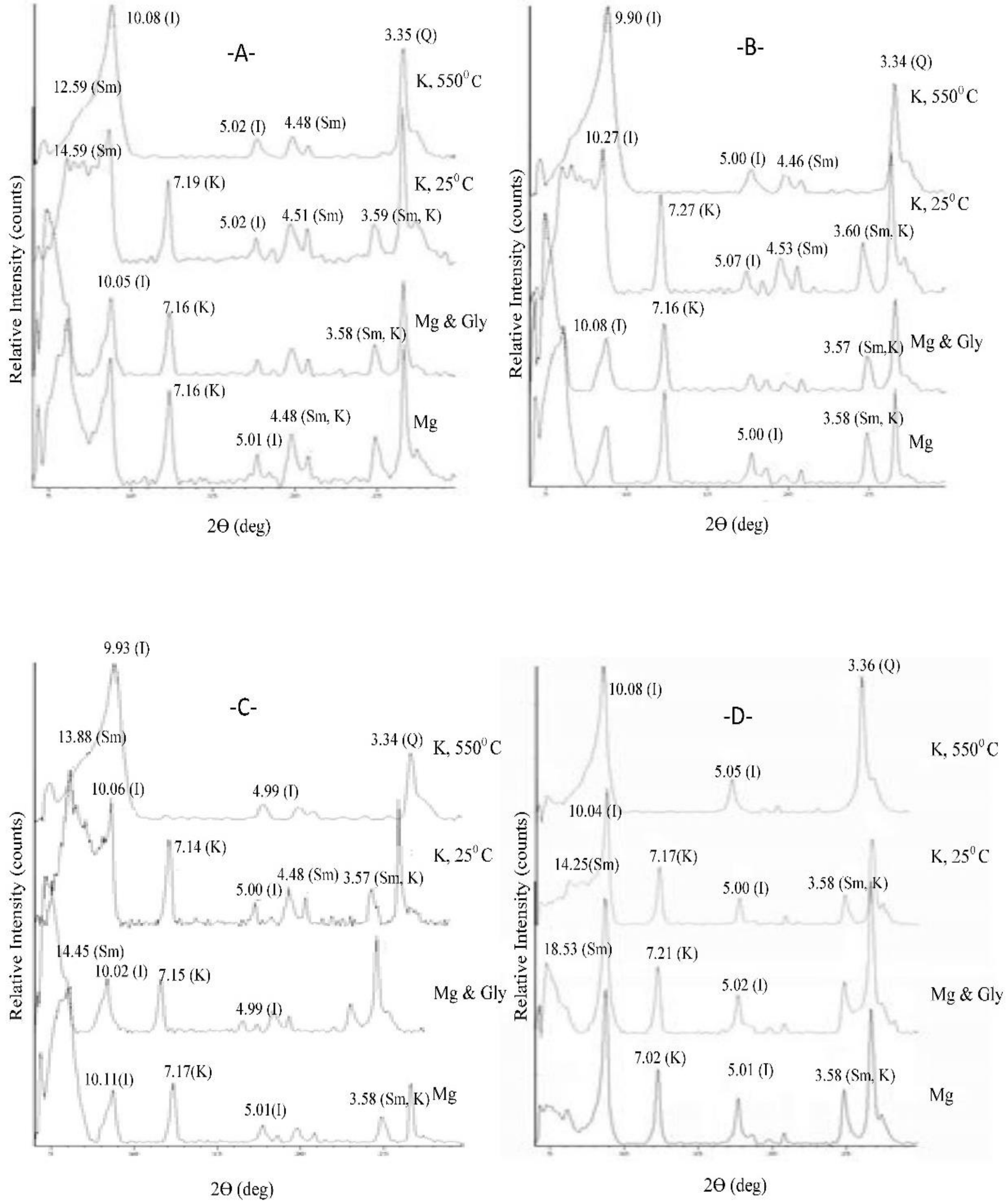

Figure 3. X-ray diffractograms of selected samples A: PI-Ap (0-21 cm), B: PII-Ap (0-21 cm), C: PIII- Ap (0-14 cm), D: PIV- Ap (0-24 cm), Smectite (Sm); Kaolinite (K); Illite (I), Quartz (Q).

Conclusion

This study tested the hypothesis that, over time and using four soil profiles, climate had a greater effect than other soil-forming factors on the formation of aridisols developed on different parent materials experiencing but under similar semi-arid climate conditions, topographical position, land use and vegetation. Jenny (1946) stated that contrasting of mass and energy is useful when interpreting the relationship between parent material and climate. Important aspects of soil formation in regions with arid and semi-arid climates are the substantial diurnal changes in temperature which cause mechanical or physical disintegration of rock, and wind-blown sands that score and abrade exposed rock surfaces. The soil depth of these regions, in particular, governs the amount of soil moisture. Soil development in the Altınova State Farm at Konya in the Central Anatolia region of Turkey is a result of slow weathering, secondary calcium carbonate illuviation, structural development and a weathering ratio greater than 2 for silicon and aluminium. All profiles, except for profile IV, were generally of fine texture due to the parent material and the intensity of the weathering process. Weakly developed soils in the taxonomic classes Xeric Haplocambid and Xeric Haplocalcid were encountered in the study area. All profiles, except for profile III, had similar pedogenetic horizons as a consequence of soil formation processes (classification and development of structural B horizon), even though they have different parent materials, such as marl, limestone and old alluvial deposits. This situation can be explained by the modifications occurring as a result of the effects of environmental factors over time. There was no significant difference found between profiles I and II which were formed on the same parent material, except for the intensity of calcification symptoms (nodules, mycelium). In addition, it is widely recognized that the chemical composition of the parent material is responsible for the origin of some soil chemical properties such as the proportion of highly exchangeable basic cations and weathering ratio. Profile III formed on limestone and displayed differences in some morphological and mineralogical properties, such as having deep soil, a high clay content, and high smectite clay mineral content when compared with the other profiles. However, the parent material cannot be said to be a major factor in soil development. For most systems under local conditions, soil type is determined by a number of different criteria related to pedogenesis. In particular, the nature and intensity of the pedogenesis is largely controlled by combinations of other soil-forming factors, namely climate, land use, land cover and time.

This study clearly showed that climatic conditions strongly affect the soil physicochemical, mineralogical and morphological properties, either directly or indirectly, in the local area. These results were supported by the application of the chemical weathering indices, namely CIA, CIW, Base/R_2O_3 (Al_2O_3 + Fe_2O_3 sesquioxide or R_2O_3) and PIA, in this study. They are commonly used for characterizing weathering profiles by incorporating bulk major element oxide chemistry into a single metric for each sample.

In this study, we evaluated previously defined chemical weathering indices for their suitability for the characterization of weathering profiles developed on limestone-marl parent rocks and in different topographical positions. The fact that the physical, chemical and mineralogical characteristics of the profiles had limited variation, and that the weathering indices and anomalies determined with the use of geochemical characteristics show a very limited variation along profiles, indicate that the profiles show similar weathering levels, despite their different ages.

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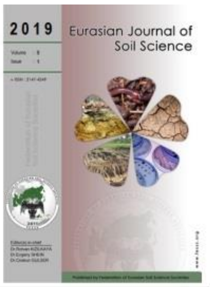

Suitability evaluation of some peri-urban soils for rainfed arable crop production in Lagos State, Southwestern Nigeria

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Abstract

A study was carried out to evaluate the suitability of some Peri-urban soils in Lagos state for arable crop production. Six pedons classified as *Alagba* (Rhodic Hapludult), *Dodokindo* (Plinthic Kandiudult), *Idesan* (Typic Endoaquept), *Owode* (Typic Kandiudult), *Atan* (Fluvaquentic Endoaquept) and *Pakoto* (Plinthic Kandiudult) Series identified at two study sites located at Igbokuta and Ibomwon communities in Ikorodu and Epe Local Government Areas of Lagos state were evaluated. The land use potentials for maize, cassava and leafy vegetables (Amaranth family) were assessed following the conventional non-parametric and the parametric (square root) methods of land suitability evaluation according to the revised FAO framework. All the pedons were rated as marginally suitable (S3) for maize except *Idesan* and *Owode* Series that made up 2.53% and 34.74% of the total area respectively, which were rated moderately suitable (S2). With respect to cassava and leafy vegetables, all the pedons were rated marginally suitable (S3) except *Atan* Series occupying 19.71 % of the total area, that was rated non-suitable (N1). The major limitations to sustainable crop production in all pedons were low nutrient supply (N, K, P and cations) coupled with high soil acidity (pH of between 3.9 and 5.8). In addition to this, *Idesan* and *Atan* series also have waterlogging problem hence may not be used for cultivating the afore-mentioned crops, but could be used for swamp rice. With appropriate liming, soil fertility management and proper drainage, most of the pedons may be rated as being moderately suitable (S2) for the cultivation of these crops. As a peri-urban area with high demand for agricultural products, year-round cropping with irrigation facilities is quite promising in most of the pedons studied.

Keywords: Land Evaluation, soil characteristics, peri-urban agriculture, land use.

Article Info

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Introduction

Recently, human populations in urban areas around major cities have increased very rapidly, especially in developing countries resulting in drastic increase in food demand (Liu and Chen, 2006). Considering the rapid growth in population in urban centres such as Lagos and other major cities and the attendant increase in demand for food and fiber, the need for effective, efficient and sustainable utilisation of peri-urban croplands is now more imperative than ever (Teklu, 2005, Behzad et al., 2009). Sustainability in agricultural production is a measure of how well the qualities of a land unit match the requirement of a particular form of land use (FAO, 2007). It is important that the land that will be used for agricultural production should be used according to its capacity for optimization and sustainability of soil productivity (Adeboye, 1994).

In order to resolve the problem of land use, there is need for the introduction of land evaluation and appropriate use of natural resources. The need for land evaluation arose from the fact that soil classification, soil map and the accompanying legends do not meet the needs of farmers and other land users (Ogunkunle, 2016). At present, the importance of land evaluation should be seen in the context of land becoming a scarce

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and non-renewable natural resource which is highly desired and for which there is a growing competition that holds a proper exchange value (Verheye, 2009). Land evaluation enables management guidelines in order to promote a more sustainable use of the soil and environmental resources (Maniyunda et al., 2007). Maize is an important tropical cereal crop both as staple and animal feed while cassava is the most important root crop in Sub Saharan African with food and industrial applications.

However, agricultural productions in many developing countries including Nigeria are carried out without proper study of the soil and optimal requirements for maximum production, which has led to low agricultural productivity. It was observed that the productivity of Nigerian soil is decreasing and the lands have been utilized intensively for all purpose regardless of its suitability and capability functions thereby resulting in land degradation and alteration of the natural ecological conservatory balances in the landscape (Senjobi, 2007); therefore, it is important that the land to be used for agricultural production should be used according to its capacity for optimisation and sustainability of soil productivity. This study was carried out to characterize some representative soils at two selected sites which are being proposed for commercial agriculture in Lagos State and evaluate the suitability of the different soil types for sustainable arable crop production.

