2016

Volume : 5

Issue : 1

Page : 1 - 83

e-ISSN : 2147-4249

Eurasian Journal of Soil Science

Federation of Eurasian Soil Science Societies

Editor(s)-in-chief

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Published by Federation of Eurasian Soil Science Societies

EURASIAN JOURNAL OF SOIL SCIENCE

(Peer Reviewed Open Access Journal)

Published by Federation of Eurasian Soil Science Societies

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SCOPE OF THE JOURNAL: Eurasian Journal of Soil Science (EJSS) is a peer-reviewed international journal published by Federation of Eurasian Soil Science Societies. EJSS is a forum for presenting articles on basic and applied research of soil science, thus making new findings, methods and techniques easily accessible and applicable in practice. It publishes original papers on research in soil science. Reviews on popular topics relating to soil science are accepted by the editorial board. Articles are published in English.

ABSTRACTING AND INDEXING: CABI, EBSCOhost, TUBITAK ULAKBIM Dergipark, ProQuest, DOAJ (Directory of Open Access Journals), CrossRef, CiteFactor

Year: 2016, Volume: 5, Issue: 1, Page: 1-83 **e-ISSN 2147-4249**

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Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

Adsorption and desorption characteristics of chlorosulfuron in selected minerals and Pakistani soils

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Article Info

Received : 17.03.2015
Accepted : 11.05.2015

Abstract

Sorption and desorption efficiency of Chlorosulfuron that is sulfonylurea herbicide was checked by selecting different minerals and two types of Pakistani soils that were different on spatial scale. In Pakistan, sulfonylurea herbicide is being used against wide varieties of broad leaf weeds and for some grasses as well. Results obtained after the experimental work showed that adsorption co-efficient isotherm for Chlorosulfuron in tested soils data well fitted the Freundlich equation. In all the cases, slope n<1 was resembling the C type curve and isotherm was nonlinear. Due to low adsorption, distribution co-efficient (K_{d}) parameters were also low. Results indicated that soil samples (silt loam) collected from northern hilly areas Ayubia, Khyber Pukhtunkhwa showed more adsorption for Chlorosulfuron herbicide i.e. 25.5% than the sandy soil of Multan Punjab. The major difference between the sorption capacities of both of the soil was due to the difference in soil organic matter and soil pH. Among both these factors, organic matter plays more significant role in sorption. Adsorption efficiency of synthesized compounds on different soil types of known composition can be predicted by the adsorption and desorption results of the present study.

Keywords: Chlorosulfuron, sorption, desorption, physicochemical properties

Introduction

One substance or mixture of different substances that are used for repelling, preventing, destroying, controlling and mitigating the undesirable effect caused by pests is called as pesticide (Kuwatsuka and Yamamoto, 1997). In the recent modern agricultural farming operations, pesticides have become an inevitable part. Almost 48 % of the world's total food production is either consumed, destroyed or lost due to different pests like insects, parasites, birds, weeds, fungi, bacteria and rodents. Pesticides are used to overcome this much loss of food production. For controlling pests, different practices have been applied since long ago like neem oil and green olive etc. These natural pesticides have been modified into broad range of chemical compounds to kill the wide varieties of pests and weeds (Hemmamda et al., 1995). Different characteristics of the pesticide like its binding capability, vapor pressure, solubility in water and degradation have an effect on its movement from the site of the application. Different physic chemical properties of soil like its texture, pH and amount of organic matter also influence the amount of pesticides migrated from an area (Cozza and Woods, 1991; Koleli et al., 2006). Soil nature and its composition also determine the amount of pesticides retained in the soil (Marinas et al., 2001).

It is necessary to understand the pesticide behavior in the natural environment to reduce the risks of contaminants for preserving the environment specially its sorption behavior. There are different active sites

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e-ISSN: 2147-4249 DOI: http://dx.doi.org/10.18393/ejss.2016.1.001-012

available on the surface of the soil. When a pesticide is applied to soil it may be attached to soil very strongly while loosely bound pesticide molecules desorbs from active sites (Wu et al., 2012). Biological efficacy and persistence of a pesticide in soil is determined by its adsorption and desorption capacity. Both these capacities not only determine the migration of pesticides in different environmental components like soil and water but also have an influence on their uptake and metabolism by different microbes and plants (Konda et al., 2002).

Distribution of pesticides in the different phases can be investigated by the nature of the soil components with different adsorption efficiency and by the physicochemical properties of the pesticides (Monkiedje and Spitteler, 2003). Electronic structure and water solubility of pesticides are the most important properties for their adsorption and desorption study. Different intermolecular forces like Vander-Waals forces, hydrogen bonding, charge transfer, ligand exchange, direct and induced ion-dipole, dipole-dipole interaction and chemisorptions monitor the sorption of pesticides (Ali and Baugh, 2003). Clayey soil with amporphous mineral matter and organic matter controls the adsorption phenomena.

In agricultural sector, large number of urea based herbicides has been used extensively. Sulfonylurea are group of herbicides applied on different crops and vegetables like wheat, barley, oats, rice, maize, turf, soybean, oil seed rap, flax, sugar beets, plantation crops, forestry, blueberries, potatoes, and tomatoes to control the growth of weeds and grasses (Verschueren, 2001). Sulfonylurea is applied in lower rates (10-40 g ha^{-1}) than higher application rate of other herbicides (e.g. 2-5 Kg ha^{-1} for atrazine) (Sarmah and Sabadie, 2002).

Sulfonylurea is less toxic to mammals and applied in low rate so it is considered safe within the environment. Except its low toxicity, it still has some other environmental concerns. It is highly toxic to plants and it can be transported to other sites by leaching and air drift. It is very persistent in the environment and affects the reproduction capability of plants specially the rotational crops. It is found both in surface water and ground water due to its higher mobility and anionic character. It has a severe effect on the non target organisms and soil microorganism (Cessna et al., 2006).

As compared to the conventional herbicides, sulfonylurea can be degraded under the field conditions and at faster rate. There are different modes of degradations but the two important modes are chemical hydrolysis and microbial breakdown (Nyström et al., 1999). At 30^{o}C, Nicosulfuron herbicide undergoes breakdown of the urea part of the molecules by alcoholysis and hydrolysis (Schneiders et al., 1993).

In alkaline soil, microbial breakdown is major degradation pathway while in acidic soils, chemical hydrolysis predominates (Sabadie, 2002). Faster degradation of pesticide is favored by warmer, moist soil with low texture and low pH while slow degradation is associated with dry, heavy textures and high pH soil (Mishra and Patel, 2008). Increase in soil pH and decrease in organic matter content of soil is also associated with the higher mobility of certain sulfonylurea herbicides. There are some cases where the situation is opposite like Nicosulfuron has irreversible sorption capacity on clay particles that is a sulfonylurea herbicide (Laird et al., 1994). In agricultural sector, many organic herbicides and insecticides have been used in past few decades that ultimately accumulate in the soil. These compounds can also enter into human food chain through drinking water and pose serious threat to human health. So there is a need of integrated research to understand the behavior and fate of the pesticides and all other organic molecules.

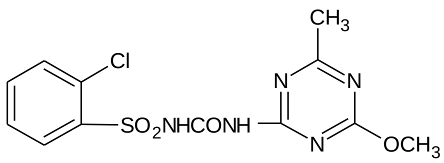
The sulfonylurea herbicide, Chlorosulfuron 1-(2-chlorophenyl) sulfonyl-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) is shown in figure 1 is a broad spectrum herbicide used against a wide range of broadleaf weeds as well as some grasses. Sulfonylurea herbicide is mostly used to control a wide range of weeds in crops of wheat in Pakistan with the Trade name of Alkanak and Logran, in which Chlorosulfuron and Triasulfuron are present (Ukrainczyk and Rashid, 1995). Different researches have indicated that the activity and adsorption efficiency of Chlorosulfuron depend on pH of soil. Like a weak acid with pKa of 3.3, Chlorosulfuron is present in ionic form in both neutral and alkaline soil solution. It has also been observed in the previous studies that there is a negative relationship soil pH and sorption of sulfonylurea herbicides (Khan et al., 2003). Nonionic pesticide has a different mechanism of binding with the soil components and it depends on the chemistry of pesticides and physic chemical properties of soil (Stork, 1998; Bailey et al., 1968). Generally, binding of pesticide with soil by physical sorption is reversible while by chemisorptions it is irreversible. Apparent hysteresis or irreversibility may be caused by some other factors than chemisorptions, such as equilibrium is not attained during desorption, pesticide loss due to biological and chemical degradation, volatilization and precipitation. Depending upon the nature of chemical bond or desorption methodology chemisorbed pesticides can be partially desorbed (Chen, 1990).

Pakistan is a country where economy is largely dependent on agricultural sector therefore most of the parts of its land are used for cultivation of crops. So pesticides are applied extensively to protect crops. Sulfonylureas based pesticides are used widely in Pakistan on different crops. Pesticides are used frequently in Pakistan but the knowledge about their toxicity is lacking. The main aim of the present research is to identify the effects of these pesticides in terms of their persistence and toxicity on different soils of Pakistan and in different environments. Four types of soils were selected from the different agricultural areas of Pakistan and main focus was on agricultural areas of KPK, central and southern Punjab districts. The selection of these areas was based on the use of pesticides. Wheat was grown in the south Punjab while other selected sites had more fruit growing area. Extensive use of sulfonylurea has raised concerns as it has potential to contaminate environment. Adsorption processes in soil play a significant role in all physical processes affecting the residue behavior of pesticides in the agro environment.

Material and Methods

Chemicals

Acetone and Methanol used were 99.9 % pure from Merck, Germany. Sodium chloride and calcium chloride anhydrous powder, extra pure used were products of Sigma Aldrich Company Germany. Analytical standard Chlorosulfuron was purchased from ACCU Standard USA.



(White crystalline pKa 3.3)

Figure 1. Chemical structure of Chlorosulfuron

Soil samples

Two soils (0-10cm) were collected from different cultivated soil areas of Punjab and KPK, with no recent history of pesticide application. Among them one was from the province of Punjab while the other one was from the KPK in Pakistan. Soil 2 was taken from chak no. 136 WB Tehsil Harpa District Multan, and soil 1 was from Ayubia, KPK. These soils having substantial differences representing a range of physical properties i.e. differences in level of clay organic matter and pH (Afyuni et al., 1997).

Sub samples of soils were mixed thoroughly, air dried at room temperature disaggregated manually using a marble mortar and a pestle. After this the soil was passed through a 2-mm screen sieve, and mixed manually to achieve homogeneity. Samples of homogenized soils were analyzed for moisture content, organic matter percentage and pH. In order to find out the moisture content of the soils, the soils were dried at 105ºC until a constant weight was achieved and the moisture content was determined by the difference in the pre and post over weights. Organic matter content was determined by the loss on Ignition Method, in this method the soil samples were heated to a temperature of 400ºC in a Ney Vulcan burnout in oven for 24 hours in order to oxidize any volatile organic matter present in the soil (Afyuni et al., 1997).

Table 1. Physiochemical properties of soils

Sample	Location	Soil Texture	OC (%)	Clay (%)	Sand (%)	Silt (%)	pH	% C	Primary Crops
Soil 1	Ayubia (KPK)	SiL	6.51	44	24	41	7.6	3.79	Maize, French beans
Soil 2	Multan (Punjab)	SC	1.89	12	52	13	8.1	1.10	Wheat, Cotton

Organic content was deduced from the loss of weight as a result of heating in the furnace. Organic carbon was determined by elemental analysis. Soil pH was measured by mixing 10 gm of dry soil and 10 ml of deionized water, after one hour of contact time the pH of the slurry was measured using Orion 420 plus pH meter equipped with a glass electrode (Laird et al., 1994; Zhang et al., 2009). The relevant physiochemical properties of two soils are given in Table 1.

Table 2. Relative physicochemical properties of selected minerals

Minerals	Formula	pH	AEC (cmol kg^{-1})	CEC (cmol kg^{-1})	d-Spacing (A^{o})	Specific Surface Area m^2g^{-1}	Types of Lattice
Geothite	FeOOH	6.0	7.0	0.4	9.6	36	N/A
Bentonite	$BaTiSi_3O_9$	9.7	N/A	10	12.06	N/A	2:1

Adsorption experiments

All experiments have been performed under isothermal conditions at 25±1ºC (Walker and Welch, 1989). Pesticide solutions were prepared in deionized water and stored at 4 ºC. For Chlorosulfuron eight different concentrations 0.25, 0.5, 0.75, 1.0, 2.5, 5.0 and 7.5 ppm were prepared, Sorbent/solution ratio was kept at 1:20. Depending on the desired Chlorosulfuron concentration, 10 ml of 0.1M sodium chloride was added as background electrolyte in each concentration to simulate ionic strength similar to that of natural soil solution. It was also added as an aqueous solvent phase in order to improve centrifugation and to minimize cation exchange.

Each sample consisted of 0.5g of soil or mineral mixed with 10ml of pesticide solution in 1:10 soil /solution ratio, placed in a 15ml Pyrex glass centrifuge tube, fitted with a screw cap. The tubes were continuously agitated on a Stuart Orbital Shaker at 90 rpm for 24 hours at room temperature (25ºC) in order to attain equilibrium. The adsorption equilibration process was done in duplicate for each concentration. In addition a blank sample containing only dissolved fungicides and 0.1M NaCl background electrolyte without any mineral or soil was prepared and treated in parallel with each set of batch experiment in order to quantify the losses and to account for possible degradation during adsorption process. The data was analyzed using XRD and HPLC techniques.

Desorption experiment

Desorption studies was conducted on the same herbicide soil solutions. After the sorption experiment, the remainder of the supernatant was decanted and the tubes were reweighed. After this 9 ml of freshly prepared 0.01M $CaCl_2$ solution was added to the soil remaining in the centrifuge tubes and the samples were again shaken for 24 hr and XRD and HPLC techniques were utilized to manipulate the data. Desorption, expressed as micrograms adsorbed/gram of soil (µg/g' soil), was obtained from the difference, taking into account the solution remaining in the soil after the supernatant was poured off.

Data analysis

The amount of the Chlorosulfuron adsorbed (µg/g of soil) was calculated by using Equation (1).

$$C_s = \frac{V}{m}.(C_b - C_a) \qquad (1)$$

where C_s is the amount adsorbed, V is the volume of solution, m is grams of soil taken, $C_b$is equilibrium concentration of blank and C_a is equilibrium concentration of treatment supernatant. The adsorption values obtained from Equation (1) were used to construct following linear type of isotherm:

$$K_{d\,(ads)} = \frac{C_s}{C_e} \qquad (2)$$

Where $K_{d(ads)}$ is linear or sorption equilibrium distribution co-efficient in (ml/µg). C_e is the concentration (µg/ml) at the equilibrium concentration. Desorption is expressed as micrograms adsorbed/gram of soil (µg/g soil) and was calculated from the difference of solution remaining in the soil after the supernatant was decant off. The sorption equilibrium distribution co-efficient $K_{d\,(des)}$ in (ml/µg) was calculated as:

$$K_{d\,(des)} = \frac{C_s}{C_e} \qquad (3)$$

The adsorption isotherms of pesticides in all the soils fitted the Freundlich adsorption relationship equation (4):

$$C_s = K_f C_e^{\frac{1}{n}} \qquad (4)$$

where C_s is the amount of adsorbed (ug/g), C_e is the equilibrium concentration (ug/ml) and K_f and n are constants determined by applying the linearized form of the Freundlich equation. The Freundlich constant normalized to organic carbon (K_{foc}) was calculated by using equation (6).

$$K_{oc} = \frac{K_d}{\%C} . 100 \quad (5)$$

Where K_{foc} and K_f are related as:

$$K_{foc} = \frac{K_f}{\%C} . 100 \quad (6)$$

The equilibrium organic matter (K_{OM}) by normalizing K_d or by normalizing K_f with the content of was calculated according to equation (7) and equation (8) respectively.

$$K_{OM} = \frac{K_d}{\%OM} . 100 \quad (7)$$

$$K_{OM} = \frac{K_f}{\%OM} . 100 \quad (8)$$

The hysteresis coefficient (H) for the adsorption isotherm was calculated using the relation;

$$H = {}^{n_d}/{n_a}$$

Where n_a and n_d are the Freundlich constants of the adsorption and the desorption isotherms. The standard free energy change of adsorption (ΔG) from the isotherm can be calculated using the following relation: (Abdullah et al., 2001; Tahir et al., 2008).

$$\Delta G = -RT\ln K_{OM} \quad (9)$$

The ΔG can be used to judge the adsorption reaction. Its value ≤ -40 $kJmol^{-1}$ indicates physical adsorption of herbicide with the soil.

Results

Chlorosulfuron adsorption and desorption were studied by HPLC attached UV- detector at λ_{max} 230 nm for Chlorosulfuron.

Adsorption isotherm

Comparative adsorption of Chlorosulfuron on 2 studied soils and selected minerals i-e Goethite and Bentonite is shown in Figure 2 and Figure 3.

Distribution coefficient (K_d), Freundlich constant (K_f), Gibbs free energy (ΔG) and Hysteresis (H) were calculated from the isotherm by using formulae given in data analysis.

Table 3. Adsorption coefficients of chlorosulfuron in selected soils

Soil	K_d	R^2	K_{oc}	K_f	n_a	R^2	K_{foc}	K_{OM}	G
Soil1	5.4	0.83	142	20	1.64	0.65	527	317	-13.31
Soil2	3.3	0.82	300	27	1.84	0.78	2454	1443	-16.81

Table 4. Adsorption coefficients of chlorosulfuron in selected minerals

Mineral	K_d	R^2	K_f	n_a	R^2
Bentonite	3.156	0.76	5.12	0.79	0.87
Geothite	2.598	0.91	4.06	1.03	0.84

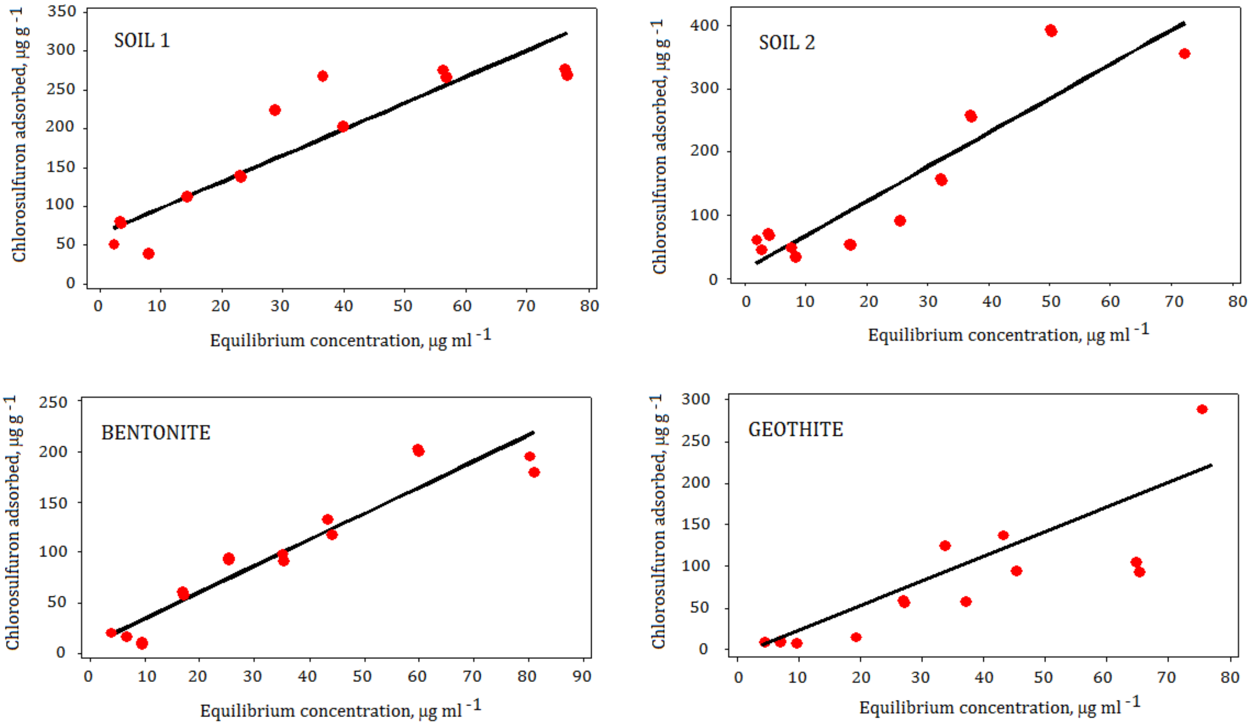


Figure 2. Simple sorption isotherms of Chlorosulfuron by soil 1, soil 2, Bentonite and Goethite.

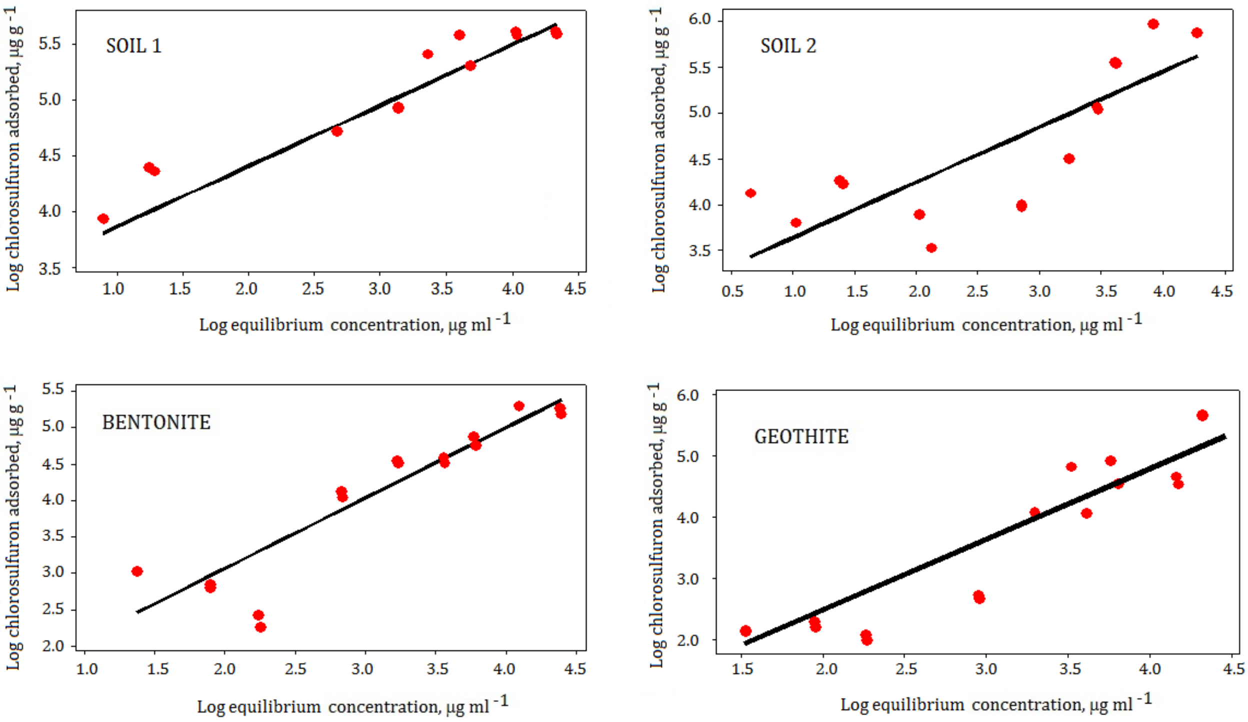


Figure 3. Freundlich Adsorption Isotherms Chlorosulfuron by soil 1, soil 2, Bentonite and Goethite

Desorption

Desorption equilibrium distribution co-efficient ($K_{d(des)}$) was calculated by plotting the desorbed pesticide concentration ($C_{s(des)}$) against the equilibrium pesticide concentration ($C_{e(des)}$) and are shown in Figure 4while Figure 5 shows Freundlich desorption isotherms.

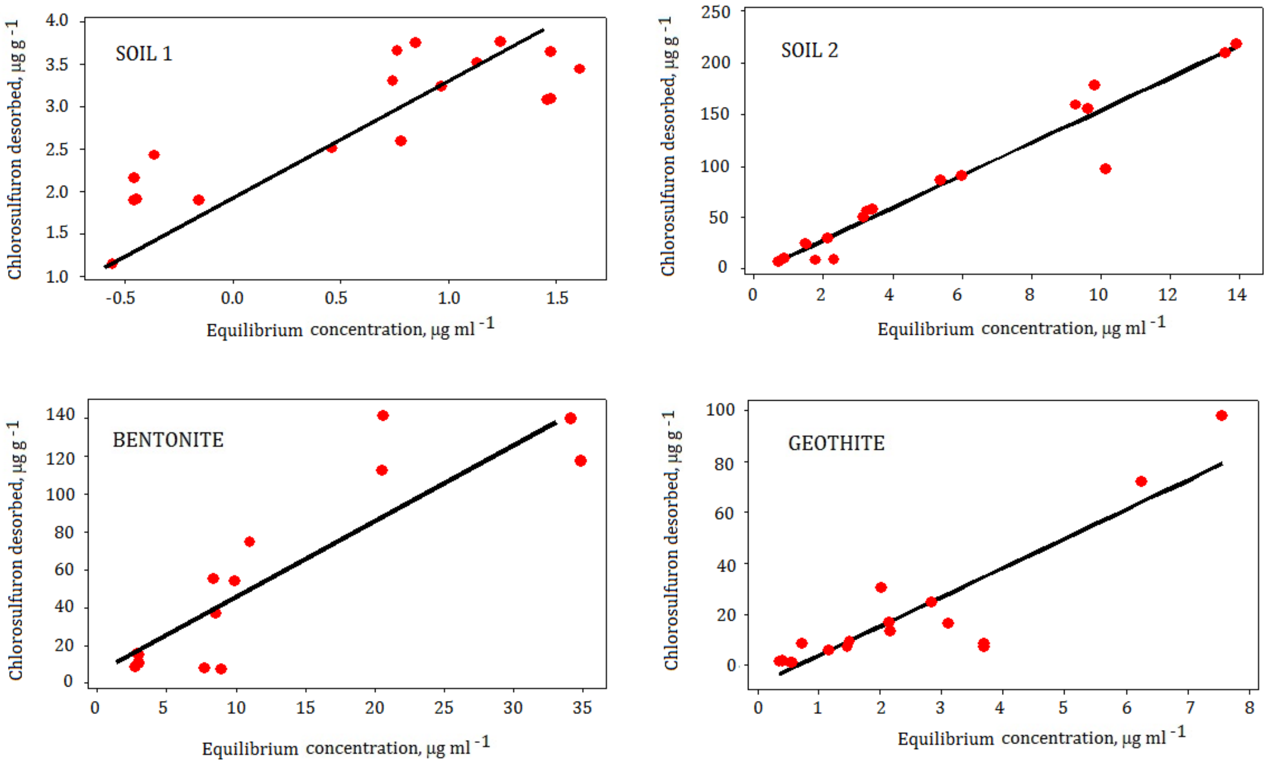


Figure 4. Simple desorption isotherms of Chlorosulfuron by soil 1, soil 2, Bentonite and Geothite

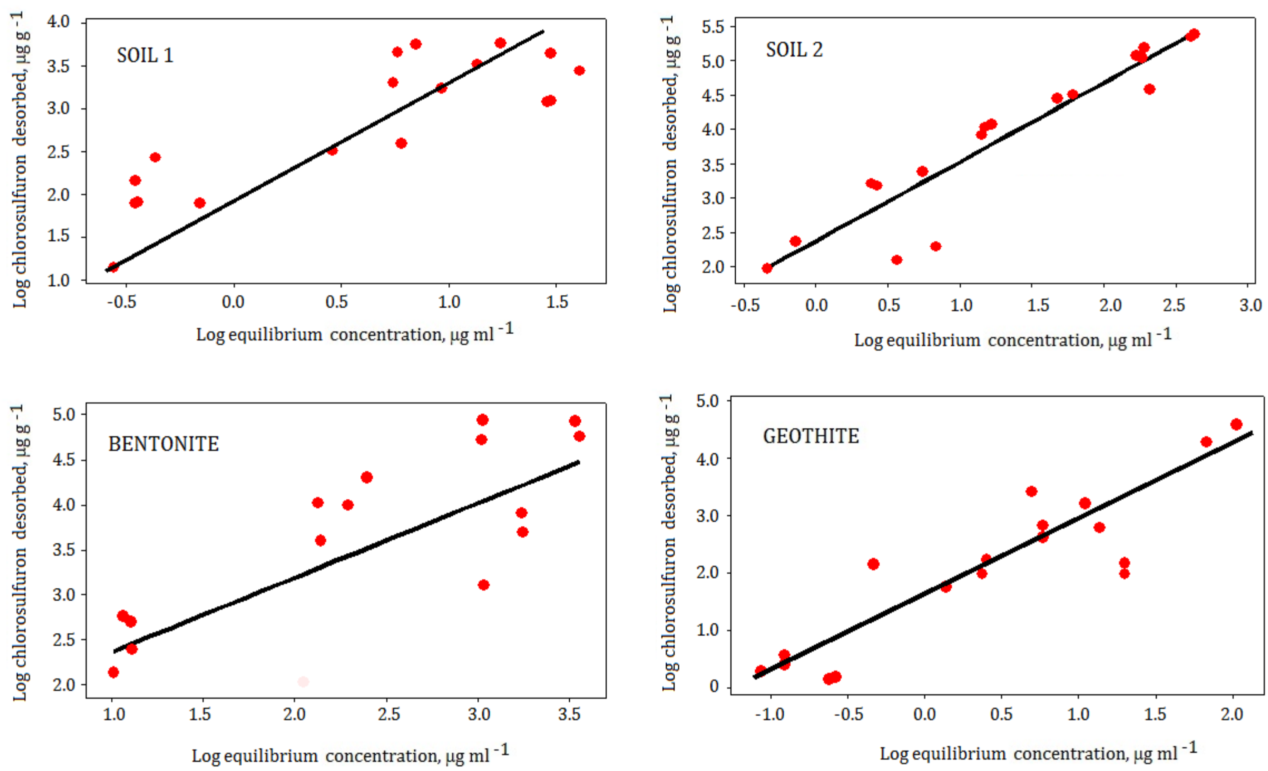


Figure 5. Freundlich desorption isotherms of chlorosulfuron by soil 1, soil 2, bentonite and geothite

Desorption kinetic studies were conducted to assess the desorption potential of adsorbed chlorosulfuron herbicide in different soils and minerals and the results are shown in Table 5 and Table 6.

Table 5. Desorption Coefficients of Chlorosulfuron in Selected Soils

Soil	$K_{d(des)}$	R^2	$K_{f(des)}$	n	R^2	H
Soil1	15.80	0.93	10.32	0.63	0.88	0.38
Soil2	6.389	0.48	10.32	1.15	0.73	0.62

Table 6. Desorption Coefficients of Chlorosulfuron in Selected Minerals

Mineral	$K_{d(des)}$	R^2	$K_{f(des)}$	n	R^2	H
Bentonite	3.044	0.48	4.60	1.19	0.51	0.9
Geothite	11.45	0.79	4.86	0.79	0.80	1

XRD Results

In XRD studies, sorptions of pesticides with minerals and soil were measured by the change in basal spacing. Results of XRD Studies for Bentonite mineral are given in figure 6 and table 7.

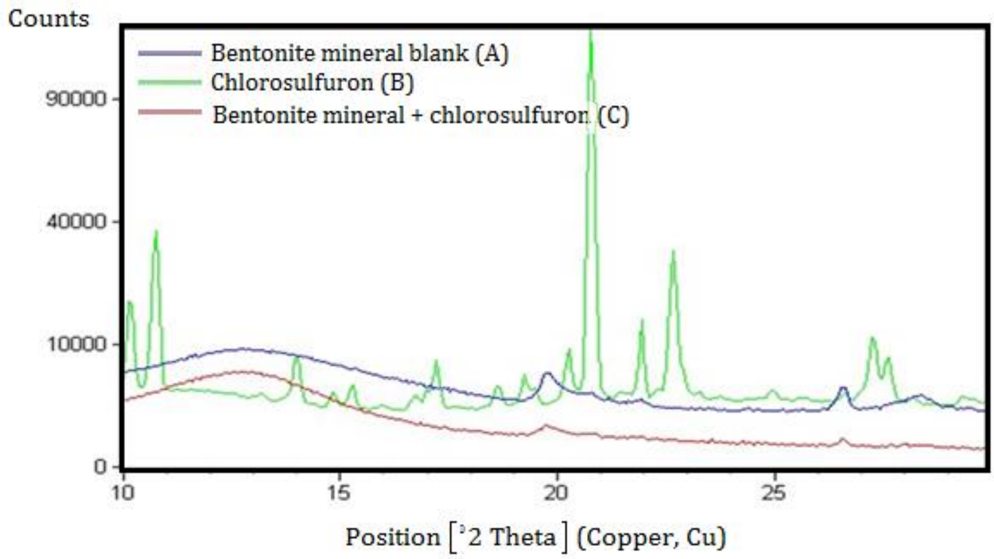


Figure 6. Bentonite Mineral (A) Untreated (B) Chlorosulfuron (C) Treated with Chlorosulfuron

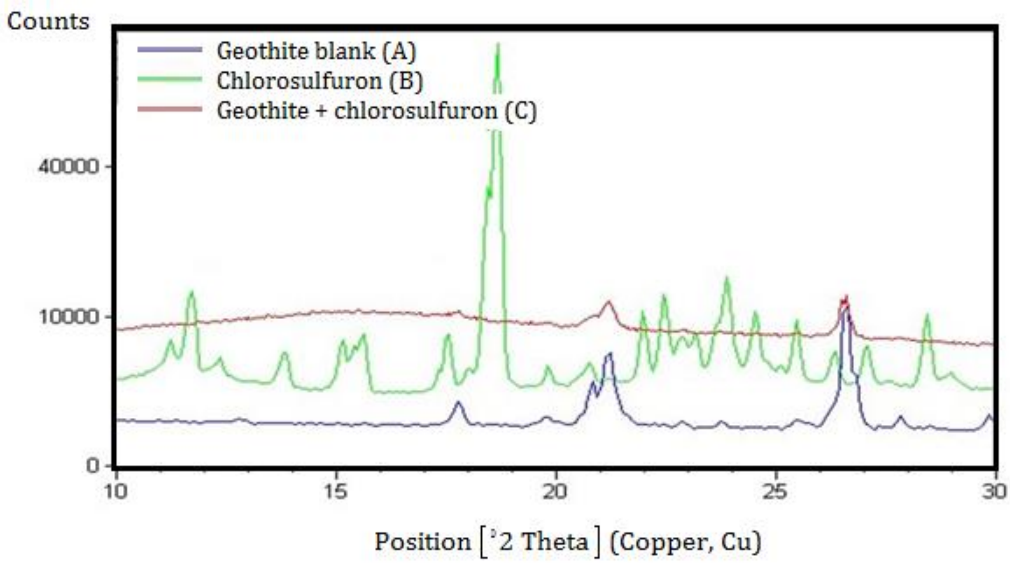


Figure 7.Geothite Mineral (A) Untreated (B) Chlorosulfuron (C) Treated with Chlorosulfuron

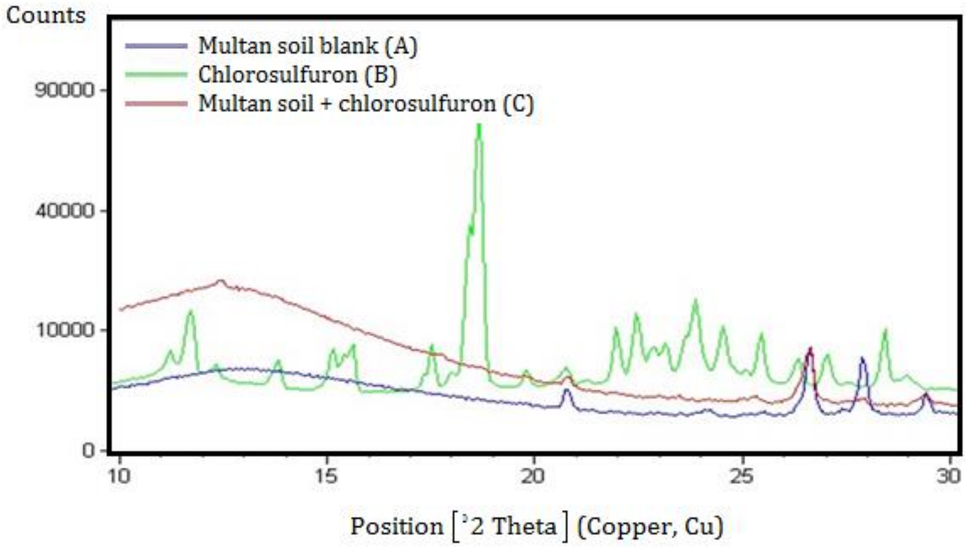


Figure 8. Multan Soil (A) Untreated (B) Chlorosulfuron (C) Treated with Chlorosulfuron

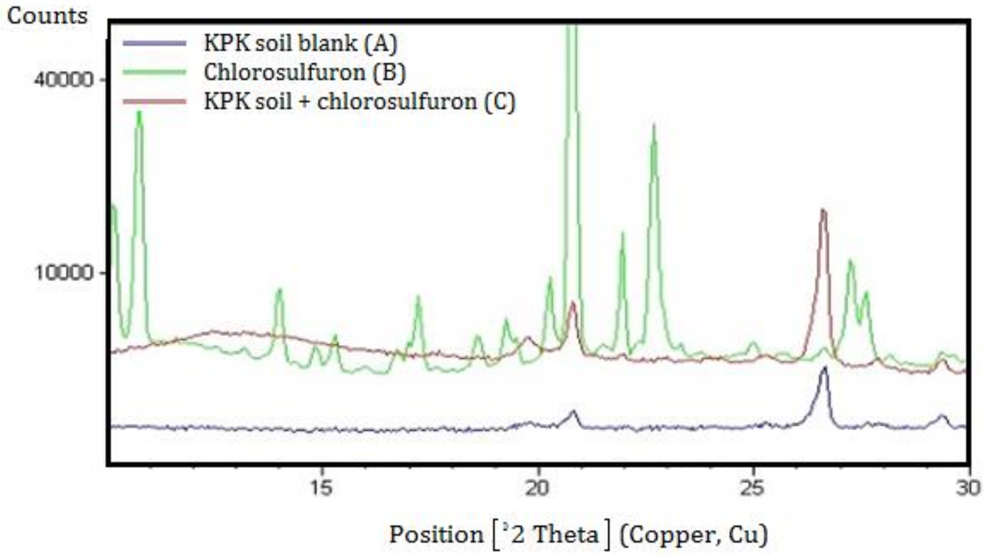


Figure 9. KPK Soil (A) Untreated (B).Chlorosulfuron (C) Treated with Chlorosulfuron

Table 7. Basal Spacing (A°) for clay minerals and soils

	MULTAN Soil	KPK Soil	Goethite Mineral	Bentonite Mineral
Untreated d (001)	9.99	9.97	10.03	12.06
Treated with Chlorosulfuron d (001)	9.99	9.97	10.03	12.06

Discussion

Adsorption studies

In this study the different values of K_f are also presented evidently in table 3 suggesting different adsorption capacities in these two soils. Further table showed that the predicted capacity for Chlorosulfuron retention normalized to the OC content (i.e.K_{foc}) differentiated significantly in these two soils. Among them soil 2 had biggest K_{foc} values. If organic matter in soils had a common capacity for Chlorosulfuron then K_{foc} value might be expected to be nearly constant. Adsorption of chlorosulfuron in soil is highly dependent on the organic matter content. Along with organic matter, iron oxide and aluminium oxides are also the important adsorbent of chlorosulfuron. Soil pH also determines the fate of chlorosulfuron in soil giving maximum adsorption at low pH and minimum at high pH. So if chlorosulfuron is applied to alkaline or neutral soils having less organic matter content and oxides, then there are more chances of leaching causing the ground water pollution (Borggaard and Streibig, 1998).

The result of the present study well agreed with the results obtained by walker *et al*. 1989, in which a significant positive correlation between organic matter contents of soil with the extent of adsorption of pesticide was observed (Walker and Welch, 1989). Soil having high sand content had less vacant sites/surface areas and probably resulted in minimum adsorption (Sprynskyy et al., 2008).

Organic carbon is crucial parameter affecting the sorption capacity of the herbicides especially when OC is greater than 2 % with the nature, form and functionality of OC not being much important in this case. In present study, soil type 1 had 6.51 % OC while soil type 2 had 1.89 % OC as shown in table 1. It means in soil 1, OC is responsible for the sorption irresepective of its nature. Presumably, when the OC of soils and their size fractions is lower than 2%, the difference in the nature and functionality of the OC makes a difference in terms of sorption as in soil 2. As compared to Kf, Koc still provides a better way for predicting hydrophobic pesticide sorption (Wang and Keller, 2009).

Shan *et al.* suggested grouping of pesticide on the basis of K_{oc} values and concluded that K_{oc} values less than 50 as a highest mobility group and those having K_{oc} values between 50 and 500 as medium mobility group (Li et al., 2003). All the K_{oc} values observed in this study suggested that Chlorosulfuron had moderately to high mobility in different soil types which might result in a leaching problem working with Chlorosulfuron.

To identify the physical and chemical mechanism of adsorption, Gibbs free energy change (ΔG)of 40 kJ/mol is considered as a threshold (Carter et al.,1995). Physical adsorption has value below the threshold. The ΔG values of Chlorosulfuron within studied soils (Table 3) ranged from -16.81 to -13.31 kJ/molsuggesting that physical adsorption have taken place. The adsorption of Chlorosulfuron by soils was also a spontaneous process for the negative value of ΔG.

