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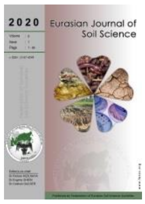




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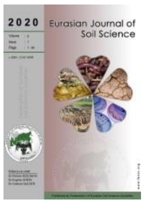



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# Hydraulic conductivity and sorptivity at unsaturated and saturated conditions as related to water infiltration in soils

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## Abstract

Sorptivity (S) has been defined in terms of the horizontal infiltration equation. At unsaturated conditions (at a very short time) S represents “maximum sorption capacity”, but in saturated conditions the sorption capacity decreases with the time. Over a long time of infiltration, sorptivity was not studied as a soil water parameter that could be determined. The purpose of this study is to apply derived equations depending on the infiltration functions to predict (1) soil water sorptivity (S) at infiltration capacity (unsaturated conditions) and at basic infiltration rate ($I_b$) (saturated conditions), (2) the hydraulic conductivity (Saturated Ks and unsaturated K(θ)) into capillary-matrix and non-capillary macro pores of soils. Five alluvial (saline and non-saline clay) and calcareous soil profiles located in the Nile Delta were investigated for applying the assumed equations. A decrease in S value was observed with an increase in soil water content. At steady infiltration rate ($I_b$), S decreased from 1.04 to 0.647cm.min$^{-0.5}$ (i.e. S decreased by 37.79%) in average in calcareous soils and from 0.537 to 0.251cm.min$^{-0.5}$ (53.25%) in alluvial clay soils. The steady $S_w$ parameter was used in prediction of the hydraulic conductivities and the basic infiltration rate $I_b$ , whereas, $S_w$ is a suggested term at steady infiltration rate. The calculated values of $I_b$ were corresponding to those obtained by infiltration experiment. This confirmed the significance of steady $S_w$ as a new functional infiltration parameter. A matching factor $u$ was calculated as a ratio between predicted $I_b$ and the measured saturated hydraulic conductivity, Ks. The mean values of $u$ were 0.895, 0.685 and 0.360 for calcareous, clay and saline clay soils respectively. Unsaturated K(θ) has been discriminated into saturated macro-pore $K(\theta)_{RDP}$ and matrix unsaturated $K(\theta)_h$. The values of $K(\theta)_{RDP}$ for macro pores remained higher than those for soil matrix pores ($K(\theta)_h$) in the studied soils. The highest value of K(θ) was obvious in calcareous soil profiles, while the lowest value was existed in saline clay soil. In conclusion, the predicted values of hydraulic conductivities of soil matrix (capillary) and macro (non-capillary) pores were reasonable and existed in the normal ranges of the investigated soils, indicating that the proposed equations are applicable and can be recommended to be used in coarse and fine textured soils with large scale of different properties.

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**Keywords**: Infiltration functions, soil pores, steady sorptivity, unsaturated hydraulic conductivity.



## Introduction

Infiltration is the passage of water into the soil surface and is distinguished from percolation, which is the movement of water through the soil profile. Irrigation water is generally infiltrated into root zone during conveyance and recession of water at the soil surface (Amer, 2004). Wu (1971) and Amer (2011a) studied the infiltrated water functions into soil during surface irrigation. Infiltration of water into soil can be described quantitatively by solving the transport equation (Richards, 1931; Klute, 1952). The solutions require knowing the relationship between water content and soil water pressure ($h$) as well as the relation

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between water content and hydraulic conductivity. The literature emphasizes the development of representative infiltration equations, e.g., those proposed by Green and Ampt (1911), Kostiakov (1932), Philip (1957), Parlange et al. (1985). The soil hydraulic properties in relation to water infiltration are essential for quantifying the rate of water flow and transport processes in the plant root zone. Water flows in the root zone occur principally through the macro non-capillary pores of soil, while the redistribution and upward flow occur in the capillary soil matrix pores (Amer, 2012). The water conductivity of soil pores is mainly controlled by pore sizes, continuity and pore size distribution in soil. On the other hand, Water flow, soil surface roughness, and infiltration rate affect the non-uniform and unsteady of flow pattern into root zone along surface irrigation (Hoogmoed and Bouma, 1980). Water inflow is expressed in a continuity equation and an equation of motion (Cahoon et al., 1995).

The purpose of this work is modeling and correlate the infiltration functions to sorptivity, hydraulic conductivity, and soil water filled pores in the root zone. In that concern, it is needed (1) to find a matching factor (*u*) between infiltration rate and hydraulic conductivity during steady state infiltration, (2) to predict water sorptivity (S) at steady state infiltration, and (3) to propose new applicable equations based on infiltration rate and soil moisture retention functions for prediction of the hydraulic conductivity [saturated, Ks and unsaturated, K(θ)] into the rapidly (non-capillary) drainable pores (RDP) and capillary-matrix pores of soils.

## Theoretical development

### Saturated hydraulic conductivity and sorptivity at steady infiltration rate

The variably saturated flow process in soils is a highly nonlinear and dynamic phenomenon. The infiltration into soil is defined with the one-dimensional differential equation (Klute, 1952, Germann, 2018). The infiltration rate (I) is defined as the volume of water infiltrating through a horizontal unit area of soil surface at any instant (infinitely small period of time), [$LT^{-1}$], while the cumulative infiltration (Z) is the total volume of water that has infiltrated through a unit of horizontal area of soil surface over a given period of time *t*, measured from the beginning of infiltration, (can be expressed in depth unit, cm or mm). For many soils a plot of Z [L] as a function of time t [T] (or opportunity time, $t_o$) is described by the equation (Kostiakov, 1932):

$$Z = ct^{m} \tag{1}$$

or

$$Z = \frac{k}{m}\ t_o^{m} \tag{2}$$

where, *c* [$LT^{-m}$] and *m* [dimensionless] are empirical coefficients for a given soil and a given moisture content, respectively, and $k = c\ m$. Both fitting parameters c and m can be determined from a simple logarithm regression analysis over the experimental Z(t) data, as:

$$\log Z = \log c + \mathrm{m} \log t \tag{3}$$

where, log *c* is the intercept and *m* the slope of the linear regression, and *Z* is equal to *c* in unit of time.
By differentiating the expression for Z (Eq. 2) with respect to time t, the infiltration rate (instantaneous) I at the soil surface defined as:

$$I = \frac{dZ}{dt} = cmt^{m-1} \qquad \text{or} \qquad I = k\ t_o^{m-1} \tag{4}$$

where, soil infiltration rate (I) is a function of time, expressed in cm/min or mm/min.
Philip (1957) showed that the cumulative infiltration Z, cm in soil changes with square root of time ($t^{0.5}$) depending on water sorptivity (S) of the soil. The S [$LT^{-1/2}$] was originally defined by the Philip equation for horizontal infiltration into an initially dry soil (equation 5),

$$Z = St^{1/2} \tag{5}$$

If Z is plotted against $t^{0.5}$ then a linear relationship is usually found for the first 1 to 3 minutes of infiltration. The slope of the linear relationship $S = \left[\frac{dZ}{d\sqrt{t}}\right]_t$ allows to determine S at the unit of time. Equation (5) corresponds to the first term of the semi-analytical solution of Philip (1957) to the governing differential equation for one-dimensional, unsaturated water flow, where the Philip infiltration equation was employed to calculate the cumulative infiltration Z using time series powers of $t^{0.5}$ as follows:

$$Z = C_1(\theta)\, t^{1/2} + C_2(\theta)\, t + C_3(\theta)\, t^{3/2} + C_4(\theta)\, t^2 + \ldots + C_m(\theta)\, t^{m/2} + \tag{6}$$

where, $C_1(\theta)$, $C_2(\theta)$, $C_3(\theta)$, $C_4(\theta)$, ..., and $C_m(\theta)$ are functions of the soil water content θ, and t is time.

The first two and three terms of the Philip infiltration equation (Eq. 6) can be used to estimate the saturated hydraulic conductivity $K_s$ (Zhang, 1997). The first two terms are applicable for relatively short times as follows:

$$Z = S\,t^{1/2} + uK_s t \qquad (7)$$

where $K_s$ is saturated hydraulic conductivity, and u is a constant such that $0 \leq u \leq 1$. Philip (1969); Swartzendruber and Young (1974) suggested that a fit of Eq. 7 to the whole elapsed time range would lead to select $u \approx 1$.