Material and Methods

Site description

The study was carried out in two areas of Lagos State (Figure 1). One of the sites was at Igbokuta village, Imota Area development Council, Ikorodu Local Government Area, Lagos State, which lies within the latitudes 6°37'51.10"N-6°38'1.18"N and longitudes 3°38'38.40"E-3°38'53.50"E. The site covered a total area of 87.3 hectares located on a gently undulating terrain with an average elevation of 15m above sea level (asl). The other site was at Ibomwon Town, Epe Local Government Area of Lagos State within the Latitudes 6°40'12.50"N-6°40'34.58"N and Longitudes 3°56'38.14"E-3°56'55.29"E. The area was on an approximately 106.8 hectares with elevations ranging from 11m to 18 m asl generally sloping south-westward in a somewhat gently rolling fashion. The two study areas have a climate of humid tropical with annual rainfall of 1554 mm. The mean maximum and minimum temperatures are 32°C and 18 °C respectively (NIMET, 2012). The natural vegetation comprises of Swamp Forest of the coastal belt and dry lowland rain forest. The geology is derived from the quaternary sedimentary rocks of the coastal plain sands.

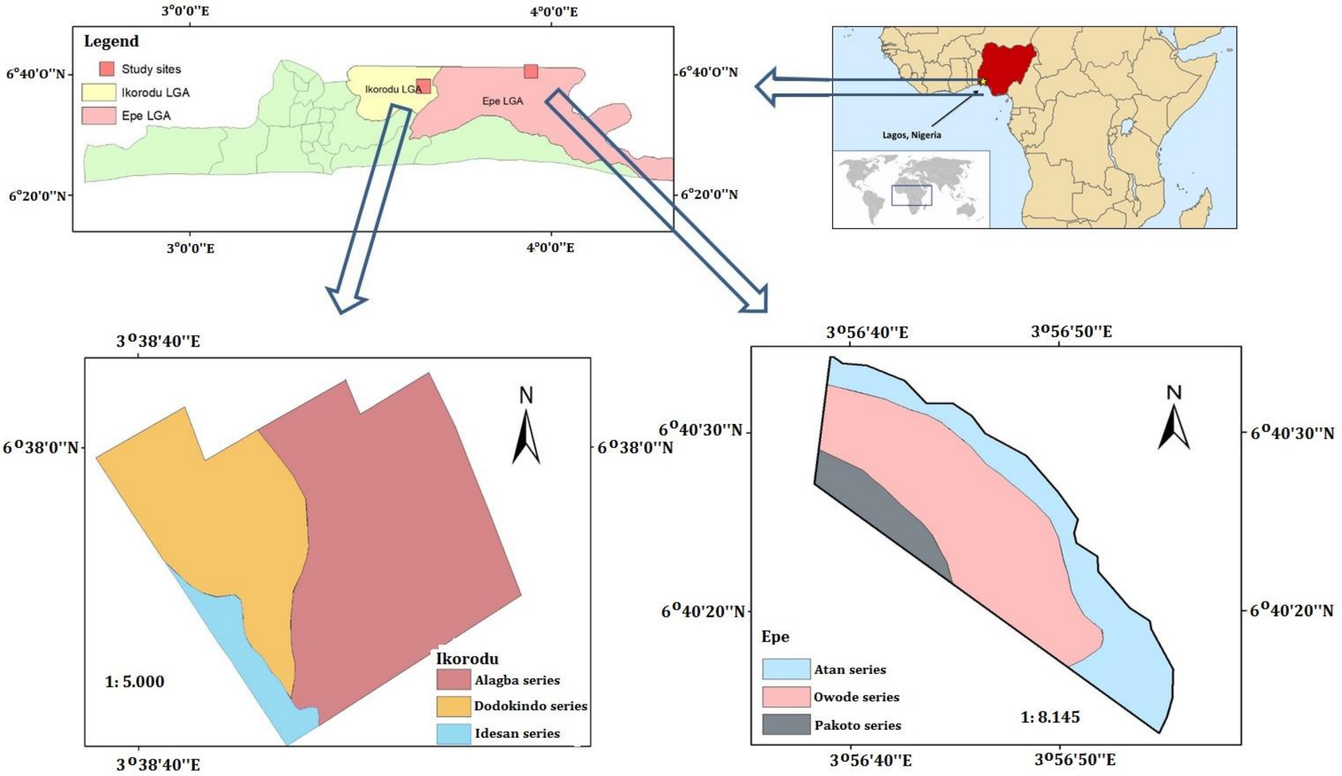

Figure 1. Location and soil maps of the study sites in Ikorodu and Epe Local Government Areas of Lagos State, Nigeria

Field survey

A detailed soil survey was conducted on the study sites. Soil morphological properties such as texture (by field method), colour (using Munsell soil colour chart), consistency, mottles, cementations etc. were examined - at each pedogenic horizons of modal soil profiles pits measuring 2x1.5x2m depth representing each of the identified soil mapping units. The pits were described according to the FAO (2006) guidelines, soil samples were collected from each horizon in each soil profile pit for laboratory analysis.

Laboratory analysis and soil classification

Soil samples collected from the field were shipped to the laboratory, and subsequently air dried, crushed and passed through 2mm sieves for physical and chemical analysis. The soils were analyzed for particle size using the modified hydrometer method, pH and electrical conductivity were determined in 1:1 soil/water ratio (ie 10g of soil in 10ml of deionised water) with glass electrode digital pH and conductivity meter. Total nitrogen was determined using Technicon Autoanalyzer while organic carbon was determined using the dichromate wet oxidation method. Available phosphorus was extracted with Mehlich III solution and concentrations were estimated colourimetrically with a UV spectrometer. Exchangeable bases (K, Ca, Mg and Na) were leached with neutral normal Ammonium Acetate solution and concentrations of Ca and Mg were determined using Atomic Absorption Spectrophotometer (AAS) while that of Na and K were measured using Flame Photometer. Exchangeable acidity was determined titrometrically using standard laboratory procedures. All parameters were determined in the Soil and Analytical Laboratory of the International Institute of Tropical Agriculture (IITA), Ibadan, Nigeria. The soils were classified according to USDA Soil Taxonomy (Soil Survey Staff, 2014) and World Reference Base (WRB) for soil resources (FAO, 2014). The classifications were correlated with the local series classification of soils (Moss, 1957).

Land Evaluation

The suitability of the soils for maize, cassava and leafy vegetable cultivation were evaluated by both non-parametric and parametric suitability evaluation methods based on the revised FAO land evaluation framework (FAO, 2007). For the non-parametric evaluation, mapping units were first placed in suitability classes by matching their characteristics with the established land use requirements for maize, cassava and leafy vegetable as presented in Tables 1, 2 and 3 respectively. The land requirement compared with the land qualities and characteristics place the soil in classes designated as S1, S2, S3, N1 and N2, which interprets to highly suitable, moderately suitable, marginally suitable, currently not suitable and permanently not suitable respectively. Land quality and factor rating for maize, cassava and leafy vegetable follows Liebig's law of minimum, the suitability class of a pedon is indicated by its most limiting characteristics for the conventional Non-Parametric approach (actual and potential) (Ogunkunle, 1993; FAO, 2007).

Table 1. Factor rating of land use requirement for maize

Land qualities	Land Characteristics	Unit	S1	S2	S3	N1
			100-85	84-60	60-40	39-20
Climate (c)						
Water availability	Mean Annual Rainfall	mm	750-1600	600-1800	>500	<500
Temperature regime	Mean annual Temp	^{0}C	32-18	18-16	16-14	<14
Wetness (w)						
Oxygen availability	Soil drainage		Well drained	Imperfectly drained	Poorly drained	Very poorly drained
Fertility(f)						
Nutrient availability	Org C (0-15cm)	%	2-1.2	1.2-0.8	0.8-0.4	<0.4
	Available P	mg/kg	>25	6-25	<6	any
	pH		5.5-7.5	5.0-5.5 or 7.5-8.0	4.0-50 or 8.0-8.5	<4.0 or >8.5
Nutrient retention	Base saturation	%	50-35	35-20	20-15	<15
Soil physical characteristics(s)						
Water retention capacity	Texture/structure		SCL	SL,LS	C	S
Rooting condition	Soil depth	cm	>75	>50	>20	<20
Salinity (n)	Ec	ms/cm	0-4	4-6	6-8	>8
Topography (t)	Slope	%	0-4	4-8	8-16	>16

Modified from Sys et al. (1991)

C, clay; LS, loamy sand; S, sand; SC, sandy clay; SCL, sandy clay loam; SL, sandy loam; EC, electrical conductivity

Table 2. Factor rating of land use requirement for cassava

Land qualities	Land Characteristics	Unit	S1 100-85	S2 84-60	S3 60-40	N1 39-20
Climate (c)						
Water availability	Mean Annual Rainfall	Mm	1000-2400	>600	>500	
Temperature regime	Mean annual Temp	^{0}C	18-30	>16	>12	Any
Wetness (w)						
Oxygen availability	Soil drainage		Well drained	Moderate or imperfectly drained	Poorly drained	Very poorly drained
Fertility (f)						
Nutrient availability	Total N	%	>0.2	0.1-0.2	<0.1	Any
	Available P	mg/kg	>25	6-25	<6	Any
	Exchangeable K	cmol/kg	>6	3-6	<3	Any
	pH		6.1-7.3	7.4-7.8 or 5.1-6.0	>8.4 or <4.0	
Nutrient retention	Base saturation	%	>35	20-35	<20	Any
	CEC	cmol/kg	>16	3-16	<3	Any
Soil physical characteristics (s)						
Water retention capacity	Texture		L,SCL, SL,CL	LS,S,CL	S, SiC	C
Rooting condition	Soil depth	cm	>105	>75	>50	<50
Salinity (n)	EC	ms/cm	0-4	4-6	6-8	>8
Topography (t)	Slope	%	0-5	5-12	12-20	>20

Modified from Sys et al. (1991).

C, clay; LS, loamy sand; S, sand; SC, sandy clay; SCL, sandy clay loam; SL, sandy loam; EC, electrical conductivity

Table 3. Factor rating of land use requirement for tropical leaf and fruit vegetables

Land qualities/characteristics	S1	S2	S3	Ns
Rainfall (mm)	$1700\text{-}2000^+$	1250-1700	850-1250	<850
No of dry months	<3	3-4	4-5	>5
Absolute temperature(^{0}C)	25-30	22-25	15-22	<15
Relative humidity during dev stage (%)	75-85	70-75	60-70	<60
Topography (t)				
Slope (%)	0-4	4-8	8-16	>16
Wetness (w)	Well drained	Moderately	Poorly drained	Poor drained
Drainage	Drained	Drained not imperfect	Drainable	Aerie
Flooding potentials	F0	F1	F2	F3
Soil physical characteristics				
Texture	CL,SL,CL,SIL	SL,LFS,LS	LCS,FS,S,C,CS,C	SIC,SC,L,SCL
Depth (cm)	>75	50-75	20-50	<20
Soil fertility (f)				
Base saturation (%)	>35	20-35	<20	
Organic matter(organic carbon in 0-15cm) %	>1.2	0.8-1.2	0.4-0.8	<0.4
pH	5.5-6.5	6.5-7.0	4.5-5.5	<4.0 >7.5

S1, Highly suitable (85-100%); S2, moderately suitable (60-85%); S3- marginally suitable (40-60%); NS Not suitable; F1, 1-2 months flooding in >10 years; F2, not more than 2-3 months flooding in 5 out of 10 years; F3 Flooding 2 months almost every year; C, clay; CL, clay loam; CS, coarse sand; Fs, fairly sand; L, loam; LCS, loamy, coarse sand; LFs loamy fine sand; LS, loamy sand; S, sand; SC, sandy clay; SCL, sandy clay loam; SIC, silty clay loam; SIL, silty loam; SL, sandy loam.

