2021

Volume : 10
Issue : 2
Page : 87 - 178

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

ABOUT THIS JOURNAL: Eurasian Journal of Soil Science is the official English language journal of the Federation of Eurasian Soil Science Societies. Eurasian Journal of Soil Science peer-reviewed open access journal that publishes research articles, critical reviews of basic and applied soil science in all related to soil and plant studies and general environmental soil science.

ABSTRACTING AND INDEXING: SCOPUS, CABI, FAO-Agris, EBSCOhost, ProQuest, DOAJ, OAJI, TR Dizin, TURKISH Journalpark, CrossRef, CiteFactor, CAS, etc.

Year: 2021, Volume: 10, Issue: 2, Page: 87 - 178 **e-ISSN 2147-4249**

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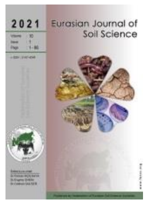

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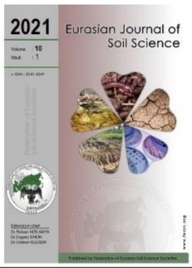
Journal homepage : http://ejss.fesss.org



Assessment of ecological state of Rostov zoo soil

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Article Info

Received : 15.06.2020
Accepted : 07.11.2020
Available online : 11.11.2020

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Abstract

A comparative study of ecological and biological parameters of soils of the Rostov-on-Don Zoo was carried out in 2017-2020. Monitoring sites were studied in areas of various purpose: aviaries with different animals, recreation area, park area. The control plot was a relatively undisturbed park section in the territory of the zoo. Different sites revealed heterogeneity of ecological conditions and soil properties. The most significant difference was in the physical properties of soils. Density, penetration resistance, and soil structure were degraded in aviaries with large animals: rhinos, zebras, deer. Using methods of bioindication, the degree of change in the soil of aviaries was determined compared with the soil of the control plot. The abundance of nitrogen-fixing bacteria of the Azotobacter genus was reduced in the soils of aviaries with zebras, rams, rhinos and giraffe due to the artificial addition of sand to the soil for the purpose of improvement of its physical properties. The activity of soil enzymes (urease and dehydrogenases) was significantly increased in the soils of aviaries due to their contamination with animal excretory products. A particularly high increase was in urease (up to 7.4 times relative to the control soil). The main problems of the topsoil of the zoo are overconsolidation, structural degradation, organic pollution, change in biological activity. The degree of change depends on the size of aviaries, the size and activity of animals and soil amelioration aimed at regulating physical properties of the soil.

Keywords: Bioindication, biology activity, chernozem, soil health, soil quality.

Introduction

The zoo is an integral part of the recreational area of any big city. The purpose of the establishment of this institution was the preservation and reproduction of animals, as well as their demonstration to visitors. In zoos accredited by the Association of Zoos and Aquariums (AZA), there are approximately 750.000 animals representing 6.000 species (AZA, 2016).

An aviary is a location for a certain type of animal. The area should be close to its natural habitat. The closeness to the natural analogue and safety make it possible for animals to feel more comfortable in the conditions of involuntary stay.

Urbanization is currently one of the main factors changing the ecological condition of nature. The condition of vegetation and topsoil in cities draws a lot of attention (Tao et al., 2016; Ivashchenko et al., 2019; Kuznetsov et al., 2019; Momirović et al., 2019). Moreover, studies of urban landscapes are insufficient for optimization of the ecological condition of large metropolises. This is especially true of soil and topsoil. The soils in the large metropolis of Rostov-on-Don with a million inhabitants have not been fully studied. There

: https://doi.org/10.18393/ejss.824654
: http://ejss.fesss.org/10.18393/ejss.824654
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

are a number of sources in the literature addressing some soil properties and features of soil formation (Gorbov and Bezuglova, 2014; Gorbov et al., 2015; Bezuglova et al., 2018). Anthropogenic impact significantly changed the properties and process of soil formation in zonal chernozems of the steppe zone of southern Russia. However, these studies were not able to reflect the functional patterns of the soils in the metropolis in full. This is especially true for the biological condition of urban soils. Rostov Zoo – one of the largest zoos in Russia – was founded 90 years ago and is located in the center of a large metropolis (Figure 1). It is a member of 38 conservation programs for rare and endangered species. The Rostov Zoo contains about 5,000 animals belonging to 400 species. The relevance of ecological studies of the territory of the Rostov Zoo is determined by a low degree of exploration, the presence of specific factors of structural and functional organization, intensive anthropogenic impact, the need for a detailed study of the ecological condition.

Figure 1. Layout of monitoring sites in the zoo: 1–zebras; 2-red deer; 3-bharals; 4- birds; 5–camels; 6-children playground; 7– control; 8– emus (2017) later red deer (2018-2019); 9–buffalo; 10–rhinoceros; 11–giraffe; 12–donkeys

There is a lack of studies of zoo soils, despite the significant role of them in the functioning of natural and anthropogenic ecosystems. Keeping animals in aviaries can lead not only to soil degradation, but also to air pollution with ammonia. Earlier, an assessment of the ecological condition of soils in the Moscow Zoo have been carried out (Yurkova et al., 2009). The results of preliminary studies of the territory of the Rostov Zoo were presented earlier (Kazeev et al., 2018).

An incorrectly selected area of the aviaries leads to overcrowding of animals. This negatively affects their habitat, including their impact on the soil cover of the territory. Also, the release of waste from zoo animals can lead to the accumulation of harmful substances in soils (Gustin and Kelley, 1971). Animal waste accumulating on the soil surface reduces the aesthetic appeal of zoos and serves as a source of pathogenic microflora, biotoxins, and unpleasant odors (Yurkova et al., 2009; Conrad et al., 2018). Zoos can be sources of air pollution from animal excrement, manure, and contaminated litter (Buzmakov et al., 2014). Thus, it becomes necessary to monitor the ecological state of the soils of the zoo aviaries in order to improve the living conditions of animals in captivity.

The aim of the study was to assess the ecological condition and function of soils in different areas of the Rostov Zoo.

The influence of animals has been established on the ecological state of the soils of the aviaries. The practical significance of the work is expressed in determining a set of indicators for environmental monitoring of the territory of zoos. Research is important for finding ways to increase the rate of biological processes in the soil in order to remove animal waste products.

Material and Methods

The studies were carried out in 2017-2020 in accordance with the methods of biological diagnostics of the ecological condition of soils (Kazeev et al., 2016). Previously, using this methodology, a study of ecological parameters of the soils in reserves and anthropogenically disturbed territories was performed (Kazeev et al., 2012, 2015, 2020). As a result, several monitoring sites were allocated in the territory of the zoo: aviaries with birds (gray cranes *Grus grus*, peacocks *Pavo cristatus*, brent geese, etc.), Chapman's zebras (*Equus burchelli chapmani*), emus (*Dromaius Vieillot*), red deer (*Cervus elaphus*), Bactrian camels (*Camelus bactrianus*), bharals (*Pseudois nayaur*), Asian buffalo (*Bubalus arnee*), Rothschild's giraffe (*Giraffa camelopardalis*), white rhinoceros (*Rhinocerotidae Gray*) and domestic donkeys (*Equus asinus asinus*). The control site is located in the Park area of the zoo and has the same soil cover and vegetation as in other areas of the zoo and aviaries. At each monitoring site, 3 individual soil samples were taken, and analytical studies were carried out in each of them; they were replicated 3-10 times. The measured indicators included the physical, chemical, physicochemical and biological properties of soils. Soil density was determined by the gravimetric method using steel rings with a volume of 135 cm^3 and replicated 3 times. Soil hardness (penetration resistance, soil structure strength) was studied in the field using an EIJKELKAMP penetrometer on a depth of 50 cm with an interval of 5 cm, replicated 10 times. The structural and aggregate analysis of the soil was carried out using dry sieving of soil through a column of sieves with 10 mm to 0.25 mm meshes. The quality of the soil structure was assessed by the percentage of the sum of soil aggregates with sizes less than 10 and more than 0.25 mm from the total sum of aggregates.

The temperature was determined with a HANNA CHECTEMP electronic thermometer, on the surface of the soil and at a depth of 5 and 10 cm. The moisture content (volumetric) of the soil was determined in the field using a Fieldscout TDR 100 moisture meter from Spectrum Technologies Inc. (USA) in 10-fold repetition on each study site.

Analytical studies were performed at the Department of Ecology and Environmental Management of the Southern Federal University (Rostov-on-Don, Russia) using methods accepted in ecology, biology and soil science (Kazeev et al., 2016). The content of organic carbon in humus was determined using the method of oxidation with a chromic mixture on a spectrophotometer UNICO 1201 (United Products & Instruments, Inc., USA). The reaction of the soil environment (pH) and the redox potential was determined by a potentiometric method (HANNA HI 98128 pHep 5, Germany) in soil suspension with a soil : water ratio of 1 : 2.5 (10 g soil to 25 ml water). The content of easily soluble salts was determined by conductometry on the basis of electrical conductivity (EC) by HANNA HI 9034, Germany. The carbonate content is determined by the volumetric method with the addition of HCl solution (AFNOR X 31-105). The total number of bacteria was determined by the method of luminescent microscopy with sample staining with acridine orange (Merck KGaA, Germany). It should be noted that staining with appropriate dyes allows only the total number of bacteria and fungi in the soil sample to be determined, but not the physiological status of the cells. The green cells of bacteria were counted with a ZEISS inverted microscope, AXIO Vert. A1 model with a 450-490 nm filter (CARL ZEISS, Germany). The intensity of carbon dioxide release – soil respiration was determined according using carbon dioxide as an absorber sodium hydroxide solution. For this purpose, 10 g of moist soil for 24 h was placed in a flask with 0.1 mol×dm^{-3} NaOH solution, which was then titrated with 0.05 mol×dm^{-3} hydrochloric acid solution.

Soil enzymes, dehydrogenases and urease, free-living nitrogen-fixing bacteria of the genus Azotobacter, which are widely used in the diagnostics of the ecological condition of soils (Kazeev et al, 2016; Martinez-Mera et al., 2017; Kolesnikov et al., 2019), were used as bioindicators. The enzymatic soil activity was estimated on the basis of the activity of different enzyme classes: oxidoreductases (dehydrogenase) and hydrolases (urease). Determination of the enzymatic soil activity was based on the amount of the substrate processed during the reaction or the formation of the reaction product under optimal conditions of temperature, pH of the medium, concentration of the substrate and soil hinge. The catalase activity (H_2O_2: H_2O_2-oxidoreductase, EC 1.11.1.6.) was determined by the volumetric method according to the volume of decomposed hydrogen peroxide per 1 min. The activity of dehydrogenases (substrate:NAD(F)-oxidoreductase, EC 1.1.1) was determined using triphenyltetrazolium reduced to triphenylformazane. The urease activity (carbamide-amidohydrolase, EC 3.5.1.5.) was determined by the amount of ammonia formed during the urea hydrolysis. The activity of soil enzymes was studied at the natural soil pH without buffer, in 3–6-fold repetition. The control for determining the activity of enzymes was carried out by the use of substrates without soil.

To combine several parameters, a methodology was used to determine the integral parameter of the biological state (IPBS) of the soil (Kazeev et al., 2015). This method allowed evaluating the set of biological parameters. For this, the value of each parameter in the control soil was taken as 100%. In the soil, this parameter value was expressed as a percentage in relation to it as follows:

$$B1 = \frac{Bx}{Bc} \times 100 \#(1)$$

where B1 is the relative score of the parameter, Bx is the actual value of the parameter in the soil, Bc is the value of the parameter in the control soil.

After that, the average estimated score of the studied parameters for the sample was calculated. The absolute values cannot be summed, since they have different units of measurement (mg, %, etc.). The integral parameter of the biological status of the soil was calculated according to the following formula:

$$B1 = \frac{Ba}{Ba.c} \times 100 \#(2)$$

where Ba – average estimated score of all parameters in post-fire soil, Ba.c – estimated score of all parameters under control.

The biological properties of the soil are characterised by a high degree of variation. Therefore, in order to obtain reliable data, thorough statistical processing is required. We determined the parameters of variation and carried out a correlation analysis. Statistical processing of the obtained results was carried out using Statistica 10.0. We used the arithmetic average value (M), and standard error of the mean (m). A correlation analysis was used to study the closeness and shape of the relationship between various parameters of the ecological and biological status of the soil. Statistical data processing was performed using Statistica 10.0 and Python 3.6.5.

Results and Discussion

The soil of the study areas is represented by ordinary heavy loamy chernozems (Haplic Chernozems). Some aviaries (zebras, rhinos, giraffe and bharals) had different amounts of sand added to the soil surface to improve the water-physical condition. The control site is located in the center of the zoo in a park area with a vegetation and topsoil characteristic of most of the territory of the zoo (Figure 2). The recreationally disturbed site is located 50 m from the control site and is characterized by a significant disturbance of the soil surface due to the construction of the playground here. The soil surface is most severely disturbed in the aviaries with deer and buffalo, which have significantly impacted the soil surface with their sharp hooves (Figure 3), as well as in aviaries with other large ungulates (rhinos, zebras), where river sand was added to improve the physical properties of the soil.

Figure 2. Zoo control site on May 2019.

Figure 3. Disturbed soil in the aviary with a male deer on May 2019.

The studies showed differences in ecological conditions and physical properties of the soils of the study area. The moisture content of the topsoil varied widely depending on the season of the year. In autumn and spring, soil moisture was high (an average of 20-22%), in the summer months, moisture decreases to its critical values for biological processes (less than 13%). However, year by year, soil moisture can vary greatly even in one month of observation. For example, in May 2018, due to the large amount of precipitation in the spring, soil moisture averaged 21.3% (the values ranged in different areas from 16.1 to 36.0), and in dry May of 2019, the soil moisture was much lower at 7.4% (the values ranged from 3.4 to 10.4%). The temperature of the soils varied even more drastically, both on the surface and throughout the soil profile. Under the conditions of the Rostov Zoo, the reaction of the soil was the most conservative indicator. In all the study areas, pH fluctuated in a small range from 7.4 to 7.8. The concentration of highly soluble salts in the soils of animal aviaries is slightly increased relative to the soils of the control plots. However, the difference in values is insignificant, although more pronounced when sampling in the dry season.

The density of the soil was the most representative parameter, reflecting the degree of disturbance of the topsoil on the territory of a number of zoo sites. This indicator is closely related to structure and porosity indicators and is one of the most important indicators of the ecological condition of soils. In all animal aviaries, soil density was increased relative to control values (Figure 4, 5). Here, the values reached high values up to 1.5-1.6 g cm^{-3}. Only in aviaries with birds bulk density was at the level of control values. This is easily explained by the size of animals and their level of mobility. Large animals exert high pressure on the soil, causing the destruction of its surface layer. However, the degree of compaction depends not only on the size of the animals, but also on their activity and the shape of the hooves. The relatively small and sharp hooves of deer and zebras create a greater destructive effect on the soil than larger camels with a wide and soft hoof. Keeping animals in aviaries significantly affects the structure of soils. All sites with animals and birds differ from the control site in a lower content of 1 to 10 mm aggregates. These aggregates determine the quality of the soil structure. In aviaries with large animals, the soil structure was also changed from lumpy (as in control) to blocky. Disturbance in the soil structure of the aviary with medium-sized birds kept together (cranes, peacocks, brent geese, chickens, etc.) is greater than that exerted by several large emus (Figure 6). That is, the effect on the soil is associated with both the size of the birds kept, and their number in the aviary, as well as the size of the aviary. Water resistance of aggregates is significantly reduced when sand is added to the soil.

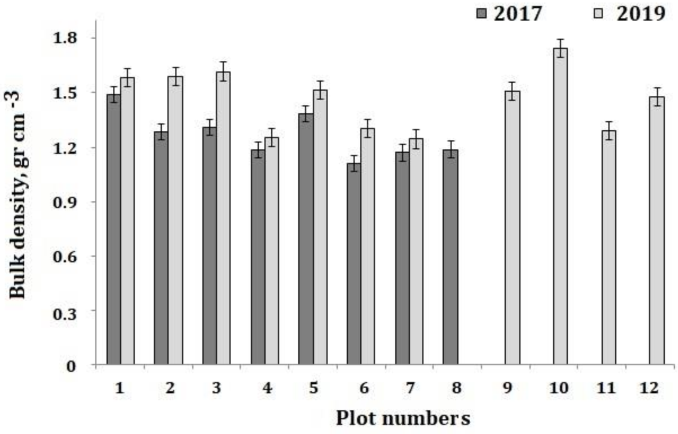

Figure 4. Bulk density values in different plots given in figure 1, May 2019

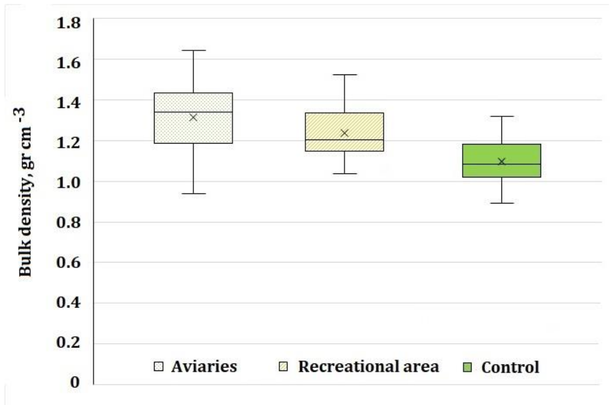

Figure 5. The bulk density of the soil in different zones of the zoo, 2017-2020

The reason for the change in the physical properties of soils is animals that have a direct impact on the soil cover in the aviaries where they live. The ratio of the number of animals and their total weight, which they load on the soil surface, to the area of the aviaries, shows the strength of the effect of this factor on the increase in density in the investigated aviaries (Table 1).

Buffaloes have a maximum impact on the soil -5.5 kg.m^{-2}, in the rhino aviary -2.8 kg.m^{-2}. Significantly less impact in aviaries with other animals. The minimum calculated load falls on the aviary with birds - 0.08 kg.m^{-2}. In addition to the size of the animal, its activity is also of great importance, as well as the direct pressure of the hooves on the soil, which depends on the weight of the animal and the size of its hooves. The relatively small and sharp hooves of deer and zebras create more damaging effects on the soil than a larger camel with a wide and soft hoof.

A significant amount of animal metabolism products enter the soil surface in aviaries (Table 1). During the year, animals introduce into the soil from 2.7 to 97.8 kg of waste per unit area. This is a significant contribution to the replenishment of organic compounds in the soils of the aviaries. The maximum biogenic pollution was found in the buffalo aviaries. In the sheep aviaries, the intake of animal waste is minimal among all aviaries (2.7 kg.m^{-2}.year^{-1}). Despite the daily cleaning, it is not possible to completely remove animal waste products. The flow of urine into the soils of the aviaries is very high due to the limited size of the aviaries. An important role is played by the specificity of animals, which determines their physiology. So for mammals and birds, the chemical composition of the secretions is different, which also matters.

In a zoo, the habitat of animals is significantly reduced. At the same time, the physiological characteristics of the inhabitants remain the same. The aviary and overcrowding of animals leads to the accumulation of nutrients in the soils. Their inability to be completely utilized leads to the accumulation of a high amount of mobile forms of nitrogen and phosphorus in the soils of the zoo's aviaries. A similar accumulation of these nutrients is characteristic of pasture soils after grazing (Sato et al., 2019; Tesfay et al., 2020). Differences in the content of nitrogen and phosphorus compounds in the soils of different parts of the zoo depend on the amount of their intake with excrement. A direct correlation dependence of the ammonium nitrogen content was revealed with animal excrement (r = 0.79 in May and 0.94 in August). This confirms the reason for the high concentrations of mobile nitrogen in the soil. A close dependence of the content of mobile phosphorus on the amount of excrement was found in August (r = 0.75).

Table 1. Impact of animals on the soil of the aviaries of the Rostov Zoo

No	Aviaries	Aviary area, m^2	The weight of animals on the aviary, kg m^{-2}	The amount of urine in the aviary, L $year^{-1}$ m^{-2}	Feces, kg year m^{-2}	Total animal waste, kg $year^{-1}$ m^{-2}
1	Birds (*Grus grus and others*)	1218	0.08	2.6	1.6	4.2
2	*Cervus elaphus*	1190	0.27	3.1	2.5	5.5
3	*Equus burchelli chapmani*	890	0.35	4.9	2.9	7.8
4	*Camelus bactrianus*	340	1.76	8.6	9.1	17.7
5	*Lama glama*	280	0.46	5.2	4.6	9.8
6	*Pseudois nayaur*	2300	0.23	1.1	1.6	2.7
7	*Equus donkeus asus*	2050	0.31	3.6	3.2	6.8
8	*Rhinocerotidaeus asusin*	1080	2.78	10.1	6.8	16.9
9	*Giraffa camelopardalis*	1390	0.43	2.9	2.6	5.5
10	*Bubalus arnee*	280	5.54	39.1	58.7	97.8

Bioindicators are often used as sensitive indicators of soil fertility under different land use systems and the degree of its degradation due to anthropogenic factors (Schwilch et al., 2016; Bünemann et al., 2018; Yertayeva et al., 2019). Biological diagnostics of soils is an important component of both local and global monitoring. Like other habitats, the soil is examined using various bioindicators. Microbial diversity and biochemical parameters are important indicators of soil condition, since they are involved in the decomposition of organic matter and the maintenance of sustainable soil function (Barrios, 2007; Akay and Sert, 2020). As a result of the studies, difference in the representation of bacteria of the Azotobacter genus has been established in soils of different plots of the Rostov Zoo. These bacteria play an important role in the nitrogen cycle, binding atmospheric nitrogen inaccessible to plants. Control sites were characterized by a high abundance of bacteria. Such values are characteristic of ordinary zonal chernozems (Kazeev et al., 2018). In aviaries and deer aviaries, no differences were found in the abundance of nitrogen-fixing bacteria of the Azotobacter genus compared with control sites. The minimal abundance of bacteria was in the soil of the aviary with zebras; the reduced abundance was in the soil of the aviary with bharals. The decrease in the abundance of bacteria was most likely due to the addition of sand into the soil of these aviaries. Sand is an inert material with minimal biological activity. Its addition into the soil leads to the "dilution" effect, reducing the number of microorganisms and biological activity. Aviaries with sand added to the soil showed the greatest variation in the values of the studied indicator as a result of different amounts of sand in soil samples.

Studies by various authors have established that the activity of soil enzymes can serve as an additional diagnostic indicator of soil fertility and its changes due to anthropogenic effects (Sinsabaugh et al., 2008; Burns et al., 2013; Raiesi and Kabiri, 2016). Much attention is drawn to the development of indicators of soil enzymes for use as a reliable indicator of soil fertility and health (Burns et al., 2013). However, despite extensive search, no single indicator has yet been found, that would allow us to draw a conclusion about the biological condition of the soil as a whole. In this paper, two classes of enzymes were used as bioindicators. From the hydrolases, the activity of urease was determined, and from the oxidoreductases, the activity of catalase and dehydrogenases was determined. Globally, Sinsabaugh et al. (2008) found that the activity of hydrolases is closely correlated to the content of organic matter in the soil, while the activity of oxidases is more susceptible to soil pH. This discovery showed that hydrolases may be more important for the decomposition of organic matter and, thus, affect nutrients and the carbon cycle. Enzymatic activity in the soil of the control site of the zoo is characterized by an average level of catalase activity during the entire observation period and varies slightly throughout all seasons. In soils of almost all aviaries, the activity of urease and dehydrogenases was significantly increased compared to the control values and varied greatly depending on the duration of observation (Figure 7).

Urease activity showed unusually high values in the soils of aviaries. This enzyme catalyzes the decomposition of urea, which enters the soil from animals in significant quantities every day. In aviaries with large animals, the flow of urine into the soil of aviaries amounts to several thousand liters per year. The correlation is detected between the animal load on the aviary soil cover and urease activity (r = 0.74). Unusually high values of urease activity have been established for the aviary with buffalo. Here, the excess of enzyme activity was 740% higher than in the soil of the control plot. This is due to the greatest pollution of the soil of this aviary, where several large animals live on a fairly small area. Urease activity was also 2-3 times higher in aviaries with deer, zebras and birds. A smaller increase is recorded in other aviaries. Only in one of the plots of the aviary with rhinoceros, a lower activity of urease was detected. This is due to two main reasons. The first is the short keeping period for rhinoceros in this aviary, which arrived at the zoo after a long break only a year and a half ago. The second reason was the addition of a significant amount of river sand used for amelioration of soil of the aviary. In this aviary, the soil surface is almost entirely covered with a layer of sand. Due to the use of sand to dilute the soil, enzyme activity was also relatively reduced in other aviaries (zebras, rams, giraffes). But still, the urease activity here was also higher than the control values.

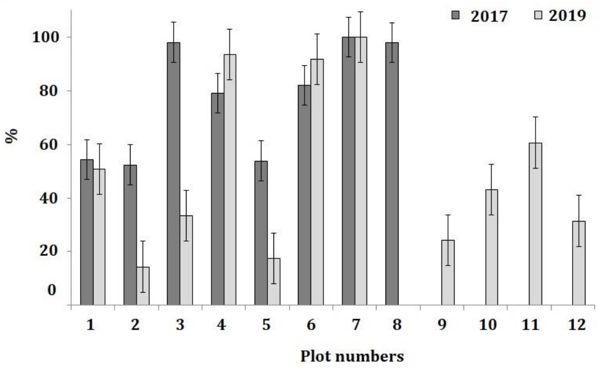

Figure 6. Changes in the structure of the soils of the zoo enclosures relative to the control values in different plots given in figure 1 according to control treatment.

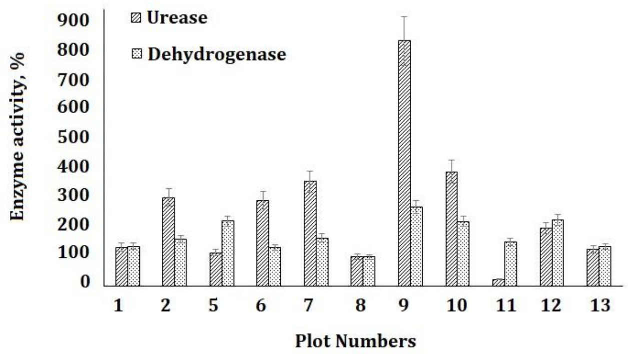

Figure 7. Changes in enzyme activities of the zoo soils in different plots given in figure 1 relative to the control site, May 2019.

The activity of dehydrogenases is associated with soil microorganisms (Kazeev et al., 2016). Its activity was also significantly increased in all observed areas relative to the control soil of the park. A large statistically significant ($p<0.01$) increase in enzyme activity was observed in the soils of aviaries with buffaloes (171%), giraffe (126%), sheep (123%) and camel (122%). In other sites, the increase ranged 32 to 65% relative to the control site ($p<0.05$). For this enzyme, such an increase in activity indicates the intensification of biological processes in the soils of animal aviaries. This is due to the increased flow of excess amounts of organic matter that serve as energy-yielding material for soil microflora. To quickly remove digestion products and metabolic waste, stimulation of the intensity of biological processes in soils is required. This will avoid the accumulation of organic waste that contribute to the associated issues of unpleasant odors and contamination of soil with pathogenic microflora.

Monitoring of the ecological condition of the aviaries of the Rostov Zoo showed a high degree of degradation of the physical properties of soils and their contamination with metabolic products of the kept animals. Possible negative effects of grazing on plant biomass and soil quality have been reported previously (Qasim et al., 2017; Hillenbrand et al., 2019; Sato et al., 2019). Keeping animals in the limited space of the zoo aviaries leads to soil compaction and a decrease in water permeability, which leads to stagnation of moisture on the surface, the formation of puddles and dirt in the conditions of heavy clay soil composition. One of the methods for soil amelioration is the technology used by the zoo designed to lighten the particle size distribution of soils using sand, which is added to the soil of some of the most degraded areas (aviaries with sheep, rhinoceros, buffalo, zebras, giraffe). The amount of added sand varies in different study plots. Under the conditions of low disturbance of the topsoil, sand is not applied at all, and in some aviaries with the largest animals (elephants, bisons), sand completely covers the soil with a thick layer, which makes monitoring the topsoil in these aviaries unproductive. Currently, studies are underway on the use of ameliorants and other substances: glauconite, wood chips and sawdust, acrylic-based hydrogel. The use of an acryl-containing hydrogel does not inhibit the heterotrophic soil microflora (Mellelo et al., 2019), which is important for maintaining a high decomposition rate of animal waste and, therefore, it may be used to regulate the water regime of soils. In addition, biologically active substances can be used to increase the rate of biodegradation of organic substances in zoo soils. For example, humic substances and preparations based on them can significantly increase the biological activity of soils (Stankevica et al., 2019).

Keeping animals in aviaries can lead not only to soil degradation, but also to air pollution with ammonia. It's can be produced not only by farm animals (Priekulis et al., 2019), but also, locally, by zoo animals. Therefore, it is important to optimize the nitrogen cycle in soils, for which it is important to maintain a high rate of biological processes in the soil and, in particular, nitrification.

In general, soils of Rostov zoo have a high biological activity comparable to the soils of natural ecosystems. This contributes to the biodestruction of a significant proportion of organic matter entering the zoo soil. The amount of animal excrements in some of the zoo aviaries is much higher than in natural ecosystems. And it continues to be so for decades. Increasing the speed of biological processes in the zoo soils is necessary for accelerated mineralization of organic pollutants and suppression of pathogenic microflora. Low biological activity of soils can lead to a decrease in the rate of biodegradation of organic substances and other negative processes (Yurkova et al., 2009). Therefore, work is currently underway to replace the main ameliorant used to improve the physical properties of soils. River sand used for this purpose in some aviaries with large animals, reduces the humus content and biological activity of soils.

Conclusion

The soils of the Rostov Zoo are subject to degradation disturbances as a result of keeping animals in aviaries, as well as the recreational impact of visitors. The difference in the ecological properties of soils at different monitoring sites of the zoo has been established. Large ungulate animals have a maximum effect on the physical properties of soils. This is especially true for deer, buffalo and zebras, which have a higher destructive effect on the soil surface compared to other animals. Minimal disturbances are showed in aviaries. Even large emus almost do not disturb the physical properties of soils. The addition of sand as an ameliorant to improve the water-physical properties of soils in aviaries with mountain sheep, zebras, rhinoceros and giraffe leads to significant changes in the physical and biological properties of soils. Biological activity is significantly reduced as a result of dilution of the soil with inert material. The most informative indicators of the ecological condition of the soils of the Rostov Zoo were the density and structure of soils. Soil enzymes, especially urease, were good bioindicators of soil contamination with animal waste products. The abundance of nitrogen-fixing bacteria, the reaction of the medium, the content of highly soluble salts, soil temperature and humidity were less informative indicators for assessing the ecological status of zoo soils.

Acknowledgements

This work was supported by government projects for the leading scientific schools of the Russian Federation (NSh-3464.2018.11; NSh-2511.2020.11).

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Eurasian Journal of Soil Science 2021, 10(2), 96 - 104

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

Carbon sequestration potential of community forests: A comparative analysis of soil organic carbon stock in community managed forests of Far-Western Nepal

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Article Info

Received : 30.06.2020
Accepted : 09.11.2020
Available online : 12.11.2020

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Abstract

Assessment of soil organic carbon (SOC) pool is an essential pace for understanding the carbon sequestration potential (CSP) of the soil system as a mitigation strategy and also investigate that they act as a source or sink for the atmospheric CO_2 subject to the level of saturation. Improved CSP has been recognized as one of the possible solutions for mitigating climate change. The CSP of soil system for the community forests (CFs) in Nepal is not well recognized. Therefore, a study was conducted in two community-managed forests viz Ganesh (degraded) and Ramnagar (non-degraded) CFs situated in the Kanchanpur district of Nepal to quantify the SOC and Bulk density (BD). For determining SOC, systematic sampling with a sampling intensity of 0.5% was used for collecting altogether 189 soil samples from both the CFs. In addition, the soil samples from varying depths (0-10, 10-20, and 20-30 cm) of each soil profile were collected from each sampling plot. The mean SOC observed upto 30 cm soil depth in Ganesh and Ramnagar CF was 42.55 ± 3.10 t ha^{-1} and 54.21 ± 3.59 t ha^{-1} respectively. While, maximum SOC was noticed at 0-10 cm whereas minimum at 20-30 cm in both the CFs. Moreover, SOC decreased and bulk density increased with increasing soil depth in both the CFs. SOC and BD was negatively correlated in both CFs. The total SOC pool exhibited a significant (p<0.05) difference between the two CFs. Hence, the outcome of study shows that the both CFs has enormous potential to sequester the atmospheric concentration of CO_2 into soil. With this concern, the participation of local people in sustainable management of community forests enhance the soil quality and meets strategy to mitigate the climate change.als and soil amelioration aimed at regulating physical properties of the soil.

Keywords: Bulk density, carbon sequestration potential, community forest, soil depth, soil organic carbon.

Introduction

Carbon sequestration through the soil system is recognized as a potential solution for climate change mitigation (Alidoust et al., 2018). The rapid increase in the atmospheric CO_2 concentration could be diminished either by reducing emissions or removing atmosphere CO_2 by sequestrating into the soil (IPCC, 2006). Forest ecosystem is known as the reservoir of carbon source that sequestered the carbon in vegetation and soil through the process of photosynthesis and respiration (Brown et al., 1996). Trees and

: https://doi.org/10.18393/ejss.825066
: http://ejss.fesss.org/10.18393/ejss.825066
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

soil are the major carbon pools that store more carbon than others in the forest ecosystem (Amir et al., 2018). According to the Global Forest Resource Assessment Report (FAO, 2020), the total forest carbon stock is 662 Giga tones and forest SOC contains 45% of total forest carbon stock (297.9 Giga tones). Furthermore, SOC is the most important carbon pool in terrestrial ecosystems and plays a major role in carbon sequestration by increasing SOC in the terrestrial biosphere carbon pool (Ali et al., 2019; Hou et al., 2019). Out of the total global terrestrial carbon pools, 60% of the carbon has been shared by forests and soil only and the carbon pool in the soil is higher than the vegetation carbon pool (Winjum et al., 1992). Thus, it is necessary to understand that the forests and soil can be well managed to sequester or safeguard substantial amounts of carbon on the land (Sharma et al., 2011).

Based on the disturbances, the forests have been classified into two group's i.e., degraded and non-degraded forests (Joshi et al., 2020). Regarding the degraded forest, the disturbance may be natural or have an anthropogenic origin (Turner et al., 2003). Anthropogenic activities are notorious for major environmental changes leading to global warming (Aryal et al., 2017). Soil organic carbon (SOC) and carbon flux are greatly affected under the land-use pattern and soil management regime (Post and Kwon, 2008). In general, Nepal is known as the pioneer of the community forestry (CF) program in which forests are handed over to community Forest User Group (Pandit et al., 2009). It was initiated to promote livelihood along with controlling environmental degradation via sustainable forest management where authority and management of forest rest upon communities in coordination with the government and other multiple stakeholders (Gautam et al., 2008). Increasingly, the recognized huge potential of CFs in carbon trading from the REDD+ mechanism can reward economic benefits for the country (Joshi et al., 2020). Meanwhile, UN-REDD (2014) indicated that REDD+ may bring between $20-86 million per year to Nepal. Additionally, most of the scientific work are concentrated on carbon and SOC stocks at different landscapes and community forest (Shrestha et al., 2004; Shrestha and Singh, 2008; Magar et al., 2020) However, there are very limited studies on soil carbon sequestration potential of community forest. Therefore, this study was intended to address the existing gap of literature by assessing the soil carbon sequestration potential of two community forests.

Material and Methods

Study area

The research was conducted in Ganesh and Ramnagar community forests of Kanchanpur district, Nepal (Figure 1). Kanchanpur district lies in Mahakali zone with the coordinates of 28.8372 ^{0}N latitude and 80.3213 ^{0}E longitude at the south-west part of Far-Western Province. Ganesh CF is situated in Bedkot Municipality-6 whereas; Ramnagar CF is in Belauri Municipality Ward Number 5 with an area of 434.48 and 197.16 ha, respectively. Each community forest user groups were handed forest at different time period i.e., Ganesh CF in year 2001 A.D. whereas Ramnagar in 2010 A.D. Both CFs are found with altitude ranging from 120-300 metres above sea level. Ganesh CF is facing towards the northern aspect (Churia foothills) and Ramnagar CF on the southern aspect of Terai belts. The soil of Ganesh CF was alluvial, sandy, and graveled whereas the soil of Ramnagar CF varies from alluvial to clay loam and is mostly black. Ganesh CF consists of scattered stands of mixed Sal broad-leaved natural forests whereas Ramnagar CF mainly consists of natural Sal forests (Joshi et al., 2019).

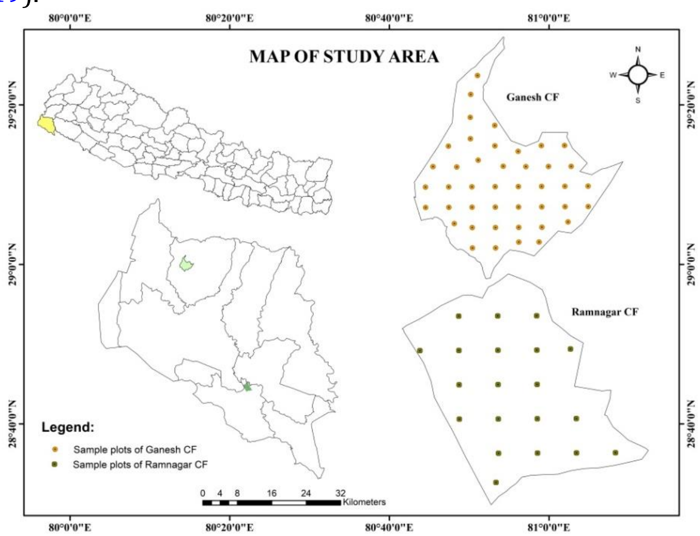

Figure 1. Map of the study area

Under this study, two CFs were divided into degraded (Ganesh CF) and non-degraded (Ramnagar CF) categories based on certain parameters (For detail explanation see Joshi et al., 2020). The degraded forest was characterized by barren and riverine areas with the presences of few trees, shrubs, and grasses susceptible to soil erosion (Ghimire et al., 2018). The study area of Ganesh CF was known as degraded CF due to the occurrence of the landslide, soil erosion, and deforestation representing. The various tending operations and major management activities are undertaken sustainably in Ramnagar CF compare to Ganesh CF. Besides, fire lines are constructed in each sub-compartments in Ramnagar CF under the scientific forest management (SFM) approach (Joshi et al., 2020). The average maximum and minimum temperature of the district is 38^{0}C (June) and 13^{0}C (January) with a mean annual precipitation of 1512.12 mm (Joshi et al., 2020).

Data collection and analysis

Sample plot design

In selected CFs, boundary surveys were carried out using GPS with the help of the forest guards and members of the forest user groups to record the latitude, longitude, and altitude of each boundary point. For the soil survey, a circle of 0.56 meter radius was made for the collection of samples as per the protocol of ANSAB (2010). Systematic sampling with a sampling intensity of 0.5% was applied for this study. For the systematic sampling, ArcMap 10.5 software was used to lay a total of 63 (43 in Ganesh CF and 20 in Ramnagar CF) sample plots though fishnet. The points generated in ArcMap was loaded in GPS and sampled were obtained from the predetermined location with the accuracy of ± 5 meters.

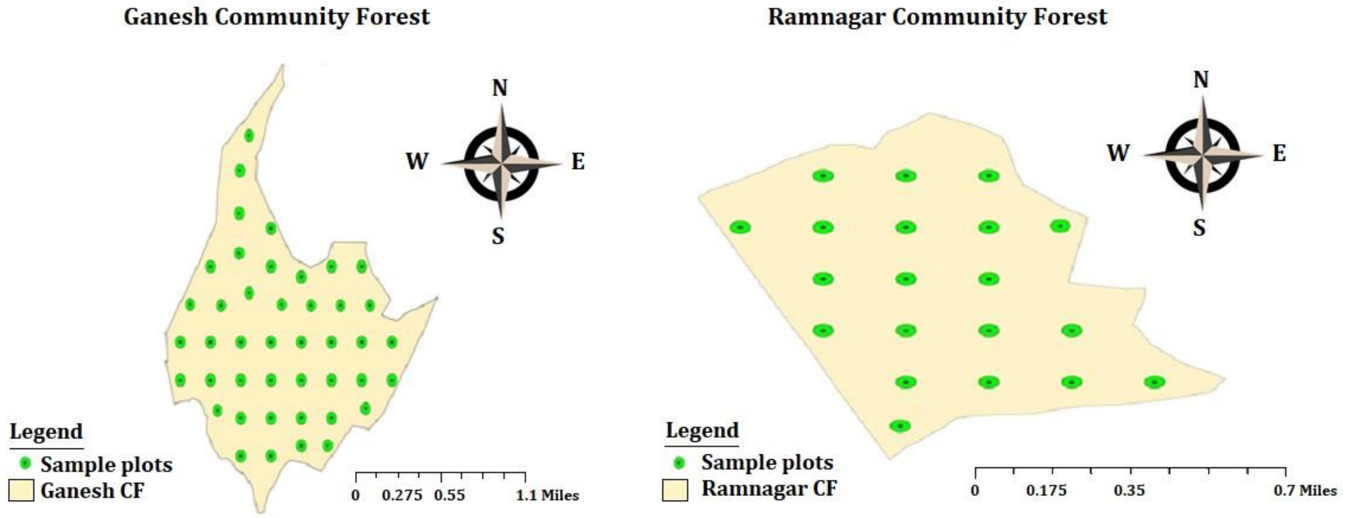

Figure 2. Sample plot design for both community forests

Soil sampling

For the estimation of soil organic carbon stock, the soil profile was dug out near the center of each sampling site up to 30 cm depth. From each community's forests, two replication of soil samples of each sample plot were collected up to 30 cm depth (0-10 cm, 10-20 cm, and 20-30 cm) by using a soil auger. Altogether 189 soil samples were collected from each sample plot (43×3 in Ganesh CF and 20×3 in Ramnagar CF) with different soil depths. To determine bulk density, a metal core ring sampler of 210 gm cm^{-3} was used to extract soil samples at 0-10 cm, 10-20 cm, and 20-30 cm depths. Finally, the extracted fresh soil samples were bagged in plastic bags and tightly closed by plastic rubber with proper labeling and transported to the laboratory of Forest Research Institute (FRI), Dehradun, India. The samples were collected during December 2018.