Desorption characteristics

Desorption study of herbicide is very important as it controls the release rate, mobility of herbicides in soil and also the treatment processes for the contaminated soils. Lower rate of desorption of an herbicide means that it can cause higher risk to the crops (Singh and Cameotra, 2013). Thus, desorption kinetic studies were conducted to assess the desorption potential of adsorbed chlorosulfuron herbicide in different soils and minerals and the results are shown in Table 5 and Table 6.

Results indicated that K_d (des) values were higher as compared to K_d (ads) in the two selected sites. Higher values of desorption of soil for chlorosulfuron showed that adsorption was reversible and chlorosulfuron did not retain after desorption has occurred. Soil type 2 was more efficient in releasing the adsorbed chlorosulfuron as the K_d (des) for soil 2 was lower (6.389) as compared with soil type 1 (15.80). The organic matter content may play an important role in the desorption process. The *Kf* values of the desorption process suggested that both soil types had higher desorption rate as compared to minerals. Among the minerals, Geothite had better desorption (4.86) than Bentonite (4.60). This observation may be attributed to the different solubility of chlorosulfuron in different media (Schneiders et al., 1993).

Hysteresis in adsorption and desorption processes shows that there are less chances of reversibility of adsorbed herbicide depending on physic chemical properties of soil and herbicides (Flores et al., 2009; Kovaios et al., 2006). Hysteresis index close to 1 indicates that sorption and desorption occur at same rate while the value less than 1 means that desorption is lower than adsorption and thus hysteresis takes place (Tang et al., 2009). Many scientists explain hysteresis in different ways as irreversible binding or sequestration of solute to the OC and/or clay mineral of soil aggregates and entrapment of sorbed molecules into meso and micropore structures within mineral structures and OC matrix of soil aggregates. Second type is called structural hysteresis (Cason and Lester, 1977).

In the both studied soils, hysteresis index values for chlorosulfuron were less than 1 as given in table 5. On the other hand, both minerals had hysteresis value 1 or close to 1 as shown in table 6. It is indicated by results that organic matter and aqueous solubility of herbicide influences the desorption hysteresis. Entrapment of herbicide in the organic matter have a significant effect on the desorption hysteresis. Hysteresis is also controlled mostly by entrapment of pesticides sorbed inside micropores, i.e., structural hysteresis. From a contaminant transport perspective, higher hysteresis associated with these fractions (clay and silt fractions) implies that these fractions bind the pesticides more 'strongly' than the bulk soils (Wang and Keller, 2009).

Soil minerals composition has also a major role in the desorption hysteresis of herbicides. The hysteresis index values observed in the present study, suggest that the adverse effect of chlorosulfuron on the succession crops should be noticed, especially when it is applied on soils with high organic matter content.

While applying it to soil with low organic matter content attention should be paid to the risk of groundwater and surface water contamination from the herbicide.

XRD of selected minerals

In XRD studies, sorptions of pesticides with minerals and soil were measured by the change in basal spacing. Results of XRD Studies for Goethite mineral are given in figure 6 and table 5 while XRD studies for Bentonite mineral are given in figure 6 and table 7. The basal spacing of Goethite did not change by the sorption of the chlorosulfuron, relative smaller difference indicates parallel arrangement of pesticide into the interlayer of mineral. In the case of Bentonite mineral again there was no change in the basal spacing by the sorption of the pesticides. When the pesticides were arranged perpendicularly in the interlayer of clay content then an increase in the basal spacing was observed while parallel arrangement of pesticides indicated relatively smaller difference. There was no significant change in the basal spacing however HPLC technique showed sorption, which may be due to surface adsorption. It can be concluded that intercalation of sulfonylurea pesticides with Bentonite mineral would not occur that why Bentonite mineral didn't show any expansion of the basal spacing.

Sorption of pesticides with soil was measured by the change in basal spacing in XRD. Results of XRD Studies for Multan soil are given in figure 8 and table 7. The basal spacing of Multan soil has no-effect with Chlorosulfuron. Results of XRD Studies for KPK are given in figure 8 and table 5. The basal spacing of KPK soil showed no effect with Chlorosulfuron whereas relative smaller difference indicates parallel arrangement of pesticide into the interlayer of mineral. In XRD, there was no any penetration observed while in HPLC, penetration may be due to surface adsorption in all six cases.

The basal spacing obtained for both soils and minerals showed no change after chlorosulfuron adsorption. The chlorosulfuron-soils and chlorosulfuron-minerals basal spacings were the same as those for the untreated soils and minerals (9.99 A^{o} for Multan soil, 9.97 A^{o} for KPK soil, 10.03 A^{o} for goethite and 12.06 A^{o} for bentonite) suggesting the absence of interlamellar adsorption (Hermosin and Perez-Rodriguez, 1981).

No change in basal spacing indicated that minerals are nonexpanding and organic herbicide was sorbed around the edges of the clay particle, owing to broken-bond charges there, rather than the interlayer structure and did not increase or decrease the 2Φ value or the d-spacing value (Cason and Lester, 1977).

Conclusion

The present study revealed that Chlorosulfuron showed weak to moderate adsorption capacity with the agricultural soils that can lead to its leaching losses creating different problems in soil. The adsorption and desorption study of Chlorosulfuron soils well fitted with the Freundlich isotherm and depended significantly on the properties of soils. Adsorption behavior of Chlorosulfuron determined by the soil pH value, organic carbon, clay contents, organic matters. Increase in pH values decreased the adsorption of the cholosulfuron while increase in adsorption was observed with the increase in organic carbon, clay contents and organic matters. Similar to other weak sulfonylurea herbicides, in this study the desorption hysteresis of Chlorosulfuron decreased from low to high solution concentrations and correlated significantly with the content of SOM, OC, Clay. Suggesting that both solute concentration gradient and physico-chemical properties of soil commonly controlled the adsorption-desorption behavior of this herbicide. XRD results show no increase or decrease in basal spacing in any of the case. This study can be used to predict the sorptivebehavior of other soils.

Acknowledgements

The authors acknowledge University of Manchester U.K. Allama Iqbal Open University Islamabad and Higher Education Commission of Pakistan for financial support.

References

Abdullah, A. R., Sinnakkannu, S., Tahir, N.M., 2001. Adsorption, desorption, and mobility of metsulfuron methyl in Malaysian agricultural soils. *Bulletin of Environmental Contamination and Toxicology* 66: 762-769.

Afyuni, M. M., Wagger, M. G., Leidy, R. B., 1997. Runoff of two sulfonylurea herbicides in relation to tillage system and rainfall intensity. *Journal of Environmental Quality* 26: 1318-1326.

Ali, M. A., Baugh, P. J., 2003. Sorption–desorption studies of six pyrethroids and mirex on soils using GC/MS-NICI. *International Journal of Environmental Analytical Chemistry* 83: 923-933.

Bailey, G. W., White, J. L., Rothberg, T., 1968. Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate. *Soil Science Society of American Journal 32*: 222-234.

Borggaard, O. K., Streibig, J. C., 1989. Chlorsulfuron adsorption by selected soil samples. *Acta Agriculturae Scandinavica* 39: 351-360.

Carter, M. C., Kilduff, J. E., Weber, W. J., 1995. Site energy distribution analysis of preloaded adsorbents. *Environmental Science & Technology* 29: 1773-1780.

Cason, R., Lester, W. R., 1977. Chemistry of two clay systems and three phenoxy herbicides. In *Proceedings of the Oklahoma Academy of Science* 57: 116-118

Cessna, A. J., Donald, D. B., Bailey, J., Waiser, M., Headley, J.V., 2006. Persistence of the sulfonylurea herbicides thifensulfuron-methyl, ethametsulfuron-methyl, and metsulfuron-methyl in farm dugouts (ponds). *Journal of Environmental Quality* 35: 2395-2401.

Cheng, H.H., 1990. Pesticides in the soil environment—an overview. In: Pesticides in the Soil Environment: Processes, Impacts, and Modeling. H.H. Cheng (ed.) Soil Science Society America Book Series No. 2, USA.

Cozza, C. L, Woods, S. L., 1991. Reductive dechlorination pathways for substituted benzenes: a correlation with electronic properties. *Biodegradation* 2: 265-278.

Flores, C., Morgante, V., González, M., Navia, R., Seeger, M., 2009. Adsorption studies of the herbicide simazine in agricultural soils of the Aconcagua valley, central Chile. *Chemosphere* 74: 1544-1549.

Hemmamda, S., Calmon, M., Calmon, J. P., 1994. Kinetics and hydrolysis mechanism of chlorsulfuron and metsulfuron-methyl. *Journal of Pesticide Science* 40: 71-76.

Hermosin, M. C, Perez-Rodriguez, J. L., 1998. Interaction of chlordimeform with clay minerals. *Clays and Clay Minerals* 29: 143-152.

Khan, M. H., Hassan, G., Khan, N., Khan, M. A., 2003. Efficacy of different herbicides for controlling broadleaf weeds in wheat. *Asian Journal of Plant Sciences 2:* 254-256.

Konda, L. N., Czinkota, I., Füleky, G., Morovján, G., 2002. Modeling of single-step and multistep adsorption isotherms of organic pesticides on soil. *Journal of Agriculture and Food Science* 50: 7326-7331.

Kuwatsuka, S., Yamamoto, I., 1997. Degradation of the herbicide halosulfuron-methyl in two soils under different environmental conditions. *Journal of Pesticides Science* 22: 282-287.

Laird, D. A., Yen, P. Y., Koskinen, W. C., Steinheimer, T. R, Dowdy, R. H., 1994. Sorption of atrazine on soil clay components. *Environmental Science & Technology* 28: 1054-1061.

Marinas, A., Guillard, C., Marinas, J.M., Fernández-Alba, A., Aguëra, A., Herrmann, J.M., 2001. Photocatalytic degradation of pesticide–acaricideformetanate in aqueous suspension of TiO2. *Applied Catalysis B: Environmental* 34:241-252.

Mishra,P.C., Patel, R.K., 2008. Removal of endosulfan by sal wood charcoal. *Journal of Hazardous Materials* 152: 730-736.

Monkiedje, A., Spiteller, M., 2002. Sorptive behavior of the phenylamide fungicides, mefenoxam and metalaxyl, and their acid metabolite in typical Cameroonian and German soils. *Chemosphere* 49: 659-668.

Nyström, B., Björnsäter, B., Blanck, H., 1999. Effects of sulfonylurea herbicides on non-target aquatic micro-organisms: growth inhibition of micro-algae and short-term inhibition of adenine and thymidine incorporation in periphyton communities. *Aquatic Toxicology* 47: 9-22.

Sabadie, J., 2002. Nicosulfuron: alcoholysis, chemical hydrolysis, and degradation on various minerals. *Journal of Agricultural and Food Chemistry* 50: 526-531.

Sarmah, A. K., Sabadie, J., 2002. Hydrolysis of sulfonylurea herbicides in soils and aqueous solutions: a review. *Journal of Agricultural and Food Chemistry* 50: 6253-6265.

Schneiders, G. E., Koeppe, M. K., Naidu, M. V., Horne, P., Brown, A. M., Mucha, C. F., 1993. Fate of rimsulfuron in the environment. *Journal of Agricultural and Food Chemistry* 41: 2404-2410.

Singh, A. K., Cameotra, S.S., 2013. Adsorption and desorption behavior of chlorotriazine herbicides in the agricultural soils. *Journal of Petroleum and Environmental Biotechnology* 4: 1-6.

Sprynskyy, M., Ligor, T., Buszewski, B., 2008. Clinoptilolite in study of lindane and aldrin sorption processes from water solution. *Journal of Hazardous Materials* 151: 570-577.

Stork, P. R., 1995. Field leaching and degradation of soil applied herbicides in a gradationally textured alkaline soil: chlorsulfuron and triasulfuron. *Australian Journal of Agricultural Research* 46: 1445-1458.

Tang, Z., Zhang, W., Chen, Y., 2009. Adsorption and desorption characteristics of monosulfuron in Chinese soils. *Journal of Hazardous Materials* 166: 1351-1356.

Ukrainczyk, L., Rashid, N., 1995. Irreversible sorption of nicosulfuron on clay minerals. *Journal of Agricultural and Food Chemistry 43:* 855-857

Verschueren, K., 2001. Handbook of environmental data on organic chemicals: Vol. 1 (No. Ed. 4). John Wiley & Sons, Inc.

Walker, A., Welch, S. J., 1989. The relative movement and persistence in soil of chlorsulfuron, metsulfuron-methyl and triasulfuron. *Weed Research* 29: 375-383.

Wang, P., Keller, A. A., 2009. Sorption and desorption of atrazine and diuron onto water dispersible soil primary size fractions. *Water Research* 43: 1448-1456.

Wu.C., Zhang, S., Nie, G., Zhang, Z., Wang, J., 2011. Adsorption and desorption of herbicide monosulfuron-ester in Chinese soils*. Journal of Environmental Sciences* 23: 1524-1532.

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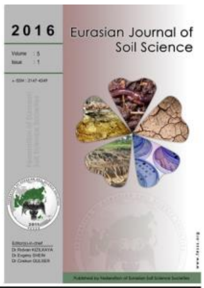

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Lithium adsorption on amorphous aluminum hydroxides and gibbsite

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Article Info

Received : 10.12.2014
Accepted : 15.06.2015

Abstract

Lithium (Li) adsorption on both amorphous aluminum hydroxides and gibbsite was studied. For the amorphous $Al(OH)_3$ the adsorption was found to be pH dependent. Generally, 1.6 times more Li was adsorbed at initial pH value 8.0 compared with pH value 6.50. Gibbsite adsorbed 11.6 to 45.5 times less Li quantities compared with amorphous $Al(OH)_3$. Lithium adsorption was not depended on equilibrium times. It remained stable for all equilibrium times used. Lithium quantities extracted with 1N CH_3COONH_4 pH 7 , represent the physical adsorption, while the remaining Li that was adsorbed on $Al(OH)_3$, represents the chemical adsorption. During the desorption process 19% of Li extracted with NH_4^+, represents the physical adsorption, while the remaining 81% of Li, which was adsorbed represents the chemical adsorption. In gibbsite, 9.6% of Li represents the physical adsorption and 90.4% the chemical one. The experimental data conformed well to Freundlich isotherm equation.

Keywords: Adsorption, aluminum hydroxides, desorption, lithium

Introduction

Lithium is trace metal and one of the alkali metals. It belongs to the IA group of the periodic table 1. Lithium occurs in basaltic tuff, rhyolite, mica schist, sedimentary rocks, gneisses, marble, calcareous rocks and in low amounts in limestones and ultra basic rocks. Lithium concentrations in the soils are 20 to 30 mg kg^{-1}. Soils derived from granitic – syenitic parent material have the highest concentration. Also it is found in minerals, irrigation waters and rivers as well as in sea or oceans. Lithium is much more mobile in soils than Rb and Cs. It is held within the structure of clay minerals produced during soil weathering, e.g. gibbsite, and it is not available to plants. Lithium is adsorbed to the soil solid phase, especially illites (Helmke and Sparks, 1996). According to Pistiner and Henderson (2003), Li is adsorbed by secondary minerals (smectite) by physisorption and onto ferrihydrite or gibbsite surfaces by chemisorption. Soils with excessive levels of organic matter have low Li concentration (3-4 mg kg^{-1}). Of the alkali elements, Li is the most toxic to plants (Bradford, 1966). Lithiophorite [$(Li,Al)MnO_2(OH)_2$] is commonly found in weathered zones of Mn deposits and in certain acid soils (De Villiers, 1983). The formation of this compound requires a relatively large concentration of Al^{3+} (Golden et al., 1993). Brümmer (1986) suggested that the adsorption of heavy metals by goethite comprises three different steps: first, surface adsorption (physical adsorption), second, diffusion into goethite particles and third, adsorption and fixation at positions within the mineral particles (chemical adsorption). These steps are able to describe the adsorption process of amorphous $Al(OH)_3$.

Metal cations adsorption on poorly crystalline or microcrystalline materials such as allophanes, imogolite and Al-hydroxide gels occurs at discrete surface sites, Al-OH groups. Amorphous $Al(OH)_3$ aging with time, increased the crystalline state of these materials and decreased the adsorption ability of the gels.

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e-ISSN: 2147-4249
DOI: http://dx.doi.org/10.18393/ejss.2016.1.013-016

The objective of this study is to investigate Li adsorption on amorphous aluminum hydroxides at different pH values, as well as on well crystallized gibbsite.

Material and Methods

Aluminum hydroxide was precipitated stoichiometrically according to reaction,

$$Al_2(SO_4)_3 + 6\,NH_4OH \rightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$$

in a series of 50 ml centrifuge tubes. The tubes were stoppered, shaken for 15 min and centrifuged at 5,000 rpm for 10 min. Then, they were washed with distilled water once (pH ~ 8.0) and twice (pH ~ 6.50). The obtained gels did not appear to be crystalline to X-ray analysis. Figure 1 gives the electron images of amorphous $Al(OH)_3$.

Well crystallized $Al(OH)_3$

Gibbsite was obtained from BDH Chem. Ltd. Figure 2 shows the x-ray diffractogram from gibbsite.

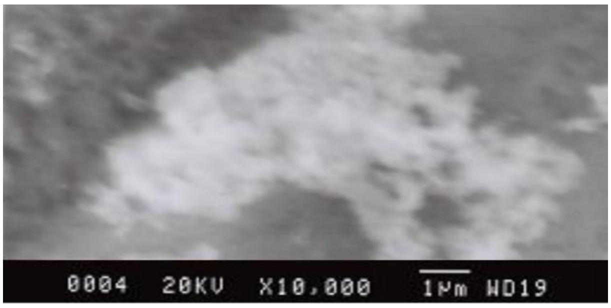

Figure 1. Electron (SEM) image of amorphous $Al(OH)_3$

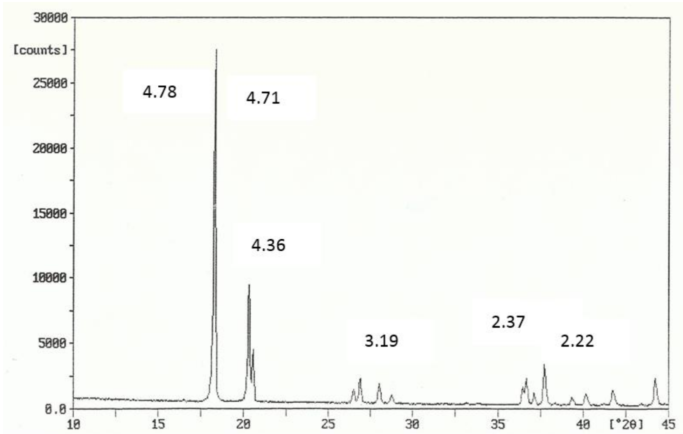

Figure 2. X-ray diffractogram obtained from gibbsite

Adsorption experiments

Samples of $Al(OH)_3$ were treated with Li solutions of different concentrations (10, 20, 40, 60, 80, 100, 120 and 160 ppm). The samples were shaken for 30 min and equilibrated with Li solutions for 0.5, 2, 24, 48, 72, 120 and 240 hours periods at a temperature of 25 ± 0,2°C. After centrifugation at 6,000 – 7,000 rpm for 10 min the supernatant liquids were filtered into volumetric flasks. Aliquots of the clear supernatant were analyzed for Li by flame photometry. The adsorption experiment took place at two different pH values 6.50 and 8.0 after the $Al(OH)_3$ precipitation.

The gibbsite sample was equilibrated with Li solutions for 24, 48, 72, 120 and 240 hours during the adsorption process, because the adsorption ability of this material is very small for 0.5 and 2 hours. All the determinations were done in triplicate.

Desorption process

After the adsorption process, the samples of $Al(OH)_3$ were equilibrated with Li solutions for 48 h at an initial pH 8.0, were washed with 30 mL CH_3COCH_3 90% two times and treated with 25 mL CH_3COONH_4 1N, pH 7.0 twice. They were shaken for 5 min and centrifuged at 6,000 rpm for 5 min. The supernatant liquids were filtered into separate volumetric flasks and Li was determined. In the case of gibbsite, the treatment with 1N CH_3COONH_4, was done once during the desorption process because the adsorption ability of this material is very small.

Results and Discussion

The experimental data fitted well to the Freundlich isotherms ($x = kC^n$), where: x is amounts of Li adsorbed per unit weight of aluminium, (mg/g Al^{3+}), C is equilibrium concentration, (μg/ml), k and n are constants.

In the linear transformation, logx = logk + nlogC, where k is the amount of Li adsorbed when C=1 which gives units of mL g^{-1} and n is related to the isotherm slope so that it usually increases with increasing slope (Table 1, Fig. 3).

Table 1. Freundlich isotherm constants and R^2 from Li adsorption on $Al(OH)_3$ and gibbsite.

Time	$Al(OH)_3$	pH	8.0	$Al(OH)_3$	pH	6.50		gibbsite	
(h)	k (ml/g)	n	R^2	k (ml/g)	n	R^2	k (ml/g)	n	R^2
½	0.767	1.01	0.7351	0.277	0.910	0.8460	-	-	-
2	1.136	0.937	0.7272	0.139	1.147	0.9850	-	-	-
24	2.532	0.741	0.8602	0.679	0.824	0.9921	0.031	0.667	0.9701
48	3.247	0.676	0.9144	0.609	0.833	0.9934	0.018	0.869	0.9768
72	3.927	0.609	0.8831	0.552	0.851	0.9898	0.020	0.841	0.9877
120	3.936	0.655	0.8805	0.749	0.786	0.9855	0.019	0.849	0.9847

Independently of the initial pH values 6.50 or 8.0, pH ranged at the same values (6.50 – 4.20 or 7.50 – 4.50) in the equilibrium solutions after the adsorption process. These final pH values depended on the equilibrium time and the concentration of Li in the equilibrium solution. Lithium adsorption by amorphous $Al(OH)_3$ was greater at pH 8.0, than at pH 6.5. Generally 1.6 times more Li was adsorbed at pH 8.0 (Fig. 4).

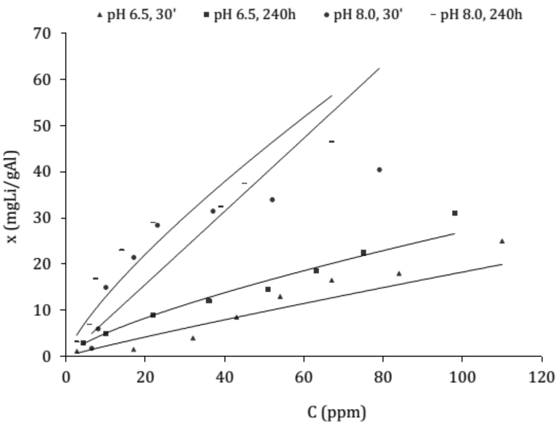

Figure 3. Lithium adsorption data on $Al(OH)_3$ plotted according to Freundlich isotherms

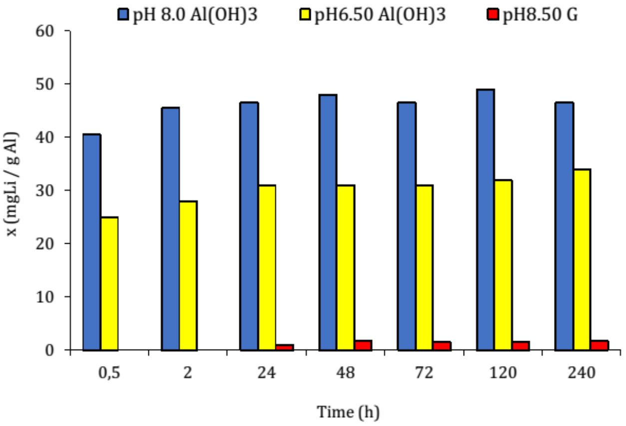

Figure 4. The histograms of Li adsorption with time for concentration of 160 ppm on $Al(OH)_3$ and gibbsite

In the case of pH 6.50, the maximum adsorption of Li occurred at 240 hours, but statistically no significant differences for the equilibrium times used were observed. Also, at pH 8.0 the maximum adsorption occurred at 48 and 120 hours, and in this case, there were no significant differences among the experimental data. However, we have to note that there were observed significant differences among the experimental data of Li adsorption occurred at the two pH values, 6.50 and 8.0. All statistical analyses were accomplished at $P<0.05$. The results showed that the initial pH value during the adsorption of Li to amorphous $Al(OH)_3$ is important regarding the amounts of Li adsorbed. The adsorption ability of amorphous $Al(OH)_3$ was not reduced with time. The maximum equilibrium time used (10 days) was not efficient to change the crystalline state of this material. Gibbsite adsorbed less quantities of Li, compared with amorphous $Al(OH)_3$. Aluminum hydroxides adsorbed 11.6 to 45.5 times more Li than gibbsite at the two pH values used. The experimental data in the case of gibbsite, fitted well to the Freundlich isotherms (Fig. 5).

Also, the Li adsorption on gibbsite was not influenced by the equilibrium time (Fig. 5). The pH values in the equilibrium solution, were 8.0 to 11.50. These values depended only on Li concentration in the equilibrium solutions. In the desorption process with CH_3COONH_4, greater Li amounts (70.5% mean-values) were extracted during the first treatment compared with the second one (29.5%). During the two treatments with CH_3COONH_4, only 19% of Li was extracted while 81% remained adsorbed on $Al(OH)_3$ (Fig. 6). In the case of gibbsite, 9.6% of Li represents the physical adsorption and 90.4% the chemical one (Fig. 6). Lithium quantities extracted with CH_3COONH_4, were weakly adsorbed on the surface charge and represent the physical adsorption. The retained Li portion was strongly adsorbed by Al-OH groups by diffusion into micropores of material particles and constitutes the chemical adsorption, under these experimental conditions.

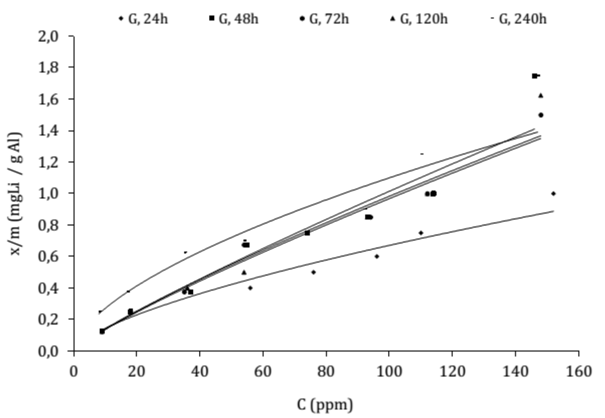

Figure 5. Lithium adsorption data on gibbsite plotted according to Freundlich isotherms

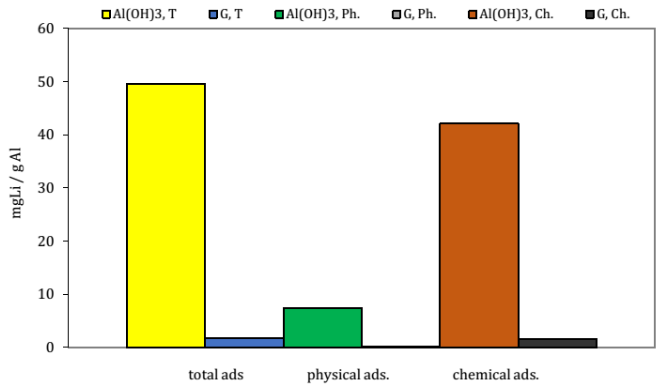

Figure 6. The histograms of Li adsorption, on the two materials, (total, physical and chemical) for concentration 160 ppm

References

Bradford, G.R., 1966. Lithium. In: *Diagnostic criteria for plant and soils.* (Chapman, H.D., ed) Agric. Sci. Univ. California, Riverside, CA. pp. 218-224.

Brümmer, G.W. 1986. In : *The Importance of Chemical Speciation in Environmental Process*. Springer – Verlag, Berlin, pp. 169-192.

De Villiers, J.E., 1983. The manganese deposits of Griqualand West, South Africa: some mineralogic aspects. *Economic Geology* 78: 1108-1118.

Golden, D.C., Dixon, J.B., Kanehiro, Y., 1993. The manganese oxide mineral, lithiophorite, in an Oxisol from Hawaii. *Australian Journal of Soil Research* 31: 51-66.

Helmke, P.A., Sparks, D.L., 1996. Lithium, Sodium, Potassium, Rubidium and Cesium. In: *Methods of Soil Analysis. Part 3. Chemical Methods*. No 5. Chapter 19 pp. 551-555.

Pistiner, J.S., Henderson. G.M., 2003. Lithium – isotope fractionation during continental weathering processes. *Earth and Planetary Science Letters* 214 (1-2): 327-339.

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Changes of C and N stocks in the subtropical Dianchi lake watershed in southwest China due to LUCC

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Article Info

Received : 02.03.2015
Accepted : 16.06.2015

Abstract

The change from forest to agricultural land in the last three decades represents a significant shift in land use in China. This study was conducted to evaluate how change from forest to greenhouse cabbage production affected soil organic carbon (SOC) and total nitrogen (TN) stocks in surface soil. Our results showed that converting forest to greenhouse vegetable production led to increases in SOC and TN concentrations and stocks, and decreases in C:N ratio in the top soil. The accumulation rates of SOC and TN in the surface soil (0-40cm) were estimated to be 4.638 Mg ha^{-1} yr^{-1} and 1.113 Mg ha^{-1} yr^{-1} respectively, over an average period of 8 years after change of forest to greenhouse vegetable production. We conclude that greenhouse vegetable production system could be an effective strategy to improve SOC and TN stocks in the subtropical Dianchi lake watershed.

Keywords: Soil organic carbon, total nitrogen, land use/land cover change, Dianchi lake watershed.

Introduction

Over the past century, China has experienced a rapid land use/land cover change (LUCC), and this process is expected to continue in the future. LUCC, in particular replacement of forest by agriculture or pasture land, strongly influences watershed nutrient fluxes (Oyarzun et al., 2007), leading to significant changes in soil properties (Karchegani et al., 2012), such as soil organic carbon (SOC) stock (Falahatkar et al., 2014) and total nitrogen (TN) level (Su et al., 2006). Understanding the storage of carbon (C) and nitrogen (N) helps us understand how ecosystems would respond to natural and anthropogenic disturbances under different management strategies (Zhang et al., 2013). Extensive studies have been conducted in the past 20 years to estimate the effects of changes in land use on soil C and N storage (Mireia et al., 2010; Khormali and Ajami, 2011; Poeplau and Don, 2013; Demessie et al., 2013; Gelaw et al., 2014). Other authors have investigated the characteristics of the carbon pool in grassland ecosystems (Wu et al., 2010) and the effect of farm management on SOC (Liang et al., 2012). Most studies have demonstrated that the change of land use results in a significant variation in the distribution and storage of organic C and N in soil (Yan et al., 2012; Zhang et al., 2013).

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e-ISSN: 2147-4249 DOI: http://dx.doi.org/10.18393/ejss.2016.1.017-023

Greenhouse is an important type of covered agriculture globally (Wang et al., 2011). The land area used for greenhouse vegetable production in China has rapidly increased and reached 3.35 million ha in 2008 (Jiang et al., 2011). It was reported that vegetable cultivation under greenhouse conditions leads to rapid accumulation of nutrients in the soil and groundwater contamination (Shi et al., 2009). For instance, Yan et al (2012) reported that, based on the paired comparisons between the greenhouse vegetable soil and cereal soil, soil C accumulation rate in the top 30 cm depth was estimated to be 1.37 Mg $ha^{-1}y^{-1}$ over an average period of 8 years. Wang et al (2011) also reported that SOC storage (0-20 cm depth) increased together with cultivation years within the plastic greenhouse vegetable cultivation system. However, these studies did not include greenhouse vegetable field that may result in substantial C accumulation in the soil converted from forest land.

In Dianchi lake watershed, southwest China, extensive deforestation, overgrazing and change of natural ecosystem into arable land are rampant due to the excessive population growth and the increasing demands for cultivable lands (Statistical Bureau of Yunnan 1985–2013). Especially from the 2000s, plastic greenhouse cultivation was started in the Dounan area for the high economic benefit. While there is already a wealth of literature on the effects of change of forest to grassland or farmland, much less is known about the consequences of change to vegetable cropping, especially in greenhouses in the subtropical Dianchi lake watershed in southwest China. The objectives of this study are: (i) to evaluate the impact of LUCC from natural forest to grassland and greenhouse vegetable production on SOC and TN concentrations and stocks in the top soils; (ii) to estimate the potential SOC- and TN-accumulation rates of grassland and greenhouse vegetable production land use. The results of the study will contribute to the development of best management practices and prediction tools for SOC and TN management in subtropical Dianchi lake watershed, southwestern China.

Material and Methods

Study area

The study area is located in the Dounan town, Chenggong country, Dianchi lake watershed of southwest China (Figure 1). The study area has an altitude of 1900 m with an area of 2490 ha. The local climate is subtropical with a mean annual air temperature and precipitation of 14.7 ºC and 1800 mm. Soil type of the studied area was predominantly classified as red soils. The soil parent materials are of base volcanic origin, principally basalts, and sedimentary rocks, such as limestones and sandstones. The minimum soil depth reaches more than 110 cm. Soils have texture-contrast profiles, with textures dominated by heavy loams and clay in upper three layers. The depths of Ah, A, and B horizon are about 12, 26 and 50 cm on average, respectively (Wang and Yang, 1997). There are three major land covers and land uses in the study area, including forest, grassland, and cultivated land. The natural vegetation is dominated by broad-leaved evergreen forests, and the secondary forest is dominated by Burma pine *Pinus yunnanensis* and China Armand pine *Pinus armandii*. Due to the early development of economy and the serious artificial damage, the original vegetation has rarely existed. The main existing secondary vegetation includes *Pinus yunnanensis*, *Pinus armandii*, Schottky oak *Cyclobalanopsis glaucoides*, Black wattle *Acacia mearnsii*, sprouted shrub and shrub grass. Grassland has been subjected to the Grain for Green program in Dianchi lake watershed from early 2000. No external inputs such as fertilizers are used and no grazing or other kinds of management techniques are practiced. Artificial farmland vegetation includes rice, corn, wheat, bean etc. Since the mid-1990s, rice field has been increasingly converted to more profitable cut flowers and vegetable crops in greenhouses. Greenhouse vegetable production has become the important pillar of rural economic development and local farmers' income (Gao and Yang, 2006). Management and harvesting practices are operated by means of manpower. Comparing with the open field soil, the number of microorganisms in the greenhouse soil was greater. The available N, P and K contents increased and soil pH value decreased with increased cultivation year.The number of bacteria, actinomyces, total microorganisms and B/F in the greenhouse soil initially increased, and then decreased with increased cultivation years (Dong et al., 2009).

Soil sampling and analysis

Soil sampling was carried out in August 2011 (just after harvest). Eighteen study sites were selected based on major land use types in this region, including six forest lands (FL), six grasslands (GL) and six greenhouse vegetable production fields (VP) (Figure 1). All investigated soils are developed from the same parent materials. A total of 180 evenly distributed soil samples (two depths, 3 land uses, 18 sites and five replications) were collected using a soil auger (44 mm internal diameter). Soil samples were taken to 40 cm depth, and separated into increments of 0–20 and 20–40 cm depths. Soil cores within each replicate were collected randomly from eight points within a rectangular plot of 10 × 10 m at each sampling site/replicate and were well mixed and combined to a composite sample by depth. Thus, a minimum of 40 point samples were represented in computing the average values of each soil parameter.

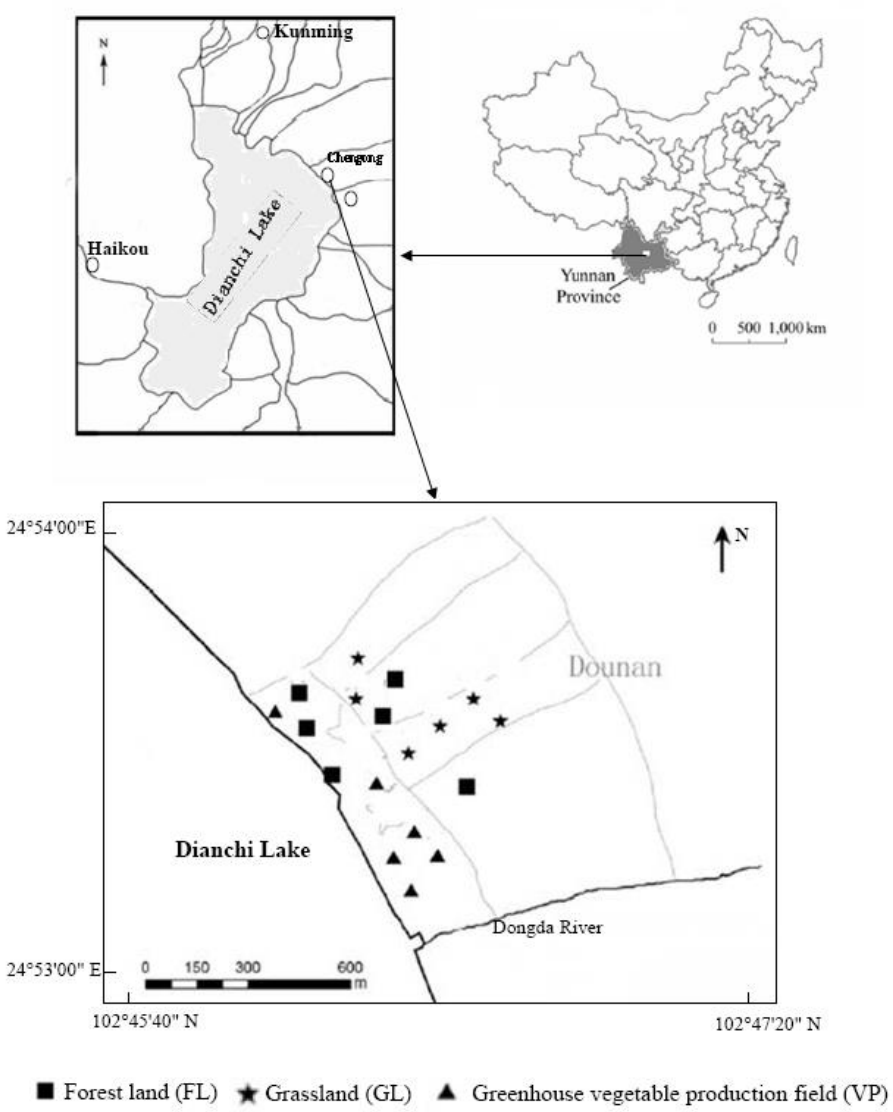

Figure 1. Sampling sites in Dounan town, subtropical Dianchi lake watershed in southwest China

All samples were air-dried, crushed, and passed through a 0.15-mm sieve for SOC and TN measurements (MOA, 2006). Concentrations of TN in the soil samples were determined after persulfate digestion using a UV-3600 spectrophotometer. The SOC concentration was measured by a TOC-analyzer (TOC-L CSH CN200, Shimadzu, Japan) (Niu et al., 2015).

Soil bulk density (BD) samples were taken for the same depth intervals as other soil samples for each replicate/plot by the core method (Blake and Hartge, 1986). The initial weight of soil core from each layer was measured in the laboratory immediately after collection. Simultaneously, soil moisture content was determined gravimetrically by oven drying the whole soil at 105°C for 24 h to calculate the dry BD. No adjustment was made for rock volume because it was rather minimal. Soil BD value for each depth interval was used to calculate the SOC and TN stocks (Mg ha^{-1}) using the model by Ellert and Bettany (1995):

SOC (or TN) Stock = Conc. · SD · T · 10000m^2 ha^{-1} · 0.001 Mg kg^{-1}

Where SOC (or TN) Stock = Soil Organic Carbon or Total Nitrogen Stock (Mg ha^{-1}).

Conc. = Soil Organic Carbon or Total Nitrogen Concentration (kg Mg^{-1}).

SD = Dry bulk density (Mg m^{-3}).

T = Thickness of soil layer (m).

The SOC (or TN) stock in the 40 cm depth for each land use was calculated by summing SOC (or TN) stocks in the 0–20 and 20–40 cm depth intervals. Accumulation of SOC (or TN) stock in the same soil depth (40 cm) for each land use was estimated by calculating the difference in SOC (or TN) stock between each one of the two land uses (GL and VP) and the control (FL) land use. Because of the variable durations of the different land uses, the rate of accumulation of SOC (or TN) stock for 0–40 cm layer for each of the two land uses (GL and VP) was estimated by dividing accumulation values by the assumed duration of each land use (Puget and Lal, 2005). Based on the survey conducted with the farmers, an average duration of 8 years was taken as the age for GL and VP land uses for adopting since early 2000s.

Statistical analysis

Data were reported as means±standard deviations. Soil parameters under different land uses and depths were subjected to one-way ANOVA. Differences between means of treatments were considered significant at the 0.05 level using the Tukey's Honestly Significant Difference (HSD) test. Correlation analysis was used to evaluate the relationships between soil variables. Regression analysis was conducted to obtain the relationships between the changes of SOC and TN. Statistical analysis was performed using the SPSS 16.0 for Windows software package and Microsoft Excel for Windows 2010.

Results

SOC and TN concentrations were significantly higher under VP than under GL and FL in both the 0–20 cm and 20-40 cm depth intervals ($p < 0.05$) (Table 1). There was no significant difference for SOC and TN concentrations between GL and FL. SOC concentrations were highly correlated with TN for all three land uses ($R^2 = 0.91$, $p < 0.05$ for FL; $R^2 = 0.92$, $p < 0.05$ for GL; $R^2 = 0.88$, $p < 0.05$ for VP). In the 0–20cm depth interval, bulk density values were significantly lower under VP than under FL and GL (Table 1). Change from FL to VP decreased average soil bulk density in the top 40 cm depth in the study area. C:N ratio decreased with soil depth and was significantly higher under FL and GL than under VP (Table 1). Change of forest to grassland and greenhouses led to a decrease trend in top soil C:N ratio. In general, C:N ratio differed significantly between VP and other land use (FL or GL). Differences in C:N ratio between the FL and GL were not significant.