For parametric evaluation, each limiting characteristic was rated by scoring using the criteria presented in Table 1, 2 and 3. The index of suitability (actual and potential) was calculated using the equation (Eq. 1):

$$IS = A\times\surd B/100\times C/100\times D/100\times E/100\times F/100 \qquad \text{Eq. 1}$$

Where IS= Index of Suitability, A= overall fertility limitation and B, C….F is the lowest characteristics rating of each land quality group (Ogunkunle, 1993; Udoh et al., 2006*)*.

Five land quality groups climate (c), topography (t), soil physical properties (s), wetness (w) and fertility (f) were used in this evaluation. Only one member in each group was used for calculation purpose because there is usually a strong correlation among members of the same group (e.g. texture and structure) (Ogunkunle, 1993). For actual suitability index, all the lowest characteristics rating for each land quality group were substituted into the index of suitability equation, for potential suitability index, the corrective limitation observed will no longer have such constraints. The final suitability indices were allocated to land suitability classes (Table 4) according to the ratings suggested by Sys et al. (1991).

Table 4. Rating of limiting factors and suitability index of land quality for parametric suitability evaluation

Suitability class	Suitability index (SI)	Designation
Highly Suitable	>75	S1
Moderately Suitable	50-75	S2
Marginally Suitable	25-50	S3
Marginally Not Suitable	10-25	N1
Permanently Not Suitable	<10	N2

Source: Sys et. al. (1991)

Results and Discussion

Soil classification and land characteristics

The six pedons were identified and based on the morphological properties, were classified as *Alagba*, *Dodokindo*, *Idesan*, *Owode*, *Atan* and *Pakoto* series respectively using the criteria and classification of Moss, (1957). This classification method was designed for soils of sedimentary origin and most of the distinguishing characteristics were based on observable morphological features of the profiles defining each pedon. The correlating classification in higher categories of USDA Soil Taxonomy (Soil Survey Staff, 2014) and World Reference Base (WRB) system (FAO, 2014) together with the summary of land characteristics of the six mapping units/pedons are shown in Table 5. The soils are generally deep with effective soil depths above 100cm with the exception of *Idesan* and *Atan* Series with effective depths of < 80 cm and 85 cm respectively. The lower effective depths of these pedons were due to seasonally high water table which is responsible for the poor drainage in both pedons because they are located at the valley bottom positions on the landscape. All the pedons are free of hard pans, gravels and stones as the gravel concentrations were below the 25% critical value of gravel concentration for arable crops as proposed by Babalola and Lal (1977) except *Pakoto* Series which had a gravel content of 50% within 50cm depth from the surface. This is in agreement with the observation of earlier workers that described soils of the sedimentary origin especially the sandstones and coastal plain sand parent materials as ‘stoneless latosols’ (Vine, 1970; FDALR, 1995; Ojanuga, 2006). The gravel concentration of soils of *Pakoto* Series was due to secondary concretions and pan rubbles obtained at the upper and middle slope positions of concretionary and ferrugenized land forms of the Maku Fasc to which the soil belongs (Ojanuga et al., 1981). The range of soil texture in the surface soils is from Loamy Sand (LS) to Sandy Loam (SL) while at the subsurface, texture ranges widely from Sandy Loam in *Dodokindo* Series to heavy clay in *Pakoto* Series. The variation in soil texture with depth in most of the pedons could be attributed to clay illuviation in the process of profile development as pointed out in similar soils of Benin area (Orimoloye and Akinbola, 2013). Though in arable cropping, more emphasis is placed on the surface texture as it influences workability, nutrient and water retention, the subsurface texture is of much importance with respect to nutrient adsorption, water infiltration and susceptibility to leaching. Soil texture therefore influences the soil's inherent fertility and directly or indirectly, erodibility and moisture characteristics which could have great impacts on soil management, rooting ability and crop yields (Jalota et al., 2010; Nciizah and Wakindiki, 2015).

The chemical properties revealed that a available P is generally deficient as none of the pedons contains the required critical level of 15 mg/kg (Fernandes and Soratto, 2012) for sustainable arable cropping. The soils are also low in potassium, with values of K ranging from 0.13 cmol/kg at the surface in *Dodokindo* Series to 0.31 cmol/kg at both *Atan* and *Pakoto* Series’ which are just within the lower limits of the critical level of 0.2 – 2.6 cmol/kg (Quezada-Crespo et al. 2017). Effective Cation Exchange Capacity is above the critical value of 5.0 cmol/kg observed by Quezada-Crespo et al. (2017) in *Dodokindo* and *Owode* Series but are lower in the other soil types. This could be as a result of leaching due to high intensity of rainfall and the parent materials that are inherently poor in weatherable cation-yielding minerals in addition to the preponderance of low activity clays of the soils. Calcium levels are generally below the minimum requirement of 3.8 cmol/kg in almost all the soils (Quezada-Crespo et al., 2017). The micro-nutrients (Fe and Zn) are at sufficiency level only at the top soil. Their critical values are 5 – 9 mg/kg and 3.0 – 3.45 mg/kg respectively. Zn is generally below 20 – 25 mg/kg critical value. So also is cupper (Cu) content of the soils which are very low, below the critical value of 1.2 – 2.0 mg/kg. Those nutrient elements that are below the critical levels need be supplied through deliberate fertilizer application to build up their levels in the soil.

Table 5. Summary of classification, land characteristics and quality of soils of Ikorodu and Epe study sites

Characteristics/Qualities	Pedons/Mapping units					
	Alagba	*Dodokindo*	*Idesan*	*Owode*	*Atan*	*Pakoto*
USDA Soil Taxonomy	Rhodic Hapludult	Plinthic Kandiudult	Typic Endoaquept	Typic Kandiudult	Fluvaquentic Endoaquept	Plinthic Kandiudult
WRB system	Haplic Acrisol (Rhodic)	Petroplinthic Acrisol (Vetic)	Gleyic Fluvisol (Oxyaquic)	Haplic Acrisol (Nitic)	Gleyic Fluvisol (Oxyaquic)	Pisoplinthic Acrisol (Vetic)
Proportion of Area covered (%)	23.91	12.78	2.53	34.74	19.79	6.25
Physiographic Location	Upper slope	Middle slope	Valley bottom	Upper slope	Valley bottom	Upper middle slope
Slope Gradient (%)	8-13	4-10	0-3	5-7	2-5	5-7
Drainage	Well drained	Well drained	Poorly drained	Well drained	Poorly drained	Well drained
Effective soil depth (cm)	180	150	<80	105	85	150
Stoniness/gravel (%) (top 50cm)	20	20	<10	20	20	50
Soil Texture	SL – SC	LS – SL	LS – SCL	SL- SC	SL- SCL	SL- C
Chemical/Fertility						
ECEC (cmol/kg)	2.21 – 3.56	7.54 – 8.92	2.98 – 9.61	6.99- 8.92	2.51- 9.16	2.69- 7.94
pH (H_2O)	4.7 – 5.3	5.0 – 5.2	5.1 – 5.4	5.3- 6.4	3.9- 5.1	4.7- 5.8
Available P (mg/kg)	0.8- 2.20	2.1-.9.1	1.00-4.81	3.81- 7.35	3.93-7.15	1.2-3.31
Organic C (g/kg)	3.2 – 14.2	3.2 – 27.8	7.4 – 20.1	9.50- 70.80	7.00- 66.40	6.70- 31.90
N (g/kg)	0.07 – 2.20	0.8 – 3. 10	1.0 – 4.90	0.01- 1.11	2.33- 7.12	0.01- 4.31
Exchangeable Acidity (cmol/kg)	0.6 – 1.4	3.6 – 4.8	0.6 – 1.0	0.6- 7.2	1.0- 7.0	1.8- 6.4
Ca (cmol/kg)	0.15 – 1.67	0.04 – 1.48	0.05 – 1.76	0.61- 4.73	0.62- 1.62	0.32- 0.89
Mg (cmol/kg)	0.31 – 0.95	0.07 – 0.66	0.06 – 1.69	0.09- 3.17	0.03- 0.21	0.02- 0.05
K (cmol/kg)	0.07 – 0.18	0.06 – 0.13	0.60 – 1.00	0.14- 0.24	0.14- 0.31	0.14- 0.31
Na (cmol/kg)	0.17 – 0.21	0.16 – 0.20	0.16 – 0.18	0.14- 0.16	0.16- 0.26	0.16- 0.22
Fe (mg/kg)	17.5 – 27.40	15.6 – 80.10	43.3 – 95.60	9.4- 73.6	22.3- 104.4	16.8- 58.4
Cu (mg/kg)	0.4 – 0.8	0.3 – 0.5	0.6 – 1.20	0.1- 0.5	0.2- 0.7	0.1- 0.6
Mn (mg/kg)	1.0 – 20.1	0.1 – 4.3	0.1 – 24.6	1.0- 12.4	1.0- 17.4	1.1- 7.4
Zn (mg/kg)	2.5 – 8.0	2.2 – 4.5	2.7 – 10.7	3.5- 6.3	3.8- 8.1	3.7- 8.1

Suitability classification

The non-parametric and parametric suitability rating of the study areas for the maize are shown in Tables 6 and 7. By non- Parametric (actual) evaluation for maize, is moderately suitable (S2) with fertility (f) and topography (t) as the limitations. If some of these constraints (fertility limitations) are ameliorated, the potential suitability evaluation remains moderately suitable with topography (t) being the only limitation that cannot be easily ameliorated. Alagba, Dodokindo, Idesan, Atan and Pakoto Series' were marginally suitable (S3) with fertility (f) as the only limitation. This limitation is also common to all therefore, the potential suitability evaluation of Alagba, Dodokindo, Atan and Pakoto, becomes moderately suitable if the fertility problem is corrected with chemical or organic soil ammendments. Topography (t) was a limitation applicable to Dodokindo and Pakoto Series while but Dodokindo Series further has soil physical characteristics (s) as additional contraints.