Laboratory analysis

Bulk density

Soil samples were oven-dried at the temperature of 105°C until a constant weight was recorded. The oven-dried soil was then passed through a 2 mm sieve to segregate stones which helps to determine moisture correction. Finally, the total amount of coarse fragments were estimated from each soil sample collected from different sample sites and subtracted from the soil weight to get a precise soil weight. According to Pearson et al. (2007) bulk density was calculated as follows:

$$\text{Bulk density (gm/cc)} = \frac{\text{Oven dry weight of soil (gm)}}{\text{Volume of the soil (cc)}}$$

where,

Volume of the soil = Volume of core – Volume of the stone

Soil Organic Carbon (SOC)

Soil samples were collected from 0-10, 10-20, and 20-30 cm depths and one composite from each sample plot. Bagged samples were transferred to the pre-weighed sampling bags. Each Soil samples were room dried for 10 days, grind into small particles, and passed through a 0.2 mm sieve. For SOC determination, the titrimetric method given by Walkley and Black (1934) was used. The SOC percent (%) was calculated by using the following formula:

Carbon (%) = 3.951/g [1 -T/S]

where,
g = Weight of sample in gram,
T= Total consumed volume of ferrous solution in sample titration (ml),
S = Total consumed volume of ferrous solution in blank titration (ml)

The carbon stock density of soil organic carbon was then calculated as follows:

Soil Organic Carbon (SOC) = § x d x % C

where,
SOC = soil organic carbon stock per unit area (t ha^{-1}),
§ = soil bulk density (gm cm^{-3}),
d = the total depth at which the sample was taken (cm)
% C = carbon concentration (%)

Further, it was expressed in ton per hectare.

Statistical analysis

The SOC of various depths was estimated by soil organic carbon concentration, soil bulk density, soil depth, and proportion of gravels. Statistical analysis such as univariate analysis under the General Linear Model and Duncan's multiple range test was performed to study the significant difference between soil variables of two community forests with various depths (p<0.05). All these statistical analysis was done by using the SPSS and R software.

Correlation between Soil Organic Carbon (SOC) and Bulk Density (BD)

Pearson's correlation was applied for the both parameter of SOC and BD. The correlation effect of both community forests on SOC and BD was analyzed by comparison of their mean values. Mean values of SOC and BD were determined by taking an average of soil depth up to 30 cm (0-10 cm, 10-20 cm, and 20-30 cm) of each sample plot of both community forests. Multiple comparisons of mean values for each variable (SOC and BD) were carried out by using R software and Microsoft Excel 2010 (Bhandari and Bam, 2014).

Results

Bulk density (BD)

The mean value of bulk density from all soil samples for each soil depth and individual CFs was calculated. The mean BD for both CFs increased slightly with increasing soil depth (Figure 3). On average, the bulk density of Ramnagar CF (non-degraded) was higher as compare to Ganesh CF (degraded). Table 1 shows bulk density mean value varies from 1.24 to 1.44 gm cm^{-3}.

Table 1. Average bulk density (gm cm^{-3}) at various depths

Depth (cm)	Mean Bulk Density (gm cm^{-3}) ± S.E	
	Ganesh CF	Ramnagar CF
0-10	1.24 ± 0.02	1.33 ± 0.03
10-20	1.25 ± 0.02	1.41 ± 0.02
20-30	1.29 ± 0.03	1.44 ± 0.02

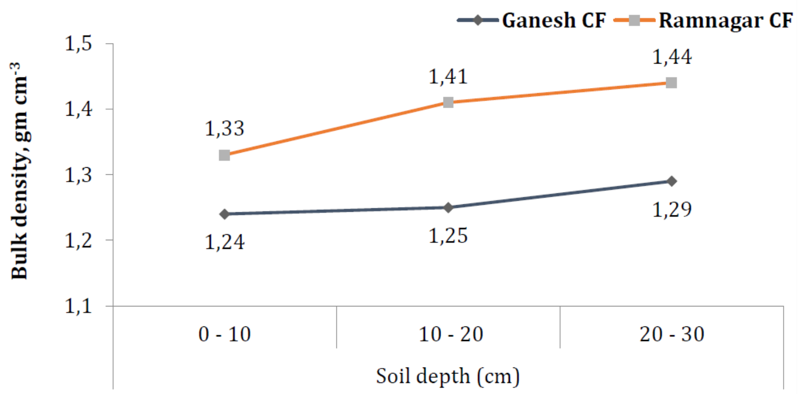

Figure 3. Graph showing the average amount of bulk density in each horizon

From the univariate analysis, it can be inferred that there is a significant impact of depth on bulk density for Ramnagar CF as $p < 0.05$. Further, Duncan's test of homogeneity was conducted to assess the relationship between these factors (Table 2). There was significant difference between values (subset 1) for depth 0-10 cm to values (subset 2) of bulk density for the ranges 10-20 cm and 20-30 cm but found insignificant between these later values of subset 2 in Ramnagar CF. However, in Ganesh CF, there was no significance difference between the values of bulk density (Subset 1) for all the different ranges (0-10, 10-20 and 20-30), (Table 2). From Duncan's subsets values it can be deduced that with increasing depth, bulk density is increasing significantly ($p \leq 0.05$) but does not found differ considerably between 10-20 cm and 20-30 cm depth.

Table 2. Duncan's test for bulk density in both CFs

Soil Depth (cm)	Ganesh CF		Ramnagar CF	
	No. of obs.	Subsets for BD	No. of obs.	Subsets for BD
0-10	43	1.2374 A	20	1.3295 A
10-20	43	1.2544 A	20	1.4110 B
20-30	43	1.2849 A	20	1.4375 B
$P_{\alpha = 0.05}$	0.175		0.459	

Soil organic carbon

The study site shows the variable of SOC percent ranges from 0.95% to 1.80%. The higher SOC (1.80 ± 0.14%) was found at the topsoil (0-10 cm) in the Ramnagar CF and lowest SOC (0.95 ± 0.07%) at the depth of 20-30 cm in the same CF (Table 3). Results demonstrated that as the depth increase SOC percentage decrease in both CFs.

Table 3. Average Soil Organic Carbon (%) at various depths

Soil Depth (cm)	Mean Soil Organic Carbon (%)± S.E	
	Ganesh CF	Ramnagar CF
0-10	1.45 ± 0.12	1.8 ± 0.14
10-20	1.2 ± 0.1	1.21 ± 0.11
20-30	1.08 ± 0.11	0.95 ± 0.07

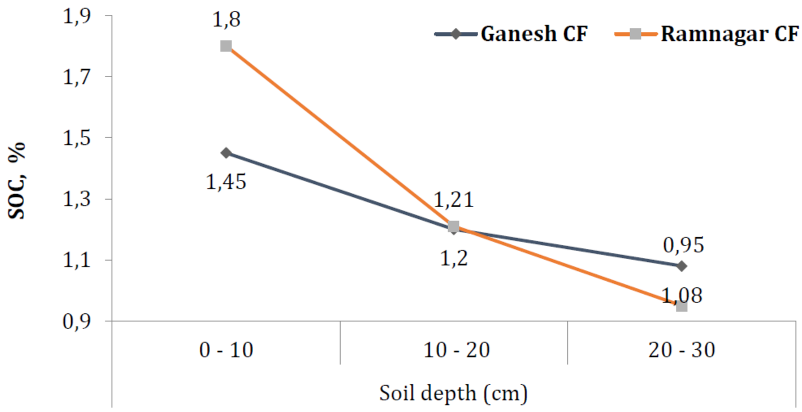

Figure 4. Average soil organic carbon at various depths

Soil organic carbon stock

In the present study, total SOC for Ganesh and Ramnagar CF was estimated to be 127.64 t ha^{-1} and 162.64 t ha^{-1} respectively. While, the average SOC was estimated to be 42.55 ± 3.10 t ha^{-1} at Ganesh CF. Similarly, the maximum SOC stock was found to be 50.51 t ha^{-1} at 0-10 cm depth and minimum (36.75 t ha^{-1}) in 20-30 cm depth. However, in case of Ramnagar CF, the mean SOC stock was calculated 54.21 ± 3.59 t ha^{-1}. SOC was highest (70.81 t ha^{-1}) for soil depth 0-10 cm and lowest (41.15 t ha^{-1}) for 20-30 cm. So, the result showed that the decreasing rate of carbon content as it goes to deeper (Figure 5). Data revealed that SOC of Ramnagar CF is more in comparison to Ganesh CF.

From the univariate analysis, it was concluded that there are significant changes of SOC with soil depth for both CFs ($p \leq 0.05$). Moreover, in both CFs, Duncan's test of homogeneity revealed no significant difference between values 10-20 and 20-30 cm (subset 2). The value of (subset 1) for depth 0-10 cm differs significantly from those two different depths. Duncan's subsets values revealed that with increasing depth, SOC was decreasing but does not differ significantly between 10-20 and 20-30 cm depth (Table 5).

Table 4. Total amount of soil organic carbon with respect to its soil depth

S.N.	Soil Depth (cm)	Mean Soil Organic Carbon (t ha^{-1}) ± S.E	
		Ganesh CF	Ramnagar CF
1	0 – 10	50.51 ± 3.74	70.81 ± 5.30
2	10 – 20	40.38 ± 3.15	50.68 ± 4.51
3	20 – 30	36.75 ± 3.41	41.15 ± 2.92
	Sum total	127.64	162.64
	Average total	42.55 ± 3.10	54.21 ± 3.59

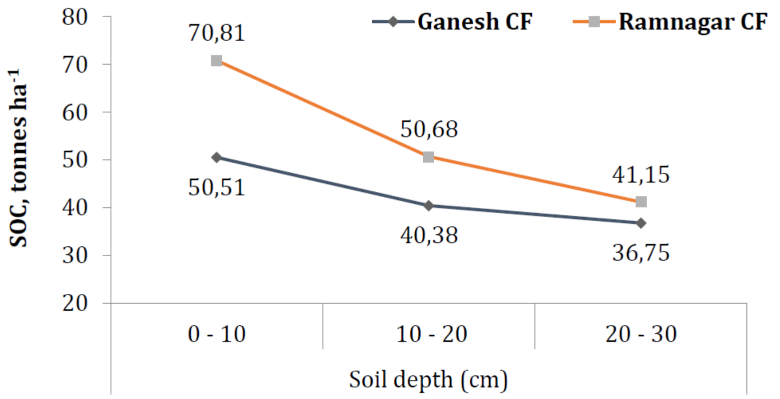

Figure 5. Graph showing the amount of carbon stock in each horizon

Table 5. Duncan's test for SOC in both CFs

Soil Depth (cm)	Ganesh CF		Ramnagar CF	
	No. of obs.	Subsets for BD	No. of obs.	Subsets for BD
0-10	43	50.51A	20	70.81A
10-20	43	40.38 A	20	50.68B
20-30	43	36.75A	20	41.15B
$P_{\alpha = 0.05}$	0.457		0.127	

Correlation between SOC and BD

In the studied CFs, SOC is found negatively correlated with bulk density which shows that the present study is in favor of the universally accepted concept (Table 6). A perfect negative correlation was observed between SOC and BD in both community forests through multiple comparison of their mean values for each variable (Figure 6 and 7).

Table 6. Correlation between SOC (t ha^{-1}) and BD (gm cm^{-3}) of both community forests (CF)

S.N.	Community forests	No.	d.f	t-value	*p*-value	*Correlation coefficient
1	Ganesh CF	43	41	-3.6543	0.0007	-0.4956
2	Ramnagar CF	20	18	-0.1730	0.8646	-0.0407

Where, *Correlation is significant at 0.05 level or 95% confidence interval. No. = number of observations

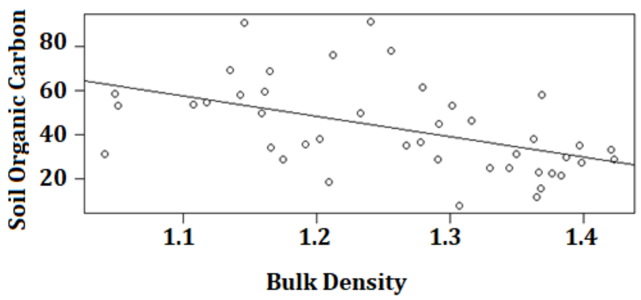

Figure 6. SOC content (t ha^{-1}) and BD (gm cm^{-3}) of Ganesh CF

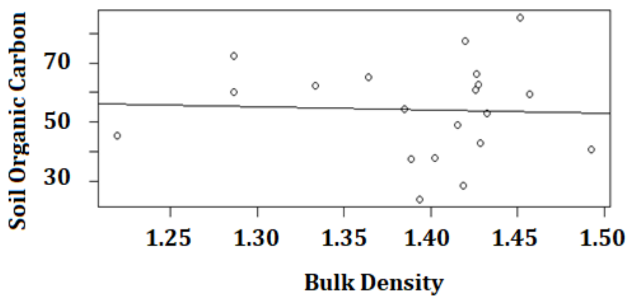

Figure 7. SOC content (t ha^{-1}) and BD (gm cm^{-3}) of Ramnagar CF

Discussion

Soil organic carbon is an indicator of soil quality that correlates with climate and land cover types such as forest, shrubland, and grassland (Chaudhari et al., 2013; Wu et al., 2017). While, there has been considerable agreement on the linkage between forest degradation and reduction in soil properties such as lower soil organic carbon and bulk density which is increased due to compaction (Sanji et al., 2020). Likewise, Morisada et al. (2004) suggested that the soil compaction due to weight or disturbance, consolidation, soil aggregates, and soil fauna has an impact on soil BD but it is inversely proportional to SOC content in natural forest. The parameters selected for this research includes soil BD and SOC. Finally, this study adds new empirical evidence that all tested variables of two community forests represent significant variation.

Soil bulk density

In the present study, distinct variation in the BD was observed with concerning soil depths at both the CFs. The diagnostic showed that the topsoil layer indicates lower BD. More positively, previous studies also suggested that low soil BD in the upper horizons of the soil is due to the existence of high organic matter in the soil facilitating plant roots (Mfaume et al., 2019). Likewise, the present research finding revealed that the mean BD for both CFs (ranging from 1.24 to 1.44 gm cm^{-3}), increased with increasing soil depth but the BD of Ramnagar CF was higher as compare to Ganesh CF for all horizons. However, Duncan's results suggest that there was no significant difference between values (subset 2) of bulk density for the ranges 10-20 cm and 20-30 cm but values (subset 1) for depth 0-10 cm differ significantly from those two different depth in Ramanagar CF whereas in Ganesh CF, there was no significance difference between the values of bulk density (subset 1) for all the different ranges (0-10, 10-20 and 20-30). Further, less variation was observed in bulk density among soil horizons in degraded Ganesh CF may be an indication of soil compaction. Additionally, mounting evidence of various study mention that a agradual increase in soil bulk density with an increase in soil depth is also evident under all forest and lower bulk density in the uppermost layers indicates soil health for plant growth (Raddad and Luukkanen, 2007; Shrestha, 2009a,b; Ghimire et al., 2018; Adhikari and Ghimire, 2019). Apart from it, the study conducted by Pandey et al. (2019) represent the reciprocal relationship between SOC and bulk density in soils of three community forests of Far Western Nepal.

Soil Organic Carbon

SOC is a major constituent in forest soils and ecosystems. SOC accretion and disintegration rates have a direct influence on terrestrial ecosystem carbon sequestration and comprehensive carbon stability. More specifically, understanding SOC allocation in forest ecosystems is significant for improving soil quality and sustaining the forest production (Liu et al., 2016). Therefore we have analyzed the SOC for both community forests. During the study period, we observed that SOC content was higher at the upper layer (0-10 cm) and decreased as depth increase. Likewise, the higher the SOC content in the upper layer is due to high soil organic matter content. Meanwhile, Khanal et al. (2010) was coinciding the similar outcomes with our study. In fact, the evident of these findings was also supported by some researchers in the tropical forests of Nepal (Pandey and Bhusal, 2016; Ghimire et al., 2018), they were observed declining SOC with increasing depth. Further, the mean SOC (up to 30 cm) of Ganesh CF was lower than Ramnagar CF which was estimated to be 42.55 ± 3.10 t ha^{-1} and 54.21 ± 3.59 t ha^{-1} respectively. Notably, the SOC below 30 cm was excluded from the research site to maintain regularity in both CFs because to extract soil samples below 30 cm from each sample plots was not possible in Ganesh CF due to the presence of intact rock mass.

In our case study, the total SOC pool (up to 30 cm) in Ganesh and Ramnagar CF was recorded up to 127.64 t ha^{-1} and 162.64 t ha^{-1} respectively. Further, total SOC for Ganesh CF is close to the value estimated by Kafle (2019) i.e. 122.36 t ha^{-1}. While, compare with the previous studies Pandey and Bhusal (2016) of Sal (*Shorea robusta*) forests in the central region of Nepal, both the CFs of our study reported higher SOC. However, the researcher uses the different soil sampling methods (up to 1m depth) and by comparing with our study area has less potential of carbon stock. Similarly, Shrestha and Singh (2008) and Shrestha (2009a,b) also indicated low SOC density than both Ganesh and Ramnagar CF. The variation in the total amount of SOC depends upon several biotic and abiotic factors such as faunal diversity, micro-climate, land use and management (Shrestha and Devkota, 2013). Further, Shrestha and Singh (2008) mention that the inputs of roots and leaf litter have a significant role in forest soil carbon dynamics. Moreover, the reduced soil organic carbon in the forested sites may be due to low vegetation cover and high anthropological activities (Yao et al., 2019). Nonetheless, the outcome results of Sheikh et al. (2009) study shows the declining rate of total SOC stock with an increase in altitude. Finally, It has been recommended that SOCs can play a vital role in land degradation/soil quality management and designing a carbon sequestration program making baseline data of SOC essential for the same (Nabiollahi et al., 2019). Thus forest management in terms of carbon sequestration, Ganesh CF has to take some additional measures to increase soil organic carbon.

Conclusion

The SOC stored in the two different CFs were reported differently. In relation to soil depth, SOC was found to be inversely proportional while BD was found to be directly proportional to it. Both SOC and BD of

Ramnagar CF were higher than those of Ganesh CF, and this contributed to the higher SOC stock in Ramnagar CF. The mean SOC in the Ganesh (degraded) CF was 42.55 t ha^{-1} whereas; the value was 54.21 t ha^{-1} in the Ramnagar CF (non-degraded) measured up to the depth of 30 cm. The topsoil is accumulated with increased SOC rather than lower profile in both forest suggesting forest management for retention of organic matter on forest floor. The presence of sandy soil in underneath may be the cause of low soil carbon content in the Ganesh CF. Statistically, the relationship between SOC and BD was tested negatively correlated. These findings suggest that the amount of SOC recorded higher at the Ramnagar (non-degraded) CF than Ganesh (degraded) CF. As per the result, we can conclude that both CFs has remarkably stored carbon serving for climate change mitigation. Finally, improved management of community forest for increased soil carbon sequestration could be a promising strategy to halt climate change.

Acknowledgements

The authors are grateful to Director, Forest Research Institute, Dehradun, India, for providing laboratory facilities during the study period. We would like to express our heartfelt gratitude to all the CFUGs members for their significant contribution and support for the successful completion of this research work. Finally, the authors would also like thankful to Antrix Soni, Durgesh Dhami, Maheshwari Bhatta, Suman Shree Neupane, Shachi Pandey and Bharat Sharma for their concern support and kind cooperation during study period.

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Eurasian Journal of Soil Science 2021, 10(2), 105- 110

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

Some soil biological and chemical properties as affected by biofertilizers and organic ameliorants application on paddy rice

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Article Info

Received : 08.04.2020

Accepted : 15.11.2020

Available online : 22.11.2020

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Abstract

Biofertilizers are compounds that contain microorganisms capable of increasing the nutrient availability to plants and increasing plant growth rate. The purpose of this research is to study the effects of biofertilizers and organic ameliorants on some of soil bio-chemical properties. The pot experiment was conducted at the field of the Faculty of Agriculture, Universitas Padjadjaran Indonesia. The experiment was conducted in a randomized block complete design format consisting of twelve treatments and three replications. The experiment consisted of control, solid biofertilizer (50 kg ha^{-1}), liquid biofertilizer (5 L ha^{-1}), a combination of solid biofertilizers (50 kg ha^{-1}) with organic ameliorants (10t ha^{-1}) (composted straw, biochar and cow manure), a combination of liquid biofertilizer (5 L ha^{-1}) and organic ameliorants (10 t ha^{-1}), and each of ameliorants (10 t ha^{-1}) independently. The results of experiment revealed that the application of solid biofertilizers and organic ameliorants significantly improved some soil biological properties (population of phosphate solubilizing microbes, N-fixing bacteria and phosphatase activity) and increased some soil chemical properties such as total N, available P, organic C and cation exchange capacity.

Keywords: Ameliorant, biofertilizers, phosphatase activity, soil, microorganism.

Introduction

Biofertilizers are compounds containing living cells of different types of microorganism which has an ability to mobilize important elements from non-available to available form through biological process. The main purposes of using biofertilizers to improve the soil quality, to substitute inorganic fertilizers, to increase productivity and to promote an eco-friendly a sustainable agriculture (Bargaz et al., 2018).

The main group of bacterial and fungal biofertilizers, such as symbiotic nitrogen-fixing biofertilizer (roots nodulation, stem nodulation and Azolla), non-symbiotic nitrogen bio-fertilizers, phosphate solubilizing and mobilizing organisms (including mycorrhizal fungi), potassium solubilizing bacteria, plant growth promoting rhizobacteria, endophytic bacteria, decomposers (mineralize of organic materials and resulting the available form of nutrients), siderophore and the mass production of biofertilizers and to evaluate the quality of biofertlizers. Islam et al. (2013) suggested that inoculation with N-fixing bacteria significantly increased chlorophyll content, and the uptake of different macro- and micro-nutrient contents enhancing

: https://doi.org/10.18393/ejss.829695

: http://ejss.fesss.org/10.18393/ejss.829695

Publisher : Federation of Eurasian Soil Science Societies

e-ISSN : 2147-4249

also in red pepper shoots. Salamone et al. (2012) states that inoculation of *Azospirillum brasilense* and *Pseudomonas fluorescens* improved paddy rice production.

In the soil, numerous biological and chemical processes are carried out, some of which include; mineralization of organic matter and fixation of mineral matter atoms into organic compounds. The processes take place within ecosystems (groups of organism interacting with their abiotic environment). Phosphate solubilizing microorganisms (PSMs) can solubilize unavailable phosphate and make them available for plant (Kalayu, 2019). The PSMs produce organic acid, phosphatase and indole acetic acid (Fitriatin et al., 2020). They have an important role in increasing the availability of insoluble P to plants. Organisms which are capable of increasing the P availability in soil belongs to diversified groups including bacteria, actinomycetes and several groups of fungi (Sharma et al., 2013).

Some result reported that biofertilizer improve nutrient available and plant growth on stress condition. Fitriatin et al (2018) reported that biofertilizers (PSMs and nitrogen-fixing bacteria) at different salinity levels (2, 4 and 6 mmhos cm^{-1}) affected the P-availibilty in the soil, phosphatase activity and dry weight of paddy rice. Soni et al. (2018) suggested that the isolated halotolerant PSMs may to be used as source to supply phosphorous to the growing plant in saline conditions.

The application methods of biofertilizers depend on the type of biofertilizers in use and the active ingredient of their inoculants. The objective of the research was to study the effect of biofertilizers (both solid and liquid biofertilizer containing of PSMs and nitrogen-fixing bacteria) on some chemical and biological properties of Inceptisols.

Material and Methods

Soil

The soil used in this study was taken from paddy soil (a depth of 0-20 cm). The soil were containing 46% clay, 41% silt, 13% sand. Soil texture can be classified as silty clay. The pH (in H_2O) was slightly acidic (6.47), soil C_{org} was low (1.30%), total N (N_{total}) was low (0.13%), the soil C/N ratio 10, soil $P_{available}$ was high (18,92 mg kg^{-1}) and cation exchange capacity (CEC) was 17.26 cmol kg^{-1}. The soil were classified Inceptisols in Soil Survey Staff (1999).

Biofertilizer

Biofertilizer contained of PSMs (*Pseudomonas mallei, Pseudomonas cepaceae, Penicillium* sp., *Aspergillus* sp.) and nitrogen-fixing bacteria (*Azotobacter* sp. and A*zosprillum* sp.) obtained from the collection of Soil Biology and Biotechnology Laboratory, Faculty of Agriculture, Universitas Padjadjaran, Indonesia. Preparation of biofertilizer begins with augmentation of each isolate. Adding 10 mL 0,85% physiological NaCl to the test tube of pure culture isolate then transferred to a tube filled with 500 mL each selective media. PSMs used Pikovskaya medium (5 g $Ca_3(PO_4)_2$, 10 g glucose, 0.5 g $(NH_4)SO_4$, 0.2 NaCl, 0.1 g $MgSO_4 \cdot 7H_2O$, 0.2 g KCl, 0.5 g yeast extract, 0.002 g $MnSO_4 \cdot H_2O$, 0.002 g $FeSO_4 \cdot 7H_2O$, 15 g agar, in 1 L distilled water, pH 7) (Nautiyal et al. 1999) and nitrogen-fixing bacteria used Nitrogen-free Ashby medium (5 g glucose, 5 g mannitol, 0.1 g $CaCl_2 \cdot 2H_2O$, 0.1 g $MgSO_4 \cdot 7H_2O$, 5mg $Na_2MoO_4 \cdot 2H_2O$, 0.9 g K_2HPO_4, 0.1 g KH_2PO_4, 0.01 g $FeSO_4 \cdot 7H_2O$, 5 g $CaCO_3$, 15g agar in 1 L distilled water, pH 7.3) and Okon medium (5 g Malic acid, 4 g KOH, 0.5 g K_2HPO_4, 0.05 g $FeSO_4.7H_2O$, 0.01 g $MnSO_4.7H_2O$, 0.1 g $MgSO_4.7H_2O$, 0.02 g NaCl, 0.01 g $CaCl_2$, 0.002 g Na_2MoO_4, 2.00 ml Bromothymol blue (0.5% in 95% methanol), Agar 1.8 g (semi-solid)/18 g(solid), NH_4Cl 1 g, Water 1 litre (Narayan et al., 2018), then incubated for 72 hours by shaking it using shaker. Solid biofertilizer used a mix of peat and compost with a ratio of 1:1 as carrier, for liquid biofertilizers use molasses (2%) + NH_4Cl 0.01 %.

Organic ameliorant

Organic ameliorant used in this research were straw compost (Organic C: 29.63%, N 1.43%. P: 1.34%, K: 2.11%, C/N: 21, and pH: 8.64), biochar (Organic C: 42.42%, N: 0.49%, P: 0.02%, K_2O: 0.16%. C/N: 87, and pH: 8,18), and cow manure (Organic C: 43.60%, N: 1.13%. P: 0.60%, K_2O: 0.59%, C/N: 29, and pH: 7.80). The three ameliorants were selected based on selection in previous studies and had different nutrients content. Doses of organic ameliorants were 10 t ha^{-1}.

Experimental design

The experiment procedure include testing and optimizing the formula for consortia of PSMs (*Pseudomonas mallei, Pseudomonas cepaceae, Penicillium* sp. and *Aspergillus* sp.) and nitrogen-fixing bacteria (*Azotobacter* sp. and A*zosprillum* sp.) with organic ameliorant with the composition of straw compost, biochar, and cow manure. Experimental soil was used for planting the rice seedlings during the pot experiment. Two rice seedlings were obtained at 14 days after seedlings (DAS) in a plastic container 40 x 30 cm with a height of 35 cm set to be transferred to pots for further experiment.

The experiment was carried out with the randomized block design (RBD) consisted of twelve treatments with three replications in greenhouse of Agricultural Faculty, Universitas Padjadjaran Indonesia.. The experiment consisted of control, solid biofertilizer (50 kg ha^{-1}), liquid biofertilizer (5 L ha^{-1}), a combination of solid biofertilizers (50 kg ha^{-1}) with organic ameliorants (10 t ha^{-1}) (composted straw, biochar and cow manure), a combination of liquid biofertilizer (5 L ha^{-1}) and organic ameliorants (10 t ha^{-1}), and each of ameliorants (10t ha^{-1}) independently. The provision of water was carried out to maintain the condition of the field capacity. The variables observed were some soil chemical properties (N_{total}, available P ($P_{available}$), CEC, organic C ($C_{org.}$)) and some soil biological properties (acid phosphatase activity and population of PSMs and nitrogen fixing-bacteria) at the end of the vegetative period. Plants are harvested at the end of the generative period at the age of 95 days.

Soil biological properties

Soil biological properties analysed in this study were total population of PSMs and nitrogen-fixing bacteria. The serial dilution plates were used to determine population of PSMs on Pikovskaya agar. One g of soil sample was taken and serially diluted using sterile distilled water upto 10^{-6} dilutions. One ml of diluted sample from 10^{-4} to 10^{-6} dilutions were taken to plate with Pikovskaya agar. The plates were incubated at 28°C for 48-72 hours until halozones appeared around the colonies. The same method to determine population of nitrogen fixing bacteria. *Azotobacter* were calculated on Nitrogen-free Ashby medium while *Azospirillum* on Okon medium (Somasegaran and Hoben, 1994). The acid phosphatase activity in soils (EC 3.1.3.2) determined according to Eivazi and Tabatabai (1977).

Soil chemical properties

Soil chemical properties analysed in this study were N_{total} content in soil using Kjeldahl method $P_{available}$ using Bray I method, $C_{org.}$ using Walkley and Black method and CEC was determined using the 1N ammonium acetate at pH 7 (van Reeuwijk, 2002).

Data analysis

Data were collected to analysis of variance (ANOVA) and treatment means were compared using Tukey HSD Advance test at p = 0.05 probability.

Results and Discussion

Soil Biological Properties

The result of experiment revealed that biofertilizer and organic ameliorant increase soil biological properties significantly. Population of soil beneficial microorganisms gave different respons by biofertilizer and organic ameliorant. Type of biofertilizer influenced to soil biological properties. The treatment of liquid biofertilizer with biochar significantly affected on population of phosphate solubilizing bacteria up to 11.70 x 10^9 CFU g^{-1} (Table 1). This indicated that the application of biochar stimulate the growth of microorganisms. Ajema (2018) reported that biochar incorporation into soil improved beneficial soil microorganisms. According to Głuszek et al. (2017) that biochar influenced soil physical and chemical properties as well as beneficial soil microorganisms.

Table 1. Population of microorganisms and phosphatase activity in soil at the end of vegetative period

Treatments	Population of soil microorganisms (CFU g^{-1})								Acid phosphatase activity	
	PSB* ($x10^9$)		PSF ** ($x10^4$)		*Azotobacter* ($x10^5$)		*Azospirillum* ($x10^7$)		(µg pNP g^{-1} h^{-1})	
Control	1.30	a	4.33	a	2.10	ab	10.38	a	32.8	a
Solid biofertilizer (S-bio)	9.00	c	9.67	ab	4.23	c	13.57	ab	56.3	c
Liquid biofertilizer (L-bio)	10.33	d	6.33	ab	1.93	ab	14.17	ab	50.3	bc
S-bio + straw compost	9.28	cd	6.00	ab	1.97	ab	16.77	ab	55.3	c
S-bio-fertilizer + biochar	6.10	bc	5.33	ab	2.03	ab	21.17	bc	50.5	bc
S-bio + cow manure	9.08	cd	7.00	ab	2.73	b	15.93	ab	53.7	bc
L-bio + straw compost	5.90	bc	6.33	ab	2.23	ab	15.33	ab	50.6	bc
L-bio + biochar	11.70	d	10.67	b	2.77	b	30.67	c	59.6	c
L-bio + cow manure	3.62	ab	4.67	ab	2.07	ab	13.83	ab	56.9	c
Straw compost	2.52	a	2.67	ab	1.73	a	8.79	a	48.4	bc
Biochar	1.18	a	6.00	ab	2.13	ab	13.60	ab	42.7	ab
Cow manure	2.32	a	6.33	ab	2.03	ab	21.18	bc	51.9	bc

Remarks: The average score followed by the same letter is not significantly different according to the Tukey HSD Advanced Test at the 5% level. *PSB : phosphate solubilizing bacteria; **PSF : phosphate solubilizing fungi

The result showed that biofertilizers application better influence than ameliorant organic on population of soil microorganisms. A previous study reported that application biofertilizer containing *Bacillus aryabatthai* increased population of phosphate solubilizing bacteria (Zulaehah et al., 2019). Bhardwaj et al (2014) stated that biofertilizers play an important role in creating a better soil environment through increase nutrient availability. The other research showed that biofertilizer (*Azotobacter* sp. *Azospirillum* sp and *Rhizobium* sp.) combined with organic fertilizer (palm oil mill effluent) increased soil bacterial population (Suliasih and Widawati, 2017).

Biofertilizers and organic ameliorant influenced enzyme activity. The result showed that biofertilizers improve soil phosphatase activity. Soil phosphatase activity was significantly higher 59.6 µg pNP g^{-1} h^{-1} recorded with liquid biofertilizers + biochar. This indicated that combination of biofertilizers and organic ameliorant stimulated soil microorganisms to produce phosphatase enzyme. According to Laxman et al. (2017) concortia of microorganisms application to soil and foliar application of macro nutrients showed remarkable influence on activity of dehydrogenase, phosphatases and urease enzymes. Rahmansyah and Antononius (2015) reported that biofertilizers and compost application improved soil phosphatase and urease activites. Furthermore, the continuous application of compost increased soil organic matter content, population of soil micoorganisms and soil enzyme activity (Chang et al., 2007).

Soil Chemical Properties

Based on the statistical analysis in Table 2, the combination of biofertilizers and ameliorants significantly affected the N_{total} and $P_{available}$ content in soil. The application of biofertilizers and organic ameliorants improve the N_{total} and $P_{available}$ significanlty. The effect of biofertilizer and organic ameliorants on N_{total} increased in the range 38.5% to 138.5%. The highest of N_{total} was shown by combination of solid biofertilizer with straw compost which increasing up to 138.5%. Our study suggests that biofertilizers without organic ameliorant have lower N_{total} content than the combined treatments of biofertilizers and organic ameliorants.

The applications of organic ameliorant significantly improved N_{total}. However, differences in the types of organic ameliorants in this case straw compost, biochar and cow manure gave effect on N_{total} non-significant each other. The other studies showed that application of ameliorant (biochar, lime and organic fertilizer) increased abundances of *Nitrosomonas* and *Nitrospira* which causes an increasing in soil N_{total} (Zhang et al., 2017).

The effect of biofertilizers and organic ameliorant on $P_{available}$ increased significantly in the range 14.7% to 79.8 % (Table 2). The highest of $P_{available}$ was shown by combination of solid biofertilizer with straw compost which increasing up to 79.8%. In general, application of organic ameliorant without biofertilizer have lower $P_{available}$ than the combined treatments of biofertilizers and organic ameliorants. Acoording to Ye et al. (2020) biofertilizer combined with organic fertilizers increased abundance of soil microorganisms and enhanced the $P_{available}$ and K contents in soil.

Table 2. N_{total} and $P_{available}$ in soil at the end of vegetative period

Treatments	N_{Total} (%)		$P_{available}$ ($mgkg^{-1}$)	
Control	0.13	a	16.36	a
Solid biofertilizer (S-bio)	0.20	bc	23.16	e
Liquid biofertilizer (L-bio)	0.18	b	19.20	bc
S-bio + straw compost	0.31	d	23.47	e
S-bio-fertilizer + biochar	0.20	bc	20.17	cd
S-bio + cow manure	0.22	bc	21.20	de
L-bio + straw compost	0.21	bc	19.90	cd
L-bio + biochar	0.24	c	21.88	de
L-bio + cow manure	0.21	bc	18.77	b
Straw compost	0.18	b	18.70	ab
Biochar	0.19	b	18.16	ab
Cow manure	0.18	b	17.77	ab

Remarks: The average score followed by the same letter is not significantly different according to the Tukey HSD Advanced Test at the 5% level

Increasing of N_{total} in soil in this research as affected by biofertilizers and organic ameliorants. This is due to the presence of N-fixing bacteria in the form of *Azotobacter* and *Azospirillum* in biofertilizers. According to Rodrigues et al. (2008) the use of organic matter with the addition of *Azotobacter* improves the fixation of N compared to without the addition of *Azotobacter*. The value of the increasing organic matter with *Azotobacter* is 11.4 kg ha^{-1}. Piccinin et al. (2013) states nitrogen fixing bacteria is associated with the plant and provides a portion of N needed by the plants. This process is through direct secretion to the plant. The addition of *Azospirillum* inoculation increases the growth of roots and upper parts of plants, and also increases crop productivity. This addition also reduces the use of N fertilizer by 15-20 kg N ha^{-1} (Rodrigues et al., 2008).

Table 3 showed the combination of biofertilizer and organic ameliorant has a significant effect on $C_{org.}$ in soil (The treatment of solid biofertilizers with ameliorant increased significantly on $C_{org.}$. Combination of solid biofertilizers with straw compost gave better effect to increase $C_{org.}$. This can be caused by C/N ratio (C/N ratio is 21) of straw compost was smallest than biochar (C/N ratio is 87) and cow manure (C/N ratio is 29), futhermore it decomposed faster and then increased $C_{org.}$ In this study, biofertilizers combined with organic ameliorant increased C_{org} up to 15.27%. The other study showed that biofertilizers (containing lactic acid bacteria, *Pseudomonas* spp., *Penicillium* and *Actinomycetes* spp.) increased the soil organic matter stability (Dębska et al., 2016). According to Mijwel (2018) combined of organic with biofertilizer were the best treatment for increasing of soil content of organic substance, $C_{org.}$ and organic phosphorus.

Table 3. $C_{org.}$ and CEC at the end of vegetative period

Treatments	C_{org} (%)		CEC (cmol kg^{-1})	
Control	1,31	a	20,43	a
Solid biofertilizer (S-bio)	1,42	bc	25,12	b
Liquid biofertilizer (L-bio)	1,37	ab	24,12	ab
S-bio + straw compost	1,51	d	25,97	b
S-bio-fertilizer + biochar	1,50	d	24,01	b
S-bio + cow manure	1,50	d	25,61	b
L-bio + straw compost	1,46	cd	23,51	ab
L-bio + biochar	1,44	cd	23,64	ab
L-bio + cow manure	1,45	cd	22,10	ab
Straw compost	1,45	cd	23,14	ab
Biochar	1,46	cd	22,70	ab
Cow manure	1,46	cd	24,41	ab

Remarks: The average score followed by the same letter is not significantly different according to the Tukey HSD Advanced Test at the 5% level.

Our study showed that application of biofertilizers combined with organic ameliorant significantly increased CEC. It may be due to that biofertilizer and organic ameliorant increased nutrient availability which further affects increasing in CEC. Arabi et al. (2018) reported that the interaction of biochar and biofertilizer significantly increased CEC. The other study showed that organic fertilizer composted with liquid biofilm biofertilizer (3-21 ton ha^{-1}) improved soil N_{total}, $P_{available}$, exchangeable-K and CEC of Lithosols and spinach yields (Sudadi et al., 2018).

Conclusion

Our study showed that combined of biofertilizer and ameliorant organic increased some soil biological properties (population of PSMs, N-fixing bacteria and acid phosphatase activity) and some soil chemical properties (N_{total}, $P_{available}$, $C_{org.}$ and CEC). The solid biofertilizers with straw compost application gave better to increase N_{total} and $P_{available}$, while the liquid biofertilizers with biochar gave better to improve population of soil microorganisms and phosphatase activity. Further studies are needed to develop organic-based biofertilizers to improve soil quality, crop production and reduce chemical fertilizers.

Acknowledgement

This research was supported by grants received from the Directorate General of Higher Education Ministry of Research and Technology Indonesia. We thank staff Laboratory of Soil Biology and Laboratory of Soil Fertility and Plant Nutrition Faculty of Agriculture, Universitas Padjadjaran for their cooperation. We thank our students for supporting us during experiment at field.

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Eurasian Journal of Soil Science 2021, 10(2), 111- 122

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

Performance of an accelerated compost as influenced by ecological zones: A case study of derived savannah and rain forest in Nigeria

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Article Info

Received : 31.07.2019
Accepted : 15.11.2020
Available online : 30.11.2020

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Abstract

Accelerated compost (AC) biotechnology that reduces composting time to less than one month is gradually finding its way to farmers. This study therefore evaluated the fertilizer potential of a brand of commercial AC (*OBD-plus*) on a degraded Alfisol in Ibadan (derived savannah) and Ultisol in Ikenne (rain forest) of Nigeria, using maize as a test crop. The experiment was laid out in Randomized Complete Block Design with three replications. The treatments were AC at 0, 60, 90, 120, 150 and 180 kg N ha^{-1}, mineral fertilizer (NPK 15-15-15) and conventional compost (CC), each at 60 kgN/ha. Data collected on biomass yield, maize grain yield (MGY, t ha^{-1}) and post-cropping soil chemical properties were subjected to ANOVA at $\alpha_{0.05}$. The average highest MGY from Ibadan (3.90) and Ikenne (3.86) were obtained from AC (180 kg N/ha), but these were not significantly different from other AC rates and NPK. The least MGY was obtained from control (2.1 and 2.0) which was significantly less than the CC (3.16 and 2.90). The AC improved the post-cropping soil pH, N and K. The mean MGY obtained from the six levels of AC in Ibadan; 3.44 and 3.98 t ha^{-1} in 2013 and 2014 were not significantly different from Ikenne (3.41 and 3.84 t ha^{-1}). However, maize in Ibadan gave significantly higher biomass yield (19.40 t ha^{-1}) than that of Ikenne (17.74 t ha-1) in 2013, with similar trend in 2014. Accelerated compost at 60 kg N ha^{-1} improved maize grain yield and post cropping soil properties in Ibadan and Ikenne, Nigeria as much as conventional compost. The performance of the accelerated compost was not location dependent in terms of MGY, but resulted in higher biomass production in the derived savannah ecology.

Keywords: Accelerated compost, ecology, maize grain yield, soil fertility enhancement, Zea mays.