Table 1. Mean SOC, TN and C:N ratio of soils of different LUCC

Land use type	Soil depth (cm)	SOC (g kg^{-1})	TN (g kg^{-1})	C:N	BD (g cm^{-3})
FL	0-20	9.43±1.69a[a]	1.28±0.19a	7.37±0.78a	1.15±0.05a
	20-40	6.08±1.53a	0.88±0.22a	6.91±0.18a	1.30±0.06a
	0-40	7.76	1.08	7.14	1.08
GL	0-20	9.59±1.78a	1.32±0.13a	7.23±0.66a	1.16±0.21a
	20-40	6.32±1.40a	0.96±0.17a	6.57±0.53a	1.25±0.23a
	0-40	7.95	1.14	6.90	1.21
VP	0-20	24.72±6.76b	4.58±1.27b	5.44±0.62b	0.71±0.21b
	20-40	20.35±5.42b	3.84±0.93b	5.31±0.6b	0.99±0.1b
	0-40	22.54	4.21	5.38	0.85

[a] Different letters in the column indicate significant differences among treatments at 0.05-probability level.

The vertical distribution (0-20 and 20-40 cm depth) of mean SOC and TN stocks for FL, GL and VP at all sites is presented in Table 2. Average SOC stocks were significantly higher in the 0-40 depth under VP (74.60 Mg ha^{-1}) than under GL (38.47 Mg ha^{-1}) and FL (37.50 Mg ha^{-1}) respectively ($p < 0.05$, Table 2), whereas no significant difference occurred between GL and FL. Trends in TN stock were similar to those of the SOC stocks. Across sites, in the 0-40 soil depth, VP had significantly higher average TN stocks (14.13 Mg ha^{-1}) than GL (5.46 Mg ha^{-1}) and FL (5.23 Mg ha^{-1}) ($p < 0.05$, Table 2). No significant differences in TN stocks were observed between GL and FL. Using SOC and TN stocks in the respective FL as baseline values, SOC and TN accumulation rates in the top 40 cm depth following LUCC increased in the order of VP < GL= FL (Table 2). The rates of SOC and TN accumulation (0–40Cm) for VP were 4.638 Mg $ha^{-1}y^{-1}$ and 1.113 Mg $ha^{-1}y^{-1}$ over an average period of 8 years, respectively (Table 2).

Table 2. Mean SOC and TN stocks and accumulation rates of soils of different LUCC

Land uses	Depth (cm)	SOC stock (Mg ha^{-1})	TN stock (Mg ha^{-1})	SOC accumulation rate (Mg ha^{-1} yr^{-1})	TN accumulation rate (Mg ha^{-1} yr^{-1})
FL	0-20	21.69±4.38a[a]	2.94±0.45a		
	20-40	15.81±4.33a	2.29±0.68a		
	0-40	37.50	5.23		
GL	0-20	22.34±6.15a	3.05±0.62a	----	----
	20-40	16.13±5.52a	2.41±0.77a	----	----
	0-40	38.47	5.46	----	----
VP	0-20	34.10±9.18b	6.50±2.21b	1.551	0.445
	20-40	40.50±11.44b	7.63±1.86b	3.086	0.668
	0-40	74.60	14.13	4.638	1.113

[a] Mean values followed by the same letters in the same column indicate no significant difference among treatments at the 0.05% significance level.

Discussion

The results in this study clearly showed that intensive agricultural practices (greenhouse) altered the vertical distribution of SOC. Concentration of SOC generally declined with soil depth, which was consistent with the results reported in the literatures (Deen et al., 2003; Gelaw et al., 2014). It is suggested that LUCC from FL to VP could increase in SOC concentrations and stocks. The higher SOC concentration and stock under greenhouse vegetable fields may be attributable to the incorporation of numerous organic materials or manures into the soil to maintain high vegetable yields (Qiu et al., 2010). For example, almost all vegetable residues (5.1 Mg C ha^{-1}yr^{-1}) were returned to the soil within the plastic greenhouses vegetable cultivation. The recycled carbon (5.5 Mg C ha^{-1}yr^{-1}) accounted for ~86% of total carbon inputs (6.4 Mg C ha^{-1}yr^{-1}) from organic fertilizer (Wu et al., 2015). Microorganisms may also make some contribution to SOC in the soil profile (Qiu et al., 2010). These factors may account for the significant difference in SOC between the two production systems at 0–40 cm depth. It is widely accepted that low agricultural inputs could result in a relatively high carbon sink (West and Marland, 2002). For instance, change from conventional tillage to no-till practices resulted in a carbon sink increment of 0.37 Mg ha^{-1} yr^{-1} (West and Marland, 2002). Plastic greenhouse vegetable field achieved an even higher carbon sink rate, showing a surprising increment of 0.91 Mg ha^{-1}yr^{-1} after being converted from a conventional vegetable cultivation system (Wang et al., 2011). In this study, VP also achieved an even significantly higher SOC accumulation rate, showing a significant increment of 4.638 Mg ha^{-1}y^{-1} after being converted from a forest system. This is primarily attributable to the higher carbon fixation capacity of VP both in terms of higher vegetable net primary production (NPP) and higher soil C sequestration (Wang et al., 2011). It indirectly suggests that most of the increase in soil organic carbon is caused by the increased NPP under VP (2.3 times than conventional, Wang et al., 2011), further showing that soil carbon sequestration is not the result of a higher fertilization rate but of benefits from greenhouses itself (Wu et al., 2015). Higher yields also increase root exudation and exudates and dissolved organic matter from manures can move deep down the soil profile with excessive irrigation (Brye et al., 2001). The vegetables harvested part account for 42% of the biomass production that removed from the greenhouses. Among them, 10% of these vegetable products will be recycled to the greenhouses indirectly by means of manure through the periphery ecosystems. 58% of the biomass production (straw) composted as manure and was applied to VP directly (Wang et al., 2011).

The higher concentration and stock of TN under VP may have resulted from excessive N fertilizer and manure applications. Collected from interviews, over triple cropping is practiced with up to about 12 irrigation events and 6 fertilizer applications in greenhouses. The amounts of N fertilizer applied in VP were found to be up to about 1500 kg ha^{-1} y^{-1}. Inefficient N uptake characteristics of the vegetable crops contributed to N accumulation in soils. The higher TN concentrations and stocks combined with large amounts of irrigation water (1800 mm per year) in the greenhouse system represent a considerable threat to groundwater quality and may be harmful to local residents.

The C:N ratio reflects the stability of soil organic matter and relative decomposition stage and the age of the humus (Russell et al., 2005). In general, agricultural use of soils reduces the soil C:N ratio (Kaffka and Koepf, 1989). In this study, we found that the soil C:N ratios significantly decreased under VP as compared to FL and GL, which was in agreement with other reports (Omonode and Vyn, 2006; Qiu et al., 2010). Excessive fertilizer N may block SOC sequestration through suppression of the microbial population or stimulation of mineralization of old native organic C (McCarty and Meisinger, 1997). This suggests that increasing management intensity in agriculture, especially with larger N inputs from fertilizer or manure application, could lead to a faster increase in soil N than C, resulting in lower soil C:N ratios. Furthermore, increased tillage operations under VP lead to enhanced decomposition rates of added organic materials and soil organic matter. This may also contribute to the decline in soil C:N ratios. Other studies have suggested that soils with lower soil C:N ratios are prone to greater N losses through leaching (Thomsen et al., 2008). Therefore, the excessive rate of N fertilizer application to greenhouse vegetable crops has been main direct reason for nitrate leaching. The lower soil C:N may partially be a consequence of higher nitrate leaching in greenhouse vegetables production systems in China.

Conclusions

This research showed that a significant shift in land use from forest to highly intensive greenhouse vegetables production in China's agriculture has resulted in higher SOC and TN concentrations and stocks, and lower C:N ratios. Using the SOC, and TN stocks in the respective FL as baseline values, the rates of SOC and TN accumulation (0–40 cm) for VP were 4.638 Mg ha^{-1} y^{-1} and 1.113 Mg ha^{-1} y^{-1} over an average period of 8 years, respectively. We conclude that greenhouse vegetable production system could be effective strategies to improve SOC and TN stocks in the subtropical Dianchi lake watershed. But the accumulation of N in greenhouse vegetable soils poses a potential threat to nearby Dianchi lake. Therefore, optimizing management strategies, which may be specific for soil C and N management, has become one of the most urgent requirements for more sustainable vegetable production in southwest China.

Acknowledgements

Financial support for this study was provided by National Key Basic Research Program (Project No. 2014CB953800), National Natural Sciences Foundation of China (Project No. 41273103 and 41173094) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

Blake, G.R., Hartge, K.H., 1986. Bulk density. In: Klute, A. (Ed.), Methods of Soil Analysis. Part 1. 2nd ed. Am. Soc. Ag., Soil Sci. Soc. Am. Madison, WI, pp. 363–375.

Brye, K.R., Norman, J.M., Bundy, L.G., Gower, S.T., 2001. Nitrogen and carbon leaching in agroecosystems and their role in denitrification. *Journal of Environmental Quality* 30: 58–70.

Chen, H.Q., Lee, J., Kuzyakov, Y., Six, J., 2012. Soil organic carbon and total nitrogen in intensively managed arable soils. *Agriculture, Ecosystems & Environment* 150:102-110.

Deen, W., Kataki, P.K., 2003. Carbon sequestration in a long-term conventional versus conservation tillage experiment. *Soil and Tillage Research* 74:143-150.

Demessie, A., Singh, B.R., Lal, R., 2013. Soil carbon and nitrogen stocks under chronosequence of farm and traditional agroforestry land uses in Gambo District, Southern Ethiopia. *Nutrient Cycling in Agroecosystems* 95: 365–375.

Dong, Y., Dong, K., Lu, Y., Zhao, P., Tang, L. 2009. Influence of greenhouse cultivation on soil chemical properties and microbial community. *Journal of Yunnan Agricultural University* 24(3): 418-424. [in Chinese, with English abstract]

Ellert, B.H., Bettany, E.T., 1995. Calculation of organic matter and nutrients stored insoils under contrasting management regimes. *Canadian Journal of Soil Science* 75: 529–538.

Falahatkar, S., Hosseini, S.M. Mahiny, A.S., Ayoubi, S., Wang, S.Q., 2014. Soil organic carbon stock as affected by land use/cover changes in the humid region of Northern Iran. *Journal of Mountain Science* 11(2): 507-518.

Gao, M., Yang, H., 2006. Distribution of soil nutrient and its environmental impact under different land utilization in Dounan of Dianchi watershed. *Journal of Anhui Agricultural Science* 34(23): 6255-6257, 6259. [in Chinese, with English abstract]

Gelaw, A.M., Singh, B.R., Lal, R. 2014. Soil organic carbon and total nitrogen stocks under different land uses in a semi-arid watershed in Tigray, Northern Ethiopia. *Agriculture, Ecosystems and Environment* 188: 256–263.

Jiang, J.B., Jia, X.S., Qiao, J., Man, C.H., Wu, G.X., 2011. Assessment of vegetable greenhouse and development for new sunlight greenhouse. *Chinese Vegetable* 11: 8-10. [in Chinese, with English abstract]

Kaffka S., Koepf H.H., 1989. A case study on the nutrient regime in sustainable farming. *Biological Agriculture and Horticulture: An International Journal for Sustainable Production Systems* 6: 89-106.

Karchegani, M.P., Ayoubi, S., Mosaddeghi, M.R., Honarjoo, N., 2012. Soil organic carbon pools in particle-size fractions as affected by slope gradient and land use change in hilly regions, Western Iran. *Journal of Mountain Science* 9: 87-95.

Khormali, F., Ajami, M., 2011. Pedogenetic investigation of soil degradation on a deforested loess hill slope of Golestan Province, Northern Iran. *Geoderma* 167-168: 274-283.

Liang, Q., Chen, H.Q., Gong, Y.S., Fan, M.S., Yang, H.F., Lal, R., Kuzyakov, Y., 2012. Effects of 15 years of manure and inorganic fertilizers on soil organic carbon fractions in a wheat-maize system in the North China Plain. *Nutrient Cycling in Agroecosystems* 92: 21-33.

McCarty, G.W., Meisinger, J.J., 1997. Effects of N fertilizer treatments on biologically active N pools in soils under plow and no tillage. *Biology and Fertility of Soils* 24: 406-412.

Mireia, L., Bruno, G.M., Belén, T., 2010. Storage of organic carbon and black carbon in density fractions of calcareous soils under different land uses. *Geoderma* 159: 31-38.

Ministry of Agriculture, People's Republic of China (MOA). 2006. Soil testing. Part 1: soil sampling, processing and reposition (NY/T 1121.1-2006). Beijing.

Niu, X.Y., Wang, Y.H., Yang, H., Zheng, J.W., Zou, J., Xu, M.N., Wu, S.S., Xie, B. 2015. Effect of land use on soil erosion and nutrients in Dianchi lake watershed, China. *Pedosphere* 25(1): 103-111.

Omonode, R.A., Vyn, T.J., 2006. Vertical distribution of soil organic carbon and nitrogen under warm-season native grasses relative to croplands in west-central Indiana, USA. *Agriculture, Ecosystems & Environment* 117: 159-170.

Oyarzun, R., Arum, J., Salgado, L., Marino, M., 2007. Sensitivity analysis and field testing of the RISK-N model in the Central Valley of Chile. *Agricultural Water Management* 87: 251-260.

Poeplau, C., Don, A., 2013. Sensitivity of soil organic carbon stocks and fractions to different land-use changes across Europe. *Geoderma* 192:189-201.

Puget, P., Lal R., 2005. Soil organic carbon and nitrogen in a Mollisol in central Ohio as affected by tillage and land use. *Soil and Tillage Research* 80: 201-213.

Qiu, S.J., Ju, X.T., Ingwersen, J., Qin, Z.C., Li, L., Streck, T., Christie, P., Zhang, F.S., 2010. Changes in soil carbon and nitrogen pools after shifting from conventional cereal to greenhouse vegetable production. *Soil and Tillage Research* 107: 80-87.

Russell, A.E., Laird, D.A., Parkin, T.B., Mallarino, A.P., 2005. Impact of nitrogen fertilization and cropping system on carbon sequestration in Midwestern Mollisols. *Soil Science Society of America Journal* 69: 413-422.

Shi, W.M., Yao, J., Yan, F., 2009. Vegetable cultivation under greenhouse conditions leads to rapid accumulation of nutrients, acidification and salinity of soils and groundwater contamination in South-Eastern China. *Nutrient Cycling in Agroecosystems* 83: 73-84.

Su, Z.Y., Xiong, Y.M., Zhu, J.Y., Ye, Y.C., Ye, M., 2006. Soil organic carbon content and distribution in a small landscape of Dongguan, South China. *Pedosphere* 16: 10-17.

Thomsen, I.K., Petersen, B.M., Bruun, S., Jensen, L.S., Christensen, B.T., 2008. Estimating soil C loss potentials from the C to N ratio. *Soil Biology and Biochemistry* 40: 849-852.

Wang, J.L., Yang, G.H., 1997. A study on soil resources and rational use of small drainage in Dianchi lake drainage area. *Resources and Environment in the Yangtze Valley* 6(2):143-148.

Wang, Y,. Xu, H., Wu, X., Zhu, Y.M., Gu, B.J., Niu, X.Y., Liu, A.Q., Peng, C.H., Ge, Y., Chang, J., 2011. Quantification of net carbon flux from plastic greenhouse vegetable cultivation: a full carbon cycle analysis. *Environmental Pollution* 159: 1427-1434.

West, T.O., Marland, G., 2002. Net carbon flux from agricultural ecosystems: methodology for full carbon cycle analyses. *Environmental Pollution* 116: 439-444.

Wu, G.L., Liu, Z.H., Zhang, L., Hu, T.M., Chen, J.M., 2010. Effects of artificial grassland establishment on soil nutrients and carbon properties in a black-soil-type degraded grassland. *Plant Soil* 333: 469-479.

Wu, X., Ge, Y., Wang, Y., Liu, D., Gu, B.J., Ren, Y., Yang, G.F., Peng, C.H., Cheng, J.H., Chang, J., 2015. Agricultural carbon flux changes driven by intensive plastic greenhouse cultivation in five climatic regions of China. *Journal of Cleaner Production* 95: 265-272.

Yan, Y., Tian, J., Fan, M.S., Zhang, F.S., Li X.L., Christie, P., Chen, H.Q., Lee, L., Kuzyakov, Y,. Six, J., 2012. Soil organic carbon and total nitrogen in intensively managed arable soils. *Agriculture, Ecosystems & Environment* 150:102-110.

Zhang, C., Liu, G.B., Xue, S., Sun, C.L., 2013. Soil organic carbon and total nitrogen storage as affected by land use in a small watershed of the Loess Plateau, China. *European Journal of Soil Biology* 54: 16-24.

Eurasian J Soil Sci 2016, 5 (1) 24 - 29

Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

Conservation agriculture increases soil organic carbon and residual water content in upland crop production systems

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Article Info

Received : 02.01.2015
Accepted : 12.07.2015

Abstract

Conservation agriculture involves minimum soil disturbance, continuous ground cover, and diversified crop rotations or mixtures. Conservation agriculture production systems (CAPS) have the potential to improve soil quality if appropriate cropping systems are developed. In this study, five CAPS including different cropping patterns and cover crops under two fertility levels, and a plow-based system as control, were studied in a typical upland agricultural area in northern Mindanao in the Philippines. Results showed that soil organic carbon (SOC) at 0- 5-cm depth for all CAPS treatments generally increased with time while SOC under the plow-based system tended to decline over time for both the high (120, 60 and 60 kg N P K ha^{-1}) and moderate (60-30-30 kg N P K ha^{-1}) fertility levels. The cropping system with maize + *Stylosanthes guianensis* in the first year followed by *Stylosanthes guianensis* and fallow in the second year, and the cassava + *Stylosanthes guianensis* exhibited the highest rate of SOC increase for high and moderate fertility levels, respectively. After one, two, and three cropping seasons, plots under CAPS had significantly higher soil residual water content (RWC) than under plow-based systems. Results of this study suggest that conservation agriculture has a positive impact on soil quality, while till systems negatively impact soil characteristics.

Keywords: Upland agriculture, soil quality, climate change adaptation, cropping systems

Introduction

The sustainability of upland crop production systems depends to a large extent on soil quality, which is affected by the nature of the farming system being implemented. In many parts of the Philippines, plow-based agriculture systems continue to be practiced, leading to serious soil degradation, especially on steep terrain. Plowing causes loss of soil organic carbon (SOC) because of greater exposure of the soil particles to microbial activity (de Morais, 2011). The loosening of the soil particles in plow-based systems may also decrease the soil residual water retention. This disruption causes carbon-protecting aggregates to disperse, a process further accelerated by cycles of wetting and drying and exposure to precipitation (Balesdent et al., 2000). Furthermore, plow-based systems increase the cost of agricultural crop production in the medium- and long-term because greater amounts of fertilizer inputs, soil amendments, and other inputs are needed to compensate for the degradation of soil quality. Traditional agricultural practices trigger excessive soil erosion and sedimentation of natural streams, reduction in channel capacities, and flooding. Adverse environmental impacts on soil quality have become even more pronounced in recent years with the

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e-ISSN: 2147-4249 DOI: http://dx.doi.org/10.18393/ejss.2016.1.024-029

occurrence of extreme rainfall events, presumably caused by climate change (Meehl et al., 2007; Follet et al., 2012).

Conservation agriculture involves minimum soil disturbance, continuous ground cover, and diversified crop rotations or mixtures (Erenstein et al., 2008). It is currently implemented in more than 110 million ha in countries such as the United States, Canada, Brazil, Argentina, Australia, Paraguay, and in the Indo Gangetic Plains (Derpsch, 2008).

Organic carbon content is a key indicator of soil quality (Govaerts et al. 2009; Jandl et al., 2013) and can increase in Conservation Agriculture Production Systems (CAPS). No-till, for example, has improved soil quality and fertility in Mediterranean areas in Spain (Madejón et al., 2009) and in Argentina (Diaz-Zorita et al., 2002), and slowed SOC decomposition in the United States (Mishra et al., 2010).

In Southeast Asia, conservation agriculture is still at a nascent stage. In Cambodia, several CAPS have shown great promise (Boulakia et al., 2009). In Laos, soil aggregation, water holding capacity, and biological activity were enhanced under CAPS (Tivet et al., 2008). In Vietnam, conservation agriculture on sloping lands reduced soil erosion by up to 96% and increased crop yield by more than 200% (Doanh and Tuan, 2008). In the Philippines, no extensive research has been done on the impacts of conservation agriculture on soil quality. Hence, a multi-year study was conducted to compare the effects of CAPS and a conventional plow-based system on SOC and residual water content (RWC) in selected crop production systems. This research aims to generate new knowledge and on the soil quality impacts of these farming systems to serve as basis for policy formulation and upscaling of conservation agriculture in steep upland crop production areas.

Material and Methods

This study was conducted at the Sustainable Agriculture and Natural Resources Management (SANREM) Innovation Lab research site in Claveria, Misamis Oriental, Philippines, which is located at 8°38’39” N and 124°55’49” E, and has an average land slope of 26% (Figure 1).

Figure 1. The SANREM research site in Claveria, Misamis Oriental, Philippines.

The area is representative of the upland agriculture landscape in northern Mindanao. Six CAPS treatments including different cropping patterns and cover crops, and a plow-based system as control (Table 1), were laid out in a randomized complete block design with four replicates and a plot size of 10 m x 20 m. Each treatment included subplots with high (120, 60 and 60 kg N P K ha^{-1}) and moderate (60-30-30 kg N P K ha^{-1}) fertility levels.

For treatment 1, seeds of the main crop, maize, were dibble-planted at a spacing of 70 cm x 20 cm resulting in a plant density of approximately 71,000 plants ha^{-1}. Cover crop *Arachis pintoi* Krapov & W.C. Gregory cuttings were planted in a single row in the middle of maize rows every 25 cm. In subsequent maize crops, NPK fertilizer was applied, and seeds were planted in furrows in the living *Arachis pintoi* mulch. For treatment 2, maize was established and managed as in treatment 1.

Table 1. Summary of conservation agriculture production systems treatments in Mindanao

Treatment	Cropping system
T1	*Arachis pintoi* + Maize- *Arachis pintoi* + Maize
T2	Maize + *Stylosanthes guianensis* – *Stylosanthes guianensis*- Fallow
T3	Maize + cowpea - Upland rice + cowpea
T4	Maize + rice bean- Maize + rice bean
T5	Cassava + *Stylosanthes guianensis*
T6	Maize-maize (conventional plow-based) (control)

The seeds of cover crop *Stylosanthes guianensis* (Aubl.) Sw were drilled between rows of maize and thinned to 10 to 15 plants m^{-1}. In subsequent croppings, *Stylosanthes* was flattened and sprayed with glyphosate before maize planting. For treatment 3, maize was established in double rows spaced 35 cm apart at 20 cm between plants resulting in a plant density of about 72,000 plants/ha, followed by two rows of cowpea (*Vigna unguiculata* (L.) Walp), as a cover crop, spaced 35 cm apart at 10 to 15 plants m^{-1}. After the harvest of cowpea, upland rice (*Oryza sativa* L.) was planted. Cowpea was planted again after the maize harvest. For treatment 4, the cover crop rice bean *Vigna umbellata* (Thunb.) Ohwi & H. Ohashi was first established. Two weeks later, maize was established as in treatment 1. During subsequent cropping, rice beans and weeds were sprayed with glyphosate before maize planting. For treatment 5, furrows were spaced at 100 cm, and cuttings of the main crop cassava were planted 50 cm apart at about 20,000 plants ha^{-1}. Seeds of the cover crop *Stylosanthes guianensis* were drilled between rows of cassava and thinned to 10 to 15 plants m^{-1}. During subsequent cropping, the cover crop was flattened and sprayed with glyphosate before cassava was planted. Treatment 5 represents the current practice for maize production for most farmers in the Philippines. Prior to maize planting, plowings by animal-drawn moldboard plow and two harrowings by animal-drawn spike-toothed harrow along with furrowing by animal-drawn moldboard plow were performed.

Soil samples were collected with an auger at 0- to 5-, 5- to 15- and 15- to 30-cm depth on July 18, 2010; December 5, 2010; April 15, 2011; September 18, 2011; February 25, 2012; August 3, 2012; and September 6, 2013. Soil samples were composited for each treatment for SOC analysis. The soil samples were brought to University of the Philippines Los Baños for laboratory analysis, and SOC was determined using the Walkley-Black method (Walkley and Black, 1934). Changes of SOC over time were analyzed using linear regression analysis.

Soil residual water content was measured in four quadrants in each experimental plot using time domain reflectometry (TDR; Field Scout 300, Spectrum Technologies Inc., Paxinos, PA) after each cropping season in the upper 12 cm which likely represents the soil layer with maximum root activity. In each quadrant, the average of three TDR readings was used to represent the quadrant. The average of the four quadrant readings was then used to represent the RWC for that plot or replicate for each of the six treatments. The TDR used enabled automatic calibration with a built-in firmware unlike other TDR meters. Also, any minute error in the automatic calibration of the TDR probe should have been offset because the overall average for each plot was based on 12 measurements. Moreover, the RWC values from TDR measurements were comparable to those obtained from gravimetric measurements of the collected soil samples used for bulk density determinations. Analysis of variance of the RWC water content was consequently performed using Dunnett's two-sided tests (Dunnett, 1955).

Results and Discussion

Effects of Conservation Agriculture Production Systems on SOC

Soil organic carbon at 0- 5-cm depth in plow-based system declined over time ($P \leq 0.10$), decreasing from 3.3% at the start of the CAPS treatments to 3.1% and 2.9% for the high and moderate fertility treatments respectively after three cropping years. These results can be attributed to the disruption in C cycling due to tillage as previously shown (e.g., Govaerts et al., 2009; Baker et al., 2006; Murty et al., 2002; Davidson and Ackerman, 1993).

On the other hand, SOC in the CAPS treatments did not decrease temporally, regardless of fertility level, and even tended to increase to 3.8% and 3.7% for the high and moderate fertility levels, respectively, after three cropping years. The strongest effect on SOC for the high fertility level was for the CAPS treatment including maize *+ Stylosanthes guianensis- Stylosanthes guianensis* - fallow ($P = 0.07$), with the treatment explaining 60% of the variance in SOC (Table 2).

Table 2. Changes in soil organic carbon (SOC; %) with time in days after imposing the treatments at 0- to 5 cm soil depth under the high fertility level

Treatment	Regression equation	R^2	P
T1	SOC = 3.460 + 0.00033 Time	0.23	0.33
T2	SOC = 3.176 + 0.00138 Time	0.60	0.07
T3	SOC = 3.243 + 0.00035 Time	0.25	0.31
T4	SOC = 3.210 + 0.00005 Time	0.02	0.77
T5	SOC = 3.446 + 0.00051 Time	0.25	0.32
T6	SOC = 3.333 - 0.00065 Time	0.54	0.09

Treatments T1 to T6 are described in Table 1

For the moderate fertility, the CAPS treatment with cassava + *Stylosanthes guianensis* exhibited the highest rate of increase in SOC (P = 0.01) and explained 82% of the variance in SOC, followed closely by the treatment with maize + *Stylosanthes guianensis – Stylosanthes guianensis*- Fallow (P = 0.02) (Table 3).

Table 3. Changes in soil organic carbon (SOC; %) with time in days after imposing the treatments at 0- to 5-cm soil depth under the moderate fertility level

Treatment	Regression equation	R^2	P
T1	SOC = -0.00026 Time + 3.578	0.14	0.47
T2	SOC = 0.00073 Time + 3.393	0.80	0.02
T3	SOC = -0.00060 Time + 3.736	0.11	0.52
T4	SOC = 0.00115 Time + 3.271	0.59	0.07
T5	SOC = 0.00120 Time + 3.142	0.82	0.01
T6	SOC = -0.00093 Time + 3.340	0.60	0.07

Treatments T1 to T6 are described in Table 1

Increased SOC could relate to the large biomass production and incorporation from *Stylosanthes guianensis,* which was allowed to decay after each cropping. In a separate study on the same site (Mercado et al., 2012), two CAPS treatments that included *Stylosanthes guianensis* as a cover crop, showed the highest biomass production after two cropping seasons, with a mean value of 27.1 and 7.0 tons ha^{-1}, respectively.

For the 5- to 15-cm and 15- to 30-cm soil depths, no distinct pattern of SOC change in the CAPS treatment was exhibited (Data not shown). Explained variance of regression functions were low (not higher than 41% with P from 0.17 to 0.99).

Although long-term monitoring is necessary to assessing the effects of conservation agriculture on SOC more conclusively, the foregoing results point to a positive effect in some cropping systems in a relatively short period while plow-based systems negatively impact the soil. The minimal disturbance of the soil under CAPS prevents the exposure of the soil particles to microbial attack, thereby minimizing the loss of organic matter. Moreover, the continuous presence of crop mulch cover appears to contribute to the increase in SOC. These are important positive effects that can reduce the ongoing global land degradation (Bail et al., 2008).

Effects of Conservation Agriculture Production System on RWC

Mean RWC in the CAPS treatments was higher than those in the plow-based system (Figure 2). Fertility levels did not affect RWC. After one cropping season, RWC ranged from 31 to 39% on a volume basis in the CAPS treatments, and from 25 to 31% in the plow-based system. After two and three cropping seasons, the RWC in the CAPS treatments varied from 21 to 25% and from 27 to 36%, respectively, compared with 18 and 20% in the plow-based system.

The CAPS treatment with maize + *Stylosanthes guianensis - Stylosanthes guianensis*-fallow yielded the highest residual moisture content (P ≤ 0.05). The significantly lower RWC under the plow-based system relative to the CAPS treatments may be attributed to the substantial soil disturbance caused by plowing at the beginning of each cropping in these plots, which loosens up the soil structure. Increased SOC in the uppermost soil layer in some of the CAPS treatments may have also contributed to higher RWC measurements as found in other studies (Balesdent et al., 2000).

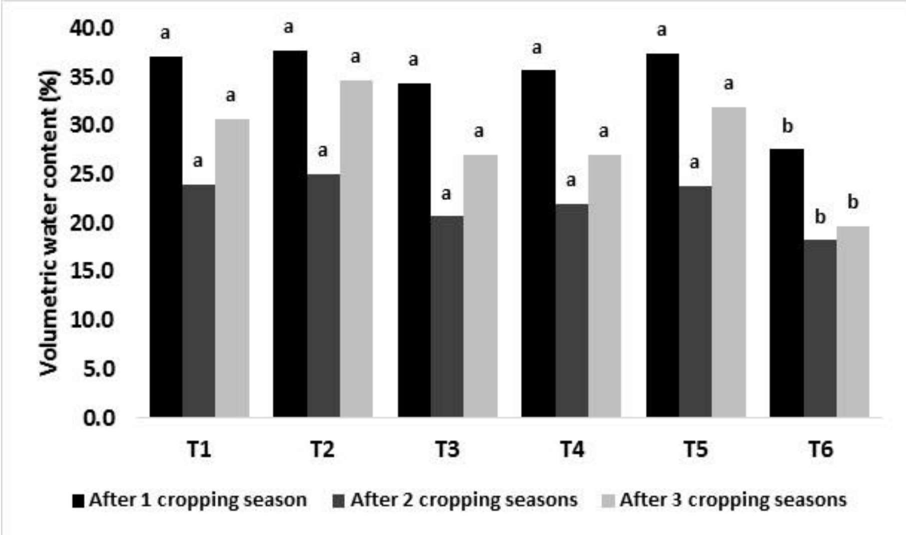

Figure 2. Residual soil water content at various CAPS treatments after one, two, and three cropping seasons.

Findings from this study indicated that conservation agriculture has a positive impact on improving the water retention capacity of the soil as found in other studies (Thierfelder and Wall, 2009; Martinez et al., 2011). Conversely, a plow-based system significantly reduces RWC. Consequently, more water is conserved under CAPS than under a plow-based system. This has practical implications in terms of the timing of the next cropping, irrigation frequencies, and the potential increased adaptation to climate change. Previous research has shown that the relationship between SOC and RWC is often not direct because of the effect of other variables such as soil textural components and bulk density (Rawls et al., 2003; Parajuli and Duffy, 2013).

Conclusions

Results of this study illustrate the potential of CAPS with no till, cover crops and crop rotations or mixtures to improve soil characteristics in steep agricultural landscapes in northern Mindanao. With CAPS, SOC generally exhibited an increase with time albeit the effect was limited to the upper part of the soil profile. In the plow-based system, SOC instead decreased with time. The high fertility level applied in this study appeared to augment the CAPS effects on SOC. The cassava crop followed by the cover crop *Stylosanthes guianensis* in the first year and *Stylosanthes guianensis* and fallow during the second year had the highest SOC increase, followed by the maize + cowpea (first year) and upland rice and cowpea (second year).

Effects of CAPS on RWC were even more marked than that those for SOC. The consistent increase in RWC over several years suggests that CAPS can have a composited effect on the soil water budget besides other positive effects such as rainwater splash and erosion reduction. Nevertheless, long-term soil quality monitoring is necessary to generate additional evidence on the impact of CAPS on soil quality. Overall, the results obtained in this study could serve as a significant takeoff point for further studies which may eventually be used for modeling studies and for policy formulation geared towards soil and water resources conservation and for sustainable upland agriculture in the humid tropics.

Acknowledgements

We are deeply grateful to USAID for funding the Southeast Asia project of the Sustainable Agriculture and Natural Resource Management Innovation Lab (SANREM).

References

Bail, Z.G., Dent, D.L., Olsson, L., Schaepman, M.E., 2008. Proxy global assessment of land degradation. *Soil Use and Management* 24: 223–234.

Baker, J.M., Ochsner, T.E., Venterea, R.T., Griffis, T.J., 2006. Tillage and soil carbon sequestration-what do we really know? *Agriculture, Ecosystems and Environment* 118: 1-5.

Balesdent, J., Chenu, C., Balabane, M., 2000. Relationship of soil organic matter dynamics to physical protection and tillage. *Soil and Tillage Research* 53: 215-230.

Boulakia, S., Phâlly, K., Sona, S., Vira, L., Kimchhorn, C., 2009. Five years of adaptative research for upland DMC based cropping systems creation in Cambodia. PADAC report.

Davidson, E.A., Ackerman, I.L., 1993. Changes in soil carbon inventories following cultivation of previously untilled soils. *Biogeochemistry* 20: 161-193.

De Morais, J.C., 2011. Carbon sequestration, soil quality, crop profitability and environmental quality. Oral presentation at the *Second International Conservation Agriculture Workshop and Conference in Southeast Asia*. July 4-7. Phnom Penh, Cambodia.

Derpsch, R., 2008. No-tillage and conservation agriculture: A progress report. In: *No-till Farming Systems*. T. Goddard, M.A. Zoebisch, Y.T. Gan, W. Ellis, A. Watson, S. Sombatpanit (*eds*.). World Association of Soil and Water Conservation, Bangkok, pp. 7-39.

Diaz-Zorita, M., Duarte, G.A., Grove, J.H., 2002. A review of no-till systems and soil management for sustainable crop production in the subhumid and semiarid Pampas of Argentina. *Soil and Tillage Research* 65: 1-18.

Doanh, L.Q., Tuan, H.D., 2008. Conservation agriculture on sloping lands in northern mountainous regions of Vietnam. *In: Proceedings of the Regional Workshop on Conservation Agriculture*. M. Chanphengxay, M., M.A. Khamhung, M.K. Panysiri, M.A. Chabanne, M. F. Jullien, M.H. T. Quoc, M.P. Lienhard, M.F. Tivet (*eds.*) October 28 to November 1. Phonsavan, Lao PDR. pp. 27-36.

Dunnett, C.W., 1955. A multiple comparison procedure for comparing several treatments with a control. *Journal of the American Statistical Association* 50: 1096 -1121.

Erenstein, O., Sayre, K., Wall, P., Dixon, J., Hellin, J., 2008. Adapting no-tillage agriculture to the conditions of smallholder maize and wheat farmers in the tropics and sub-tropics. *In: No-till Farming Systems.* T. Goddard, M.A. Zoebisch, Y.T. Gan, W. Ellis, A. Watson, S. Sombatpanit (eds.). World Association of Soil and Water Conservation, Bangkok, pp. 253-278.

Follet, R.F., Stewart, C.E., Pruessner, E.G., Kimble, J.M., 2012. Effects of climate change on soil carbon and nitrogen storage in the US Great Plains. *Journal of Soil and Water Conservation* 67: 331-342.

Govaerts, B., Verhulst, N., Castellanos-Navarette, A., Sayre, K.D. Dixon J., Dendooven, L., 2009. Conservation agriculture and soil carbon sequestration: Between myth and farmer reality. *Critical Reviews in Plant Sciences* 28: 97-122.

Jandl, R., Rodeghiero, M., Martinez, C., Cotrufo, M.F., Bampa, F., van Wesemael, B., Harrison, R.B., Guerrini, I.A., D. Richter Jr., D., Rustad, L., K. Lorenz, K., Chabbi, A. Miglietta, F., 2013. Current status, uncertainty and future needs in soil organic carbon monitoring. *Science of the Total Environment* 468-469: 376-383.

Madejón, E., Murillo, J.M., Moreno, F., López, M.V., Arrue, J.L., Alvaro-Fuentes, J., Cantero, C., 2009. Effect of long-term conservation tillage on soil biochemical properties in Mediterranean Spanish areas. *Soil and Tillage Research* 105: 55-62.

Martinez, I., Ovalle, C., Del Pozo, A., Uribe, H., Valderrama, N., Prat, Ch., Sandoval, M., Fernández, F., Zagal, E. (2011). Influence of conservation tillage and soil wáter content on crop yield in dryland compacted alfisol of central Chile. *Chilean Journal of Agriculture Research* 71: 615-622.

Meehl, G.A., Stocker, T.F., Collins, W.D., Friedlingstein, P., Gaye, A.T., Gregory, J.M., Kitoh, A., Knutti, R., Murphy, J.M., Noda, J.A., Raper, S.C.B., Watterson, I.G., A.J. Weaver, A.J., Zhao, Z.C., 2007. Global climate projections. *In Climate change: The physical science basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor, H.L. Miller (eds.). Cambridge University Press, Cambridge, UK, and New York, USA.

Mercado, Jr., A.R., Ella, V.B., Reyes, M.R., 2012. Yield, biomass and soil quality of conservation agriculture systems in the Philippines. In Proceedings 3rd International Conference on Conservation Agriculture in Southeast Asia. Hauswirth et al. (eds.), December 10-15, Hanoi, Vietnam, p. 256-58.

Mishra, U., Ussiri, D.A.N., Lal, R., 2010. Tillage effects on soil organic carbon storage and dynamics in Corn Belt of Ohio USA. *Soil and Tillage Research* 107: 88-96.

Murty, D., Kirschbaum, M.U.F., McMurtrie, R.E., McGilvray, H.M., 2002. Does conversion of forest to agricultural land change soil carbon and nitrogen? A review of literature. *Global Change Biology* 8: 105-123.

Parajuli, P.B., Duffy, S. 2013. Evaluation of soil organic carbón and soil moisture content from agricultural fields in Mississippi. *Open Journal of Soil Science* 3: 81-90.

Rawls, W.J., Pachepsky, Y.A., Ritchie, J.C., Sobecki, T.M., Bloodworth, H., 2003. Effect of soil organic carbon on soil water retention. *Geoderma* 116: 61-76.

Thierfelder Ch., Wall, P.C., 2009. Effects of conservation agriculture techniques on infiltration and soil water content in Zambia and Zimbabwe. *Soil and Tillage Research* 105:217-227.

Tivet, F., Quoc, H.T., Boyer, J., Chabanne, A., Inthavong, C., S. Senephansiri, S., Keodouangsy, L., Chounlamountry, T., Khamxaykhay, C., K. Panyasiri, K., Seguy, L., 2008. Soil aggregation, water holding capacity and biological activity under no-till systems and cropping sequences in the Lao PDR. *In* Proceedings of the Regional Workshop on Conservation Agriculture, XX (eds.). October 28 to November 1, Phonsavan, Lao PDR, p. 130.

Walkley, A., Black, I.A., 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science* 37: 29-38.

Eurasian J Soil Sci 2016, 5 (1) 30 - 38

Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

Predicting saturated hydraulic conductivity using soil morphological properties

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Article Info

Received : 04.04.2015
Accepted : 13.08.2015

Abstract

Many studies have been conducted to predict soil saturated hydraulic conductivity (K_s) by parametric soil properties such as bulk density and particle-size distribution. Although soil morphological properties have a strong effect on K_s, studies predicting K_s by soil morphological properties such as type, size, and strength of soil structure; type, orientation and quantity of soil pores and roots and consistency are rare. This study aimed at evaluating soil morphological properties to predict K_s. Undisturbed soil samples (15 cm length and 8.0 cm id.) were collected from topsoil (0-15 cm) and subsoil (15-30 cm) (120 samples) with a tractor operated soil sampler at sixty randomly selected sampling sites on a paddy field and an adjecent grassland in Central Anatolia (Cankırı), Turkey. Synchronized disturbed soil samples were taken from the same sampling sites and sampling depths for basic soil analyses. Saturated hydraulic conductivity was measured on the soil columns using a constant-head permeameter. Following the K_s measurements, the upper part of soil columns were covered to prevent evaporation and colums were left to drain in the laboratory. When the water flow through the column was stopped, a subsample were taken for bulk density and then soil columns were disturbed for describing the soil morphological properties. In addition, soil texture, bulk density, pH, field capacity, wilting point, cation exchange capacity, specific surface area, aggregate stability, organic matter, and calcium carbonate were measured on the synchronized disturbed soil samples. The data were divided into training (80 data values) and validation (40 data values) sets. Measured values of K_s ranged from 0.0036 to 2.14 cmh^{-1} with a mean of 0.86 cmh^{-1}. The K_s was predicted from the soil morphological and parametric properties by stepwise multiple linear regression analysis. Soil structure class, stickiness, pore-size, root-size, and pore-quantity contributed to the K_s prediction significantly ($P<0.001$, $R^2 = 0.95$). Soil morphological properties can be used along with basic soil properties in predicting K_s.