Equations 2, 4, and 7 have the same functional form, so S can be replaced by C;

$$S = c^{0.5/m} \quad \text{or} \quad S = C^{-m}\,C^{1/2} \qquad (8)$$

At steady-state infiltration, the infiltration rate, I, becomes constant and denoted as basic (final) infiltration rate, $I_b$. The time that must elapse before the instantaneously infiltration rate, I, becomes approximately constant can be expressed in terms of the soil property, m (Amer, 2011a);

$$t = 10\,(1-m) \quad \text{hr} \qquad (9)$$

By differentiation of Eq.7 at unsaturated conditions, the corresponding flux equation becomes:

$$dZ / dt = S / 2t^{0.5} + uK_s \qquad (10)$$

The sorptivity S is thus:

$$S = 2t^{0.5}\,(I - uK_s) \qquad (11)$$

At steady state infiltration, where $I = I_b$, the Eq. 1 and 4 can be rearranged as:

$$Z = \frac{I_b . t}{m} = \frac{uK_s . t}{m} \qquad (12)$$

By combination of Eq. 7 in the form $S = 1/t^{0.5}\,[Z - K_s t]$ with Eq. 12, the result is:

$$I_{b(calculated)} = \frac{S\ m}{(1-m)\sqrt{t}} \qquad (13)$$

Valiantzas et al. (2009) pointed out that the variation of soil initial water content affected the value of S. So, it may be of interest to define the sorptivity S at measured steady state infiltration $I_b$ in term steady sorptivity, $S_w$.

According to Eq.13, steady sorptivity ($S_w$) becomes:

$$S_w = I_{b(measured)}\left(\frac{1-m}{m}\right)\sqrt{t} \qquad (14)$$

where measured $I_b$ is obtained from experimental data at the time $\sqrt{t} = [10(1\text{-}m)]^{0.5}$.

At steady state infiltration, where the gravitational potential is predominant, the basic (final) infiltration rate $I_b$ [$LT^{-1}$] could be identical with the saturated hydraulic conductivity of soil as $I_b \approx uK_s$ (Eq. 7), and then the constant *u* is considered as a matching factor or an adjustment between $K_s$ and $I_b$. By combining Eq. 7 with Eqs.10 and 13, the matching factor *u* (dimensionless) between $I_b$ and $K_s$, has been obtained as;

$$u = \frac{mI_b . \sqrt{t}}{I_b . \sqrt{t} - mS} \qquad (15)$$

with respect to Eqns. 7, 12 and 13, the saturated hydraulic conductivity ($K_s$) can be then estimated theoretically as follows:

$$K_{s(calculated)} = \frac{Sm}{u(1-m)\sqrt{t}} \qquad (16)$$

### Unsaturated hydraulic conductivity K(θ) in transmission zone

By measuring sorptivity and using it as a scaling factor, the unsaturated hydraulic conductivity K(θ) can be predicted fairly accurately (Moldrup et al., 1993). Application of the one-dimensional form of Darcy's equation using the average K(θ) and hydraulic gradient with reference to steady infiltration rate may be useful in prediction of water flow in unsaturated soils. During infiltration, the application rate of water to soil surface is often greater than $K(\theta)_{RDP} + K(\theta)_h$, where $K(\theta)_{RDP}$ is the hydraulic conductivity into the rapidly drainable pores and $K(\theta)_h$ is the matrix unsaturated hydraulic conductivity (Germann and Prasuhn, 2018). At steady state infiltration and steady sorptivity ($S = S_w$), and when ponding water depth (h) on the upper surface of the soil reaches zero ($h_0$) [i.e., $\Delta h = h_0 - (-\psi_i)$, where $\psi_i$ is the water potential at particular moisture content θi that corresponds to the boundary limit of soil-water filled pore class], Amer (2011b) proposed the following model;

$$K(\theta) = \frac{Z.S_w}{\Delta h.\Delta\theta.\sqrt{t}}[\frac{1+m}{2(1-m)}] \tag{17}$$

where K(θ) is unsaturated hydraulic conductivity in the transmission zone of the infiltration moisture profile in soil, Z is the cumulative infiltration at the time $\sqrt{t}$ = $[10(1\text{-}m)]^{0.5}$ which should be equal to the product of the wetting front depth $L_f$ (i.e., the distance from the soil surface to the wetting front), Δh is the pressure head change from soil surface to the wetting front ($h\text{-}h_f$). The latter corresponds to $\Delta\theta = \theta s\text{-}\ \theta in$ in the soil profile.

The solution of Philip's equation (Eq. 6) indicates that at small times, the advance of any θ value proceeds as $\sqrt{t}$ (just as in horizontal infiltration), while at larger times the downward advance of the wetting front approaches a constant rate $(K_0 - Ki)/(\theta_0 - \theta i)$. Here $K_o$ and Ki are the conductivities at the soil water contents of $\theta_0$ (wetted surface) and $\theta_i$ (initial soil wetness), respectively. For different soil pore classes, K(θ) can be calculated by applying $\Delta h = h_0 - (-\psi)_{0\text{-}10kPa}$, $\Delta h = h_0 - (-\psi)_{0\text{-}33kPa}$, $\Delta h = h_0 - (-\psi)_{0\text{-}1500kPa}$, and $\Delta h = h_0 - (-\psi)_{>1500kPa}$ (in cm $H_2O$) for RDP, SDP, WHP, and FCP respectively. The corresponding Δθ values of water filled pore classes can be derived from soil-moisture retention curve. Thus, the equation 17 can be developed (Amer, 2011b) into:

$$K(\theta) = \frac{C.Z.S_w}{\Delta h.\Delta\theta}\ [\frac{(1+m)}{(1-m)^{1.5}}] \tag{18}$$

The calculated values of K(θ) (in cm/hr) by Eq. 18 represent the accumulative drainable and matrix pore classes in transmission and wetting zones. In order to calculate K(θ) for individual class of pore size, Eq. 18 should contain saturation degree (*a*) as a representative for that particular pore class size:

$$K(\theta)_i = \frac{CZS_w.a}{(\Delta\psi)i\ (\Delta\theta)i}\ [\frac{(1+m)}{(1-m)^{1.5}}] \tag{19}$$

where the subscript i denotes the soil pore class, C is a numerical coefficient = 0.1581, Δψ is the matric potential of the particular pore class, and *a* represents $\frac{(\Delta\theta)_{RDP}}{\theta_s}$, $\frac{(\Delta\theta)_{SDP}}{\theta_s}$, $\frac{(\Delta\theta)_{WHP}}{\theta_s}$, and $\frac{(\Delta\theta)_{FCP}}{\theta_s}$ for RDP, SDP, WHP, and FCP respectively.

## Material and Methods

Five soil profiles; calcareous sandy loam, alluvial saline and non-saline clay, located at the Nile Delta (Egypt) were used for testing the applicability of proposed equations (Table 1). The 1st and 2nd profiles located at Nubaria and Borg El-Arab areas (northern west of the Nile Delta), and 3rd, 4th and 5th located at Shebin El-Kom, Ebshan, and El-Khamsin (middle Nile Delta) areas, respectively. Disturbed and undisturbed soil samples were taken from three successive depths of the concerned soil profiles. Soil samples were subjected to chemical and physical analyses (as given in Table 1) according to Page (1982), Sparks et al. (1996), Dane and Topp (2002). Saturated hydraulic conductivity (Ks) was measured with the constant head method as discussed in Klute (1986). Darcy's law was applied to calculate Ks;

$$\text{Ks} = \frac{V.L}{A.t.\Delta H} \tag{20}$$

where V is the volume of discharged water ($cm^3$), L is the length of the core (cm), A is the cross-sectional area of the core ($cm^2$), t is the discharge time (sec), and ΔH is the hydraulic head difference across a distance L (cm). The $[\theta]_{0-10kPa}$ soil water content on volume basis at suction pressure head $h$ =10 kPa was determined using undisturbed samples for clay alluvial and saline soils (profiles III, IV, and V), while neutron probe and tensiometers in situ were used for calcareous soils (profiles I and II). Disturbed samples were air-dried, gently crushed, sieved through a 2 mm sieve, and used for analysis of saturation water content ($\theta_s$), $CaCO_3$, salinity (EC), sodium adsorption ratio (*SAR*), and particle size distribution. The hydration envelopes in which water content is considered to be immobile in soil should be subtracted from FCP, can be

expressed as moisture adsorption capacity (*Wa*) (Amer, 2009);

$$Wa = Wm + 2Wme \tag{21}$$

where *Wm* is the mono-adsorbed layer of water molecules on soil particles, and *Wme* is the external mono-adsorbed layer of water molecules. The water vapour adsorption isotherm method with applying BET theory was used to estimate Wm and Wme.

The infiltration rate was measured using the double ring method (Ankeny, 1992; Reynolds et al., 2002) in thefield for the concerned soils.