Introduction

The application of organic wastes generated from domestic, agricultural and industrial activities as soil amendment on agricultural land is known as a popular means of their disposal (Baharuddin et al., 2009; Soretire and Olayinka, 2013). The conversion of such wastes to soil amendments fosters sustainability of production, a more balanced nutrition for plants, improvement in soil properties and reduction in greenhouse gases emissions, hence mitigate climate change (Embrandiri et al., 2012; Ibrahim and Fadni 2013; AyanfeOluwa et al. 2015). Moreover, organic fertilizers are the store house of plant nutrients in the

: https://doi.org/10.18393/ejss.833544
: http://ejss.fesss.org/10.18393/ejss.833544
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

soil. They improve the cation exchangeable capacity of the soil and thus has the potential to enhance crop yield (Bekeko, 2013; Natsheh and Mousa, 2014; Moyin-Jesu, 2015).

However, the process of composting various organic wastes into organic fertilizers ideally often requires a long period which poses a major limitation. This could take as long as eight months depending on factors such as the procedure adopted, nature of the organic materials, particle size, environmental conditions, etc. (Cooperband, 2002). However, with recent technological development, it is possible to reduce the period of composting to as short as three weeks and such compost is called rapid /accelerated which have been reported highly innovative in improving soil fertility for improved yields of crops (Mowa and Maass 2012; Hu and Qi 2013; Mbouobda et al., 2014; Patidar et al., 2014).

Although, the composting acceleration technology is relatively new in Nigeria, AyanfeOluwa et al. (2017) found that the compost mineralized properly comparable to the conventional compost in an incubation study. In a further work, AyanfeOluwa (2019) also reported that nutrients from accelerated compost are also available for maize production comparable to conventional compost and mineral fertilizer in a screen house study. Accelerated compost thus fulfilled two of the conditions of a good fertilizer in spite of the shortness in the process of composting, relative to compost from conventional composting method. However, there is a need to validate the performance of accelerated compost on the field to substantiate its fertilizer potential for crop production.

Maize is rated globally as the second most important cereal and the most important in sub-Saharan Africa (OECD/FAO, 2015) with Nigeria recognised as the largest producer in the region. Maize plant performance on the field is very sensitive to soil nutrient supply for good growth and high yield (Gul et al., 2015). However, the average grain yield of maize obtained by farmers in Africa has been very low with an estimate of 2 t ha^{-1}, due to low fertilizer application rate (Fanadzo et al., 2010). Alfisols and Ultisols are major agricultural soil types in the world which are highly weathered, leached and inherently low in soil nutrients, hence, require soil amendments to enhance their productivity (Blum and Eswaran 2004; FFD, 2012). Derived savannah and rainforest are two of the major agro ecology in Nigeria. Thus this research work evaluated the potential of an accelerated compost 'OBD plus' on a degraded Alfisol in the derived savannah and Ultisol in the rainforest of Nigeria, with maize as the test crop.

Material and Methods

The trials took place in two locations. The first was conducted at the Federal College of Agriculture, Ibadan, Nigeria (Lat. 7°22.5′N and Long. 3°50.5′E), on a soil described as Alfisol belonging to Iwo series (Smyth and Montgomery 1962). The second was carried out at the Institute of Agricultural Research and Training, substation in Ikenne, Nigeria (Lat. 6°51'N and Long. 3°42'E), on a soil described as Ultisol belonging to Alagba series (Periaswamy and Ashaye, 1982).

Ibadan is located in the derived savannah agro-ecological zone of Nigeria. The zone is characterized by bimodal rainfall distribution and an average annual rainfall of 1288±158 mm over a period of 10 years (2005 to 2014), average temperature range of 6.1˚C (max. temp.; 29.0˚C, min temp.; 22.9˚C) over the same period. The average relative humidity (RH) was 86.3% over the same period of 10 years (NASA-Power, 2016). This zone is covered with scattered trees and tall grasses. Conversely, Ikenne is located in the tropical rain forest ecological zone of Nigeria, characterized with bimodal rainfall distribution with distinct dry and rainy seasons. The zone has an average annual rainfall of 1532±227 mm over a period of 10 years (2005 to 2014), average temperature range of 2.2˚C (max. temp.; 27.8˚C, min temp.; 25.6˚C) and average RH of 86.1% over the same period (NASA-Power, 2016). The vegetation is classified into two; low and top layers. The low layer vegetation is characterized with abundance of herbs, shrubs and grasses while the top layer is characterized with valuable economic trees such as *Chlorophora Excelsa*, *Eucalyptus marginata*, *Khaya ivorensis* among others (Sowunmi and Akintola, 2010).

The rainfall data obtained for Ibadan in the three months (May – July) period of the maize cropping was 380 and 515 mm for the years 2013 and 2014, respectively. However at Ikenne, it was 570 and 735 mm in 2013 and 2014, respectively. The average maximum temperature obtained for Ibadan in 2013 and 2014 was 31.6˚C and 31.8˚C, respectively, while it was 28.2 and 28.3˚C in 2013 and 2014, respectively, in Ikenne (NASA-Power, 2016).

The accelerated compost; OBD-plus evaluated in this study is a company's product, obtained from Gateway Fertiliser Company, Abeokuta, Ogun State, Nigeria. The compost matured in a month. The conventional compost used as a check was also a company's product, obtained from Alesinloye Compost Company, Alesinloye market, Ibadan, Oyo State, Nigeria. Chemical analyses of the composts (Table 1) were carried out using standard procedures (Olsen and Dean, 1965; Okalebo et al., 1993; Bremner, 1996; Thomas, 1996).

Table 1. Chemical analysis of the accelerated and conventional composts

Parameter	pH (H_2O)	Total Carbon	N	P	K	Ca	Mg	Na	C:N ratio	Fe	Cu	Mn	Zn
		-------------------- ($g\ kg^{-1}$)						--------------------------------		----------- $mg\ kg^{-1}$	-----------		
AC	6.2	170	12.3	46	5	3.1	1.1	2	140	2860	71	495	464
CC	9.7	170	12.0	8	17	3.2	1.0	4	140	1670	78	393	186

AC; Accelerated compost, CC; Conventional compost

The physical and chemical analyses of the pre-treated soils were also carried out using standard procedures (Bray and Kurtz, 1945; Murphy and Riley, 1962; Hendershot and Lalande, 1993; Bremner, 1996; Nelson and Sommers, 1996; Thomas, 1996; Gee and Or, 2002) and are shown in Table 2. The Ibadan location soil (Alfisol) was low in N, P and organic carbon, but marginal in K for the two years, while Ikenne soil (Ultisol) was low in N, P, K and organic carbon (FFD, 2012). The textural classes of the Alfisol in the two years were loamy sand while that of Ultisol was loamy sand in the first year and sandy loam in the second year based on USDA textural triangle (Soil Survey Division Staff, 1993).

Table 2. Physical, chemical and biological characteristics of soil in the experimental field

Parameters	Ibadan		Ikenne	
	2013	2014	2013	2014
pH (H_2O) 1:1	6.2	6.1	5.9	5.8
Organic C ($g\ kg^{-1}$)	7.2	9.1	7.8	6.7
Total N ($g\ kg^{-1}$)	0.4	0.9	0.7	0.7
Available P ($mg\ kg^{-1}$)	8.0	4.0	7.0	5.0
Exchangeable cations ($cmol\ kg^{-1}$)				
Ca^{2+}	1.8	1.8	1.6	2.0
Mg^{2+}	0.7	1.1	0.4	0.9
K^+	0.4	0.4	0.2	0.1
Na^+	0.4	0.5	0.2	0.4
Ex. Acidity ($cmol\ kg^{-1}$)	0.1	0.1	0.4	0.4
ECEC ($cmol\ kg^{-1}$)	3.4	3.9	2.7	3.8
Extractable Micronutrients ($mg\ kg^{-1}$)				
Mn	423	157	265	215
Fe	191	133	113	136
Cu	3.0	3.0	2.0	3.0
Total microbial count (x 10^6 CFU g^{-1})	3.4	3.8	3.5	6.2
Fungi count (x 10^6 CFU g^{-1})	3.0	4.0	2.0	4.0
Particle size ($g\ kg^{-1}$)				
Sand	840	876	820	776
Silt	108	24	108	84
Clay	52	100	72	140
Textural class (USDA)	Loamy sand	Loamy sand	Loamy sand	Sandy loam

The treatments applied were accelerated compost at 0, 60, 90, 120, 150, 180 kg N ha^{-1}, mineral fertilizer (NPK 15:15:15) and conventional compost at 60 kg N ha^{-1} each. The maize variety planted was TZEE1 14 X TZEE1 57 X TZEE1 12 (extra early maturing Hybrid maize) and the design was randomized complete block replicated three times. Each plot size was 3.3 x 3.3 m and the planting spacing was 75 x 25 cm with one plant per stand, giving a plant population of 48 stands per plot. The total land area used for the experiment was 360 m^2. The compost treatments were applied a week before sowing while the inorganic fertilizer was applied at two weeks after sowing (WAS) and weeding was carried out as necessary.

Data were collected on growth parameters; number of leaves, stem diameter at 4 and 6 WAS and yield parameters; stover weight, ear weight, husk weight, dry cobs weight (sun dried), 100 grain weight (with the use of Mettler PM 4000 balance) and grain yield (with the use of a kitchen scale). The post-maize cropping soil analysis was carried out; a total number of four samples were randomly collected per plot and bulked together. The parameters considered were soil pH, organic carbon, total N, available phosphorus (P), exchangeable bases (Ca, Mg, K and Na), particle size distribution and total microbial and fungi, following standard procedures. The data obtained were subjected to analysis of variance (ANOVA) and the means separated using Duncan Multiple Range Test (DMRT). Data collected from the six rates of AC were also compared for the two agro-ecologies for relationship and difference using T-test and correlation.

Results

The result showed significant differences among the treatment means for all the parameters (Table 3). In 2013, AC at 150 kg N ha^{-1} recorded the highest stover weight (16.7 t ha^{-1}), which differed not significantly from AC at 180 kg N ha^{-1} (14.8t ha^{-1}), but higher than other treatments. The control gave the least stover weight (7.8 t ha^{-1}). In terms of ear weight of maize, AC at 180 kg N ha^{-1} produced the highest value (8.6 tha^{-1}), which differed not significantly from others apart from the control (6.6 t ha^{-1}). The AC at 180 kg N ha^{-1} gave the highest dry cob weight (5.3 t ha^{-1}), which differed not significantly from others except AC at 90 kg N ha^{-1} (4.4 t ha^{-1}) while control treatment had the least value (3.4 t ha^{-1}). The NPK had the highest mean dry shaft weight (1.0 t ha^{-1}), which differed not significantly from others, except AC at 90 kg N ha^{-1} (0.8 t ha^{-1}) and control treatment (0.7 t ha^{-1}). In 2014, 120 kg N ha^{-1} AC gave the highest mean stover weight (18.4 t ha^{-1}), which was at par with AC at 180 kg N ha^{-1} (18.2 t ha^{-1}), 150 kg N ha^{-1} (17.3 t ha^{-1}) and NPK (16.3 t ha^{-1}), but significantly higher than others. The control gave the lowest stover weight (11.9 t ha^{-1}). The AC at 180 kg N ha^{-1} produced the highest ear weight (7.8 t ha^{-1}), which differed not significantly from other treatments, except CC (5.6 t ha^{-1}) and control (5.5 t ha^{-1}). In terms of the dry cob weight, 90 kg N ha^{-1} AC treatment recorded the highest mean value (4.8 t ha^{-1}), which differed significantly from every other treatment. The control treatment gave the least significant value (2.6 t ha^{-1}). The AC at 120 kg N ha^{-1} produced the highest dry shaft weight (0.9 t ha^{-1}), which was at par with AC at 90 kg N ha^{-1} (0.8 t ha^{-1}) and CC (0.8 t ha^{-1}), but differed significantly from others. Meanwhile, differences among AC at 60 kg N ha^{-1}, CC and NPK were not significant in all the parameters in the two years.

Table 3. Effects of accelerated compost on yield parameters of maize

		Year							
		2013				2014			
	Treatments (kg N ha^{-1})	Mean stover weight	Mean ear weight	Mean dry cob weight	Mean dry shaft weight	Mean stover weight	Mean ear weight	Mean dry cob weight	Mean dry shaft weight
Ibadan	AC	t ha^{-1}				t ha^{-1}			
	0	7.8 c	6.6 b	3.4 c	0.7 c	11.9 d	5.5 b	2.6 c	0.7 bcd
	60	12.0 b	7.2 a	4.4 ab	0.9 ab	15.0 bc	7.6 a	4.0 b	0.6 cd
	90	12.2 b	7.2 a	4.4 b	0.8 bc	15.1 bc	7.4 a	4.8 a	0.8 ab
	120	12.8 b	7.9 a	5.0 ab	0.9 ab	18.4 a	7.6 a	3.9 b	0.9 a
	150	16.7 a	8.4 a	5.0 ab	0.9 ab	17.3 ab	7.4 a	4.1 b	0.6 de
	180	14.6 ab	8.6 a	5.3 a	0.9 ab	18.2 a	7.8 a	3.8 b	0.4 e
	Checks(60 kg N ha^{-1})								
	NPK	12.6 b	8.2 a	4.9 ab	1.0 a	16.3 abc	6.8 ab	3.6 b	0.6 cd
	CC	12.0 b	7.4 a	4.5 ab	1.0 a	14.2 c	5.6 b	3.5 b	0.8 abc
Ikenne	AC	t ha^{-1}				t ha^{-1}			
	0	9.1 c	4.7 b	2.6 c	0.7	11.0 b	5.4 c	2.5 e	0.7 bc
	60	12.8 ab	7.0 a	4.8 ab	0.8	16.4 a	6.7 ab	4.1 bc	0.7 bc
	90	13.9 ab	7.1 a	3.6 c	1.1	15.5 a	6.9 ab	4.7 a	0.8 a
	120	13.3 ab	7.3 a	4.9 ab	1.0	15.2 a	6.6 ab	3.7 bcd	0.9 a
	150	14.4 ab	7.4 a	4.9 ab	1.0	16.9 a	7.3 a	4.1 b	0.6 c
	180	15.5 a	8.2 a	5.3 a	1.3	16.6 a	7.1 ab	3.7 bcd	0.4 d
	Checks (60 kg N ha^{-1})								
	NPK	13.3 ab	7.2 a	4.7 ab	1.1	16.3 a	7.3 a	3.4 d	0.6 c
	CC	10.1 bc	5.4 b	3.7 bc	1.1	15.1 a	6.3 b	3.5 cd	0.8 ab
					ns				

ns: not significant, Means with different letters among treatments do not differ significantly at α0.05 by DMRT
AC, Accelerated Compost; CC, Conventional Compost; NPK, 15-15-15

In Ikenne, the result obtained (Table 3) showed significant differences among the treatments in all the parameters in the two years, except in the dry shaft weight in year 2013. In 2013, AC at 180 kg N ha^{-1} resulted into the highest stover weight (15.5 t ha^{-1}), which was at par with AC at 150 kg N ha^{-1} (14.4 t ha^{-1}), 120 kg N ha^{-1} (13.3 t ha^{-1}) and NPK (13.3 t ha^{-1}) but significantly higher than other treatments. The control treatment recorded the lowest significant stover weight (9.1 t ha^{-1}). In terms of ear weight, AC at 180 kg N ha^{-1} produced the highest (8.2 t ha^{-1}), which was at par with others, except CC (5.4 t ha^{-1}) and control (4.7 t ha^{-1}). The 180 kg N ha^{-1} AC gave the highest mean dry cob weight (5.3 t ha^{-1}), which differed not significantly from others except CC (3.7 t ha^{-1}), AC at 90 kg N ha^{-1} AC (3.6 t ha^{-1}) and control (2.6 t ha^{-1}).

In 2014, the AC at 150 kg N ha^{-1} (16.9 t ha^{-1}) produced the highest stover weight, which differed not significantly from other treatments, apart from the control (11.0 t ha^{-1}). The AC at 150 kg N ha^{-1} also gave the highest ear weight (7.3 t ha^{-1}), which differed not significantly from others, except CC (6.3 t ha^{-1}) and the control (5.4 t ha^{-1}) gave the least significant value. The AC at 90 kg N ha^{-1} had the highest dry cob weight (4.7 t ha^{-1}), while control recorded the lowest (2.5 t ha^{-1}). In terms of the dry shaft weight, AC at 120 kg N ha^{-1}

recorded the highest (0.9 t ha^{-1}), which differ significantly from other treatments, apart from AC at 90 kg N ha^{-1} (0.8 t ha^{-1}) and CC (0.6 t ha^{-1}). The AC at 180 kg N ha^{-1} gave the lowest value (0.4 t ha^{-1}). Also, the result showed no significant difference among the 60 kg N ha^{-1} of AC, CC and NPK in all the parameters in the two years of trials.

In terms of yield (Table 4), at Ibadan, in 2013, the AC at 180 kg N ha^{-1} recorded the highest grain yield (4.41 t ha^{-1}), which differed not significantly from AC at 150 kg N ha^{-1} (4.14 t ha^{-1}), AC at 120 kg N ha^{-1} (4.18 t ha^{-1}) and NPK (3.95 t ha^{-1}). This was however significantly higher than others, while the control gave the lowest yield (2.29 t ha^{-1}). In 2014 at Ibadan, the 90 kg N ha^{-1} AC produced the highest grain yield (3.96 t ha^{-1}), which was at par with 150 kg N ha^{-1} AC (3.53 t ha^{-1}), but significantly higher than others. The control recorded the significantly lowest mean yield (1.92 t ha^{-1}). Averaged over the two years, AC at 180 kg N ha^{-1} produced the highest yield (3.90 t ha^{-1}), which differed not from AC at 150 kg N ha^{-1} (3.83 t ha^{-1}), AC at 90 kg N ha^{-1} (3.76 t ha^{-1}), AC at 120 kg N ha^{-1} (3.6 t ha^{-1}), NPK (3.46 t ha^{-1}) and AC at 60 kg N ha^{-1} (3.41 t ha^{-1}), but higher than CC (3.16 t ha^{-1}). The control recorded the lowest yield (2.10 t ha^{-1}).

At Ikenne, in 2013, 180 kg N ha^{-1} AC produced the highest grain yield (4.43 t ha^{-1}), which differed not significantly from others except 90 kg N ha^{-1} AC (3.14 t ha^{-1}) and CC (3.07 t ha^{-1}), while control produced the lowest yield of 2.07 t ha^{-1} (Table 4). In 2014, the 90 kg N ha^{-1} AC gave the highest yield (3.92 t ha^{-1}), which differed not from 150 kg N ha^{-1} AC (3.58 t ha-1), 60 kg N ha^{-1} AC (3.42 t ha^{-1}), but significantly higher than others. The control recorded the significant least yield (1.89 t ha^{-1}). Averaged over the two years, 180 kg N ha^{-1} AC recorded the highest maize grain yield (3.86 t ha-1), which was at par with others except 120 kg N ha^{-1} AC (3.13 t ha^{-1}) and CC (2.90 t ha^{-1}) while control still gave the least yield (1.98 t ha^{-1}). The AC at 60 kg N ha^{-1} (3.75 t ha^{-1}) was at par with NPK (3.35 t ha^{-1}), but significantly higher than 60 kg N ha^{-1} CC (2.90 t ha^{-1}).

Table 4. Effects of accelerated compost on maize grain yield (t ha^{-1})

Treatments	Ibadan						Ikenne					
(kg N ha^{-1})	2013		2014		Average		2013		2014		Average	
AC												
0	2.29	c	1.92	e	2.10	c	2.07	c	1.89	e	1.98	d
60	3.50	b	3.33	bc	3.41	ab	4.09	ab	3.42	ab	3.75	a
90	3.56	b	3.96	a	3.76	a	3.14	b	3.92	a	3.53	ab
120	4.18	ab	3.02	bcd	3.60	ab	3.39	ab	2.86	cd	3.13	bc
150	4.14	ab	3.53	ab	3.83	a	4.10	ab	3.58	ab	3.84	a
180	4.41	a	3.39	bc	3.90	a	4.43	a	3.28	bc	3.86	a
Checks (60 kg N ha^{-1})												
NPK	3.95	ab	2.97	cd	3.46	ab	3.91	ab	2.79	cd	3.35	abc
CC	3.57	b	2.76	d	3.16	b	3.07	bc	2.74	d	2.90	c

Means with different letters among treatments do not differ significantly at α0.05 by DMRT
AC, Accelerated Compost; CC, Conventional Compost; NPK, 15-15-15

In terms of post-cropping soil chemical properties, at Ibadan in 2013, the two years is shown in Table 5. The results revealed that the fertilizer treatments had significant ($p<0.05$) effects on the soil properties as follows. In Ibadan, in year 2013, plot treated with AC at 120 kg N ha^{-1} recorded the highest pH (6.7), which was at par with soils from other treatments, except the NPK treated soil (6.1). Plot treated with AC at 180 kg N ha^{-1} recorded the highest organic carbon (9.5 g kg^{-1}), which was at par with CC (7.8 g kg^{-1}) and the control (7.6 g kg^{-1}) but significantly higher than other treatments while soil treated with NPK gave the lowest value (3.6 g kg^{-1}). Plot that received 180 kg N ha^{-1} AC recorded the highest total N (2.0 g kg^{-1}), which was at par with 90 kg N ha^{-1} AC treated plot (1.7 g kg^{-1}), 120 kg N ha^{-1} AC plot (1.7 g kg^{-1}) and 150 kg N ha^{-1} AC plot (1.6 g kg^{-1}), followed by 60 kg N ha^{-1} AC (1.4 g kg^{-1}) and CC (1.3 g kg^{-1}) while NPK treated soil had the lowest value (0.8 g kg^{-1}). The 90 kg N ha^{-1} AC gave the highest available P (81 mg kg^{-1}) which differed significantly from others, while the control recorded the lowest value (16 mg kg^{-1}). The 60 kg N ha^{-1} AC (4.5 cmol kg^{-1}) treated soil had the highest significant Ca. The 150 kg N ha^{-1} AC (7.5 cmol kg^{-1}) treated soil gave the highest significant Mg. All the treatments differed not from one another regarding K and Na. The AC at 60 kg N ha^{-1} treated soil recorded the highest ECEC (14.4 cmol kg^{-1}) while NPK had the lowest value (5.0 cmol kg^{-1}).

In year 2014, 180 and 150 kg N ha^{-1} AC treated soils had the highest pH (6.4), which was at par with other treatments except NPK with the lowest pH (5.6). The plot that received AC at 180 kg N ha^{-1} had significantly highest organic carbon (13.8 g kg^{-1}), followed by AC at 150 kg N ha^{-1} (10.4 g kg^{-1}), which differed not significantly from the soils that received CC (10.2 g kg^{-1}) and 60 kg N ha^{-1} AC (9.8 g kg^{-1}) while NPK and the control gave the lowest value (5.8 and 5.6 g kg-1, respectively). The plot that received AC at 150 kg N ha^{-1} recorded highest N value (1.4 g kg^{-1}), which differed not significantly from AC rates at 180 kg N ha^{-1} (1.3 g kg^{-1}) and 60 kg N ha-1 (1.2 g kg^{-1}), while NPK gave the lowest mean value (0.9 g kg^{-1}). The 180 kg N ha^{-1} AC plot gave the highest significant available P (67 mg kg^{-1}), followed by the 150 kg N ha-1 AC (28 mg kg^{-1}), which differed not significantly from other rates while the CC plot gave the lowest mean value (8 mg kg-1). The 120 kg N ha-1 AC treated soil had the highest significant Ca (3.5 cmol kg-1), Mg (1.8 cmol kg-1) and ECEC (6.4 cmol kg-1) while all the treatments differed not from one another regarding K and Na.

Table 5. Effects of accelerated compost on post-cropping soil chemical properties at Ibadan

Year	Treatments (kg N ha-1)	pH $_{H20}$ 1:2		Organic C (g kg-1)		Total N (g kg-1)		Avai. P (mg kg-1)		Exchangeable cations (cmol kg-1) Ca		Mg		K	Na	ECEC (cmol kg-1)	
2013	AC																
	0	6.5	ab	7.6	ab	0.9	c	16	e	2.0	b	3.9	b	0.3	0.2	7.3	c
	60	6.3	ab	4.0	c	1.4	b	19	e	4.5	a	3.3	b	0.3	0.2	14.4	a
	90	6.5	ab	4.4	bc	1.7	ab	81	a	2.7	b	2.4	b	0.3	0.2	5.7	cd
	120	6.7	a	4.5	bc	1.7	ab	33	d	1.2	b	3.0	b	0.3	0.2	5.9	cd
	150	5.5	c	5.9	bc	1.6	ab	41	c	1.9	b	7.5	a	0.3	0.2	10.0	b
	180	6.5	ab	9.5	a	2.0	a	56	b	2.6	b	3.6	b	0.3	0.2	6.7	c
	Checks (60 kg N ha-1)																
	NPK	6.1	b	3.6	c	0.8	c	17	e	1.2	b	3.2	b	0.3	0.2	5.0	d
	CC	6.6	a	7.8	ab	1.3	b	35	d	2.6	b	2.9	b	0.3	0.2	6.1	cd
														ns	ns		
2014	AC																
	0	6.1	a	5.6	d	1.1	bcd	14	bc	2.1	b	1.3	abc	0.3	0.5	4.3	b
	60	6.2	a	9.8	b	1.2	abc	16	bc	2.1	b	1.3	abc	0.3	0.4	4.2	b
	90	6.3	a	8.7	c	1.1	bcd	15	bc	2.3	b	1.3	abc	0.3	0.4	4.4	b
	120	6.3	a	8.2	c	1.0	cd	18	bc	3.5	a	1.8	a	0.4	0.5	6.4	a
	150	6.4	a	10.4	b	1.4	a	28	b	2.3	b	1.1	bc	0.3	0.4	4.1	b
	180	6.4	a	13.8	a	1.3	ab	67	a	2.5	b	1.3	abc	0.4	0.5	4.7	b
	Checks (60 kg N ha-1)																
	NPK	5.6	b	5.8	d	0.9	d	9	c	2.2	b	1.4	ab	0.3	0.5	4.5	b
	CC	6.3	a	10.2	b	1.0	cd	8	c	2.5	b	0.8	c	0.3	0.5	4.1	b
														ns	ns		

ns: not significant, Means with different letters among treatments do not differ significantly at α0.05 by DMRT
AC, Accelerated Compost; CC, Conventional Compost; NPK, 15-15-15

In Ikenne (Table 6), in year 2013, the plot treated with AC at 180 kg N ha-1 gave the highest pH (6.2), which was at par with other treatments, except 60 kgN/ha AC (5.5), NPK (5.3) and control (5.3). The plot with AC at 150 kg N ha-1 recorded the highest mean organic carbon (10.7 g kg-1), which differed not significantly from other AC rates and CC (10.4 g kg-1), but significantly higher than NPK (9.0 g kg-1). The control gave the least organic carbon (7.6 g kg-1).

The no fertiliser treated soil (control) recorded the highest value of N (1.2 g kg-1) which differed not significantly from plots that received AC at 90 kg N ha-1 (1.0 g kg-1), NPK (1.0 g kg-1) and (0.9 g kg-1) while AC at 60 kg N ha-1 gave the least value of 0.4 g kg-1. The 150 kg N ha-1 AC plot had the highest available P (26 mg kg-1), which differed not significantly from AC at 60-120 kg N ha-1 plots (23 - 24 mg kg-1) but significantly higher than others, while NPK gave the lowest value (16 mg kg-1). The plot that received AC at 60 kg N ha-1 had the highest value of Mg (5 cmol kg-1), which differed not significantly from all other plots except the control (0.7 cmol kg-1). In terms of K, CC plot gave the highest significant value (0.7 cmol kg-1) while the plots with AC at 180 kg N ha-1 and the control treatment gave the lowest values of 0.2 cmol kg-1 each. The CC treated soil had the highest value of Na (1.1 cmol kg-1), which differed not significantly from others except AC at 180 kg N ha-1, NPK and the control (0.7 cmol kg-1 each).

In terms of ECEC, plot that received AC at 60 kg N ha-1 gave the highest value (7.9 cmol kg-1) which differed not significantly from other treatments but higher than control (3.3 cmol kg-1).

In 2014, soil treated with AC at 60 kg N ha-1 recorded the highest pH value (5.9), which differed not significantly from soils from plots that received other treatments, except the control (5.2). The CC treated soil resulted into the highest significant organic carbon (10.4 g kg-1) which was at par with soils from other various rates of AC apart from 120 kg N ha-1 (9.4 g kg-1). The NPK gave the least significant value (8.6 g kg-1). The AC at 120 kg N ha-1 plot gave the highest value of total N (1.6 g kg-1) which differed not significantly from CC (1.5 g kg-1), followed by 90 kg N ha-1 AC (1.3 g kg-1) which was at par with others, while the 60 kg N ha-1 AC (1.3 g kg-1) gave the lowest value (1.0 g kg-1). The 150 kg N ha-1 AC plot gave the highest available P (32 mg kg-1), which differed significantly from other treatments. The next treatment in line was 120 kg N ha-1 AC (20 mg kg-1), which differed not significantly from AC rates at 180 kg N ha-1 (19 mg kg-1) and 60 kg N ha-1 (17 mg kg-1), and CC (18 mg kg-1). The NPK treated plot recorded the lowest significant value (7 mg kg-1). There was no significant difference among the treated soils regarding Ca and Mg.

The CC treated plot still had the highest significant K value of 0.2 cmol kg^{-1} and Na (0.4 cmol kg^{-1}) while the differences among others were not significant. The CC plot gave the highest ECEC value (4.1 cmol kg^{-1}), which was at par with AC rates of 180 kg N ha^{-1} (3.9 cmol kg^{-1}) and 150 kg N ha^{-1} (3.9 cmol kg^{-1}) while there was no difference between 60 kgN/ha AC (3.5 cmol kg^{-1}) and NPK (3.5 cmol kg^{-1}).

Table 6. Effects of accelerated compost on post-cropping soil chemical properties at Ikenne

Year	Treatments (kg N ha^{-1})	pH_{H20} 1:2	Organic C (g kg^{-1})	Total N (g kg^{-1})	Avai. P (mg kg^{-1})	Exchangeable cations (cmol kg^{-1}) Ca	Mg	K	Na	ECEC (cmol kg^{-1})
2013	AC									
	0	5.3 b	7.6 c	1.2 a	17 b	1.5	0.7 b	0.2 c	0.7 bc	3.3 b
	60	5.5 b	9.4 ab	0.4 c	23 a	1.3	5.0 a	0.2 c	1.1 a	7.9 a
	90	6.1 a	9.4 ab	1.0 ab	24 a	1.4	4.0 a	0.3 b	0.9 ab	7.0 a
	120	5.9 a	10.1 ab	0.4 d	23 a	1.4	4.0 a	0.3 b	1.0 a	7.1 a
	150	6.2 a	10.7 a	0.6 c	26 a	1.4	3.6 a	0.3 b	0.8 ab	6.4 a
	180	6.2 a	10.5 ab	0.6 c	17 b	1.5	4.2 a	0.2 c	0.7 bc	6.7 a
	Checks (60 kg N ha^{-1})									
	NPK	5.3 b	9.0 b	1.0 ab	16 b	1.2	4.2 a	0.2 c	0.7 bc	6.6 a
	CC	6.0 a	10.4 ab	0.9 abc	18 b	1.4	2.7 a	0.7 a	1.0 a	6.3 a
						ns				
2014	AC									
	0	5.2 c	8.9 bcd	1.2 cd	7 e	2.5	0.7	*	0.3 b	3.7 bc
	60	5.9 a	9.6 abc	1.0 d	17 cd	2.1	1.0	*	0.3 b	3.5 c
	90	5.5 b	10.3 a	1.3 bc	15 d	2.1	1.1	*	0.3 b	3.7 bc
	120	5.7 ab	9.4 bc	1.6 a	20 b	2.4	0.8	0.1 b	0.3 b	3.6 c
	150	5.7 ab	10.1 ab	1.2 cd	32 a	2.3	1.2	0.1 b	0.3 b	3.9 ab
	180	5.7 ab	10.0 ab	1.2 cd	19 bc	2.5	0.9	*	0.3 b	3.9 ab
	Checks (60 kg N ha^{-1})									
	NPK					1.9	1.1	0.1 b	0.3 b	3.5 c
	CC					2.0	1.3	0.2 a	0.4 a	4.1 a
						ns	ns			

*value less than 0.05; ns: not significant, Means with different letters among treatments do not differ significantly at α0.05 by DMRT; AC, Accelerated Compost; CC, Conventional Compost; NPK, 15-15-15

The result of the comparative effects of application rates of AC on maize cropping in Ibadan, the derived savannah zone and in Ikenne, the rain forest in two years are shown in Tables 7. In 2013 trial, the AC gave a significantly (P<0.05) higher mean plant height (154.8 cm), stem diameter (20.0 mm), no. of leaves (11.0) all at 6 WAS and mean biomass yield (19.40 t ha-1) of maize at Ibadan than Ikenne (plant height; 122.3 cm, stem diameter; 16.1 mm, no. of leaves; 9.8, mean biomass yield (17.74 t ha^{-1}). However, there was no significant difference in the effect of the AC on maize performance at the two locations in terms of cob yield (Ibadan; 4.86 t ha^{-1} and Ikenne; 4.66 t ha^{-1}) and grain yield (Ibadan; 3.98 t ha^{-1} and Ikenne; 3.84 t ha^{-1}).

Table 7. Comparative effects of application rates of accelerated compost on the growth at 6 WAS and yield of maize at Ibadan and Ikenne in 2013 and 2014

Year	Parameter	Ibadan[a]	Ikenne[b]	Mean difference	t-value	Correlation coefficient
2013	Plant height (cm)	154.80	122.30	42.60	8.03**	0.55*
	Stem diameter (mm)	20.00	16.10	6.90	16.83**	0.76*
	No. of leaves	11.00	9.80	1.20	8.04**	0.49*
	Biomass yield (t ha^{-1})	19.40	17.74	1.66	0.97**	3.48**
	Cob yield (t ha^{-1})	4.86	4.66	0.20	1.35ns	0.77**
	Grain yield (t ha^{-1})	3.98	3.84	0.13	0.89ns	0.74**
2014	Plant height (cm)	162.60	133.60	29.00	5.35**	0.03ns
	Stem diameter (mm)	20.60	16.80	3.80	15.81**	0.69**
	No. of leaves	11.20	10.10	1.08	5.09**	-0.08ns
	Biomass yield (t ha^{-1})	18.61	18.11	0.50	1.00**	6.33**
	Cob yield (t ha^{-1})	4.11	4.07	0.04	0.98ns	0.96**
	Grain yield (t ha^{-1})	3.44	3.41	0.03	0.96ns	0.97**

* Significant at p<0.05; ** Significant at p<0.01; ns, not significant; WAS, Weeks after sowing ; [a] Derived savannah ; [b] Rain forest

The correlation coefficients were significant (p<0.05) for plant height (r = 0.55), stem diameter (r = 0.76), no. of leaves (r = 0.49), mean biomass yield, (r = 0.97), mean cob yield (r = 0.77) and grain yield (r = 0.74) and the correlation were positive in all cases. The result of the 2014 trial followed the same trend as in 2013. It showed that the AC gave a significantly (P<0.05) higher mean plant height (162.6 cm), stem diameter (20.6

mm), no. of leaves (11.2), all at 6 WAS and mean biomass yield (18.61 t ha^{-1}) of maize at Ibadan compared to Ikenne (plant height; 133.6 cm, stem diameter; 16.8 mm, no. of leaves; 10.1, biomass yield; 18.11 t ha^{-1}). Also, there was no significant difference in the effect of the AC on maize performance at Ibadan and Ikenne with respect to cob yield (Ibadan; 4.11 t ha^{-1} and Ikenne; 4.07 t ha^{-1}) and grain yield (Ibadan; 3.44 t ha^{-1} and Ikenne; 3.41 t ha^{-1}). The correlation also followed the same trend as in 2013. There was high significant ($p<0.05$) correlation coefficients for stem diameter at 6 WAS (r = 0.69), biomass yield (r = 1.00), cob yield (r = 0.96) and grain yield (r = 0.97), and the correlation were positive in all cases.

In terms of the soil chemical properties (Tables 8), in 2013 trial, the t-values were significant ($P<0.05$) for total N, available P, organic carbon and Na. The result showed that significantly higher values were recorded at Ibadan for N (1.7 g kg^{-1}) and P (47 mg kg^{-1}), and at Ikenne for organic carbon (10 g kg^{-1}) and Na (0.9 cmol kg^{-1}). However, in the 2014 trial, significantly higher values were recorded at Ibadan for pH (6.2), K (0.3 cmol kg^{-1}), Mg (1.3 cmol kg^{-1}), Na (0.4 cmol kg^{-1}) and ECEC (4.6 cmol kg^{-1}). The correlation coefficients (r) were not significant for all the parameters in the two years.

Table 8. Comparative effects of application rates of accelerated compost on post-cropping soil chemical properties at Ibadan and Ikenne after cropping in 2013 and 2014

Year	Parameter	Ibadan[a] soil	Ikenne[b] soil	Mean difference	t-value	Correlation coefficient
2013	pH (H_2O) 1:1	6.3	6.0	0.32	1.17ns	-0.25ns
	Organic C (g kg^{-1})	5.7	10.0	-4.36	5.12*	0.68ns
	Total N (g kg^{-1})	1.7	0.6	1.08	8.70*	0.28ns
	P (mg kg^{-1})	47	23	24.20	2.32*	-0.13ns
	Ca^{2+} (cmol kg^{-1})	3.8	1.4	2.38	1.38ns	-0.73ns
	Mg^{2+} (cmol kg^{-1})	4.0	4.2	-0.20	0.19ns	-0.51ns
	K^{+} (cmol kg^{-1})	0.3	0.3	0.04	2.30ns	-0.18ns
	Na^{+} (cmol kg^{-1})	0.2	0.9	-0.70	9.90*	-0.31ns
	ECEC (cmol kg^{-1})	8.5	7.0	1.5	0.32ns	-0.07ns
2014	pH (H_2O) 1:1	6.2	5.6	0.6	7.94**	0.30ns
	Organic C (g kg^{-1})	10.2	9.9	0.3	0.32ns	-0.41ns
	Total N (g kg^{-1})	1.2	1.3	-0.1	2.45ns	-0.49ns
	P (mg kg^{-1})	21.9	17.0	4.9	1.27ns	0.33ns
	Ca^{2+} (cmol kg^{-1})	2.4	2.3	0.2	1.56ns	0.21ns
	Mg^{2+} (cmol kg^{-1})	1.3	1.0	0.3	2.29**	-0.27ns
	K^{+} (cmol kg^{-1})	0.3	0.1	0.3	12.56**	-0.09ns
	Na^{+} (cmol kg^{-1})	0.4	0.3	0.2	8.65**	0.00ns
	ECEC (cmol kg^{-1})	4.6	3.7	0.9	4.60**	0.30ns

*Significant at $p<0.05$; **Significant at $p<0.01$; ns, not significant; WAS, Weeks after sowing; [a] Derived savannah ; [b] Rain forest

Discussion

The accelerated compost at 60 kg N ha^{-1} compared favourably with both conventional compost and NPK, with respect to yield parameters; dry stover weight, dry ear weight, dry cob weight and dry shaft weight, at both locations, in the two years. The average grain yield from AC at 60 kg N ha^{-1} (equivalent of 5 t ha^{-1} compost) comparing favourably with 180 kg N ha^{-1} (equivalent of 15 t ha^{-1} compost) indicated that the preferred rate of application for the accelerated compost for maize production is 60 kg N ha^{-1}. This is in line with the report of Udom et al. (2013), where 5 t ha^{-1} (equivalent of 60 kg N ha^{-1}) poultry manure compared favourably with 10 t ha^{-1} (equivalent of 120 kg N ha^{-1}) in terms of maize grain yield. Furthermore, that the accelerated compost compared favourably with the conventional compost at Ibadan and better at Ikenne showed that its soil amendment ability was not negatively affected by the shortness in the duration of composting. The accelerated compost comparing favourably with NPK at the same N rate in terms of maize grain yield showed that it could be a suitable fertiliser for crop production, in place of mineral fertiliser.

This confirmed the report of Eghball et al. (2004); Abou Ed-magd et al. (2005); Tejada and Gonzalez (2007); Ayeni et al. (2008); AdeOluwa and AyanfeOluwa (2015), that organic materials are known to release soil nutrients slowly and guarantees the longer supply of nutrients. This is because the soil nutrients contained in organic fertilisers would first be utilized by soil microorganisms and the nutrients released gradually as the microorganisms die (Abou Ed-magd et al., 2005; Deenik, 2006). Furthermore, in the yield obtained from residual cropping in 2014 at Ikenne, the 60 kg N ha^{-1} AC (1.14 t ha^{-1}) and 60 kg N ha^{-1} CC (0.90 t ha^{-1}) were more than double and almost double respectively, compared to that of NPK (0.51 t ha^{-1}). Although the yields were generally low, the result re-affirmed the well-known fact that organic fertilisers have better residual yields than mineral NPK fertiliser (Olowoake and Adeoye, 2013; AdeOluwa and AyanfeOluwa, 2015).

In summary, accelerated compost improving the growth and yield parameters suggested a good mineralization of the compost in the soil and subsequent availability of the nutrients for the maize plants. This implies that the reduction in the period of composting of OBD plus accelerated compost did not pose any limitation to its fertiliser potential. This is in agreement with the findings of some other authors (Lindani and Brutsch, 2012; Dehghani et al., 2013) that accelerated compost improved growth and yield of crops.

The accelerated compost treatments improved the soil pH at a level comparable to conventional compost after cropping at 60 kg N ha^{-1} mostly, in the two locations, for the two years. The compost improving the soil pH might be due to its ability to influence retention of cations and reduction of nutrient leaching. Compost could also improve good buffering capacity of soils for hydrogen and aluminium ions in the soil (Bot and Benites, 2005). This is in line with the reports of Valarini et al. (2009); Adeyemo and Agele (2010); Ogunwole et al. (2012); Kayode et al. (2013) that organic fertilisers improved the soil pH.