Keywords: Saturated hydraulic conductivity, soil morphological properties, multiple linear regression, pedotransfer functions, soil stickness, soil structure

Introduction

Soil is a complex system, comprising solid, liquid and gas phases. The liquid and gas phase fill the pores that located between the solid portions. The water in these pores moves continuously by the action of evaporation, precipitation or gravitational forces even though its speed is very slow. The driving force of soil water movement is potential difference exerted from differences in water potential at different regions in

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e-ISSN: 2147-4249
DOI: http://dx.doi.org/10.18393/ejss.2016.1.030-038

soil. Hydraulic conductivity is the unique soil property that determines the water flow rate under specified soil water potential gradient (Jurry et al., 1991).

Soil hydraulic properties vary spatially and temporally, and direct measurement of these properties is time consuming and expensive. Therefore, indirect methods such as pedotransfer functions (PTFs) have been used frequently to predict soil hydraulic properties. Hydraulic conductivity is one of the most commonly predicted soil properties by PTFs. Knowing the relationship between hydraulic conductivity and other soil properties are very useful for understanding water flow in soils. Soil physical and chemical properties such as bulk density, organic matter content, porosity, and pore-size distribution are used quite a lot to model saturated and unsaturated hydraulic conductivity of soils (Wösten et al., 2001).

Soil morphologic properties such as soil structural features, soil pores, and roots are expected to affect saturated water flow in soils. Pachepsky et al. (2008) stressed that since soil structural properties are closely related to soil hydraulic parameters, including them in the list of PTF inputs may substantially improve predictions of soil hydraulic parameters. However, use of morphological properties in modeling saturated hydraulic conductivity (K_s) has been ignored for a long time (Lin et al., 1999).

Accoring to Abbaspour and Moon (1992),'Recent trends in PTF's research, however, indicate attempts to expand methods and data collections to better link hydraulic properties to morphological properties. An earlier attempt to bring structural parameters from the horizon/pedon scale to improve predictions of soil hydraulic properties at the aggregate/ped scale was generally unsuccessful'. On the other hand, Lilly et al. (2008) showed that morphological indicators could be used to predict soil hydraulic properties as well as commonly used laboratory data.

Soil morphological features, particularly those pertaining to structure may explain some of the variations in K_s (Sharma and Uehara, 1968; Keng and Lin, 1982; Field et al. 1984; Bouma, 1992). Saturated hydraulic conductivity can also be related to soil morphological criteria based on the expert assessment (McKenzie et al., 2000). The aim of this study was to evaluate potential of some readily avalable soil morphological properties in soil survey reports to predict K_s.

Material and Methods

Material

This study was carried out on paddy and adjacent grassland soils (total 9-ha) in Kızılırmak Township in Cankırı Province in Central Anatolia, Turkey. The study area is located 40º 30' 41º North latitude and 32º 30' 34º East longitudes in the north of Central Anatolia Region of Turkey (Fig. 1). The climate in the region is semi-arid and annual temperature, humidity, evaporation, and rainfall is 11 ºC, 64%, and 418 mm, respectively. Cankırı is surrounded by bare mountains and plateaus (Anonymous, 2011). The parent material within the study area comprises gypsum, andesite, spilite, basalt, marl, clay, and limestone and soils are classified as Gypsic Ustorthends.

Figure 1. Map showing location of the study area (Anonymous, 2014)

Methods

Undisturbed soil samples (15 cm length and 8.0 cm id) were taken from topsoil (0-15 cm) and subsoil (15-30 cm) at randomly selected sixty sampling points) with a tractor mounted sampling apparatus. Saturated hydraulic conductivity (K_s) was measured on the soil columns using a constant-head permeameter (Klute and Dirksen, 1986). After K_s measurement, the soil column was left standing on a desk to dry and when the water flow through the column was stopped (approximately 3 days after the test), a 100 cm^3 sample was taken by a steel cylinder for bulk density measurement and the rest of the column was disturbed and used for diagnosis of morphological properties. Bulk density was measured by the method from Blake and Hartge (1986).

Basic soil properties were measured on disturbed soil samples taken concomitantly with undisturbed samples. Particle–size distribution (Gee and Bauder, 1986), aggregate stability index (Kemper ve Rosenau, 1986), field capacity and wilting point (Klute, 1986), pH and electrical conductivity (Page et al., 1982), specific surface area (Carter et al., 1986), soil organic matter content (Page et al., 1982), cation exchange capacity (Page et al., 1982), $CaCO_3$ (Page et al., 1982), and Coefficient of Linear Extensibility; COLE (Schafer and Singer, 1976*)* were measured on the disturbed samples.

Soil morphological properties (structure, pores, consistence, stickiness, plasticity, roots, and mottles) were described with standard soil description charts (USDA-NRCS, 2002) used in soil survey studies. The morphological properties and soil colors were converted into numerical values. The strategy "greatest is the best" was applied in coding, depending on the expert idea on relationship between K_s and subjected property (Tables 1-7).

Table 1. Criteria applied to soil color coding in undisturbed soil samples (Munsell Color Scala)

Soil Color	Code	Soil Color	Code	Soil Color	Code	Soil Color	Code
Gley	1	7.5 YR 4/2	3	7.5 YR 5/2	4	7.5 YR 6/2	5
7.5 YR 3/2	2	7.5 YR 4/3	3	7.5 YR 5/3	4	7.5 YR 6/3	5
7.5 YR 3/3	2	7.5 YR 4/4	3	7.5 YR 5/4	4		
7.5 YR 3/4	2						

Soil structure was coded according to type, grade (Table 2), and size (Table 3), and code numbers was attained, accordingly (Table 2).

Table 2. Criteria applied to soil structure coding in undisturbed soil columns(USDA-NRCS, 2002)

Type	Code	Grade	Code
Masive	1	Structureless	1
Platy	2	Weak	2
Prismatic	3	Moderate	3
Blocky/Angular	4	Strong	4
Blocky/Sub-angular	5	Very strong	5
Granular	6		
Single grain	7		

Table 3. Criteria applied to soil structure coding in undisturbed soil columns(USDA-NRCS, 2002)

Size	Granular/Platy (mm)	Block-Angular / Subangular (mm)	Code
Very thin	< 1	< 5	1
Thin	1 – 2	5 – 10	2
Medium	3 – 5	11 – 20	3
Coarse	6 – 10	21 – 50	4
Very coarse	>10	>50	5

Pores in soil samples were classified according to quantity, size, and type and code numbers was given (Table 4).

Table 4. Criteria applied to coding soil pores in undisturbed soil columns (USDA-NRCS, 2002)

Quantity	Code	Size	Size (mm)	Code	Type	Code
Few	1	Micro	< 0,075	1	Irregular	1
Common	2	Very fine	0,075-1	2	Vesicular	2
Many	3	Fine	1-2	3	Dendritic tubular	3
		Medium	2-5	4	Tubular	4
		Coarse	5-10	5	Interstitial	5
		Very coarse	≥ 10	6		

Rupture resistance of soils were determined. Parts of soil samples with size about 3 cm were taken, and strength was evaluated by applying pressure to crash the aggregate and then consistency was evaluated according to Table 5.

Table 5. Consistency Classification Criteria of undisturbed soil columns (USDA-NRCS, 2002)

Consistency	Code	Definition
Loose	5	There is no adhesion between grains.
Soft	4	Adhesion between grains is weak, it becomes powder with light pressure
Slightly hard	3	Soils breakable and disintegrate with light pressure
Hard	2	It is quite resistant to pressure, crushed difficultly between the fingers, and it breakable in the palm.
Very hard	1	It is very durable to pressure, not breakable between the fingers, and hardly breakable in the palm.

Soil stickiness was evaluated at soil moisture slightly above field capacity. Stickiness was observed on the sample squeezed between thumb and forefinger and classified according to degree of adhesion (Table 6). Soil plasticity was determined on the soil yarns at field capacity. The strength of yarns were evaluated according to the state to support when they were standed with approximately 45-degree angle with vertical (Table 7).

Table 6. Criteria applied to stickness coding in undisturbed soil samples (USDA-NRCS, 2002)

Stickiness	Code	Definition
Not sticky	1	Soil does not stick when squeezed between the fingers.
Slightly sticky	2	Soil sticks to one finger
Moderatelystick	3	Soil sticks to two fingers and mud elongate slightly when fingers opened
Very sticky	4	Soil sticks firmly to two fingers and mud extend in certain ways when fingers opened

Table 7. Criteria applied to plasticity coding in undisturbed soil samples (USDA-NRCS, 2002)

Plasticity	Code	Definition
Not plastic	1	Soil does not form yarn.
Slightly plastic	2	Soil forms yarn, but easily breaks
Plastic	3	Soil forms yarn, and it resist somehow against breaking
Very plastic	4	Soil forms yarn and it resists agains breaking

Roots in soil samples were classified according to their quantity and size, and code numbers were given, accordingly (Table 8). Mottles of soil samples were evaluated according to percentage of the soil surface covered and they were coded in three classes (Table 8).

Table 8. Criteria applied to root and mottles coding in undisturbed soil samples (USDA-NRCS, 2002)

Root Quantity		Code	Root Size		Code	Mottle Quantity	Code	Mottle Percentage(%)
Not or few	<1	1	Very thin	<1mm	1	Not or few	3	%2
Common	1-5	2	Thin	1-2mm	2	Common	2	%3 - %20
Many	>5	3	Medium	3-5 mm	3	Many	1	>% 20
			Coarse	6-10 mm	4			
			Very coarse	>10 mm	5			

Of the 120 soil columns, 80 were selected randomly for training and 40 for validation of the predicitons. Saturated hydraulic conductivity (K_s) was predicted by forward stepwise linear regression technique usingcodes of soil morphological properties given in Tables 2-8. Independent variables, which significantly ($P<0.05$) contributed to prediction of K_s were selected as predicting variables.

The accuracy of the developed model was evaluated using validation data set. The predicted K_s were compared with their corresponding measured values. The coefficient of determination (R^2), root mean square error, mean absolute error, and correlation coefficient between measured and predicted K_s-values were used as criteria for sucsess of the developed PTF.

Results and Discussion

Laboratory measured saturated hydraulic conductivity (K_s) values ranged from 2.76 and 0.0036 cmh^{-1} with a mean of 0.82 cmh^{-1} for training and 0.83 cm h^{-1} for validation data sets. Coefficient of variation (CV) was 79.7% for calibration and 80.3% for validation data set, indicating that validation and calibration data sets have similar distributions (Tables 9 and 10).

Greatest variation occurred for K_s and lowest for pH in physical and chemical properties of soils. These results agreed to those reported in literature (Mulla and McBratney 2002). Most of the soil properties exhibited medium variation, and this agreed to those reported by many different authors. Unexpectedly, soil textural components exhibited somehow greater variations than frequently reported values in the literature, and it was attributed that the study area is highly variable in topography and to that soils have been derived from alluvial and colluvial parent materials. Root size have greatest and structure type have lowest variation among soil morphological properties. The soils generally have a high clay content and have angular and subangular bolocky structure.

Table 9. Exploratory statistics of physical, chemical, and morphological properties of the calibration soils (N =80)

Soil properties	Maximum	Minimum	Mean	Std.Deviation	%VC
K_s, cm h^{-1}	2.25	0.0036	0.82	0.65	79.78
Sand, %	74.17	1.49	27.36	17.44	63.74
Silt, %	65.54	4.89	26.83	11.24	41.89
Clay, %	76.8	7.88	45.79	17.06	37.26
BD, gcm^{-3}	1.62	1.08	1.25	0.09	7.89
SSA, m^{2}g^{-1}	284.85	96.75	207.19	48.84	23.57
CEC, meg/100 g	73.85	31.58	55.74	8.07	14.48
COLE, %	9.8	4.5	8.14	1.49	18.30
FC, %	43	21	35.26	6.55	18.57
WP, %	31.0	9.0	22.93	6.32	27.52
pH	9.7	7	8.42	0.46	5.57
EC	0.48	0.01	0.13	0.09	73.1
ASI	0.589	0.19	0.49	0.04	9.05
SOM, %	7.12	0.40	4.09	1.23	30.23
$CaCO_3$, %	24.15	5.11	15.22	4.35	28.63
Structure Grade	4	1	2.03	1.02	50.27
Structure Type	6	2	4.58	0.83	18.25
Structure Size	4	1	2.82	0.95	33.68
Pore Size	5	1	2.43	1.38	56.84
Pore Quantity	3	1	1.85	0.76	41.33
Consistency	6	1	3.63	1.22	33.66
Plasticity	4	1	2.21	0.88	39.84
Stickiness	4	1	2.35	0.76	32.54
Root Size	4	1	1.33	0.70	53.40
Root Quantity	4	1	1.39	0.83	60.12
Mottles	3	1	1.09	0.32	29.96
Color	5	2	3.45	1.00	29.13

K_s: saturated hydraulic conductivity, ρ_b: Bulk Density, SSA: spesific surface area, CEC: cation exchange capasity, COLE:coefficient of linear extensibility, FC: field capacity, WP: wilting point, ASI: agregatte stability index, SOM: soil organic matter

Table 10. Exploratory statistics of physical, chemical, and morphological properties of the validation soils (N =40)

Soil properties	Maximum	Minimum	Mean	Std.Deviation	%VC
K_s, cmh^{-1}	2.71	0.0036	0.84	0.68	80.30
Sand, %	62.75	2.48	29.00	17.0	58.61
Silt, %	52.5	10.09	25.07	8.74	34.86
Clay, %	82.7	2.48	45.91	19.67	42.86
BD, gcm^{-3}	1.51	1.06	1.25	0.094	7.53
SSA, m^2g^{-1}	271.36	82.081	198.45	42.87	21.60
CEC, meg/100 g	70.86	21.8	54.09	8.81	16.29
COLE, %	9.8	4	8.22	1.53	18.62
FC, %	43	20	35.42	6.78	19.15
WP, %	31	8	23.32	6.91	29.61
pH	9.77	6.7	8.36	0.49	5.87
EC	0.47	0.01	0.13	0.08	73.0
ASI	0.57	0.42	0.49	0.02	3.96
SOM, %	7.98	0.94	4.21	1.42	33.45
$CaCO_3$, %	22.69	5.69	15.10	4.05	26.79
Structure Grade	4	1	2.07	1.03	49.83
Structure Type	6	2	4.47	0.92	20.59
Structure Size	4	1	2.85	1.06	37.25
Pore Size	5	1	2.4	1.32	54.96
Pore Quantity	3	1	1.87	0.81	43.31
Consistency	6	1	3.6	1.32	36.64
Plasticity	4	1	2.3	0.93	40.83
Stickiness	4	1	2.42	0.81	33.52
Root Size	4	1	1.15	0.57	49.76
Root Quantity	4	1	1.25	0.80	63.87
Mottles	2	1	1.05	0.22	20.75
Color	5	2	3.5	0.92	26.34

K_s: saturated hydraulic conductivity, ρ_b: bulk density, SSA: spesific surface area, CEC: cation exchange capasity, COLE: coefficient of linear extensibility, FC: field capacity, WP: wilting point, ASI: agregatte stability index, SOM: soil organic matter

The forward stepwise multiple linear regression was performed for developing a PTF that predicts K_s from soil morphological and parametric properties. Soil properties, which significiantly contributed the K_s prediction are shown in Table 11.

Table 11. Soil morphological properties contributed to K_S prediction significantly ($P \leq 0.05$)

Independent Variables					R^2	SSE
Stickiness					90.40	0.206
Stickiness	Structure-grade				93.24	0.174
Stickiness	Structure-grade	Pore-size			93.63	0.170
Stickiness	Structure-grade	Pore-size	Plasticity		93.98	0.167
Stickiness	Structure-grade	Pore-size	Plasticity	Pore-quantity	94.55	0.160

Greatest correlation occurred between K_s and Stickiness (Table 10). Stickness, structure grade, pore size, plasticity, and pore quantity contributed the K_s prediction significantly as shown by Eq (1).

$$K_s = 0.565 - 0.331x(\text{Stickiness}) + 0.184x(\text{Structure Grade}) + 0.0625 \text{ x } (\text{Pore Size}) + 0.182x(\text{Plasticity}) + 0.217 \text{ x } (\text{Pore Quantity}) \quad (1)$$

The Eq. (1) described 95% of the total variation in K_s. Eq.(1) was used with validation data to evaluate its prediction success using mean error (ME), root mean squared error (RMSE), and mean absolute error (MAE). The results were highly successful (MAE= 0.0042, RMSE = 0.203, MAE = 1.145). In addition, predicted and measured K_s values of validation data set were correlated and related to each other by a 1:1-line (Fig. 2). The results suggested that the Eq (1) was successfully predicted K_s in studied soils.

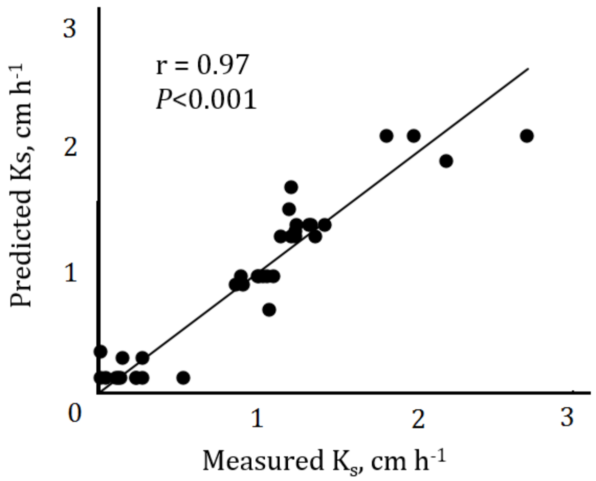

Figure 2. Correlation between measured and calculated K_s-values of validation data set

Effects of clay content on soilphysical and chemical properties have long been known. Besides clay content, clay type is an important factor,controlling many soil properties such as specific surface area, CEC, water hold capacity, COLE index, swelling, shrinking, plasticity, and stickiness. Swelling, stickiness, and plastisity are main soil properties controlled by amount and type of soil clay. Stickiness is greater in soils rich in high activity clays (montmorillonite and vermiculite). These clays are 2:1 type and they have high expansion, adsorptivity, and water retention capacities. When these clays wet, they swell, resulting in decreased soil porosity and decreased water conductivity. In addition, soils rich in these clays can be compacted easily. It was reported in Rahman (2000) that 'The smectite mineral particles have a large specific surface area of up to 800 m^2 g^{-1} and have a high adsorptive capacity and can be compacted to give very low hydraulic conductivity (10^{-11} to 10^{-13} ms^{-1})'. Boivin et al. (2004) reported that swelling capacity of the soil increases with clay content, which is related to clay type, pore size, and moisture content.

Soil clay influence on the soil plasticity and soil stickiness are highly similar since the point of stickiness usually lies above the upper plastic limit on the moisture scale (Baver, 1956). Greater liquid limit, plastic limit, and surface activity are associated with soils having a greater quantity of clay particles (Mitchell, 1976). Soils containing a large quantity of expanding minerals generally have a high plasticity index. The liquid limit and the plastic limit reflect the consistency of the soilstructure. All other factors being equal, more plastic clays should have lower hydraulic conductivity (Day and Daniel, 1985; Mesri and Olson, 1971). The results of this study showed that, expectedly, soil stickiness had a significantly negative correlation with K_s. Soil consistency and structural parameters can serve as predictors of soil water retention because those parameters are related to soil basic properties that affect soil hydraulic properties (Rawls and Pachepsky, 2002).

According to Pachepsky et al. (2006), typical PTF inputs such as soil texture, bulk density, or organic carbon content, are related to the pore structure in a broad sense, but are not sufficient to fully characterize the pore structure of a specific soil. Soil structure type affects the soil structure grade. The absence of large structural units might mean absence of large pores and a wide pore-size distribution that should provide relatively large water retention near field capacity (Pachepsky et al., 2006). Majority of the soil samples (87%) used in this study had medium to strong angular and subangular blocky structure and a significant positive correlation occurred between soil structure type and K_s in our study, agreed to those reported by Mckeagu et al. (1982).

Soil clay content and clay type have a considerable influence on soil structure and pore geometry, which in turn affects K_s. Type, size, spatial orientation, and arrangement of soil pores have significant influence on K_s (Beven and German, 1982). Increased macro porosity in soil structure results in an increased soil hydraulic conductivity (Ahuja et al. 1985). Large and continuous pores have far grater water conductivity than smaller pores. Soils with high clay content generally have lower K_s than sandy soils. Sandy soils generally have greater bulk density and lower total porosity than clayey soils. However, pore-size distribution in sandy soil favors large pores, which promote K_s (Soil Survey Staff, 1993). The results of Keren and Singer (1988) and

Kosmas and Moustakas (1990) suggest that there may be interactions between the dispersion of clays and the swelling processes and their impact on pore size and continuity, and thus on K_s.

Water flow is faster in inter-granular pores in granularly structured soils. In addition, preferential flow is common in saturated structured soils. Presence of root channels and earthworm channels enhances saturated water flow in soils. Water flow in sandy soils is generally higher; however, comparable high K_s values were reported in structured clay soils due to presence of structural features such as cracks, earthworn channels and root channels and large inter-aggregate openings. Anderson and Bouma (1973) reported that excellent estimates of K_s were obtained when void sizes have been measured directly.

A significant positive correlation between observed inter-aggregate pore quantity and K_s was obtained (Eq.1). In this study, amount of the voids (interstitial, tubular, dendritic, irregular, vasicular in shape) between soil aggregates, which detecteable by naked eye, were considered as structural pores.These pores, mainly located between aggregates (inter-aggregate),rapidly conduct waterin saturated soils. However, intra-aggregate pores are not as important as inter-aggregate pores in K_s since water flow very slowly in narrow intra-aggregate pores. In general, total porosity increases with soil clay content as there are many pores between fine soil particles, while most of these pores are small in size and hold water tidily.

Saturated hydraulic conductivity depends on many soils parametric (clay, sand, silt, organic matter contents; specific surface area, cation exchange capacity, soil sodicity and electrolyte concentration of soil solution; and morphological properties such as soil structure, soil porosity and pore geometry, macrospores and roots, and consistency). In K_s modeling studies, soil parametric variables are generally preferred. However, it's well known that a slight change in soil structure has a considerable impact on K_s since K_s is strongly controlled by soil pores and their geometry and their orientations in soils. In this study, significant relations between K_s and soil morphological properties of stickiness, structure grade, structural pore-size, plasticity, and pore quantity were obtained and it was clearly shown that these variables could successfully be used in prediction of K_s in paddy and adjacent grassland soils by forward stepwise multiple regression analysis. The results were highly promising, suggesting that soil morphological properties can be used besides soil parametric variables in K_s modeling studies. Further studies are needed across different soil and management conditions to adapt use of soil morphology in K_s modeling.

Acknowledgements

The authors thank Scientific and Technological Council of Turkey (TUBİTAK) for financial support under the grant of the BİDEP (2233) and Cankırı Karatekin University for partially supporting this study under the BAP (2012/08). We grant of thank Dr. Ali ECE for his assistance in soil sampling. The authors are indebted to Prof. Evgeny SHEIN for his kind technical advice.

References

Abbaspour, K.C., Moon, D.E., 1992. Relationships between conventional field information and some soil properties measured in the laboratory. *Geoderma* 55(1-2): 119-140.

Ahuja, L. R., Naney, J. W., Williams, R. D.1985. Estimating soil water characteristics from simpler properties or limited data. *Soil Science Society of America Journal* 49: 1100–1105.

Anderson, J.L., Bouma, J., 1973. Relationships between saturated hydraulic conductivity and morphometric data of an argillic horizon. *Soil Science Society of American Proceedings* 37: 408– 413.

Anonymous, 2011. Çankırı İl Çevre Durum Raporu. Çankırı Valiliği Çevre ve Şehircilik İl Müdürlüğü. Available at : http://www.csb.gov.tr/turkce/dosya/ced/icdr2011/cankiri_icdr2011.pdf

Anonymous, 2014. Maps of World. Available at: http://www.mapsofworld.com

Baver, LD. 1956. Soil Physics. Third Edition. John Willey& Sons, Inc., New York.

Beven, K., Germann, P. 1982. Macropores and water flow in soils. *Water Resources Research* 18: 1311-1325.

Blake, G.R., Hartge, K.H., 1986. Bulk density. In: Methods of soil analysis. Klute, A., (Ed.), Part 1, 2nd edition pp. 363-373. American Society of Agronomy, Madison, WI.

Boivin, P., Garnier, P.P., Tessier, D., 2004. Relationship between clay content, clay type and shrinkage properties of soil samples. *Soil Science Society of America Journal* 68(4): 1145-1153.

Bouma, J., 1992. Effect of Soil Structure, Tillage, and Aggregation upon Soil Hydraulic Properties. Book Chapter. Interacting Processes in Soil Science (Ed; RJ Wagenet, P Baveye, BA Stewart).

Carter, D.L., Mortland, M.M., Kemper, W.D.1986. Specific Surface. Book Chapter 16. Eprints.nwisrl.ars.usda.gov.

Day, S. R., Daniel, D. E. 1985. Hydraulic conductivity of two prototype clay liners. *Journal of Geotechnical Engineering* 111: 957-970.

Field, J.A., Parker, J.C., Powell., N.L., 1984. Comparison of field and laboratory-measured and predicted hydraulic properties of soil with macropores. *Soil Science* 138: 385–396.

Gee, G.W., Bauder, J.W., 1986. Particle-size analysis. p. 383–411. In A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Manag. 9. ASA and SSSA, Madison, WI.

Jurry, W.A., Gardner, W.R., Gardner, W.H., 1991. Soil Physics. 5th. Ed. W, NY, 328 p.

Kemper, W. D., Rosenau, R. C., 1986. Aggregate stability and size distribution. In: Methods of soil analysis. Klute, A., (Ed.), Part 1, 2nd edition pp. 425-442. American Society of Agronomy, Madison, WI.

Keng, J.C., Lin, C.S., 1982. A two-line approximation of hydraulic conductivity for structured soils. *Canadian Agricultural Engineering* 24: 77–80.

Keren, R., Singer, M.J., 1988. Effect of low electrolyte concentration on hydraulic conductivity of Na/Ca-montmorillonite-sand system. *Soil Science Society of America Journal* 52: 368-373.

Klute, A. 1986. Methods of soil analysis, Part 1: Physical and mineralogical methods, 2nd edition, American Society of Agronomy, Madison, WI. 1188 p.

Klute, A., Dirksen, C., 1986. Hydraulic conductivity and diffusivity: laboratory methods. In: Methods of soil analysis. Klute, A., (Ed.), Part 1, 2nd edition pp. 687-734. American Society of Agronomy, Madison, WI.

Kosmas, C., Moustakas, N., 1990. Hydraulic conductivity and leaching of an organic saline-sodic soil. *Geoderma* 46: 363-370.

Lilly, A., Nemes, A., Rawls, W.J., Pachepsky, Ya.A., 2008. Probabilistic approach to the identification of input variables to estimate hydraulic conductivity. *Soil Science Society of America Journal* 72: 16–24.

Lin, H.S., McInnes, K.J., Wilding, L.P., Hallmark, C.T., 1999. Effects of soil morphology on hydraulic properties: II. Hydraulic pedotransfer functions. *Soil Science Society of America Journal* 63(4): 955-961.

McKeague, J.A., Wang, C., Topp, G.C., 1982. Estimating saturated hydraulic conductivity from soil morphology. Soil *Science Society of America Journal* 46: 1239–1244.

McKenzie, N.J., Jacquier, D.W., Ashton, L.J., Cresswell, H.P., 2000. Estimation of Soil Properties Using the Atlas of Australian Soils. Technical Report 11/00, CSIRO Land and Water, Canberra ACT.

Mesri, G., Olson, R. E., 1971. Mechanisms controlling the permeability of clays. *Clays and Clay Minerals* 19(3): 151-158.

Mitchell, J. K. 1976. Fundamentals of Soil Behavior. Series in Geotechnical Engineering, John Wiley & Sons, 422.

Mulla, D.J., McBratney, A.B., 2002. Soil spatial variability. In A.W. Warrick (Ed.), Soil Physics Companion (pp. 343-373). CRC Press, Boca Raton, FL.

Pachepsky, Y.A, Rawls, W.J, Lin, H.S., 2006. Hydropedology and pedotransfer functions. *Geoderma* 131(3-4): 308–316.

Pachepsky, Y., Nez, D.G., Lilly, A., Nemes, A., 2008. Promises of hydropedology. *CAB Reviews: Perspectives in Agriculture, Veterinary Science, Nutrition and Natural Resources* 3 (040): 1-19.

Page, A.L., Miller, R.H., Keeney, D.R., 1982. Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties Second Edition. SSSA Publisher, Madison, Wisconsin USA.

Rahman, F. 2000. Hydraulic conductivity and chemical compatibility of some Victorian soils used as liners for waste containment. Ph.D Thesis. School of the Built Environment. Victoria University of Technology. Melbourne, Australia.

Rawls, W.J., Pachepsky, Ya. A., 2002. Soil consistence and structure as predictors of water retention. *Soil Science Society of America Journal* 66: 1115–1126.

Schafer, W.M., Singer, M.J., 1976. A new method of measuring shrink -swell potential using soil pastes. *Soil Science Society of America Journal* 40: 805-806.

Sharma, M., Uehara, G., 1968. Influence of soil structure on water relations in low humic latosols: I. Water retention. *Soil Science Society of America Journal* 32: 765-770.

Soil Survey Staff. 1993. Soil Survey Manuel. United States Department of Agriculture Handbook No: 18, USDA, Washington.

USDA-NRCS, 2002. Version 2.0. National Soil Survey Center Natural Resources Conservation Service U.S. Department of Agriculture, Lincoln, Nebraska.

Wösten, J.H.M., Pachepsky, Y.A., Rawls, W.J., 2001. Pedotranfer functions: Bridging the gap between available basic soil data and missing soil hydraulic characteristics. *Journal of Hydrology* 251: 123–150.

Eurasian J Soil Sci 2016, 5 (1) 39 - 46

Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

Seed germination and seedling growth of bean (*Phaseolus vulgaris*) as influenced by magnetized saline water

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Article Info

Received : 13.04.2015
Accepted : 18.08.2015

Abstract

Magnetized water is considered eco-friendly physical presowing seed germination.The aim of this study was to evaluate the effects of magnetized watertreatments on bean (*Phaseolus vulgaris*) germination under saline conditions (0, 25, 50, 75, 100 and 120 mM NaCl). This experiment was performed as factorial in a complete randomized design (CRD) with three replications. The results revealed that the roots and shoots length, fresh and dry weight of shoots and roots and roots to shoots ratio, chlorophyll content index, water uptake, tissue water contentwere significantly affected by magnetized water.Irrigation with magnetized water significantly increased the physiologic factors such as germination percentage and index, vigor index and salt tolerance index, compared to untreated control seeds.Mean germination time and parameters T_1, T_{10}, T_{25}, $T_{50}$and T_{90} (required time for germination of one to 90 percent of seeds) were reduced significantly in all magnetized water treated plants in comparison to control.The results also demonstrated that magnetized water was conducive to promote the growth of bean seedlings under saline conditions.

Keywords: Chlorophyll content index, physiological parameters, salinity, vigor index

Introduction

Magnetic and electromagnetic treatments arebeingused in agriculture, as a noninvasive technique, to improve the germination of seeds and increase crops and yields (Martinez et al., 2009). A safe method for enhancing seed germination includes the reasonable use of chemical additives and substitution by appropriate physical treatment. In recent years, there are growing concerns of eco-friendly physical presowing seed treatments by newly developed methods such as magnetic field (MF) (Jamil et al., 2012). The effects of different MFs varies depending on the age during exposure as well as the induction of the field (magnetic field strength), period of exposure and environmental conditions such as temperature, humidity, etc. (Pang and Dang, 2008).

In the beginning of 1980s, Fujio Shimazaki, a Japanese researcher, reveal that some physical andchemical properties of water changed when it pass through MF; hecalled the passed water through MF, "magnetized water" (MW) which lead to special functions (Cai et al., 2009); however,many researchers reported that MW could promote germination and early growth (Qiuet al., 2011). Hilal and Hilal (2000) showed that comparision between MF and MW in different treatment seeds. Magneticfieldtreatments had doubled germination compared to MW ones on pepper seeds; however, tomato and cucumber seeds had responded more to MW rather than MF. Soaking seeds is a crucial factor to enable MF effects because of the water's role

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e-ISSN: 2147-4249 DOI: http://dx.doi.org/10.18393/ejss.2016.1.039-046

as MF mediator.Both MW and MF treatments have succeeded to given the highest germination percentage for cucumber cousing 86% increase over control (Hilal and Hilal, 2000). Magnetization of both seeds and water has come to be the most effective treatment in seed germination as compared with control (Selim, 2008). Function of MW depends on induction, types (dynamicorstatic), length, andconfigurations of homogeneous and heterogeneous of MF, numbers of repetitions of the process (flow revalations), water flowpressure, material of pipeand composition of dissolved salts (Vashisth and Nagarajan, 2010). Dynamic and static MW treatment improved rice seed germination and significant differences compared to control were only obtained for the dynamic method (Carbonell et al., 2000).

Extensive research has revealed that the effects of MW depend on a wide range of factors including specialenvironmental conditions such as temperature, humidity, and salinity (Gutzeit, 2001). Despite, MW improved crop resistance in the alkali and salt conditions (Dandan and Yan, 2013) and the mechanism of its effects highly depending on the concentration and composition of the dissolved salts (Ibrahim Mohamed and Mohsen Ebead, 2013), there is a relatively little scientific literature on germination mechanism of MW in saline condition. The present study was conducted to analyze the effects of MW, with six different salt concentrations, on bean germination and seedling growth parameters.

Material and Methods

The magnetized water was produced byan electromagnetic field generator (Water Clear Environment Technologies Company-SB 150) with signal cable is changed any where from 2000 to 24000 times a second produces an oscillating and complex modulating frequency wave from the produces an inaudible sonic impluse magnetic field strength (0.05-0.5mT).

Seed germination tests were conducted as a factorial experiment arranged in a complete randomized design (CRD) with three replications. Seeds were sterilized by sodium hypochlorite and distilled water, placed in petri dishes on a wet filter paper. Each treatment category (100 seeds) was irrigated with 20 ml of MW and non MW (0, 25, 50, 75, 100 and 120mM NaCl). Seeds germinated in an incubator at 25°C and a relative humidity of 50% (ISTA, 2004). Water uptake percentage (WUP) was recorded for 15 hours calculated by the formula 1 according to Mujeeb-ur-Rahman et al. (2008).

$$WUP = \frac{W_2 - W_1}{W_1} \times 100 \qquad [1]$$

Where W_1= initial weight of seed, and W_2= weight of seed after absorbing water in a particular time. The pot experiment was conducted with the aforementioned treatments "MW and non MWin a cultivated media box filled with peatmoss and perlite (1:1). For each treatment category, 100 seeds was sown at the depth of 2cm with three replications. The boxes were placed in green house at 25°C. After 2 weeks, plants harvested and then the growth paramerets, including the roots and shoots length (RL and SL), fresh and dry weight of shoots and roots (FWR, DWR, FWS and DWS) and roots to shoots ratio (R/S) were measured with scale 0.001 g.

Dry weights were determined after samples were oven-dried at 70°C for 48 h. Chlorophyll content index (CCI) of fresh seedling leaves was determined using a portable chlorophyll content meter (CCM-200, OPTI-SCIENCES, Tyngsboro, MA,USA) based on absorbance measurements at 660 and 940 nm (Markwell et al., 1995).

The tissue water content (TWC) was calculated based on equation 2 (Black and Pritchard, 2002).

$$TWC = \frac{Fresh\,weight - Dry\,weight}{Fresh\,weight} \times 100 \qquad [2]$$

The physiological factors consisted of germination percentage (GP), germination index (GI), vigor index (VI), salt tolerance index (STI), required time for germination of one to 90 percent of seeds (parameters T_1, T_{10}, T_{25}, T_{50}, and T_{90}) and mean germination time (MGT) were calculated based on equations 3 and 4.

$$GP = \frac{n}{N} \times 100 \qquad [3]$$

$$GI = \sum \frac{(n_i \times T_i)}{N} \qquad [4]$$

Where n represents the number of newly germinating seeds, and N total number of seeds; $n_i$is number of seeds germinated at day T_i and T_i is number of days after starting the test (Panwar and Bhardwaj, 2005). Seedling vigor index was calculated based on Abdul-Baki and Anderson (1973).

$$VI(I) = GP\% \times Seedling\ Lenght\,(Root + Shoot) \quad [5]$$

$$VI(II) = GP\% \times Seedling\ Dry\ Weight\,(Root + Shoot) \quad [6]$$

$$STI = \frac{Seedling\ Dry\ Weight\,(Root + Shoot)\,atS_x}{Seedling\ Dry\ Weight\,(Root + Shoot)\,atS_0} \quad [7]$$

Where, $S_o$represents control and S_x a given salt concentration.The rate of germination was assessed by determining the required time for germination of 1, 10, 25, 50, 75 and 90% of seeds (T_1, T_{10} ,T_{25} ,T_{50}, T_{90}) (Carbonell et al., 2008) and the mean time germinating (MTG) calculated according to the equation 8 (Panwar and Bhardwaj, 2005).

$$MTG = \sum(\frac{n_i}{T_i} \times 100) \quad [8]$$

Where, T_i is the number of days after starting the experiment and n_i represent the total number of germinated seeds on the i^{th} day.

Statistical Analysis

ANOVA test was used for analyzing the data by using Minitab software at 5% probality level.

Results and Discussion

Analysis of variance of bean seed germination parameters are presented in Tables 1 and 2, and Figures 1 and 2.

Table 1. Analysis of variance for growth and developmental parameters of corn under different salinity levels and magnetized water regimes; RL and SL (roots and shoots length, FWR, DWR, FWS, DWS (fresh and dry weight of shoots and roots), R/S (roots to shoots ratio), TWC (tissue water content), WUP (water uptake percentage, WT (water treatment: magnetized and non-magnetized) and EC (electrical conductivity).

Source	df	RL	SL	FWR	DWR	FWS	DWS
WT	1	273.903**	110.600**	8.107**	0.088**	6.003**	0.046**
EC	5	102.170**	42.357**	0.831**	0.008**	2.276**	0.015**
WT*EC	5	3.294**	6.736**	0.259**	0.003**	0.374**	0.002**
Source	df	FWP	DWP	R_f/S_f	R_d/S_d	TWC	WUP
WT	1	28.062**	0.260**	0.968**	0.773**	1189.53**	785.401**
EC	5	5.850**	0.045**	0.006*	0.012*	431.22**	252.516**
WT*EC	5	1.029**	0.008**	0.173**	0.038**	12.12**	10.528**

** and *: significant at *P=0.01*, and *P=0.05*, respectively; *df*: degree of freedom.

Table 2. Analysis of variance for corn physiological parameters as effected by magnetized water regimes and salinity; CCI (chlorophyll content index), GP (germination percentage), GI (germination index), VI (vigor index), STI (salt tolerance index), MTG (mean time generation), T_1,T_{10},T_{25},T_{50}, T_{75},T_{90} (required time for germination of seeds from one to 90%), WT (water treatment: magnetized and non-magnetized) and EC (electrical conductivity).

Source	df	CCI	GP	GI	VI(I)	VI(II)	STI
WT	1	312.111**	1133.44**	6.996**	4489172**	1470.340**	1.046**
EC	5	97.019**	1178.24**	8.004**	2010007**	416.450**	0.332**
WT*EC	5	4.208**	27.78**	0.402**	144379**	57.490**	0.056**
Source	df	MTG	T1	T10	T25	T50	T90-T10
WT	1	18.431**	20.026**	6.003**	20.25**	8.028**	4.694**
EC	5	1.454**	1.447**	2.306**	2.583**	0.628ns	10.094**
WT*EC	5	0.347**	0.187**	0.415*	1.117**	0.494ns	0.228ns

**, * and, ns: significant at *P=0.01, P=0.05* and no significant, respectively; *df*: degree of freedom.

Growth parameters

Analysis of variance of the growth parameters including roots and shoots lenght, fresh and dry weight of roots and shoots, roots to shoots ratio, tissue water content and water uptake percentage exposed to magnetized water are shown in Table 1 and Figure 1.