Table 1. Physical and chemical properties of the studied soils.

| Soil profile and location | Soil depth,cm | EC†, dS m-1 | $\rho_b$, g.cm-3 | $CaCO_3$, % | Particle size distribution, Sand, % | Silt, % | Clay, % | Texture class | $\theta_s$, $m^3\ m^{-3}$ | *Ks, cm.h-1 | Wa, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I Nubaria | 0-20 | 0.34 | 1.48 | 22.00 | 55.98 | 19.90 | 24.12 | SCL | 0.512 | 3.81 | 5.90 |
| | 20-40 | 0.26 | 1.52 | 23.00 | 55.79 | 20.31 | 23.90 | SCL | 0.489 | 3.67 | 4.98 |
| | 40-60 | 0.24 | 1.50 | 26.00 | 54.85 | 22.15 | 23.00 | SCL | 0.487 | 3.45 | 4.34 |
| II Borg El-Arab | 0-20 | 0.38 | 1.46 | 36.00 | 71.33 | 17.30 | 10.37 | SL | 0.449 | 3.32 | 5.40 |
| | 20-40 | 0.42 | 1.48 | 38.00 | 73.32 | 15.30 | 11.38 | SL | 0.444 | 3.10 | 5.16 |
| | 40-70 | 0.41 | 1.48 | 32.00 | 77.91 | 13.00 | 9.90 | LS | 0.431 | 3.59 | 4.70 |
| III Shebin El-Kom | 0-30 | 1.90 | 1.30 | 2.10 | 23.76 | 35.28 | 40.96 | C | 0.657 | 2.20 | 13.46 |
| | 30-60 | 1.60 | 1.38 | 1.84 | 23.60 | 34.75 | 41.65 | C | 0.693 | 1.78 | 12.17 |
| | 60-90 | 2.00 | 1.35 | 0.92 | 22.29 | 32.91 | 44.80 | C | 0.662 | 1.72 | 9.63 |
| IV Ebshan | 0-30 | 2.30 | 1.27 | 0.84 | 21.98 | 15.37 | 62.65 | C | 0.721 | 1.25 | 12.32 |
| | 30-60 | 1.89 | 1.28 | 0.98 | 14.31 | 18.69 | 67.00 | C | 0.768 | 1.04 | 13.70 |
| | 60-90 | 1.22 | 1.28 | 0.79 | 16.44 | 24.38 | 59.18 | C | 0.732 | 1.13 | 13.56 |
| V El-Khamsin | 0-30 | 6.00 | 1.21 | 0.67 | 8.26 | 28.50 | 63.24 | C | 0.743 | 0.98 | 13.07 |
| | 30-60 | 6.44 | 1.19 | 0.82 | 7.38 | 23.62 | 69.00 | C | 0.782 | 0.81 | 14.75 |
| | 60-90 | 8.12 | 1.18 | 0.56 | 9.04 | 20.46 | 70.50 | C | 0.754 | 0.75 | 14.39 |

†EC is electrical conductivity, $\rho_b$ is bulk density, $\theta_s$ is saturation water content and *$K_s$ is measured saturated hydraulic conductivity.

## Results and Discussion

### Pore class size distinctions

Water is held in soil pores by cohesive and adhesive capillary forces. The size of pores in unsaturated soil state can be determined through the so-called hydraulic radius ($r$) of a section of pore space. The relation between $r$ and capillary forces expressed as pressure head potential ($h$ in m) is represented by the following capillary rise equation (Hillel, 1980, Amer et al., 2009):

$$h = \frac{2\gamma \cos\alpha}{\rho_w g r} \tag{22}$$

where, γ is surface tension between water and air (at 20ºC = 0.0727 kg $s^{-2}$), $r$ (in m) is equivalent cylindrical pore size (hydraulic) radius related to meniscus curvature radius (R) via equation; r = R cos α, and cos α is assumed to be 1 for the wet surface, $g$ is acceleration due to gravity (9.8 m $s^{-2}$), and $\rho_w$ is density of water (998 kg $m^{-3}$ at 20ºC). As soil dries out, increasing suction occurs due to progressive empty of capillary pores. Pore size diameters were determined for the ranges of soil matric potentials by applying Eq. (22) with respect to soil water retention curves (Table 2).

The K(θ) of capillary pores was divided into $K(\theta)_{SDP}$, $K(\theta)_{WHP}$, and $K(\theta)_{FCP}$ within slowly drainable pores, SDP, water holding pores, WHP and fine capillary pores FCP, respectively. These categories can be combined into total draining pores (*TDP*) (0-330 hPa), and total water-storage pores (*WSP*) (> 330 hPa), as well as into macro (non-capillary) pores (<100 hPa) and soil matrix (capillary) pores (>100 hPa). The pressure head corresponding with the cutoff between capillary and non-capillary pores varies widely, ranging from 1.0 hPa (Beven and Germann, 1982) to 100 hPa (Marshall, 1956). However, $h$ = 100 hPa is selected by Amer et al. (2009) as corresponding to the limit between capillary and non-capillary pores.

Table 2. Pore size classes as a percent of soil bulk volume (Δθ%) and ratio of total volume pores $\frac{\Delta\theta}{\theta_s}$

| Soil profile and location | Soil depth (cm) | RDP Δθ % $\frac{\Delta\theta}{\theta_s}$ | SDP Δθ % $\frac{\Delta\theta}{\theta_s}$ | TDP Δθ % $\frac{\Delta\theta}{\theta_s}$ | WHP Δθ % $\frac{\Delta\theta}{\theta_s}$ | CCP Δθ % $\frac{\Delta\theta}{\theta_s}$ | FCP Δθ % $\frac{\Delta\theta}{\theta_s}$ | TVP A/W % |
|---|---|---|---|---|---|---|---|---|
| **I** Nubaria (SL) | 0-20 | 14.6<br>0.369 | 11.10<br>0.280 | 25.72<br>0.649 | 6.40<br>0.162 | 17.50<br>0.442 | 7.50<br>0.189 | 39.62<br>1.85 |
| | 20-40 | 13.8<br>0.385 | 10.01<br>0.278 | 23.86<br>0.663 | 4.93<br>0.137 | 14.94<br>0.415 | 7.18<br>0.199 | 35.97<br>1.97 |
| | 40-60 | 12.8<br>0.364 | 9.42<br>0.267 | 22.24<br>0.631 | 6.00<br>0.170 | 15.42<br>0.437 | 7.00<br>0.198 | 35.24<br>1.71 |
| **II** Shebin El-Kom (Clay) | 0-30 | 1.25<br>0.190 | 8.10<br>0.123 | 9.35<br>0.142 | 31.68<br>0.482 | 39.78<br>0.605 | 24.74<br>0.376 | 65.77<br>0.17 |
| | 30-60 | 1.33<br>0.192 | 16.30<br>0.235 | 17.63<br>0.254 | 28.90<br>0.417 | 45.20<br>0.652 | 22.78<br>0.328 | 69.31<br>0.34 |
| | 60-90 | 2.00<br>0.302 | 13.28<br>0.200 | 15.28<br>0.231 | 29.54<br>0.446 | 42.82<br>0.646 | 21.46<br>0.324 | 66.28<br>0.30 |

A/W is Air/Water ratio or A/W = TDP/(WHP+FCP)

The radii and volumes of the drainable and capillary pores were determined (such as in Table 2) from the soil water retention curves SWRC, ψ(θ) (Figure 1) by applying equation (22).

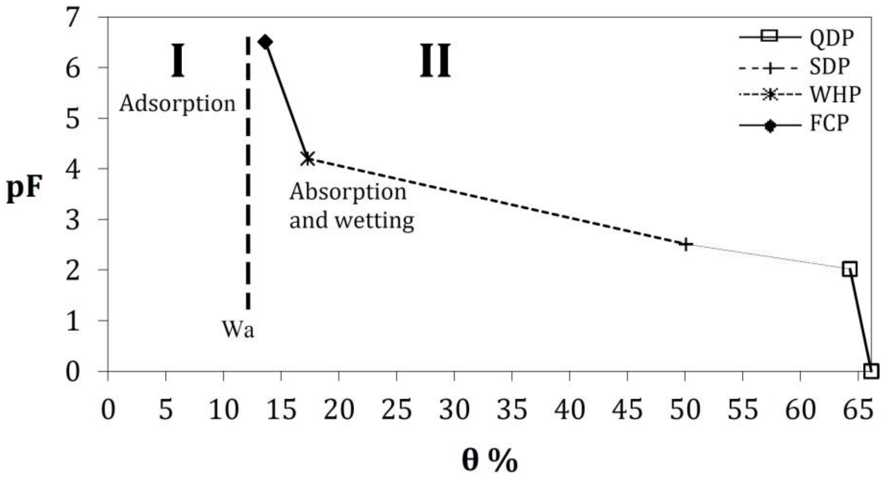


Figure 1. Pore size distribution (%) expressed in volumetric water content (θ%) and soil moisture suction (pF=log $h$) or [$h$(θ)] function in Shebin El-Kom soil profile.