Table 6. Non Parametric suitability classification for maize in the peri-urban soils of Ikorodu and Epe study sites

Land qualities	Land Characteristics	Unit	Pedons					
			Alagba	*Dodokindo*	*Idesan*	*Owode*	*Atan*	*Pakoto*
Climate(c)								
Water availability	Mean Annual Rainfall	mm	1554(S1)	1554(S1)	1554(S1)	1554(S1)	1554(S1)	1554(S1)
Temperature regime	Mean annual temp	^{0}C	25(S1)	25(S1)	25(S1)	25(S1)	25(S1)	25(S1)
Wetness (w)								
Oxygen availability	Soil drainage		Well drained (S1)	Well drained (S1)	Poorly drained (S3)	Well drained (S1)	Poorly drained (S3)	Well Drained (S1)
Fertility(f)								
Nutrient availability	Org C (0-15cm)	%	0.83(S2)	2.35(S1)	1.60(S1)			
	Available P	mg/kg	0.15(S3)	0.16(S3)	0.15(S3)	7.32(S2)	7.02(S2)	2.36(S3)
	pH		5.3(S2)	5.15 (S2)	5.3(S2)	5.9(S1)	5.1 (S2)	5.8(S1)
Nutrient retention	Base saturation	%	67.69(S1)	22.78(S2)	53.17(S1)	58.85(S1)	41.80(S1)	19.79(S3)
Soil physical characteristics(s)								
Water retention capacity	Texture/structure		SCL(S1)	SL,LS(S2)	SL(S2)	SCL(S1)	SL,LS(S2)	SCL(S1)
Rooting condition	Soil depth	cm	180(S1)	150(S1)	107(S1)	155(S1)	85(S1)	150(S1)
Salinity (n)	EC	ms/cm						
Topography (t)	Slope	%	4-6(S2)	5-7(S2)	0-2(S1)	5-7(S2)	2-5(S1)	5-7(S2)
Actual			S3f	S3f	S3fw	S2ft	S3w	S3f
Potential			S2t	S2ts	S3w	S2t	S3w	S2t

S1, highly suitable; S2, moderately suitable; S3, marginally suitable; Ns, not suitable; f, low fertility status; w, wetness; s, soil physical characteristics; t, topography, c, climate.

Table 7. Parametric suitability classification for maize in the peri-urban soils of Ikorodu and Epe study sites

Land qualities	Land Characteristics	Unit	Pedons					
			Alagba	*Dodokindo*	*Idesan*	*Owode*	*Atan*	*Pakoto*
Climate(c)								
Water availability	Mean Annual Rainfall	mm	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
Temperature regime	Mean annual temp	^{0}C	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
Wetness (w)								
Oxygen availability	Soil drainage		100 (S1)	100(S1)	40(S3)	100 (S1)	40(S3)	100(S1)
Fertility(f)								
Nutrient availability	Org C (0-15cm)	%	85(S2)	100(S1)	100(S1)			
	Available P	mg/kg	40(S3)	40(S3)	40(S3)	85(S2)	85(S2)	40(S3)
	pH		85(S2)	85 (S2)	85(S2)	100(S1)	85 (S2)	100(S1)
Nutrient retention	Base saturation	%	100(S1)	85(S2)	100(S1)	100(S1)	100(S1)	40(S3)
Soil physical characteristics(s)								
Water retention capacity	Texture/structure		100(S1)	85(S2)	85(S2)	100(S1)	85(S2)	100(S1)
Rooting condition	Soil depth	Cm	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
Salinity (n)	EC	ms/cm						
Topography (t)	Slope	%	85(S2)	85(S2)	100(S1)	85(S2)	100(S1)	85(S2)
Actual			40(S3)	34(S3)	23.32(N1)	78.36(S1)	34(S3)	36.88(S3)
Potential			85 (S1)	78.4 (S1)	36.9 (S3)	85 (S1)	36.9 (S3)	85 (S1)

S1, highly suitable; S2, moderately suitable; S3, marginally suitable; Ns, not suitable; f, low fertility status; w, wetness; s, soil physical characteristics; t, topography, c, climate.

Idesan and Atan have wetness as limitations and the potential suitability evaluation remains marginally suitable with wetness as constraint which will cost a lot to drain.

For parametric actual suitability evaluation, Alagba, Dokindo, Atan and Pakoto are marginally suitable (S3), Idesan is not suitable (N1) and Owode is highly suitable (S1). With proper management practices such as mulching, addition of organic manure etc. (the potential suitability evaluation) of Alagba and Atan remain marginally suitable (S3), Dodokindo, Owode and Pakoto become highly suitable (S1), while Idesan becomes marginally suitable (S3) and Atan remains marginaly suitable (S3).

By non- Parametric (actual) evaluation for cassava (Table 8), the entire mapping unit are marginally suitable (S3) with fertility (f) as the major limitations and wetness as additional limitation in Idesan and Atan soil series. With proper soil fertility amelioration, the potential suitability evaluation is moderately suitable (S2) for Alagba, Dodokindo, Owode and Pakoto soil series with topography (t) as the only limitation that cannot be easily ameliorated for Alagba, Owode and Pakoto soil series while Dodokindo has topography and soil physical characteristics (s) as its limitations. Idesan and Atan remains marginally suitable with wetness as constraint that cannot be easily corrected except by drainage which might not be economically significant with respect to cassava production.

For parametric actual suitability evaluation for cassava (Table 9), Alagba, Dodokindo, Idesan Owode and Pakoto are marginally suitable (S3) and Atan is not suitable (N1) with proper management practices such as mulching, addition of organic manure e.t.c (the potential suitability evaluation), Alagba, Dodokindo, Owode and Pakoto may become highly suitable (S1), Atan becomes marginally suitable (S3) while Idesan remains marginally suitable (S3).

Table 8. Non parametric suitability classification for cassava in the soils of Ikorodu and Epe study sites

Land qualities	Land Characteristics	Unit	Pedons					
			Alagba	*Dodokindo*	*Idesan*	*Owode*	*Atan*	*Pakoto*
Climate(c)								
Water availability	Mean Annual Rainfall	mm	1554(S1)	1554(S1)	1554(S1)	1554(S1)	1554(S1)	1554(S1)
Temperature regime	Mean annual temp	^{0}C	25(S1)	25(S1)	25(S1)	25(S1)	25(S1)	25(S1)
Wetness (w)								
Oxygen availability	Soil drainage		Well drained(S1)	Well drained(S1)	Poorly drained(S3)	Well drained(S1)	Poorly drained(S3)	Well drained(S1)
Fertility(f)								
Nutrient availability	Org C (0-15cm)	%	0.19(S2)	0.31(S1)	0.26(S1)	0.21(S1)	0.47(S1)	0.29(S1)
	Available P	mg/kg	0.15(S3)	0.16(S3)	0.15(S3)	7.32(S2)	7.02(S2)	2.36(S3)
	pH		0.13(S3)	0.11(S3)	0.05(S3)	0.2(S3)	0.17(S3)	0.15(S3)
Nutrient retention	Base saturation	%	5.3(S2)	5.15(S2)	5.3(S2)	5.9(S2)	5.1(S2)	5.8(S2)
Soil physical characteristics (s)								
Water retention capacity	Texture/structure		3.25(S2)	6.22(S2)	2.20(S3)	8.85(S2)	5.84(S2)	7.65(S2)
Rooting condition	Soil depth	cm						
Salinity (n)	EC	ms/cm	SL, SCL(S1)	SL,LS(S2)	SL(S1)	SC, SCL(S1)	SC(S1)	SC,CL(S1)
Topography (t)	Slope	%	180(S1)	150(S1)	107(S1)	155(S1)	85(S2)	150(S1)
Actual								
Potential			4-6(S2)	5-7(S2)	0-2(S1)	5-7(S2)	2-5(S1)	5-7(S2)

S1, highly suitable; S2, moderately suitable; S3, marginally suitable; Ns, not suitable; f, low fertility status; w, wetness; s, soil physical characteristics; t, topography, c, climate.

Table 9. Parametric suitability classification for cassava in the soils of Ikorodu and Epe study sites

Land qualities	Land Characteristics	Unit	Pedons					
			Alagba	*Dodokindo*	*Idesan*	*Owode*	*Atan*	*Pakoto*
Climate(c)								
Water availability	Mean Annual Rainfall	mm	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
Temperature regime	Mean annual temp	^{0}C	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
Wetness (w)								
Oxygen availability	Soil drainage		100(S1)	100(S1)	40(S3)	100(S1)	40(S3)	100(S1)
Fertility(f)								
Nutrient availability	Org C (0-15cm)	%	85(S2)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
	Available P	mg/kg	40(S3)	40(S3)	40(S3)	85(S2)	85(S2)	40(S3)
	pH		40(S3)	40(S3)	40(S3)	40(S3)	40(S3)	40(S3)
Nutrient retention	Base saturation	%	85(S2)	85(S2)	85(S2)	85(S2)	85(S2)	85(S2)
Soil physical characteristics(s)								
Water retention capacity	Texture/structure		85(S2)	85(S2)	40(S3)	85(S2)	85(S2)	85(S2)
Rooting condition	Soil depth	Cm						
Salinity (n)	EC	ms/cm	100(S1)	85(S2)	100(S1)	100(S1)	100(S1)	100(S1)
Topography (t)	Slope	%	100(S1)	100(S1)	100(S1)	100(S1)	85(S2)	100(S1)
Actual			36.88(S3)	34(S3)	25.30(S3)	36.88(S3)	23.32(N1)	36.88(S3)
Potential			85(S1)	78.37(S1)	40(S3)	85(S1)	36.88(S3)	85(S1)

S1, highly suitable; S2, moderately suitable; S3, marginally suitable; Ns, not suitable; f, low fertility status; w, wetness; s, soil physical characteristics; t, topography, c, climate.

By non-Parametric (actual) evaluation for Leafy vegetables (Table 10), the entire mapping unit are marginally suitable (S3) with fertility (f) and wetness as their limitations. However with proper amelioration such as fertilizer application, liming and proper organic matter management; the potential suitability could be moderately suitable (S2) for Dodokindo, Owode and Pakoto with climate as a limitation common to all, Dodokindo has topography and soil characteristics (s) as its other limitations, Pakoto has topography as another limitation. Idesan and Atan remain marginally suitable with wetness (w) as the major limitation for Idesan and Atan while Alagba has topography (t) as a constraint. Off-season cultivation with irrigation may favour leafy vegetable production in Idesan and Atan soil series but these could not be factored in here under rainfed system

For parametric actual suitability evaluation for vegetables (Table 11), Owode is moderately suitable (S2), Alagba, Dodokindo and Pakoto are marginally suitable (S3) while Idesan and Atan are not suitable (N1), with proper amelioration (the potential suitability evaluation), Owode and Pakoto become highly suitable (S1), Alagba and Dodokindo become moderately suitable (S2) while Idesan and Atan becomes marginally suitable (S3).