The accelerated compost treatments (at 60 kg N ha^{-1} and other rates) improved the soil organic carbon comparable to the conventional compost after both the main and residual cropping, at the two locations, in the two years. This is in agreement with the findings of Adeyemo and Agele (2010); Šimon and Czakó (2014). The result showing that some of the organic carbon contained in accelerated compost and conventional compost was stored in the soil, substantiates the submission of Rees (2009), that organic carbon contained in composts will be sequestered, when organic fertiliser is applied. The result further supports the inclusion of composting as an official method for greenhouse gas emission reduction projects (UNFCCC/CCNUCC, 2007). The accelerated compost, by sequestrating more carbon than the conventional compost, even at the same N rate of application (60 kg N ha^{-1}) at both Ibadan and Ikenne, indicated that the reduction in the composting duration for accelerated compost posed no limitation to its ability to sequester carbon.

The soil N was significantly improved by the accelerated compost treatments in Ibadan. This is in accordance with the findings of several authors (Kayode et al., 2013; Šimon and Czakó, 2014; Moyin-Jesu, 2015), where organic fertilisers improved the post cropping soil N. The accelerated compost improved the soil available P better than mineral fertiliser when applied at the same 60 kg N ha^{-1}, at both locations. The increase in soil available P due to the addition of accelerated compost is in line with the reports of Eghball et al. (2004), where organic fertiliser applications increased the soil available P in the post cropping soil analysis. Soil nutrients improvement by accelerated compost suggested good mineralization of the compost in the soils. The compost treatments improving the soil ECEC could be attributed to organic matter having negatively charged sites which attract and hold positively charged particles. This result agrees with the reports of several authors that compost application improved the soil ECEC and soil fertility generally (Hansen and Strawn, 2003).

Although, higher values were recorded for most of the post cropping soil chemical properties measured, at Ibadan than Ikenne, in the two years, only the case of N and P in 2013 stood out. Others could be explained by the differences in the initial soil values. Again, the improvement in the post cropping soil properties by accelerated compost suggests its ability to resist nutrient leaching and also conserve nitrogen against volatilization, which is a hallmark of organic fertilisers. Hence, the accelerated compost could compare favourably with the conventional compost in spite of its shortness in the time of maturity.

The application of accelerated compost in the derived savannah resulted into higher plant height, stem diameter, number of leaves and biomass yield than in rain forest, in both 2013 and 2014 trials. This consistency of better growth and biomass yield in the derived savannah than rain forest suggests that accelerated compost could have the potential to support biomass production better in the derived savannah than the rain forest. This is probably because more nitrogen and phosphorus were available from the compost treatments for the maize plant in the derived savannah, than rain forest. Khan et al. (2014) had reported that N and P improved the vegetative growth of maize plant as they were found significant on fresh weight of maize plants. Some other studies have shown positive correlation between fresh fodder yield and nitrogen level (Masood et al., 2011; El Zubair et al., 2015).

This result suggests the effect of the different weather conditions characterizing the different ecologies, especially the higher amount of rainfall in the rainforest zone and the tendency for higher temperature in the derived savannah zone (NASA-Power, 2016; Sowunmi and Akintola, 2010). The rainfall data obtained for Ibadan; derived savannah (380 and 515 mm) and Ikenne; rain forest (570 and 735 mm) in 2013 and 2014, respectively for the period of the field trial (May-July) confirmed that the rainforest zone received much more rainfall than the derived savannah.

Benbi and Khosa (2014) reported that the rate of decomposition of organic matter vis-à-vis compost could be slowed down during periods of water saturation leading to poor aeration. This is because most soil organisms require oxygen for the decomposition activities. Hence, the insufficient oxygen in the soil would slow down the rate of mineralization as these organisms become inactive or even die. The probable higher rate of decomposition of the compost in the derived savannah could also be traced to the higher temperature that was observed in the ecology during the trial. It has been widely reported that organic matter decomposition correlated positively with temperature (Joshi et al., 2005; Reich et al., 2006; van Opheusden et al., 2012; Brevik, 2013). However, this higher growth rate and biomass yield of maize recorded from accelerated compost in the derived savannah, compared to rainforest zone, did not translate into significant higher grain yield as there was no significant difference in the mean cob yield and grain yield obtained from the two locations, both in 2013 and 2014 trials.

The correlation analysis showed that the performance of the accelerated compost followed the same pattern across the six levels of accelerated compost, in the two locations, as revealed by all the growth and yield parameters considered in 2013 as well as stem diameter, biomass yield, cob yield and grain yield in 2014. This suggests that the response of maize plants to each of the different levels of accelerated compost used for this study followed the same trend in the two locations. This is in line with the report of Ayoola and Adeniyan (2006) who reported that maize grain yield followed the same trend in both derived savannah and rain forest for two cropping seasons.

Although, higher values were recorded for most of the post cropping soil chemical properties measured in the derived savannah than rainforest in the two years of field trials, only the case of N and P in the 2013 trial stood out. Others were traceable to the differences in the initial soil values. The higher values of N and P recorded in the derived savannah confirmed a higher level of mineralisation of the applied compost in the ecological zone than rainforest, and corroborate the higher vegetative growth and biomass yield in the zone.

Conclusion

In conclusion, the result revealed that the performance of the accelerated compost was not significantly influenced by the locations of this trial in terms of maize grain yield. The performance of the accelerated compost in the derived savannah and in the rain forest zone followed the same pattern across the six levels of accelerated compost, and with no significant difference between the two locations in terms of the grain yield. However, the biomass production was significantly better in the derived savannah ecology.

The result of this study also showed that accelerated compost has the potential to support the production of maize in spite of the shortness in duration to maturity. It is as adequate as mineral fertiliser (NPK 15-15-15) and conventional compost as revealed by maize grain yield at both Ibadan and Ikenne in the derived savannah and rain forest agro ecologies, respectively. The optimal rate of application of accelerated compost for maize at both Ibadan and Ikenne was 60 kg N ha^{-1}. It was also found out that accelerated compost improved the soil chemical properties, than the conventional compost.

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Eurasian Journal of Soil Science 2021, 10(2), 123- 131

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

Partitioning of heavy metals in different particle-size fractions of soils from former mining and smelting locations in Austria

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Article Info

Received : 17.07.2020
Accepted : 26.11.2020
Available online : 07.12.2020

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Abstract

Austrian soils from mainly historical mining and smelting sites were separated into four particle size fractions (coarse sand, fine sand, silt and clay) to distinguish the possible origins and pathways of heavy metals. Each fraction was extracted with *aqua regia* to determine the pseudo-total content and with $CaCl_2$ to determine the available content of metals. The soil mineralogical composition of the < 2000 µm fraction was determined by X-ray diffraction (XRD). In general, the concentration of heavy metals and metalloids increased as soil particle size decreased. Based on the correlations of concentrations vs. the log of the mean particle size, obtained from each fraction the presence of unweathered allochthonous minerals were especially present in samples from locations at Rabenstein for most trace elements, at Arzwaldgraben for Cd, Co, Mn and Pb, at Johnsbach for Cd, Co, Mn, Pb and Zn and at Pilgersdorf for Cr. The opposite trend was found for the samples of the industrial area of Arnoldstein, Zeltweg and Hinterlobming suggesting that their metal load was derived from the discharge of effluents or from weathered phases.

Keywords: Heavy metals, minerals, soil particle size fractions, separation.

Introduction

Heavy metals in soils pose a major challenge for humanity due to their toxic effects on living things. They can occur in soil in various forms; dissolved in soil solution, adsorbed to organic and inorganic soil exchangers, trapped in mineral constituents, precipitated in conjunction with other soil constituents, incorporated into living soil organisms (Adriano, 1986; Bradl, 2004).

The size of soil particles is one of the main parameters which play an important role in mobility and bioavailability of heavy metals. Finer soil particles or soil colloids (with a diameter less than 2 µm) have the ability to accumulate higher concentrations of heavy metals due to the high content of secondary minerals like clay minerals, Fe/Mn/Al oxides and hydroxides, and carbonates and organic matter, which can efficiently adsorb heavy metals due to their high specific surface areas (Mandzhieva et al., 2014; Yao et al., 2015). The inorganic colloids can adsorb heavy metals via coprecipitation, adsorption, surface complex formation, ion exchange and penetration of the crystal lattice (Chao and Theobald, 1976). Organic matter possesses high affinity for heavy metals, resulting from complexation of various functional groups (-OH, -COOH, etc.) (Bradl, 2004). The silt fraction (2-63 µm) mainly contains secondary mineral phases, like clay minerals, iron and aluminum oxides, allophanes, mono- and polysilicic acids, and organic and organomineral compounds. Sand particles with a diameter higher than 63 µm are largely composed of quartz (predominantly) feldspars and heavy minerals like amphiboles (Mandzhieva et al., 2014). The sand fraction

: https://doi.org/10.18393/ejss.837139
: http://ejss.fesss.org/10.18393/ejss.837139
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

is a weak adsorbent for heavy metals as its specific surface area is much lower. In general, metal inputs transported via soil solution are adsorbed at fine soil particles (Zhang et al., 2013; Gong et al., 2014), while the contents of metals from mineral abrasion show no clear dependence from soil particle size (Sager and Belocky, 1990; Ajmone-Marsan et al., 2008). In case of chemical weathering the concentrations of trace elements are thus linear versus the negative logarithm of the mean grain size diameter (Sager and Belocky, 1990). This is not the case, however, if trace elements are present in lower soluble minerals, or if transportation effects in rivers change the skewness of this distribution. In adjacent soils, metals from geogenic sources, are usually present in smaller amounts than in the corresponding ores. In general, the solubility of metals is determined by their incorporation into minerals or adsorption at their surfaces (Adriano, 1986).

Soils in the vicinity of mining and smelting industries contain metal-bearing deposited particulates. Whereas heavy minerals in the mine tailing samples investigated, made 4% of the fraction < 2mm, they contained 24% of the metal loads. Metal-bearing phases can be investigated in detail by automated scanning electron microscopy equipped with energy dispersion spectroscopy, to avoid bias in searching and identifying metal bearing phases. Pre-selected sample areas can be further imaged by use of an electron probe micro-analyzer. In mining and smelting areas, the majority of contaminations is generally concentrated in the topsoil layer. Geogenic particles originate from the geological environment or from mechanical processing of the ore, like pyrite FeS_2, chalcopyrite $CuFeS_2$, or enargite Cu_3AsS_4. The sulphides usually exhibit well-developed alteration rims composed of metal-bearing Fe-oxides (Tuhý et al., 2020). Mine tailings present an important source of heavy metals like Cu, Pb, Zn, Cd, Cr and As (Chung et al., 2005, Lim et al., 2008). Under acid conditions, heavy metals become mobile and are easily leached out of the tailing deposits ("Acid mine drainage") (Pandey et al., 2007). In mine tailings from a historic zinc-mine within freely draining cambisols, in the clay fraction (< 2 µm) mainly quartz, mica and kaolinite were identified by X-ray diffraction. Heavier density fractions were separated by tetrabromoethane (density > 2.7 g/cm^3) and further by diodomethane (density > 3.3 g/cm^3), which contained goethite, hematite, rutile, and barite as main minerals, as well as the metalliferous minerals smithsonite ($ZnCO_3$) and leadhillite ($Pb_4SO_4(CO_3)_2(OH)_2$) as weathering products. Smithsonite and barite tended to increase in coarser fractions, whereas leadhillite and rutile were enhanced in fine size fractions. No crystalline phases were found for Cu and Cd because they were associated with organics or other minerals (Mattigod et al., 1986).

In Austria due to construction works, large amounts of excavated soils and subsoils do not meet the requirements for recycling (due to exceeding of permitted values for heavy metals) and have to be landfilled (Jelecevic et al., 2018, 2019). Although the Federal Management Waste allows in some cases higher values for geogenic heavy metals this generalized expert opinion does not provide a method how the possible origin of heavy metals can be determined. It is therefore assumed that a certain amount of excavated material is not adequately classified and is disposed of in landfills (Jelecevic et al., 2018). The aim of this work, was to separate four particle size fractions; coarse sand/2000-200 µm, fine sand/200-63 µm, silt/63-2 µm and clay/< 2 µm from soils mainly at historical mining and smelting sites in Austria and to determine the total and available content of these fractions which should help to distinguish the possible origins and the toxic potential of each metal.

Material and Methods

Materials

In this study eight soil samples (seven with high metal levels) were investigated (Figure 1). The Styrian soils; Arzwaldgraben (Arz), Johnsbach (Joh) and Rabenstein (Rab) are from former mining and mineral processing sites while the others (Hinterlombing (Hin), Kraubath (Kra) and Zeltweg (Zel)) are grassland soils without known information about their industrial use in the past. The soil samples Arnoldstein - A(C) from Carinthia and Pilgersdorf – P (C) from Burgenland were used as control soils for an anthorpogenic respectively geogenic metal contamination. The samples were taken with a geological drill (so called "Pürckhauer") and the upper 25 cm were used for subsequent studies. The main characteristics of the sampled soils are presented in Table 1.

Methods

X-ray diffraction

The mineralogical compositions of the samples were determined by X-ray diffraction (XRD) at the Graz University of Technology (Panalytical XPert Pro, step size 0.001° 2 Theta, Kα = 1.78901 Å, 409 mA, 40 kV). Rietveld refinement for phase quantification was conducted using the automated mode, which includes refinement of the scale factors, the background, the zero shift, the lattice parameters, and the peak shape parameter W.

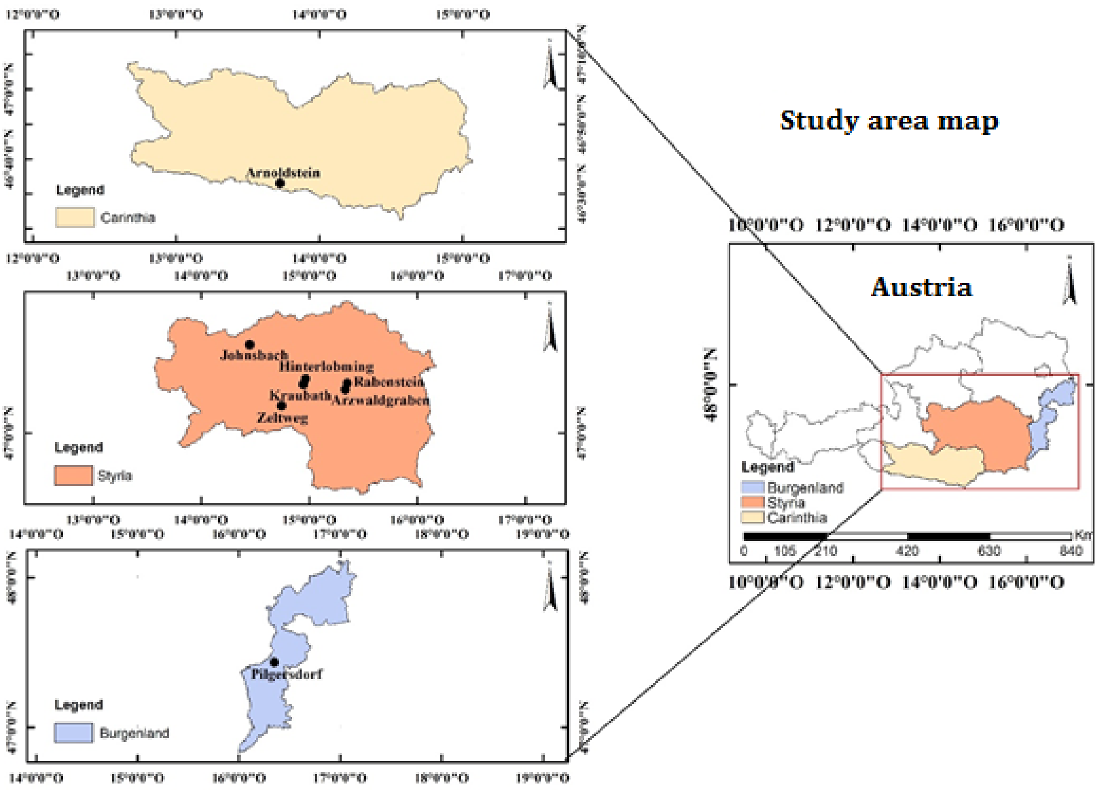

Figure 1. Sampling map of the selected area

Table 1. List of soil samples used in this study with their characteristics

Sample	Region and Geographic coordinates	Present Use	Past Use	Substrate	Soil type	Soil texture	pH	Total Organic Carbon
Arz (Jelecevic et al., 2019)	Styria 47° 14.261´ N 15° 16.798´ E	Grassland	Pb-Zn mining	Alluvial fan	Gley	Silty loam	7.4	5.4%
Hin	Styria 47° 17.556´ N 15° 02.300´E	Grassland	none	Alluvial fan	Alluvial soil	Sandy loam	6.8	3.7%
Joh (Jelecevic et al., 2019)	Styria 47° 31.723´ N 14° 36.857´ E	Grassland	Cu-As mining	Alluvial fan	Gley	Sandy loam	5.9	14%
Kra (Jelecevic et al., 2019)	Styria 47° 18.034´ N 14° 55.955´ E	Grassland and farmland in crop rotation	none	Mica shist	Cambisol	Loam	7.3	4.6%
Rab (Jelecevic et al., 2019)	Styria 47° 15.023´ N 15° 18.450´ E	Grassland	Pb-Zn mining and processing	Phyllite	Cambisol	Loam	6.9	2.8%
Zel (Jelecevic et al., 2019)	Styria 47° 11.575´ N 14° 43.325´ E	Grassland	Not known	Alluvial fan	Cambisol	Silty loam	6.2	4.1%
A (C) (Kuffner et al., 2008)	Carinthia Not given	Not known	Pb-Zn mining and processing	Not known	Leptosol	Silty loam	6.6	1.3% *
P (C) (Redlschlag in Wenzel et al., 2003)*	Burgenland Not given	Serpentine quarry	Serpentine quarry	Serpentine	Leptosol	Silty loam	7.2	2.5% *

* In Kuffner et al. (2018) and Wenzel et al. (2003) described as Organic Carbon

Soil partitioning

The soil samples were passed through a 2-mm sieve and then weighed into a 100 mL plastic beaker (about 30 g dry matter) and mixed with about 70 mL distilled water. The beaker was then placed on a lift table under the ultrasound probe. Thereafter the disaggregated soil suspension was passed through a 200 µm and then through a 63 µm sieve to separate the fractions 200 µm – 2 mm (coarse sand) and 63 µm – 200 µm (fine sand). These fractions were thoroughly rinsed with deionized water, transferred into glass beakers and dried in the oven at 60 °C to constant weight. Further separation of the fraction < 63 µm was carried out by sedimentation in a centrifuge.

The sedimentation time of a given particle size in a rotating fluid over a given distance was calculated by the following formula:

$$t = \frac{63.0 * 10^8 * \eta * \log\frac{R}{S}}{rpm^2 * d^2 * (p - p_{fl})}$$

t	:	centrifugation time [min]	rpm	:	revolutions per minute 600
η	:	Liquid viscosity [0.001 g s^{-1}]	d	:	analiscopic particle diameter [2 µm]
R	:	outer radius of the rotating fluid [13.3 cm]	ρ	:	Density of the solid [2.61 g cm^{-3}]
S	:	Inner radius of the rotating fluid [9.3 cm]	ρ_{fl}	:	density of liquid [1 g cm^{-3}]

According to the given equation, the sedimentation time of particles < 63 µm was reached in t = 4.22 min. This was measured from the start time of the centrifuge until the beginning of the braking phase. If the acceleration phase of the centrifuge is taken into account, the optimal running time at 1000 rpm is 2 minutes (Stemmer et al., 1998). After that the suspension containing the fraction < 63 µm was transferred to four 250 mL centrifuge beakers, leveled to 10 cm level and tared to at least 0.1 g accuracy in a swing-bucket rotor in the centrifuge. After centrifugation at 600 rpm for 4.22 min, the cups were carefully removed from the rotor and the supernatant suspension (fraction < 2 µm) decanted into a 2 L beaker and put into an oven at 80°C and finally at 105 °C until complete dryness. The residue (63 - 2 µm) of the four cups was resuspended and transferred to a centrifuge cup. It was refilled to cm sinking distance and tared with a complementary cup. The suspension was well homogenized and centrifuged against the balance weight to the above conditions. This process for purifying the silt fraction was repeated a total 3 times. The now cleaned silt pellet was transferred to a beaker and dried in a drying oven at 105 °C to constant weight.

All soil fractions were treated with aqua regia (for the determination of the pseudo-total metal content) and $CaCl_2$ (for the determination of available metals) in a soil/solution ratio 1 : 10 w/v. After that the metal concentrations in all samples were analyzed with ICP-MS (Inductively coupled plasma mass spectrometry, Elan 9000 DRCe, Perkin Elmer). For each sample two digestions were made (3 g per 250 mL). Two different dilutions of each digested samples were made to assure that the resulting concentrations were in the calibration range. Each of these samples was analyzed three times. The mean values of these three runs were calculated internally by the Elan software. The mean values of the runs of those solutions which were in the calibration range were used to calculate a new mean value. This is the value which is given in the results. The values of the dilutions which were not in the calibration range were discarded.

All experimental results including the mean values were analyzed by using Microsoft Excel 2013 and SigmaPlot 14.0. Correlations coefficient of mean particle size and heavy metal concentrations were performed to determine the statistical relationship of different soil fractions and the Grubbs test to identify the outliers from the selected locations.

Results and Discussion

The X-ray diffraction patterns of the investigated samples are displayed in Table 2. Most samples are mainly composed of quartz, muscovite and feldspars. Only the sample from Pilgersdorf is dominated by serpentine. Metal bearing phases could not be identified, except PbO at Zeltweg. This can be explained by the detection limit of XRD which is within the range of 2 wt%.

Table 2. Mineralogical composition of selected soils in wt%

Mineral	Soil (wt %)							
	Arz	Hin	Joh	Kra	Rab	Zel	P (C)	A (C)
Quartz, α-SiO_2	31	43	39	40	25	28	18	45
Muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$	30	5	39	14	51	27	<1	30
Albite, $NaAlSi_3O_8$	9	41	12	31	15	23	-	-
Anorthite, $CaAl_2Si_2O_8$	-	-	-	-	-	1	7	12
Kalifeldspar, (Microcline), $KAlSi_3O_8$	-	-	1	9	-	-	-	-
Chlorite, $(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$	27	9	9	6	6	21	34	12
Rutile, α-TiO_2	2	-	-	-	4	-	-	-
Calcite, $CaCO_3$	2	-	-	-	-	-	-	-
Litharge, PbO	-	-	-	-	-	1	-	-
Serpentine Mg_3 [$Si_2O_5(OH_4)$]	-	-	-	-	-	-	41	-
Dolomite CaMg $(CO_3)_2$	-	1	-	-	-	-	-	1

Grubbs tests reveal that Mn is the only element which does not show outliers in individual particle size fractions. All elements show positive outliers within the particle size fractions. As and Pb distributions show several outliers in all particle size fractions above 2 µm. The number of outliers does not vary significantly between different particle size fractions (Table 3).

Table 3. Grubbs test, G statistic and p-value for the most extreme heavy metals

Fraction	Unit	Heavy metals								
		Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb
2000-200 µm	Mean	241.4	1243.8	30.6	244.2	310.8	394.2	22.6	3.9	954.3
	Std.Dev.	570.1	559.1	20.5	573.8	772.9	514.2	42.6	8.6	2065.4
	Ex. value	1651.0	1990.0	68.6	1664.0	2223.0	1548.5	124.0	25.0	5996.4
	G value	2.47	1.33	1.69	2.47	2.47	2.45	2.38	2.46	2.47
	$P_{2 \text{ tail of G}}$	0.0001	0.1679	0.2120	< 0.0001	<0.0001	<0.0001	0.0001	< 0.0001	< 0.0001
	n. outliers	1	0	0	1	1	1	2	1	2
200-63 µm	Mean	194.1	1193.6	32.2	285.2	413.0	492.2	24.3	5.8	1415.5
	Std.Dev.	406.4	414.1	30.0	652.3	1025.4	765.2	41.7	13.2	3349.8
	Ex. value	1197.0	732.0	171.9	1898.0	2950.0	2295.7	117.0	38.3	9668.9
	G value	2.47	1.11	2.45	2.47	2.47	2.36	2.22	2.47	2.46
	$P_{2 \text{ tail of G}}$	<0.0001	0.2628	< 0.0001	< 0.0001	<0.0001	0.0003	0.0025	< 0.0001	< 0.0001
	n. outliers	1	0	1	2	1	1	2	1	3
63-2 µm	Mean	162.1	1128.3	32.2	256.9	428.5	567.7	28.9	6.4	1609.2
	Std.Dev.	290.1	342.2	30.0	564.1	1052.0	925.1	49.3	15.2	3855.6
	Ex. value	873.0	1620.0	104.3	1651.0	3031.0	2769.0	138.0	43.8	11108.4
	G value	2.45	1.44	2.40	2.47	2.47	2.38	2.21	2.47	2.46
	$P_{2 \text{ tail of G}}$	<0.0001	0.1313	< 0.0001	< 0.0001	<0.0001	0.0001	0.0027	< 0.0001	< 0.0001
	n. outliers	1	0	1	2	1	1	4	1	2
< 2 µm	Mean	225.4	1337.5	46.4	380.7	682.0	721.5	48.9	7.7	2012.6
	Std.Dev.	349.0	369.5	56.7	825.7	1711.0	1155.3	79.8	19.2	4966.1
	Ex. value	1060.0	816.0	185.6	2417.0	4916.0	3512.4	232.0	55.2	14282.8
	G value	2.39	1.52	2.46	2.47	2.47	2.42	2.29	2.47	2.47
	$P_{2 \text{ tail of G}}$	<0.0001	0.1054	< 0.0001	< 0.0001	<0.0001	< 0.0001	0.0009	< 0.0001	< 0.0001
	n. outliers	2	0	1	2	1	1	1	1	1

Note: the value of 2.1266 is the $G_{\text{critical value}}$ (0.05) based on the numbers of samples (8). The test has been repeated several times till the identifications of outlier number. The G value was calculated from the most extreme value of all selected locations.

In most of the soils the concentration of heavy metals and metalloids increased as soil particle size decreased (Table 4). Correlations of obtained concentrations versus the log means of the particle size fractions indicate the presence of other phases than sorbed on particle surfaces; in other words, the presence of unweathered allochthonous minerals. This is the case in Arzwaldgraben for Cd, Co, Mn, and Pb, in case of Hinterlobming for some Pb, in case of Kraubath for Cd, in case of Johnsbach for Cd, Co, Mn, Pb and Zn in case of Pilgersdorf for Cr and some As, Cd, Co, Mn, Ni and Pb, in case of Rabenstein for almost all trace elements investigated (except Cu) and in case of Zeltweg just for some Mn and Cd. This trend was also found by many researchers (Sager and Belocky, 1991; Chopin and Alloway, 2007; Liu et al., 2018). To the contrary, the control soil in the industrial area of Arnoldstein had received their metal loads exclusively from effluents or from weathered phases, where the metal concentrations were significantly higher in the finer soil particles (Figure 2). The general increase of metal concentration with decreasing grain size is most pronounced for As and less pronounced for Cu and Cd in our study. However, differences between the soil samples are more significant than differences between the elements.

It is suggested that heavy metals and metalloids, which are enriched in the finer fractions, entered the soil via aqueous solutions and precipitated as fine-grained minerals in the pores, or were adsorbed at the mineral surfaces. The samples from Johnsbach and Arzwaldgraben are gley soils, i.e. groundwater influence played an important role in pedogenesis. However, as only the upper 25 cm of these soils were used for the experiments, it is suggested that the metal-bearing aqueous solutions infiltrated the soil rather from the surface than from the groundwater. Interestingly the two gley samples are the only ones, in which Mn concentrations were highest in the coarsest fraction. Mn is a redox-sensitive element, of which the oxidized state Mn (IV) is less mobile than its reduced state Mn (II). Gley-reducing conditions in the lower B_r horizon mobilize Mn and transport it into the upper oxidizing B_o horizon, where it gets oxidized and precipitates. However, if this process would take place in topsoil samples, Mn should be enriched in finer particle size fractions.

Table 4. Metal total concentrations (mg kg^{-1}) in different particle sizes and the correlation of obtained concentrations versus the log means of particle sizes

Location	Heavy metals concentration (mg kg^{-1})								
	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb
Arz 2000-200 µm	78.3	1719	32.4	59.2	40.3	618.5	<0.3	3.20	1020.0
Arz 200-63 µm	78.5	1373	28.3	65.9	50.1	679.2	<0.3	3.31	937.2
Arz 63-2 µm	97.0	1607	34.5	72.1	65.0	777.7	<0.3	3.75	1103.7
Arz < 2 µm	126.8	1092	29.6	76.3	60.6	804.8	<0.3	2.38	878.4
correlation coeff. (r)	-0.96	0.85	0.23	-0.96	-0.79	-0.93	-	0.60	0.49
Hin 2000-200 µm	63.4	657	12.8	62.2	19.4	50.7	0.3	0.03	13.9
Hin 200-63 µm	102.1	732	16.5	117.4	22.5	64.8	1.2	0.13	9.3
Hin 63-2 µm	132.2	1017	19.2	126.7	29.5	90.2	1.3	0.14	12.5
Hin < 2 µm	304.5	1790	37.5	256.3	67.2	187.8	12.5	0.42	30.6
correlation coeff. (r)	-0.97	-0.96	-0.96	-0.98	´-0.94	-0.96	-0.90	-0.97	-0.81
Joh 2000-200 µm	<0.4	1990	58.2	28.7	2223	349	124	0.99	169
Joh 200-63 µm	1.2	1194	30.8	27.8	2950	107	117	1.54	130
Joh 63-2 µm	2.0	689	26.5	32.9	3031	110	138	0.46	109
Joh < 2 µm	8.5	816	23.8	43.1	4916	140	232	< 0.05	163
correlation coeff. (r)	-0.94	0.81	0.82	-0.93	-0.97	0.63	-0.90	0.77	0.02
Kra 2000-200 µm	20.4	705	7.6	18.5	11.5	43.7	< 0.3	0.14	17.0
Kra 200-63 µm	39.4	907	11.3	37.6	29.8	107	< 0.3	0.63	25.3
Kra 63-2 µm	36.4	801	10.9	32.7	24.8	106	< 0.3	0.19	22.5
Kra < 2 µm	65.3	1249	18.2	53.4	45.3	205	0.7	0.35	42.5
correlation coeff. (r)	-0.97	-0.91	-0.97	-0.94	-0.94	-0.98	-0.87	-0.16	-0.94
Rab 2000-200 µm	43.1	1951	34.8	51.4	56.6	422	6.2	1.67	339
Rab 200-63 µm	36.3	1966	33.8	52.1	65.2	512	6.4	2.15	422
Rab 63-2 µm	35.1	1620	25.9	46.9	59.5	492	4.4	2.04	359
Rab < 2 µm	49.1	1495	23.8	56.6	67.9	602	5.7	1.63	390
correlation coeff. (r)	-0.47	0.90	0.91	-0.50	-0.78	-0.95	0.35	0.11	-0.37
Zel 2000-200 µm	46.5	1104	16.7	35.8	37.4	88.2	12.0	0.36	76.2
Zel 200-63 µm	60.1	969	18.3	46.0	43.2	113.7	12.9	0.24	119.0
Zel 63-2 µm	77.6	1150	20.6	54.2	56.3	140.0	21.6	0.45	149.6
Zel < 2 µm	127.8	1727	34.3	96.3	99.7	238.6	54.0	0.93	298.8
correlation coeff. (r)	-0.99	-0.86	-0.95	-0.97	-0.96	-0.98	-0.94	-0.88	-0.98
A (C) 2000-200 µm	28.4	786	14.0	33.9	65.2	1548.5	35.2	25.00	5996.4
A (C) 200-63 µm	38.3	868	14.5	36.5	100.2	2295.7	54.8	38.31	9668.9
A (C) 63-2 µm	43.8	950	15.3	39.0	121.6	2769.0	64.4	43.83	11108.4
A (C) < 2 µm	61.2	1085	18.2	46.7	141.2	3512.4	82.2	55.21	14282.8
correlation coeff. (r)	-0.99	-0.99	-0.97	-0.99	-0.96	-0.99	-0.99	-0.98	-0.98
P (C) 2000-200 µm	1651	1039	68.6	1664	32.8	33.0	2.3	0.14	2.8
P (C) 200-63 µm	1197	1540	171.9	1898	42.6	58.0	1.2	0.17	12.4
P (C) 63-2 µm	873	1192	104.3	1651	40.3	56.5	0.9	<0.05	9.3
P (C) < 2 µm	1060	1766	185.6	2417	57.7	81.4	3.7	0.30	14.8
correlation coeff. (r)	0.71	-0.80	-0.72	-0.84	-0.96	-0.97	-0.53	-0.60	-0.84

Some elements in certain soil samples, however, are enriched in the coarse fractions. For example, in the soil of Pilgersdorf, where we had assumed geogenic enrichments, this is the case for Cr. This soil had developed upon serpentinite, a rock type in which Cr is in most cases present as chromite (Vollprecht et al., 2019), which is highly resistant against chemical and physical weathering due to its low solubility and high hardness, respectively. Consequently, chromite grains survive during pedogenesis and remain present in the coarse fraction of the soil. Ni is enriched in ultramafic rocks and soils in olivine as well as in serpentine minerals (lizardite, antogorite, chrysotile) (Sager, 2019).

Mn and Co contents dominate the sand fractions of the soil at Johnsbach, and to a lesser extent, at Arzwaldgraben and Rabenstein. All these soils have developed on substrates which contain sulfide ore deposits. Weathering of sulfide ores may lead to the precipitation of secondary minerals, like Co sulfates or arsenates. Enrichment of Co in the coarse fraction, however, suggests that a significant proportion of Co is still present in weathering relicts, e.g. as substitutes in silicates or oxides. The same might be valid for Zn at Johnsbach and for As at Rabenstein.

To the contrary, emissions from modern steel works include spherulic micro-particles of iron oxides, fly ash particles from the combustion of fossil fuels, whereas irregular and angular particles of Fe-oxides are associated with abrasions of combustion cylinders, pads and disc brakes of vehicles. Whereas spherical particles originate from the smelting and flue gas cleaning processes, angular particles have either geogenic origins or they are windblown from waste disposal sites. Sulphides from ores and mine tailings often exhibit weathering rims in contrast to smelter-derived high-temperature sulphides. Mixed Fe-oxides are weathering features (Ettler and Johan, 2014).

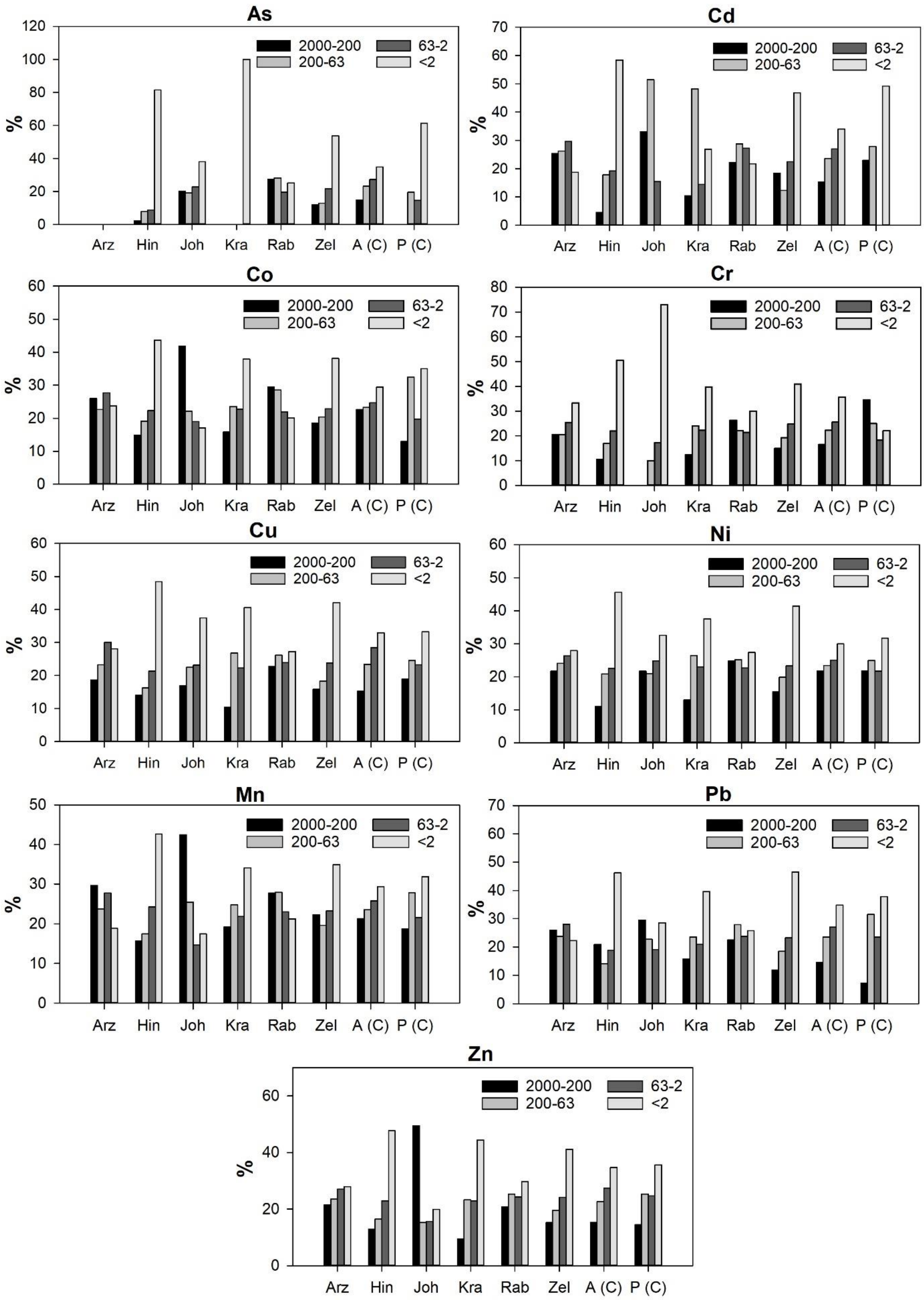

Figure 2. Distribution of heavy metals and metalloids in different particle grain sizes of selected soils

Grain-size fractionation of calcareous fluvisols by shaking in water led to lower percentage of the clay fraction versus ultrasonic or chemical pretreatment with dilute HCl (decarbonisation) and H_2O_2 (oxidation of organics). Ultrasonic vibrations broke the associations of fine minerals with organic matter down to 0.2-2.0 µm size and transferred C and N from coarser to the clay fraction. The phyllosilicates were concentrated in the clay fraction, and the carbonates in the silt and sand, but were broken by ultrasonic treatment. After densimetric fractionation with tetrabromoethane-polyvinylpyrolidone-ethanol, Cd from polluted samples dissolved at about 10%, but other metals negligibly (Ducaroir et al., 1990).

Extracts with $CaCl_2$

Though the water-soluble fractions had been lost during the sample preparation step, extraction with $CaCl_2$ –solution might give an indication of exchangeable respectively weathered phases (Table 5). The proportion of exchangeable over aqua regia extractable fractions did not depend on the particle size fractions. Exchangeable Mn could be an indicator for carbonaceous- bound Mn, because reaction of $MnCO_3$ with $CaCl_2$ to yield soluble $MnCl_2$ and $CaCO_3$ seems feasible. In 0.5 M $MgCl_2$-extract 1:10, which is comparable to the $CaCl_2$-extract data presented in, about 12% of total Mn was found exchangeable in a calcareous cambisol, like in the current sample from Johnsbach. In a podsol, an acid cambisol, and a calcareous leptosol profile, about 5% of Mn were exchangeable, like current samples from Arzwaldgraben, Hinterlobming and Arnoldstein (Sager and Mutsch, 2007). Precipitation of Fe and Mn from oxygenated water at circumneutral pH is known to produce ferric oxide plus manganous carbonate (Mettler et al., 2001). Amounts at 1% of exchangeable Mn or less indicate non-weathered Mn-containing phases. Similarly, about 3% of exchangeable Zn at Johnsbach and 3% of exchangeable Cd in the Arnoldstein-samples indicate rather high weathering of Zn/Cd minerals or additional Zn respectively Cd input, because exchangeable Zn in non-contaminated forest soils is expectable at 1%, and in podsoils at 2% (Sager and Mutsch, 2007). In case of Cu, exchangeable < 0.5-1% are typical for ambient levels. At non-contaminated sites, exchangeable Pb, Cr, Ni, and Co were negligible, but at Hinterlobming and Johnsbach, some % of Ni and Co were detected. At Pilgersdorf, exchangeables were negligible, except for Pb. Thus, the proportion of exchangeables indicates the weathering status of the given sample.

Table 5. Metals soluble in $CaCl_2$ extract of sand (2000-63) and silt-clay (< 63) fractions

Location	Heavy metals concentration (mg kg^{-1})							
	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Arz 2000-63 µm	0.00	77.92	0.00	0.13	0.17	0.53	0.00	0.07
Arz < 63 µm	0.00	84.93	0.00	0.10	0.20	0.51	0.00	0.07
Hin 2000-63 µm	0.00	64.23	0.42	1.51	0.00	0.45	0.00	0.05
Hin < 63 µm	0.00	46.82	0.39	2.15	0.04	0.73	0.00	0.05
Joh 2000-63 µm	0.00	130.41	1.15	0.73	16.28	3.03	0.00	0.03
Joh < 63 µm	0.00	78.21	0.51	0.86	13.47	3.24	0.00	0.02
Kra 2000-63 µm	0.00	9.24	0.00	0.05	0.00	0.11	0.00	0.03
Kra < 63 µm	0.00	10.15	0.00	0.06	0.00	0.12	0.00	0.02
Rab 2000-63 µm	0.00	40.99	0.00	0.21	0.00	2.30	0.00	0.00
Rab < 63 µm	0.00	45.29	0.03	0.25	0.07	3.64	0.00	0.06
Zel 2000-63 µm	0.00	8.19	0.00	0.05	0.00	0.11	0.00	0.05
Zel < 63 µm	0.00	11.84	0.00	0.06	0.04	0.12	0.00	0.04
A (C) 2000-63 µm	0.00	55.83	0.00	0.04	0.34	3.08	1.22	5.81
A (C) < 63 µm	0.00	54.95	0.00	0.07	0.77	2.99	1.16	7.87
P (C) 2000-63 µm	0.17	1.71	0.00	1.78	0.00	0.12	0.00	0.08
P (C) < 63 µm	0.10	1.44	0.00	1.98	0.00	0.12	0.00	0.06

Conclusion

This study demonstrates that the heavy metal distribution between different particle size fractions of Austrian soils is a tool to identify the sources of the pollution. Four out of seven investigated soil samples show an increase in heavy metal concentration with increasing particle size suggesting their incorporation into primary mineral phases which survived weathering. The other three samples show a decrease in heavy metal concentration with increasing particle size which can be explained by their presence as fine-grained secondary minerals which have precipitated from heavy metal bearing aqueous soil solutions. However, by distinguishing between anthropogenic and geogenic pollution two other facts must be taken into account: Firstly, anthropogenic pollution can be due to the disposal of heavy metal containing solid waste as well as from the discharge of heavy metal bearing waste water, yielding to an enrichment of heavy metals in the coarse and fine fraction, respectively. Secondly, also geogenic pollution can be due to the enrichment of heavy metals in secondary minerals, e.g. of Ni during a laterization process, i.e. in the fine fractions, but also due to the presence of heavy metals in weathering relicts such as chromite, $FeCr_2O_4$.