## Infiltration power functions and water sorptivity

The typical trends in cumulative infiltration, *Z, cm* versus time t minute and infiltration rate, *I, cm/h* are illustrated by empirical power functions according to Eqns.1 and 4 (Table 3 and Figure 2). The constants *c* and *m* of the equations ranged from 1.12 to 0.51 and from 0.58 to 0.38 respectively, in the investigated soils. The highest values of *c* and *m* were evident in calcareous soils (profiles I and II) and the lowest value was in alluvial saline clay soil (profile V). As the onset of wetting, the moisture gradient was the greatest, hence more rapid infiltration was obtained. The infiltration rate $I$ ($LT^{-1}$) slowed gradually with time t and reached the steady state of flow (basic infiltration rate, $I_b$) after 4.2- 4.5 h from the beginning of infiltration for calcareous I and II soil profiles, and after 5.4-6.2 h in alluvial clay IV and V soil profiles. The steady-state infiltration was occurred in Shebin El-Kom soil (III profile) after 4.7 hour. Values of steady infiltration rate can be calculated using Eq.9 or by experimental infiltration curves of Z(t) function.

Sorptivity (S) in unsaturated condition represents the highest capacity of “absorption” but the capacity decreases with increasing water content in soil due to accumulated infiltration depth. It may be of interest to propose sorptivity as a soil hydro-physical property. Thus, the term “sorptivity” (S) at unsaturated conditions [at a very short time (1 – 3 minutes)] represents “maximum sorption capacity”, while at saturation conditions S represents “minimum sorption capacity”. With respect to water infiltration in soil, the term wet or steady sorptivity (Sw) after a long time of infiltration (saturation case) may be suggested for application in similar way to the term “steady infiltration rate”.

Table 3. Infiltration functions and hydraulic conductivities for the studied soils

| Soil profile and location | Soil depth (cm) | Z, cm& I, cm/h | S, cm/min$^{0.5}$ | $S_w$ cm/min$^{0.5}$ | $K_S$ (=$I_b$), cm/min | $K(\theta)_{RDP}$, cm.min$^{-1}$ | $K(\theta)_h$, cm.min$^{-1}$ | (u) $I_b/^*K_s$ | $[\theta]_{0-10kPa}$ m$^3$.m$^{-3}$ |
|---|---|---|---|---|---|---|---|---|---|
| I Nubaria | 0-20 | $Z=0.97\ T^{0.58}$ $I=33.8\ T^{-0.42}$ | 0.974 | 0.633 | 0.055 | $7.11x10^{-1}$ | $3.83x10^{-3}$ | 0.866 | 0.0662 |
| | 20-40 | | | | | $6.58x10^{-3}$ | $3.55x10^{-3}$ | 0.899 | 0.0585 |
| | 40-60 | | | | | $5.45x10^{-3}$ | $2.93x10^{-3}$ | 0.956 | 0.0482 |
| II Borg El-Arab | 0-20 | $Z=1.12T^{0.55}$ $I=36.9T^{-0.45}$ | 1.108 | 0.661 | 0.049 | $8.23x10^{-3}$ | $5.58x10^{-3}$ | 0.885 | 0.0754 |
| | 20-40 | | | | | $8.06x10^{-3}$ | $5.46x10^{-3}$ | 0.948 | 0.0731 |
| | 40-70 | | | | | $9.53x10^{-3}$ | $6.47x10^{-3}$ | 0.819 | 0.0840 |
| III Shebin El-Kom | 0-30 | $Z=0.61T^{0.53}$ $I=19.3T^{-0.47}$ | 0.627 | 0.340 | 0.023 | $8.75x10^{-4}$ | $7.38x10^{-4}$ | 0.623 | 0.0252 |
| | 30-60 | | | | | $8.16x10^{-4}$ | $6.89x10^{-4}$ | 0.769 | 0.0248 |
| | 60-90 | | | | | $1.02x10^{-3}$ | $8.63x10^{-4}$ | 0.796 | 0.0297 |
| IV Ebshan | 0-30 | $Z=0.59T^{0.46}$ $I=16.4T^{-0.54}$ | 0.574 | 0.257 | 0.012 | $3.71x10^{-4}$ | $4.59x10^{-4}$ | 0.584 | 0.0221 |
| | 30-60 | | | | | $3.12x10^{-4}$ | $3.86x10^{-4}$ | 0.702 | 0.0198 |
| | 60-90 | | | | | $3.30x10^{-4}$ | $4.09x10^{-4}$ | 0.646 | 0.0200 |
| V El-Khamsin | 0-30 | $Z=0.51T^{0.38}$ $I=11.6T^{-0.62}$ | 0.412 | 0.157 | 0.005 | $1.29x10^{-4}$ | $2.09x10^{-4}$ | 0.306 | 0.0192 |
| | 30-60 | | | | | $1.19x10^{-4}$ | $1.92x10^{-4}$ | 0.370 | 0.0186 |
| | 60-90 | | | | | $1.42x10^{-4}$ | $2.31x10^{-4}$ | 0.400 | 0.0215 |

$[\theta]_{0-10kPa}$ is drained water of macro pores, and Ks is predicted saturated hydraulic conductivity.

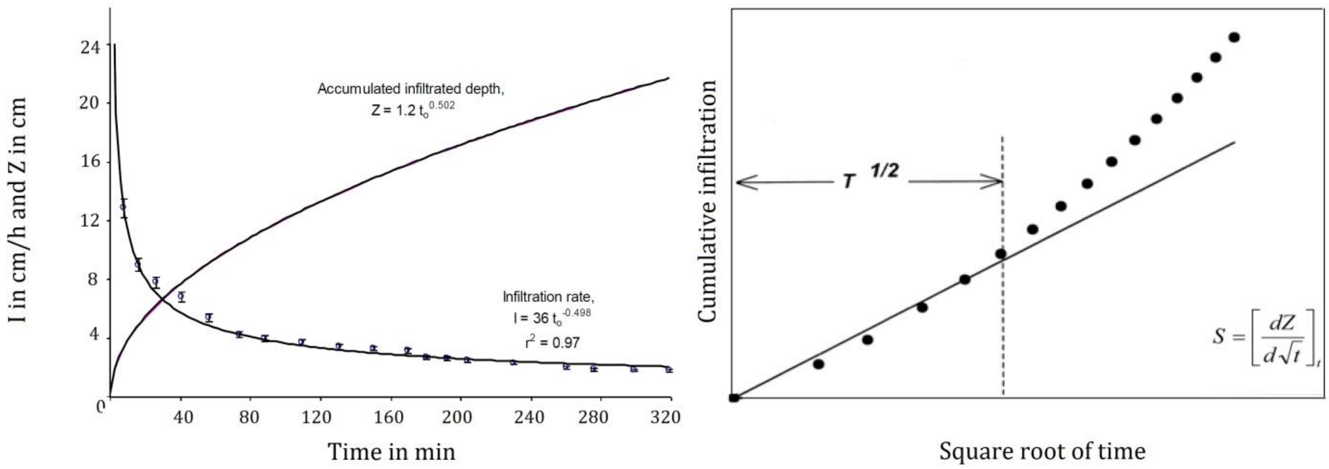


Figure 2. Cumulative infiltration (Z), infiltration rate (I) and Prediction of Sorptivity (S) at square root time (T $^{0.5}$) for Borg El-Arab soil profile

Data of infiltration parameters and water sorptivity are given in Table 3. Hallett (2008) mentioned that sorptivity is the capacity of soil to absorb (suck up) water and is dominated by the antecedent water content of the soil. At the beginning of infiltration in an initial dry soil (un-saturation conditions), the sorptivity, S can be calculated using *Z* as functioned to time *t* and adjusted to *m* = 0.5 (Eq. 5). The S values were found to be ranged from 1.108 to 0.412cm/min$^{0.5}$ in the studied soils. The values were in the following order: Borg El-Arab>Nubaria>Shebin El-Kom>Ebshan>El-Khamsin. Sorptivity (S) at steady-state infiltration was denoted as wet or steady sorptivity ($S_W$) and calculated using Equation14. It worthy to mention that the data of the infiltration rate at steady-state infiltration $I_b$ which calculated via steady sorptivity ($S_w$) (Eq.13) were correspondent to those obtained by the experimental data. This confirm the significance of $S_W$ in predicting the hydrological soil parameters such as $I_b$, $Ks$ and $K(\theta)_i$. It was observed that sorptivity was decreased at steady-state infiltration by 37.79% in average in calcareous soils and by (53.25%) in average in alluvial clay soils. This means that a dry soil typically has a much greater sorptivity than a wet soil (Hallett, 2008). These results attributed to soil texture and salinity in alluvial clay soils and to abundance of $CaCO_3$ fraction which has a great ability to suck up water in such calcareous soils (Ghazy, 1993).