Table 10. Non parametric suitability classification for tropical leaf and fruit vegetables the soils of Ikorodu and Epe study sites

Land qualities/characteristics	Pedons					
	Alagba	*Dodokindo*	*Idesan*	*Owode*	*Atan*	*Pakoto*
Rainfall(mm)	1554(S2)	1554(S2)	1554(S2)	1554(S2)	1554(S2)	1554(S2)
No of dry months	4(S1)	4(S1)	4(S1)	4(S1)	4(S1)	4(S1)
Absolute temperature(ºC)	25(S1)	25(S1)	25(S1)	25(S1)	25(S1)	25(S1)
Topography(t)						
Slope (%)	4-6(S2)	5-7(S2)	0-2(S1)	5-7(S2)	2-5(S1)	5-7(S2)
Wetness(w)	Well drained(S1)	Well drained(S1)	Poorly drained(S3)	Well drained(S1)	Poorly drained(S3)	Well drained(S1)
Drainage	Drained(S1)	Drained(S1)	Drainable(S3)	Drained(S1)	Drained not (S2)	Drained(S1)
Flooding potentials	F0(S1)	F1(S2)	F2(S3)	F0(S1)	F2(S3)	F0(S1)
Soil physical characteristics						
Texture	SL,SC(S1)	SL, LS(S2)	SL,SC(S1)	SL,SC(S1)	SL, LS(S2)	SL,SC(S1)
Depth (cm)	180(S1)	150(S1)	107(S1)	155(S1)	85(S1)	150(S1)
Soil fertility (f)						
Apparent CEC (mol/kg)	3.25(NS)	6.22(NS)	2.20(NS)	8.85(S3)	5.84(NS)	7.65(NS)
Base saturation (%)	67.69(S1)	22.78(S2)	53.17(S1)	58.85(S1)	41.80(S1)	19.76(S3)
Organic matter (organic carbon in 0-15cm) %	1.42(S1)	4.05(S1)	2.75(S1)	7.08(S1)	6.64(S1)	4.5(S1)
pH	5.3(S3)	5.15(S3)	5.3(S3)	5.9(S1)	5.1(S3)	5.8(S1)
Actual	S3f	S3f	S3fw	S3f	S3fw	S3f
Potential	S2tc	S2ts	S3w	S2c	S3w	S2ct

S1, highly suitable; S2, moderately suitable; S3, marginally suitable; Ns, not suitable; f, low fertility status; w, wetness; s, soil physical characteristics; t, topography, c, climate.

Table 11. Parametric suitability classification for tropical leaf and fruit vegetables at Ikorodu and Epe study areas in Lagos State

Land qualities/characteristics	Pedons					
	Alagba	*Dodokindo*	*Idesan*	*Owode*	*Atan*	*Pakoto*
Rainfall(mm)	85(S2)	85(S2)	85(S2)	85(S2)	85(S2)	85(S2)
No of dry months	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
Absolute temperature(ºC)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
Topography(t)						
Slope (%)	85(S2)	85(S2)	100(S1)	85(S2)	100(S1)	85(S2)
Wetness(w)	100(S1)	100(S1)	60(S3)	100(S1)	60(S3)	100(S1)
Drainage	100(S1)	100(S1)	60(S3)	100(S1)	85(S2)	100(S1)
Flooding potentials	100(S1)	85(S2)	60(S3)	100(S1)	60(S3)	100(S1)
Soil physical characteristics (s)						
Texture	100(S1)	85(S2)	100(S1)	100(S1)	85(S2)	100(S1)
Depth (cm)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
Soil fertility (f)						
CEC (cmol/kg)	40(NS)	40(NS)	40(NS)	60(S3)	40(NS)	40(NS)
Base saturation (%)	100(S1)	85(S2)	100(S1)	100(S1)	100(S1)	60(S3)
Organic carbon (0-15cm) %	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)	100(S1)
pH	60(S3)	60(S3)	60(S3)	100(S1)	60(S3)	100(S1)
Actual	34(S3)	28.9(S3)	17.14(N1)	51(S2)	18.81(N1)	34(S3)
Potential	78.37(S1)	66.61(S2)	33.19(S3)	78.37(S1)	36.42(S3)	78.37(S1)

S1, highly suitable; S2, moderately suitable; S3, marginally suitable; Ns, not suitable

Conclusion

Land suitability ranges from moderately suitable (S2) to marginally suitable (S3) for the three crops (maize, cassava and leafy vegetable). Major limitations are low soil fertility, drainage and surface texture. However, with proper management, the potential land suitability ranges from highly suitable (S1) to marginally suitable (S3) for the three crops in the study areas. In order to correct the major limitations, management practices such as incorporation of crop residues and organic manure to the soil should be adopted to improve soil physical and chemical properties. Application of organic and inorganic fertilizers to increase the nutrient in the soil and use of drainage operation or planting of water tolerant crops to control the waterlogging condition of some part of the land would ensure optimum productivity.

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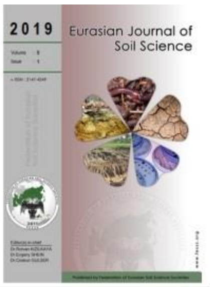

Impact of Resource Conserving Technologies (RCT) on soil physical properties and rapeseed (*Brassica napus* L.) yield in irrigated agriculture areas of the South-Eastern Kazakhstan

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Abstract

The aim of this resarch was to determine the effects of Resource Conserving Technologies (RCT) system and Conventional Tillage (CT) on soil physical properties and Rapeseed (*Brassica napus* L.) yield in irrigated agriculture areas of the South-Eastern Kazakhstan. The experimental study was conducted according to a radomized block design with three replications between 2015 and 2018. The CT system had maximum anthropogenic effect and caused loosening of arable soil layer, had the lowest bulk density values (1.19 -1.21 g/cm^3). The CT had a bulk density ranged between 1.13 and 1.30 g/cm^3. With a RCT tillage, the bulk density during the growing season of rape was located in optimal density zone between 1.20 and 1.22 g/cm^3. The RCT of rapeseed provided the greatest efficiency, where the yield of rapeseed increased by 13.3% and 22.0%. It has been revealed that with RCT of rapeseed cultivation, minimum technology (Mini-till) ensures sustainability of soil environment and its ecological condition, improves structure and raises water resistance of agroecosystem's soil aggregate. In turn the structure of soil's arable layer stabilizes with optimal soil density, which contributes to normal growth and development of rapeseed. It is proved that minimal technology of tillage is the leading agricultural practice ensuring preservation and improvement of qualitative and quantitative indicators of soil resource and productivity of oilseed rape.

Keywords: Conservation tillage, agrophysical factors, fertility, yield.

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Introduction

At the beginning of the third millennium, humanity was faced with ecosystem's limited ecological capabilities (Carpenter et al., 2006). Particularly, this case refers to the arable lands which have been used intensively under field traffic leading to decrease not only fertility and crop yield in soil but also to reduce usage of sustainable land and soil resources (Gomiero, 2016). In addition to that, in connection with the tillage systems also have the potential not only to accelerate ecological deterioration such as soil fertility loss and soil erosion but also, to reduce economical income such as increasing financial, energy and labor costs by reducing the long-term sustainability of dryland agriculture (Telles et al., 2011). A certain sequence of multiple methods of tillage takes place under traditional technology of agricultural crops' cultivation. Between 30 and 40 % of the total cost for crop growth is tillage application (Townsend et al., 2016). In general for those main reasons, concept of conservation agriculture was developed. Conservation agriculture is a part of sustainable agriculture, aiming at optimizing yields and prots but also at protecting land resources and the environment. Therefore, it is necessary to focus on effective and environmentally friendly methods in terms of resource conserving technologies for field cultivation activities (Hobbs et al., 2008).

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In recent years, systemic measures have been taken in agriculture field in the Republic of Kazakhstan to apply highly efficient Resource Conserving Technologies (RCT). Separate elements of this (No-tillage) technology were introduced in northern Kazakhstan as a system for soil protection which contributed to slow down soil erosion processes and increased the yield of grain crops (FAO, 2013: Saparov, 2014). Moreover, in different agricultural zones of the Republic of Kazakhstan, the basic principles of resource conserving agriculture has been developed by applying mulch system with plant residues and reduction or completely non mechanical tillage. Thus, zero tillage technology is contributing to enhanced sustainability of dryland agriculture in the region by reducing erosion, and improving soil quality and soil ecosystem services (Franzluebbers, 2002; Bessam and Mrabet, 2003; Kassam et al., 2009; Palm et al., 2013; Acar et al., 2018).

Conservation agriculture involves zero or minimum soil disturbance through tillage (no-tillage, reduced tillage, mulch tillage and strip-tillage), a balanced use of fertilizers and herbicides, a permanent soil biomass cover enhancing water and soil conservation, crop rotation and integrated pest management, reduced production costs and increased farming efficiency (Mrabet et al., 2001; Kassam et al., 2009; Ruiz-Colmenero et al. 2013; Chauhan et al., 2012). As for minimal technology (Mini-till), the number of soil's mechanical treatments is also reduced, continuous action herbicides replace the systems of mechanical pre-sowing and intermediate tillage and instead of deep processing, and small flat-cutting treatment is used. The use of environmentally correct techniques of technology that fit into biochemical circulation of agroecosystem resources ensures creation of sustainable competitive agrophytocenosis (Duru et al., 2015). Therefore, the objective of this manuscript was to investigate the effects of resource conserving technology techniques on soil physical properties and rapeseed (*Brassica napus* L.) yield in irrigated agriculture areas of the South-Eastern Kazakhstan.

Material and Methods

Study site description

Experimenal studies were carried out at the Turgen private farm "Agrouniversity" training and experimental farm of KazNAU found on the foot slope position of the Northern part of the Ili Alatau in the irrigated agriculture zone used under intensive acricultural activity and located at in South-Eastren part of the Kazakhistan (Figure 1). The study area is situated between 550 and 700 m elevation from sea level.

Figure 1. Location map of the study area

The climate type of study area is "Continental Climate" which can be described as low humidity, plenty of sunlight, a short but rather cold winter. The average annual air temperature is 7.7°C. The average long-term sum of precipitation for a period with temperature above 10°C is 240-350 mm with a total evaporation volume of moisture during this period (1550-1720 mm). The duration of the frost-free period is 158-175 days. Monthly average precipitation and temperature values of the study area is given Figure 2.