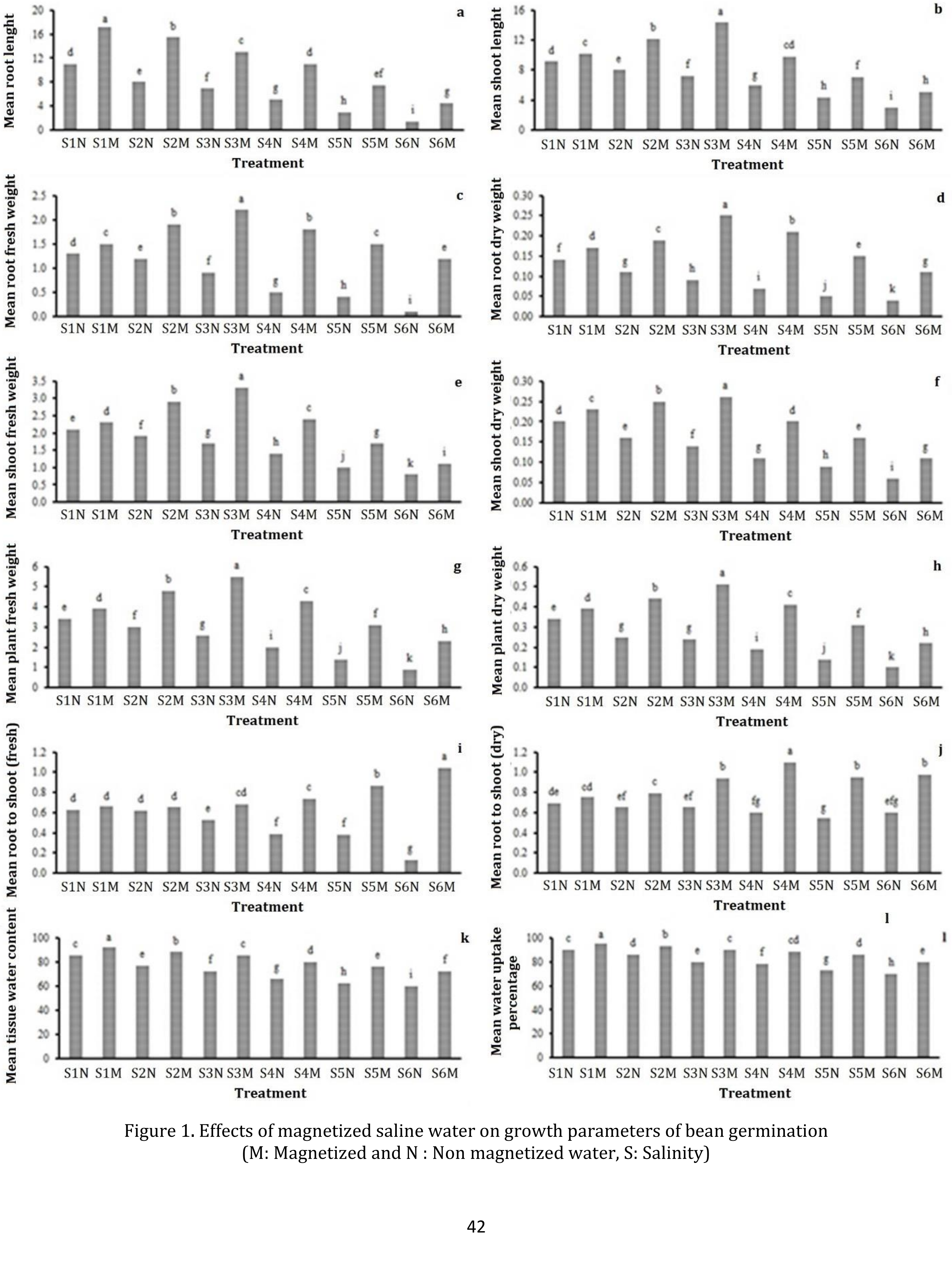

Figure 1. Effects of magnetized saline water on growth parameters of bean germination
(M: Magnetized and N : Non magnetized water, S: Salinity)

Roots and shoots length

Root length provides an important clue to the response of plants to salinity stress. Analysis of variance in table 1 showed that shoot and root length of the magnetized saline water treated seedlings were higher than seedlings treated by saline water. Salt stress inhibited the growth of root more than shoot in all treatments. Root and shoot length decreased by increasing NaCl concentration. A marked reduction in RL and SL of non-MW treatments was observed following salt stress (Figure 1a,b). The result showed that RL and SL of the magnetized saline water treatments siginificantly were higher than control by 69 and 40%, respectively (Table1). Mahmood and Usman (2014) reported similar results on maize seed germination, as in their experiment, magnetized saline water significantly increased SL up to 10.24% compared to saline water.

Roots and shoots dry and fresh weight

Salt stress decreased FWR, DWR, FWS and DWS in non-MW treatments (Figure 1c,d,e,f). Reduction in weight can be due to proportional increase in Na^+ concentration which disturbs ionic and osmotic balances; however, dry weights were not much affected compared to the fresh weights. A significant increase in FWR, DWR, FWS and DWSoccured in the magnetized saline water treated seedlings as compared to the control (Table 1). There were significant differences between treatments for roots to shoots ratio (R/S) (Table 1). As NaCl concentration increased, it unequally affected roots and shoots weight. The result of R/S represented that salt stress inhibited the growth of roots more than shoots in all non-MW treatments (Figure 1i,j). Other authors have reported similar findings (Jamil et al., 2006). As NaCl levels increased the ratio of roots to shoots dry weight remarkably decreased. Reduction of dry weights relatively depended on shoot or root lengths. Along with increase in NaCl concentration in magnetized saline water treatments, the R/S gradually increased (up to 75 mM NaCl) (Figure 1 i, j), then decreased; however, it was significantly higher than non-MW treatments.

Tissue water content (TWC)

Magnetized water increased TWC significantly in compairison with non-MW treatments (Table 1 and Figure 1k). Along with increase in the salinity intensity, Kang and Saltvett (2002) reported that the osmotic pressure leads to a reduction of water absorbance and inhibition cell division and differentiation;, which adversely affects metabolic and physiological processes, and this causes more delay in initiation of germination followed by prolonged seed germination duration, and ultimately reduces germination parameter and seedling growth. It seems that MW decreases injurious effects of salinity by increaseing water absorption.

Water uptake percentage

As NaCl concentration increased (up to 120 Mm) WUP decreased in all treatments (Figure 1l). Increase in salinity level decreased germination parameters and seedling growth which are directly related to external osmotic potential preventing water uptake. Bean seeds exposure to MW increased WUP significantly compaired to non-MW treatments (Table 1). The result are in agreement with other researchers, which indicates that MW treated seeds absorbed more water and absorbed it faster than untreated seeds (Kaya et al., 2006); moreover, results of this study are in agreement with findings which lettuce seeds exposure to static MF causes increase in water uptake rate (Reina et al., 2001). MF changes both osmotic pressure and ionic concentrations in the membrane angles, which regulates the water absorbance (Azharonok et al., 2009).

Physiological parameters

Analysis of variance of physiological factors included chlorophyll content index, germination percentage, germination index, vigor index, salt tolerance index, mean germination time and required time for germination of seeds from one to 90%, whichare shown in Table 2 and Figure 2.

Chlorophyll content index (CCI)

As NaCl levels increased, the CCI decreased remarkably (Figure 2a) due to enzymatic chlorophyll degradation (Xu et al., 2000). Magnetized saline water significantly increases CCI as compared to non-MW (Table 2). This result was in agreement with previous works as it has been reported that MW increased chlorophyll content of wheat, flax, and lentil (Qados and Hozayn, 2010) byincreasing the activity of the chlorophyll degrading enzyme: Chlorophyllase (Jamil et al., 2007).

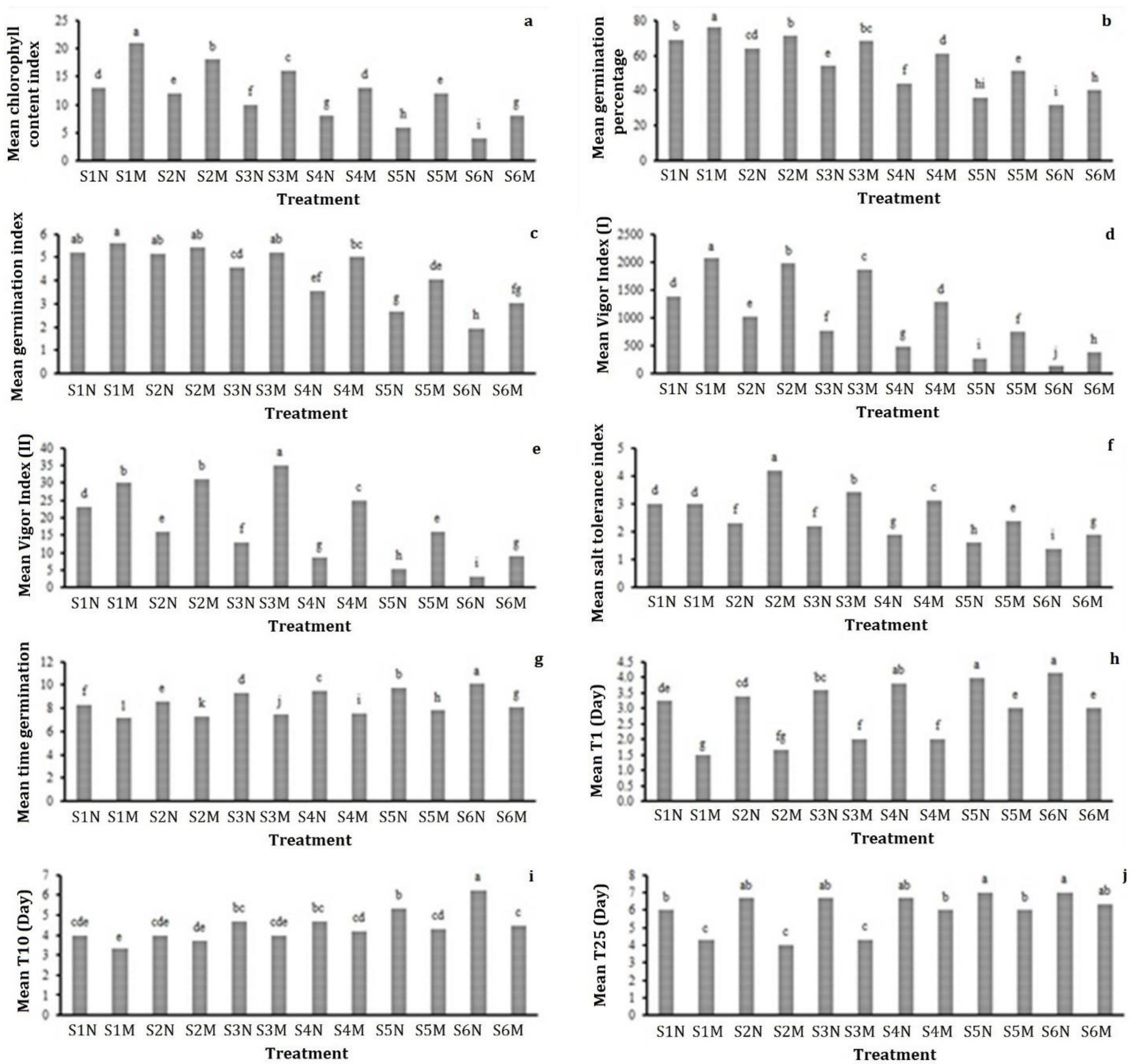

Figure 2. The bean physiological parameters as affected by magnetized water and salinity
(M: Magnetized and N : Non magnetized water, S: Salinity)

Germination Percentage(GP)

The analysis of variance showed magnetized saline water had significant effect on GP compared with non magnetized saline water (Table 2). Previous studies have shown that static and dynamic MW improved GP of rice seeds (Carbonell et al., 2000); moreover, it increased GP of pepper 35.8% over control (Ahamed et al., 2013). Increasing the salinity level increases the time required for germination. Some studies have reported that increasing the salt concentration delays the tomato seeds germination (Mohamed and Ebead, 2013).

Germination Index (GI)

Germination test showed magnetized saline water had a significant effect on GI in comparison to control seeds (Table 2). The result confirmed the study of Mahmood and Usman (2014), who indicated improvement of GI from 10.20 to 11.85 in seedlings treated with saline magnetized water in comparison with the control. The enhanced speed of seedgermination does suggest that magnetized water hasacquired some structural changes; perhaps promotingwater flow and bioactive molecules availability.

Vigor index (VI)

Vigor Index (I) values based on seedling length and GP showed a trend similar to seedling shoots and roots length in non-MW treated seedlings. In magnetized saline water treatments, as NaCl levels increased, the VI(I) gradually decreased (Figure 2d); however, it was significantly higher than non-MW treatments. MW improved VI(II) values based on seedling dry weight and GP (Table 2). Along with increase in NaCl levels, VI(II) increased (up to 50 Mm NaCl) in all magnetized saline water treatments, then decreasded (Figures 1 and 2); however, it was significantly higher than non-MW treatments (Table 2).

Salt tolerance index (STI)

At different levels of NaCl, STI was significantly different and decreased with increasing in salinity intensity (Figure 2f). The magnetized saline water had significant effect on increasing STI in comparison to control seeds (Table 2). This results were in agreement with the findings of Dandan and Yan (2013) who indicated that applications of magnetically saline water increased STI of wheat and guinea grass.

Mean time germination (MTG)

Magnetized saline water treatment had significantly lower MTG than the control treatments (Table 2 and Figure 2g). Results are in agreement with the germination data obtained by Mahmood and Usman (2014) that magnetized saline water reduced MTG from 9.15 to 8.73 and germination completed two to three days earlier than control. Time parameters (T_1 ,T_{10} ,T_{25} , T_{50}, and T_{90}) in magnetized saline water treatments significantly were lower than control (Table2), indicated less time required for seed germination, and germination speed is higher. Parameters T_1 and T_{10} are related to the beginning of germination, this study represents a progress in germination and a reduction in the induction phase in most of the magnetized saline water treatments applied.

Conclusion

Results of the current study revealed the positive and significant impacts of magnetic water on physiologic factors, and growth and development parameters of bean (*Phaseolus vulgaris*) comparison with the control. The stimulatory effect of magnetic water on the growth in this research may be due to the increase in roots and shoots growth. Therefore, as a simple and safe method, irrigation with magnetic water can be used to improve plant growth and water use efficiency. The results also demonstrated that magnetized water increased the bean seedling tolerance under salinity conditions. Generally, using magnetic water treatment could be a promising technique for agricultural improvements but extensive research is required on different crops.

References

Abdul-Baki, A.A., Anderson, J.D., 1973. Vigor determination in soybean by multiple criteria. *Crop Science* 13: 630-633.

Ahamed, M.E.M., Elzaawely, A.A., Bayoumi, Y.A., 2013. Effect of magnetic field on seed germination, growth and yield of sweet pepper *(Capsicum annuum* L.). *Asian Journal of Crop Science* 5: 286-294

Azharonok, V.V., Goncharik, S.V., Filatova, I.I., Shik, A.S., Antonyuk, A.S., 2009. The effect of the high frequency electromagnetic treatment of the sowing material for legumes on their sowing quality and productivity. *Surface Engineering and Applied Electrochemistry* 45: 317-327.

Black, M., Pritchard, H., 2002. Desiccation and survival in plants drying without dying. New York: CABI publishing.

Cai, R., Yang, H., He, J., Zhu, W., 2009. The effects of magnetic fields on water molecular hydrogen bonds. *Journal of Molecular Structure* 938: 15–19.

Carbonell, M.V., Martinez, E., Amaya, J.M., 2000. Stimulation of germination in rice *(Oriza sativa* L.) by a static magnetic field. *Electromagnetic Biology and Medicine* 19: 121-128.

Carbonell, M.V., Martinez, E., Florez, M., Maqueda, R., Lopez-Pintor, A., Amaya, J.M., 2008. Magnetic field treatments improve germination and seedling growth in *Festuca arundinacea* Schreb and *Loliumperenne* L. *Seed Science and Technology* 36: 31-37.

Dandan, L., Yan, S., 2013. Effects of magnetized saline on growth and development of winter wheat seedlings. *Advance Journal of Food Science and Technology* 5(12): 1596-1599.

Gutzeit, H.O., 2001. Biological effects of ELF-EMF enhanced stress response: new insights and new questions. *Electro- and Magnetobiology* 20(1): 15-26.

Hilal, M.H., Hilal, M.M., 2000. Application of magnetic technologies in desert agriculture: I-Seed germination and seedling emergence of some crops in a saline calcareous soil. *Egyptian Journal of Soil Science* 40(3): 413-423.

Ibrahim Mohamed, A., Mohsen Ebead, B., 2013. Effect of irrigation with magnetically treated water on faba bean growth and composition. *International Journal of Agricultural Policy and Research* 1(2): 24-40.

ISTA., 2004. International Rules for Seed Testing. International Seed Testing Association. Zurich.

Jamil, M., Lee, D.B., Jung, K.Y., Ashraf, M., Lee, S.C., Rha, E.S., 2006. Effect of salt (NaCl) stress on germination and early seedling growth of four vegetables. *Journal of Central European Agriculture* 7(2): 273-282.

Jamil, M., Rehman, S., Lee, K.J., Kim, J.M., Kim, H.S., Rha, E.S., 2007. Salinity reduced growth PS II photochemistry and chlorophyll content in radish. *Scientia Agricola* 64: 1-10.

Jamil, Y., Haq, Z., Iqbal, M., Jamil, T., Amin, N., 2012. Enhancement in growth and yield of mushroom (*Pleurotus ostreatus*) using magnetic field treatment. *International Agrophysics* 26 (4): 375–380.

Kang, H.M., Saltveit, M.E., 2002. Chilling tolerance of maize, cucumber and rice seedlings leaves and roots are differently affected by salicylic acid. *Physiologia Plantarum* 115: 571–576.

Kaya, M.D., Okcu, G., Atak, M., 2006. Seed treatments to overcome salt and drought stress during germination in sunflower (*Helianthus annuus* L.). *European Journal of Agronomy* 24: 291-295.

Mahmood, S., Usman, M., 2014. Consequences of magnetized water application on maize seed emergence in sand culture. *Journal of Agricultural Science and Technology* 16: 47-55.

Markwell, J., Osterman, J.C., Mitchell, J.L., 1995. Calibration of the Minolta SPAD-502 leaf chlorophyll meter. *Photosynthesis Research* 46: 467–472.

Martinez, E., Carbonell, M.V., Flórez, M., Amaya, J.M., Maqueda, R., 2009. Germination of tomato seeds (*Lycopersicon esculentum*L.) under magnetic field. *International Agrophysics* 23: 45-49.

Mohamed, A.I., Ebead, B.M., 2013. Effect of magnetic treated irrigation water on salt removal from a sandy soil and on the availability of certain nutrients. *International Journal of Engineering*2(2): 2305-8269.

Mujeeb-ur-Rahman, U.A.S., Mohammad, Z., Shereen, G., 2008. Effects of NaCl Salinity on Wheat (*Triticum aestivum* L.) Cultivars. *World Journal of Agricultural Sciences* 4(3): 398-403.

Pang, X.F., Deng, B., 2008. The changes of macroscopic features and microscopic structures of water under influence of magnetic field. *Physica B: Condensed Matter* 403: 3571–3577.

Panwar, P., Bhardwaj, S.D., 2005. Handbook of Practical Forestry. Agrobios, India.191p.

Qados, A., Hozayn, M., 2010. Magnetic water technology, a novel tool to increase growth, yield, and chemical constituents of Lentil (*Lens esculenta*) under greenhouse condition. *American-Eurasian Journal of Agricultural and Environmental Sciences* 7(4): 457-462.

Qiu, N.W., Tan, T.H., Dai, H., Shen, X., Han, R., Lin, Y., Ma, Z.Q., 2011. Biological effects of magnetized water on seed germination, seedling growth and physiological characteristics of wheat. *Plant Physiology Journal* 47(8): 803-810.

Reina, F.G., Pascual, L.A., Fundora, I.A., 2001. Influence of a stationary magnetic field on water relations in lettuce seeds. Part II: Experimental Results. *Bioelectromagnetics* 22: 596-602.

Selim, M.M., 2008. Application of magnetic technologies in correcting underground brackish water for irrigation in the arid and semi-arid ecosystem. The 3rd International Conference on Water Resources and Arid Environments.

Vashisth, A., Nagarajan, S., 2010. Effect on germination and early growth characteristics in sunflower (*Helianthus annuus*) seeds exposed to static magnetic field. *Journal of Plant Physiology* 167: 149–156.

Xu, X.M., Ye, H.C., Li, G.F., 2000. Progress in research of plant tolerance to saline stress. *Chinese Journal of Applied & Environmental Biology* 6(4): 379-387.

Eurasian J Soil Sci 2016, 5 (1) 47 - 52

Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

Response of earthworm's biomass and soil properties in different afforested type areas in the North Iran

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Article Info

Received : 14.03.2015
Accepted : 19.08.2015

Abstract

The study was conducted to evaluate the effects of spruce (*Picea abies*), alder (*Alnus subcordata*), and spruce with alder and maple (*Picea abies* with *Alnus Subcordata* and *Acer cappadocicum*) plantations on the soil properties and earthworm's abundance and biomass in the Lajim, north of Iran. Soil sampling with 50 × 50 cm samples to 50 cm depth in the studied stands was conducted in order to measure soil and earthworm abundance and biomass. Soil texture, C, N, pH, K, and P were measured in all samples in the laboratory. Earthworm's abundance was measured by handpicked and dried for 48 h at 60 °C and then the biomass was measured per unit area. The results showed that the percentage of organic carbon, N, and C/N ratio reached the climax and acidity had the lowest value in spruce stand, and K was significantly higher in alder stand. The maximum and minimum abundance of earthworms was observed in alder and spruce stands, respectively. The results of this study support the effects of plantations on soil properties, earthworm abundance, and biomass.

Keywords: Alder, earthworms, plantation, soil, spruce

Introduction

Because of forest degradation and increase in population, plantation is a vital issue for now and the future. Due to the reduction in forested areas and the shortages in obtaining sufficient amount of forest products, Iran has developed a new policy on forest management. The new policy promotes developing plantations to reduce the need for excessive and early harvesting of natural forest trees and strong dependence of wood industries on the natural forests' products (Asadi, 2001). Plantation with native and nonnative species besides the environmental and economic effects, has a significant impact on the fauna and flora variety of forest floor and physical and chemical properties of forest soil and subsequently can make adverse effects such as loss of biodiversity, the increase of soil acidity, and the reduction of soil micro and macro organisms especially earthworms in temperate climate (Razavi, 2010). Tree composition is one of the main factors determining the soil properties in the long term (Augusto et al., 2002). In addition, Tree species have different effects on soil including biological, chemical and physical properties (Antunes et al., 2008). The importance of soil organisms in the formation and maintenance of soil fertility and structure is not completely understood by soil scientists. Soil fauna is considered as the most important factor in assessing the soil health that its abundance and biomass are influenced by ecological conditions of the site (Moghimian and Kooch, 2013). Moreover, soil fauna is considered as the important component in forest ecosystems due its significant role on decomposing the organic matter and transporting the nutrients (Yang and Chen, 2009). Soil fauna such as earthworms accelerates the decomposition of organic matter and mineralization of nutrients (Rashid et al., 2014). The earthworms are introduced as soil ecosystem engineers because they affect the physical, chemical, and biological properties of the soil (Uchida et al., 2004) and also are one of the important components of soil formation, structure, and fertility (Edwards, 1994). Depending on the

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e-ISSN: 2147-4249
DOI: http://dx.doi.org/10.18393/ejss.2016.1.047-052

environment type and ecosystem function, earthworms are splitted into three classes of Litterfall, Litterfall and soil fauna and soil fauna. The effective degree of earthworms depends on their ecological group, size, soil parent material, and climate (Shen and Yang, 2008). Physical, chemical and biological features of soil are essential for soil fertility and ecological classification (Schoenholtz et al. 2000). Forest stand composition and density directly and indirectly affect soil organisms and inorganic soil fauna has significant promotes on humification and can influences the soil nutrients. Pure and mixed plantations have different effects on the soil particularly via their humus type, litterfall quality, and lignin content. Hence, evaluating the success of reforestation activities in rehabilitation and development of destroyed areas is necessary. The purpose of this study was to evaluate the effect of different plantation on many earthworms and soil physical and chemical properties.

Material and Methods

Site description

The present study was conducted in Lajim region located in Mazandaran province, north of Iran, with 965 meters above sea level, 20 percent of the general slope, and longitude 26.5° N and latitude 53.10° E (Figure 1). The studied stands include the species of spruce (*Picea abies*), alder (*Alnus subcordata*), spruce with alder and maple (*Picea abies* with *Alnus Subcordata* and *Acer cappadocicum*). The regional climate is humid-temperate on the basis of Domarten climate system. Soil characteristics include undeveloped soil, profile of AC to AC (B) C, pH of weak alkaline to neutral, parent limestone, clay soil, poor drainage, and rooting medium (Aqbash et al., 2002).

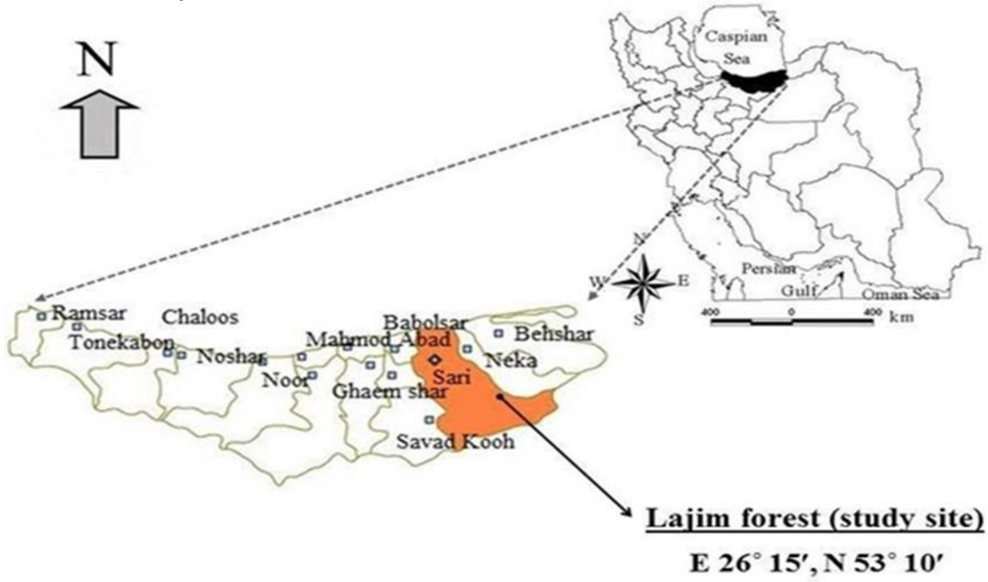

Figure 1. Study site location in the Mazandaran Province, Hyrcanian forests, in north of Iran.

Methods

Ten soil samples were randomly collected from each afforested type. Whole of soil earthworms were collected using plots of 50 × 50 cm to 50 cm depth. The samples transferred to lab then the earthworms in them were manually separated. Subsequently, the samples were dried for 48 h at 60° C in oven. Finally, after weighing the dried samples, earthworm biomass was measured per unit area (m^2). Soil samples were kept simultaneously with earthworms sampling and then conveyed to laboratory due to physico-chemical analysis.

Soil samples were air dried and crushed to pass a two-mm sieve before size fractionation and chemical analyses. Soil physical characteristics such as texture was measured by Hydrometer Method and chemical properties such as pH by potentiometric method using a pH meter, total N by Kjeldahl method, organic carbon by Walkey-Black method, K by flame photometry and P by spectrophotometer were measured (Ghazanshahi, 1997; Jafari Haghighi, 2003).

Statistical Analyses

The normality of the data was evaluated using Kolmograph-Smirnoff. ANOVA and Duncan's test were used to indicate differences and no differences in soil characteristics and the abundance and biomass of earthworms in the three studied stands. All data were submitted in SPSS 16.0.

Results

Earthworm's abundance and biomass

The results showed that earthworm abundance in alder stands was significantly more than that in other stands (Figure 2), while there was not fount a significant difference for earthworm biomass among all stands. The following analysis of earthworm biomass results indicated that despite the lack of significant differences between the different populations studied,the maximum amount of this attribute has been observed in the alder stand (Figure 3).

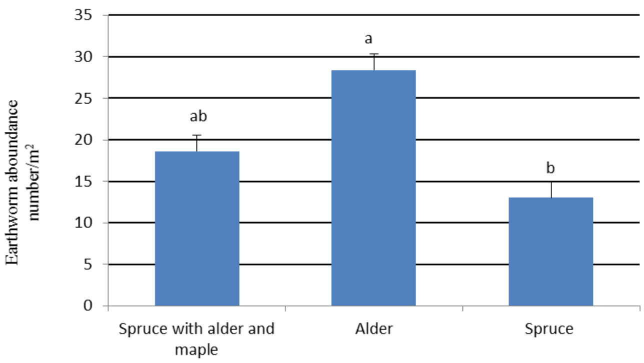

Figure 2. The mean comparison of earthworm aboundance in the stands. Different letters indicate significant differrence (P< 0.05).

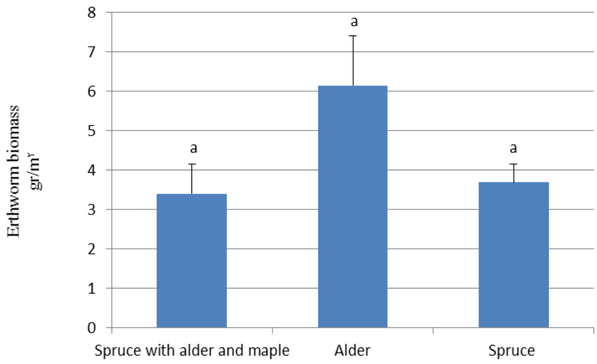

Figure 3. The mean comparison of earthworm biomass in the stands. Different letters indicate significant differrence (P< 0.05).

Physical and chemical characteristics of the soil

Soil analyses indicated the presence of significant differences among all stands with respect to sand, silt and clay contents (Table 1). The results indicated that pH of the soil under the spruce stand was significantly less than that other stands (Table 1).

Table 1. Soil chemical and physical properties in the three stands (mean ± standard error)

Property / Stand		Sand, %	Silt, %	Clay, %	Bulk density, gr/cm^2
Spruce		10±0.56 a	26.5±0.37 a	63.5± 0.24 c	1.37±0.03 a
Alder		8±0.6 b	24±0.57 b	68±0.61 b	1.07±0.02 c
Spruce with alder and maple		9±0.56 ab	17±0.6 c	74±0.56 a	1.26 ±0.05 b
pH	Organic C, %	Total N%	C/N	P, %	K, %
4.31±0.03 c	2.3±0.03 a	0.09±0.004 a	26.74±1.32 a	24.4±0.64 b	256.25±1.66 b
6.15±0.12 b	0.65±0.02 c	0.06±0.005 b	11.63±1.39 c	24±0.54 b	191.55±1.48 c
6.75±0.07 a	1.13±0.03 b	0.07±0.01 b	15.28±1.32 b	26.80±0.72 a	311.60±1.88 a

Different letters indicate significant differences (p<0/05) between different stands

ANOVA results indicated that the organic carbon was significantly higher among the stands so that the highest and lowest value were recorded in spruce and alder, respectively (Table 1). The results analyses indicated total N was significantly different among all stands (Table 1). Results of ANOVA showed that the C/N ratio in the stands studied showed a significant difference as the largest and lowest amount of it were in spruce and alder, respectively. Comparison of means of K in alder, spruce, and spruce with maple and alder stands orderly increased and significantly were different (Table 1). Also, comparison of means of P in the spruce with alder and maple stand was significantly more that in other two stands (Table 1). ANOVA results indicated the presence of significant differences among all stands with respect to bulk density of soil so that the maximum and minimum were recorded in spruce and alder, respectively (Table 1).

Discussion

Forest species can cause different changes in soil properties which due to species type, stand age, and biomass growth. Immediately after the plantation, small and gradual changes occur in physical, chemical and biological parameters of the soil. Influence of tree species on soil fertility is the result of interactions between trees and all components of the ecosystem and only the species effect varies on soil fertility in different areas (Augusto et al., 2002). Planting by fast-growing species is one of the most effective ways of demand for fuel, wood and biomass. Choosing a suitable species depends on its adaptability, survival ability, optimal growth, and toleration of positive or negative changes in the soil.

Physical and chemical properties

Significant differences in soil characteristics have shown among the stands. pH affects soil physical, chemical and biological properties and has an eminent compact on plantation performance through effects on the availability of essential nutrients and the solubility of toxic elements (Rhoades and Binkley, 1996). The minimum pH was observed in spruce stand which can be due to the slow decomposition of spruce litterfall. Different authors have shown that conifers reduce the soil pH and the litterfall layer of conifers is more thicker than that in hardwoods (Zhang et al., 2012). Augusto et al. (2002) showed that soil acidity in spruce stands were lower than that in beech and oak stand. Obviously, changes in soil acidity can lead to changes in nitrogen uptake, activity of soil microorganisms, and nutrient uptake by trees (Khanhasani et al., 2009). Organic carbon, as a functional and structural component of soil fertility, has been most commonly used in management of forest soils and site richness (Moghimian and Kooch, 2013). N plays an important role in the decomposition of organic material, so that a high concentration of N in the fresh litterfall can accelerate the decomposition process (Agren et al., 2001). C/N ratio is an indicator of humus and litterfall decomposition, and thereby weight and volume loss of litterfall can be measured (Taylor et al., 1989). The results indicate the amount of C and N in the soil are significantly different in the stands that spruce has reached the maximum of them. It appears that the accumulation of litterfall on the soil surface doesn't permit C to leave the soil. Nobakht et al. (2011) revealed that Norway spruce uptaked more N from the soil which it played an important role on increasing soil organic carbon. C/N ratio showed a significant difference among stands which the maximum amount of it was found in the spruce stand. High ratio of C/N as an index of slow litterfall decomposition shows that organic matter increases in soil surface horizons.

Cannel and Dewar (1993) concluded that coniferous species increase the density of surface litterfall and in other words, causes soil organic carbon. K and P in spruce with alder and maple were maximum which this value is due to rapid decomposition of alder and maple litterfall and then rapid decomposition of litterfall releases the high concentration of cations in the soil (Yugai, 1980). The soil texture of the the present study in all stands was clay. it indicates that changes in soil texture requires more time, while chemical properties have shown significant differences among different stands; i.e. chemical ch anges ocuure more rapid than physical change.

Characterized by the abundance and biomass of earthworms

The low abundance and biomass of earthworms in spruce stand can be due to high acidity, C/N ratio, and organic carbon in the spruce soil, while and high abundance and biomass of earthworms in alder stand are resulted from low C/N and organic carbon. Most species of earthworms play an important role on mineralization, soil structure, and constant of soil pH in 6-7 (Rashid et al., 2014). Brinkley (1994) concluded that the abundance of earthworms in pine and spruce stands was less than that in hardwood species. Lower C/N ratio makes small population size and biomass of earthworms (Rahmani and Saleh-Rastin, 2000). Nanoosi et al. (2008) found a significant and negative correlation between the abundance of earthworms and organic carbon. Moreover, Jalilvand and Kooch (2012) recorded that earthworm abundance and biomass had a strong relationship with N, C, and C/N ratio. Neirynck et al. (2000) showed that a low ratio of C/N in maple stand resulted in an increase of the earthworm population. Irannejad and Rahmani (2009) obtained a negative correlation between the density of the dry weight of earthworms and the soil bulk density. The research shows that the lowest bulk density of soil and the highest aboundence of earthworms belong to alder stand and also the high aboundence of earthworms in alder stand is attributed to low bulk density of the soil. Plantation by hardwoods and conifers affects physical and chemical properties of soil and thereby leads to significant changes in the abundance and biomass of earthworms. Therefore, choosing the appropriate species for plantation needs a comperhensive study about the soil properties and the species demands. According to findings of the present study, alder will be suggested as a suitable species for planattion, because it can increase soil fertility and the aboundence of earthworms.

References

Agren, G.I., Bosatta, E., Magill, A.H., 2001. Combining theory and experiment to understand effects of inorganic nitrogen on litter decomposition. *Oecologia* 128 (1): 94-98.

Antunes, S.C., Pereira, R., Sousa, J.P., Santas, M.C., Goncalvels, F., 2008. Spatial and temporal distribution of litter arthropods in different vegetation covers of Porto Santo Island (Madeira Archipelago, Portugal). *European Journal of Soil Biology* 44: 45-56.

Asadi, F., 2001. Evaluation of genetic diversity and between plant communities of different species of poplar. PhD thesis. Tarbiat Modares University, Iran. p.145

Augusto, L., Ranger, J., Binkley, D., Rothe, A., 2002. Impact of several common tree species of European temperate forests on soil fertility. *Annals of Forest Science* 59: 233-253.

Brinkley, D., 1994. The influence of tree species on forest soils: Processes and patterns. In: Mead, D.J., Cornforth, I.S. (Eds.), Proceedings of the Trees and Soil Workshop. 1994. Agronomy Society of New Zealand. Special Publication 10, Lincoln Univ. Press, Canterburg NZ, pp.1-33.

Cannel, M.G.R., Dewar, R.C., 1993. The carbon Sinks provided by plantation forests and their products in Britain. *Forestry* 68: 35-48.

Edwards, C.A., 1994. Earthworm Ecology. Boca Raton, FL: CRC Press. 456p.

Ghazanshahi, J., 1997. Plant and Soil Analysis. Tehran, Iran: Homa Publications. 311 p.

Irannejad, E. Rahmani, R., 2009. Evaluation of earthworm abundance and vertical distribution pattern in some forest types of Shast-Kolateh. *Journal of Forest and Wood Products* 62: 145–157

Jafari Haghighi M., 2003. Methods of soil sampling and analysis, Nedaye Zohi Publications, pp.236. (In Persian).

Jalilvand, H., Kooch, Y., 2012. Factors influence the distribution and abundance of earthworm communities in difference forest types (man – made and natural forests). *International Journal of Green and Herbal Chemistry* 1(1): 26-38.

Khanhasani, M., Sharifi, M., Tavakoli, A., 2009. Alteration in composition of understory plants in Pine plantations with different ages in Kermanshah province. *Iranian Journal of Forest and Poplar Research* 17(2): 188-199.

Moghimian, N., Kooch, Y., 2013. The effect some of physiographic factors and soil physico-chemical features of hornbeam forest ecosystem on earthworms biomass. *Journal of Wood and Forest Science and Technology* 20(2): 1-21.

Nano-osi, K.M., Joann, K.W., Sazelle, B., 2008. Earthworm abundance related to soil physicochemical and microbial properties in Accra, Ghana. *African Journal of Agricultural Research* 3(3): 186-194.

Neirynck, J., Mirtcheva, S., Sioen, G., Lust, N., 2000. Impact of Tilia platyphyllos Scop., Fraxinus excelsior L., Acer pseudoplatanus L., Quercus robur L. and Fagus sylvatica L. on earthworm biomass and physico-chemical properties of a loamy topsoil. *Forest Ecology and Management* 133(3): 275-286.

Nobakht, A., Pourmajidian, M., Hojjati, S.M., Fallah, A., 2011. A comparison of soil carbon sequestration in hardwood and softwood monocultures (Case study: Dehmian forest management plan, Mazindaran). *Iranian Journal of Forest* 3(1), 13-23.

Rahmani, R., Saleh-Rastin, N., 2000. Abundance vertical distribution and seasonal changes in earthworm's populations of Oak-Hornbeam, Hornbeam and Beech Forest in Neka, Caspian Forests, Iran. *Iranian Journal of Natural Resources* 53: 37-52.

Rashid, M.I., de Goede, R.G.M., Nunez, G.AC., Brussaard, L., Lantinga, E.A., 2014. Soil pH and earthworms affect herbage nitrogen recovery from solid cattle manure in production grassland. *Soil Biology and Biochemistry* 68: 1-8.

Razavi, S.A., 2010. Comparison of soil characteristics and biodiversity in plantations of bald cypress and Caucasian Alder (Case Study: Kludeh-Mazandaran Province). *Iranian Journal of Wood & Forest Science and Technology* 17(2): 41-56.

Rhoades, C., Binkley, D., 1996. Forest influencing decline in soil pH in Hawaiian Eucalyptus and Albizia plantation. *Forest Ecology Management* 80: 47-56.

Schoenholtz, S.H., Van Miegroet, H., Burger, J.A., 2000. A review of chemical and physical properties as indicators of forest soil quality: challenges and opportunities. *Forest Ecology and Management* 138(2): 335-356.

Taylor, B.R., Parkinson, D., Parson, W.F., 1989. Nitrogen and lignin content as predictors of lignin decay rates. A microcosm test. *Ecology* 70: 97-104.

Uchida, T., Kaneko, N., Ito, MT., Futagami, K., Sasaki, T., Sugimoto, A., 2004. Analysis of the feeding ecology of earthworms (Megascolecidae) in Japanese forests using gut content fractionation and δ^{15}N and δ^{13}C stable isotope natural abundances. *Applied Soil Ecology* 27: 153-163.

Shen, W.B., Yang, H.Q., 2008. Effects of earthworm and microbe on soil nutrients and heavy metals. *Agrricultural Sciences in China* 7: 599-605.

Yang, X., Chen, J., 2009. Plant litter quality influences the contribution of soil fauna to litter decomposition in humid tropical forests, southwestern China. *Soil Biology and Biochemistry* 41: 910-918.

Yugai A.N., 1980. Effect of lime tilia cordata trees on forest growing soil properties. *Izvestiya Timiryazevskoi Sel'Skokhozyaistvennoi Akademii*: 1-115

Zhang, K., Dang, H., Tan, S., Wang, Z., Zhang, Q., 2012. Vegetation community and soil characteristics of abandoned agricultural land and pine plantation in the Qinling Mountains, China. *Forest Ecology and Management* 259: 2036-2047.

Eurasian J Soil Sci 2016, 5 (1) 53 - 61

Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

Growth and yield response of wheat (*Triticum aestivum* L.) to tillage and row spacing in maize-wheat cropping system in semi-arid region

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Article Info

Received : 13.08.2015
Accepted : 16.09.2015

Abstract

Tillage practices and row spacing can be manipulated to optimize spatial distribution and plant growth, therefore maximizing sunlight, soil water use efficiency, nutrients and grain yield on sustainable basis. A field study was conducted to determine the effect of tillage and row spacing on growth and yield of wheat (*Triticum aestivum* L.) at Agronomic Research Area, University of Agriculture, Faisalabad, Pakistan during wheat season. The treatments were comprised of two tillage practices viz. zero tillage and conventional tillage and four row spacing viz. 15 cm, 20 cm, 25 cm and 30 cm. The experimental results revealed that zero tillage significantly enhanced the plant height, tillers m^{-2}, spike length, 1000 kernel weight and yield and yield components of wheat plants as compared to conventional tillage. Wheat plants resulted in a significant increase in tillers m^{-2} and accumulated higher biomass and grain yield under 15-cm row spacing than all three other row spacing. The grain yield increase was mainly attributed to more tillers m^{-2} at 15-cm than the other row spacing. So, zero tillage and narrow row spacing (15 cm) proved to be involved in higher wheat yield for the wheat-maize cropping system in semi-arid regions.