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Eurasian Journal of Soil Science 2021, 10(2), 132- 141

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

Exchangeable form of potentially toxic elements in floodplain soils along the river-marine systems of Southern Russia

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Article Info

Received : 11.05.2020
Accepted : 01.12.2020
Available online : 10.12.2020

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Abstract

Large rivers and especially their deltaic parts and adjacent coastal zones are subjected to strong anthropogenic influence and are often considered as hotspots of environmental pollution. The Don River is one of the largest and most important rivers in the South of Russia. The Don River basin is a highly urbanized area with developed agriculture and industry which negatively affect water quality, aquatic ecosystems and soils. The main objectives of the proposed research were to determine the levels exchangeable form of PHEs in soils of various aquatic landscapes of the study area, as well as to reveal the relationships between the content of exchangeable PTEs and the physical–chemical properties of floodplain soils. The obtained results showed that soils of the Lower Don and Taganrog Bay coastal zone are rather contrast in terms of properties and metal contents, which indicates the variability of landscapes, natural and anthropogenic processes in the studied systems. High CV values for a number of metals such as Pb, Zn, Cd and Cr indirectly indicate strong anthropogenic influence on these environments. The group median values for extractable forms for most of the metals except for Cu and Ni were higher for urbanized areas. The results of PCA analysis showed that there are two association of metals in terms of geochemical behavior and sources. The first one included Cr-Zn-Pb-Cd, the elements of anthropogenic origin, the second Mn, Ni, and Cu, which are probably of mixed origin. The obtained results showed that the Lower Don and Taganrog Bay coastal zone is a diverse and complex system subjected to anthropogenic activities, which is pronounced in the enrichment of aquatic soils with a number of metals and higher proportions of exchangeable forms from different types of sources that likely can be of both local and whole basin scale.

Keywords: Floodplain, heavy metals, Fluvisols, the Don River, Taganrog Bay, Azov Sea.

Introduction

Deltas of large rivers and adjacent coastal areas are transitional environments, where parameters of the media and element mobility change significantly at rather short distances, and interactions between fluvial and marine processes significantly affect their geochemistry (Dada et al., 2016; Botsou et al., 2019). Chemical and physical gradients typical for such systems lead to the partial removal of both suspended and dissolved matter, which sequentially results in the formation of barrier zones (Chen et al., 2020; Savenko and Pokrovsky, 2020). The filtration capacity of river deltas is important for the protection of marine

: https://doi.org/10.18393/ejss.838700
: http://ejss.fesss.org/10.18393/ejss.838700
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

ecosystems, but the accumulation of pollutants in deltaic landscapes aggravates their degradation (Lychagin et al., 2015; Kasimov et al., 2020a,b; Chalov et al., 2020). Thus, delta geochemistry studies are very informative for tracking anthropogenic activities within the entire river basin, since various components of such systems provide information on both current and historic pollution (Beltrame et al., 2009; Loureiro et al., 2009; Uluturhan et al., 2011; Dhanakumar et al., 2015; Birch et al., 2015; Buscaroli et al., 2021).

River deltas and adjacent coastal zones are highly dynamic systems subject to seasonal and long-term fluctuations of stream runoff and fluxes of dissolved and suspended matter, storms or floods, as well as anthropogenic processes in basins (Kasimov et al., 2020a,b). Consequently, environmental management and pollution control for deltaic landscapes requires consideration of many factors, including the geomorphological structure and hydrology of a particular river mouth, land-use and erosion processes in the basin (Greening et al., 2014; Chapman and Darby, 2016; Ahn et al., 2020; Fulford et al., 2020). Moreover, efficient management of deltas is impossible without systematic geochemical monitoring of water, sediments, macrophytes and soils. The latter are of particular interest, since they are complex heterogenous systems subject to flooding and redox fluctuations. It is important to note, that deltaic alluvial soils in highly urbanized regions are affected by strong anthropogenic pressure, which leads to their transformation due to agricultural or recreational activities, atmospheric and hydrogenic pollution (Arafa et al., 2015; Shokr et al., 2016; Thinh et al., 2018; Yan et al., 2018; Enya et al., 2019; Elbehiry et al., 2019; Ge et al., 2019; Hu et al., 2020; Lu et al., 2020).

The Don River is one of the most important rivers in European part of Russia. The entire Don basin has been greatly transformed as a result of long-term intensive anthropogenic load (Bartsev et al., 2016). Highly productive arable land in southern Russia, industrial and mining clusters, concentrated mainly in the watershed of the Seversky Donets tributary, and intensive development of the Rostov-on-Don agglomeration are the main factors that negatively affect the lower part of the Don basin (Nikanorov and Khoruzhaya, 2012; Matishov et al., 2016; Bauer et al., 2018; Konstantinova et al., 2020; Linnik et al., 2020; Minkina et al., 2020; Sushkova et al., 2020). The highest degree of anthropogenic load is characteristic of the Don Delta and the coastal zone of the Taganrog Bay due to urbanization, river and sea transport, as well as recreational activities, which leads to a decrease in water quality, soil and sediment pollution, degradation of coastal and deltaic landscapes and vegetation (Chichaeva et al., 2020).

Potentially toxic elements (PTEs) are one of the most dangerous pollutants for aquatic and subaqueous landscapes of the Lower Don and the Taganrog Bay (Nikanorov, 2014; Tkachenko et al., 2016, 2017). Previous geochemical studies within the Don Delta and the coastal zone of the Taganrog Bay revealed a strong variability in the PTEs content in soils and plants (Minkina et al., 2017a, b, 2019; Nevidomskaya et al., 2020). The main objectives of this study were (1) to determine the levels of total and exchangeable form of PHEs in soils of various aquatic landscapes of the study area, (2) to reveal the relationships between the content of exchangeable PTEs and the physical–chemical properties of floodplain soils.

Material and Methods

Study area and soil sampling

The floodplain soils, representing various zones of the Lower Don–Taganrog Bay system, have been analyzed in this study. Depending on the soil-landscape and hydrological conditions and taking into account the intensity of anthropogenic influence, the following zones were identified: the lower Don floodplain from the Tsimlyansk Reservoir to the source of the Mertvy Donets River, Don Delta, the coastal zone of the Taganrog Bay, the mouths of small rivers flowing into the bay, and Taganrog city, an industrial port center on the northern coast of the bay (Figure 1).

The the valley of the Lower Don is characterized by the presence of wide floodplain develops with an abundance of above-water and meadow vegetation. The Don Delta is represented by several sandy islands, densely indented by gently sloping depressions of dried old riverbeds. Delta arms and ducts have natural riverbed shafts up to 1.5 m above low-water level (Korotaev and Chernov, 2018). The total area occupied by modern Don Delta is estimated at 540 km^2 (Ivanov et al, 2013). The northern shore of the coast of the Taganrog Bay is characterized by the predominance of abrasion and erosion processes, the southern part, from the Dolgaya Spit, is distinguished by relatively more intense accumulative processes (Krylenko et al., 2017). In addition to the Don River, floodplains of smaller rivers, that flow into the bay, such as the Kagalnik, Mius, Sukhaya Chuburka, and Mokraya Chuburka were also analyzed. The degree of the anthropogenic impact on coastal soils due to the urbanization was assessed on the example of the city of Taganrog.

The climate of the studied territory is moderately continental, the average annual temperature is 9.9 °C, and annual precipitation is 615 mm (Kazakov, 2020). In terms of hydrology and hydrochemistry, the Don estuary is complex system strongly controlled by surges up and down with frequent flows of marine water into the delta branches, especially during periods of low water (Chikin et al., 2019). The chemical composition of the water varies from sulphate-calcium at the upper delta to chloride-sulphate-sodium at the seaside, mineralization varies form 300-500 mg L^{-1} in the middle part of the river mouth to 1–2 g L^{-1} near the sea, while the pH values fluctuate in a smaller range (7.5-8.5) (Tkachenko et al., 2016).

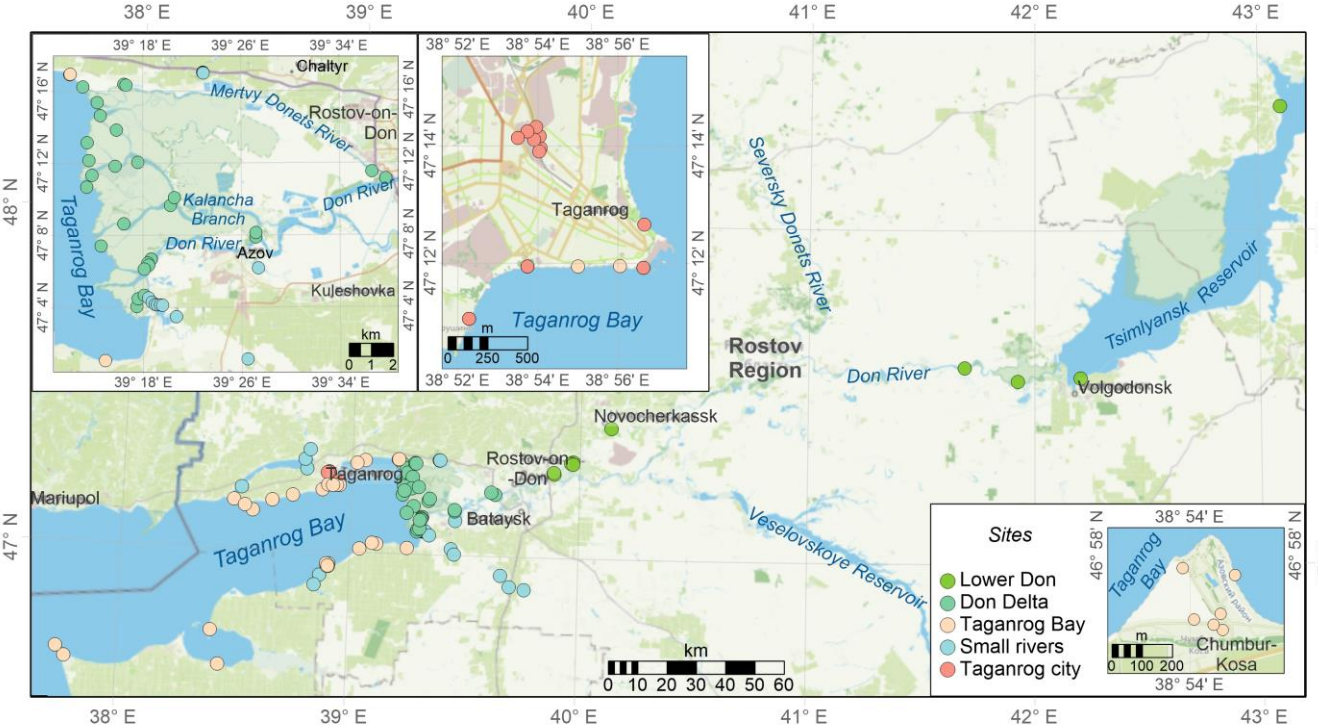

Figure 1. Simplified map of study area, showing various key sites and location of sampling points (basemap from www.openstreetmap.org).

Floodplain and coastal landscapes of the Lower Don and Taganrog Bay are represented by alternation water bodies, coppice willows, floodplain meadows, sand dunes, beaches and spits, parks, gardens and other tree plantations. The most common macrophytes of the Lower Don and coastal zones of the Taganrog Bay belong to the families *Asteraceae*, *Poaceae*, *Fabaceae*, *Brassicaceae*, *Apiaceae*, *Lamiacea*, and *Scrophulariaceae* (Kolomyichuk and Fedyaeva, 2012; Matishov et al., 2014). The floodplain and coastal landscapes of the study area are dominated by *Fluvisols* (according to IUSS, 2015), which differ significantly in texture, salinity, and organic matter content. *Fluvisols* are formed on medium and fine alluvial sands and sandy loams, characterized by a stratification of the profile and underdeveloped genetic due to periodic flooding and redeposition of particles (Minkina et al., 2017a,b). *Solonchaks*, *Arenosols* and *Haplic Chernozems* which are background soils of the region are less common.

Soil samples were collected in summer 2020 using an envelope method (GOST 17.4.4.02-2017, 2018) from the surface soil horizon (0–20 cm deep). The soil samples were air-dried, mixed, ground, and passed through a 1-mm sieve (Vorobyova, 2006).

Physical and chemical analyses

The particle size analysis was conducted using the pipette method to obtain the clay fraction (<0.001 mm) and physical clay fraction (<0.01 mm). The total organic carbon (TOC) content in the soils was determined using the dichromate oxidation method according to Tyurin. The pH was measured by potentiometry in the supernatant suspension of soil and water in a ratio of 1:2.5. The $CaCO_3$ content was determined by the complexometric method proposed by Kudrin (Vorobyova, 2006). The exchangeable cations Ca^{2+} and Mg^{2+} were determined using the method described by Shaimukhametov (1993).

The total concentrations of Cr, Mn, Ni, Cu, Zn, Cd, and Pb were determined by X-ray fluorescence analysis using a Spectroscan MAX-GV spectrometer (Spectron, Russia) (OST 10-259-2000, 2001), and the content of exchangeable forms extracted from the soil by NH_4Ac buffer solution with pH 4.8 and soil/solution ratio of 1:10 for 18 h was determined by atomic absorption spectrophotometry (AAS) (KVANT 2-AT,Kortec Ltd, Russia) (RD 52.18.289-90, 1990). All laboratory tests were performed in triplicate. The accuracy of element determination was verified using duplicates, reagent blanks, and state standard reference samples (no. GSS 10412-2014, State Service for Standard Specimens Relating to Composition and Properties of Substances and Materials) and complies with standards of certified methods (RD 52.18.289-90, 1990; OST 10-259-2000, 2001).

Statistical analysis

Descriptive statistics of PHEs concentrations and soil properties, including mean, median maximum, minimum values, standard deviation (SD), and coefficients of variation (CV) were calculated. The Kolmogorov–Smirnov test with Lilliefors correction disposed the normal distribution of all data; therefore, raw data was standardized by means of z-score before multivariate statistical analysis.

To analyze the significant differences in exchangeable PTE content in the soils of various zones of the Lower Don–Taganrog Bay system, one-way analysis of variance (ANOVA) and Fisher LSD. Pearson correlation coefficients (r) were calculated to determine the relationship between exchangeable PTEs and physical–chemical properties of soils. Principal component analysis (PCA) was carried out in order to identify relationship between the measured parameters by achieving individual component loadings. Only components with eigenvalues above 1.0 were considered, following the Kaiser criteria. All of these analyses were performed using STATISTICA 12 (Statsoft, USA), and statistical significance was determined at $p < 0.05$.

Results and Discussion

Soil physical–chemical properties

The descriptive statistics for physical–chemical properties of soils of the Lower Don and Taganrog Bay coastal zone are present in Table 1. One can see that most of the studied parameters varied significantly. The $CaCO_3$ content varied from 0.1 to 8.3 %, the TOC content – from 0.1 to 3.9 %, Ca^{2+} and Mg^{2+} 3.2 to 36.3 and from 0.2 to 8.3 $cmol_c\ kg^{-1}$ respectively and the clay from 0.1 to 33.1 %. The differences in the content of SiO_2, Fe_2O_3 and Al_2O_3 correspond to the variations of soil texture with maximum SiO_2 values characteristic for soils of sandy beaches and higher proportion of Fe_2O_3 and Al_2O_3 is characteristic for well-developed accumulative *Fluvisols* with higher contents of clay fraction. The values of the CV are rather high for $CaCO_3$ (78.4%), TOC (61.5%), Ca^{2+} (50.4%), Mg^{2+} (66.9%), and clay fraction (70.0%). High heterogeneity of soil properties indicates the diversity of landscapes and parent material within the large river system and coastal environment. Studied soils develop whin various geomorphic forms that may differ significantly in hydrological regime, current sedimentation processed and, in general, by their timing of pedogenic processes. All studied soils were alkaline, from slightly to strongly. At the same time pH values showed smaller variation (CV=4.1%), which can be explained by the fact that all studied soils appear in semi-arid climatic condition and carbonate-reach loess is the most common type of covering deposits within the Lower Don basin.

Table 1. Descriptive statistics for physical–chemical properties of soils of the Lower Don and Taganrog Bay coastal zone (N=97)

Statistics*	pH H_2O	$CaCO_3$	TOC	Ca^{2+}	Mg^{2+}	SiO_2	Fe_2O_3	Al_2O_3	Clay	Physical clay
			%	$cmol_c\ kg^{-1}$						%
Mean	7.9	2.4	1.3	16.1	2.7	63.8	3.6	8.1	14.1	29.7
Median	7.9	1.9	1.1	16.0	2.0	63.8	3.9	8.5	12.2	26.4
Minimum	7.2	0.1	0.1	3.2	0.2	37.0	0.4	1.2	0.1	1.3
Maximum	8.9	8.3	3.9	36.3	8.3	85.2	6.7	11.8	33.1	67.8
SD	0.3	1.9	0.8	8.1	1.8	9.9	1.3	2.6	9.8	17.3
CV	4.1	78.4	61.5	50.4	66.9	15.5	36.1	32.3	70.0	58.4

* TOC total organic carbon content, SD standard deviation, CV coefficient of variance.

Levels of PTEs in the studied area

The data on the concentrations of total and exchangeable forms of metals is summarized in Table 2. Based on the descriptive statistics it is possible to conclude, that total concentrations of all PHEs showed significantly variability in soils of the Lower Don and Taganrog Bay coastal zone. The studied PHEs can be subdivided in two groups based on the values of CV. The first group includes Mn (47.2%), Ni (38.1%) and Cu (46.2%), and the second group includes Cr (84%), Zn (116.8%), Cd (111.7%) and Pb (101.3%). High CVs are characteristic of the second group, and confirm the heterogeneity of PHEs. The fact that the CV for the second group of elements is 2–3 times higher than for the first indicates that they are better indicators of anthropogenic activities and pollution in soils of the studied aquatic system. This is consistent with the data on the exchangeable forms of PHEs. In general, we can mention that the CV values for exchangeable forms of all studied metals were higher than for total concentration, especially for Zn (182.0) and Pb (175.5). It can be explained as consequence of anthropogenic impact on the Lower Don basin, as well as Zn and Pb are good indicators of anthropogenic activity. It should be noted that studied soils are rather different in terms of carbonate, organic carbon and clay content, which strongly affect their sorption properties and geochemical status.

Table 2. Descriptive statistics for PTEs (mg kg^{-1}) in soils of the studied area (N=97)

Concentration	Element	Mean	Median	Minimum	Maximum	SD	CV
Total	Cr	109.2	94.9	34.1	871.0	91.7	84.0
	Mn	861.6	729.3	110.3	2466.2	406.6	47.2
	Ni	46.5	45.3	19.0	98.0	17.7	38.1
	Cu	43.9	40.5	4.1	143.4	20.3	46.2
	Zn	147.9	94.3	19.4	1389.7	172.7	116.8
	Cd	1.7	0.9	0.1	10.0	1.9	111.7
	Pb	47.5	33.0	5.3	317.0	48.1	101.3
Exchangeable	Cr	3.8	2.8	0.3	62.6	6.6	173.7
	Mn	80.9	65.2	7.7	363.0	61.1	75.5
	Ni	2.5	1.9	0.6	8.5	1.8	70.7
	Cu	2.6	1.7	0.2	23.3	3.4	130.0
	Zn	20.5	7.0	1.3	295.5	37.3	182.0
	Cd	0.14	0.08	0.01	0.90	0.16	116.0
	Pb	4.8	2.7	0.2	60.4	8.3	175.5
Exchangeable percentage	Cr	3.0	3.0	0.6	7.2	1.4	46.7
	Mn	8.7	7.9	4.2	14.7	2.8	32.6
	Ni	5.3	5.3	1.5	10.1	2.2	40.9
	Cu	5.3	4.6	0.6	21.8	3.9	72.4
	Zn	10.0	8.5	1.5	21.3	5.0	50.4
	Cd	8.5	8.3	2.3	20.0	4.1	47.6
	Pb	8.3	8.0	2.6	19.1	3.5	42.3

The Figure 2 illustrates variability of the exchangeable PTE content in soils of the studied area. The highest level of variability for Pb, Cr and Zn were observed for soils from Taganrog. Soils of small rivers showed significant variability of Mn, Cu and Ni. For exchangeable Cd, the greatest variability was observed in the Don Delta soils, which can be interpreted as an evidence of geochemical barrier, related to the changes in pH values. According to the Wilks lambda criterion, the confinement of soils to a specific zone of the river-marine system is highly significant for all studied PHEs ($p < 0.0005$).

Significant differences in exchangeable PHE content for different zones were observed: highly significant for Zn and Pb, strongly significant for Cd, and statistically significant for Cr and Cu (Table 3). In the urban soils of Taganrog, an excess of the average level of exchangeable Cr, Zn, Cd, and Pb was shown (Figure 2), which indicate the anthropogenic origin of these PHEs in the soils of the territory under consideration.

Table 3. Effects of the soil location within the Lower Don–Taganrog Bay system on exchangeable PTEs content as indicated by one-way ANOVA

Exchangeable metals	Sum of squares (*SS*)	Mean square (*MS*)	*F*	*p*
Cr	12.248	3.062	3.363	0.0129*
Mn	6.395	1.599	1.642	0.1705
Ni	8.187	2.047	2.144	0.0816
Cu	11.766	2.941	3.213	0.0162*
Zn	33.716	8.429	12.450	0.0000*
Cd	14.825	3.706	4.201	0.0036*
Pb	35.415	8.854	13.444	0.0000*

* significant at $p < 0.05$.

The soils of small rivers were characterized by increased values of exchangeable Cu, the content of which was 2 times higher than in the soils of other zones. Copper exhibits organophilic properties in soils (Kabata-Pendias, 2011); its accumulation can be associated with more pronounced processes of humus accumulation, since the soils small river floodplains are enriched with organic matter transported from local arable land due to the erosional processes.

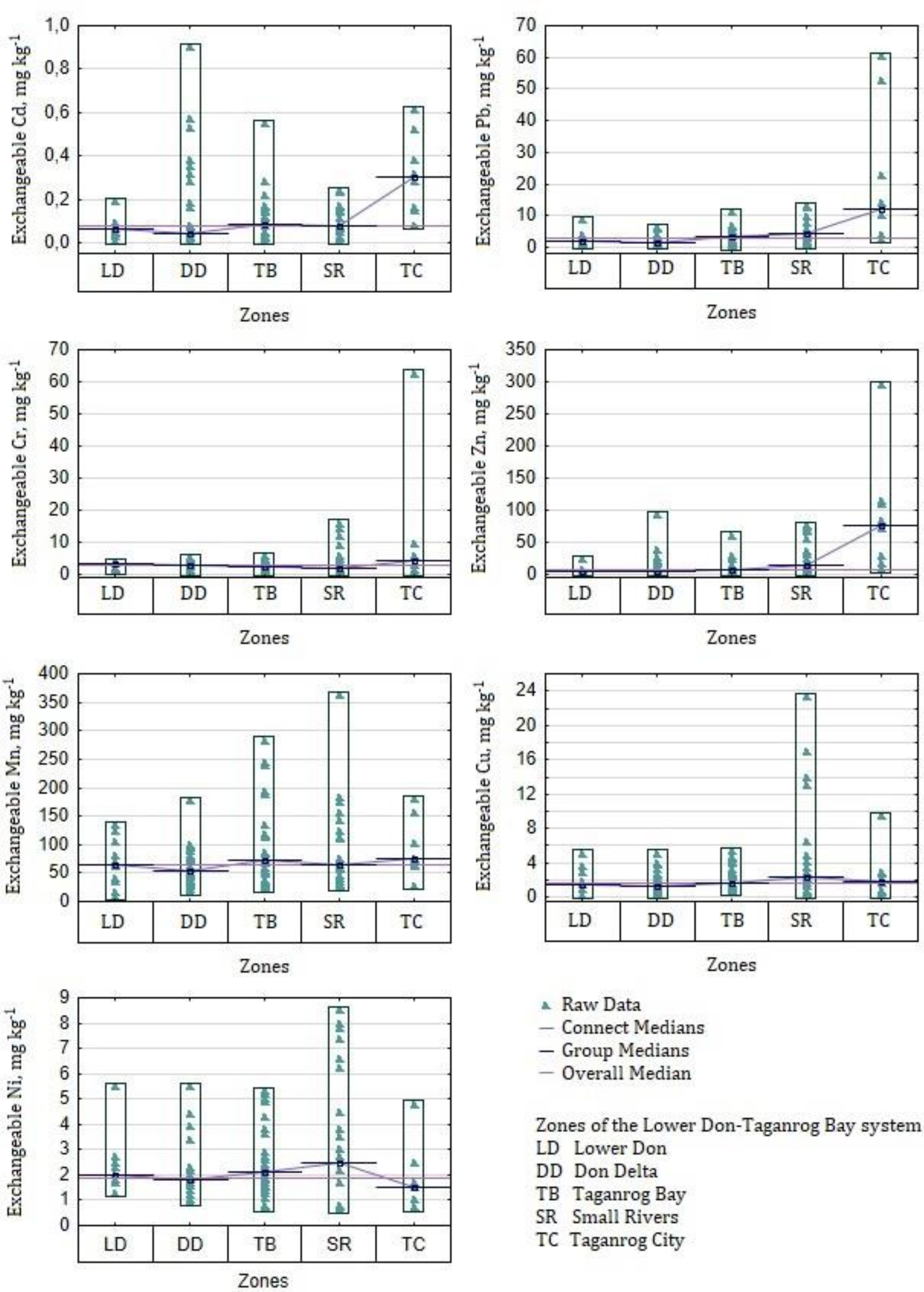

Figure 2. Variability plots of the exchangeable PTE content in soils within the study area.

Relationship between soil properties and exchangeable PTEs content

The results of correlation analysis showed that soil properties have weak effect on the accumulation of exchangeable PHEs (Table 4). Statistically significant ($p< 0.05$) low negative correlations were observed between physical clay and Ni, SiO_2 and Zn and Pb, as well as low positive correlations were observed between Fe_2O_3 and Zn and Pb, $Mg^{2=}$and Pb. Moderate correlations were found only between Mn and SiO_2. The data obtained indicate the absence of a linear relationship between the studied parameters.

Table 4. Pearson correlations between exchangeable PTE content and soils properties

N=97	Cr	Mn	Ni	Cu	Zn	Cd	Pb
pH	0.136	0.044	-0.108	0.011	0.181	0.167	0.182
$CaCO_3$	0.192	-0.045	-0.118	0.005	0.300*	0.043	0.244*
TOC	-0.046	0.018	-0.222*	-0.151	0.179	0.153	0.223*
Ca^{2+}	-0.036	-0.048	-0.276*	-0.209*	0.113	0.004	0.163
Mg^{2+}	0.099	-0.004	-0.183	-0.070	0.246*	0.147	0.319*
SiO_2	-0.174	-0.569*	-0.117	-0.243*	-0.339*	-0.201*	-0.331*
Fe_2O_3	0.274*	0.127	0.133	0.078	0.339*	0.230*	0.317*
Al_2O_3	0.155	0.051	0.125	0.041	0.183	0.081	0.131
Clay	-0.035	-0.106	-0.299*	-0.202*	0.134	0.055	0.197
Physical clay	-0.014	-0.081	-0.307*	-0.191	0.161	0.122	0.223*

* significant at $p< 0.05$.

Two principal components (PC) were identified, accounting for 67% of the total variance (Figure 3). Exchangeable forms of PTEs with high factor loadings were distributed among the factors as follows. The first PC characterized by the Cr-Zn-Pb association had the most significant strong negative value. The same factor had a moderate negative loading for Ni, Cu, and Cd. Moderate positive loadings for Mn, Ni, and Cu were characterized by PC2. The first PC also weakly correlates with content of Fe_2O_3 (-0.333) and SiO_2 (0.388). Fractions of clay and physical clay showed weakly negative effects on PC2. Other soil properties were not associated with either PC1 or PC2. For each sampling site, factor loadings were calculated, which were projected onto the plane of PC1 and PC2. The first PC has the greatest influence on urban soils, while the PC2 manifests itself most strongly in relation to the soils of small rivers. Thus, it can be assumed that the PC1 is associated with anthropogenic impact, and the PC2 is associated with the natural processes.

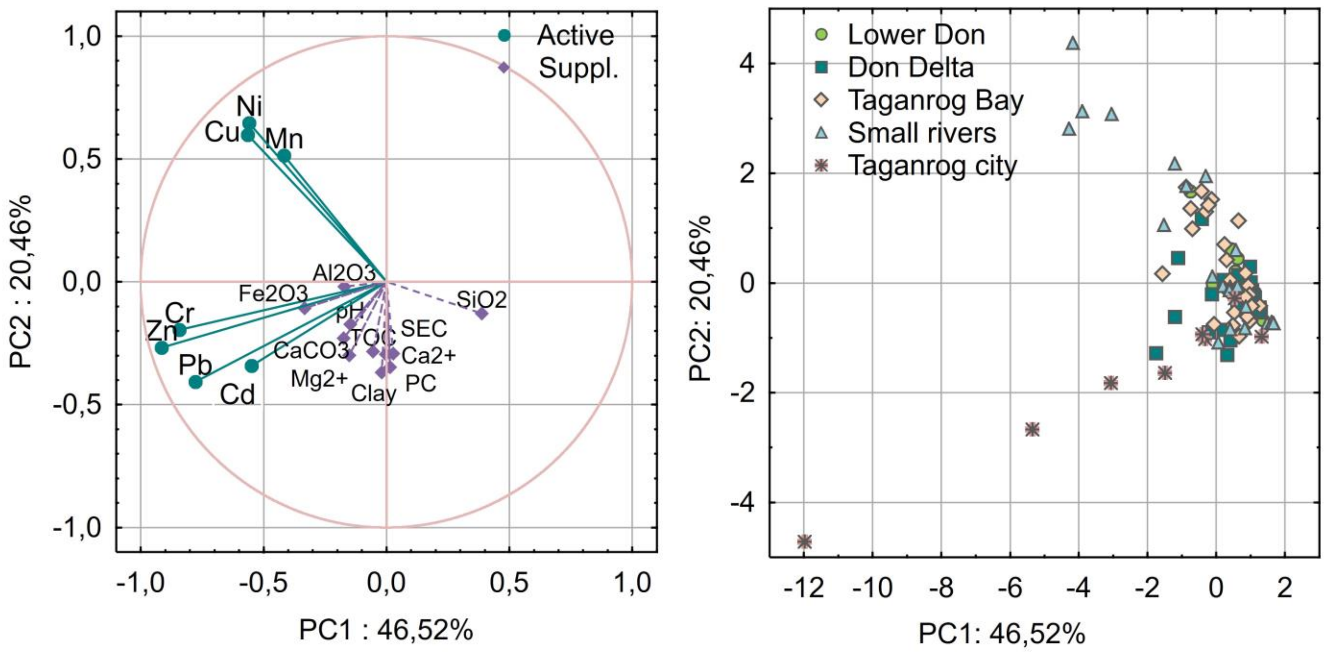

Figure 3. Plots of factor loadings revealed from principal component analysis, indicating the relationships between exchangeable PTE content and soil properties (left), and reflecting the degree of influence of factors on exchangeable PTE content in the soils of sampling sites (right).

Conclusion

The study results have shown that the Lower Don and Taganrog Bay coastal zone is a complex system with a wide diversity of environments. This thesis is supported by the data on the properties of soils, representing different landscapes of the study areas. It was shown that most of the studied metals, especially Pb, Zn, Cd and Cr, have showed high CV values for both total concentrations and their exchangeable forms. This fact supported by the results of PCA analysis can be interpreted as signs of strong anthropogenic influence on this aquatic system. The obtained results showed that different parts the Lower Don and Taganrog Bay coastal zone are rather contrast in terms of soils, their properties and the degree of anthropogenic impact, which is manifested in significant variance of metals exchangeable forms and their proportions. Thus, the studies on the soil-geochemical features of the studied aquatic environments require complex investigation of mechanisms responsible for the geochemical behavior of potentially toxic elements.

Acknowledgements

This project was funded by the Russian Science Foundation, Grant no. 20-14-00317.

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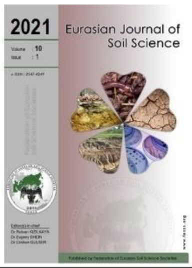
Journal homepage : http://ejss.fesss.org



Effect of biogas waste applications on soil moisture characteristic curve and assessment of the predictive accuracy of the Van Genuchten model

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Article Info

Received : 11.04.2020
Accepted : 05.12.2020
Available online : 15.12.2020

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Abstract

Biogas production has recently become an important issue in countries where alternative energy sources are gaining importance. The study investigates the use of waste, the final product of production, as a soil conditioner and fertilizer for sustainable soil management. The study examines the effects of different amounts of biogas waste [0 (B0), 1 (B1), 2 (B2), 3 (B3) and 4 (B4) ton da^{-1}] on some soil properties and soil moisture characteristic curve (pF). In addition, the van Genuchten model, which has been long and widely used in many studies for the prediction of hydraulic properties, was compared with the pF curves that were obtained using the predicted and real values obtained from the applications. The results of the study showed that although biogas waste applications were more effective in the wet region of the moisture characteristic curve, B3 was the most effective dose that improved the physical properties of the soil. The B4 application had a decrease of about 16% in the penetration resistance and an increase of about 21% in the wilting point compared with those of the control group. The decrease in the macro pore volume due to biogas waste applications was not statistically significant, while biogas waste applications caused a statistically significant increase in the micro pore volume ($P < 0.05$). Among the van Genuchten model parameters, the moisture content in saturation (θ_S) and residual water (θ_r) had realistic results in all biogas waste applications. Moreover, the air entry value ($1 / \alpha$) was estimated to be 41.667 cm in the B0 application and 55.556 cm in the B4 application. In conclusion, high-accuracy estimates were obtained using the van Genuchten model with a R^2 value of 0.901 and root mean square error (RMSE) value of 0.061 cm^3 cm^{-3} in the moisture characteristic curve of the control (B0) soil.

Keywords: Biogas waste, van Genuchten model, pF, soil physical properties.

Introduction

In recent years, available water amount has decreased due to global warming and unconscious water consumption. Thus, its importance is increasing day by day. Furthermore, its increasing consumption due to rapidly increasing population will inevitably cause drought. The scenarios of climate change point to growing risks of drought and land degradation due to the limited use of technological developments in agricultural production as opposed to excessive resource consumption (IPCC, 2019). Turkey, which has a surface area that is mostly dominated by arid, semi-arid or semi humid climatic characteristics, uses 70% of its fresh water resources for agricultural activities (TUIK, 2012). The unconscious and unplanned use of

: https://doi.org/10.18393/ejss.841287
: http://ejss.fesss.org/10.18393/ejss.841287
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

these resources can lead both to the decrease of the already scarce water supply and land degradation (salinification, runoff, etc.). Therefore, knowing the soil-plant-water relationships in soils on which agricultural activities are carried out especially in regions with arid and semi-arid ecosystems are highly important to improve issues such as the preservation of soil water and development of irrigation programs.

The soil-water dynamic and soil-water potential can considerably change depending on texture, structure and compaction (Liyanage and Leelamanie, 2016; Fashi et al., 2017). The soil-water dynamic includes the entry of water to soil, water storage, water losses and water use by plants and is evaluated using the water retention curves of soils. Water can move or be retained in the pores of soils. The water retention characteristics of soils change depending on the pore structure of soils, infiltration rate and hydraulic conductivity. The water retention curve explains the relationship between the amount of water held in the soil and retention forces. In their study on the effects of organic material applications on water retention and water-entry value, Liyanage and Leelamanie (2016) reported that the soil water content significantly and linearly increased with increasing organic material content. Again, Müjdeci et al. (2020) reported that stable manure and green manure applications increased volumetric water content at all retention pressure. Barzegar et al. (2002) stated that organic material applications increased the water content held at levels below 100 kPa.

Various numerical models have been developed to predict soil water retention curves due to the difficulty and cost of determining the curves. The applicability of the models varies depending on the region and soil properties (Alaboz and Işıldar, 2019). The model developed by van Genuchten (1980) is one of the most used equations. Retc and Rosetta are widely used programs for the prediction of the parameters of the van Genuchten equation. Unguraşu et al. (2012) reported that they successfully predicted all hydraulic properties (water retention parameters, hydraulic conductivity values under saturated and unsaturated conditions) within the scope of the Rosetta neural network using the parameters of sand, clay and silt contents, bulk density and water contents at 33 kPa and 1500 kPa.

Energy need and consumption are constantly increasing due to the increasing population in Turkey and the world. There is a need for different energy resources and biogas is one of these alternative energy resources. Organic wastes of animal and plant origin are generally used in biogas production (Şenol et al., 2017). Biogas production involves an anaerobic degradation process and the wastes of its production are turned into valuable organic fertilizers (Kılıç, 2011). Yaraşır et al. (2018) reported that biogas waste applications had a positive effect on wheat yield and quality parameters. Again, Islam et al. (2010) reported that biogas applications positively affected the yield and quality parameters of corn silage.

The study investigates the effect of biogas waste applications on water retention characteristic curve and assesses the predictive accuracy of the van Genuchten equation, a model widely used for the prediction of soil-water dynamic.

Material and Methods

Study Area

The study area is located in the east of the Isparta–Burdur Highway within the borders of Isparta Applied Sciences University. Its coordinates are WGS 1984 UTM Zone 36N 283100- 282921 North longitude and 4190355-4191399 East latitude (Figure 1). The study area is on a land opening to the Isparta plain in the southeast direction and surrounded by high hills and ridges in the other direction. According to the long-term meteorological data (1974-2017) of the study area, the region has a semi-arid climate. The annual mean temperature and precipitation are 12.3ºC and 467 mm, respectively. According to the Newhall simulation model (Figure 2) for the soil climate regime, the soil temperature and moisture regime of the study area are mesic and xeric (dry xeric in the subgroup) (van Wambeke, 2000).

Application material and experimental setup

The study was carried out in accordance with the randomized block experimental design. The biogas waste (B) used as the organic material was obtained from a biogas production facility. Farmyard manure was used in biogas production and the waste that contain 15% moisture and leave the Separator Press as an end product was used as the organic material. Different ratios of biogas waste were used [0(B0), 1(B1), 2(B2), 3(B3), 4(B4) ton da^{-1}] and the waste was applied in 5 repetitions to parcels of 3*5 m^2. The study area was ploughed and seed bed was prepared using a rotary harrow at the time of harvest. The experiment was set up on 19.11.2019 and B was mixed into a depth of about 0-20 and, then, 2 rows of barley (Tarım-92) was planted using a 6-split row planter with an automatic piston. As the main fertilizer, 10 kg da^{-1} N, 8 kg da^{-1} P and 8 kg da^{-1} K were applied. The trial was harvested on 05.07.2020. Prior to the harvest, disturbed and undisturbed soil samples were collected in three repetitions and brought to the laboratory. Then, preparations were made for the soil analyses.