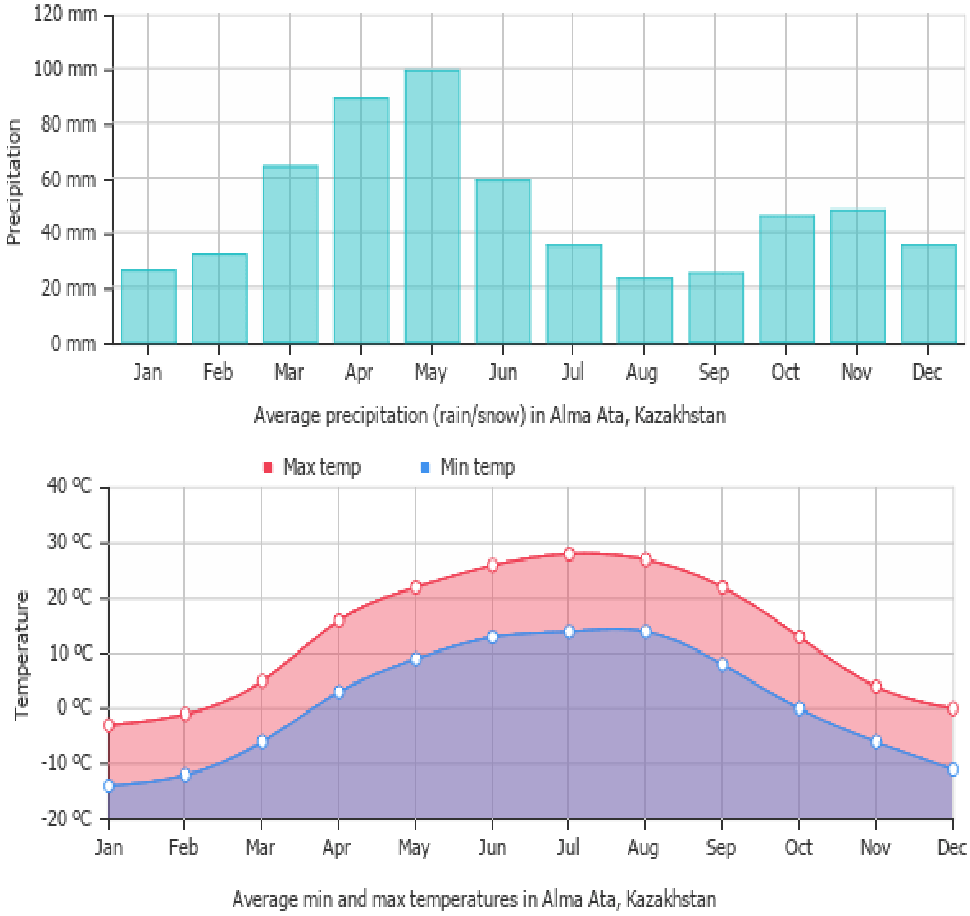

Figure 2. Monthly average precipitation and temperature values of the study area

Soil properties in study site

Before the beginning of the experiment, some properties of the soil were determined. After taking soil samples from surface depth (0-20 cm), some phsico-chemical analyses were conducted on air-dried samples stored at room temperature and from which crop residues, root fragments and rock larger than 2 mm in diameter had been removed. Selected some soil chemical properties were determined by the methods of Rowell (1994) and Jones, Jr. (2001). Research area soil is slightly alkaline with 7.3 pH value in 1:1 (w/v), while amount of their average $CaCO_3$ is about 5.8%. In addition, organic matter content, C/N ratio and total mineral nitrogen (NH_4+NO_3), available phosphorus and available potassium of the surface soil are 4.45%, 11.8, 87 mg/kg, 435.1 mg/kg and 22 mg/kg, respectively. These ratios decreased with increasing soil depth. According to the soil classification system, soil of experimanetal area was calssifed as meadow chesnut. In addition, some soil chemical characteristic values of meadow chesnut are given in Table 1. Moreover, physical properties of meadow chestnut soil is potentially fertil and satisfies the conditions to cultivate all types of crops particularly for oilseed rape.

Table 1. Some properties of meadow chestnut soil

Depth, cm	Organic matter, %	Total nitrogen,%	C:N	Total potassium, %	Total phosphorus, %	$CaCO_3$, %
0-24	4,45	0,120	21,51	2,60	0,19	5,80
24-32	4,40	0,119	21.44	2,10	0,16	5,84
32-59	1,00	0,060	9,66	1,09	0,17	5,88
59-103	0,46	0,039	6,84	1,10	0,14	7,30

Experimental design and tillage systems

In order to determine effect of different soil tillage systems on some soil physical properties such as soil aggregate stability, bulk density, and yield of Rapseed (*Brassica napus* L.), the experimental studies were performed between 2015 and 2018. In this study, main plot treatments were the two soil tillage methods, Conventional Tillage (CT) and Resource Conserving Technology (RCT), sub-plot treatments were three primary soil tillage methods (Tillage at 20-22 cm, Flat-cut tillage at 16-18 cm and Flat-cut tillage at 12-14 cm), and sub-sub-plot treatments were three Pre-sowing soil tillage methods (Cultivation at 10-12 cm by harrowing, Loosening at 12-14 cm and Disking at 8-10 cm). Each sub-sub plot was sized as 20m x 5m (100 m^2) and total plot number was 27. Each treatment was performed in three replicate plots. The plant densities of 15x10^4 – 45x10^4 plant ha^{-1} and row spacings from 15–35 cm used in the study are widely used for Rapeseed production in the Almaty region. Different tillage methods used in the study were given in Table 2.

Table 2. Different tillage applications

Soil Tillage Methodology- A	**Primary soil tillage-B**	**Soil Tillage system** **Pre-sowing soil tillage – C**
A_1 Conventional Tillage (CT)	**B_1** Tillage at 20-22 cm	**C_1** - Cultivation at 10-12 cm by harrowing **C_2** - Loosening at 12-14 cm **C_3** - Disking at 8-10 cm
A_2 Resource Conserving Technology (RCT)	**B_2** Flat-cut tillage at 16-18 cm	**C_1** - Cultivation at 10-12 cm by harrowing **C_2** - Loosening at 12-14 cm **C_3** - Disking at 8-10 cm
	B_3 Flat-cut tillage at 12-14 cm	**C_1** - Cultivation at 10-12 cm by harrowing **C_2** - Loosening at 12-14 cm **C_3** - Disking at 8-10 cm

In all plot, Rapseed (*Brassica napus* L.) seeds were placed at 2–2.5 cm depth in dry soil. Sowing of rapeseed carried out with a seeding rate of 2.5 million pieces/ha. Rapeseed was manually sown on the September. The seed density was evaluated directly after seedling emergence and adjusted for precise planting density at the five-leaf growth stage for all plots. Before sowing, Phosphorus and potassium fertilizer, as an agricultural background were applied as a basal fertilizer. Pest, disease (Cruiser -the active ingredient is Thiamethoxam, and Karate -the active ingredient is Lambda-cyhlothrin) and irrigation (two to three times at a rate of 400-420 m^3/ha) were performed according to local management practices. In the fight against weeds in the sowing of rapeseed, the herbicide (Impulse) was also used in an environmentally safe dose (0.7 L/ha) in RCT plots.

Harvesting and harvest measurements

Plots were harvested when approximately 2/3 of the seed was brown. Rapeseed (*Brassica napus* L.) yield and yield components were determined by adopting the standardized Crop Cut Method (Sapkoda et al., 2016). On each plot, the following measurements and observations were made: the plant density (m^2), pods per plant, seeds per plant and the 1000-seed-weight (g). Then, the remaining plants in each plot were manually harvested to measure the manually harvesting seed yield (t/ha). After the fresh weight was determined, the roots and the aboveground tissues were dried in an oven for 30 min at 105 °C to deactivate enzymes and then dried at 70 °C until a constant weight was reached for dry weight determination.

Soil sampling and analysis

Bulk soil samples were taken 2015-2018 period in undisturbed state from the experiment within each parcel at at 0-20 cm soil depth and kept in laboratory for analyses. Soil bulk density was analized by volume weight using the Kachinsky method (Kachinsky, 1958). Porosity and degree of aeration were determined by calculation. Aggregate size distribution was determined by the standard dry-sieving method (Savinov, 1936).

Economic analysis

A simple economic analysis was done based on total production. Production cost included rental charge of the land and input cost. The input cost was calculated by considering cost of seed, fuel, fertilizers, pesticide, hiring charges of labour. Fuel consumption was measured by filling the fuel tank twice, before and after each operation, with the re-filled volume being the actual fuel consumption. The gross income and net returns were calculated on the basis of market price for Rapseed. Price of the product was based on local market to compute total production cost, gross return, gross margin and benefit-cost ratio. The net returns were calculated by subtracting total variable costs from the gross income.

Statistical analysis

Analysis of variance (ANOVA) was performed using Duncan's multiple range test. ANOVA and the LSD test were conducted using the KazNAU using data processing methods.

Results and Discussion

In addressing the problem of developing and introducing RCT for cultivation of oilseed crops such as rape (*Brassica napus* L.), it was identified that resupply techniques provide and enable to reveal hidden forms of stability disorders to maintain agro-ecosystem's stability. Thus, agro-ecosystem made it possible to determine the ecological situation under traditional and resource conserving cultivation technology. As a result of controlling abiotic, biotic and anthropogenic factors, the negative influence of traditional technology of rapeseed cultivation on agroecosystem's ecological situation was revealed.

Bulk density

The tillage applications did lead significant differences on bulk density in average of 3 years of the experiment (Table 3). Generally, soil bulk density was increased in RCT, while decreased in CT. Kanwar (1989) and Meek et al. (1992) reported that tillage systems have altered bulk density and porosity of soils. Decreasing the number, intensity and depth of tillage induced to obtain higher bulk density values (Table 3). The increases in bulk density of the soil with no-tillage treatments have previously been reported by Xu and Mermoud (2001). Contrasting results have been reported for the effects of soil tillage systems on bulk density. Greater bulk density values under conventional tillage systems were reported when compared to no-tillage (Dao, 1996; Roscoe and Buurman, 2003).

When compared soil bulk density in two different tillage methods (CT and RCT), it was found that under CT, which has maximum anthropogenic effect and causes loosening of arable soil layer, has the lowest values (1.19 -1.21 g/cm^3) in 16-18 cm. This case can be explained that after preparing seed bed, the density of soil in arable layer was naturally decreased, thus, it created optimal condition for the initial period of growing season. On the other hand, in soil bulk density of 12-14 cm soil depth slightly increased about 1.20–1.22 g/cm^3. With tillage minimization (RCT), the soil bulk density is on average 1.20 g/cm^3. The data obtained by volume mass indicate the close dependence of arable soil layer's composition on the system of primary tillage. The value of the bulk mass of 0-30 cm of soil layer, with the conventional tillage indicates a loose composition with a bulk mass within range of 1.13 g/cm^3 and 1.30 g/cm^3 (Table 3).

The influence of main and pre-sowing treatment on soil bulk density, the day of sowing rape by horizons, average over the years of research indicates that comparing to main flat-cutting of soil to a depth of 16-18 cm, provides an increase in soil bulk density at a depth of 0-30 cm from 1.19 to 1.21 g/cm^3. Against the same background, at depth of 12–14 cm of tillage in all variants of pre-sowing tillage, an increase in the soil bulk density revealed up to 1.20–1.22 g/cm^3. With tillage minimization (RCT), the soil density varies within the limits of optimal addition, where the bulk density is an average of 1.20 g/cm^3. The data obtained by volume mass indicated that there was the close dependence of arable soil layer's composition with the system of primary tillage. The value of the bulk mass of 0-30 cm of soil layer, with the CT indicates a loose composition with a bulk density ranged between 1.13 g/cm^3 and 1.17 g / cm^3 (Table 3).

Table 3. Effect of Conventional Tillage (CT) and Resource Conserving Technology (RCT) on bulk density (average of 3 years)

A	**B**	**C**	**Bulk density of 0-30 cm soil layer, g/cm^3**	
			Before sowing	**Before harvesting**
A1	B1	C1	1.14	1.27
		C2	1.17	1.28
		C3	1.13	1.30
A2	B2	C1	1.19	1.30
		C2	1.20	1.31
		C3	1.21	1.32
	B3	C1	1.20	1.31
		C2	1.20	1.32
		C3	1.22	1.32

A1: Conventional Tillage (CT), A2: Resource Conserving Technology (RCT)

When studying soil density by volume mass in dynamics, it was found that under CT system, the maximum anthropogenic effect of dump plowing manifests itself which causes loosening of arable soil layer. After preparing the field for sowing, the bulk density of arable soil layer naturally decreased, and it was optimal at the initial period of growing season and development of rape growth. The obtained results of soil's bulk mass before sowing rape showed that replacement of costly, energy-saturated traditional dump plowing with RCT with flat-cut treatments to a depth of 16-18 cm and 12-14 cm contributes to creating an optimal composition of soil's arable layer in initial period of rapeseed development.