**Hydraulic conductivity in soil pores and matching factor**

Data presented in Table 3 show the values of hydraulic conductivity K(θ) as calculated by the derived equations for matrix and macro pores of the investigated soils. The $K(\theta)$ values were discriminated into saturated hydraulic conductivity ($Ks$), macro pore saturated $K(\theta)_{RDP}$ and matrix unsaturated $K(\theta)_h$ of soil (Amer, 2012; Weiler, 2017). The values of $K(\theta)_{RDP}$ remained higher than those for lateral $K(\theta)_L$ in I, II, III soil profiles, particularly, in calcareous soils. The opposite trend was observed for VI and V heavy clay soil profiles. It was evident that $K(\theta)_{RDP}$ values increased gradually with increasing sand and $CaCO_3$ fractions in soil profiles. The hydraulic conductivity K(θ) values into soil matrix were higher as much as in Borg El-Arab calcareous soil (profile II) due to the prevalence of $CaCO_3$ fraction in that calcareous soil. As expected, the values of $K(\theta)_h$ and $K(\theta)_{RDP}$ increased with increase in pore sizes, soil porosity, and water content; θ and $[\theta]_{0-10kPa}$. On the other hand, the values are decreased by the prevailing fine clay fraction, salinity, fine and coarse capillary pores in the soil matrix of such clay soils. A matching factor *u* was calculated as a ratio between predicted $I_b$ (Eq.13) and the measured Ks (Table 2). The mean values of *u* ranged from 0.91-0.88 in calcareous soils (I&II profiles) to 0.73-0.64 in clay soils (III&IV profiles). The *u* values decreased to 0.36 in saline clay soil (V profile) indicating that the matching factor decreases with increasing clay fraction and salinity of soils.

## Conclusion

Equations were proposed to estimate the hydraulic conductivity K(θ) and sorptivity (S) in soils. Five soil profiles - located in the Nile Delta - differ in their texture, salinity, and $CaCO_3$ % were used for applying the assumed equations. The equations based on the measurements of infiltration functions in particular, steady infiltration rate ($I_b$). The K(θ) was considered into macro-pore saturated $K(\theta)_{RDP}$ and matrix unsaturated $K(\theta)_h$. Using the assumed equations, the values of $K(\theta)_{RDP}$ remained higher in macro pores particularly for calcareous soils than those for soil matrix. Generally, the highest values of hydraulic conductivities [Ks, $cm.h^{-1}$, $K(\theta)_{RDP}$, and $K(\theta)_h$ $cm.min^{-1}$] were observed in calcareous soils and the lowest were existed in saline clay soil profile. The predicted values of hydraulic conductivities were reasonable and existed in the normal ranges of the investigated soils, indicating that the proposed equations are applicable and can be recommended to be used in coarse and fine textured soils with large scale of different properties. Sorptivity (S) at unsaturated conditions represents “maximum sorption capacity”, while at saturation conditions S represents “minimum sorption capacity”. With respect to water infiltration in soil, the term wet or steady sorptivity (Sw) after a long time of infiltration (saturation case) may be applied in a similar way to the term “steady infiltration rate”. Water sorptivity (S) was determined for the studied soils at unsteady state (S) and at steady state ($S_w$) of infiltration. It was found that S decreased from S to $S_W$ by 37.79% in average in calcareous soils, and by (53.25%) in average in alluvial clay soils indicating that dry soils typically has a much greater sorptivity than wet soils. The steady $S_w$ parameter was used in prediction of the hydraulic conductivities and the basic (steady) infiltration rate $I_b$. The calculated values of $I_b$ were corresponding to those obtained by infiltration experiment. This confirmed the significance of steady $S_w$ as a new functional infiltration parameter. A matching factor *u* was calculated as a ratio between predicted $I_b$ and the measured saturated Ks. The mean values of *u* were 0.895, 0.685 and 0.360 for calcareous, clay and saline clay soils respectively.

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# Modelling soil properties from horizon depth functions and terrain attributes: An example with cation exchange capacity

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## Abstract

The objective of this study was to, through the distribution of some soil properties, model cation exchange capacity (CEC) in soils formed on gently undulating coastal plain sands of southeastern Nigeria using genetic horizon functions and terrain attributes. A total of 19 profile pits were prepared, described and 104 genetic horizons were identified and sampled, processed and analysed in the laboratory. Data were generated on the soil characteristics, including particle size fractions, hydraulic conductivity, bulk density, organic carbon, pH and electrical conductivity. Terrain attributes that were generated from digital elevation model include aspect, compound topographic index (CTI), Flow direction, curvatures, slope and stream power index (SPI). Data generated were analysed using descriptive statistics, correlation and regression. The terrain attributes were modified with genetic horizon depths, bulk density and clay content for the modelling process. Sand content, bulk density and cation exchange capacity possess geogenic rather than pedogenic characteristics and were normally distributed. The indication is that the two groups of terrain attributes depended on the mass per unit area of soil and clay content in their influence on these ultisol profiles. Paired comparison, root mean square error and normalized root mean square error indicated that the model was a good fit and could be useful in the prediction of soil properties and management of coastal plain sands.

## Article Info

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## Introduction

Genetic horizons are imprints of pedogenesis that manifest in the characteristics of a pedon. The direction and progression of pedogenesis is largely dependent on the predominant factors of soil formation. The humid tropical environment characteristically encourages argeluviation -argiluviation with progression of pedogenesis. This is particularly manifest in the coastal plain sands that are dominantly sandy, kaolinitic and classified as ultisols (Lekwa and Whiteside. 1986) inherently low in organic matter content and fertility (Obi, 2015a; Obi et al., 2016).

Ultisols are highly leached, low in weatherable minerals, cation exchange capacity (CEC) and base saturation. The cation exchange capacity, which reflects the nature of the mineral component of the exchange complex, measures the quantity of negatively charged sites that can retain positively charged ions electrostatically and occurs in kaolinitic clays due to the broken bonds around the crystal edges, the substitutions within the lattice, and the hydrogen ions on exposed surface hydroxyls that may be exchanged (Ma and Eggleton, 1999).

The effects of topography (as endogenous and exogenous factors of soil formation) on soil moisture characteristics has been reported (Seibert et al., 2007; Debella-Gilo et al., 2007; Behrens et al., 2010; Obi, 2015b). This relationship between soil water content and landscape is encapsulated in the digital terrain analysis (DTA) as a component of the environmental variables that influence pedogenesis and variability of

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soil properties (Swarowsky et al., 2011). Therefore, terrain attributes influence pedogenesis and could be useful in the study of variations within the profiles of coastal plain sands. The dominant factors in the formation of ultisols have been associated with the influence of terrain attributes (Obi et al., 2014; Obi, 2015b). Cation exchange capacity is a good indicator of pegogenesis and could be directly influenced by terrain attributes. Therefore this study modelled the cation exchange capacity of the coastal plain sands using terrain attributes and genetic horizon depth.

## Material and Methods

### Study area

The study was carried out in Akwa Ibom State located in the Southeastern Nigeria and enclosed between 4°30' and 5°30' N and 7°28' and 8°20' E (Figure 1). The climate is characterized by distinct rainy (March/April to October) and dry (November to March) seasons. There is bimodal rainfall distribution in each year with high intensity varying between 2000 mm in the northernmost part and 4000 mm along the coast (Udosen, 2014). Temperature is uniformly high averaging between 28 °C and 30 °C and relative humidity is high (approximately 75%). Vegetation is characterized by secondary forest of predominantly wild oil palm trees of various densities, woody shrubs and various grass undergrowth.