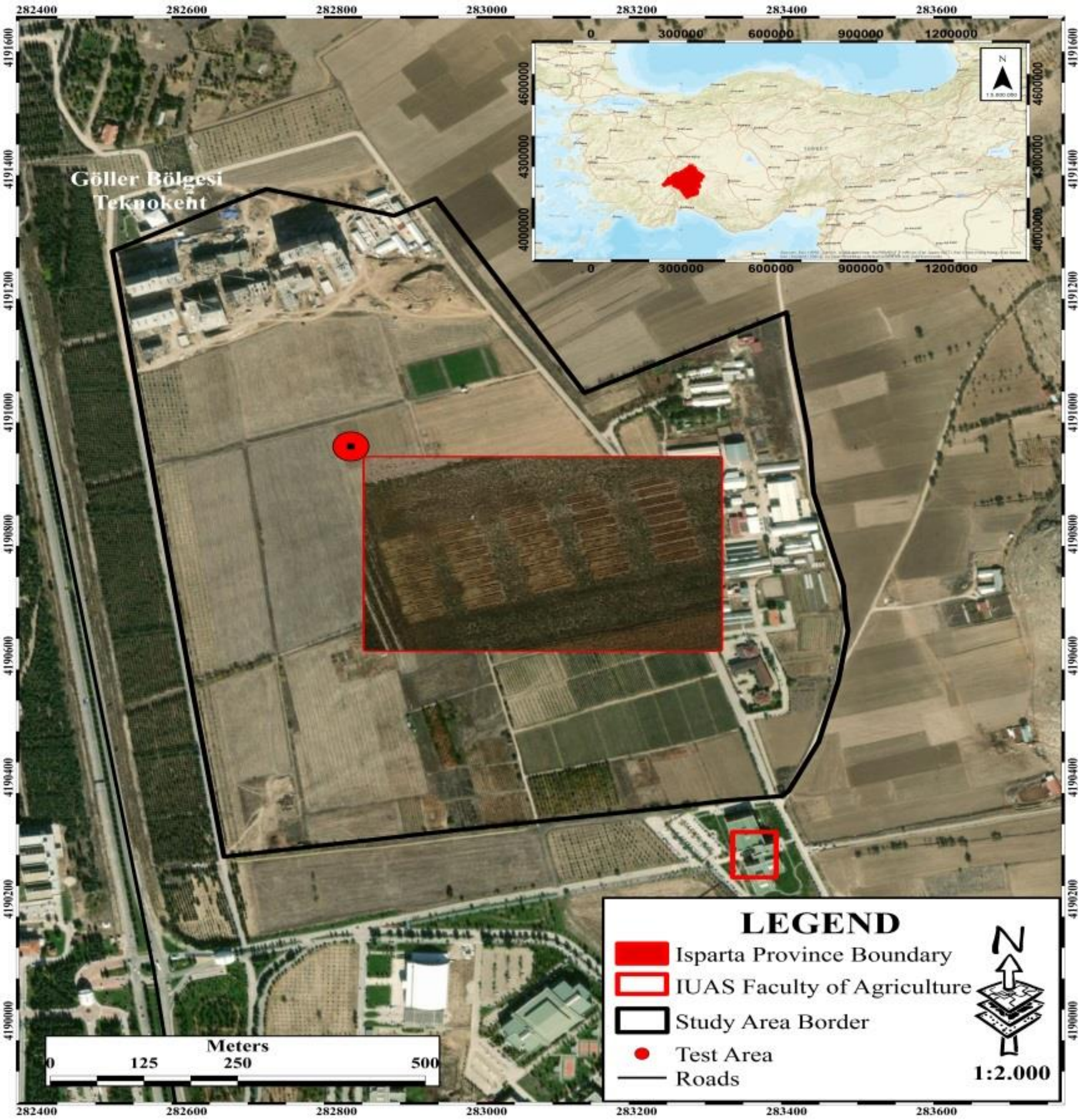

Figure 1. Study area

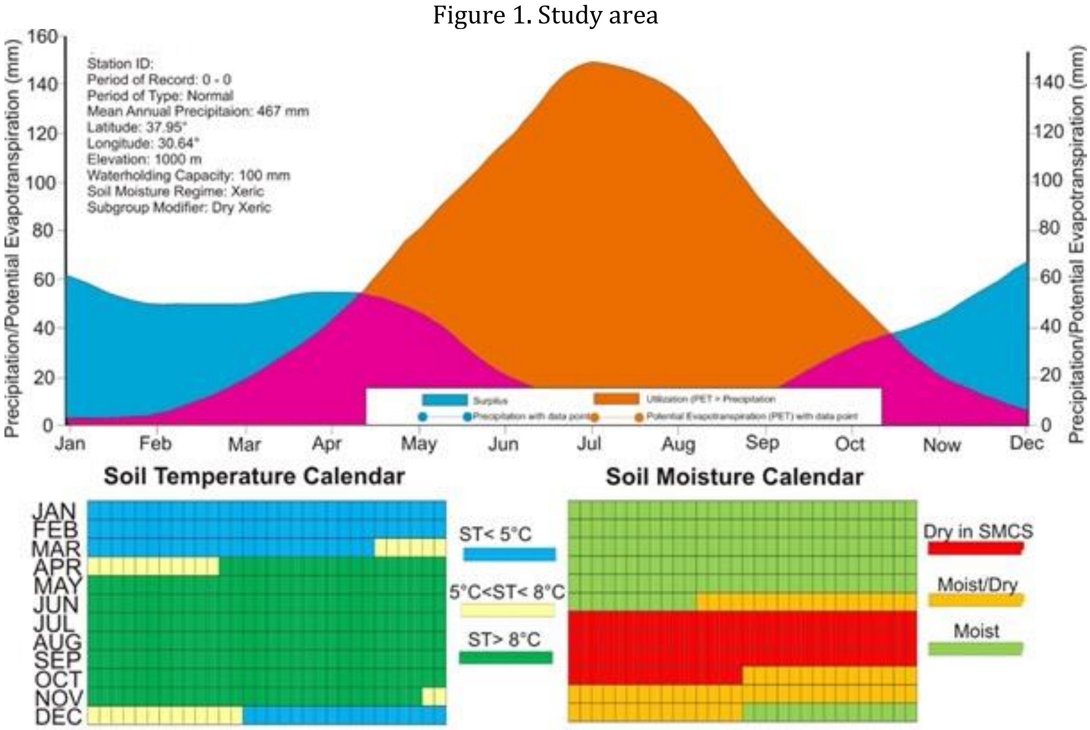

Figure 2. Diagram of the soil moisture and temperature regimes

Method

The texture analysis of the soils (sand, silt and clay %) was determined with the Bouyoucos hydrometer method (Bouyoucos, 1962). Bulk density (P_b) was determined using sampling cylinders (100 cm^3). The electrical conductivity (EC) and pH values of the soils and biogas waste were measured using 1:1 soil-water and 1:5 organic material-water suspensions. The $CaCO_3$ % content was determined using volumetric calcimeter and organic matter content was determined using the Walkley-Black and dry combustion methods (Soil Survey Staff, 1993). The nitrogen content was determined by following the Kjeldahl method (Kacar, 2009) and the moisture characteristic curve was determined in volumes using a pF set with ceramic plate (U.S.A, Soil Moisture Equipment Corp.) (Soil Survey Field and Laboratory Methods Manual, 2014). The 0.001(θ_S)-, 0.1-, 0.33(θ_{TK})-, 1.0-, 5-, 10- and 15(θ_{SN})-bar moisture contents were used to form the pF curves. The air-dry moisture contents of the soils were evaluated as water kept at 1000-atm pressure. The total pore volume was obtained from the water volumes at saturation and micro pore volume was obtained from the water volumes kept at 0.33 bar (field capacity). The macro pore volume was obtained by subtracting the micro pore volume from the total pore volume (Danielson and Sutherland, 1986). The penetration resistance (PR) measurements were made with a cone penetrologger (Eijkelkamp) using the conical edge with 60º (NEN 5140, 1996) and base surface of 1 cm^2. The moisture corrections in the penetration resistance value was made using the correction equation proposed by Alaboz (2019).

Van Genuchten model

The van Genuchten model (van Genuchten, 1980) (Equation 1) was used in the prediction of the soil moisture characteristic curve. Retention Curve (RETC) program-Rosetta neural network was used in the evaluation of the moisture characteristic parameters. For the determination of the coefficients of the shape parameters, (1) texture class, (2) sand, clay and silt contents, (3) sand, clay and silt contents, bulk density, (4) sand, clay and silt contents, bulk density, water content at 33kPa and (5) sand, clay and silt contents, bulk density, water contents at 33kPa and 1500 kPa properties and their predictions were used.

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{(1+|ah|^n)^m} \quad \text{(Eq. 1)}$$

θ(h): volumetric water content in soil water potential (cm^3 cm^{-3}) h: soil water potential (cm), θr: residual water content (cm^3 cm^{-3}), θs: saturated water content (cm^3 cm^{-3}), α (cm^{-1}), n ve m: are shape parameters. n>1, ve m : 1−1/ n (Mualem, 1976), 0<m<1.

Assessment of the predictions

The coefficient of determination (R^2) and root mean square error (RMSE) values were used to evaluate the relationship between the real data obtained from the soil moisture characteristic curve and predicted values obtained using the Van Genuchten model (Equation 2, 3).

$$RMSE = \sqrt{\frac{\sum (Zi-Z)^2}{n}} \quad \text{(Eq. 2)}$$

$$R^2 = \left[\frac{\sum ZiZ - \frac{\sum Zi \sum Z}{n}}{\left[\sum Zi^2 - \frac{(\sum Zi)^2}{n}\right]\left[\sum Z^2 - \frac{(\sum Z^2)}{n}\right]} \right]^2 \quad \text{(Eq. 3)}$$

Zi: predictive value, Z: actual value, n: number of observations.

The effects of the application on certain soil properties were examined using the Tukey test among the multiple comparison tests and Minitab 16 package program.

Results and Discussion

Table 1 shows the properties of the soil and biogas waste. According to Kacar (2009) and Hazelton and Murphy (2016), soils from the loamy clay texture class contain high levels of lime and low levels of organic material and have a slight alkaline reaction and do not have a salinity problem. The organic material content of the biogas waste was 46.7%. The biogas waste had a pH value of 7.70 and its C/N ratio was 12.1.

Table 1. Some properties of soil and Biogas waste

	Texture	$CaCO_3$, %	OM, %	pH	EC, dS m^{-1}	C/N
Soil	CL	25.43	1.69	7.89	0.38	10.9
Biogas waste			46.70	7.70	1.44	12.1

Table 2 shows the effects of biogas waste applications at different ratios on some soil properties and Figure 3 shows their effects on soil moisture characteristic curve.

Table 2. The effect of biogas waste applications on soil properties

	P_b, g cm^3	PR, MPa	Macro pore volume	Micro pore volume	θ_S, cm^3 cm^3	θ_{FC}, cm^3 cm^3	θ_{WP}, cm^3 cm^3	θ_{AWC}, cm^3 cm^3	OM, %
B0	1.46a	1.56a	0.26	0.28c	0.54b	0.28c	0.18b	0.10c	1.69e
B1	1.35b	1.37b	0.25	0.29bc	0.54b	0.29bc	0.18b	0.11c	2.03d
B2	1.29c	1.30c	0.24	0.33 b	0.57ab	0.33b	0.19b	0.14bc	2.47c
B3	1.22d	1.28c	0.24	0.38a	0.62a	0.39a	0.19b	0.20a	2.86b
B4	1.20d	1.22d	0.22	0.39a	0.61a	0.38a	0.23a	0.15b	2.97a
P	*	*	NS	**	**	**	*	*	*

P_b : bulk density, PR: penetration resistance, θ_S: saturated water content, θ_{FC}: field capacity, θ_{WP}: wilting point θ_{AWC}: available water content, OM: organic matter, P: significance level, * : P<0.01, ** : P<0.05, NS : not significant

The changes in the effects of different levels of biogas waste applications on the investigated properties were statistically significant, except for macro pore volume. The organic material contents of the soils significantly increased due to the biogas waste applications (P<0.01) and these increases caused expected decreases in bulk density and penetration resistance. The bulk density in the control application was 1.46 g cm^{-3}, while the bulk density in the B4 application was 1.20 g cm^{-3}. Compared with the control application, penetration resistance decreased by about 16% in the B4 application. The increase in porosity due to the application of organic materials with a porous structure decreases penetration resistance and bulk density. The negative relationship between penetration resistance and porosity is in compliance with the literature (Gülser and Candemir, 2012; Mujdeci et al., 2017). The biogas waste applications did not have a significant effect on the macro pore volume of the soils, but the micro pore volume significantly changed depending on the applications (P<0.05). The 0.28-cm cm^{-3} micro pore volume in the control sample increased by 39% in the B4 application. The B3 and B4 and the B0 and B1 applications were statistically similar. Micro pores retain higher levels of water than macro pores (air-filled pores) (Calonego and Rosolem, 2011). Organic material particles enter the large pores in soils and create smaller-diameter pores. Thus, the B3 application was considered effective on water retention. The statistically-not-significant decrease in the macro pores is due to the increase in micro pores. The inverse proportionality of the air-filled pores to water-holding pores has also been reported in the literature (Birol, 2010).

Increasing doses of biogas waste application caused statistically significant changes in the soil moisture constants (θ_S, θ_{FC}, θ_{WP}, θ_{AWC}) (P<0.05; 0.01). The moisture content at saturation (θ_S) was at the same level in the B0 and B1 applications (0.54 cm cm^{-3}), while an application-caused increase, albeit unstable, was observed in other applications. The highest θ_S was obtained in the B3 application. The low saturation values are attributable to the number of large drainage pores and decreases in the total pore volume due to increasing bulk density with compaction. The θ_{FC} level in the control application was 0.28 cm cm^{-3}, while the other applications had θ_{FC} levels of 0.29, 0.33, 0.38 and 0.39 cm cm^{-3}, respectively. The θ_{WP} levels were 0.18, 0.18, 0.19, 0.19 and 0.23 cm cm^{-3}, respectively. The wilting point was stable until the B4 application and resulted in an increase in θ_{AWC}, while the increase in θ_{WP} in the B4 application caused a decrease in θ_{AWC}. The biogas waste application increased the number of water-holding pores in the soils. Until the B4 application, more water was held by plants by lowering the water-holding energy. Abdulwahhab (2020) reported that, with the application of cattle manure, the values at wilting point decreased leading to decreased water-holding energy and, thus, increased available water amount. The B4 application caused an increase in the wilting point by about 21%, which led to a decrease of about 25% in the plant-available water content.

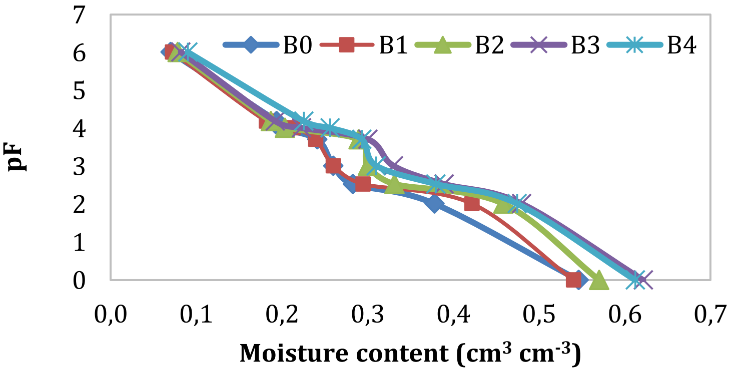

Figure 3. Soil moisture characteristic curve

Air-dry soil moisture (pF: 6) were 0.07, 0.072, 0.078, 0.082 and 0.09 cm cm^{-3}, respectively, depending on the application. The addition of organic material increases surface area and water-holding capacity increases at higher tensions (Gliński et al., 2011). The remaining water in soil approaches to zero as soil water potential increases and water retention curve begins to bend after a point and remains stable. The inflection point corresponds to the residual water content. Some studies refer to the residual water content either as the remaining moisture content below 1500 kPa or air-dry soil moisture content (Abdulwahhab, 2020). Within this framework, considering the air-dry moisture as the residual water content, residual water content with the increases in the applications. The soil moisture characteristic curve (Figure 3) revealed that the differences between the applications did not cause significant changes in the dry region. Especially after pF 4.2, the changes in the B0 and B1 applications were close to each other in water contents kept at lower pressures, while differences in the curves emerged as other applications differed when compared with the control application.

Prediction of the moisture characteristic curve using the Van Genuchten model

Table 3 shows the parameters that were obtained by assessing the combinations of five different soil properties using the Rosetta neural network for the prediction of the parameters of the van Genuchten model. For the prediction of the parameters, the closest results to the real θ_r and θ_S values were obtained by using the sand, silt, clay, bulk density, θ_{FC} and θ_{WP} properties. The air-dry moisture was taken into consideration for the comparison of the θ_r values. Unguraşu et al. (2012) reported that the Rosetta program successfully predicted the water-holding parameters and hydraulic conductivity at saturated and unsaturated conditions.

Table 3.Van Genuchten model parameters

	θ_S, cm^3 cm^{3}	θ_r, cm^3 cm^{3}	α, cm^{-1}	1/ α, cm	n	m
B_0	0.565	0.089	0.024	41.667	1.383	0.277
B_1	0.473	0.098	0.023	43.478	3.634	0.725
B_2	0.560	0.128	0.023	43.478	1.395	0.283
B_3	0.487	0.096	0.019	52.632	4.374	0.771
B_4	0.566	0.122	0.018	55.556	4.327	0.769

θr: residual water content (cm^3 cm^{-3}), θs: saturated water content (cm^3 cm^{-3}), α (cm^{-1}), n and m: are shape parameters.

The parameters that were predicted using the Rect-Rosetta program varied depending on the application. In the applications, θ_S levels were around the levels of 0.473-0.566 cm cm^{-3}, while θ_r ranged from 0.089 to 0.128 cm cm^{-3} and α ranged from 0.018 to 0.024 cm^{-1}. The inverse of the parameter α (1/α, cm) is known to be the air entry value. The beginning of the entry of air to the large pores in soils is described as the matric potential of water, which is the beginning of drainage. The decreases in the air entry values with the increase in macro porosity (Wang et al., 2015) and increases due to compaction (Abdulwahhab, 2020) have been reported in the literature. n and m are shape parameters and are based on the minimization of the difference between the predicted volumetric water content at a certain soil water pressure and measured water content value. n is a dimensionless parameter related to the shape of the curve. The equation m=1-1/n proposed by Mualem (1976) was used for the constant m. The constant m determines the shape of the pF curve and is affected by various soil properties such as texture, organic material content, structural conditions, compaction, etc. (Van Genuchten et al., 1991). The constant n ranged from 1.383 to 4.374 and generally increased as the application dose increased, except for the B2 application. The constant m ranged from 0.277 to 0.771 and exhibited a similar change to that in the constant n. Figure 4 shows the changes in the pF curves that were predicted using the van Genuchten model (VG) and real pF values. Table 4 shows the R^2 and RMSE values that were used in the assessment of the predicted and real data.

The pF curves revealed that the predictions of the van Genuchten model was more realistic for the B0 and B2 applications both in the dry and wet regions. However, in other applications, although the θ_S and θ_r were similar, the real and predicted values of the moisture constants were significantly different. Abdulwahhab (2020) reported that θ_r can be predicted with a high accuracy in the dry region and stated that there were significant differences in the measured and calculated values depending on the increase in the application dose. This study was in compliance with the literature. In their study in which some algorithms and the Retc – Rosetta programs are compared in terms of their effectiveness in the determination of the van Genuchten model, Yang and You (2013) reported that Rect well-reflected the moisture content but failed to determine the θ_r values used in the model.

The highest R^2 value between the real and predicted values was obtained in the B0 application with a value of 0.901 and the other R^2 values were 0.601, 0.833, 0.544 and 0.582. The lowest RMSE value was obtained in the B0 application with a value of 0.061 cm^3 cm^{-3}, followed by 0.078 (B2), 0.155 (B1), 0.177 (B4) and 0.207(B3) cm^3 cm^{-3}, respectively. A high R^2 and low RMSE improve the reliability of the models in the assessment of the accuracy of the models. Thus, the highest reliability with the van Genuchten model was obtained in the control (B0) application. The lowest accuracy was obtained in the moisture characteristic curves obtained in the B3 and B4 applications. The lack of regular increases in the moisture constants resulting from the application of organic material led to differences in the shapes of the curves. Therefore, the values predicted by the van Genuchten model differed due to the differences in the shape parameters.

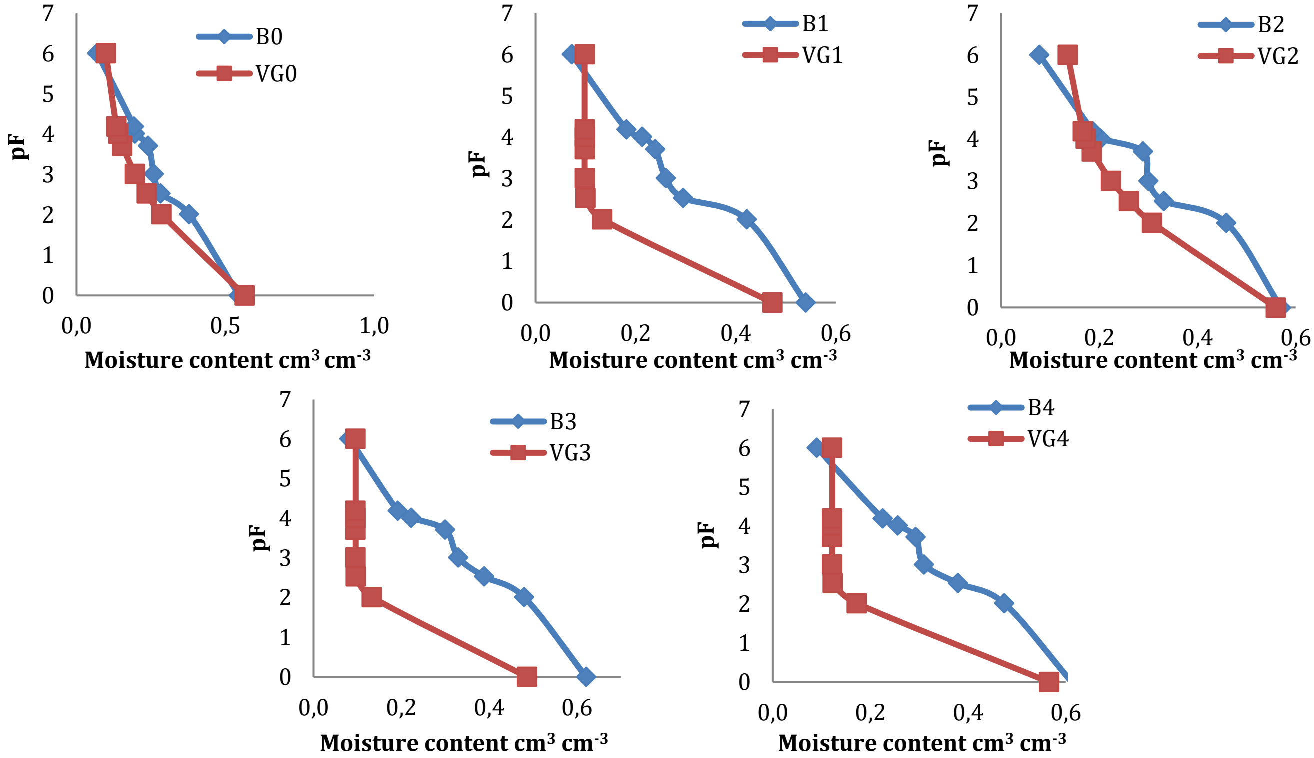

Figure 4. Variation of pF curves estimated by Van Genuchten model and determined in reality

Table 4. Model evaluation for soil moisture curve

Applications	Equation	R^2	RMSE
B0	Y= 1.0089X-0.0471	0.901	0.061
B1	Y=0.7018X-0.0455	0.601	0.155
B2	Y=0.7981X+0.0104	0.833	0.078
B3	Y=0.5926X-0.0443	0.544	0.207
B4	Y=0.7421X-0.061	0.582	0.177

R^2:coefficient of determination, RMSE: root mean square error; Y: actually determined water content, X: predicted water content

Conclusion

The study investigates the effects of the applications of different ratios of biogas waste on some soil properties and soil moisture characteristic curve (pF). The predictive accuracy of the van Genuchten model for hydraulic properties was also examined. The biogas waste applications were determined to be more effective on the increase in moisture in the wet region of the moisture characteristic curve than in the dry region. The effects of the B3 and B4 applications on the soil properties were either generally similar or the B3 application can be considered more effective. Therefore, we recommend the B3 application as the effective dose considering the economic aspects of its use and improvements in the soil physical properties.

Using the van Genuchten model, the most realistic predictions were obtained in the control (B0) application and the model had high predictive accuracy. The lack of a regular change in the moisture constants with the biogas waste applications led to changing shape parameters that were determined on the pF curve and, thus, the predictive accuracy of the applications was lower. The van Genuchten model achieved an accuracy of about 70% in the examined region. We recommend testing the model for larger areas and different soils. Conventional agriculture is carried out in the study area. Therefore, organic materials of different forms are applied to the soils. The results of this study revealed the need to investigate the relationship between the diversity of the organic materials added to soils and soil moisture characteristics. Moreover, expanding the study area will greatly contribute to the irrigation and soil management in the area in terms of labor and economy by improving the predictive power.

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Eurasian Journal of Soil Science 2021, 10(2), 150- 160

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

Impact of deforestation and subsequent land-use change on soil quality

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Article Info

Received : 11.06.2020
Accepted : 19.11.2020
Available online : 20.12.2020

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Abstract

Deforestation for conventional farming has affected soil quality (SQ) worldwide. The goal of our study was to evaluate the impact of land use change, from forest to subsistence farming, on SQ in Benin. Composite soils from forest, horticultural, agricultural, fallow, and degraded lands were collected to analyze for chemical and physical properties. Using inductive additive approach and principal component analysis (PCA), generalized (SQI_g) and minimum dataset SQ (SQI_{MDS}) indices were calculated. Results showed that upon conversion of forest, total organic carbon (TOC) decreased by more than 2 folds in fallow and degraded soils. A similar impact was observed on total nitrogen (TN). Soil cation exchange capacity (CEC) and base saturation (BS) were significantly higher under horticulture than in degraded lands. In contrast, carbon protection capacity (CPC) was significantly higher by 12-41% in forest soils compared to the lowest in degraded soils. Among the land uses, aggregate stability index (ASI) was, by far, the lowest (3.2%) in degraded soils and highest (7.5%) in horticulture soils. Soils under fallow and degraded lands had SQI_g decreased by 5 to 16%, when compared with forest, indicating a significant SQ degradation. In contrast, SQI_g under horticulture increased by 5%, suggesting a similar or even an improvement in SQ comparable to the forest. The PCA-based SQI_{MDS} significantly and positively accounted for 70% of the variability in SQI_g with a non-significant biasness ($6 \pm 3.8\%$ at $p<0.12$). The TOC and CPC contributed most (20.9% and 21.1%) followed by clay (14.1%) and Ca^{+2}:(Mg^{+2} + K^{+1} + Na^{+}) (13.7%), TOC (11%), and ASI (10.5%) compared to lowest by K^{+} (9.7%) to account for SQI_{MDS} variability. Our results concluded that there was no significant difference between SQI_g and SQI_{MDS}, which justified our results to use SQI_{MDS} detecting management-induced changes in SQ.

Keywords: Soil degradation, slush-burn agriculture, Carbon protection capacity, minimum dataset, Soil quality.

Introduction

Developing and improving soil quality (SQ) is urgently needed to support global food security. Management-induced temporal changes in SQ attributes and its processes, in turn, can affect soil functions to influence plant growth and food production; therefore, understanding and evaluating the impact of land use change on SQ is critical to enhance ecosystem services (Tellen and Yerima, 2018; Nguemezi et al., 2020). In Africa, SQ has been degrading rapidly due to subsistence farming by an ever-rising population, this is a critical issue in

: https://doi.org/10.18393/ejss.843861
: http://ejss.fesss.org/10.18393/ejss.843861
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

Africa that is adversely impacting agriculture and food security (Moebius-Clune et al., 2011; Alarima et al., 2020). It is reported that subsistence farming, is often associated with poor SQ, leading to a decline in agricultural productivity (Obalum et al., 2012).

In Benin, as one of the small Sub-Saharan West African countries, the impact of subsistence farming on SQ is a major growing agronomic and environmental concern. Due to rapid population growth, large areas under primary natural forest were deforested and subsequently converted into conventional agriculture and other anthropogenic activities (Ouedraogo et al., 2010). Increasing population growth, particularly in southern Benin, has led to the degradation of natural forest and shrubby fallows due to subsistence farming, resulting in accumulation of marginal lands (Félix et al., 2015). The assessment of soil degradation in Benin showed negative balances and consequently, the performance of agricultural production was reduced by 62% (Félix et al., 2015). Due to lack of available alternative technologies and knowledge, small-scale farmers are over-exploiting natural resources and consequently, affected soil's functional capacity.

Agricultural land use in Benin depends largely on topographic position, as rain fed subsistence cropping is less intensified in the foothills of the valleys compared to the fringes and uplands (Prasad and Nolte, 1995). While about 35% of the area in the foothills of the valleys is under cultivation, 74% of the area is under cultivation on the fringes, and 30% of the area is under cultivation on the uplands. However, agriculture in Benin remains vulnerable due to the use of low yield crop varieties, lack of inputs, and subsistence farming practices that are not adapted to climate change impacts.

To maintain soil productivity, chemical fertilizers and animal manures are applied to agronomic crops, homestead gardens, and other production areas (Sangare et al., 2012; Perrin et al., 2015). In recent years, the orchard growers (such as pineapples) in southern Benin have started to apply unconventional sources of nutrients and soil amendments, such as biosolids and greywater, to enhance SQ to support for economic crop production (Kpera et al., 2019).

Evaluation of SQ is commonly performed using laboratory analysis of antecedent soil physical, chemical, and biological properties in response to management practices (Marzaioli et al., 2010; Aziz et al., 2013; Davari et al., 2020). There is an urgent need to assess the impact of on-going land-use change, upon deforestation and conversion of forest, on SQ in Benin. Moreover, climate change is not just a threat to terrestrial ecosystems in the distant future; it is already affecting African agroecosystems, including Benin (Sintayehu, 2018).

The most common and effective strategy for adapting to deforestation and climate change is to develop sustainable agricultural practices to maintain and develop SQ. However, there is a lack of information on the effects of deforestation and conversion of land on SQ in Benin. The objective of our study was to evaluate the impact of diverse land use changes on soil chemical and physical properties, and their contribution to mathematical- and statistical model based SQ evaluation in southern Benin.

Material and Methods

Study area and soil sampling

The study was conducted in the vicinity of the Ze region of southern Benin, West Africa. While the highest precipitation (1200 to 1300 mm) is confined to the southern region, the lowest values are recorded in the northern region (900 to 950 mm) of Benin. Mean annual air temperatures range from 26-28°C and occasionally reach 35-40°C in northern localities.

Ferrallitic-ferruginous soil (Ferrasols and Acrisols according to the USDA and FAO classification, respectively) with a dominant sandy loam-loamy sand texture. Geo-referenced composite soils (0 to 15 cm depth) were collected from (1) Forest (n = 18) that consists of Pawpaw (*Asimina triloba*), teak (*Tectona grandis*), and palm (*Elaies guinenses*); (2) Horticulture (n = 36) that consists of lands under banana (*Musa × paradisiaca*), pineapple (*Ananas comosus*), and tomato (*Solanum lycopersicum*); (3) Agriculture (n = 24) that consists of lands under cassava (*Manihot esculenta*), yams (*Dioscorea* spp.), green beans (*Phaseolus vulgaris*), maize (*Zea mays*), and cotton (*Gossypium* spp.); (4) Fallow (n = 42); and (5) Degraded (n = 18) what consists of lands under the dominance of elephant grass (*Imperata cylindrica*).

Soil management and cultural practices

Soil management and cultural practices differed among land uses. While the routine application of liming materials and chemical fertilizers by small-scale farmers is economically unfeasible, soils under small-scale both horticultural and agricultural crops were seasonally amended with household ashes, animal manures, composts, and other unconventional organic sources as a neutralizer of soil acidity and supplier of nutrients for tropical acid soils. Annual household animal manuring of soil generally in between 4 to 10 ton ha^{-1}, on a wet weight basis. However, liming and chemical fertilizations were performed occasionally more for agricultural crops than for horticultural crops. Liming @ 0.5 to 2 ton ha^{-1} was applied to the field with along with N, P, and K fertilization 30-50, 25-45, and 120-45 kg ha^{-1}. The horticultural crops were occasionally irrigated manually. Standard cultural practices associated with planting and harvesting of crops were performed.

Soil processing and analysis

The field-moist soils were collected in sealable plastic bags, then gently sieved through 4-mm mesh to remove stones, roots, and large organic residues, air-dried under shade at room temperature (~ 25°C) for a period of 15-days, grinded with porcelain mortar and pestle, and finally passed thru a 2-mm sieve before analysis.

Soil pH was determined in distilled water at a soil: water ratio of 1:2.5 using a pH glass electrode. Total organic C (TOC) content was determined by the modified Walkley-Black wet digestion method (Jackson, 1958). Total N (TN) was determined by microkjeldahl digestion and distillation method. The available P (AP) was measured by following the Bray-1 method after extracting the soil with a 0.3M NH_4F in 0.5M HC1 mixture followed by spectrophotometric determination by the ascorbic acid method (Murphy and Riley, 1962).

Soil cation exchange capacity (CEC) was determined by NH_4-acetate extraction and stem distillation method (Rhoades, 1982). The exchangeable cations were extracted with a 1M neutral NH_4-acetate solution and were determined by atomic absorption spectrophotometry. Using the exchangeable cations data, the Ca^{2+}: Mg^{2+} and Ca^{2+}: (Mg^{2+} + K^{2+} + Na^{+}), as measures of soil balancing and dispersion, were calculated (Schulte and Kelling, 1993). Aggregate stability index (ASI) relating soil resistance to external disruption forces was assessed using Pieri (1992). Soil particle size analysis (sand, silt, and clay contents) was determined by the standard Bouyoucos hydrometer method. While total surface area of soil was calculated by following Thein and Graveel (1997), the carbon protection capacity (CPC) was calculated by following Hassink (1997).

Derivation and calibration of soil quality

A modified inductive additive approach (Huddleston, 1984; Wymore, 1993; Aziz et al., 2013) was followed to calculate for SQ. First, a generalized SQ index (SQI_g) was calculated by accounting the status or concentration of all measured or calculated soil properties' potential SQ indicators under agriculture, horticulture, fallow, and degraded lands considering those were once the same as that of the soils under the adjacent natural forests prior to conversion.

Data were normalized considering assumptions "higher values of soil properties are better indicators of SQ" in response to management practices (Wymore, 1993; Aziz et al., 2013). Datum (x) of each individual soil property was normalized (x_i) relative to the maximum value (x_{max}) of that particular property to transform into ≥ 0 to 100 based on linear scoring functions, $x_i = (x \times x_{max}^{-1})$. By summing all the x_i's and dividing by the number of x_i's (n), the SQI_g was calculated:

$$SQI_g = \Sigma\,(x_i + ... + x_n)\, n^{-1}$$

The calculated SQI_g ranged from ≥0 to 100, with 100 being excellent soil quality and >0 being extremely poor soil quality. Data were normalized to convert for removing variable units into a unit-less format, reducing heterogeneous variances of the errors, and simplifying the relationship between random errors influencing the SQ properties.

To avoid any biasness and data redundancy in SQI_g, a minimum dataset (MDS) of orthogonal soil properties was selected using Principle Component Analysis (PCA) to derive for SQI_{MDS} (Chandel et al., 2018). All the original untransformed data of each soil property were included in the PCA model using Origin Pro 2018. Under a given PC, each variable had corresponding eigenvector weight value or factor loading. The PCs that had eigen value >1.0 and explained at least 5% of the variation in the data were selected (Rezaei et al., 2006). When more than one factor was retained under one PC, the multivariate correlation was performed to select orthogonal soil attributes for calculating the SQI_{MDS}. To calibrate, the SQI_g was then regressed on the SQI_{MDS} for accounting significant variations in SQI_g as explained by the PCA selected SQI_{MDS}.

Statistical analysis

One-way analysis of variance procedure of the SAS 9.3 was used to evaluate the effects of land use on soil properties and SQ indices. The Least Significant Difference (LSD) test was used to separate the means of the dependent variables in response to predictor variables at $p \leq 0.05$ unless otherwise mentioned. Averaged across all the data, a separate one-way ANOVA was performed to test whether the SQI_g and SQI_{MDS} comparisons produced similar differences in all the dataset. SigmaPlot® was used for regression and correlation analyses.

Results and Discussion

Impact of land-use changes on soil properties

Soil pH varied significantly by the impact of land-use changes upon conversion of forest (Table 1), with lowest pH (5.7) in degraded soils and highest pH (7.1) in horticultural soils. Upon conversion of forest, TOC content decreased by 1.6 to 2.7 folds in soils under agriculture and degraded lands. Soils under horticulture and fallow had more than 2 folds less TOC than in soils under forest. A similar impact was observed on TN content. The AP availability was low, with highest AP content in horticultural and agriculture soils relative to forest and degraded soils. While a significantly higher Ca content was measured in both horticultural and agricultural soils than in degraded, fallow, and forest soils (Table 2), K^+ content was higher in horticultural soils in soils under other land use systems. Soils under agriculture and horticulture had significantly higher Ca^{2+}: Mg^{2+} and Ca^{2+}: (Mg^{2+} + K^+ + Na^+) and degraded soils had the lowest Ca^{2+}: Mg^{2+} and Ca^{2+}: (Mg^{2+} + K^+ + Na^+) values.

Table 1. Impact of land-use change on soil pH, total organic carbon, total nitrogen, and available phosphorus upon conversion of primary natural forest in Southern Benin.

Land-use/ Land covers	pHw (1:2.5)	TOC (g kg^{-1})	TN (g kg^{-1})	CN ratio	AP (mg kg^{-1})
Forest (control)	6.6 $^{b¥}$	9.3 ^{a}	0.85 ^{a}	11.0 ^{a}	4 ^{c}
Horticulture	7.1 ^{a}	7.1 ^{b}	0.61 ^{b}	12.4 ^{a}	10 ^{a}
Agriculture	6.8 ^{ab}	5.7 ^{b}	0.49 ^{b}	11.8 ^{a}	8 ^{ab}
Fallow	6.8 ^{ab}	7.0 ^{b}	0.61 ^{b}	11.3 ^{a}	6 ^{bc}
Degraded	5.7 ^{c}	3.5 ^{c}	0.28 ^{c}	12.5 ^{a}	4 ^{c}

¥ Means separated by same lower-case letter under each column were not significantly different at p≤0.05 among land uses.

Table 2. Impact of land-use change on soil exchangeable calcium, magnesium, potassium, and sodium contents, cation exchange capacity, and base saturation upon conversion of primary natural forest in southern Benin.

Land-use/ Land covers	Ca^{2+}	Mg^{2+}	K^+	Na^+	Ca^{2+}: Mg^{2+}	Ca^{2+}: (Mg^{2+} K^+ Na^+)	CEC	BS
	(mg/kg)						(cmol/kg)	(%)
Forest (control)	126 $^{b¥}$	20 ^{a}	20 ^{b}	2 ^{a}	3.8 ^{b}	2.8 ^{bc}	3.8 ^{b}	33.9 ^{b}
Horticulture	220 ^{a}	23 ^{a}	37 ^{a}	4 ^{a}	5.6 ^{a}	3.6 ^{ab}	4.7 ^{a}	44.7 ^{a}
Agriculture	199 ^{a}	17 ^{a}	18 ^{b}	2 ^{a}	6.9 ^{a}	4.9 ^{a}	3.8 ^{b}	46.7 ^{a}
Fallow	110 ^{b}	20 ^{a}	24 ^{b}	3 ^{a}	3.4 ^{b}	2.3 ^{bc}	3.6 ^{b}	33.3 ^{b}
Degraded	69 ^{c}	20 ^{a}	16 ^{b}	2 ^{a}	2 ^{c}	1.6 ^{c}	4.2 ^{ab}	20.2 ^{c}

¥Means separated by same lower-case letter under each column were not significantly different at p≤0.05 among land uses.

Similarly, CEC was significantly higher by 19 to 24% in soils under horticulture compared to lowest in degraded soils. Soils under both agriculture and horticulture had the highest base saturation (BS) as compared lowest in fallow and degraded soils. Highest values of TOC: Ca^{2+} were measured in soils under forest followed by fallow and degraded soils when compared with soils under horticulture and agriculture, respectively (Table 3). The TOC: clay was highest in soils under forest compared to lowest in degraded soils. Similarly, the CPC was significantly higher by 12 to 41% in forest soils followed by agriculture, horticulture, and fallow soils compared to the lowest in degraded soils. The silt content was significantly lower in degraded soils when compared with forest (Table 3). Even soils under horticulture, agriculture, and fallow had lower silt content than in forest soils. In contrast, soils under horticulture had the highest surface area (18.8 m^2 g^{-1}) relative to lowest surface area (14 m^2 g^{-1}) in agriculture soils (Table 3). The impact of land-use change on ASI with conversion of primary natural forest showed that the ASI was, by far, the lowest (3.2%) in degraded soils and highest (7.5%) in horticulture soils (Figure 1). Likewise, soils under forest and agriculture had higher ASI values than the degraded soils. Even the fallow soils had higher ASI (6%) than the degraded soils.

Table 3. Impact of land-use change on sand, silt and clay, carbon protection capacity, and surface area in soils upon conversion of primary natural forest in southern Benin.

Land-use/ Land covers	Sand	Clay	Silt	Surface area	TOC: Ca	TOC: Clay	CPC
		(%)		(m^2 g^{-1})			(g kg^{-1})
Forest (control)	126 $^{b¥}$	20 ^{a}	20 ^{b}	2 ^{a}	3.8 ^{b}	2.8 ^{bc}	3.8 ^{b}
Horticulture	220 ^{a}	23 ^{a}	37 ^{a}	4 ^{a}	5.6 ^{a}	3.6 ^{ab}	4.7 ^{a}
Agriculture	199 ^{a}	17 ^{a}	18 ^{b}	2 ^{a}	6.9 ^{a}	4.9 ^{a}	3.8 ^{b}
Fallow	110 ^{b}	20 ^{a}	24 ^{b}	3 ^{a}	3.4 ^{b}	2.3 ^{bc}	3.6 ^{b}
Degraded	69 ^{c}	20 ^{a}	16 ^{b}	2 ^{a}	2.0 ^{c}	1.6 ^{c}	4.2 ^{ab}

¥Means separated by same lower-case letter under each column were not significantly different at p≤0.05 among land uses.

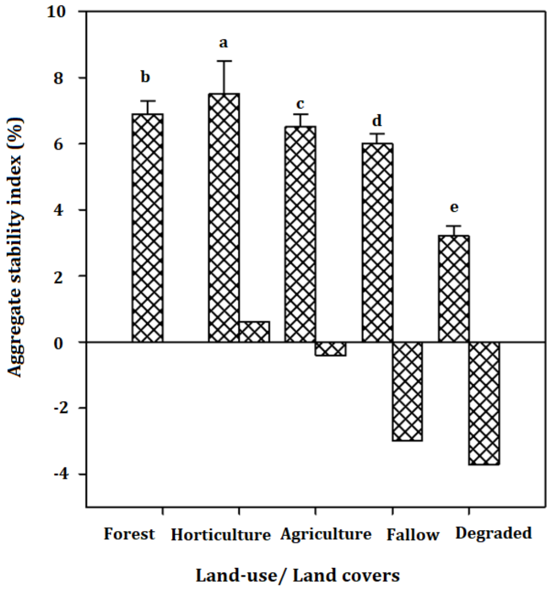

Figure 1. Impact of land-use change on soil aggregate stability index (ASI) upon conversion of primary natural forest in Southern Benin (The upward and downward second bar represented the increased and decreased ASI in comparison with forest, respectively).

Significantly lowest pH in degraded soils was due to the consequences of the leaching of basic cations and dominance of exchangeable H^+ and Al^{+3} compared to other soils (Neina, 2019). Accelerated leaching of basic cations (Ca, Mg, K, etc.) due to high rainfall and erosion was also responsible for causing acidity in degraded soils. A greater demand for, and uptake, of basic cations by forest vegetation over time was responsible for the more acidic nature of soils than horticulture, agriculture, and fallow soils.