Soil bulk density of 0-30 cm soil layer by the end of rapeseed growing season in all treatments increased from 1.20 g / cm^3 to 1.27 g / cm^3. Under CT with dumping plowing, the top 0-30 cm layer of soil is compacted to the maximum, the bulk density increased from 1.13 g / cm^3 to 1.30 g / cm^3. A sharp compaction of soil's arable layer causes a disturbance of soil's water regime due to high physical evaporation of moisture and numerous gaps in root system of plants associated with a sharp compaction of the entire root-soil layer.

On the variants of minimal tillage (RCT) during the growing season of rape, soil is compacted moderately and risks for development of plant root system are not created. Before harvesting rapeseed, the bulk density increased from 1.19 to 1.30 g/cm^3 minimally under flat-cut processing for a depth of 16-18 cm, and from 1.20 g / cm^3 to 1.30 g / cm^3 for a depth of 12-14 cm (Figure 3).

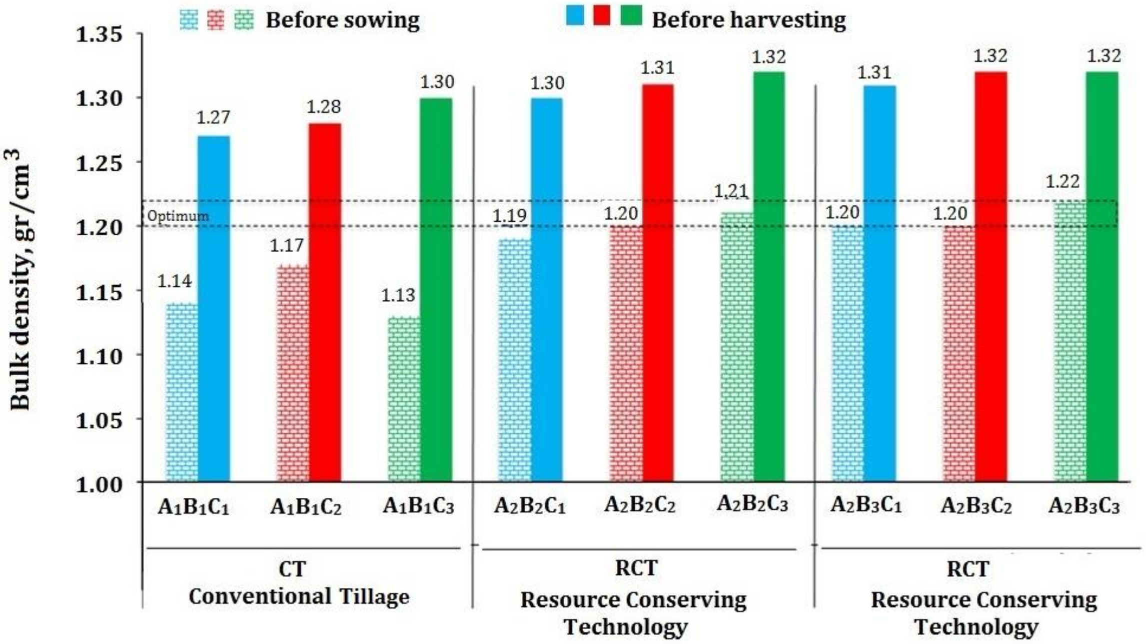

Figure 3. Effect of different tillage systems (CT and RCT) on dynamics of soil bulk density (average of 3 years)

With a RCT (implemented by flat-cut) tillage, the bulk density during the growing season of rape was located in optimal density zone between 1.20 and 1.22 g/cm^3. Namely, the optimal addition of arable layer of soil takes place in variants of RCT of rapeseed cultivation with Mini-till. The soil bulk density in both studied variants of flat-cut tillage to a depth of 16-18 cm and 12-14 cm, as well as in case of RCT is within the optimum value (1.19-1.20 g/cm^3) for normal growth and development of rapeseed.

Aggregate stability

The overall results of the experiment revealed a strong influence of tillage on aggregate size distribution and mean weight diameter in the average of 3 years, at the 0- 20 cm soil depth (Table 4). The quantity of fine aggregates (<0.25 mm) in RCT compared to CT. Tisdall and Oades (1982) also reported that the stability of macro-aggregates (>0.25 mm) was controlled by soil management (tillage, rotations, etc.), but the stability of micro-aggregates (<0.25 mm) depended on amount and stability of organic sementing agents and seemed to be independent of soil management.

Of the two tillage systems, better aggregate stability of the soil was observed in RCT, as seen by the high percentage of micro-aggregates of diameter <0.25 mm at a depth of 0 to 10 cm (range from a minimum of 42.5% to a maximum of 48.3%) with respect to that calculated in CT (28.1% to 37.0%) (Table 4). The better structure in RCT could be attributed to the effect of different agents that intervene in the aggregate stability. On the one hand, this could be due to a higher organic matter content as a consequence of the incorporation to the soil of residues coming from winter cropping and on the other hand, to that during the tillage operations, by the effect of soil turning, compacted horizons would be taken to the surface, forming stable aggregates that would arise from the compression (Silva and Mielniczuk, 1998) and not from the biological action of roots or microorganisms.

Effects of CT and RCT on water stable aggregates in average of 3 years of the experiment are given in Table 4. Generally, sum of water stabile aggregates was increased in RCT, while decreased in CT. There were differences between sum of water stable aggregates of tillage systems in all plots. The highest sum of water stable aggregates values were found for RCT (40%-42.1%), in in the average of 3 years. However, the lowest sum of water stable aggregates was reported for CT (22.3%-23.5%). These results were supported by Arshad et al. (1999), where no-tillage improved aggregate stability in surface soil compared to CT. Intensive tillage systems can cause the disruption of water stable aggregates and loss of organic content.

Table 4. Effects of tillage systems on sum of microaggregates and water stable aggregates as a percentage coefficient of soil structure

A	**B**	**C**	**Sum of micro-aggregates (%)**			**Sum of water stable aggregates, %**	**Coefficient of soil structure**
			0-10 cm	**10-20 cm**	**0-20 cm**		
A1	B1	C1	37.0	35.2	36.1±1.25	22.4±0.29	0.56±0.004
		C2	32.5	31.9	32.2±1.20	23.5±0.51	0.58±0.003
		C3	28.1	30.0	29.0±1.11	22.3±0.66	0.57±0.011
A2	B2	C1	45.8	43.2	44.5±2.12	40.0±1.75	0.91±0.012
		C2	42.5	44.1	43.3±1.51	41.1±1.97	0.83±0.011
		C3	43.5	45.5	44.5±1.56	40.8±2.25	0.87±0.010
	B3	C1	47.2	46.8	47.0±1.75	41.5±2.09	0.90±0.013
		C2	44.2	46.2	45.2±2.14	42.1±2.04	0.94±0.018
		C3	48.3	46.5	47.4±2.28	41.9±2.16	0.98±0.019

A1: Conventional Tillage (CT), A2: Resource Conserving Technology (RCT)

The analysis of soil structure during rapeseed vegetation period with minimal soil treatment, shows a satisfactory structural condition of arable layer (0-20 cm), the share of valuable macro-aggregates was between 43.3 ± 1.51% and 47.4 ± 2.28%, aggregates was between 40.0 ± 1.75% and 42.1 ± 2.04%. In the 0-10 cm section of arable soil layer, these indicators indicate a more visible change. After flat cutting soil to a depth of 16-18 cm, the amount of soil macro-aggregates was between 43.3 ± 1.51 and 44.5 ± 1.56%, and water-resistant aggregates was between 40.0 ± 1.75 and 41.1 ± 1, 97%. Flat cutting to a depth of 12-14 cm had a significant impact on these indicators, where the sum of macro-aggregates rised from 45.2 ± 2.14% to 47.4 ± 2.28% and water stable aggregates from 41.5 ± 2.09% to 42.1 ± 2.04%.

In the soil management, persistency and stability of soil aggregation is associated with the size of aggregates (Traore et al. 2000; Whalen and Chang, 2002). Nyamangar et al. (1999) indicated that there is need to root secretions in the soil for aggregates to be increased. Martens (2000) reported increases of water stable aggregates as a result of corn crop residues, and suggested less soil inverting methods to increase soil aggregation. Shaver et al. (2002) noted that no till cropping in wheat-corn rotation returned more crop residue, decreased bulk density, increased porosity and improved soil aggregation compared to wheat-fallow. Bronik and Lal (2005) noticed the effectiveness of organic matter and decomposition degree on the stability of aggregates. On the other hand, Abiven et al. (2008) determined the correlation between decomposition characters of crop residues and soil aggregates. Meanwhile Shaver et al. (2002) determined increase of macro aggregates and total porosity due to high aggregate stability which in turn causes in high infiltration and water use efficiency. Kasper et al. (2009) determined the amounts of water stable aggregates under conventional and reduced tillage treatments as 18,2 % and 18,9%, respectively, whereas it was found as 37,6% at minimum tillage practice. Besides, authors noted conventional tillage interfere more natural soil properties than reduced and minimum tillage.

Soil aggregates are a reflection of soil structure and texture. The combined group of soil particles is stronger rather than a single one. Aggregate stability is prominently a multi-parameter effect on the soil properties (Kalhoro et al., 2017). Along with soil water-resistance, the effectiveness of minimal tillage was estimated by the soil structure coefficient. Under CT of rapeseed cultivation, the value of this indicator, depending on pre-sowing tillage, ranged between 0.56 ± 0.004 and 0.58 ± 0.003, which indicated that soil structure was unsatisfactory. Under RCT, tillage minimization provided restoration of aggregate composition and soil structure, where structural coefficient increased with an average from 0.56 ± 0.004 to 0.98 ± 0.019, which indicated good soil structure (Figure 4).

These results confirm the typical beneficial effect of the lack of disruption of the soil structure (RCT). In Rapseed cultivation, this is consequence of the protection of the dense vegetation, without handling disturbances. According to Eltz et al. (1989), the larger values found for soil aggregate stability and soil structure under RCT, when compared to CT, are related to the lack of mechanical disruption of the soil and to the protection that plant residues offer to the surface, contributing to better aggregation. The increase of the stability of aggregates in the surface layer in RCT soil is a good effect because it reduces the susceptibility of the soil to erosion and losses caused by heavy rainfall, management, and wind (Freitas et al., 1999; Hevia et al., 2007). In this present study RCT improved soil aggregation properties after continuous CT, turning them more similar to the original state under native vegetation.