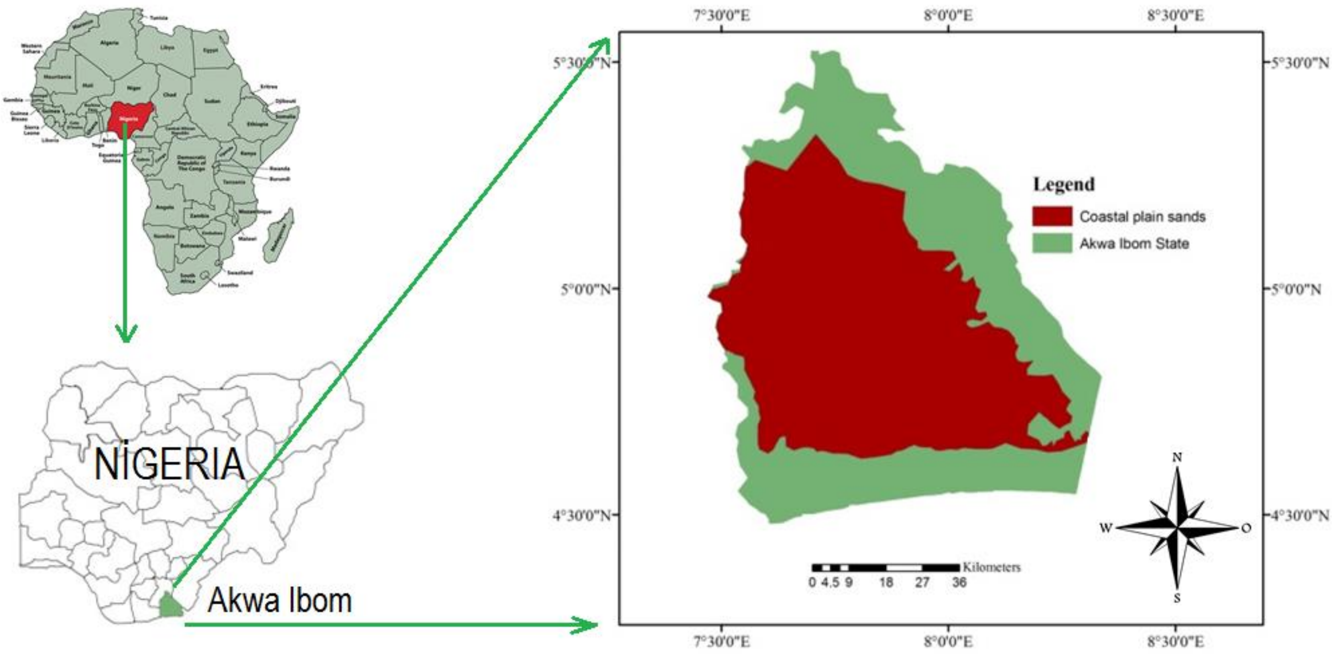


Figure 1. Map of Akwa Ibom State showing area covered by coastal plain sands

Soils of Akwa Ibom State are formed on six geomorphic units among which coastal plain sands constitute approximately 55% (Figure 1). According to Ibia *et al*. (2015) the spatial coverage of these geomorphic units are beach ridge sands (9.4%), tertiary sandstones (17.1%), strongly undulating coastal plain sands (4.2%), gently undulating coastal plain sands (51.2%), mangrove mudflat (6.5%) and alluvium covering (11.6%). These are indications that coastal plain sands is the predominant material and could largely influence the extensive rain fed low input agricultural production system practiced in the area.

The profiles of the coastal plain sands are characterized by the dominance of sandy textured grains comprising higher proportion of coarse fractions over fine textured materials, low physical and chemical fertility due to dominance of low-activity kaolinitic clays, and low organic matter content (Ofomata, 1981; Ojanuga et al., 1981). They are well drained, deeply weathered, have udic moisture regime and isohypertermic temperature regime.

### Soil sampling and laboratory analysis

A total of 19 profile pits were prepared and georeferenced (Table 1) to represent the landscape of the study area. The landscapes of coastal plain sands characteristically comprised upper, middle and lower slopes because they are largely gently undulating. The profile pits were described and sampled according to genetic horizons. There were between 5 and 6 horizons in the profiles and a total of 104 representative genetic horizons were identified and corresponding bulk and core samples collected for the study. The samples were processed and analysed in the laboratory for particle size fractions, bulk density and hydraulic conductivity using the method of Dane and Topp (2002). Organic carbon (OC) content was determined as described in Sparks (1996). Soil pH and electrical conductivity (EC) were determined in 1:2.5 (soil:water) solution using pH meter (McLean, 1982) and conductivity bridge (Rhoades, 1996), respectively. Cation exchange capacity (CEC) was determined by ammonium saturation ($NH_4OAc$) displacement method conducted at pH 7.0 following the approach by (Odu et al., 1986).

Table 1. Coordinates of representative profile pits sampled for the study

| Location | Latitude | Longitude | Location | Latitude | Longitude |
|---|---|---|---|---|---|
| Atai obio ediene | 5.2111333 | 7.8278000 | Use offot | 5.0339333 | 7.9789500 |
| Atai obio ediene | 5.2111000 | 7.8287167 | Ntak inyang | 5.0787333 | 7.9250333 |
| Atai obio ediene | 5.2111333 | 7.8293333 | Uyo | 5.0546833 | 7.9395000 |
| Edem iyere | 5.1949167 | 7.8328167 | Uyo | 5.1270667 | 7.9595333 |
| Edem iyere | 5.1948833 | 7.8327167 | Use atai | 5.0485000 | 7.9751167 |
| Edem iyere | 5.1948833 | 7.8327000 | Ikot anyang | 5.0483833 | 7.9745833 |
| Etip ediene | 5.1945833 | 7.7977167 | Nduetong oku | 5.1406167 | 7.9677667 |
| Etip ediene | 5.1943667 | 7.7977333 | Uyo obio | 5.1540200 | 7.8322167 |
| Etip ediene | 5.1941000 | 7.7978667 | Uyo obio | 5.1539167 | 7.8328333 |
| Uyo obio | 5.1544000 | 7.8318000 | | | |

## Terrain analysis

Digital elevation model is differentiated into primary and secondary attributes. Primary terrain attributes including slope, aspect, curvatures, flow direction and hill shade, are estimates of local geomorphometric terrain characteristics. Secondary terrain attributes include compound topographic index or topographic wetness index and the sediment transport index or stream power index (Moore et al., 1993). The terrain attributes were generated from digital elevation model (DEM) using Spatial Analyst extension of Arcgis 9.2 of ESRI© (Figure 2), and sampling points were georeferenced and added as coordinates. The terrain attributes and sampling points were brought into the same Arcgis environment and thereafter the terrain attributes were extracted for further processing and analysis. The terrain attributes extracted include slope, aspect, total curvature, profile curvature, plan curvature, tangent curvature, flow direction, hill shade, stream power index and compound topographic index (Obi et al., 2014).

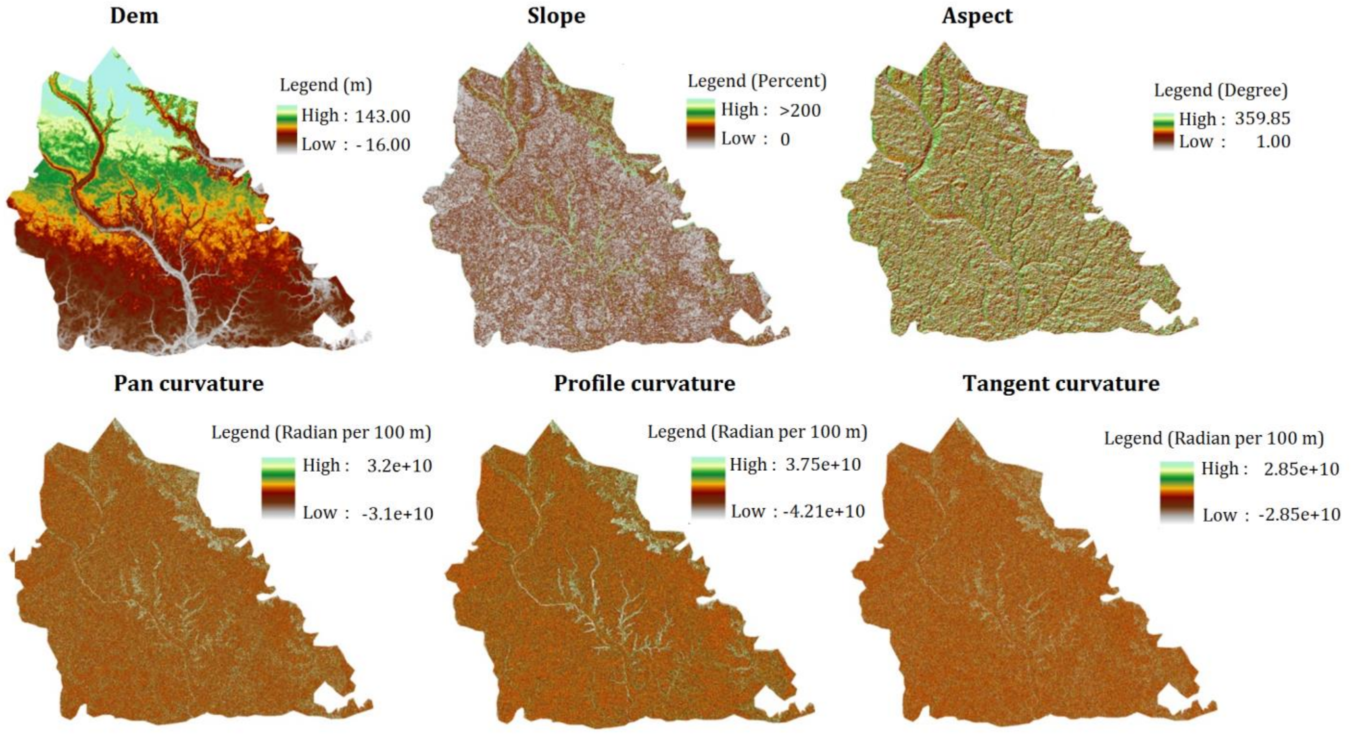


Figure 2. Some topographic attributes of coastal plain sands of south eastern Nigeria

Curvature of a surface at a point is the second derivative of the altitude or elevation and generally varies with orientation. Curvature is associated with gravity field constraints, measures related to stress fields, surface and subsurface water and sediment flows. Profile curvature (cp) is the rate of change of slope gradient (in the direction of greatest change), and contour or plan curvature (cc), the rate of change of direction of a contour line associated with a particular elevation reference field (Carson and Kirkby, 1972). Plan curvature is the rate at which flow direction changes with direction (i.e. following a contour line). Tangential curvatures (ct) are evaluated perpendicularly to slope gradient. Hill shade is the estimate of the intensity of the sun achieved using the altitude and azimuth properties. The stream power index is an estimate of effects of rainfall intensity and scouring inflow rate on runoff formation, soil erosion and solute transport on the surface runoff (Guo et al., 2010). Compound topographic index (CTI) reflects flow accumulation and is estimates as the ratio between the catchment area and slope. Stream power index is the erosive power of the terrain.