In contrast, biomass ash amended from traditional slush-burn practices on horticulture, agriculture, and fallow soils could have recycled basic cations to maintain or increase pH, at least temporarily (Voundi Nkana et al., 1998). Moreover, liming of intensively managed horticultural and agricultural fields is likely one of the contributing factors for slightly higher pH relative to low pH values in degraded soils. Greater biomass additions to the soil surface through leaf fall under forest might have contributed to higher TOC contents.

A reduced contact between surface accumulated high C: N litter-fall and microbial diversity favored slower decomposition of residues with a higher anabolism under physically undisturbed forest ecosystems (Islam and Weil 2000a; Adaikwu et al., 2012). In contrast, the lower levels of TOC in degraded soils may have resulted over time from a combination of several factors, such as lower C inputs because of sparse vegetation and less biomass return, slush-burn practices, accelerated soil erosion, rapid decomposition due to high relative humidity and temperatures, and uncontrolled livestock grazing (Mullar-Harvey et al., 1985). Likewise, a relatively lower TOC content in soils under horticulture and agriculture than in forest soils could be due to the reduced amount of crop residues being returned to the soil, higher rates of soil organic matter (SOM) oxidation as a result of frequent plowing and slush-burn practices, and removal of harvested green leafy materials (Moges and Holden, 2008; Yimer et al., 2007). In addition, frequent plowing may have accelerated the breakdown of soil aggregates and exposure of aggregate protected carbon to microbial oxidation by changing the O_2 diffusion, moisture, and temperature regimes (Reicosky and Forcella, 1998).

As N is stoichiometrically linked with C in SOM (Kirkby et al., 2013), a greater TN content in forest soils than in horticultural and agricultural soils was probably due to higher litter input, C: N stoichiometry, and biological N fixation by the naturally grown leguminous vegetation (Moges et al., 2013). In contrary, a lower amount of TN in soils under horticulture and agriculture was due to removal of N-enriched leafy biomass and grains during harvest and insufficient replenishment of N through manure or chemical fertilizers. The lowest TN content in degraded soils was due to C:N stoichiometry, soil erosion, and lack of continuity of N fertilization. Likewise, a significantly lower amount of AP in degraded soils was likely associated with lack of P fertilization and higher P fixation by ferruginous minerals (Yimer et al., 2007; Koda et al., 2018). While P fixation is a problem in Ferrallitic-ferruginous soils, the higher TOC content in horticulture soils might have decreased P fixation and increased AP (Moges et al., 2013; Kalu et al., 2015). Moreover, a relatively higher AP content in soils under horticultural might be due to biomass ash application, manure amendments, and P fertilization to support growing crops and vegetables.

A higher content of Ca^{2+} and K^+ in soils under horticulture was probably due to the application of household biomass ashes, liming, and fertilization, as biomass ash is a good source of calcium, potassium, phosphorous and magnesium (Voundi Nkana et al., 1998). Moreover, diverse vegetative cover reportedly increased the recycling of Ca contents in soil (Moges et al., 2013). The increased availability of K^+ in soils under horticulture might also have resulted from reduced K^+ fixation and a release of K^+ due to the interaction of TOC with clay minerals (Sharma et al., 2001). The Ca^{2+}: (Mg^{2+} + K^+ + Na^+), as measures of soil's resistance to aggregate dispersion in response to rainfall impacts, erosion, and flooding, was higher in soils under horticulture and agriculture. This may be associated with the application of household biomass ashes, liming, and recycling of basic cations from the subsoil by the vegetation and returning them into the topsoil (Yimer et al., 2007).

The BS, as an indicator of the cationic fertility status of soil (Chesworth, 2008), was significantly higher under agriculture and horticulture compared to forest, in response to manure and biomass ash amendments, liming, and chemical fertilization. Biomass ash from traditional slush-burn practices, lime, and unconventional sources of fertilization (Kpera et al., 2019) could have recycled basic cations to maintain and/or improve both CEC and BS in soils under horticulture and agriculture. On the contrary, the lower CEC and BS were related to the low SOM and nutrient content, erosion, and lack of chemical fertilization and liming. A greater recycling of Ca^{2+} showed higher Ca^{2+}: Mg^{2+} and Ca^{2+}: (Mg^{2+} + K^+ + Na^+) values in soils under horticulture and agriculture compared to degraded soils. However, both Ca^{2+}: Mg^{2+} and Ca^{2+}: (Mg^{2+} + K^+ + Na^+) values in all soils were below the critical limits of a balanced soil. In contrast, a relative shortage of Ca, CEC, and BS in degraded soils was readily reflected in the lower Ca^{2+}: (Mg^{2+} + K^+ + Na^+) levels as an indicator of degraded and unbalanced soils.

A considerably lower silt content soil, especially in degraded soils than in forest soils, was most likely because of preferential removal of silt by soil erosion. In contrast, degraded soils with lower values of surface area reflected in the lower values of CPC. A greater amount of TOC with improved aggregate stability in forest soils might have developed more CPC than in horticultural, agricultural, fallow, and degraded soils because physical disturbance periodically breaks down macroaggregates and exposes aggregate protected C (e.g. particulate organic matter) and accelerates SOM decomposition by opportunistic microbes (Islam and Weil, 2000b). The soils under horticulture had higher ASI than agriculture, which suggested that soils under horticulture had improved fertility more than the soils under agriculture (Zhang et al., 2016). The difference of ASI between horticulture and agriculture was probably associated with variable TOC contents, which influenced the API (Onweremadu et al., 2007; Durigan et al., 2017). In addition, both horticulture and agriculture soils might have created conditions for the accumulation of SOM, thereby causing improved ASI (Nimmo et. al., 2002). It is reported that a decrease in ASI leads to the degradation of macroaggregates, dispersion of finer soil particles, and sealing of pores with dispersed finer particles (Schwartz et al., 2003; Ezeaku, 2015).

Impact of land-use change on soil quality

The SQI_g, calculated by including all the data, reflected an overall status of the integrated soil properties by the impact of land-use changes (Figure 2). The fallow and degraded soils had lower SQ by 5 and 16%, respectively, indicating a significant SQ degradation over time when compared with the forest. The values of SQ of degraded lands were also significantly lower by 9 to 11% than that of agriculture and fallow lands. On the contrary, the SQ under horticulture was significantly higher by 5%, suggesting a similar or even an improvement in SQ compared to forest. Islam and Weil (2000a) reported similar results upon the conversion of forests for conventional agriculture.

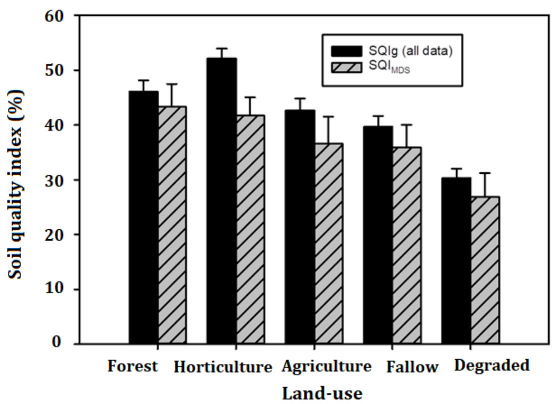

Figure 2. Impact of land-use change on generalized (SQIg) and minimum dataset (SQIMDS) based soil quality indices upon conversion of primary natural forest in Southern Benin.

The use of PCA to identify weighted soil attributes showed dissimilarities within land use systems (Figure 3). Thus, the Ca^{2+}: Mg^{2+}, Ca^{2+}: (Mg^{2+} + K^+ + Na^+) and BS for PC-1, the K, Na and TOC: clay for PC-2, the CPC for PC-3, the ASI for PC-4, and the clay for PC-5 were identified based on highly weighted eigenvectors, therefore those were selected to further calculate for SQI_{MDS} and calibrate with SQI_g to evaluate its applicability.

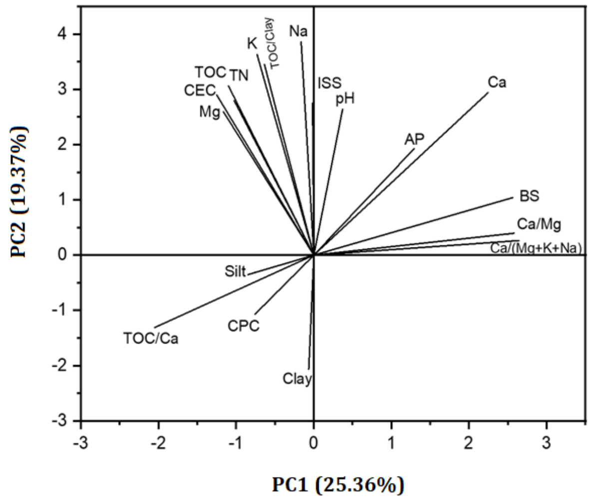

Figure 3. Impact of land-use change on distribution of weighted variables using principal component analysis.

The highly weighted attributes of PC-1, the Ca^{2+}: Mg^{2+}, and Ca^{2+}: (Mg^{2+} + K^+ + Na^+) were significantly correlated with each other (Table 4), thereby the Ca^{2+}: (Mg^{2+} + K^+ + Na^+) with the highest factor loading (0.42) was chosen for SQI_{MDS} computation. In PC-2, Na^+, K^+ and TOC: clay showed highest factor loading; however, Na showed a significant correlation with K^+, thus, only K^+ and TOC: clay were included because K^+ (0.35) is one of the important attributes in African soil. The CPC (0.49) was the only attribute chosen from PC-3.

Table 4. Principal component analysis to select attributes for calculation of soil quality index based on minimum datasets (SQI_{MDS}) under diverse land-use systems.

Soil attributes	Components				
	PC-1	PC-2	PC-3	PC-4	PC-5
pH	0.06	0.25	-0.17	0.18	-0.08
TOC	-0.17	0.27	0.37	-0.20	0.16
TN	-0.18	0.29	0.35	-0.20	0.15
Ca	0.36	0.28	0.12	0.05	0.01
Mg	-0.19	0.25	-0.21	0.26	0.11
Ca: Mg	**0.42**	0.04	0.19	-0.05	-0.02
K	-0.12	**0.35**	-0.02	0.25	0.20
Ca: (Mg^{2+} + K^+ + Na^+)	**0.43**	0.03	0.19	-0.09	-0.02
Na	-0.03	**0.37**	0.02	0.26	0.11
CEC	-0.20	0.28	-0.10	0.22	-0.13
BS	**0.41**	0.10	0.12	-0.01	0.09
AP	0.21	0.19	0.01	0.22	0.14
Clay	-0.01	-0.20	0.25	0.24	**0.59**
Silt	-0.14	-0.03	0.45	0.22	-0.37
TOC: Ca	-0.33	-0.13	0.15	-0.22	0.22
TOC: Clay	-0.10	**0.33**	0.10	-0.28	-0.47
CPC	-0.12	-0.10	**0.49**	0.28	-0.10
ASI	-0.01	0.27	-0.14	**-0.48**	0.28
Eigen Values	4.60	3.50	3.00	1.90	1.30
Variance (%)	25.4	19.40	16.70	10.80	7.00
Cumulative Variance (%)	25.4	44.70	61.40	72.20	79.30

Bold numbers are 'highly weighted' eigenvectors which are within 10% of the highest values under same PC

The TOC factor loading was (0.35), which is one of the most important attributes and thus, TOC was included in SQI_{MDS}. In PC-4 and PC-5, the ASI (0.48) and clay (0.59) were shown as the highest factor loadings. Considering both eigenvectors and correlation matrix (Table 4 and 5), seven weighted soil attributes Ca^{2+}: (Mg^{+2} + K^+ + Na^+), K^+, TOC: Clay, CPC, TOC, ASI and clay were selected for SQI_{MDS} computation.

Table 5. Correlation among the different soil physical and chemical attributes.

Soil attributes	pH	TOC	TN	Ca	Mg	Ca: Mg	K	Ca: (Mg+K+Na)	Na	CEC	BS	AP	Clay	Silt	TOC: Ca	TOC: clay	CPC
TOC	-0.01																
TN	0.03	0.99															
Ca	0.27	0.13	0.12														
Mg	0.21	0.08	0.12	-0.03													
Ca: Mg	0.05	-0.06	-0.10	0.75**	-0.54												
K	0.29*	0.22	0.26	0.09	0.43	-0.14											
Ca:(Mg^{2+}K^{+}Na^{+})	0.04	-0.04	-0.08	0.79**	-0.52**	0.95**	-0.28										
Na	0.24	0.19	0.23	0.27	0.30	0.03	0.83**	-0.07									
CEC	0.38**	0.23	0.27	0.01	0.58	-0.36	0.35**	-0.37	0.27								
BS	0.07	-0.08	-0.10	0.83**	-0.22	0.82**	-0.02	0.84**	0.11	-0.49**							
AP	0.15	-0.03	-0.02	0.52**	0.15	0.31	0.07	0.31*	0.34*	0.01	0.42*						
Clay	-0.21	0.13	0.10	-0.05	-0.11	0.06	-0.07	0.08	-0.15	-0.12	0.02	-0.01					
Silt	-0.21	0.39**	0.36**	-0.08	-0.13	-0.03	0.03	-0.06	0.07	0.08	-0.14	-0.10	0.18				
TOC: Ca	-0.37**	0.41**	0.40**	-0.69**	-0.08	-0.50	0.05	-0.55**	-0.05	-0.15	-0.53**	-0.35**	0.18	0.21			
TOC: Clay	0.06	0.49**	0.53**	0.16	0.13	-0.07	0.24	-0.08	0.30	0.26	-0.05	-0.03	-0.61**	0.24	0.09		
CPC	-0.26	0.39**	0.35**	-0.09	-0.15	-0.01	-0.01	-0.02	0.01	0.02	-0.11	-0.09	0.52**	0.93**	0.24	-0.02	
ASI	0.07	0.35**	0.39**	0.19	0.10	-0.02	0.14	0.02	0.10	0.13	0.03	-0.03	-0.26	-0.51**	0.01	0.33*	-0.54**

*Correlation is significant at the 0.05 level (2-tailed) & **Correlation is significant at the 0.01 level (2-tailed).

Figure 4 showed that contribution of TOC towards SQI_{MDS} was highest in forest (25.2%) followed by fallow (22.7%), horticultural (20.1%), agricultural (18.2%), and degraded lands (0.15). For K^+, the highest contribution toward SQI_{MDS} was observed under horticulture (13.1%) and lowest contribution under forest (6.6%) and agriculture (7.4%). The Ca^{2+}: (Mg^{2+} + K^+ + Na^+) contributed maximum to SQI_{MDS} under agriculture (22.5%) compared to minimum under forest (9.3%). In contrast, clay content exerted highest contribution for SQI_{MDS} in degraded land (18.9%) and minimum under forest (10.7%). The TOC: clay contribution toward SQI_{MDS} was highest under forest (15.4%) and lowest with agriculture (6.2%). CPC contribution to SQI_{MDS} was maximum under degraded soils (29.3%) compared to others (17.2 to 20.7%). However, the ASI contribution for SQI_{MDS} was highest for forest (12.1%) and lowest of 8.1% in degraded soils.

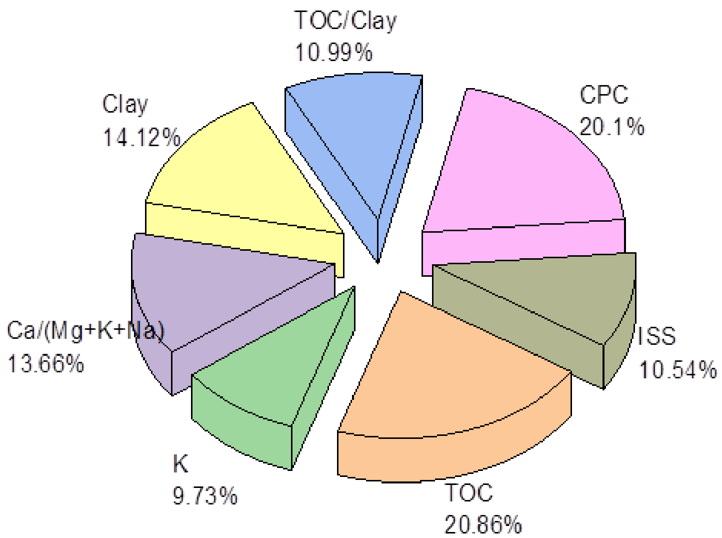

Figure 5. Impact of land-use change on overall contribution of weighted variables.

Results showed that among the selected MDS, the TOC and CPC contributed most (20.9% and 21.1%) followed by clay (14.1%) and Ca^{2+}: (Mg^{2+} + K^+ + Na^+) (13.7%), TOC: clay (11%), and ASI (10.5%) compared to the lowest by K^+ (9.7%) to account for variability in SQI_{MDS} (Figure 5). The PCA-based SQI_{MDS} showed a similar pattern, but slightly lower SQ values in response to land use changes (Fig. 2). While the highest SQ was calculated for forest (43.3%) in SQI_{MDS}, the highest SQI_g calculated for horticulture (52.1%). When regressed (Figure 6), the SQI_{MDS} linearly accounted for 70% of the variability (R^2) in SQI_g, with a significant slope (Δy: Δx as b) of 0.988 ($p \geq 0.0001$). The intercept (a) of the linear equation (y = a + bx) suggested that SQI_{MDS} was slightly underestimated (6 ± 3.8%) to predict SQIg; however, that was statistically non-significant ($p \geq 0.12$) between SQI_g and SQI_{MDS}. The t-test showed that there was no significance between SQI_g and SQI_{MDS} to predict for SQ in response to land use change.

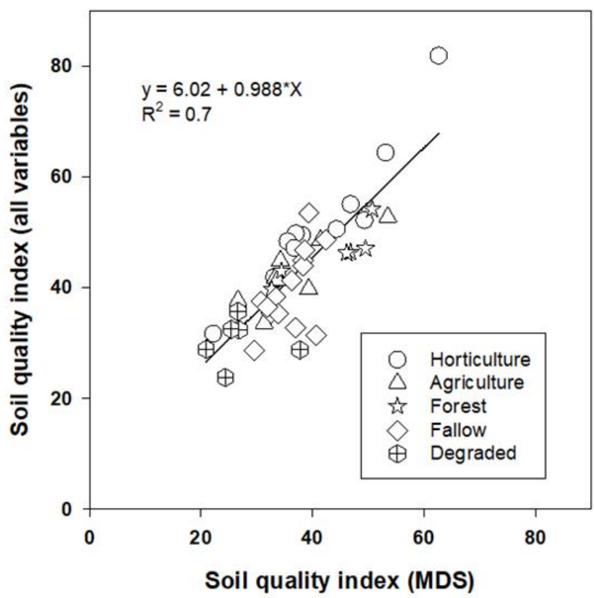

Figure 6. Impact of land-use change on relationship between generalized (SQIg) and minimum dataset based (SQIMDS) soil quality indices.

Conclusion

Results showed that the impact of deforestation for land use changes resulted in the deterioration of SQ in Benin. Soil physical and chemical parameters were significantly influenced by land use changes that impacted SQ. Horticulture soils had better SQ than other land uses upon the conversion of natural forest. The PCA identified seven soil attributes including TOC, Ca^{2+}: (Mg^{+} + K^{+} + Na^{+}), K, TOC: clay, CPC, ASI and clay for SQI_{MDS} computation. The PCA-based SQI_{MDS} showed a similar pattern, but slightly lower values in SQI_{g} by the impact of land-use changes upon conversion of primary forest. The SQI_{MDS} significantly accounted for 70% of the variability in predicting SQI_{g}. Results showed that there was no significance between SQI_{g} and SQI_{MDS} to predict SQ in response to land-use change. While temporal deforestation for land use change significantly degrading SQ over time, future research is needed to aware the policy makers and farmers for adopting sustainable agricultural practices to improve SQ with enhanced ecosystems services in Benin.

Acknowledgements

The USDA Norman Borlaug World Food Prize Fellowship provided funding to Drs. Emmanuel Amoakwah (Ghana) and Nataliia Didenko (Ukraine) to conduct their studies on the soil at the Ohio State University, Ohio, USA.

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Eurasian Journal of Soil Science 2021, 10(2), 161- 170

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

Performance of vermicompost in zinc and boron nutrition for quality production of cabbage

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Article Info

Received : 24.02.2020
Accepted : 05.01.2021
Available online : 12.01.2021

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Abstract

The quality and efficacy of vermicompost are greatly influenced by the respective feeding materials as well as earthworm species used in vermicomposting. Consequently, the variable role of applied vermicompost is reflected in crop production. With a view to observe the efficacy of vermicompost produced from various sources in supplementing zinc and boron requirement for quality production of cabbage, a field study was conducted in Floodplain soil of Bangladesh. Six treatment combinations comprising of vermicompost from different sources, and different levels of zinc and boron from mineral fertilizers were tested in the study. The vermicompost used in different treatments were produced from different combinations of feeding materials (cowdung and poultry litter) and earthworm species (*Eisenia fetida* and *Eudrilus eugeniae*). A control treatment having no supplement of Zn and B was tested in the study. Higher measurements were recorded for most of the parameters studied, i.e., head diameter, marketable yield and total yield in the vermicompost treated plots than the solely mineral fertilizer treated plot. Except for P, the highest uptake of each of the elements by cabbage was observed due to the application of T_3 treatment (VC-ECD @2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}). The findings of this research work indicate the additional benefit of using vermicompost over the mineral fertilizer in supplying zinc and boron for better production of cabbage.

Keywords: Vermicompost, performance, zinc, boron, quality, cabbage.

Introduction

Producing food for an ever-increasing population from limited land resources is one of the big challenges in Bangladesh. To cope up with the situation, the arable land is being intensively used in the recent previous years. Hence, there is an increasing trend of cropping intensity in this country and it was 171 and 194.28% in the year 1983-84 and 2015-16, respectively (BBS, 2017). Consequently, the soil resource of this country has been impacted negatively and deficiency of different nutrients diagnosed one after another. Micronutrients like Zn and B deficiency along with macronutrient deficiency (N, P, K, and S) have already emerged in soils of the country (Islam, 2008).

In Bangladesh, it is a common practice to use urea in over-dose while other fertilizers like TSP, MoP, and gypsum in sub-optimal doses. The use of micronutrient-containing fertilizers is very rare in crop cultivation. This unbalanced management of fertilizers is hampering the successful production of crops (Rijpma and Jahiruddin, 2004). Usually, a very small amount of micronutrient than macronutrient is required in crop production; but micronutrient deficiency can make a plant unable to complete its life cycle. Again, excessive application of micronutrients may create phytotoxicity as well as threaten food safety. The toxic and deficient status of boron in soil and plant is very close to each other (Reisenauer et al., 1973). Deviation in proper doses of

: https://doi.org/10.18393/ejss.859136
: http://ejss.fesss.org/10.18393/ejss.859136
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

micronutrients might hamper crop growth and quality also. Different mineral fertilizer sources are commonly used in the country to meet up the requirement of micronutrients as organic sources are very limited there. In such a situation application of vermicompost can be an excellent option to address the problem.

Vermicompost is one of the highly nutritive manures as well as a potential growth promoter in crop cultivation. It has ten times higher nutritive value for a plant than farmyard manure (Lourduraj and Yadav, 2005). Prabakaran (2005) reported the considerable content of vitamins, hormones, enzymes and different plant nutrients in vermicompost. Theunissen et al. (2010) reported higher content of micronutrients namely iron, copper, zinc, and manganese in vermicompost. Increased content of Zn along with other micronutrients was showed in vermicompost applied soil than the control plot (Abdelmonem et al., 2016). The nutrient content of vermicompost greatly depends on the feeding materials and species of earthworm used in vermicomposting. The growth as well as performance of earthworms, was impacted a lot by the palatability and nutrient content of various organic materials used in vermicomposting (Suthar, 2007). The growth of earthworm in specific organic substrate is determined by the palatability as well as suitability to eat by worms (Yadav and Garg, 2011). Rajendran and Thivyatharsan (2014) found the highest content of different macronutrients (N, P, and K) and organic carbon in vermicompost produced by using E. eugeniae among four different earthworm species. Such variations among vermicompost produced from using different earthworm species were also reported by Singh et al. (2014).

Different micronutrients have specific role in cabbage production. Among the micronutrients, zinc and boron are more important than others due to their availability in soil, mobility in soil-plant system, especially in the case of cole crops. Zinc deficiency in soil was reported in the early 1990s. From the nutritional point of view, different reports suggested that about one-fourth of the total world's population is threatened by Zn deficiency (Maret and Standstead, 2006). Improving Zn status in food crops through various means may be one of the options to mitigate the problem. For addressing this issue, many scientists planned different strategies including Zn fertilization in crop production through mineral sources as well as from various organic fertilizers (Yilmaz et al., 1997; Cakmak et al., 1998; Khattak et al., 2006; Maqsood et al., 2009). Light-textured acid soils and soils having low organic matter are usually deficient in boron (Keren and Bingham, 1985; Mandal et al., 2004). Boron deficiency has been diagnosed for various field crops in different countries throughout the world (Shorrocks, 1997).

Among the thirty agro-ecological zones (AEZs) of Bangladesh, the Surma-Kushiyara Floodplain (AEZ 20) is an important one formed on sediments of the rivers graining into the Meghna catchment area from the hills. The soils of this area are featured with low to medium organic matter content where zinc content is medium and boron content is low to medium (BARC, 2012). Considering above-mentioned points, a study was conducted to evaluate the response of cabbage to zinc and boron application through both vermicomposts as well as chemical fertilizers in Surma-Kushiyara Floodplain soil.

Material and Methods

Experimental location

Field study, as well as chemical analysis of soil-plant samples in the laboratory, was included in the study. Farmer's field in Sunamgonj sadar upazila under Sunamgonj district was selected to conduct the field experiment. Duration of the field experimentation was November/2018 to January/2019. The experimental plot lies under the Eastern Surma-Kushiyara Floodplain (AEZ 20) (FAO and UNDP, 1988). The analytical part of the study was performed in the laboratory located in the Department of Soil Science (Sylhet Agricultural University) as well as the Sylhet regional soil laboratory of SRDI (Soil Resource Development Institute).

Collection, preparation and analysis of soil samples

At the very beginning of field experimentation, the soil sample (at 0-15 cm depth) from the research plot was collected and processed as per standard methods. Different basic soil properties and some macro- and micronutrients were analyzed from the processed soil sample following standard methodology as described in Table 1. The analytical results of this initial soil are presented in Table 2.

Crop variety, treatments, and design used

A widely cultivated popular hybrid variety of cabbage, Atlas 70 was used in the experiment. Six treatment combinations were tested in the experiment which are given below-

T_1: Control

T_2: 3 kg Zn ha^{-1}+ 2 kg B ha^{-1}

T_3: VC-ECD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}

T_4: VC-EuCD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}

T_5: VC-ECDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}

T_6: VC-EuCDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}

Table 1. Methods for analyses of soil properties

Soil properties	Analytical methods
pH	Soil pH was determined by glass-electrode pH meter maintaining 1:2.5 soil-water ratio (McLean, 1982)
Texture	Mechanical analysis of soil was done by hydrometer method (Gee and Bauder, 1986) and the textural class was determined by fitting the values for %sand, %silt, and %clay to the Marshall's triangular co-ordinate following USDA system
Organic carbon	Following the wet oxidation method (Nelson and Sommers, 1996), the soil organic carbon was oxidized by 1N potassium dichromate and the amount of organic carbon in the aliquot was determined by titration with 0.5 N ferrous sulphate solution. Percent organic matter was calculated by multiplying the percent organic carbon with the van Bemmelen factor 1.73 (Piper, 1950)
Total N	Total N content of the soil was determined by the micro-Kjeldahl method (Bremner and Mulvaney, 1982). Soil sample was digested with conc. H_2SO_4 in presence of catalyst mixture (K_2SO_4:$CuSO_4.5H_2O$: Se= 10:1:0.1). Nitrogen in the digest was estimated by distilling the digest with 10N NaOH followed by titration of the distillate trapped into H_3BO_3 indicator solution with 0.01N H_2SO_4
Available P	Soils having pH smaller than 7.0 were extracted with ammonium fluoride extracting solution (Bray and Kurtz, 1945), and soils having pH greater than 7.0 were extracted with 0.5M $NaHCO_3$ solution (Olsen and Sommers, 1982). The P in the extract was then determined by developing blue colour with $SnCl_2$ reduction of phosphomolybdate complex and measuring the colour by spectrophotometer at 660 nm wavelength
Exchangeable K	The element was extracted from soil by 1M CH_3COONH_4 with a 1:10 soil-extractant ratio and the extractable amount of K was determined by flame photometer (Knudsen et al., 1982)
Available S	Extraction was done with $CaCl_2$ (0.15%) solution as described by Tabatabai (1996). The S content in the extract was determined turbidimetrically using a spectrophotometer at 420 nm wavelength (Fox et al., 1964; Jones et al., 1972)
Available Zn	The micronutrient was extracted by 0.05M DTPA solution (pH 7.3) maintaining 1:2 soil-extractant ratio. The extracted level was measured by flame AAS (Lindsay and Norvell, 1978)
Available B	Soil B was extracted by hot water-0.02M $CaCl_2$ solution (1:2). The extractable B was determined by spectrophotometer following azomethine-H method (Keren, 1996)

In different treatment combinations, vermicompost from various sources was denoted as VC-ECD (vermicompost from *E. fetida*-cowdung), VC-EuCD (vermicompost from *E. eugeniae*-cowdung), VC-ECDPL (vermicompost from *E. fetida*-cowdung-poultry litter) and VC-EuCDPL (vermicompost from *E. eugeniae*-cowdung-poultry litter. Different doses of Zn and B shown in various treatment combinations were applied from mineral fertilizer sources (zinc sulfate and boric acid). Each of the treatment combinations was replicated thrice following RCBD. The size of individual plots was 4 m × 2.5 m. The gap between two sub-plots was 0.6 m and it was 1 m between two blocks.

Table 2. Soil physical and chemical characteristics of the experimental field

Characteristics	Analytical results
Mechanical fractions (USDA system)	
% Sand (2.0-0.05 mm)	67.68
% Silt (0.05-0.002 mm)	15.28
% Clay (<0.002 mm)	17.04
Textural class	Sandy loam
Organic matter (%)	1.06
pH	5.10
Total N (%)	0.07
Available P (mg kg^{-1})	3.10
Exchangeable K ($cmol_c$ kg^{-1})	0.11
Available S (mg kg^{-1})	13.9
Available Zn (mg kg^{-1})	1.25
Available B (mg kg^{-1})	0.14

Macronutrient doses and their application

In the experiment, the soil was applied with different macronutrients (N, P, K, and S) through vermicompost as well as chemical fertilizers. Fertilizer Recommendation Guide was used to calculate the required amount of macronutrients other than the amount received from the applied vermicompost (BARC, 2012). The respective doses applied in the experiment are presented Table 3. Urea, triple super phosphate, muriate of potash, and gypsum were applied as inorganic sources of N, P, K, and S, respectively. The full amount of all recommended fertilizers and manures other than urea was mixed with the soil of experimental plots before transplanting cabbage seedling. At 10, 25 and 35 DAT (Days after transplanting) the recommended amount of urea was side-dressed in equal split doses.

Table 3. Application doses of different macronutrients

Macronutrients	Application doses
Nitrogen	130 kg ha^{-1}
Phosphorus	55 kg ha^{-1}
Potassium	85 kg ha^{-1}
Sulphur	25 kg ha^{-1}

Intercultural operations

Various intercultural activities were performed during the experimentation to achieve better growth and performance of cabbage. Immediate after the transplantation, banana leaf sheath was used at day time to protect the tender cabbage seedlings from direct scorching sunlight. Besides, the seedlings were watered two times (morning and evening) in a day for three days after transplanting. Other intercultural operations like irrigation and pesticide application were performed as per requirement.

Data collection

At the proper edible stage, cabbage head yield was recorded by harvesting an area of 4 m^2 in each of the sub-plots. Head yield was recorded by weighing the immediately harvested heads. Data on different growth and yield contributing characters as well as yield were collected from five pre-selected cabbage plants. Such plants were selected randomly from the sub-plots excluding the area to be harvested for yield data.

Collection, preparation and nutrient analysis of cabbage samples

Samples of cabbage head including stem were collected while harvesting head for yield data. After air drying those samples were cut off into finer parts and placed into an electric oven at 65°C. This oven drying process was continued for about twenty-four hours and then the well-dried crispy plant materials ground finely using a plant grinder. Thus ground samples were analyzed chemically to determine the nutrient (N, P, K, S, Zn, and B) content using standard protocols as described in Table 4. Uptakes of different nutrient elements were determined using respective nutrient concentration data and yield of cabbage.

Table 4. Methods used for plant analysis

Elements	Analytical methods
N	The micro-Kjeldahl method (Bremner and Mulvaney, 1982) was followed.
P	Colorimetric method: The concentration of P was determined colorimetrically using molybdovanadate solution (Yoshida et al., 1976).
K	The concentration of K in the digest was determined directly by a flame photometer (Yoshida et al., 1976).
S	Turbidimetric method: The S concentration in the digest was determined by developing turbid using $BaCl_2$ (Chapman and Pratt, 1961).
Zn	The concentration of Zn in the digest was determined directly by an atomic absorption spectrophotometer (Yoshida et al., 1976).
B	The B concentration in the digest in terms of color was determined by a spectrophotometer following the azomethine-H method (Keren, 1996).

Statistical analysis of data

A computer-based statistical package software R was used for the analysis of collected data. Different standard statistical methodologies were followed to determine the significant effects of the treatments. The treatment mean separation was adjudged by Duncan's Multiple Range Test (Gomez and Gomez, 1984).

Results

Effects on growth parameters of cabbage

Plant height at harvest

Cabbage plant heights at different DAT were not significantly affected by the treatments applied and it was ranged from 11.13 to 11.64, 20.46 to 22.69, and 27.33 to 32.11 cm at 20 DAT, 40 DAT, and at harvest, respectively (Table 5).

Number of loose leaves plant^{-1} at harvest

Like plant height, the number of loose leaves plant-1 was also varied non-significantly by the treatments used (Table 5). In T_4 treatment, the number of loose leaves was the highest where in T_2 treatment it was the lowest.

Table 5. Effects of sources of vermicompost on growth parameters of cabbage

Treatment	Plant height at different growth stage (cm)			No. of loose leaves at harvest (No)	Length of the largest leaf (cm)	Breadth of the largest leaf (cm)
	At 20 DAT	At 40 DAT	At harvest			
T_1: Control	11.15	20.46	27.33	17.14	32.00b	27.50b
T_2: 3 kg Zn ha^{-1}+ 2 kg B ha^{-1}	11.13	21.93	30.33	16.93	34.67ab	34.75a
T_3: VC-ECD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	11.60	22.69	32.11	16.30	38.67a	36.67a
T_4: VC-EuCD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	11.64	21.06	30.44	16.61	36.67a	35.33a
T_5: VC-ECDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	11.28	21.73	31.11	17.44	35.00ab	35.50a
T_6: VC-EuCDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	11.52	22.13	32.00	16.40	38.08a	36.33a
CV (%)	4.93	3.70	7.57	3.47	6.47	9.06
Significance level	NS	NS	NS	NS	0.05	0.05

Means followed by the same letter in a column are not significantly different at 5% level by DMRT
CV= Co-efficient of variation
VC-ECD= Vermicompost produced from cowdung using *Eisenia fetida* earthworm species
VC-EuCD= Vermicompost produced from cowdung using *Eudrilus eugeniae* earthworm species
VC-ECDPL= Vermicompost produced from cowdung + poultry litter using *Eisenia fetida* earthworm species
VC-EuCDPL= Vermicompost produced from cowdung +poultry litter using *Eudrilus eugeniae* earthworm species

Length of the largest leaf

The application of different treatments affected the length of the largest leaf significantly and it ranged from 32.00 to 38.67 cm (Table 5). The largest leaf was produced by T_3 treatment and at par result was recorded in the remaining treatments other than T_1. On the other hand, the shortest leaf was measured in T_1 treatment and at par result also recorded in both T_2 and T_5 treatments.

Breadth of the largest leaf

Like the length of the largest leaf, the breadth of the largest leaf was also significantly differed by the treatments where the broadest leaf (36.67 cm) was produced in T_3 treatment and it was at par with that of all other treatments except the control treatment (Table 5). The narrowest leaf (27.50 cm) was resulted from the control treatment where no Zn and B were applied.

Effects on yield contributing parameter and yield of cabbage

The parameters included head diameter, marketable head yield, and gross yield.

Head diameter

The head diameter of cabbage varied significantly by different treatments of the study (Table 6). The largest diameter (24.70 cm) was produced in the T3 treatment and it had statistical similarity with that of remaining treatments other than T1 and T2. Again, the lowest diameter (22.57 cm) was recorded in the control treatment and it was statistically similar to that of T2 and T4 treatments.

Marketable head yield

Significant differences were observed in the marketable head yield of cabbage produced by different treatments and it ranged from 33.71 to 51.71 t ha^{-1} (Table 6). Marketable yield was the highest for T_3 treatment and it had statistical similarity with the remaining treatments other than T_2 and the control. The lowest yield was produced by the T_1 treatment and it had statistical similarities with the yield of the T_2 treatment (40.16 t ha^{-1}) where Zn-B was applied through mineral fertilizers only.

Gross yield

The application of different treatments affected the gross yield of cabbage significantly where it varied from 51.71 to 63.36 t ha^{-1} (Table 6). The highest gross yield producing treatment was T_3 and at par result was found for all other treatments except the control. The T_2 treatment produced gross head yield (57.74 t ha^{-1}) which was higher than that of the T1 treatment; whereas it was lower than the gross yield of all other treatments.

Effects on nutrient uptake by cabbage

The concentration of various nutrients (N, P, K, S, Zn, and B) in cabbage samples as presented in Table 7 was estimated as fresh weight basis. The nutrient uptake which was calculated based on nutrient concentration and yield data has shown in Table 8.

Table 6. Effects of sources of vermicompost on yield and yield contributing characters of cabbage

Treatment	Head diameter (cm)	Marketable head yield (t ha^{-1})	Total yield (t ha^{-1})
T_1: Control	22.57c	33.77c	51.71c
T_2: 3 kg Zn ha^{-1}+ 2 kg B ha^{-1}	23.55bc	40.16bc	57.74b
T_3: VC-ECD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	24.70a	51.71a	63.36a
T_4: VC-EuCD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	23.66abc	45.49ab	58.71ab
T_5: VC-ECDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	23.86ab	44.83ab	58.74ab
T_6: VC-EuCDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	24.12ab	49.10a	61.13ab
CV (%)	2.58	9.20	5.17
Significance level	0.05	0.01	0.05

Means followed by the same letter in a column are not significantly different at 5% level by DMRT
CV= Co-efficient of variation
VC-ECD= Vermicompost produced from cowdung using *Eisenia fetida* earthworm species
VC-EuCD= Vermicompost produced from cowdung using *Eudrilus eugeniae* earthworm species
VC-ECDPL= Vermicompost produced from cowdung + poultry litter using *Eisenia fetida* earthworm species
VC-EuCDPL= Vermicompost produced from cowdung + poultry litter using *Eudrilus eugeniae* earthworm species

Table 7. Effects of sources of vermicompost on nutrient content of cabbage

Treatments	N (%)	P (%)	K (%)	S (%)	Zn (μg g^{-1})	B (μg g^{-1})
T_1: Control	0.164	0.0219	0.121b	0.0243	6.05c	5.07b
T_2: 3 kg Zn ha^{-1}+ 2 kg B ha^{-1}	0.174	0.0190	0.127ab	0.0295	9.23ab	7.87a
T_3: VC-ECD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	0.174	0.0191	0.139a	0.0303	9.62a	8.92a
T_4: VC-EuCD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	0.169	0.0197	0.141a	0.0292	8.52b	8.45a
T_5: VC-ECDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	0.171	0.0194	0.137a	0.0280	8.65ab	8.15a
T_6: VC-EuCDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	0.178	0.0200	0.141a	0.0290	9.30ab	8.55a
CV (%)	4.01	6.22	5.73	7.70	5.99	7.91
Significance level	NS	NS	0.05	NS	0.001	0.001

Note: Nutrient concentration of cabbage was expressed as fresh weight basis
Means followed by the same letter in a column are not significantly different at 5% level by DMRT
CV= Co-efficient of variation
VC-ECD= Vermicompost produced from cowdung using *Eisenia fetida* earthworm species
VC-EuCD= Vermicompost produced from cowdung using *Eudrilus eugeniae* earthworm species
VC-ECDPL= Vermicompost produced from cowdung + poultry litter using *Eisenia fetida* earthworm species
VC-EuCDPL= Vermicompost produced from cowdung + poultry litter using *Eudrilus eugeniae* earthworm species

Nitrogen uptake

Significant effect of different applied treatments on N uptake was observed. The T_3 treatment helped for the highest uptake (110.05 kg ha^{-1}) of N which had statistical similarity with that of T_2, T_5, and T_6 treatments. The control treatment showed the lowest uptake of N.

Phosphorus uptake

Non-significant effect of various treatments was noticed for P uptake by cabbage and it varied from 11.01 to 12.18 kg ha^{-1}. There was a higher P concentration in the control treatment than T_2 treatment (Table 7) and consequently this situation contributed to estimate higher P uptake in the control than in the T_2 treatment.

Potassium uptake

Significant influence of different treatments on K uptake by cabbage was recorded. The T_3 treatment had induced the highest uptake (87.90 kg ha^{-1}) and at par results were observed for all vermicompost applied treatments. Potassium uptake was the lowest in T_1 treatment.

Sulphur uptake

Significant variations were observed among the S uptakes by cabbage in different treatments where it varied from 12.54 to 19.14 kg ha^{-1}. The lowest and the highest values of uptake were found in the control and T_3 treatments, respectively.

Zinc uptake

Different treatments had significant effects on Zn uptake by cabbage. The T_3 treatment had induced the highest uptake (609.42 g ha^{-1}) where the lowest uptake was calculated for control treatment. The T_2 treatment which received no Zn and B containing mineral fertilizers had induced for 531.82 kg ha^{-1} Zn uptake.