Keywords: Grain, growth, maize, tillage, wheat, yield

Introduction

Wheat (*Triticum aestivum* L.), "King of the cereals" is an important staple food crop of Pakistan and is grown under different climatic conditions (Mirbahar et al. 2009). It is used as staple food by about 35% of the world population and its demand is growing faster than other major food crops. It contributes 13.1 percent to the value added in agriculture and 2.8 percent to GDP of Pakistan. It was grown in around 9,062 thousand hectares of area having annual production of 23,421 thousand tones during 2008-09 (GOP, 2009). However, the wheat yield in Pakistan is still quite low when compared with the world average. There are several factors responsible for low yield of wheat in Pakistan. The prime reasons being poor soil fertility, late planting, traditional sowing methods, irrigation water deficiency, weed infestation and poor crop husbandry.

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e-ISSN: 2147-4249 DOI: http://dx.doi.org/10.18393/ejss.2016.1.053-061

Managerial practices help to sustain the crop production at higher level without deteriorating natural resources. In the conventional tillage system crop residues and weeds are burned, used as feed or incorporated with soil. But, in conservation tillage more importance is given to conserving the soil properties. Here the plant cover is used to provide organic matter and higher infiltration of irrigation and rain water (Ortega, 1991) into soil. The concept of zero tillage has become a very common practice in many countries of the world, because it is ecologically, agronomically, economically and environmentally beneficial. Maintaining crop residues on the soil surface improved soil properties (Franchini et al. 2007; Sidiras et al. 1982). Zero tillage increases soil moisture retention capacity, minimizes soil temperature fluctuations, and decreases soil erosion by wind and water, enhances organic matter content in soil with time, improves soil micro-organisms activity, resulting in increased crop growth and yield (Malhi et al. 2006; Carter, 1992; Franzluebbers et al. 1999; Franchini et al. 2007; Derpsch, 1999; Warren, 1983). Zero tillage also reduces the cost of production and contributes to early sowing of wheat by 10-15 days (Erenstein and Laxmi, 2008; Sayre and Ramose, 1997) as compared to conventional tillage. Late wheat sowing can decrease wheat yield due to reduction in tillering period and enhances the risk of high temperature during grain filling stage (Razzaq et al. 1986; Bahera et al. 1994). Hussain et al. (1998) reported that with every single day delay in sowing of wheat from 20th November onward in Punjab (Pakistan) can decrease grain yields at 36 kg ha^{-1} d^{-1}.

Similarly, row spacing also plays a vital role in wheat production. In Pakistan wheat is normally sown by broadcasting or at 25 cm row to row distance, whereas in leading wheat producing countries it is much lower (10-15 cm) (Wibberley, 1989). Narrow row spacing in wheat caused suppression of weeds by increasing ground cover, leaf area, light interception, and even spatial plant distribution (Weiner et al. 2001; Drews et al. 2009). It also reduced soil evaporation and increased nutrient use efficiency by deploying nutrients (Johri et al. 1992; Chen et al. 2010). It has been shown by many studies, carried out in different climates, that narrow row spacing increased yield as compared to wider row spacing (Johnson et al., 1988; Marshall and Ohm, 1987; Chen et al. 2008). However, in contrast some reports have also found that wider row spacing in wheat produced higher yield or was same as compared to narrow spacing (Lafond, 1994; Lafond and Gan, 1999; Hiltbrunner et al. 2005). This indicated that the response of wheat yield to row spacing varied with environment and genotype (Marshall and Ohm, 1987).

Wheat is grown in Pakistan in a diverse cropping system following rice, maize, cotton, sugarcane, vegetables and fodders. Maize was planted on an area of 1,118 thousand hectares during 2008-2009 in Pakistan (GOP, 2009). To date, zero tillage wheat after rice has been most widely adopted resource conserving technology in the south Asian Indo-Gangatic Plains (Erenstein and Laxmi, 2008). Zero tillage technology is being rapidly adopted by the farmers in India but comparatively very slow progress has been seen in Pakistan (Malik et al. 2005; Erenstein and Laxmi, 2008; Erenstein et al. 2007). Mostly researchers are focused on sowing of wheat by zero tillage after rice harvesting in rice-wheat cropping system in India and Pakistan (Erenstein and Laxmi, 2008, Gupta et al. 2004; Iqbal et al. 2002; Sarwar and Goheer, 2007). However, wheat grown by zero tillage after maize harvesting in maize-wheat cropping system in Pakistan has rarely been reported. Thus, it is very imperative to study the feasibility of zero tillage in wheat-maize cropping system and the effect of row spacing on wheat plants. Hence, a field experiment was conducted to investigate effects of tillage and row spacing on growth and yield of wheat plants in a semiarid region wheat-maize copping system in Pakistan.

Material and Methods

Experimental site and treatments

Studies pertaining to investigate the effect of tillage and row spacing on the growth and yield of wheat cultivars "Auqab 2000" was carried out at the at the Agronomic Research Area, University of Agriculture, Faisalabad during wheat season. After maize harvesting (latitude = 31°30/N, longitude = 73°10/E and altitude = 184.4 m). The experiment was laid out in randomized complete block design (RCBD) with split plot arrangement (tillage practices in main plots and row spacing in subplots, respectively) having three replications. Net plot size was 3m × 6m. Soil under study belonged to Lyallpur Soil Series (Aridisol fine-silty, hyperthermic ustalfic, haplargid, mixed in USDA classification and Haplic Yermosols in FAO classification scheme). The soil pH and electrical conductivity (EC) were observed 7.7 and 1.2 dS m^{-1}, respectively. The treatments were comprised of two tillage practices (T_1= conventional tillage and T_2= zero tillage) and four row spacings (S_1 = 15 cm, S_2 = 20 cm, S_3 = 25 cm and S_4 = 30 cm). Conventional tillage was comprised of three cultivations, each followed by planking).

Crop husbandry

The crop was sown with the help of single row hand drill maintaining variable row spacing as per treatment 15, 20, 25 and 30 cm after maize harvesting. Seed rate was maintained and accomplished manually at a rate of 130 kg ha^{-1} for all the treatments. Urea and ammonium phosphate were used as source of Nitrogen and Phosphorus, respectively. Half of nitrogen and full dose of phosphorus was applied at the time of sowing. The remaining half of the nitrogen was applied along with fist irrigation. No water stress in plants happened in the whole growing season, and all essential nutrients were not considered to limit growth. All other agronomic practices were kept normal and uniform for all the treatments during the entire course of study. Harvesting of crop was done on its physiological maturity. Observations on growth and yield parameters of the crop were recorded using standard procedures.

Measurements

Plant height, spike length, number of spikelets per spike, number of grains per spike was recorded from twenty randomly selected plants from each plot. Total number of tillers taken at random from each plot, measuring 1 m^2 were counted, averaged and recorded. Crop harvest was completed by using a plot combine and air dried. Biological, straw and grain yield of wheat plants were measured from each plot and then converted into t ha^{-1}. 1000-grain weight was measured at random from the produce of each plot. Harvest index was calculated by using the following formula.

H.I. = grain yield/ biological yield x 100.

Crop harvest was completed by using a plot combine. After harvesting, grains were air-dried, and plot yield and 1000 seed weight were determined.

Statistical analysis

Data collected on different parameters were analyzed statistically by using a statistical package, SPSS version 16.0 (SPSS, Chicago, IL) and differences among the treatments means were compared by using the least significant difference (LSD) test at 5% probability level. Pearson correlation coefficients were calculated to determine the relationship among quantitative and qualitative growth and yield traits in wheat plants.

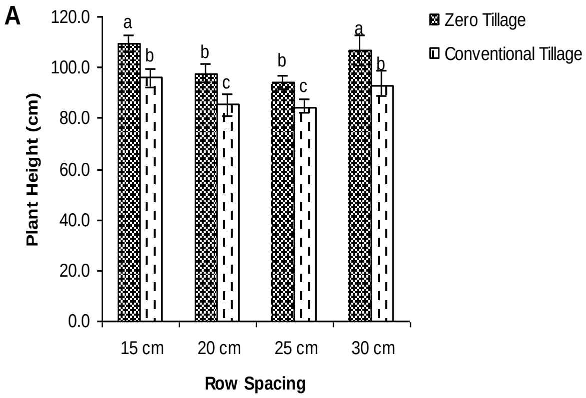
Results

Plant height and tillers m^{-2}

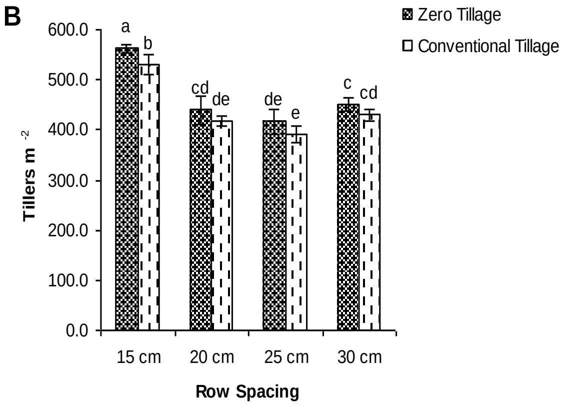
The effects of tillage practices on plant height and tillers m^{-2} of wheat plants are presented in Fig. 1A and B, respectively. Zero tillage led to significant increase in plant height at all levels of row spacing as compared to conventional tillage. But in case of tillers m^{-2} zero tillage showed significantly higher value at 15 cm row spacing and slightly higher values at all other three row spacing levels than conventional tillage but no significant difference was detected. Plant height and tillers m^{-2} were significantly affected by row spacing. In case of plant height the treatments 15 cm and 30 cm were statistically at par but significantly higher than the treatments 20 cm and 25 cm in both tillage levels. As regarding tillers m^{-2}, the treatment 15 cm had significantly higher value as compared to other three treatments; those were found statistically at par among each other. The interaction between tillage practices and row spacing on plant height and tillers m^{-2} was observed non-significant.

Spike length, number of kernels $spike^{-1}$ and 1000 kernel weight

The data regarding spike length, number of kernel $spike^{-1}$ and 1000 kernel weight of wheat plant as affected by different tillage practices and row spacings are shown in Fig 2A, B and C. Zero tillage had significantly higher spike length at 30 cm row spacing than conventional tillage but at other row spacings no significant difference was found. It is evident from the figure 2B and C that zero tillage had significantly higher number of kernel $spike^{-1}$ and 1000 kernel weight than conventional tillage on all row spacing treatments. While the row spacing the treatment 30 cm gave significantly more spike length over the rest of treatments in both tillage treatments, but the other treatments were statistically at par among each other. Row spacing at 30 cm had significantly higher values number of kernel $spike^{-1}$ than the other three row spacing levels in conventional tillage, while these treatments statistically at par among each other. But in case of zero tillage 30 cm row spacing had significantly higher values followed by 15 cm and 25 cm and 20 cm. While the 25 cm and 20 cm statistically had no difference with each other. As regarding 1000 kernel weight, slight increase was observed with increasing row spacing, though not statistically significant. . The interaction between tillage practices and row spacing on spike length, number of kernel $spike^{-1}$ and 1000 kernel weight was found non-significant.

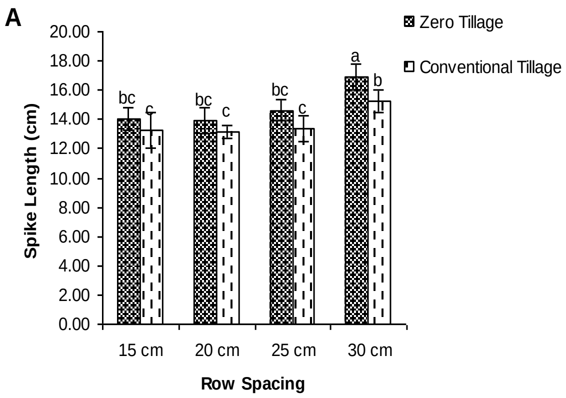


Variance analysis = Tillage** (F=63.8)
Row spacing** (F=13.9)
Tillage × Row spacing^{ns} (F=0.6)

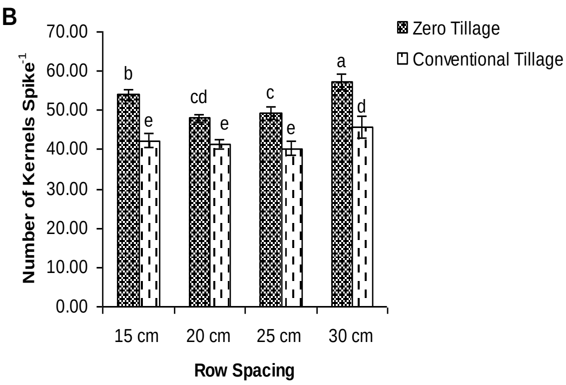


Variance analysis = Tillage** (F=95.0)
Row spacing** (F=58.2)
Tillage × Row spacing^{ns} (F=0.1)

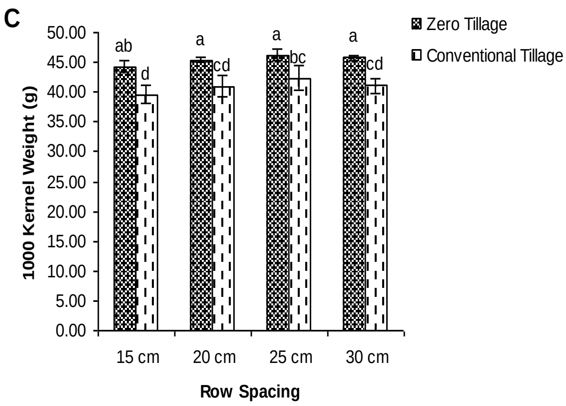
Figure 1. Effect of tillage practices and row spacing on plant height (A) and tillers m^{-2} (B). Data are means ± S.D. (n=3). F-value indicates significance level based on two-way ANOVA.
ns= non significant, * significant at *P*<0.05, ** significant at *P*<0.01



Variance analysis = Tillage** (F=116.2)
Row spacing** (F=9.2)
Tillage × Row spacing^{ns} (F=0.3)



Variance analysis = Tillage** (F=0.0)
Row spacing** (F=16.3)
Tillage × Row spacing^{ns} (F=2.1)

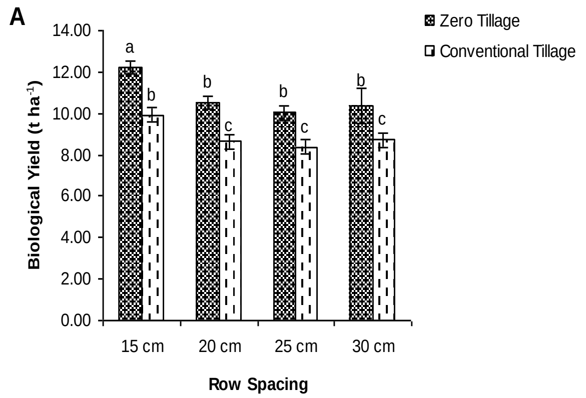


Variance analysis = Tillage** (F=106.9)
Row spacing** (F=2.9)
Tillage × Row spacing^{ns} (F=0.1)

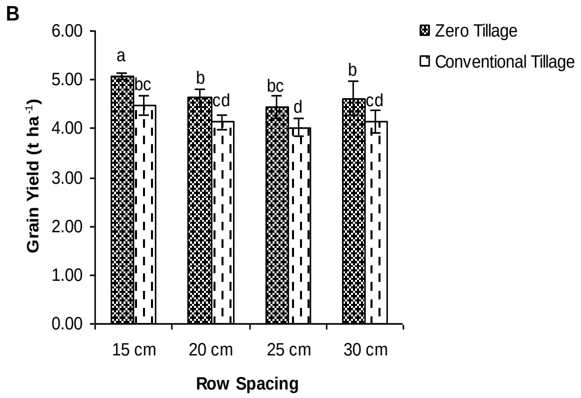
Figure 2. Effect of tillage practices and row spacing on spike length (A), number of kernels spike^{-1} (B) and 1000 kernel weight (C). Data are means ± S.D. (n=3). F-value indicates significance level based on two-way ANOVA.
ns= non significant, * significant at *P*<0.05, ** significant at *P*<0.01

Biological yield, grain yield, straw yield and harvest index

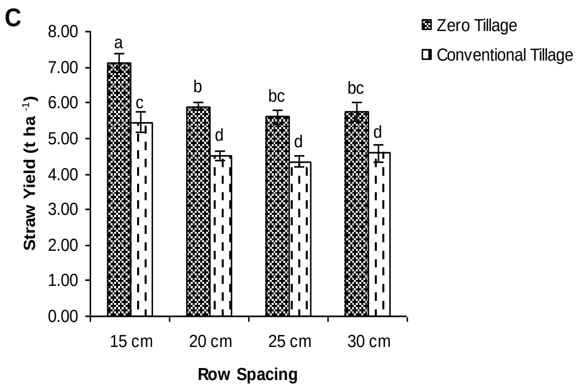
Data shown in Fig.3A, B and C revealed that sowing of wheat by zero tillage significantly increased biological yield, grain yield and straw yield at all row spacings than wheat sown by conventional tillage. But, in case of harvest index the results were just opposite (Fig.3D), mainly due to higher biomass production for zero tillage than for conventional tillage. Row spacing significantly affected the biological yield, grain yield, straw yield and harvest index. 15 cm row spacing had significantly higher biological yield, grain yield and straw yield in both tillage practices. While in the other three row spacing, no significant difference could be detected. But, in case of harvest index 15 cm had significantly lower value than other treatments. 20 cm, 25 cm and 30 cm treatments are statistically at par among each other. . The interaction between tillage practices and row spacing on biological yield, grain yield, straw yield and harvest index was found to be non-significant.



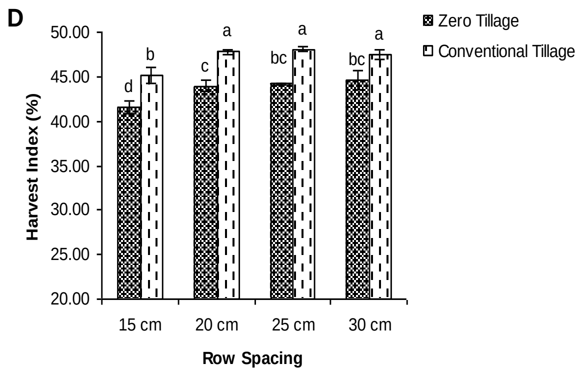
Variance analysis = Tillage** (F=437.7)
Row spacing** (F=15.7)
Tillage × Row spacing^{ns} (F=0.5)



Variance analysis = Tillage** (F=76.8)
Row spacing** (F=5.6)
Tillage × Row spacing^{ns} (F=0.2)



Variance analysis = Tillage** (F=648.7)
Row spacing** (F=23.4)
Tillage × Row spacing^{ns} (F=0.0)



Variance analysis = Tillage** (F=132.4)
Row spacing** (F=14,3)
Tillage × Row spacing^{ns} (F=0.4)

Figure 3. Effect of tillage practices and row spacing on biological yield (A), grain yield (B), straw yield (C) and harvest index (D). Data are means ± S.D. (n=3). F-value indicates significance level based on two-way ANOVA.

ns= non significant, * significant at *P*<0.05 , ** significant at *P*<0.01

Pearson correlation coefficients among qualitative and quantitative traits

The relationships among qualitative and quantitative traits in wheat plants are presented in Table 1. The results showed that grain yield was very remarkably and positively correlated with the plant height, tillers m^{-2}, number of kernel $spike^{-1}$, straw yield and biological yield but significantly and negatively correlated with harvest index. But there was no significant relationship found between grain yield and Spike length or 1000 Kernel weight. There was observed a significant and positive correlation between tillers m^{-2} and biological yield, grain yield or straw yield (Table 2). Plant height had significantly positive correlation with tillers m^{-2}, number of kernel $spike^{-1}$, straw yield, biological yield and harvest index.

Table 1. Weather data during the course of the study
Source: Agricultural Meteorology Cell, Department of Crop Physiology, University of Agriculture, Faisalabad, Pakistan

Months	Mean monthly Temperature	Mean monthly relative humidity	Total monthly rainfall
	°C	%	mm
November	19.7	58.9	0.0
December	15.5	68.9	14.6
January	13.5	68.0	13.1
February	20.3	52.4	14.6
March	21.0	57.0	37.0
April	25.0	57.0	0.0
May	29.5	57.0	24.0

Table 2. Pearson correlation coefficients among qualitative and quantitative traits of wheat

	PH	TL	SL	NKPS	1000KW	BY	GY	SY
TL	0.716*							
SL	0.546	-0.081						
NKPS	0.900**	0.364	0.766*					
1000KW	0.497	-0.119	0.517	0.753*				
BY	0.898**	0.766*	0.189	0.754*	0.533			
GY	0.918**	0.782*	0.214	0.765*	0.508	0.997**		
SY	0.889**	0.758*	0.180	0.749*	0.542	1.000**	0.994**	
HI	0.861**	-0.707	-0.188	-0.743	-0.596	-.986**	-.973**	-.989**

**Significance at 1% probability level; *Significance at 5% probability level; PH: Plant height, NT: Tillers m^{-2}, SL: Spike length, NKPS: Number of kernel $spike^{-1}$, 1000KW: 1000 Kernel weight, BY: Biological yield, GY: Grain yield, SY: Straw yield, HI: Harvest index.

Discussion

In this investigation, tillage practices had significant effect on plant growth and yield of wheat plants. Zero tillage had higher values of plant growth and yield parameters such as plant height, tillers m^{-2}, spike length, number of kernel $spike^{-1}$, 1000 kernel weight, biological yield, grain yield and straw yield as compared to conventional tillage. These results confirmed the findings of the previous studies who reported that zero tillage increased the growth and yield of plants (Munoz-Romero et al. 2010; Mehla et al. 2000; Sen et al. 2002; Bonfil et al. 1999; Halvorson et al. 2000). Increasing growth and yield of wheat plants under zero tillage than conventional tillage could be attributed to the following benefits of zero tillage over conventional tillage. Soil moisture and water use efficiency is affected significantly by the type of soil tillage (Moitra et al. 1996). Zero tillage enhances the rate of water stable aggregates and increases the size of soil aggregates. In the result, it improves the soil structure (Beare et al. 1994). Under conventional tillage aggregates formation process is disturbed regularly (Green et al. 2007). Heavy use of agricultural machinery in the soil causes soil compaction and increased soil bulk density (Miransari et al. 2007), which results in increased thermal conductivity of soil (Sarkar and Singh 2007). Tillage affects the structure of the soil porosity by disturbing shape, size and continuity of soil pores. Cassel et al. (1995) reported that zero tillage increased soil bulk density, resulting in decreased porosity of soil and soil resistance ultimately increased compared with conventional tillage methods viz. chisel plow and moldboard plow. Zero tillage also increases soil microbial biomass N and C as compared to other conventional methods (Franchini et al. 2007). Under conventional tillage, little amount of plant residues are changed into microbial biomass, because higher microbial respiration increased CO_2 emission from the soil (Lopez-Garrido et al. 2009). Zero tillage protest soil organic matter from microbial degradation. However, under disturbed soil conditions, mineralization rate increases and it becomes more exposed to microbial biomass (Balesdent et al. 2000). Moreover, there was very highly significant correlation found between soil moisture and soil microbial biomass (Torabi et al. 2008). So, it is worth mentioning that zero tillage has positive environmental impacts (reduced emissions of greenhouse, gas savings of fossil fuel, water savings) and ecologically, agronomically, economically and environmentally advantageous as compared with conventional tillage.

Row spacing affect on growth and yield of wheat plants. A number of researchers revealed that narrow row spacing gave better yield in wheat than wider row spacing (Johnson et al. 1988; Tompkins et al. 1991; Marshall and Ohm, 1987; Joseph et al. 1985). In this study, narrow row spacing (15 cm) increased tillers per unit area and yield of wheat plants. Although 15-cm treatment had lower 1000 kernel weight than wider rows but the difference was observed slight and compensated by increased tiller per unit area. So, the higher grain yield at the 15-cm compared with other row spacings in this investigation was chiefly attributed to the increased spike density per unit area. Our results confirmed the earlier findings of Frederick and Marshall (1985) who reported that by decreasing row spacing to 12.7 cm, grain yield increased by 8.2%, and the main contributing factor was higher number of tillers per unit area. Narrow row spacing caused more even spatial plant distribution, increased leaf area index, crop ground cover, light interception and dry matter. Thus, narrow spacing also decreased weed population and reduced soil evaporation (Drews et al. 2009; Weiner et al. 2001; Chen et al. 2010). Our results also agreed with the findings of Lafond (1994), who revealed that by increased row spacings caused decreased number of spikes m^{-2}. Similarly, it was reported that narrow row spacing had higher plant density than at wider row spacing (McLeod et al. 1996). The higher values of tiller m^{-2} in 15-cm row spacing in this study was likely due to more uniform and accurate spatial distribution and less plant-to-plant competition (Auld et al. 1983). In our study, higher biomass was produced at the 15-cm row spacing indicating better resource utilization at this row spacing level.

Conclusion

The investigation results indicate that sowing wheat by zero tillage is an efficient tillage system and resource conservation technology. The results obtained also confirmed the validity of innovative tillage system for energy conservation in broad sense with assurance of satisfactory yield production. The row spacings also significantly affected growth and yield of wheat plants. Row spacing 15-cm should be adopted for its contribution towards higher grain yield. Therefore, zero tillage with 15-cm row spacing may be recommended for the wheat-maize cropping system in semi-arid region of Pakistan.

Acknowledgement

Thanks to Ministry of Education Pakistan and Higher Education Commission of Pakistan for financial support.

References

Auld, B.A., Kemp, D.R., Medd, R.W., 1983. The influence of spatial arrangement on grain yield of wheat. *Australian Journal of Agricultural Research* 34: 99-108.

Bahera, A.K., 1994. Response of wheat to sowing dates. *Indian Journal of Agronomy* 39: 171-173.

Balesdent, J., Chenu, D., Balabane, M., 2000. Relationship of soil organic matter dynamics to physical protection and tillage. *Soil and Tillage Research* 53: 215-230.

Beare, M.H., Hendrix, P.F., Coleman, D.C., 1994. Water stable aggregates and organic carbon fractions in conventional and no-tillage soils. *Soil Science Society of America Journal* 58: 777-786.

Bonfil, D.J., Mufradi, I., Klitman, S., Asido, S., 1999. Wheat grain yield and soil profile water distribution in a no-till arid environment. *Agronomy Journal* 91: 368-373.

Carter, M.R., 1992. Influence of reduced tillage systems on organic matter, microbial biomass, macro-aggregate distribution and structural stability of the surface soil in humid climate. *Soil and Tillage Research* 23: 361-372.

Cassel, D.K., Raczkowski, C.W., Denton H.P., 1995. Tillage effects on corn production and soil physical conditions. *Soil Science Society of America Journal* 59: 1436-1443.

Chen, C., Neill, K., Wichman, D., Westcott, M., 2008. Hard red spring wheat response to row spacing, seeding rate, and nitrogen. *Agronomy Journal* 100: 1296-1302.

Chen, S., Zhang, X., Sun, H., Ren, T., Wang, Y., 2010. Effects of winter wheat row spacing on evapotranspiration, grain yield and water use efficiency. *Agricultural Water Management* 97: 1126–1132.

Derpsch, R., 1999. Frontiers in conservation tillage and advances in conservation practice. 10th International Soil Conservation Organization Meeting, May 24-29, 1999. Purdue University and USDA-ARS National Soil Erosion Research Laboratory, USA.

Drews, S., Neuhoff, D., Köpke, U., 2009. Weed suppression ability of three winter wheat varieties at different row spacing under organic farming conditions. *Weed Research* 49: 526-533.

Erenstein, O., Farooq, U., Malik, R.K., Sharif, M., 2007. Adoption and impacts of zero tillage as a resource conserving technology in the ırrigated plains of South Asia. Comprehensive Assessment of Water Management in Agriculture-Research Report 19. IWMI, Colombo, Sri Lanka.

Erenstein, O., Laxmi, V., 2008. Zero tillage impacts in India's rice-wheat systems: A review. *Soil and Tillage Research* 100: 1-14.

Franchini, J.C., Crispino, C.C., Souza, R.A., Torres, E., Hungria, M., 2007. Microbiological parameters as indicators of soil quality under various soil management and crop rotation systems in Southern Brazil. *Soil and Tillage Research* 92: 18-29.

Franzluebbers, A.J., Langdale, G.W., Schomberg, H.H., 1999. Soil carbon, nitrogen, and aggregation in response to type and frequency of tillage. *Soil Science Society of America Journal* 63: 349-355.

Frederick, J.R., Marshall, H.G., 1985. Grain yield and yield components of soft red winter wheat as affected by management practices. *Agronomy Journal* 77: 495-499.

GOP, 2009. *Pakistan Economic Survey*. Government of Pakistan (2008-09), Ministry of Food, Agriculture and Live Stock, Federal Beauru of Statistics Islamabad.

Green, V.S., Stott, D.E., Cruz, J.C., Curi, N., 2007. Tillage impacts on soil biological activity and aggregation in a Brazilian Cerrado Oxisol. *Soil and Tillage Research* 92: 114-121.

Gupta, P.K., Sahai, S., Singh, N., Dixit C.K., Singh, D.P., Sharma, C., Tiwari, M.K., Gupta, R.K., Garg, S.C., 2004. Residue burning in rice–wheat cropping system: Causes and implications. *Current Science* 87: 1713-1717.

Halvorson, A.D., Black, A.L., Krupinsky, J.M., Merrill, S.D., Weinhold, B.J., Tanaka, D.L., 2000. Spring wheat response to tillage and nitrogen fertilization in rotation with sunflower and winter wheat. *Agronomy Journal* 92: 136-144.

Hiltbrunner, J., Liedgens, M., Stamp, P., Streit, B., 2005. Effects of row spacing and liquid manure on directly drilled winter wheat in organic farming. *European Journal of Agronomy* 22: 441- 47.

Hussain, T., 1997. Comparative growth and yield performance of various wheat cultivars. Master's Thesis, University of Agriculture Faisalabad, Pakistan.

Iqbal, M., Khan, A., Anwar, M.Z., 2002. Zero-tillage Technology and Farm Profits: A Case Study of Wheat Growers in the Rice Zone of Punjab. *The Pakistan Development Review* 41, 665-682.

Johnson, J.W., Hargrove, W.L., Moss, R.B., 1988. Optimizing row spacing and seeding rate for soft red winter wheat. *Agronomy Journal* 80: 164-166.

Johri, A.K., Singh, G., Sharma, D., 1992. Nutrient-uptake by wheat and associated weeds as influenced by management-practices. *Journal of Tropical Agriculture* 69: 391-393.

Joseph, K.D.S.M., Alley, M.M., Brann, D.E., Gravelle, W.D., 1985. Row spacing and seeding rate effects on yield and yield components of soft red winter wheat. *Agronomy Journal* 77: 211-214.

Lafond, G.P., 1994. Effects of row spacing, seeding rate, and nitrogen on yield of barley and wheat under zero-till management. *Canadian Journal of Plant Science* 74: 703-711.

Lafond, G.P., Gan, Y., 1999. Row spacing and seeding rate studies in no-till winter wheat for the northern Great Plains. *Journal of Production Agriculture* 12: 624-629.

Lopez-Garrido, R., Díaz-Espejo, A., Madejón, E., Murillo, J.M., Moreno, F., 2009. Carbon losses by tillage under semi-arid Mediterranean rainfed agriculture (SW Spain). *Spanish Journal of Agricultural Research* 7: 706-716.

Malhi, S.S., Lemke, R., Wang, Z.H., Chhabra, B.S., 2006. Tillage, nitrogen and crop residue effects on crop yield, nutrient uptake, soil quality, and greenhouse gas emissions. *Soil and Tillage Research* 90: 171-183.

Malik, R.K., Yadav, A., Gupta, R.K., Singh. S., Hobbs, P.R., Bellinder, R.R., 2005. Introduction and success of zero tillage in wheat under rice–wheat cropping system in Haryana, India-related stories. In Accelerating the Adoption of Resource Conservation Technologies in Rice-Wheat System of the Indo-Gangetic Plains, Proceedings of the Project Workshop June 1-2, 2005. Directorate of Extension Education, CCS HAU, Hisar, Haryana, India, pp. 1-17.

Marshall, G.C., Ohm, H.W., 1987. Yield responses of 16 winter wheat cultivars to row spacing and seeding rate. *Agronomy Journal* 79: 1027-1030.

Mcleod, J.G., Campbell, C.A., Gan, Y., Dyck, F.B., Vera, C.L., 1996. Seeding depth, rate and row spacing for winter wheat grown on stubble and chemical fallow in the semiarid prairies. *Canadian Journal Plant Science* 76: 207-214.

Mehla, R.S., Verma, J.K., Gupta, R.K., Hobbs, P.R., 2000. Stagnation in the productivity of wheat in the indo-gangetic plains: Zero-till-seed-cum-fertilizer drill as an ıntegrated solution. Rice-Wheat Consortium Paper Series 8 RWC, New Delhi, India.

Miransari, M., Bahrami, H.A., Rejali, F., Malakouti, M.J., Torabi, H., 2007. Using arbuscular mycorrhiza to reduce the stressful effects of soil compaction on corn (*Zea mays* L.) growth. *Soil Biology and Biochemistry* 39: 2014-2026.

Mirbahar, A.A., Markhand, G.S., Mahar, A.R., Saeed, A., Kanhar, N.A., 2009. Effect of water on yield and yield components of wheat (*Triticum aestivum* L.) varieties. *Pakistan Journal of Botany* 41: 1303-1310.

Moitra, R., Ghosh, D.C., Sarkar, S., 1996. Water use pattern and productivity of rainfed yellow sarson (*Brassica rapa* L. var *glauca*) in relation to tillage and mulching. *Soil and Tillage Research* 38: 153-160.

Muñoz-Romero, V., Benítez-Vega, J., López-Bellido, R.J., Fontán, J.M., López-Bellido, L., 2010. Effect of tillage system on the root growth of spring wheat. *Plant and Soil* 326: 97-107.

Ortega A., 1991. Relative importance of pests in conventional and conservation tillage: A review of the literature. Maize conservation tillage: CIMMYT, pp. 71-96.

Razzaq, A., Shah, P., Zada, K., Saeed, K., 1986. Effect of date of sowing on emergence, growth rate and days to earings of wheat varieties. *Sarhad Journal of Agriculture* 2: 23-28.

Sarkar, S., Singh, S.R., 2007. Interactive effect of tillage depth and mulch on soil temperature, productivity and water use pattern of rainfed barley (*Hordium vulgare* L.). *Soil and Tillage Research* 92: 79-86.

Sarwar, M.N., Goheer, M.A., 2007. Adoption and Impact of Zero Tillage technology for wheat in Rice-Wheat System- water and cost saving technology. Proc. International Forum on Water Environmental Governance in Asia, Bangkok March 14-15, 2007.

Sayre, K.D., Ramos, O.H.M., 1997. Application of raised bed planting system to wheat. CIMMYT Report. WPSR No. 37 A.

Sen, A., Sharma, S.N., Singh, R.K., Pandey, M.D., 2002. Effect of different tillage systems on the performance of wheat. In Herbicide Resistance Management and Zero Tillage in Rice– Wheat Cropping System. CCSHAU, Hisar, India, pp. 115-116.

Sidiras, N., Henklain, J.C., Derpsch, R., 1982. Comparison of three different tillage systems with respect to aggregate stability, the soil and water conservation and the yields of soybean and wheat on an Oxisol. *Journal of Agronomy and Crop Sciences* 151: 137-148.

Tompkins, D.K., Hultgreen, G.E., Wright, A.T., Fowler, D.B., 1991. Seed rate and row spacing of no-till winter wheat. *Agronomy Journal* 83: 684-689.

Torabi, H., Naghdibadi, H.A., Omidi, H., Amirshekari, H., Miransari, M., 2008. Effects of soil tillage, canola (*Brassica napus* L.) cultivars and planting date on canola yield, and oil and some biological and physical properties of soil. *Archives of Agronomy and Soil Sciences* 54: 175-188.

Warren, R., 1983. Technology transfer in zero tillage crop production in the third world agriculture. No-tillage Crop Production in the Tropics. Proc. Symp., Monrovia, Liberia. Int. Plant. Prot. Center, Oregon State Univ., Corvallis, OR, USA, pp. 25-31.

Weiner, J., Griepentrog, H.W., Kristensen, L., 2001. Suppression of weeds by spring wheat triticum aestivum ıncreases with crop density and spatial uniformity*. Journal of Applied Ecology* 38: 784-790.

Wibberley, F.J., 1989. Cereal Husbandry Farming Press Book, Ipswich, U.K. pp. 93.

Eurasian J Soil Sci 2016, 5 (1) 62 - 73

Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

Comparison of kriging interpolation precision between grid sampling scheme and simple random sampling scheme for precision agriculture

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Abstract

Sampling methods are important factors that can potentially limit the accuracy of predictions of spatial distribution patterns. A 10 ha tobacco-planted field was selected to compared the accuracy in predicting the spatial distribution of soil properties by using ordinary kriging and cross validation methods between grid sampling and simple random sampling scheme (SRS). To achieve this objective, we collected soil samples from the topsoil (0-20 cm) in March 2012. Sample numbers of grid sampling and SRS were both 115 points each. Accuracies of spatial interpolation using the two sampling schemes were then evaluated based on validation samples (36 points) and deviations of the estimates. The results suggested that soil pH and nitrate-N (NO_3-N) had low variation, whereas all other soil properties exhibited medium variation. Soil pH, organic matter (OM), total nitrogen (TN), cation exchange capacity (CEC), total phosphorus (TP) and available phosphorus (AP) matched the spherical model, whereas the remaining variables fit an exponential model with both sampling methods. The interpolation error of soil pH, TP, and AP was the lowest in SRS. The errors of interpolation for OM, CEC, TN, available potassium (AK) and total potassium (TK) were the lowest for grid sampling. The interpolation precisions of the soil NO_3-N showed no significant differences between the two sampling schemes. Considering our data on interpolation precision and the importance of minerals for cultivation of flue-cured tobacco, the grid-sampling scheme should be used in tobacco-planted fields to determine the spatial distribution of soil properties. The grid-sampling method can be applied in a practical and cost-effective manner to facilitate soil sampling in tobacco-planted field.

Article Info

Received : 13.08.2015
Accepted : 18.09.2015

Keywords: Grid sampling scheme, Interpolation precision, simple random sampling scheme, precision agriculture

Introduction

Among nutrients necessary for plant growth, potassium, nitrogen and phosphorus are the most important and sensitive for yield and quality of flue-cured tobacco. Tobacco plants receive potassium, nitrogen and phosphorus not only from fertilizers, but also from soil minerals. However, soil is characterized by a high degree of spatial variability because of geological and soil-forming factors that operate at different intensities and scales (Goovaerts, 1998; Quine and Zhang, 2002). Therefore, uniform fertilizer application likely leads to over-application in areas with high nutrient levels and under-application in areas with low nutrient levels (Ferguson et al., 2002), which results in extremely uneven tobacco yield and quality. Variable-rate fertilizer application, which is an efficient method of solving such problems, is possible if spatial variation in nutrient contents across a field is known (Cahn et al., 1994). The spatial distribution of soil

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e-ISSN: 2147-4249
DOI: http://dx.doi.org/10.18393/ejss.2016.1.062-073

properties can be predicted accurately by soil spatial sampling (Zhu et al., 2005). In soil sampling, point information is used to estimate soil fertility levels at locations where samples are not obtained. Soil sampling schemes are important because of their effect on the quality of spatial interpolation maps, and the corresponding values to manage such maps depend on the accuracy of predicted values (Frogbrook, 1999). Therefore, a suitable sampling method is necessary to estimate correctly the values of soil properties in areas of specified sizes.

An optimal and time-effective sampling method in any study should provide maximum estimation precision with the least sample cost. The number of soil samples and sampling strategies required to represent field variability has been extensively studied since the 1920s (Lindsley and Bauer, 1929). This requirement is possibly based on economic values (Peck, 1990). Increased agricultural income from reduced input, increased yield, and improved quality should offset not only the costs of characterizing soil variability but also the technology required for variable application. Studies have indicated that appropriate sampling or a combination of systematic is effective when the density of rare or clustered populations is estimated (Thompson and Seber, 1996; Christman, 2000). The sample pattern and sample spacing are important factors that affect the accuracy of the kriging interpolation (Wollenhaupt et al., 1994; Gotway et al., 1996), which is a technology for estimating the soil property values in nonsampled areas and generating the spatial distribution (Goovaerts, 2000). Few previous studies evaluated the effect of sample design and intensity on the accuracy of assessment (McBratney et al., 1999; Caeiro et al., 2002; Zhu and Stein, 2006; Brus et al., 2006; Li et al., 2007; Kumar,2009; Liu et al., 2010). That research provides a starting point in developing a sampling strategy for analyzing effectively the spatial variability of soil properties in tobacco-planted field.

Furthermore, sampling strategies should be carefully selected to represent fields in which known sources of variability are considered. Field observation has been traditionally based on discrete sampling procedures by using either grid sampling or SRS (Li et al., 2007). A grid pattern is commonly an optimum sampling scheme to ensure that an entire field is represented. However, sampling with a grid pattern can be laborious if large areas are examined (Li et al., 2007). Therefore, the present study compared kriging interpolation precision between the grid sampling method and the SRS.