**Statistical analysis**

Soil profile pit characteristics and terrain attributes were analysed using descriptive statistics, correlation and regression. The descriptive statistics were used to summarise the soil profile characteristics of the study area and evaluate their distribution. Correlation analysis evaluated the relationship between the soil characteristics and the terrain attributes while regression was used to model the determinants of the variability of cation exchange capacity of the profiles of coastal plain sands. In the stepwise multiple regression analysis, both genetic horizon depth and bulk density were used as modifiers for the terrain attributes as an indication of the soil mass. Bulk density is influenced by the amount of organic matter, texture, constituent minerals and porosity. Soil bulk density measurements are often required as an input parameter for models that predict soil processes. Such models often use bulk density measurements to account for horizon mass when aggregating soil data (Chaudhari et al., 2013). Each profile should possess same terrain attributes but the influences of the attributes are not the same at different portions of the profiles as could be differentiated with genetic horizons. Equally, soil bulk density varies with depth and their interactions with factors of soil formation manifests in the characteristics of different genetic horizons.

Predictability of cation exchange capacity was evaluated using analysis of variance and significantly different means were compared with least significant difference ($p<0.05$). Further evaluation of the accuracy of prediction was carried out using root mean square error (RMSE) and normalized root mean square error (NRMSE). Root mean square error compares predicted and observed values through the aggregation of residual to a single measure of predictive power. Normalization transforms RMSE into dimensionless quantities and renders them suitable for direct comparison especially of variables that have different units. Statistical analysis system (SAS)/STAT® software version 9.2 for Windows (SAS Institute, 2011) was used to perform the statistical analyses.

## Results and Discussion

**Distribution of soil properties within the study area**

The distribution of the soil properties within the study area were as shown in Table 2. Normality of distribution of the soil variable determined in this study was used as indication of the characteristics of the representative profiles. It was not expected that the characteristics of the profiles will be homogenous within the study area. This is explained by the fact that pedogenesis is a process that depends on diverse factor and these act independently. Hence the combination at different rates could lead to different degrees of variations. For instance the distribution of the horizon depth of the profiles was not normally distributed as other variables with the exception of sand, bulk density and cation exchange capacity. It was expected that even at non-normal distribution, variable that originated from the same population should have the indicator of the central tendencies (mean, median and mode) to fall within the same periphery indicating that though they are not normally distributed, yet they are neither skewed nor kurtosis. This event has been reported for the coastal plain sands (Obi and Udoh, 2011). The non-normal distribution is anticipated because the characteristics of the pedons are manifestations of pedogenesis and as the samples are not uniformly from a single horizon but a combination of different horizons of different slope configurations. Then they are not expected to be a representation of a single population. Coastal plain sands are formed from pedogenic processes characterized by the dominance of sand fractions (Obi, 2015b). The major point of deviation is the different configuration and slope forms from which the profiles were formed. These are not expected to lead to the formation of similar features or profile characteristics as they have been used in the differentiation of soil classes on both sedimentary and metamorphic materials (Moss, 1957; Smyth and Mongomery, 1962).

The normally distributed soil properties (Pr<W) as shown in Table 2 established with the aid of Shipiro Wilk test (Shapiro and Wilk, 1965) included sand content, bulk density and cation exchange capacity. It is

established that the most common feature of the coastal plain sands is the dominance of the sand particles, low-activity kaolinitic clays, and low organic matter content (Ofomata 1981; Ojanuga et al., 1981). This characteristic is inherited by the profiles from their mineralogy (quartz arenitic) which is highly resistant to weathering and may not have experienced major modifications. The bulk density is dependent on the particle sizes which are dominantly sandy and organic matter among others (Chaudhari et al., 2013). The cation exchange of the humid tropical regions are largely pH dependent and influenced more by soil texture than organic matter which has been reported to be very low.

Table 2: Statistical status and normality test of some soil properties in the study area

| | | Range | Mean | Median | Mode | CV | Std. Dev. | Skewness | Kurtosis | Pr<W |
|---|---|---|---|---|---|---|---|---|---|---|
| Depth | | 185.00 | 97.49 | 105.00 | 200.000 | 59.57 | 59.48 | 0.18 | -1.15 | 0.00 |
| Horizon depth interval | | 80.00 | 35.73 | 32.00 | 40.00 | 44.52 | 15.91 | 1.88 | 3.99 | 0.00 |
| Sand | Very coarse | 100.00 | 59.93 | 58.8 | 40.00 | 36.90 | 22.13 | 0.29 | -0.67 | 0.00 |
| | Coarse | 280.00 | 129.00 | 96.00 | 70.00 | 56.00 | 72.39 | 1.09 | -0.10 | 0.00 |
| | Medium | 476.00 | 380.79 | 432.00 | 200.00 | 36.93 | 139.88 | -0.59 | -1.19 | 0.00 |
| | Fine | 220.00 | 61.50 | 40.00 | 140.00 | 92.54 | 56.91 | 1.20 | 0.20 | 0.00 |
| | Very fine | 360.00 | 259.68 | 252.00 | 200.00 | 24.13 | 62.67 | 1.07 | 2.06 | 0.00 |
| | Total | 194.20 | 890.91 | 895.00 | 866.00 | 4.96 | 44.23 | -0.37 | -0.39 | 0.05* |
| Silt | | 65.80 | 22.94 | 22.2 | 14.00 | 61.43 | 14.11 | 0.64 | 0.26 | 0.00 |
| Clay | | 183.80 | 85.19 | 77.4 | 22.20 | 45.59 | 38.84 | 0.74 | 0.38 | 0.00 |
| Hydraulic conductivity | | 1.18 | 0.22 | 0.10 | 0.05 | 117.28 | 0.26 | 2.02 | 4.55 | 0.00 |
| Bulk density | | 1.20 | 1.54 | 1.56 | 1.09 | 17.22 | 0.27 | -0.33 | -0.58 | 0.02** |
| Organic carbon | | 3.11 | 1.37 | 1.4 | 0.28 | 57.29 | 0.78 | 0.07 | -1.04 | 0.00 |
| pH | | 1.41 | 5.82 | 5.79 | 5.79 | 5.28 | 0.31 | 0.48 | -0.13 | 0.00 |
| Electrical conductivity | | 0.63 | 0.07 | 0.02 | 0.01 | 154.00 | 0.11 | 2.86 | 8.99 | 0.00 |
| Cation exc. capacity | | 5.50 | 4.68 | 4.70 | 3.50 | 24.28 | 1.14 | 0.28 | -0.57 | 0.06* |
| CECclay | | 0.82 | 0.20 | 0.09 | 0.05 | 104 | 0.21 | 1.38 | 0.95 | 0.00 |

* and ** Significant at 5% and 1% level of probability respectively

**Relationship between the terrain attributes and some profile soil characteristics**

The relationships between terrain attributes and soil profile characteristics within the coastal plain sands were as shown in Table 3. Terrain curvature comprising total, plan, profile and tangent is associated with the configuration of the landscape. Configuration and slope were major criteria for selection of the toposequences utilized in the study and their components have manifested their influence in the process of pedogenesis by dominating the significant correlation among the attributes used in the study.