Table 8. Effects of sources of vermicompost on nutrient uptake by cabbage

Treatments	N uptake (kg ha^{-1})	P uptake (kg ha^{-1})	K uptake (kg ha^{-1})	S uptake (kg ha^{-1})	Zn uptake (g ha^{-1})	B uptake (g ha^{-1})
T_1: Control	0.164	0.0219	0.121b	0.0243	6.05c	5.07b
T_2: 3 kg Zn ha^{-1}+ 2 kg B ha^{-1}	0.174	0.0190	0.127ab	0.0295	9.23ab	7.87a
T_3: VC-ECD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	0.174	0.0191	0.139a	0.0303	9.62a	8.92a
T_4: VC-EuCD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	0.169	0.0197	0.141a	0.0292	8.52b	8.45a
T_5: VC-ECDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	0.171	0.0194	0.137a	0.0280	8.65ab	8.15a
T_6: VC-EuCDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	0.178	0.0200	0.141a	0.0290	9.30ab	8.55a
CV (%)	4.01	6.22	5.73	7.70	5.99	7.91
Significance level	NS	NS	0.05	NS	0.001	0.001

Means followed by the same letter in a column are not significantly different at 5% level by DMRT
CV= Co-efficient of variation
VC-ECD= Vermicompost produced from cowdung using Eisenia fetida earthworm species
VC-EuCD= Vermicompost produced from cowdung using Eudrilus eugeniae earthworm species
VC-ECDPL= Vermicompost produced from cowdung + poultry litter using Eisenia fetida earthworm species
VC-EuCDPL= Vermicompost produced from cowdung + poultry litter using Eudrilus eugeniae earthworm species

Boron uptake

Boron uptake by cabbage was varied significantly due to the effect of various treatments applied and it ranged from 262.61 to 565.04 g ha^{-1}. The highest and the lowest uptakes were found in T_3 and T_1 treatments, respectively. The highest uptake-inducing treatment (T_3) had statistical similarity with that of remaining all vermicompost applied treatments other than T_5.

Changes in soil properties after experimentation with cabbage

Analytical results of different soil parameters and nutrient elements in the initial (before initiation of the experiment) and post-harvest soils (after 1-crop) have presented in Table 9. There were few changes in soil properties due to the application of different mineral fertilizers and vermicompost to supplement Zn and B for cabbage production.

Table 9. Changes in soil properties as influenced by different treatments applied in cabbage

Treatment	pH	Org. C (%)	Tot. N (%)	Ex. K (cmol$_c$ kg^{-1})	Av. P (mg kg^{-1})	Av. S (mg kg^{-1})	Av.Zn (mg kg^{-1})	Av. B (mg kg^{-1})
Initial soil:	5.1	1.06	0.072	0.110	3.1	13.90	1.25	0.136
Post-harvest soil:								
T_1: Control	4.9	1.11b	0.095b	0.173	8.31a	14.97	1.26c	0.150c
T_2: 3 kg Zn ha^{-1}+ 2 kg B ha^{-1}	4.9	1.09b	0.112a	0.174	6.10c	15.35	2.50ab	0.280b
T_3: VC-ECD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	4.8	1.23a	0.117a	0.194	7.20b	17.42	2.60a	0.313ab
T_4: VC-EuCD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	4.7	1.23a	0.116a	0.180	6.97bc	16.91	2.15ab	0.300ab
T_5: VC-ECDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}	4.8	1.19ab	0.120a	0.180	7.02bc	17.09	2.02b	0.310ab
T_6: VC-EuCDPL@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} +1.0 kg B ha^{-1}	4.7	1.24a	0.114a	0.186	7.14bc	17.23	2.32ab	0.323a
CV (%)	2.49	3.14	4.83	6.00	7.53	6.17	12.64	7.24
Significance level	NS	0.01	0.01	NS	0.05	NS	0.01	0.001

Means followed by the same letter in a column are not significantly different at 5% level by DMRT
CV: Co-efficient of variation
VC-ECD= Vermicompost produced from cowdung using *Eisenia fetida* earthworm species
VC-EuCD= Vermicompost produced from cowdung using *Eudrilus eugeniae* earthworm species
VC-ECDPL= Vermicompost produced from cowdung + poultry litter using *Eisenia fetida* earthworm species
VC-EuCDPL= Vermicompost produced from cowdung + poultry litter using *Eudrilus eugeniae* earthworm species

The decreased pH value was recorded in post-harvest soils than the initial soil. The values were non-significantly varied with the applied treatments. After completion of the experiment, the organic carbon content of the soil was found to be increased slightly and it varied from 1.11 to 1.24%. The organic carbon content was found as the highest in the T_6 treatment and it had statistical similarity with that of all other vermicompost receiving treatments. Like organic carbon, total N content in soil was higher in post-harvest soils over all the treatments, with the range of 0.095 - 0.120% (initial level 0.072%). Available P content showed a remarkable increase in post-harvest soils than the initial content which ranged from 6.10 to 8.31 mg kg^{-1} (initial status 3.1 mg kg^{-1}). Significant differences were observed in soil P contents of different treatments where the highest and the lowest contents were in control and T_2 treatments, respectively. Though increased content (0.173 - 0.194 cmolc kg^{-1}) was found for exchangeable K level from the initial soil test value (0.110 cmolc kg^{-1}), those were not significantly varied from each other. Like K, the S level of post-harvest soils also non-significantly varied from 14.97 to 17.42 mg kg^{-1} where the initial status was 13.90 mg kg^{-1}. The Zn content of soil increased considerably in Zn-treated plots, as expected due to Zn application but almost static in the control treatment. After 1-crop experimentation, the available Zn status of the soil varied from 1.26 to 2.60 mg kg^{-1} against the initial level of 1.25 mg kg^{-1}. Similarly, higher content of B was found in post-harvest soils as compared to the initial content. Those contents have significantly differed from each other where the highest value (0.323 mg kg^{-1}) was recorded for the soil of T6 treatment and the other vermicompost receiving treatments had at par results.

Discussion

All the yield parameters studied, i.e., head diameter, marketable yield, and total yield recorded in the vermicompost plus mineral fertilizer treated plots differed from those of solely mineral fertilizer treated plots as well as the control plot. This finding indicates the suitability of vermicompost comparing with the mineral fertilizer for yield components of cabbage.

Except for P, uptake of all the nutrients by cabbage was significantly differed by the treatments added. The highest value of uptake in each of the elements was observed due to the application of T_3 treatment (VC-ECD@2.0 t ha^{-1} + 1.5 kg Zn ha^{-1} + 1.0 kg B ha^{-1}). Such a result has agreed with the previous findings of other researches. The combined application of mineral fertilizers with vermicompost has induced the highest uptake of various nutrients (N, P, K, and Mg) by rice plant (Jadhav et al., 1997). Sreenivas et al. (2000) found an almost similar result in the case of N uptake by ridge gourd by applying a combination of inorganic fertilizer and vermicompost. Phosphorus uptake was found higher in the control treatment than all other treatments; it is because of the higher P concentration in T_1 than the remaining treatments. The interaction effect between applied P and Zn might be responsible for reduced uptake of P in different treatments other than the control. Except for the control all other treatments received Zn either from mineral fertilizer or from both the mineral and organic source. Antagonistic interactions of Zn and P have been confirmed from numerous studies (Webb and Loneagan, 1988; Hu et al., 1996; Bukviċ et al., 2003; Mousavi, 2011). There was the superiority of the vermicompost applied treatments in nutrient uptake issue for most of the elements. The high potentiality of vermicompost in supplying plant nutrients might be contributed to this. Vermicompost is rich in plant nutrients, vitamins, and hormones which consequently have impacted on better growth and performance of plants (Kale et al., 1992; Edwards, 1988; Makulec, 2002; Sinha et al., 2009). Due to larger particular surface area, vermicompost have the capability to provide huge micro-sites for microbial activity as well as for plant nutrient adsorption (Shi-wei and Fu-zhen, 1991).

From the analytical results of post-harvest soil and initial soil, it is found that the pH of vermicompost treated soils (T_3-T_6) was found lower than the control treatment and even than the initial pH value. Though such a decrease is not statistically significant there might be some influence of applied vermicompost. After completion of the experiment, the organic carbon and B content of soil of vermicompost treated plots was found to be increased to some extent and these values are higher than those of the only mineral Zn-B treated plot as well as the control plot. Such higher content of organic carbon and B may be attributed to the applied vermicompost. Available P content showed a remarkable increase in post-harvest soils than the initial content. The highest content of P was observed in T1 (control) treatment while the lowest was found in T2 treatment (3 kg Zn ha-1 + 2 kg B ha-1) where Zn and B were supplied only through chemical fertilizer). This situation might be arisen because of the negative interaction between P and Zn in the soil-plant system; because all but control plots were treated with Zn through applying either mineral fertilizer only or with a combination of mineral fertilizer and vermicompost. The Zn content of the soil in all the treatments increased considerably except the control. It is because those plots were received Zn through fertilization.

Conclusion

Sole application of chemical fertilizers can supplement zinc-boron nutrition for cabbage production. But the application of vermicompost in combination with chemical fertilizers is better performing to supply required zinc and boron nutrition for quality production of cabbage. Such practice of vermicompost application might be helpful for retaining degraded soil health.

Acknowledgements

We gratefully acknowledge UGC (University Grants Commission) of Bangladesh for the fellowship and financial assistance provided in the way of accomplishing the concern research work.

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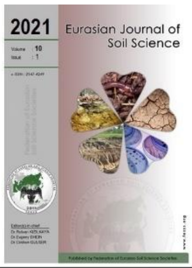
Eurasian Journal of Soil Science 2021, 10(2), 171- 178

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org



Comparison of Fuzzy logic and Boolean methods in mapping nitrogen and phosphorus nutrients

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Article Info

Received : 14.09.2019
Accepted : 09.01.2021
Available online : 18.01.2021

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Abstract

One of the approaches for increasing of yield and reduction of rice production costs is precision agriculture. Complete and correct determination of nutrition status of paddy soils is necessary in precise agriculture. To compare fuzz y and Boolean methods and mapping of nutrition status of nitrogen and phosphorus, 370 compound samples were collected from 306 ha of paddy soils of Rice Research Institute in Rasht County from plots with the dimension of 50 × 100 m. Total nitrogen and available phosphorus contents were measured. Results showed that interpolation and mapping by fuzzy logic was more accurate and correct in comparison with Boolean method and had greater distinguishing power to indicate deficiency of nutrients. Evaluation of dependency of paddy soils using of fuzzy function and Boolean method, showed that the southwest of study area have nitrogen and phosphorus deficiency and the other parts have minor limitation for these elements.

Keywords: Fuzzy logic, mapping, nutrients, precision agriculture.

Introduction

Determination of homogeneous management zones is an appropriate tool used in precision agriculture that improves crop management and reduce the destructive effects of environmental (Franzen et al., 2002; Khosla et al., 2002). Administrative regions in precision agriculture shows similar characteristics and soil conditions in landscape and spatial similarity of them leads to the same potential crop yield, inputs efficiency, and environmental effects (Schepers et al., 2004). Due to a lot of changes within the farm and dynamic nature of soil nutrients, a traditional soil map does not offer enough information. One common method of soil fertility evaluation is Boolean method (Heuvlink and Burrough, 1993; McBratney and Odeh, 1997). However, using appropriate methods such as fuzzy set causes less data loss at different stages of analysis (Burrogh et al., 1992). Fuzzy set for the first time Zadeh (1965) introduced the fuzzy system as a possible method for the expression of uncertainty in the processes or uncertain vague of experts knowledge (Freissinet et al., 1998). Based on Zadeh comments, fuzzy logic theory is an effective way for recreation of the relations between accuracy and math class ambiguity and lack of precision in the real world (Zadeh, 1965).

Fuzzy Logic philosophy is creation of a network in which mathematical concepts in uncertain decisions is being studied accurately. This logic can be used especially when that sufficient data to determine the uncertainty through the use of standard statistics (e.g. mean, standard deviation and distribution type) is not present (Martin-Clouaire et al., 2000). Today in Soil Science, the fuzzy logic theory has broad applications that include: numerical classification of soil and mapping, land evaluation, modelling and simulation of soil physical processes, fuzzy spatial statistics of soil, soil quality indicators, and measurements for fuzzy defined

: https://doi.org/10.18393/ejss.863606
: http://ejss.fesss.org/10.18393/ejss.863606
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

soil phenomena (McBratney and Pringle, 1997). Reyniers et al. (2006) used from fuzzy logic changes of yield potential changes in relation to characteristics of loamy soils of Central Belgium. Fuzzy set leaded the field into 5 regions with different yield potential. This information caused to accurate management and optimized performance in the field. Amini et al. (2005) used from a combination of fuzzy classification and spatial prediction for assessment of soil pollution for 225 samples in Isfahan. Concentrations of heavy metals based on the optimal number of classes and Fuzzy c-mean method were grouped into 4 classes and the results showed that fuzzy classification is a proper method for grouping of soil contamination data.

Related researches

In a case study, Sicat et al. (2005) used fuzzy model of farmer's knowledge and GIS to evaluate of fertility of agricultural lands. The results of their study showed that the usefulness of fuzzy model for determining land suitability classes and optimal land use. Ping and Dobermann (2003) evaluated the spatial variation of rice yield in relation to soil properties in paddy lands using fuzzy logic and classical statistics and indicated that the relative advantages of the fuzzy logic and emphasized on the necessity of further research about interpolation method. This study was carried out with the aim of comparison of Boolean and fuzzy logic method for diagnosis of real requirement of paddy lands to nitrogen and phosphorus fertilizers.

Material and Methods

Study area and sampling

The study area was 306 ha of paddy fields in Rice Research Institute, located in Rasht city. This field stands in the rice cultivation area of Gilan province in north of Iran.

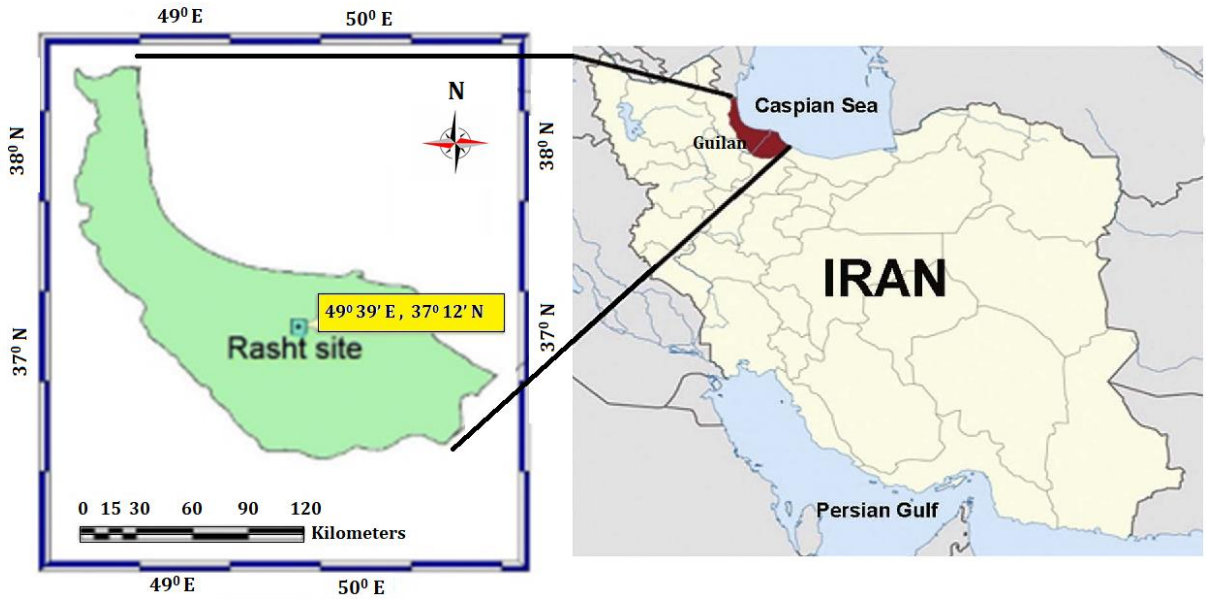


Figure 1. Rice cultivation area of Gilan province in north of Iran.

Gilan province with the 238,000 ha paddy farms has the second rank of rice cultivation area in Iran (37% of total) (Khodabande and GhasempourAlamdari, 2005). This region has a humid climate with average annual rainfall of 1200 mm. 370 soil samples were collected from the plots with the dimensions of 50 × 100 m. Sampling procedure was a compound 9 points that the first sample were collected from the centre of the plot and the rest with a radius between 15 and 25 m from around it, then mixed with equal weight and transferred to the laboratory. After air drying the samples were passed through 2 mm sieve. The main soil taxonomy class of study field was xeralf according to US Taxonomy (Soil Survey Staff, 2014). The characteristics of study field were measured in former researches and the average of them is presented in Table 1. Because of high potassium content of Gilan province (as soils, no potassium fertilizers usually used by farmers, therefore, nitrogen and phosphorous were studied in this research.

Table 1. Mean soil characteristics of paddy fields of Rice Research Institute

Soil Depth (cm)	Electrical conductivity ($dS.m^{-1}$)	pH	OC (%)	Total nitrogen (%)	Available phosphorus ($mg.kg^{-1}$)	Available potassium ($mg.kg^{-1}$)	Sand (%)	Silt (%)	Clay (%)	Soil texture
0-30	1.2	7.4	1.9	0.187	26.7	224	10	42	48	Silt-Clay

Chemical analysis

Total nitrogen was measured by Kjeldal method (Boltz and Howell, 1978) and available phosphorus extracted by Olsen method and measured with spectrophotometer (Murphy and Riley, 1988).

Descriptive statistics

Statistical parameters related to the position distribution (mean, median, mode), frequency distribution parameters (variance, standard deviation and range) and the distribution parameters (skewness, traction coefficient of variation) were calculated. Assessment for normal distribution of data done using Histogram test and skewness significance test by the SPSS software version 11.5 (Lund Research Ltd, 2018).

Boolean and Fuzzy logic theory

In Boolean method, for converting of input variables to a set of explicit values membership function, membership for conditions of deficiency or severe limitation Class (relationships 1 and 2) and conditions of adequacy or without limitation Class (relationships 3 and 4), were defined as follows:

$$\text{if } Z \leq b_1 \; BMF_Z = 1 \tag{1}$$

$$\text{if } Z > b_1 \; BMF_Z = 0 \tag{2}$$

$$\text{if } Z < b_2 \; BMF_Z = 0 \tag{3}$$

$$\text{if } Z \geq b_2 \; BMF_Z = 1 \tag{4}$$

Where: Z; variable, b_1; critical level lower than that in the plant is accompanied by severe shortages b_2; critical upper limit that the plant doesn't face to any restrictions and BMF; membership of Boolean function.

In fuzzy logic, for converting the value of each variables to the fuzzy membership function, use from a continuous range from 0 to 1; 1 indicates full membership, and 0, indicating non-membership. Fuzzy membership function for the class of deficiency or severe limitation (relationships 5 and 6) and adequacy class or conditions without limitation (relationships 7 and 8) were defined as follows:

$$\text{if } Z < (b_1 - d) \; FMF_Z = 1 \tag{5}$$

$$\text{if } Z \geq (b_1 - d) \quad FMF_Z = \frac{1}{1 + \left(\frac{Z - b_1 + d}{d}\right)^{\rho}} \tag{6}$$

$$\text{if } Z > (b_2 + d) \; FMF_Z = 1 \tag{7}$$

$$\text{if } Z \leq (b_2 - d) \quad FMF_Z = \frac{1}{1 + \left(\frac{Z - b_2 - d}{d}\right)^{\rho}} \tag{8}$$

where: Z; variable, FMF; fuzzy membership function, b_1; critical level that the plant shows severely deficiency in the values lower than it, b_2; critical upper limit that the plant doesn't not faced with restrictions, d; width of transitional range ρ; indicate curve slope is based on the desired element behaviour in the study area, is determined by plant nutrition specialist.

To determine the upper and lower critical level of nutrient table 2 was used. b1; lower critical level of nitrogen and phosphorus concentrations, which in the amounts less than it the plant has a severe shortage of these 2 elements n paddy lands and yields loss is the possible. b2; critical upper limit (adequacy), which in higher nitrogen and phosphorus concentrations than it the plant doesn't faced to any restrictions in these nutrients uptake and, if other production factors likely to be optimized, high performance is archived.

Table 2. Critical level of nitrogen and phosphorus for rice in paddy soils

Soil properties	b1	b2	d
Total Nitrogen %	0.1	0.2	0.02
Available Phosphorus (mg. kg^{-1})	6.0	12.0	2.0

Statistical analysis

In this research, GS + 5.1 software was used for semi-variogram and representation of Boolean and fuzzy membership functions. For the representation of spatial distribution of fuzzy membership functions and Boolean by kriging first fitting and selection of varogram model were done. Fitted models, a model which remains the lowest sum of squares (RSS) and the highest coefficient explained (R^2) was selected as the best model for fitting of experimental values on semi-variance of practical values. To realize the spatial power structure (dependency) of each variable, the ratio of item variance (C0) to the total variance (C0 + C) were used. The ration of item variance to the threshold of a piece showed the share of piece variance from the total variance. This ratio helps us to compare the relative effect of piece variance between the different characteristics (Trangmar et al., 1985). the value of less than 25% of this ratio shows that the variable has a strong spatial dependency, 25 to 75% indicates the average spatial dependency and the values more than 75% considered as a weak spatial dependency (Sun et al., 2003).

Results and Discussion

Frequency distributions of the studied variables were shown in Table 3. Skewness of soil nitrogen and phosphorus was not significant at 5% level and their mean (0.16 and 7.0) is close to median (0.16 and 6.6) therefore the distribution of them is normal because the mean and median are approximately equal (Hasani Pak, 1997). If only random factors were affective in creating of differences, the distribution of values is normal or close to it (Rezaee, 1995).

Table 3. Statistical distribution of the studied properties

Properties	mean	min	max	median	mode	Var	S.D	skewness	kurtosis	C.V%
N%	0.16	0.07	0.28	0.16	0.17	0.00089	0.02981	0.336^{ns}	0.467	18.1%
P (mg. kg^{-1})	7.00	0.40	19.20	6.6	5.60	9.93232	3.15156	0.728^{ns}	1.020	44.6%

ns: insignificant at 5% level؛

Division of properties based on coefficient of variation (CV) and grouping based on Dahiya et al. (1985) and Wilding and Deres (1983) were shown in the Table 4. Parameter of coefficient of variation (CV) was dimensionless and can be use to compare of variation of a variable among the sampling units of 2 or more statistical populations with heterogeneous or incongruous observations between different properties of a sampling unit that have different observation size (Rezaee, 1995; McBratney and Odeh, 1997).

Table 4. Grouping properties based on coefficient variation (CV %)

Properties	Classification of Dahiya et al.			Classification of Wilding and Deres		
	high variation CV>75	medium variation 75CV<<15	low variation 75CV<	high variation CV>35	medium variation 35CV<<15	low variation 15CV<
N %		*			*	
P (mg. kg^{-1})		*		*		

With considering the grouping based on Dahiya et al. (1985) nitrogen and phosphorus has changes were moderate, while Wilding and Deres (1983) grouping resulted that phosphorus was had an extremely deficit. Coefficient of variation of more than 30% shows substantial variations of soil, more dissimilarity between the data and the requirement of more sample collection from the study population (Schöning et al., 2006). Boolean and fuzzy membership functions of nitrogen deficiency and sufficiency conditions are shown in the figures of 1 to 2. According to Figure 2a, the fuzzy membership function, number of examples with a concentration of less than 0.1% had a full dependence to severe limitation class, but samples with higher N 0.1 to close 0.2% had also relative dependence to deficiency class (severe restriction), but Boolean method was very rigid and samples with more than 0.1% N showed without dependence to severe restriction class (Figure 2a). Fuzzy membership function in the class of without nitrogen limitation. Figure 3a showed that samples with higher N 0.2% with complete dependence to adequacy class (without limitation and high fertility) are almost rare. While Boolean membership function, considered samples with less than 0.2% N without dependence on the class of without limitation (Figure 3b).

Fuzzy membership function for phosphorus in deficiency conditions (severe limitation) was shown in Figure 4a. Number of samples in class with severe limitations was very high and samples with the phosphorus concentrations of more than 6 mg kg^{-1} had also the relative dependence on severe limitations class. However, in severe limitations class of membership Boolean function this dependence did not exist (Figure 3b). Fuzzy membership function for class of without limitation phosphorus (Figure 5) showed that the number of samples in the class of high fertility and low limitation was very low. These results showed that the studied soils had more limitation for phosphorus than nitrogen.

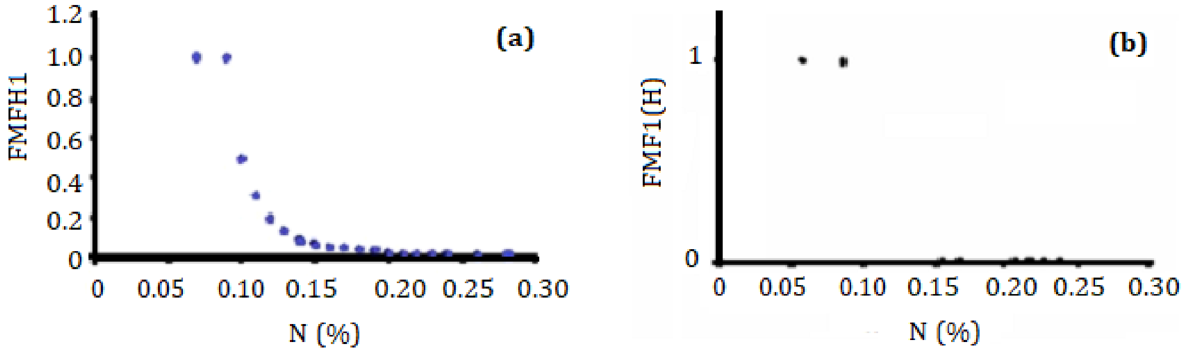


Figure 2. Fuzzy membership function (a) and Boolean membership function (b) of severe N limitation

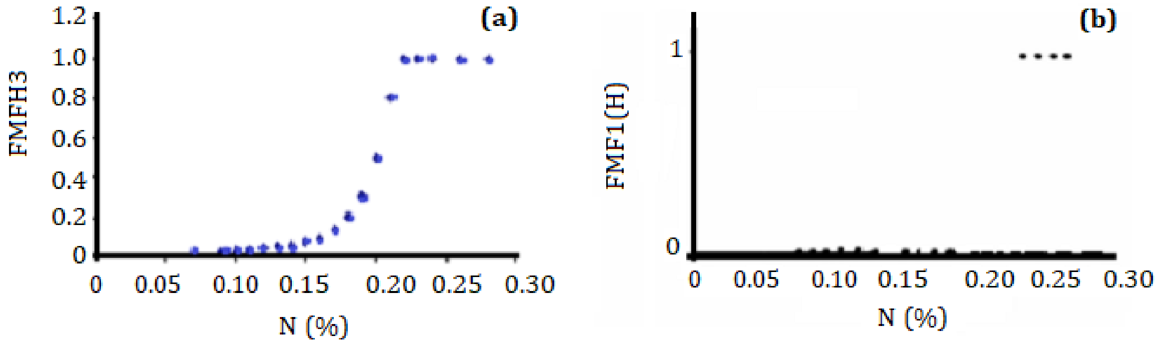


Figure 3. Fuzzy membership function (a) and Boolean membership function (b) of without N limitation

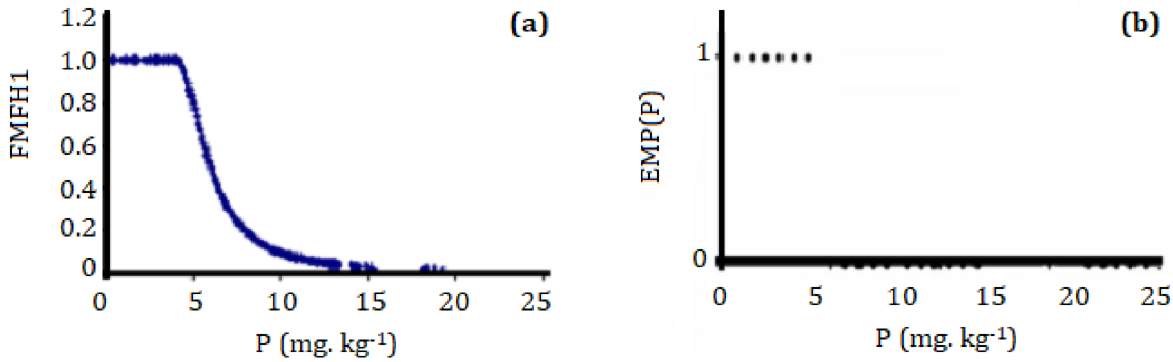


Figure 4. Fuzzy membership function (a) and Boolean membership function (b) of severe limitation of P

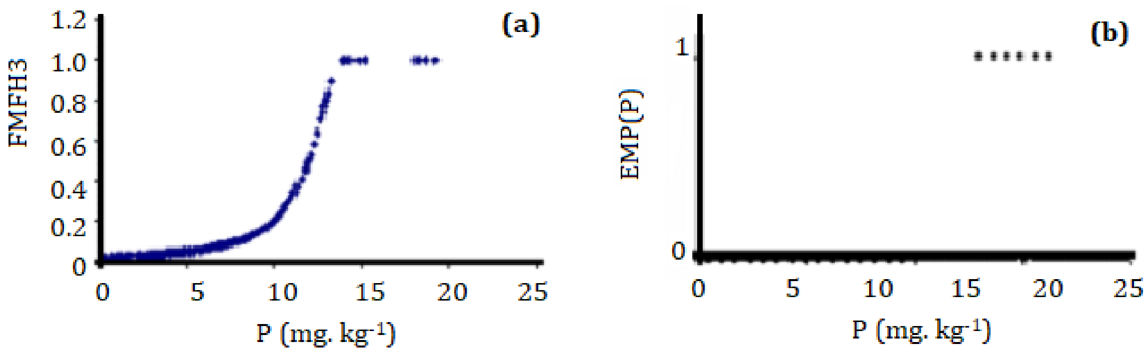


Figure 5. Fuzzy membership function (a) and Boolean membership function (b) of without limitation of P

The best fitted model of variogram for the data on membership functions of nitrogen and phosphorus, along with the spatial structure parameters of these variables were shown in the Table 5. Fuzzy membership functions and Boolean of N in severe limitation class followed from spherical variogram model and fuzzy membership functions and Boolean phosphorus in both classes (severe limitation or low fertility) (Figure 6) and adequacy (without limitation or high fertility) (Figure 7) also followed from spherical variogram model. Spherical variogram model shows a specific spatial dependence of a variable in a distinct range.

Table 5. Model of parameters estimated of N and P

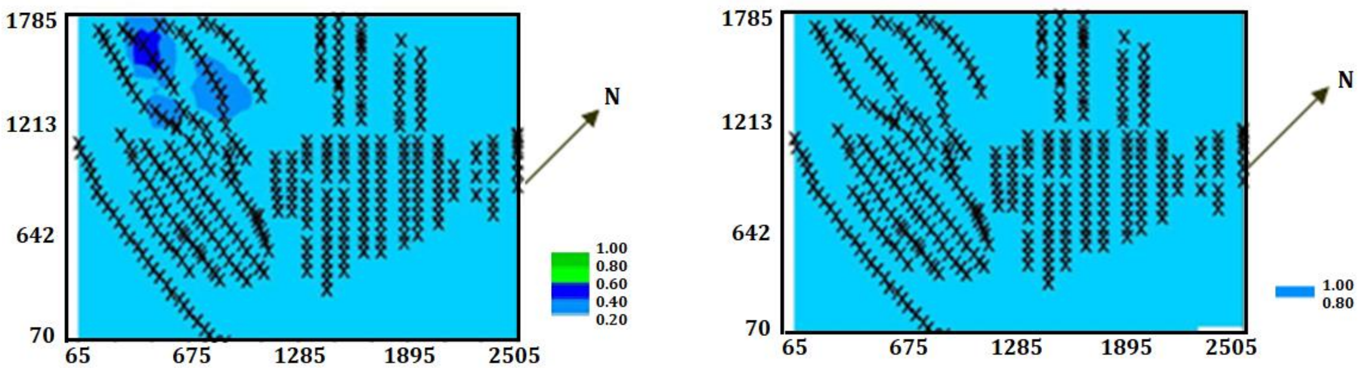
Properties	Method	Class	Model	C_0	C_0+C	A_0	R^2	RSS	$\frac{C_0}{C_0+C}\times 100$
N	Boolean	low fertility	spherical	0.00750	0.01430	1000	0.094	7.284×10^{-4}	52.4
		high fertility	linear	0.12382	-	-	0.052	9.499×10^{-3}	-
	Fuzzy	low fertility	spherical	0.00329	0.01132	1400	0.379	4.199×10^{-4}	29.0
		high fertility	spherical	0.03900	0.06590	300	0.088	5.185×10^{-3}	59.1
P	Boolean	low fertility	spherical	0.17000	0.26500	1000	0.399	0.0161	64.1
		high fertility	spherical	0.05020	0.06500	1100	0.193	0.0360	77.2
	Fuzzy	low fertility	spherical	007278	0.15877	2222	0.634	0.0111	45.9
		high fertility	spherical	0.03100	0.04210	1000	0.189	8.418×10^{-3}	73.6

Note. C_0: Piece variance, C_0 + C: Threshold, A_0: Effective range, R^2: Coefficient of determination, RSS: Residual sum of square

Effective ranges of nitrogen and phosphorus membership function were variable and fuzzy membership function for class of without nitrogen limitation was the lowest. This range indicates the magnitude of spatial dependence. Although, inherent soil forming factors have the greatest effect on the amount of effective range, but reduction of nitrogen effective range is further under the control of management factors such as differences in the amount of fertilizer applied and land leveling program (Sun et al., 2003), in addition, the effective range was used o determine of neighborhood radios in kriging.

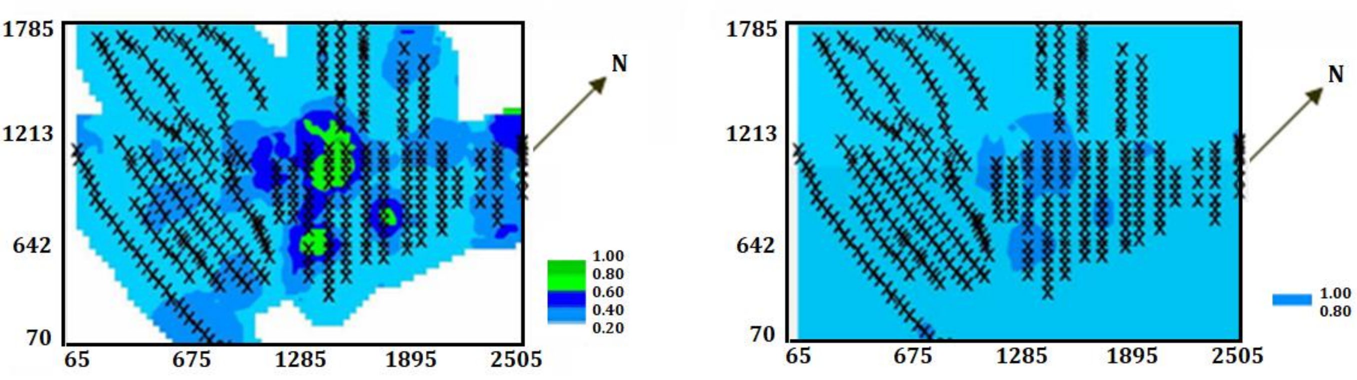
Fuzzy membership function of N in severe restriction class followed from the spherical model. Range of its dependence was high (1400 m) and had the medium spatial structure (29.0). Fuzzy membership function of phosphorus in both classes of severe restriction and without limitation followed from spherical model, but the extent and power dependency in the class of severe limitation were similar to the class of without limitations. Range of dependence for phosphorus in severe limitation class was high (2222 m) which indicates high range of spatial dependence and the spatial similarity of the study farm to the class of deficiency or severe restriction.

Parts of the paddy lands in of the southwest of study farm with the N fuzzy membership function between 0.2 to 0.6 had the highest values. But in other parts, there was no serious problem of nitrogen. Boolean method didn't able to detect severe limitation range in the Southwest and all of the studied paddy lands have dependence of more than 50% to the severe limitations class for nitrogen. Dobermann and Oberthür (1997) believed that nitrogen management is the key factor in control of yield throughout the study region. Representation of spatial membership distribution function of nitrogen in the class of without limitation showed that the central parts of the studied land with the fuzzy membership function of 0.6 to 1 and the Boolean membership function 0.5 to 1, had optimum status for nitrogen and had no limitation for supplying of plant nitrogen. But Boolean membership function unlike to fuzzy membership function could not separate the other parts of the land and determine the degree of their dependency to the class of without limitations (Figures 7).



(a) (b)

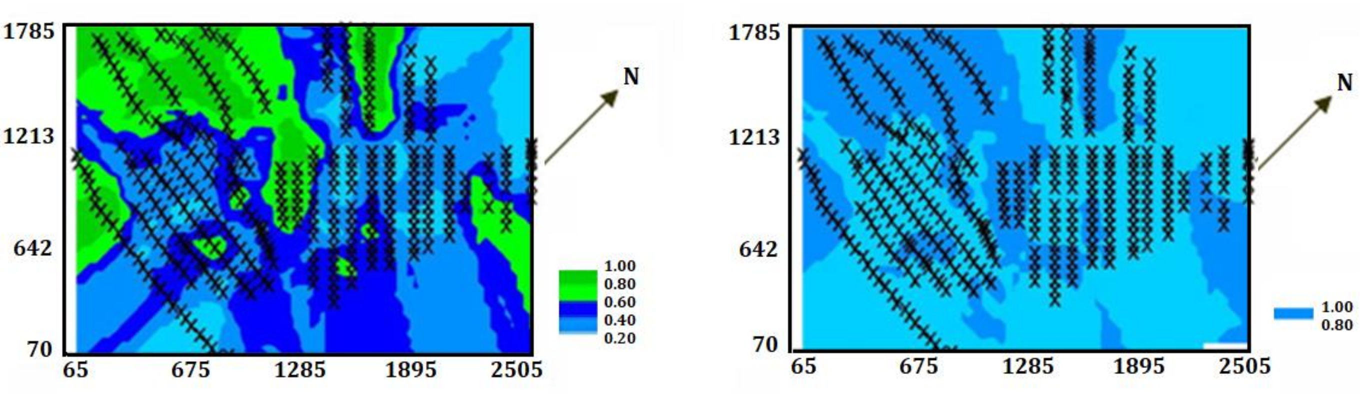
Figure 6. Map of fuzzy (a) and Map of Boolean (b) nitrogen severe limitations class



(a) **(b)**

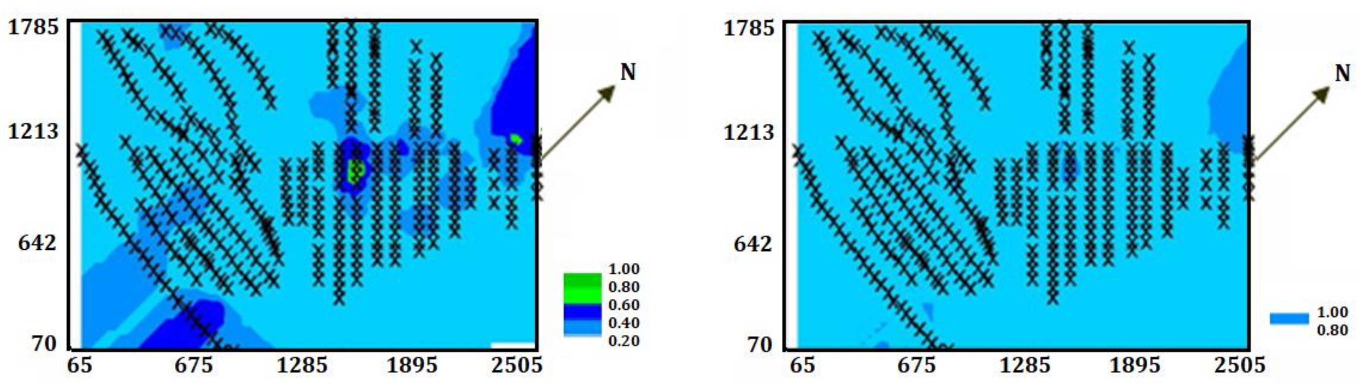
Figure 7. Map of fuzzy (a) and Map of Boolean (b) nitrogen without limitations class

North, south, south west and some parts of the centre of study field, with the fuzzy membership function of 0.6 to 0.8 and 0.8 to 1, had the most dependency to severe limitation class, and these had phosphorus shortage (Figure 8a). Spatial distribution of Boolean membership function also showed that these areas have limitations but with the lower resolution and considered the other parts of field without dependency on the class of severe limitation (Figure 8b). Only very small areas in north-central of studied paddy lands with fuzzy membership function of 0.6 to 0.8 had a dependence on middle limitation class for phosphorus (Figure 9). Except to very small area in centre and north of land with the Boolean membership function of 0.5 to 1 had minimum dependence on the class of without limitation. But the land separation ability of this function was weaker. Deficiency of P in the most of paddy-lands is partly related to the lack of phosphorus application for a long time, therefore, a suitable phosphorus fertilizer consumption is recommended for the almost all of the study area, especially to the parts belonging to class of severe restrictions and if the achievement of the yield more than 5-6 t/ha is considered the consumption of nitrogen and potassium should be considered.



(a) **(b)**

Figure 8. Map of fuzzy (a) and Map of Boolean (b) phosphorus severe limitations class



(a) **(b)**

Figure 9. Map of fuzzy (a) and Map of Boolean (b) phosphorus without limitations class

Fuzzy system was better in mapping of soil fertility for plant's nutrients and its prediction was also more accurate compare to the Boolean method. The efficiency of this method for phosphorous was superior to the nitrogen.

Conclusion

Preparation of soil fertility maps with fuzzy system improves precision and accuracy. Distingusing of nutrient deficiencies using fuzzy logic much better than regular approaches; so that, severe nitrogen deficiency in some part of study farm was distinguished in fuzzy system, but not with Boolean method.

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