There are more than one million ha of agricultural soil for flue-cured tobacco plantation that serve as an important source of income for tobacco growers as well as local administration in China. In order to improve the quality of flue-cured tobacco, the Tobacco Company of China has requested that farmers adopt variable-rate fertilizer application. The objectives of this study were: (i) to quantify the spatial variability of soil properties across flue-cured tobacco (Nicotiana tabacum) plantation fields, (ii) to identify the appropriate sampling scheme for nine soil properties in order to minimize cost and maximize evaluation accuracy, and (iii) to provide a theoretical basis for establishing a reasonable sampling scheme in tobacco-planting fields.

Material and Methods

Study site

The study was performed at an agricultural experiment station in Southeast Pengshui County (29°8'14'4672"N, 107°57'3081"E) of Chongqing City in Southwest China in 2012. The site is characterized by a subtropical moist monsoon climate with an average annual temperature of 17.5 °C, a mean annual potential evapotranspiration of 950.4 mm, and an annual precipitation of approximately 1104.2 mm. The main soil type at this site ranges from light clay (80.6%) to heavy loam (3.5%), and the remaining 15.9% is medium clay. In addition, the soil is slightly acidic (pH = 5.87).

Soil sampling and laboratory analysis

A 10-hectare area was selected for soil sampling, and the overview of the boundary of the study site is illustrated in Figure 1. This area is surrounded by a hill and the field was bare at the time of observation. Soil samples were collected in March 4, 2012. All of the samples were taken from the topsoil (0-20 cm), and a real-time kinematic global positioning system (GPS) survey was used to identify sampling locations. At each point, the values were recorded by differential GPS (DGPS) and then converted to coordinates (x, y; Fig. 1). The soil samples of the grid sampling scheme were collected using an approximately 32 m grid sampling design (n=115, Fig. 1). The soil samples of the regular simple random sampling scheme were regularly taken from spaces that ranged between approximately 16 m and 32 m (n=115, Fig. 1).

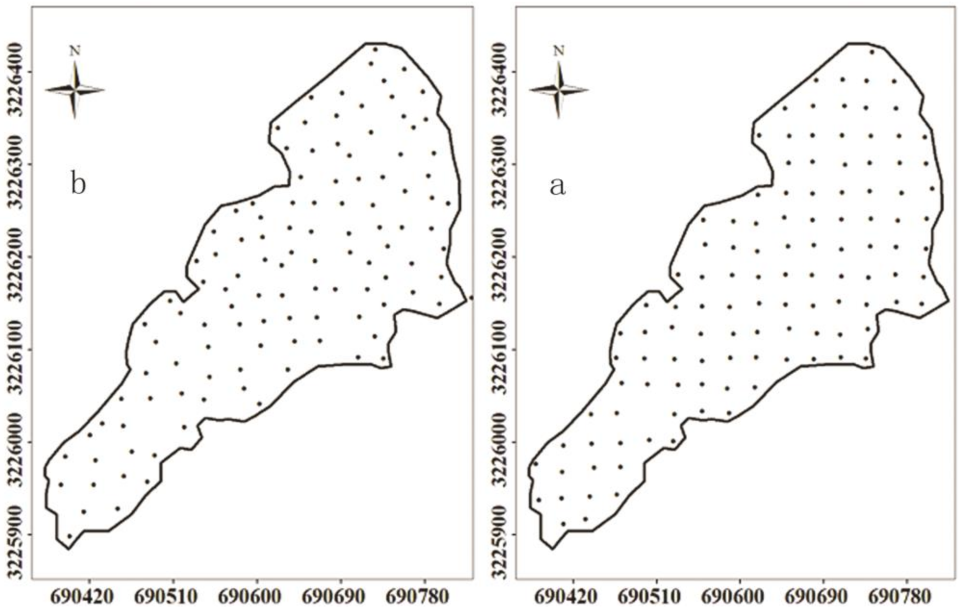

Figure 1. Soil sample distribution under two sampling schemes (a: grid sampling scheme, b: simple random sampling scheme) in the 10-ha area.

Soil samples were packed in plastic bags, air-dried, divided, and ground to a sufficient size to pass through a 2 mm sieve before analysis was conducted. The soil pH of the samples was subsequently measured using a pH meter with a glass electrode (soil-H_2O ratio = 1:2.5, W-V). The organic matter (OM) content was analyzed using the wet oxidation method of Walkley and Black (Nelson and Sommers, 1982). Cation exchange capacity (CEC) was determined by extraction using neutral sodium acetate (Chapman, 1965). Total nitrogen (TN) was determined using the Kjeldahl method (Bremner and Mulvaney, 1984). Nitrate nitrogen (NO_3-N) of a fresh sample was determined using a continuous flowing analyzer (Paramasivam et.al., 2002). Total phosphorus (TP) was then determined by sulfate-perchlorate acid heating digestion-MoSb colorimetry (Lu, 1999). Available phosphorus (AP) was determined using the Olsen extraction method with alkaline sodium bicarbonate as an extractant at a ratio of 20:1 (Olsen et al., 1954). Total potassium (TK) was analyzed by inductively coupled plasma-atomic emission spectroscopy. Available potassium (AK) was determined using the neutral ammonium acetate method (Richards, 1954).

Evaluation method

In order to evaluate the accuracy of our estimates, 36 sites were selected by probability sampling for external validation. The interpolation values of these 36 points were compared with the actual measurements.

As an alternative method of evaluating the accuracy of our estimates, we determined the performance of each interpolation obtained using the two sampling methods. Deviations of the estimates from the measured data were then compared by cross-validation (Webster and Oliver, 2001). Comparison of performance of the two sampling methods was done using the following statistics:

In order to evaluate the accuracy of the estimates, the performance of each interpolation under different intervals was assessed by comparing the deviation of estimates from the measured data through cross-validation (Webster and Oliver, 2001). Comparison of performance between the two sampling schemes was done using the following statistics: mean absolute error (MAE), mean error (ME), mean square error (MSE), average standardized error (ASE), root mean square error (RMSE), and root mean square standardized error (RMSSE). The ME was used to determine the degree of bias in the estimates; MSE provided a measure of the size of MSE; ASE was used to identify the degree of ASE; RMSE provided a measure of the error size that it is sensitive to outliers; and RMSSE was used to determine the degree of RMSSE. The five error statistics of predictions were used in the cross-validation analysis. The equations are as follows (Johnston et al., 2001):

$$\text{ME} = \frac{1}{N}\sum_{i=1}^{N}[Z(x_i) - Z(\hat{x}_i)] \tag{1}$$

$$\text{MSE} = \frac{1}{N}\sum_{i=1}^{N}\frac{Z(x_i) - Z(\hat{x}_i)}{\sigma(i)} \tag{2}$$

$$\text{ASE}=\sqrt{\frac{1}{N}\sum_{i=1}^{N}\sigma(i)} \tag{3}$$

$$\text{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}[Z(x_i) - \hat{Z}(x_i)^2]} \tag{4}$$

$$\text{RMSSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\{\frac{Z(x_i) - \hat{Z}(x_i)}{\sigma(i)}\}^2} \tag{5}$$

where $\hat{Z}(x_i)$ is the predicted value, $Z(x_i)$ is the observed value, n is the number of values, and σ is the standard error for location i.

The criteria for cross-validation were as follows. ME and MSE indicate the degree of bias in the model prediction, and should be approximately zero. RMSE and ASE indicate the precision of prediction. Their values should be as small as possible. RMSSE compares the error variance with the kriging variance. RMSSE should be approximately 1. If RMSE equals ASE, then all errors are of small If ASE>RMSE or RMSSE<1, the model-predicted values are larger than the actual values (Tang and Yang, 2006). MAE indicates the precision of prediction, such that low MAE values indicate more accurate point-by-point predictions.

The measured variables in the data set were analyzed using descriptive statistical methods to obtain the mean, S.D., minimum, median, maximum, skewness, kurtosis, and coefficient of variation (CV) using SPSS 17.0 software. Distributions of these variables were evaluated to determine normality using Kolmogorov-Smirnov statistics. Semi-variance calculation, semi-variogram function model fitting, and cross validation were performed using the geostastistical software ArcGIS 9.3 for Windows.

Results

Descriptive statistics

Summary statistics of soil parameters is shown in Table 1. Distributions of all variables were only slightly skewed (skewness < 1), and their median values were close to their mean values. In addition, results showed that all data were normally distributed (Kolmogorov-Smirnov test, P > 0.05; Table 1).

Table 1. Descriptive statistics of soil properties (*n* = 289) in the topsoil (0-16cm) at different sampling dates.

Soil properties	Min.	Median	Mean	Max.	S.D.	# CV %	Skewness	Kurtosis	※ $P_{K\text{-}S}$
pH	5.00	5.85	5.87	7.00	0.45	7.67	0.32	-0.25	0.59
OM, g kg^{-1}	14.26	25.00	25.24	39.34	5.01	19.85	0.32	-0.11	0.59
CEC, cmol kg^{-1}	6.23	17.19	17.65	31.09	5.34	30.25	0.35	-0.34	0.21
TN, g kg^{-1}	0.34	0.79	0.81	1.35	0.20	24.69	0.09	-0.4	0.63
NO_3-N, mg kg^{-1}	137.3	174.3	177.33	221.3	16.79	9.47	0.52	-0.23	0.08
TP, g kg^{-1}	0.35	0.75	0.79	1.33	0.22	27.85	0.61	-0.12	0.01
AP, mg kg^{-1}	13.54	19.95	20.46	29.51	3.42	16.72	0.57	-0.48	0.01
TK, g kg^{-1}	10.85	17.26	17.22	24.57	2.93	17.02	0.27	-0.32	0.52
AK, mg kg^{-1}	62.41	202.31	199.78	374.11	65.76	32.92	0.22	0.56	0.16

CV, coefficient of variation (%).

※ K-S Test, Kolmogorov-Smirnov test was used to test the significance level of normality, all variables were normally distributed (*P* > 0.05).

The greatest variability was observed in AK (32.92%), whereas the least variability was found in pH (7.67%). The variability in pH and NO_3-N were low (CV < 15%), whereas all of the other soil variables exhibited moderate variation (CV: 15%-50%). AK also exhibits a localized pattern of enrichment according to the National Soil Survey Office (1993). In conclusion, the soil possesses high variability, which results in extremely uneven tobacco yield, quality, and agricultural benefits, which suggests that variable-rate fertilization application is necessary for improving tobacco quality in this area.

Geostatistical analysis

Semi-variograms were calculated to identify the possible spatial structure of different soil variables. Cross-validation was performed to compare the prediction performances of geostatistical interpolation algorithms with a particular sampling method. Cross-validation indicators and additional model parameters (nugget, sill, and range) helped determine the optimal model of the prediction maps for each soil property (Issaks and Srivastava, 1989). In this study, the optimal model that could describe specific spatial structures was identified. The result of the geostatistical analysis is shown in Table 2. In this analysis, several spatial distribution models were fitted, which revealed different spatial dependence levels of the soil variables based on the cross-validation model.

Our results suggested that NO_3-N, TK, and AK ideally matched an exponential model, whereas the remaining variables suitably fit the spherical model with the two sampling methods. The coefficient of determination (R^2) of all variables, except for NO_3-N and AK, was greater than 0.90, indicating good fits. The spatial variability of soil nutrients may be affected by extrinsic (soil management practices such as fertilization and cultivation) and intrinsic factors (soil formation factors, such as soil parent materials). The strong spatial dependence of soil variables can typically be attributed to extrinsic factors (Cambardella et al., 1994). The value nugget % was used to qualitatively define spatial dependence values. Our results showed that pH, OM, CEC, TN, and NO_3-N exhibited <25% except NO_3-N in the SRS, which suggested strong spatial dependence. Rodríguez et al. (2009) found that spatial dependence of NO_3-N was high in sandy and loam soils. All of the other soil variables were moderately spatially dependent with nugget % ranging from 33.33% to 57.14%. This range could be interpreted as the zone of influence diameter. This result represented the average maximum distance at which the soil properties of the two sampling points are related. The ranges of spatial dependences exhibited large variation (from 95.78 m for OM of grid sampling to 558.41 m for AK of SRS, as shown in table 2).

Accuracy of validation samples

The spatial distributions of nine soil properties were completed with the optimal models using the two sampling schemes in the study area. The predicted values of evaluation samples (115 points) and validation samples (36 points) were obtained using the two sampling schemes.

The scatter diagrams, in which the predicted values are on the vertical axis and the measured values are on the horizontal axis, were constructed and a trend line was subsequently added (Fig. 2). The trend line was closer to the 45-degree line, indicating a more accurate prediction than other lines (Li et al., 2008). In the scatter diagram, the prediction accuracies of pH, TP, and AP in the SRS were bigger than that of the grid-sampling scheme, while the prediction accuracy of soil OM, CEC, TN, NO_3-N, TK and AK in the grid-sampling scheme was bigger than that of the SRS.

Analysis of interpolation results for SRS and Grid sampling

Results of cross-validation from the 115 points arranged in the SRS are shown in Table 3. These data may be more useful in comparing prediction errors. ME was always nearly equal to MSE, ASE was almost equal to RMSE, and RMSSE values were always close to 1. Consequently, kriging was shown to be accurate for soil pH, TP and AP by the five statistical criteria in the SRS, while the interpolation results of soil OM, CEC, TN, TK and AK in the SRS were poor than that in the grid-sampling scheme. The difference in accuracy of the soil NO_3-N between the two sampling schemes was not markedly significant.

For pH, TP, and AP, the absolute values of ME and MSE were slightly greater than zero, whereas the absolute value of RMSE was remarkably close to and less than that of ASE, and the RMSSE values were less than one, indicating that they were underestimated in the SRS. The absolute values of ME, RMSE, ASE, and MSE of TN and AK were very close to zero, and RMSE > ASE, RMSSE > 1, suggesting that they were slightly overestimated at the grid sampling scheme. However, it was underestimated by kriging for OM and TK in the grid sampling scheme (RMSE < ASE, RMSSE < 1).

Table 2. Characteristic of calculated semivariograms for all soil properties under two sampling methods in study area

Variable	Grid sampling scheme							Simple random sampling scheme						
	※Model	Co	§Co+C	Nugget, %	#Spatial dependence class	R^2	Range	Model	Co	Co+C	Nugget, %	Spatial dependence class	R^2	Range
pH	S	0.02	0.1	20	S	0.99	358.97	S	0.03	0.14	21.43	S	0.97	148.3
OM	S	4.17	17.15	24.31	S	0.95	95.78	S	3.02	18.21	16.58	S	0.94	107.2
CEC	S	4.05	22.33	18.14	S	0.97	154.43	S	4.09	17.57	23.28	S	0.97	139.95
TN	S	0	0.01	18.65	S	0.92	553.58	S	0	0.04	13.56	S	0.92	460.17
NO_3-N	E	24.78	143.31	17.29	S	0.87	325.42	E	64.15	165.41	38.78	M	0.87	439.56
TP	S	0.04	0.11	36.36	M	0.95	553.58	S	0.03	0.09	33.33	M	0.96	495.04
AP	S	6.2	16.01	38.73	M	0.92	478	S	4.82	13.78	34.98	M	0.93	558.41
TK	E	2.13	5	42.6	M	0.9	257.28	E	3.07	8.02	38.28	M	0.9	258.41
AK	E	833.7	2333.7	35.72	M	0.81	553.58	E	1409.2	4244.9	33.2	M	0.84	558.41

※ S: spherical models; E: exponential models.

§ Co: nugget variance; C: structural variance.

\# Nugget %: Co/(Co + C)×100. Nugget between 25% and 75%: moderate spatial dependence. Nugget < 25%: strong spatial dependence.

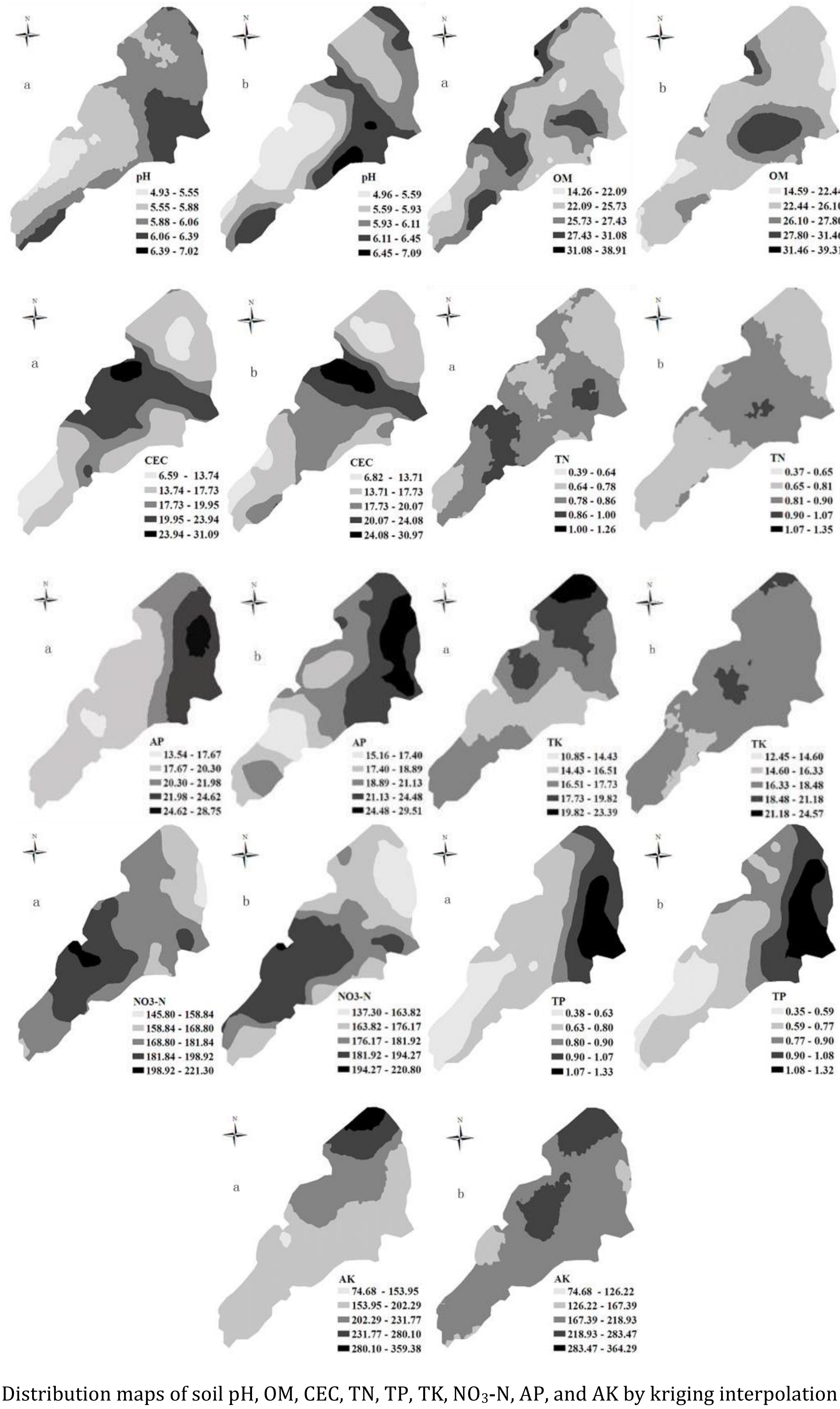

Figure 2. Distribution maps of soil pH, OM, CEC, TN, TP, TK, NO_3-N, AP, and AK by kriging interpolation under two sampling methods.

Thus, the results of cross-validation of soil OM, CEC, TN, TK and AK indicate that the interpolation results of the grid-sampling scheme were better than the regular simple random sampling scheme, and soil pH, TP and AP provided worse interpolation results in grid-sampling scheme. The interpolation results of soil NO_3-N have no markedly significant in the two sampling schemes.

Table 3. Results of cross-validation (ME, MSE, ASE, RMSE and RMSSE) from the 115 points, respectively, in the simple random sampling scheme and grid sampling scheme

Item		pH	OM	CEC	TN	NO_3-N	TP	AP	TK	AK
Simple random sampling scheme	ME	0.002	0.039	0.057	0.004	-0.010	0.001	0.023	-0.001	0.671
	MSE	0.003	0.008	0.010	0.019	-0.001	0.004	0.006	0.000	0.009
	ASE	0.378	4.882	4.274	0.195	13.370	0.142	2.748	2.921	68.900
	RMSE	0.376	4.870	4.350	0.198	14.350	0.130	2.635	2.863	66.690
	RMSSE	0.996	0.997	1.017	1.015	1.071	0.892	0.907	0.981	0.968
Grid sampling scheme	ME	-0.005	-0.033	-0.018	0.002	0.187	-0.001	0.010	-0.005	-0.016
	MSE	-0.010	-0.003	-0.002	0.010	0.009	-0.001	0.004	-0.006	-0.001
	ASE	0.421	4.859	4.410	0.179	14.770	0.145	2.757	2.537	56.180
	RMSE	0.397	4.857	4.252	0.184	14.680	0.130	2.496	2.474	56.300
	RMSSE	0.944	0.998	0.969	1.028	0.999	0.914	0.966	0.978	1.006

Interpolation Maps

Kriging interpolation was performed to obtain a filled contour map using ArcGIS 9.3 with the two sampling methods to determine the spatial distribution and status of soil properties. The contour maps of the soil properties are shown in Figure 3. For each of the soil properties, the spatial distribution trend was similar using the two sampling schemes. Analysis of distributions of soil nutrients revealed that TP and AP have similar spatial distributions. High levels of TP and AP were detected at the east section and low distribution was observed in the southwest sections of the study area. The contour map of TK content showed the highest positional similarity with the krigged AK map. The distributions of pH, OM, and CEC were consistent with high values in the middle section of the field.

Discussion

Coefficients of variation (CVs) were very different among the variables, ranging from approximately 7.67% (pH) to nearly 32.92% (AP), indicating large heterogeneity in soil properties. Nitrogen (N), phosphorus (P) and potassium (K), which are the major minerals needed for tobacco growth and development. In addition, they had particularly high CVs in this study area. This is consistent with the findings of Wang et al. (2009). Our results differed from those reported by Gupta et al. (1999), who showed that soil NO_3-N exhibits moderate variation. This is mainly because of different planting patterns, uneven crop growth and non-uniform management practices, resulting in marked changes in topsoil over small distances. Therefore, site-specific management of nutrients may be necessary to achieve maximum economic and environmental benefits (Jiang et al., 2010). However, classical statistics do not show the spatial distribution of soil properties. The spatial distribution maps of soil nutrients based on geostatistical analysis provide a basis for variable-rate application.

It is important to determine the spatial dependence of soil properties because soil properties with strong spatial dependence are more readily managed (Jiang et al., 2010). The nugget-sill ratio can be used to classify the spatial dependence of soil properties (Jiang et al., 2011). The lower ratios for pH, OM, CEC, and TN were less than 25, indicating that the four soil variables had strong spatial dependence and the structural factors strongly influenced the spatial variability of these properties (Cambardella et al., 1994). Consistent with other reports, the spatial dependence of pH, TN, OM, and CEC were fairly strong (Jiang et al., 2010; Liu et al., 2008). Meanwhile, all other soil variables, except for NO_3-N of grid sampling, were moderately spatially variable, with the nugget/sill ratios ranging from 33.33% to 42.60%. Ranges of spatial dependence that varied from 95.78 m for OM of grid sampling to 558.41 m for AK of SRS were larger than the smallest sampling distance (16 m), suggesting that the two sampling schemes can satisfy the requirement of spatial variability structure analysis of soil properties in the study. Knowledge of the range of influence for various soil variables allows for construction of independent data sets that can be used for classical statistical analysis. A small range indicated that a small sampling interval is required for OM.

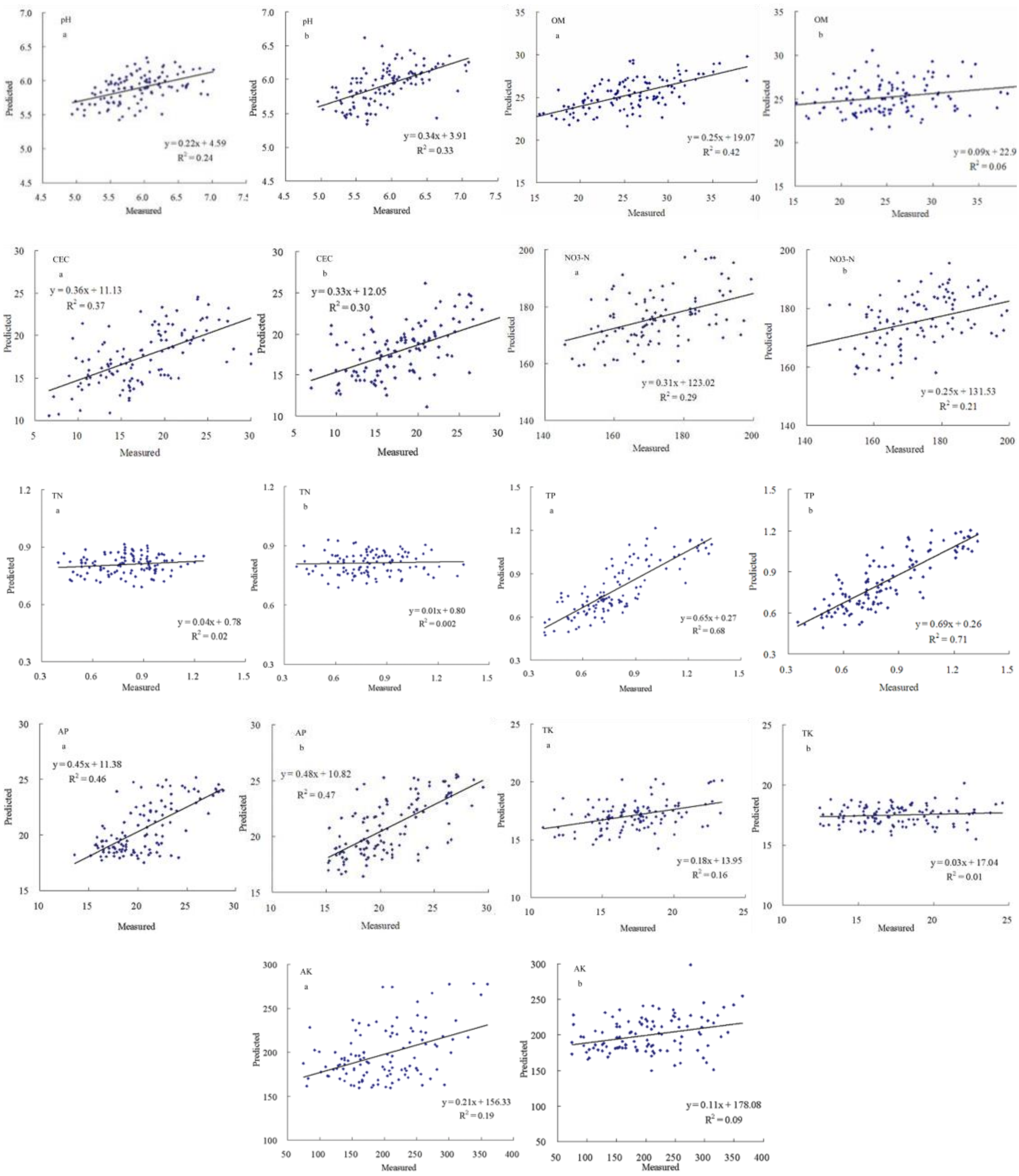

Figure 3. Smoothed contour maps produced by kriging for pH, OM, CEC, TN, TP, TK, NO3-N, AP, AK under two sampling methods in the 10-ha area (a: grid sampling scheme, b: simple random sampling scheme).

For the same soil properties, the nugget-sill ratios of pH, CEC and NO_3-N of grid sampling were lower than those of SRS (Table 2). The other soil properties were just the opposite. Results of cross-validation of the soil properties indicated that a reasonable sampling scheme of pH, CEC and NO_3-N at the site was SRS, whereas that for the remaining soil properties was grid sampling. Therefore, we can speculate that the sampling scheme with bigger nugget-sill ratio was optimal within a certain range of nugget-sill ratio. However, whether this is applicable to other soil properties or other fields must be verified further.

Variable-rate fertilizer application is only possible if the spatial variation in nutrient status across a field is known (Cahn et al., 1994). Geostatistics is an important tool for characterizing the spatial variability of soil properties, and it has been widely used in variable-rate fertilizer application. The accuracy of kriging interpolation also depends on the sample pattern and sample spacing (Gotway et al., 1996). Sampling design is also very important when the objective is to interpolate in an optimal fashion and to generate spatial distribution maps for soil properties within a region (Haining, 1990). Results of the present study revealed that the interpolation errors of soil OM, CEC, TN, TK and AK were the lowest with the grid sampling scheme. On the other hand, interpolation error of soil pH, TP, and AP was the lowest with the SRS. The interpolation results of soil TN, CEC, AK, and TK obtained by grid sampling were better than SRS, while the interpolation accuracy of soil NO_3-N was no markedly significant in the two sampling scheme. Our results differ from the findings reported by Mallarino and Wittry (2004), which found that grid sampling was the most effective for phosphorus, potassium, pH, and organic matter. Discrepancy between these results and those reported in previous studies may be attributed to inconsistencies in agricultural experimental treatments among different studies.

Potassium is one of the major minerals needed for tobacco growth and development (Liu, 2003). The potassium content of tobacco leaves is highly correlated to tobacco leaf quality and cigarette safety, and potassium content is an important index for measuring tobacco leaf quality (Yang et al., 2007). Potassium deficiency is the most common problem in tobacco planting fields in China, and is seen as a major constraint for improving tobacco quality. In this study, we found that the interpolation errors of soil potassium data in the topsoil layer were lowest in the grid sampling scheme. Similarly, It should be noted that the grid-sampling scheme has previously been shown to be more effective for potassium (Mallarino and Wittry, 2004). Thus, it can be deduced that the optimal spatial sampling scheme is grid sampling if the land was previously planted with flue-cured tobacco. Additionally, plants derive nitrogen and phosphorus, which are important for tobacco plant growth and development, not only from fertilizers, but also from soil minerals.

Our results clearly showed that the prediction accuracies of soil OM, CEC, TN, TK, and AK were smaller in grid-sampling scheme than SRS. The pH, TP, and AP had the smallest kriging errors in the SRS, the interpolation errors of NO_3-N were not markedly different between the two sampling schemes. We instead found that the grid sampling method is optimal for tobacco planting fields because soil properties, which are important for tobacco quality, are predicted with better accuracy, and an accurate site-specific fertilization scheme for precision farming can be more easily developed using this method.

This study provides a theoretical basis for the practice of precision agriculture in tobacco-planted field. For tobacco production, examining the distribution and abundance and shortage situation of key-nutrients is necessary, especially for the nutrient crucial for tobacco such as potassium (Liu, 2003). If we continue to use the experience based homogenization fertilization management, the variability of tobacco yield and quality will increase. Therefore, the key-nutrient must be closely considered by the producer when determining the sampling scheme. From the analytical results of this study, the interpolation error of AK and TK were the smallest, revealing that the best sampling scheme was grid sampling. In actual production, the grid-sampling scheme could be used as the basis for site-specific fertilizer management because potassium, which is key-nutrient for tobacco quality, is predicted with better accuracy. In the future, a reasonable sampling scheme should be selected in accordance with spatial autocorrelation, trend effect, anisotropy effect of soil properties, and the restrictions of monetary, time, workforce.

Conclusion

Classical statistical analysis showed considerable spatial variability of all soil properties. Soil pH and NO_3-N had low variation (CV, <15%), whereas all other soil properties exhibited medium variation (CV, 15%-15%). Geostatistical analysis of soil properties indicated that pH, OM, TN, CEC, TP and AP ideally matched the spherical model, whereas the remaining variables suitably fit the exponential model with two sampling methods. Classical statistical analysis and geostatistical analysis of soil properties revealed considerable spatial variability in the study area, suggesting that variable-rate fertilizer application is required. In addition, interpolation error analysis revealed that soil OM, CEC, TN, TK and AK had the smallest kriging errors in the grid sampling scheme. The smallest interpolation error for pH, TP, AP was obtained by SRS. Moreover, the interpolation precisions of NO_3-N were not markedly different between the two sampling schemes, while the SRS was slightly better for soil pH, TP, AP, and grid sampling was slightly more appropriate for all other soil properties. Therefore, considering the fact that potassium is one of the major minerals needed for tobacco, the grid sampling scheme should be used for variable-rate fertilizer application to improve the quality of flue-cured tobacco.

References

Bremner, J.M., Mulvaney, C.S., 1984. Total nitrogen In: Methods of Soil Analysis, page, A.L. (ED.). 2nd Edn. Agron. No. 9, Part 2: Chemical and microbiological properties. Am. Soc. Argon. Madison, WI. USA. pp. 595-624.

Brus, D.J., de Gruijter, I.J., van Groenigen, J.W., 2006. Designing spatial coverage samples using the k-means clustering algorithm. In: Digital Soil Mapping: An Introductory Perspective. P. Lagachene, A. B. McBratney, M. Voltz (eds.). Elsevier, Amsterdam, Netherlands.

Caeiro, S., Goovaerts, P., Painho, M., Costa, H., Sousa, S., 2002. Optimal spatial sampling design for mapping estuarine sediment management areas. AGILE Conference on Geographic Information Science, Palma, p. 1-6.

Cahn, M.D., Hummel, J.W., Brouer, B.H., 1994. Spatial analysis of soil fertility for site-specific crop management. *Soil Science Society America Journal* 58: 1240-1248.

Cambardella, C.A., Moorman, T.B., Parkin, T.B., Karlen, D.L., Novak, J.M., Truko, R.F., Konopka, A.E., 1994. Field-scale variability of soil properties in central Iowa soils. *Soil Science Society America Journal* 58: 1501-1511.

Chapman, H.D., 1965. Cation exchange capacity. In: methods of soil analysis, black, C.A. (ED.). Part 2. Number 9 in the series agronomy: American institute agronomy, Madison, Wisconsin. pp. 891-901.

Christman, M.C., 2000., A review of quadrat-based sampling of rare geographically clustered populations. *Journal of Agricultural Biological and Environmental Statistics* 5: 168–201.

Ferguson, R.B., Hergert, G.W., Schepers, J.S., Gotway, C.A., Cahoon, J.E., Peterson, T.A., 2002. Site-specific nitrogen management of irrigated maize: Yield and soil residual nitrate effects. *Soil Science Society America Journal* 66: 544-553.

Frogbrook, Z.L., 1999. The effect of sampling intensity on the reliability of predictions and maps of soil properties. In: Proceedings of the 2nd European Conference on Precision Agriculture. Sheffield Academic Press, Sheffield, UK. pp. 71-80.

Goovaerts, P., 1998. Geostatistical tools for characterizing the spatial variability of microbiological and physico-chemical soil properties. *Biology and Fertility of Soils* 27: 315-334.

Goovaerts, P., 2000. Estimation or simulation of soil properties? An optimization problem with conflicting criteria. *Geoderma* 97: 165-186.

Gotway, C.A., Ferguson, R.B., Hergert, G.W., Peterson, T.A., 1996. Comparison of kriging and inverse-distance methods for mapping soil parameters. *Soil Science Society America Journal* 60: 1237-1247.

Gupta, R.K., Mostaghimi, S., McClellan, P.W., Birch, J.B., Brann, D.E. 1999. Modeling spatial variability of soil chemical parameters for site-specific farming using stochastic. *Water Air and Soil Pollution* 110: 17–34.

Haining, R. 1990. Spatial data analysis in the social and environmental sciences. Cambridge University Press. 409 pp.

Issaks, E., Srivastava, R.M. 1989. An Introduction to Applied Geostatistics. Oxford University Press, New York.

Jiang H.L., Liu G.S., Wang X.Z., Song, W.F., Zhang, R.N., Zhang, C.H., Hu, H.C., Li, Y.T., 2010. Spatial variability of soil properties in a long-term tobacco plantation in central China. *Soil Science* 175: 137-144.

Jiang H.L., Liu G.S., Wang, R., Liu, S.D., Han, F.G., Yang, Y.F., Ye, X.F., Zhang, Q.J., Wang, X.J., Wang, Z.H., Hu, H.C., 2011. Delineating site-specific quality-based management zones for a tobacco field. *Soil Science* 176: 206-212.

Johnston, K., Hoef, J.M.V., Krivoruchko, K., Lucas. N., 2001. Using ArcGIS Geostatistical Analysis. GIS User Manual by ESRI, New York.

Kumar, N. 2009. An optimal spatial sampling design for intra-urban population exposure assessment. *Atmospheric Environment* 43: 1153–1155.

Li, Q.Q., Wang, C.Q., Yue, T.X., Li, B., Yang, J., Shi, W.J., 2008. Error analysis of soil property spatial interpolation with RBF artificial neural network with different input methods. *Acta Pedologica Sinica* 459: 360-365.

Li, Y., Shi, Z., Wu, C.F., Li, F., Li, H.Y., 2007. Optimised spatial sampling scheme for soil electriclal conductivity based on Variance Quad-Tree (VQT) method. *Agricultural Sciences in China* 6: 1463-1471.

Lindsley, C. M., Bauer, F. C. 1929. Test your soil for acidity. University of Illinosis, College of Agriculture and Agricultural Experiment Station, Circular No. 346. USA.

Liu, G.S., 2003. Tobacco Cultivation. China Agricultural Press, Beijing, China. (In Chinese)

Liu, G.S., Wang, X.Z., Zhang, Z.Y., Zhang, C.H., 2008. Spatial variability of soil properties in a tobacco field of central China. *Soil Science* 173: 659-667.

Liu, G.S., Jiang, H.L., Liu, S.D., Wang, X.Z., Yang, X.M., Hu, H.C., Liu, Q.H., Xie, D.P., Gu, J.G.., Li, Y.T., 2010. Comparison of kriging interpolation precision with different soil sampling intervals for precision agriculture. *Soil Science* 175: 405-415.

Lu, R.K., 1999. Chemical analysis of agricultural soil, Beijing, China. *Agricultural Science Technology Press*, p. 34–56. (In Chinese)

Mallarino, A.P., Wittry, D.J., 2004. Efficacy of grid and zone soil sampling approaches for site-specific assessment of phosphorus, potassium, pH, and organic matter. *Precision Agriculture* 5: 131–144.

McBratney, A.B., Whelan, B.M., Walvoort, D.J.J., Minasny, B., 1999. A purposive sampling scheme for precision agriculture. In: Proceedings of the 2nd European Conference on Precision Agriculture. Sheffield Academic Press, Sheffield, UK. p. 101-110.

National Soil Survey Office. 1993. Soil series of China. Beijing, China Agriculture. Press.

Nelson, D.W., Sommers, L.E., 1982. Total carbon, organic carbon and organic matter. In: methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI. P. 539-577.

Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. United States Department of Agriculture, Circular No. 939, Washington, DC. USA.

Paramasivam, S., Alva, A.K., Fares, A., Sajwan, K.S., 2002. Fate of nitrate and bromide in an unsaturated zone of a sandy soil under citrus production. *Journal of Environmental Quality* 31: 671-681.

Peck, T.R., 1990. Soil testing: Past, present and future. *Communication in Soil Science and Plant Analysis* 21: 1165-1186.

Pooler, P.S., Smith, D.R., 2005. Optimal sampling design for estimating spatial distribution and abundance of a freshwater mussel population. *Journal of the North American Benthological Society* 24: 525–537.

Quine, T.A., Zhang, Y., 2002. An investigation of spatial variation in soil erosion, soil properties and crop production within an agricultural field in Devon, UK. *Journal of Soil and Water Conservation* 57: 55-65.

Richards, L.A., 1954. Diagnosis and improvement of saline and alkaline soil. Unites States Department of Agriculture, Agriculture HandBook. No. 60. Washington, DC. USA.

Rodríguez, A., Durán, J., Fernández-Palacios, J. Gallardo, A., 2009. Spatial variability of soil properties under Pinus canariensis canopy in two contrasting soil textures. *Plant and Soil* 322: 139–150.

Tang, G.A., Yang, X. 2006. ArcGIS experimental tutorial of spatial analysis GIS [In Chinese]. Science Press, Beijing, China, 384-385.

Thompson, S.K., Seber, G.A.F., 1996. Adaptive sampling. Wiley, New York.

Wang, X.Z., Liu, G.S., Hu, H.C., Wang, Z.H., Liu, Q.H., Liu, X.F., Hao, W.H., Li, Y.T., 2009. Determination of management zones for a tobacco field based on soil fertility. *Computers and Electronics in Agriculture* 65: 168-175.

Webster, R., Oliver, M.A. 2001. Geostatistics for Environmental Science. John Wiley and Sons, LTD, Toronto, Ontario, Canada. pp. 271.

Wollenhaupt, N.C., Wolkowski, R.P., Clayton, M.K., 1994. Mapping soil test phosphorus and potassium for variable-rate fertilizer application. *Journal of Production Agriculture* 7: 441-448.

Yang, T.Z., Lu, L. M., Xia, W., Fan, J.H., 2007. Characteristics of potassium-enriched, flue-cured tobacco genotype in potassium absorption, accumulation, and ın-ward potassium currents of root cortex. *Agricultural Sciences in China* 6: 1479-1486.

Zhu, Z., Stein, M.L., 2006. Spatial sampling design for prediction with estimated parameters. *Journal of Agricultural, Biological & Environmental Statistics* 11: 24-44.

Zhu, X.H., Yang, X.C., Cai, Y.L., 2005. Fractal and fractal dimension of spatial distribution of China soil system. *Acta Pedologica Sinica* 42: 881-888.