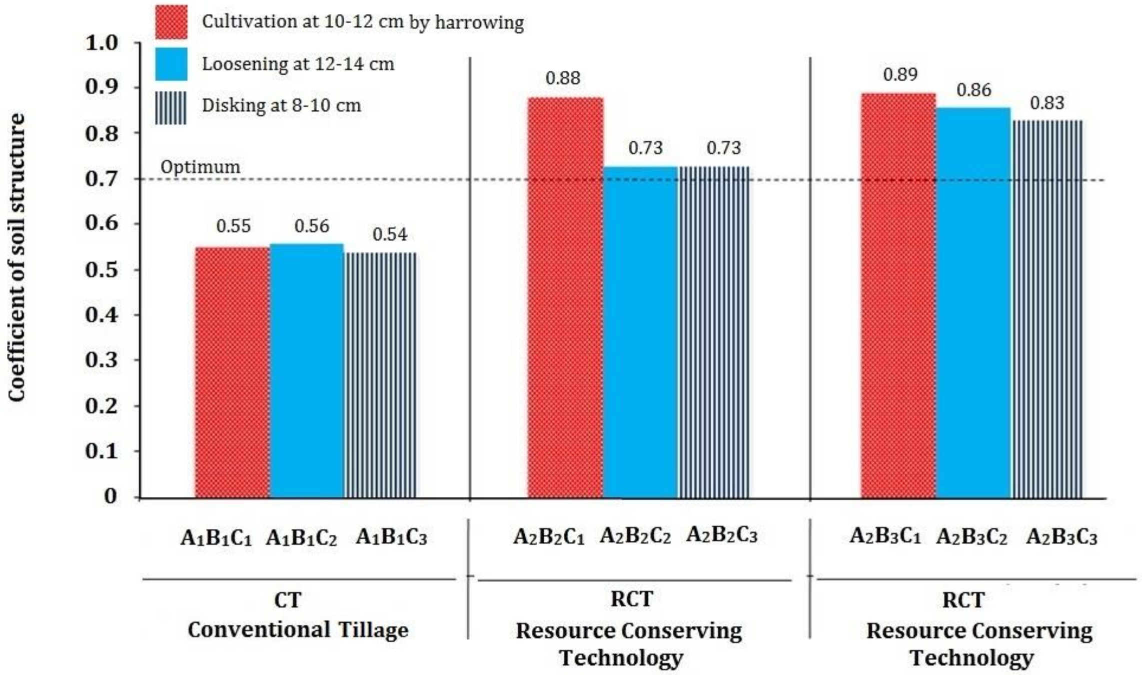

Figure 4. Effects of Conventional Tillage (CT) and Resource Conserving Technology on coefficient of soil structure

Rapeseed yield and yield components

The investigation results revealed that the rapeseed density, number of pods, number of seeds, 1000 seed weight and rapeseed yield were affected by tillage treatments as shown in Table 5. Under RCT, where flat-cut treatment (A2B2) was carried out to a depth of 16-18 cm, the rapeseed density was 80.1%, and with a processing depth of 12-14 cm, it was 78.6%. The density of growing rape plants depends on technology of cultivation and agrophysical indicators of soil fertility. Density of plants increases with improvement of aggregate composition and structure of soil. With a satisfactory soil structure after flat-cut treatment, due to improvement in moisture content of sowing rapeseed, the plant density increased, where the number of plants per m^2 was between 78.6 and 80.1%.

Table 5. Impact of tillage practices on mean values of rapeseed density, number of pods, number of seeds, 1000 seed weight and rapeseed yield

	Rapeseed density (Number/m^2)	Number of pods (pieces / plant)	Number of seeds, (pieces/plant)	1000 seed weight (gr)	Rapeseed Yield (t/ha)
A_1 B_1 (CT)	69.7±2.6	12.4±0.36	297±11.5	5.8±0.06	1.73±0.059
A_2 B_2 (RCT)	80.1±2.9	18.1±0.88	405±19.5	6.4±0.11	2.11±0.082
A_2 B_3 (RCT)	78.6±2.1	17.8±0.61	389±13.7	6.2±0.07	1.96±0.071

One of the elements of crop structure - the number of pods on one plant, depending on primary tillage, showed that the best result was obtained on average with 17.8–18.1 pieces/plant, and the same number of seeds per plant plants 389-405. The number of seeds in one plant was 92 -108 pieces less compared to CT. The most basic indicator of crop structure is the 1000 seed weight. Under RCT of rapeseed cultivation compared to CT, the mass of 1000 seed weight averages were over the years between 5.8g and 6.2-6.4g.

The magnitude of tillage effects varies with the use of tillage implements. CT decreases the bulk density, increases the soil porosity, infiltration rate and hydraulic conductivity (Kanwar, 1989; Meek et al., 1992; Dao, 1996; Xu and Mermoud, 2001; Shaver et al., 2002; Roscoe and Buurman, 2003; Bronik and Lal, 2005). As a result, soil becomes permeable, aerated and having good physical condition for rapseed growing. On the other hand, RCT increases the bulk density, soil resistance and mechanical impedance of soil for which poor physical condition may be developed. In our experiment, soil perhaps were more loose compared to other tillage treatments, which might have permited the roots to enter into the deeper layer for uptaking water and mineral nutrients. Positive physiological and metabolic activities of rapseed were indicated by higher density, number of pods, number of seeds, 1000 seed weight. Hence, highest yield of rapseed was obtained using RCT because of higher density, number of pods, number of seeds, 1000 seed weight. The pattern of changes in the addition of the arable layer of soil as a result of the application of the technique of RCT–Minimum (Mini-till) tillage revealed indicated an increase in the quality indicators of the soil resource and the restoration of the agro-physical factors of soil fertility.

The yield of rapeseed with the cultivation of RCT in 2016, 2017, 2018 and 3-year average yield are given in Table 6. The yield of rapeseed in the years of research with the CT was 1.73 t/ha, and with the RCT, it increased to 1.96-2.11 t / ha.

Table 6. Impact of tillage practices on rapeseed yield

Soil Tillage Methodology	**Research Years**			**Average yield (t/ha)**	**Yield gain**	
	2016	**2017**	**2018**		**(t/ha)**	**%**
A_1 B_1	1,76	1,69	1,75	1,73	St	-
A_2 B_2	2,16	2,04	2,14	2,11	0,38	22,0
A_2 B_3	1,98	1,93	1,99	1,96	0,23	13,3
Sd_{05}, t/ha	1,21	0,12	0,16	0,11		
S_x, %	2,43	2,43	2,87	3,04		

Yield results were processed by analysis of variance, where the lowest value of the standard deviation (Sd_{05}) between the control and the studied variants was 0.12t / ha and the accuracy of the experiment was Sx,% = 2.43%. According to the results of ANOVA, it is considered significant when the obtained difference of the studied variants exceeds the Sd_{05}. For example, in 2016, the yield difference between RCT and CT was within 0.22-0.40 t/ha. If we compare, the yield difference of the cultivation with RCT (0.40 t/ha) where Sd_{05} = 0.12, it was proved that the RCT provided a reliable significant yield increase up to 22.7%. In all the years of studying both methods of RCT, a significant yield increase was achieved, within 0.23-0.38 t/ha. Thus, the RCT of rapeseed provided the greatest efficiency, where the yield of rapeseed increased by 13.3% and 22.0%.

Economic Evaluation

In the series, under the conditions of the foothill zone of south-east of Kazakhstan, we gave the economic efficiency of RCT techniques. Economic efficiency was calculated to assess the effectiveness of economic and natural resources in the agro-ecosystem, as well as to assess specific areas of increasing economic efficiency in the cultivation of crops, ensuring the preservation and reproduction of the natural environment and increasing yields. The economic efficiency of rapeseed cultivation technology was carried out on the basis of rapeseed cultivation technology maps, taking into account the direct costs of CT and RCT according to the standards, rates and prices existing at the farm.

The following indicators were used in the comparative assessment of the efficiency of the methods of using the RCT of rapeseed cultivation:

- Rapeseed crop yield when studying the effect of minimization (Mini-Till) of tillage,
- Production costs per 1 hectare of rapeseed (based on rapeseed cultivation maps) from 1 ha (yield multiplied by the cost of 1 ton of rapeseed),
- Net income (sales revenue minus costs of rapeseed cultivation),
- Production profitability in rapeseed cultivation (net income divided by the cost and multiplied by 100%) depending on the studied techniques of the technology.

Crop yield was the main indicator for assessing the economic efficiency of rapeseed, while evaluating the ratio of yield and production costs. Increasing the yield of a cultivated rapeseed crop implies its economic efficiency (Table 7).

Table 7. Economic efficiency of rapeseed under Conventional Tillage (CT) and Resource Conserving Technology (RCT) in foothill zone conditions of South-Eastern Kazakhstan

Economic efficiency indicators	**CT**	**RCT**
Average yield, t/ha	1,73	2,10
Cost of 1 tonna of production, $	165,7	165,7
Sales revenue, $/ha	286,6	347,9
Cultivating expenses, $/ha	219,1	171,7
Relative net profit, $/ha	67,5	176,2
Rentability of soy cultivation , %	30,8	102,6
Net profit from application of resource- saving technology, $/ha		38,0 $/ha

Evaluation of the economic efficiency of RCT in the foothill zone of the south-east of Kazakhstan shows that with CT of rapeseed, the yield was 1.73 tones/ha , where the direct costs of its cultivation was 219.1 $/ha. With the sale of the harvest, revenue amounted to 286.6 $/ha, conditionally net income – 67.5 $/ha, which ensured the profitability of rapeseed cultivation only 30.8%.

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With the use of elements of RCT, the amount of costs was reduced due to the minimum cost of fuel and lubricants and additional funds with minimal tillage of RCT equal to 47.4 $/ha and the cost of applying an environmentally safe dose of herbicide in the fight against debris and other types works on the cultivation of rapeseed from 219.1 to 171.7 $/ha, where the cost of production decreased.

Comparative evaluation of economic indicators from the use of techniques of RCT shows that minimizing tillage contributed to an increase in income from 67.5 $/ha (CT) to 176.2 $/ha (RCT). On the basis of economic efficiency, the purity of the use of RCT of rapeseed cultivation, where the conditional net income from the use of RCT techniques (where the tillage technology pass is reduced by 2 times) rises to 176.2, $/ha, which increases the profitability of cultivation from 30, 8% to 102.6%.

Conclusion

Thus, for the first time, the possibility of efficient use of resources and energy saving in an agroecosystem has been established. The restored parameters of the agrophysical indicators of soil fertility are determined. The decrease in total energy costs by 47.4 $/ha , which is 21.6% due to the cost of fuel and additional funds with minimal tillage of RCT. In comparison with the waste treatment, while minimizing the cost processing is reduced. It has been established that with CT, the cost is 219.1 $/ha, and with RCT, only 171.7 $/ha. Where conditional net income is 67.5 to 176.2 $/ ha, additional income from each hectare of 38.0 thousand tenge is received. Indicators of the economic efficiency of the methods of RCT of rapeseed proves that the replacement of the main dump processing with small-plow cutting (Mini-till) is abundant, ensuring the effective use of soil resources and the conservation and restoration of the soil fertility agro-physical factors and the rapeseed agroecosystem energy saving in the foothill zone of South-East Kazakhstan.

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