Eurasian J Soil Sci 2016, 5 (1) 74 - 83

Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

The effect of zeolite and some plant residues on soil organic carbon changes in density and soluble fractions: Incubation study

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Article Info

Received : 27.08.2015
Accepted : 12.10.2015

Abstract

Organic carbon (OC) fractions play an important role in soil and many ecosystem processes. This study focuses on changing of OC in different fractions in a soil treated with different levels of zeolite and plant residue that incubated for 90 days. The results showed that the amounts of light fraction (LF) and heavy fraction (HF) increased with increasing the percentage of zeolite and plant residues in the soil. The highest amounts of LF (22.7 g LF. Kg^{-1}_{Soil}) and HF (26.7 g. Kg^{-1}_{Soil}) were found when 30% zeolite, 5% wheat and alfalfa straws was added to the soil respectively. Accordingly, wheat straw and alfalfa straw were effective for increasing the LF and HF respectively. However they declined with decreasing the OC from the 1st day of experiment until the 90th day of experiment. Soluble OC in hot (2.80 g. Kg^{-1}_{Soil}) and cool (2.25 g. Kg^{-1}_{Soil}) water fractions increased with the addition of 30% zeolite and 5% plant residues particularly alfalfa straw in comparison with control. Although they increased after 30 days of starting incubation but, then they decreased in the continuation of the experiment. In fact, OC contents in density and soluble fractions increased with application and addition of 30% zeolite and 5% plant residues into the soil; however they decreased after 30 days of incubation with decreasing the OC. The findings of this research revealed the application of zeolite and plant residues improved carbon pools in density and soluble fractions and carbon sequestration increase by increasing the OC contents in soil.

Keywords: Alfalfa straw, wheat straw, light fraction, heavy fraction, hot water, cool water

Introduction

It has been recognized in recent decades that the quantity of carbon stored in soils is important on a global scale. Therefore, land management practices affecting the soil organic carbon (SOC) content may have a global impact, if they are applied over large areas (Bronick and Lal, 2005). Global warming concerns have led to a surge of interest in evaluating the effect of management practices on carbon sequestration in soils (Adesodun and Odejimi, 2010). This interest is justified because soils as a sink for atmospheric CO_2 play a key role in the global carbon budget as well as in the global carbon cycle (Eshel et al., 2007). Soils are the third largest active carbon pool after the hydrosphere and the lithosphere. The role of soils as either a source or a sink for greenhouse gases, in general, and that of CO_2, in particular, has been a focus of recent studies (Bhattacharyya et al., 2009; Majumder et al., 2008).

Since the largest terrestrial pool of carbon is located in the soils (Bhattacharyya et al., 2009), factors that affect its retention and release also influence its exchange between soil and atmosphere (Borkowska and Stêpniewska, 2011). Storage of SOC in agricultural systems is a balance between carbon additions from non-

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e-ISSN: 2147-4249 DOI: http://dx.doi.org/10.18393/ejss.2016.1.074-083

harvested portions of crops (Wu et al., 2008), organic sources (Thelen et al., 2010), and carbon losses, primarily through organic matter decomposition and release of respired CO_2 to the atmosphere (Bird et al., 2002). For centuries, organic matter has been applied to agricultural soils as a means of supplying the crops with nutrients and maintaining the required SOC content with benefits to soil structure (Balashov et al., 2010). Organic substances improve soil aggregation, reduce soil compaction and surface sealing, increase carbon sequestration and nutrient availability, and enhance infiltration rate and water holding capacity (Ohu et al., 2009).

Density fractionation

Changes total organic carbon (TOC) in soil with changes in land use and management can be partly explained by the way carbon (C) is allocated in different fractions of soil organic matter (SOM) (Tan et al., 2007). These fractions exhibit different rates of biochemical and microbial degradation (Stevenson, 1994) as well as different accessibility and interactions (Sollins et al., 1999). The dynamics of SOC are usually described by dividing SOM into two or more fractions. Physical fractionation of SOM is useful for distinguishing specific carbon pools responsive to management, identifying the physical control of SOM (Cambardella and Elliott, 1993; Collins et al., 1997), and characterizing the relationship between SOM and size distribution of aggregates (Feller et al., 1996).

Density fractionation is a laboratory procedure that physically separates soil into light and heavy fractions (Wander and Traina 1996; Sollins et al. 1999). The procedure is useful for assessing labile pools of SOM that are more sensitive to cropping practice than is the total SOC pool in temperate soils (Janzenet et al., 1992). Among liquids for density fractionation, sodium polytungstate (SPT) solution of 1.85 g $.mL^{-1}$ is often used (Magid et al., 1996; Six et al., 1998, 2002). Light fraction is commonly referred to a plant-like and less stable fraction with high organic carbon (OC) concentration (Golchin et al., 1994; Gregorich et al., 1996). Heavy fraction is a more stable and high-density organo-mineral fraction having lower C concentrations (Golchin et al., 1995a, b).

Light fraction of SOM is not only sensitive to changes in management practices (Cambardella and Elliott, 1992; Bremer et al., 1994), but also correlates well with the rate of N mineralization (Hassink 1995; Barrios et al., 1996). By incubating bulk soil and density fractions, Alvarez and Alvarez (2000) observed that light fraction was the driving factor in soil respiration. Light fraction supposedly represents an intermediate pool between undecomposed residues and humified SOM (Gregorich and Janzen, 1996). In contrast, the heavy fraction contains more processed SOM (Hassink 1995; Wander and Traina, 1996) and can be a major sink for C storage in soil because it has a little mineralizable carbon (Barrios et al., 1996; Whalen et al., 2000), although it is demonstrated by poor relationships with soil respiration (Alvarez and Alvarez, 2000). Meanwhile, the importance of light fraction (including free and occluded organic C within aggregates) is widely recognized for its role in formation and stability of soil structure, especially in stabilization of soil macroaggregates (>250 mm) (Miller and Jastrow, 1990; Kay 1998). Janzen et al (1992) reported that light fraction of surface soil (0–7.5 cm) accounted for 2–17% of SOC, depending largely on cropping systems. However, there are few direct data quantifying these two fractions and their contributions to total SOC storage as related to changes in land use and tillage practices.

Water soluble organic carbon

Soluble organic matter in soils plays an important role in many ecosystem processes. For example, the size of this pool of organic matter and its availability as a substrate are critical to nutrient fluxes in agricultural systems. The amount and biodegradation of soluble organic matter in soil also have implication for different parts of the ecosystem, from the atmosphere (e.g., Production of greenhouse gases) to the hydrosphere (e.g., Water quality) (Gregorich et al., 2003). Plant residue and humus are the most significant sources of soluble organic carbon in soil (Kalbitz et al., 2000). In studies using ^{13}C natural abundance technique to identify the source of carbon in labile organic matter fractions, Gregorich et al. (2000) observed that carbon isotope signature of water-soluble carbon was similar to that of humus, whereas for the microbial biomass carbon, it was similar to recent maize residue. They hypothesized that, although the water-soluble carbon pool was small, it had a high turnover and was in equilibrium with soil humus.

Results of Boyer and Groffman (1996) suggested that, the difference in water-soluble and biodegradable C between agricultural soils and forest soils (values were higher in agricultural soils) was due to increases in soluble humic materials in agricultural soils. Therefore, humus is likely the major source of water-soluble C because of the relatively large amount of humus present in soil relative to that contributed by the microbial biomass or recently deposited plant residues. Soluble organic matter is an important substrate for microorganisms (Marschner and Bredow, 2002) and is quickly depleted during incubation. Laboratory studies (Boissier and Fontvieille, 1993; Nelson et al., 1994; Boyer and Groffman, 1996) have shown that microorganisms can decompose different amounts of the water-soluble organic matter fraction. These studies, which ranged in duration from hours to months, indicated that 10–40% of the water-soluble organic carbon was decomposable under laboratory conditions. Boyer and Groffman (1996) reported that land use and soil depth had significant effects on the proportion of soluble organic C that was readily biodegradable C (i.e., Labile C). In order to fully understand the dynamics of soluble organic C, it is useful to have some knowledge of the biological nature of soluble organic N. But in contrast to soluble organic C, little work has been done to characterize soluble organic N.

The quantity and the biological nature of dissolved organic matter are affected by the extraction procedure used. Extraction procedures involving higher temperatures extract a greater amount of soluble organic matter than extractions carried out at the room temperature. High temperature is known to hydrolyze organic structures, lyse cells, and dissociate organic materials from inorganic colloids (Nelson et al., 1994). Davidson et al (1987) found strong correlations between organic C extracted with hot water and mineralizable C, but noted that the extent to which heterotrophs could decompose the extracted C was uncertain. Non-microbial pools contribute to the hot water-extractable C (Sparling et al., 1998), and this material may represent a pool of organic matter involved in the formation of stable aggregates (Haynes and Swift, 1990).

During last years, great strides have been made in a number of research topics such as characterizing the spatial and temporal variations in the concentration and flux of dissolved organic carbon (DOC) reviewed by Kalbitz et al (2000) and Aitkenhead-Peterson et al (2003), quantifying its role in soil chemistry and pedogenesis (e.g., Kaiser and Zech, 1998; Jansen et al., 2003; Cances et al., 2003), describing the chemical composition of DOM (Guggenberger and Zech, 1994; Kaiser et al., 2001; Strobel et al., 2001), and quantifying the availability of DOC to soil microflora (Zsolnay and Gorlitz, 1994; Yano et al., 2000; Kalbitz et al., 2003; Marschner and Kalbitz, 2003). The main objectives of this study were to determine water soluble and density fractions of organic carbon in soils treated by different percentage of zeolite and some plant residues and incubation them in field capacity for 90 days.

Material and Methods

Study area

This study was conducted in Hamedan province, western part of Iran. This area is located between longitudes 47° 42' and 48° 45' E and latitudes 33° 28' and 34° 29' N. The climate of the region is semiarid with a mean annual precipitation of 300 mm and a mean annual temperature of 10 °C. Agriculture is an industry and principal land use in Hamadan. The soil of this area was classified as Typic Haplocalcids (Aminiyan et al., 2015).

Sampling, treatment and analysis of soil

The methods used for soil sampling, treatment and analysis were reported in Aminiyan et al (2015). The treated and moistened soils were incubated in lab condition (20-25 °C) for 90 days. After 1, 5, 10, 20, 30, 45, 60, 75 and 90 days of incubation, a portion of each soil was taken for the study of in density (light and heavy) and soluble (hot water and cool water) organic carbon fractions.

Density fractionation

About 10 g dried sample was transferred to a 20 ml graduated centrifuge tube, and 50 ml of NaI solution (d = 1.3 g cm^{-3}) was added. Suspensions were immediately centrifuged at 3000rpm for 10 min. The supernatant containing the light fraction (LF) was decanted onto Whatman no. 50 filters (2.7-pm retention) and vacuum-filtered. The heavy fraction (HF) residue was re-suspended twice in fresh NaI solution and the LFs were combined. Light and heavy fractions were then washed four times into pre weighed tins with deionized water, afterwards dried at 55°C for 24 h in the oven, and weighed (Strickland and Sollins, 1987). Then organic carbon content in heavy fraction was determined by Walkley and Black (1934) method.

Soluble water organic carbon fractions

The soluble water organic carbon in the whole soil and the three aggregate fractions were extracted using cold water followed by hot water. Soluble organic matter in cold water was extracted from soils by adding 150 ml of distilled/deionized water to a tube containing 15g of air-dried whole soil or aggregate fraction. The soil water suspension was shaken for30 min and centrifuged at 4500 rpm for 20 min. The supernatant solutions were decanted and passed through a 0.45-µm cellulose nitrate filter. The weight of extraction tubes with remaining wet soil was recorded in order to calculate the amount of cold water extract remaining. Hot water-soluble organic matter was extracted from these soils by adding water to the wet soil remaining in each tube to return the water volume to 150 ml, then by placing the tubes in a water bath at 80 °C for 16 h. After this period of time, the samples were centrifuged, decanted, and filtered as above. Filtered solutions were stored in a refrigerator (4°C) prior to incubation (Gregorich et al., 2003). Then organic carbon content in heavy fraction was determined by Walkley and Black, (1934) method.

Statistical data analysis

The experiment was a completely randomized factorial design with three replicates. The factors applied were alfalfa straw (0 and 5%), wheat straw (0 and 5%), Zeolite (0, 10 and 30%) and incubation time (1, 5, 10, 20, 30, 45, 60, 75 and 90 days). All statistical analyses were performed in the SAS Ver.9.2 statistical framework (SAS Institute, 2008); to obtain the main differences between the treatments, the Duncan's (α = 0.01) test was applied.

Results and Discussion

Some of soil, plant residues and zeolite properties

Table 1 shows the sand, silt and clay contents were 69, 19 and 12%, respectively in the soil corresponding to a loamy sand texture. The soil was not saline (EC 1.1 dS. m^{-1}); equivalent calcium carbonate ($CaCO_3$) and pH values were 1.79% and 7.2 respectively, with low cation exchange capacity (CEC 4.80 Cmolc Kg^{-1}), organic matter (OC 3.41 g Kg^{-1}). Table 2 presents some properties of applied plant residues. Alfalfa and wheat straw had neutral pH (6 and 7.97), high OC (511 and 532 g. Kg^{-1}) values and C/N (23.30 and 90.75) and C/P (85.20 and 123.50) ratios respectively. Table 3 reveals some of applied zeolite properties.

Table 1. Some of chemical and physical properties of applied soil.

EC (dS. m^{-1})	pH	CEC (Cmol c Kg soil^{-1})	Total organic C (g Kg^{-1})	CCE*	Sand	Clay	Silt
				%			
1.10	7.20	4.80	3.41	1.79	69	12	19

* Carbonate Calcium Equivalent

Table 2. Some properties of applied plant residues in this study.

	pH	EC (dS m^{-1})	Total Organic C (g Kg^{-1})	Total Nitrogen (g Kg^{-1})	Total Phosphorous (g Kg^{-1})	C/N	C/P
Alfalfa straw	6.00	9.50	511	22	5.98	23.30	85.20
Wheat straw	7.97	4.30	532	7	4.31	90.75	123.50

Table 3. Some properties of applied Zeolite

EC (dS. m^{-1})	pH	Organic C (g Kg^{-1})	CEC (Cmol c Kg soil^{-1})
0.98	7.20	0.93	169.30

The effect of zeolite and plant residues on OC in density fractions

Table 4 shows the analysis of variance of the effects of applied zeolite, plant residues, incubation time, and their interaction on light fraction (LF), heavy fraction (HF), Soluble OC in Cool water and hot water fractions in soil. Also this table shows that the significant (p <0.01) effects of application of zeolite, alfalfa and wheat straws, their interaction and incubation time on LF and HF, Soluble OC in Cool water and hot water fractions in soil. Although, the interactions between zeolite and incubation time, plant residues and incubation time and zeolite, plant residues and incubation time did not have significant effects on mentioned organic carbon fractions in the soil.

Table 4. Analysis of variance (mean square) of the effects of zeolite, plant residues application, incubation time and their interaction on light (LF) and heavy fraction (HF), Soluble OC in Cool water and hot water fractions in soil.

Source	DF	Organic Carbon (gr/Kg soil)			
		LF (g LF. Kg^{-1}_{Soil})	OC in HF (g .Kg^{-1}_{Soil})	Soluble OC in Cool water (g .Kg^{-1}_{Soil})	Soluble OC in Hot water (g .Kg^{-1}_{Soil})
Zeolite	2	524.45 **	1144.33 **	1.54 **	1.43 **
Plant Residues	3	54 **	201.44 **	0.19 **	0.80 **
Time	8	65.45 **	353.87 **	5.00 **	11.59 **
Zeolite*Time	16	60.48 ns	1.97 ns	1.66 ns	3.67 ns
Plant Residues*Time	24	19.59 ns	0.98 ns	1.16 ns	2.72 ns
Zeolite* Plant Residues	6	111.15 **	3.90 **	0.34 **	0.49 **
Zeolite*Plant Residues*Time	48	16.32 ns	0.54 ns	0.41 ns	0.92 ns
Error	216	6.02	0.5	0.1	0.1

**) Mean square of the treatment is significant at the 0.01 level.
ns) Mean square of the treatment is not significant.

Table 5 reveals the OC content in LF and HF increased by the addition of zeolite and plant residues (p <0.01). LF value in 30% zeolite plus 5% wheat straw (Z30W5) treatment was greater than the other treatments; as its value 6.38 (g LF Kg^{-1}_{Soil}) was greater than control, because C:N ratio in wheat straw was higher than alfalfa straw thus subsequently wheat straw had lower stage of biodegradation by microorganisms in soil. This fraction of organic carbon decreased from the 1^{th} day (20.61 g LF Kg^{-1}_{Soil}) to the 90^{th} day (16.99 g LF Kg^{-1}_{Soil}) during soil incubation (Figure 1).

Table 5. Light fraction and heavy fraction content in all of treatment.

Treatment	LF (g LF. Kg^{-1}_{Soil})	OC in HF (g .Kg^{-1}_{Soil})
Control	16.32±1.30* f	17.60±3.00 f
Z0A5	17.08±1.27 f	20.50±3.01 de
Z0W5	18.04±1.28 e	19.70±3.02 ef
Z10PR0	18.36±1.29 e	21.90±3.04 cd
Z10A5	18.85±1.30 de	25.80±3.02 ab
Z10W5	19.52±1.26 d	24.60±3.03 bc
Z30PR0	20.48±1.30 c	24.10±3.01 bc
Z30A5	21.60±1.29 b	26.70±3.04 a
Z30W5	22.70±1.28 a	25.40±3.03 ab

*. Mean ± Standard deviation
The same letter are not significantly different at p < 0.01 using Duncan's LSD.
Note: Z0A5 (0% zeolite+5% alfalfa straw), Z0W5 (0% zeolite+5% wheat straw), Z10PR0 (10% zeolite+0% Plant Residue), Z10A5 (10% zeolite+5% alfalfa straw), Z10W5 (10% zeolite+5% wheat straw), Z30PR0 (30% zeolite+0% Plant Residue), Z30A5 (30% zeolite+5% alfalfa straw), Z30W5 (30% zeolite+5% wheat straw).

The heavy fraction value in Z30A5 treatment was significantly increased (9.1 g C/Kg $_{Soil}$) in comparison with the control treatment (Table 5). Also this table investigates that Z30A5 treatment increased heavy fraction (approximately 1 g Kg^{-1}_{Soil}) and (6.2 g Kg^{-1}_{Soil}) in comparison with the Z10A5 and Z0A5 treatments respectively. Actually, it is known that the alfalfa straw was more efficiency due to increasing organic carbon in heavy fraction than wheat straw in all of the treatments with the similarity percentage of zeolite (Table 5).

Soil organic carbon (SOC) in the light fraction plays an important role in retaining of cellulase molecule from washing out and nutrition of soil microorganisms and subsequently humus production. Thus soil organic matter quality is an important factor in its disintegration rate (Schmidt et al., 2002; Beheshti et al., 2012). According to the Figure 2, OC in heavy fraction had a distinct downward trend from the 1^{st} day (27 g Kg^{-1}_{Soil}) until the 90^{th} day (18.4 g Kg^{-1}_{Soil}). The recent research on organic carbon decay dynamics showed that LF and HF were decreased during of soil incubation (Hassink et al., 1995; Creamer et al., 2012). This is consistent with the finding of Rovira and Vallejo'studies (2003) who also found that LF and HF contents were declined in during of soil incubation period.

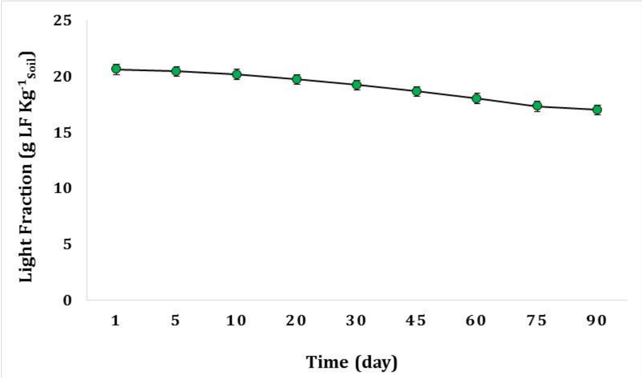

Figure 1. Light fraction changes with the passage of time

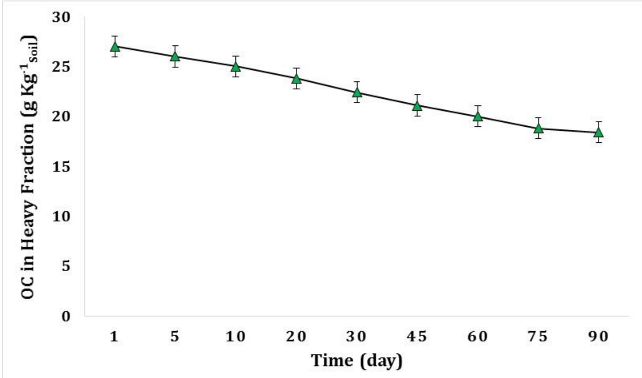

Figure 2. Organic carbon changes in heavy fraction with the passage of time.

The effect of zeolite and plant residues on water soluble organic carbon fractions

As shown in Table 6, soluble organic carbon contents in hot water and cool water increased by the addition of zeolite and plant residues especially alfalfa straw. The results showed that soluble OC in hot water in Z30A5 treatment was 0.46 (g Kg^{-1}_{Soil}), 0.18 (g Kg^{-1}_{Soil}) and 0.3 (g Kg^{-1}_{Soil}) greater than control, Z10A5 and Z0A5 treatments respectively (Table 6). Studying on the chemical composition of dissolved organic carbon (DOC) suggested that, most DOM is an end product of microbial metabolism (Guggenberger and Zech, 1994); however short-term experimental manipulations of organic matter sources showed that fresh litter also contributes significantly to the production of DOC (Park et al., 2002). These two views are not necessarily mutually exclusive, but they do point out the considerable difficulty in determining the influence of substrate (litter, soil organic matter), microbial community composition (Muller et al., 1999), and abiotic factors such as temperature and water flux on DOC production and flux (Brooks et al., 1999). Aminiyan et al (2015) reported that the addition of 30% zeolite with 5% alfalfa straw to the soil redounded increasing OC in different aggregate particle size classes.

Table 6. Soluble organic carbon in Hot and Cool water content in all of treatments.

Treatment	Soluble OC in Cool water (g .Kg^{-1}_{Soil})	Soluble OC in Hot water (g .Kg^{-1}_{Soil})
Control	1.93±0.348* b	2.34±0.552 e
Z0A5	2.01±0.353 ab	2.50±0.546 de
Z0W5	1.94±0.357 b	2.42±0.561 de
Z10PR0	1.97±0.352 ab	2.44±0.454 cd
Z10A5	2.10±0.355 ab	2.62±0.461 ab
Z10W5	2.04±0.357 ab	2.52±0.477 ab
Z30PR0	2.15±0.360 ab	2.58±0.480 ab
Z30A5	2.25±0.358 a	2.80±0.491 a
Z30W5	2.19±0.349 ab	2.68±0.473 ab

*. Mean ± Standard deviation

The same letter are not significantly different at $p < 0.01$ using Duncan's LSD.

Note: Z0A5 (0% zeolite+5% alfalfa straw), Z0W5 (0% zeolite+5% wheat straw), Z10PR0 (10% zeolite+0% Plant Residue), Z10A5 (10% zeolite+5% alfalfa straw), Z10W5 (10% zeolite+5% wheat straw), Z30PR0 (30% zeolite+0% Plant Residue), Z30A5 (30% zeolite+5% alfalfa straw), Z30W5 (30% zeolite+5% wheat straw).

According to the Table 6, the same results were achieved similar the results of hot water to cool water, accordingly soluble OC in cool water increased with the greater percentage of zeolite and plant residues particularly alfalfa straw. Soluble OC in cool water content was 0.32 (g Kg^{-1}_{Soil}) and 0.26 (g Kg^{-1}_{Soil}) greater than the control in Z30A5 and Z30W5 treatments respectively. Thus Z30A5 treatment more effective to increasing soluble OC in cool water than Z30W5 treatment. Soluble OC content in hot water was greater than soluble OC content in cool water (Table 6), because hot water had greater ability to extract of lysis microbial cells and extractable soluble organic matter may be adsorbed to clay or complexed with other organic material produced by plants or decomposing organic matter than cool water (Guggenberger and Zech, 1994;

Muller et al., 1999). The plant residues with lower C:N ratio are a readily decomposable substrate for microorganisms and they have additional soluble OC content than plant residues with higher C:N ratio (Gregorich et al., 2003). Also these researchers found that the quantity of biodegradable soluble organic matter was related to the extraction procedure and the quantity of organic matter present in the soil.

Figure 3 indicates that, soluble OC in both hot water and cool water increased with over time from 1st day until the 30th day of incubation period but then decreased by the end of the experiment. Accordingly, the soluble OC in cool water increased from 2 (g Kg^{-1}_{Soil}) in the 1st day to 2.63 (g Kg^{-1}_{Soil}) in the 30th day and then it decreased by the end of experiment 1.68 (g Kg^{-1}_{Soil}). As shown in Figure 3, Soluble OC in hot water value increased from 2.41 (g. Kg^{-1}_{Soil}) in the 1th day to 3.37 (g Kg^{-1}_{Soil}) in the 30th day and finally it decreased by the 90th day 1.95 (g Kg^{-1}_{Soil}). Since soluble organic carbon was increased with the development and promoting plant residues biodegradation in the initial 30 days and when the growth and development of microbial communities were increased with the passage of time and subsequently soluble organic carbon decreased with the passage of time. Kalbitz et al (2003) observed that soluble OC increased with the passage of time, but in another study soluble OC decreased by over the time (Gregorich et al., 2003). Alfalfa straw had greater Soluble organic carbon than wheat straw, thus its degradation rate and OC content decreasing was done by higher rate in this fraction (Swanston et al., 2002; Preston and Schmidt, 2006). It is known in recent reviews that the organic matter quality is particularly important for SOC stabilization (Amelung et al., 2008; Schmidt et al., 2011).

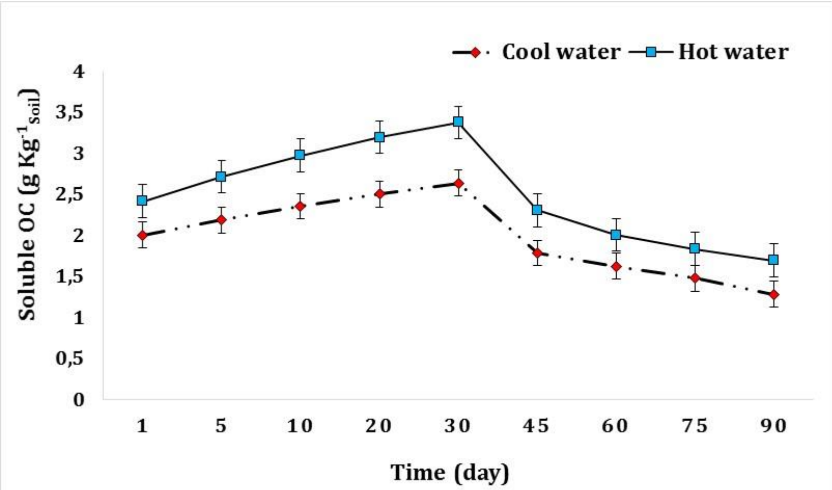

Figure 3. Soluble OC changes in hot and cool water with the passage of time

Conclusion

The results of this study showed that, light fraction, heavy fraction and water soluble organic carbon were increased by addition of greater percentage of zeolite and plant residues into the soil. The results of this study showed that light fraction was greater in Z30W5 treatment than the other treatments. But OC in heavy fraction, Soluble organic carbon in hot water and cool water were maximum in (Z30A5) than the other treatments. LF and HF decreased with the passage of time from the 1st day until the 90th day. Soluble organic carbon in hot water and cool water increased from 1st day until the 30th day and then they decreased by the end of the experiment. In fact, organic carbon content increased by application and addition of zeolite and plant residues into the soil, but these pools decreased with the passage of time. Finally it can be said that the application of zeolite and plant residues improve carbon sequestration process in soil.

Acknowledgments

The authors sincerely thank editor and the anonymous reviewers for reviewing the manuscript and providing critical comments to improve the paper. Thanks so much for Fadak institute in Isfahan and Afrazand factory in Tehran.

References

Aitkenhead-Peterson, J.A., McDowell, W.H., Neff, J.C., 2003. Sources, production, and regulation of allochthonous dissolved organic matter. In: Findlay, S. (Ed.), dissolved organic matter sources, transport, and transformation in aquatic ecosystems. Academic Press, New York.

Alvarez, R., Alvarez, C.R., 2000. Soil organic matter pools and their associations with carbon mineralization kinetics. *Soil Science Society of American Journal* 64: 184–189.

Amelung, W., Brodowski, S., Sandhage-Hofmann, A., Bol, R., 2008. Combining biomarker with stable isotope analyses for assessing the transformation and turnover of soil organic matter. In: Sparks, D.L. (Ed.), Advances in Agronomy. Academic Press, Burlington, pp. 155-250

Aminiyan, M.M., Sinegani, A.A.S., Sheklabadi, M., 2015. Aggregation stability and organic carbon fraction in a soil amended with some plant residues, zeolite, and natural zeolite. *International Journal of Recycling of Organic Waste in Agriculture* 4: 11-22.

Barrios, E., Buresh, R.J., Sprent, J.I., 1996. Nitrogen mineralization in density fractions of soil organic matter from maize and legume cropping systems. *Soil Biology and Biochemistry* 28: 1459–1465.

Beheshti, A., Raiesi, F., Golchin, A., 2012. Soil properties, C fractions and their dynamics in land use conversion from native forests to croplands in northern Iran. *Agriculture, Ecosystems & Environment* 148: 121–133.

Boissier, J.M., Fontvieille, D., 1993. Biodegradable dissolved organic carbon in seepage waters from two forest soils. *Soil Biology and Biochemistry* 25: 1257–1261.

Boyer, J.N., Groffman, P.M., 1996. Bioavailability of water extractable organic carbon fractions in forest and agricultural soil profiles. *Soil Biology and Biochemistry* 28: 783– 790.

Bremer, E., Jansen, H.H., Johnston, A.M., 1994. Sensitivity of total, light fraction and mineralizable organic matter to management practices in a Lethbridge soil. *Canadian Journal of Soil Science* 74: 131–138.

Brooks, P.D., McKnight, D.M., Bencala, K.E., 1999. The relationship between soil heterotrophic activity, soil dissolved organic carbon (DOC) leachate, and catchment-scale DOC export in headwater catchments. *Water Resources Research* 35: 1895– 1902.

Cambardella, C.A., Elliott, E.T., 1992. Particulate soil organic matter changes across a grassland sequence. *Soil Science Society of American Journal* 56: 777–783.

Cambardella, C.A., Elliott, E.T., 1993. Carbon and nitrogen mineralization in aggregates from cultivated and native grassland soils. *Soil Science Society of American Journal* 57: 1071–1076.

Cances, B., Ponthieu, M., Castrec-Rouelle, M., Aubry, E., Benedetti, M.F., 2003. Metal ions speciation in a soil and its solution: experimental data and model results. *Geoderma* 113: 341– 355.

Collins, H.P., Paul, E.A., Paustian, K., Elliott, E.T., 1997. Characterization of soil organic carbon relative to its stability and turnover. In: Paul E A, Elliott E T, Paustian K, Cole C V. (Eds.), Soil Organic Matter in Temperate Agroecosystems, Long-term Experiments in North America. CRC Press, Boca Raton, FL, pp. 51–72.

Creamer, C., Filley, T., Boutton, T., 2012. Long-term incubations of size and density separated soil fractions to inform soil organic carbon decay dynamics. *Soil Biology and Biochemistry* 51: 8-11.

Davidson, E.A., Galloway, L.F., Strand, M.K., 1987. Assessing available carbon: comparison of techniques across selected forest soils. *Communication in Soil Science and Plant Analyses* 18: 45– 64.

Feller, C., Albrecht, A., Tessier, D., 1996. Aggregation and organic matter storage in kaolinitic and smectitic tropical soils. In: Carter, M.R., Stewart, B.A. (Eds.), Structure and Organic Matter Storage in Agricultural Soils. CRC Press, Boca Raton, FL, pp 309–359.

Gianello, C., Bremner, J.M., 1986. A simple chemical method of assessing potentially available organic nitrogen in soil. *Communication in Soil Science and Plant Analyses* 17: 195– 214.

Golchin, A., Oades, J.M., Skjemstad, J.O., Clarke, P., 1994. Study of free and occluded particulate organic matter in soils by solid-state 13C NMR spectroscopy and scanning electron microscopy. *Australian Journal of Soil Research* 32: 285–309.

Golchin, A., Clarke, P., Oades, J.M., Skjemstad, J.O., 1995a. The effects of cultivation on the composition of organic matter and structural stability of soils. *Australian Journal of Soil Research* 33: 975–993.

Golchin, A., Oades, J.M., Skjemstad, J.O., Clarke, P., 1995b. Structure and dynamic properties of soil organic matter reflected by ^{13}C natural abundance, pyrolysis mass spectrometry and solid-state 13C NMR spectroscopy in density fractions of an Oxisol under forest and pasture. *Australian Journal of Soil Research* 33: 59–76.

Gregorich, E.G., Beare, M.H., Stoklas, U., St-Georges, P., 2003. Biodegradability of soluble organic matter in maize-cropped soils. *Geoderma* 113: 237– 252.

Gregorich, E.G., Janzen, H.H., 1996. Storage of soil carbon in the light fraction and macro organic matter. In: Carter M R, Stewart B A. (Eds.), Advances in Soil Science. Structure and Organic Matter Storage in Agricultural Soils. CRC Press, Boca Raton, FL, pp.167–190.

Gregorich, E.G., Liang, B.C., Mackenzie, A.F., Drury, C.F., McGill, W.B., 2000. Elucidation of the source and turnover of water soluble and microbial biomass carbon in agricultural soils. *Soil Biology and Biochemistry* 32: 581– 587.

Gregorich, E.G., Monreal, C.M., Schnitzer, M., Schulten, H.R., 1996. Transformation of plant residues into soil organic matter; chemical characterization of plant tissue, isolated soil fraction, and whole soil. *Soil Science* 161: 680–693.

Guggenberger, G., Zech, W., 1994. Composition and dynamics of dissolved organic carbohydrates and lignin degradation products in two coniferous forests, N.E. Bavaria, Germany. *Soil Biology and Biochemistry* 26: 19–27.

Hassink, J., 1995. Density fractions of soil macroorganic matter and microbial biomass as predictors of C and N mineralization. *Soil Biology and Biochemistry* 27: 1099–1108.

Haynes, R.J., Swift, R.S., 1990. Stability of soil aggregates in relation to organic constituents and soil water content. *European Journal of Soil Science* 41: 73– 83.

Hinds, A., Lowe, L.E., 1980. Ammonium-N determination soil nitrogen Berthelot reaction. *Soil Science and Plant Analysis* 11: 469-475.

Jansen, B., Nierop, K.G.J., Verstraten, J.M., 2003. Mobility of Fe(II), Fe(III) and Al in acidic forest soils mediated by dissolved organic matter: influence of solution pH and metal/organic carbon ratios. *Geoderma* 113: 323–340.

Janzen, H.H., Campbell, C.A., Brandt, S.A., Lafond, G.P., Townley-Smith, L., 1992. Light-fraction organic matter in soils from long-term crop rotations. *Soil Science Society of American Journal* 56: 1799–1806.

Kaiser, K., Zech, W., 1998. Rates of dissolved organic matter release and sorption in forest soils. *Soil Science* 168: 714–725.

Kalbitz, K., Schmerwitz, J., Schwesig, D., Matzer, E., 2003. Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* 113: 273–291.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Science* 165: 277– 304.

Kay, B.D., 1998. Soil structure and organic carbon, a review. In: Lal R, Kimble, J M, Follett R F, Stewart B A. (Eds.), Soil Processes and the Carbon Cycle. CRC Press, Boca Raton, FL, pp. 169–197.

Magid, J., Gorissen, A., Giller, K.E., 1996. In search of the elusive ''active'' fraction of soil organic carbon: three size-density fractionation methods for tracing the fate of homogeneously ^{14}C labeled plant materials. *Soil Biology and Biochemistry* 28: 89–99.

Marschner, B., Bredow, A., 2002. Temperature effects on release and ecologically relevant properties of dissolved organic carbon in sterilized and biologically active soil samples. *Soil Biology and Biochemistry* 34: 459– 466.

Marschner, B., Kalbitz, K., 2003. Controls of bioavailability and biodegradability of dissolved organic matter in soils. *Geoderma* 113: 211– 235.

Miller, R.M., Jastrow, J.D., 1990. Hierarchy of root and mycorrhizal fungal interactions with soil aggregation. *Soil Biology and Biochemistry* 22: 579–584.

Muller, J., Miller, M., Kjuller, A., 1999. Fungal–bacterial interaction on beech leaves: influence on decomposition and dissolved organic carbon quality. *Soil Biology and Biochemistry* 31: 367– 374.

Murphy, D.V., Macdonald, A.J., Stockdale, E.A., Goulding, K.W.T., Fortune, S., Gaunt, J.L,. Poulton, P.R., Wakefield, J.A., Webster, C.P., Wilmer, W.S., 2000. Soluble organic nitrogen in agricultural soils. *Biology and Fertility of Soils* 30: 374–387.

Nelson, P.N., Dictor, M.C., Soulas, G., 1994. Availability of organic carbon in soluble and particle-size fractions from a soil profile. *Soil Biology and Biochemistry* 26: 1549-1555.

Park, J.H., Kalbitz, K., Matzner, E., 2002. Resource control on the production of dissolved organic carbon and nitrogen in a deciduous forest floor. *Soil Biology and Biochemistry* 34: 813-822.

Peperzak, P., Caldwell, A.G., Hunziker, R., Black, C.A., 1959. Phosphorus fractions in manures. *Soil Science* 87: 293-302.

Pratt, P.F., 1965. Potassium. In: Black, C.A. (Ed.), Methods of Soil Analysis: Part 2. Chemical and Microbiological Properties. American Society of Agronomy, Madison, WI, pp. 1022–1030.

Preston, C.M., Schmidt, M.W.I., 2006. Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* 3: 397-420.

Rovira, P., Ramo´n, Vallejo, V., 2003. Physical protection and biochemical quality of organic matter in Mediterranean calcareous forest soils: a density fractionation approach. *Soil Biology and Biochemistry* 35: 245–261.

SAS Institute (2008) SAS Procedures Guide. Version 9.2, SAS Inst, Cary, NC.

Schmidt, M.W.I., Skjemstad, J.O., Jager, C., 2002. Carbon isotope geochemistry and nanomorphology of soil black carbon: black chernozemic soils in central Europe originate from ancient biomass burning. *Global Biogeochemical Cycles* 16(4), 1-70.

Schmidt, M.W.I., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D.A.C., Nannipieri, P., Rasse, D.P., Weiner, S., Trumbore, S.E., 2011. Persistence of soil organic matter as an ecosystem property. *Nature* 478: 49-56.

Six, J., Callewaert, P., Lenders, S., De Gryze, S., 2002. Measuring and understanding carbon storage in afforested soils by physical fractionation. *Soil Science Society of American Journal* 66: 1981–1987.

Sollins, P., Glassman, C., Paul, E.A., Swanston, C., Lajtha, K., Heil, J.W., Elliott, E.A., 1999. Soil carbon and nitrogen: pools and fractions. In: Robertson, G.P., Bledsoc, C.S., Coleman C, Sollins P. (Eds.), Standard Soil Methods for Long-Term Ecological Research. Oxford Univ. Press, New York, pp. 89–105.

Sparling, G., Vojvodic´-Vukovic´, M., Schipper, L.A., 1998. Hot-water-soluble C as a simple measure of labile soil organic matter: the relationship with microbial biomass C. *Soil Biology and Biochemistry* 30:1469– 1472.

Stevenson, F.J., 1994. Humus Chemistry: Genesis, Composition, Reaction, 2nd ed. Wiley, New York, p. 496.

Strobel, B.W., Hansen, H.C.B., Borggaard, O.K., Andersen, M.K., Raulund-Rasmussen, K., 2001. Composition and reactivity of DOC in forest floor soil solutions in relation to tree species and soil type. *Biogeochemistry* 56: 1– 26.

Swanston, C.W., Caldwell, B.A., Homann, P.S., Ganio, L., Sollins, P., 2002. Carbon dynamics during a long-term incubation of separate and recombined density fractions from seven forest soils. *Soil Biology and Biochemistry* 34: 1121-1130.

Tan, Z., Lal, R., Owens, L., Izaurralde, R.C., 2007. Distribution of light and heavy fractions of soil organic carbon as related to land use and tillage practice. *Soil and Tillage Research* 92: 53–59.

Walkley, A., Black, I.A., 1934. An examination of digestion method for determining soil organic matter and a proposed modification of the chromic acid titration. *Soil Science* 37: 29-38.

Wander, M.M., Traina, S.J., 1996. Organic matter fractions from organically and conventionally managed soils. 1. Carbon and nitrogen distribution. *Soil Science Society of American Journal* 60: 1081–1087.

Whalen, J.K., Bottomley, P.J., Myrold, D.D., 2000. Carbon and nitrogen mineralization from light and heavy fraction additions to soil. *Soil Biology and Biochemistry* 32: 1345–1352.

Yano, Y., McDowell, W.H., Aber, J.D., 2000. Biodegradable dissolved organic carbon in forest soil solution and effects of chronic nitrogen deposition. *Soil Biology and Biochemistry* 32: 1743–1751.

Zsolnay, A., Gorlitz, H., 1994. Water-extractable organic matter in arable soils: effects of drought and long-term fertilization. *Soil Biology and Biochemistry* 26: 1257–1261.