Table 3. Correlation coefficients between the soil properties and terrain attributes of the study area

| Soil properties | | Aspect | CTI | Flow Direction | Curvature | | | | Slope | SPI |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Plan | Profile | Tangent | Total | | |
| Profile depth | | 0.02 | -0.04 | -0.04 | 0.03 | -0.05 | 0.06 | 0.02 | 0.02 | -0.01 |
| Horizon depth | | -0.07 | 0.03 | -0.12 | 0.03 | -0.04 | 0.21* | 0.05 | 0.11 | 0.09 |
| Sand | Very coarse | -0.14 | -0.01 | -0.03 | 0.10 | 0.30** | -0.03 | -0.14 | -0.55** | -0.56** |
| | Coarse | -0.19 | 0.18 | -0.07 | 0.30** | -0.26** | -0.49** | 0.36** | -0.12 | -0.04 |
| | Medium | 0.12 | -0.29 | 0.09 | 0.16 | 0.18 | 0.56** | -0.25* | 0.03 | 0.03 |
| | Fine | 0.01 | 0.17 | -0.22* | 0.31** | -0.33** | -0.46** | 0.42** | 0.25* | 0.25* |
| | Very fine | -0.03 | 0.22* | -0.14 | -0.30** | 0.29** | -0.66** | -0.35** | 0.66** | 0.12 |
| | Total | -0.05 | 0.10 | -0.28** | -0.01 | 0.29** | 0.28** | -0.22* | 0.20* | 0.23* |
| Silt | | 0.38** | -0.17 | 0.33** | 0.03 | -0.11 | 0.15 | 0.13 | -0.17 | -0.16 |
| Clay | | -0.08 | 0.19 | 0.22* | 0.05 | -0.32** | -0.20 | 0.25* | -0.21* | -0.24* |
| Hydraulic conductivity | | 0.07 | -0.14 | -0.14 | 0.06 | -0.06 | 0.07 | 0.07 | -0.03 | 0.01 |
| Bulk density | | 0.25* | -0.23 | 0.04 | 0.12 | 0.08 | 0.09 | 0.01 | -0.05 | -0.09 |
| Organic carbon | | 0.17 | -0.16 | 0.38** | 0.02 | -0.37** | -0.33** | 0.24* | 0.08 | 0.09 |
| pH | | 0.22 | -0.17 | 0.01 | -0.29** | 0.27** | 0.61** | -0.34** | 0.12 | 0.14 |
| Electrical conductivity | | -0.05 | 0.08 | -0.02 | 0.36** | 0.12 | -0.56** | 0.23* | -0.15 | -0.10 |
| Cation exc. capacity | | 0.29** | 0.02 | 0.26** | -0.01 | -0.18 | -0.02 | 0.14 | 0.06 | 0.04 |
| CECclay | | -0.03 | 0.21* | -0.22* | 0.32** | -0.09 | -0.62** | 0.28** | 0.14 | 0.16 |

The results in Table 3 reveal that tangent curvature significantly correlated with horizon depth (r=0.21, p<0.05) and the entire particle size fraction except very coarse sand as with total curvature. Stream power index (r=-0.56), slope (r = -0.55) and profile curvature (r = 0.30) are the terrain attributes that significantly correlated with very coarse sand. The stream power index is an estimate of effects of rainfall intensity and scouring inflow rate on runoff formation, soil erosion and solute transport on the surface runoff (Guo et al., 2010). This is an indication that these three terrain attributes play important role in the development of these profiles, thus supporting the view that pedogenesis of coastal plain sands is dependent on the particle size fraction which is dominated by coarse sand fractions (Obi, 2015b). The slope and aspect of a vegetated surface strongly affects the amount of solar radiation intercepted by that surface. Solar radiation is the dominant component of the surface energy balance and influences ecologically critical factors of microclimate, including near surface temperatures, evaporative demand and soil moisture content (Bennie et al., 2008). Aspect describes moisture and energy component of the landscape characteristics and was found to significantly correlate with silt content (r=0.38, p<0.01), bulk density (r=0.25, p<0.05) and cation exchange capacity (r=0.29, p<0.01) of the soils. Bulk density and cation exchange capacity are influenced by moisture and temperature as a microclimatic phenomenon characteristically known as aspect and largely influence horizon morphology.

**Modelling of cation exchange capacity using terrain attributes**

The terrain attributes were modified by multiplying them with the bulk density and horizon depth which is a factor that could estimate the mass per unit depth of soil. The estimate of terrain attributes for a pedon is unity but the influence of terrain attribute within the profile will vary. This is because as different terrain attributes influences the landscape differently their effects are not the same with all horizons of the profile. This is simply because the different characteristics of the profile interact with each other. For instance moisture dynamics within the profile are influenced by the particle sizes that change both laterally and horizontally. In this case clay content with soils classified as ultisols will increase with depth and affect moisture dynamics. Therefore horizon characteristics modify the influence of the terrain attributes. The bulk density estimates the relationships between the components that made up soil and dependent on organic matter, texture, the density of soil mineral (sand, silt, and clay) and their packing arrangement. Bulk density typically increases with soil depth since subsurface layers are more compact and have lower organic matter, aggregation, and root penetration compared to surface layers, therefore they have lower pore spaces. Soil processes have been predicted with the aid of bulk density as horizon mass aggregation index (Bernoux et al., 1998; Calhoun et al., 2001).

It was possible to model the variability of the cation exchange capacity of the coastal plain sands using terrain attributes modified with bulk density and depth of each genetic horizon as shown in Table 4. The terrain attributes that were used in the modelling of cation exchange capacity were aspect and stream power index. The two terrain attributes influence moisture dynamics, energy distribution, physical movement of particles and solute transport. The coastal plain sands are dominated by kaolinitic clays and low organic carbon content that decrease with increase in depth within a profile, the consequence is the dependence of the cation exchange capacity solely on the clay content of the soils. Clay in soils classified as ultisol increases with increase in depth. The result revealed that clay is the only soil physical property considered in this study that influenced variability of cation exchange capacity (Table 4) and could be used in its prediction due to its role in the process of pedogenesis. Clay is intrinsically associated with stream power index as a major participant in the solute dynamics within soil profiles (Obi, et al., 2014; Obi, 2015a).

Table 4. Model of cation exchange capacity of coastal plain sands using terrain attributes and horizon interval

| Variable | Model | P-value | $R^2$ | Observed | Predicted | $LSD_{(0.05)}$ | RMSE | NRMSE |
|---|---|---|---|---|---|---|---|---|
| CEC | 3.62335 + 0.00005015 (aspect*bulk density*genetic horizon depth) – 0.00119 (stream power index* bulk density*genetic horizon depth) + clay | 0.02 | 0.25 | 4.69 | 4.68 | 0.19 | 0.97 | 1.01 |

The model accounted for approximately 25% of variability of cation exchange capacity of the profiles of coastal plain sand. The observed and predicted cation exchange capacity of the profiles were found not to be significantly (p<0.05) different from each other (Table 4). Root MSE and NRMSE for the model were 0.97 and 1.01 respectively indicating the superiority of the model and its capacity to predict especially for use in soil classification and management. The prediction model revealed the effectiveness of modification of the terrain characteristics with the bulk density and genetic horizon depth. The dimension of the factors of bulk density and horizon depth results to mass per unit area of soil as shown below:

$$\text{Bulk density } = \frac{mass}{volume} = \frac{g}{cm^3}$$

$$\text{Horizon depth} = \text{cm}$$

$$\text{Bulk density x horizon depth} = \frac{\text{g}}{\text{cm}^3} \text{x cm} = \frac{\text{g}}{\text{cm}^2} = \text{mass per unit area}$$

The above formula is an indication that the aspect, stream power index and mass per unit area of soil and clay content could effectively provide appropriate information on the cation exchange capacity of profiles formed on the gently undulating profiles of coastal plain sands.

## Conclusion

The soil profile characteristics considered for the prediction of cation exchange capacity of coastal plain sands were easily determinable, inexpensive and associated with other soil properties. These include particle size fractions, hydraulic conductivity, bulk density, organic carbon, pH and electrical conductivity. Most of the soil properties were not normally distributed except sand, bulk density and cation exchange capacity which possess characteristics that are more associated with their geogenic than pedogenic origin. The profile characteristics that were non-normally distributed were those that are usually influenced by pedogenesis and since the landscape characteristics and genesis are different, then they are from different populations and their characteristics should not be normally distributed. The terrain attributes that could be used to predict cation exchange capacity of the coastal plain sands were aspect and stream power index modified by genetic horizon depth, bulk density and clay content.

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# Soil hydraulic properties: A simple and practical approach to estimate the number of samples

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## Abstract

There have been a number of studies dealing with soil hydraulic properties. Yet, there is a poor discussion on the number of samples necessary to represent such variables that usually vary orders of magnitude in space. In the present paper, we examine the adequate number of samples for two soil saturated hydraulic conductivity (Ksat) data sets: (1) normal distribution (a 40 year-old pasture) and (2) non-normal distribution (primary forest). To assess the adequate number of samples in each case, we used for normal distribution, an statistical criterion of standard deviation lower than 5% compared to a high sampling effort (n = 25) as an indicative of a proper representation of Ksat variability. In the case of non-normal distribution, we used the same criterion but using median absolute deviation (a non-parametric statistics). Both data sets were available in Salemi et al. (2013) and were Ksat measured at 0.15 m soil depth for medium-textured inceptisols in São Paulo State, Brazil. For each data set, we simulated 10 'new' samplings in which we calculated mean and standard deviation from sample 1 to 25 (for normal data) and median and median absolute deviation (for non-normal data). We found that, on average, at least 17 to 22 samples had to be collected to meet the adopted criterion for normal data whereas 20 to 25 had to be collected for non-normal data. Such numbers of samples exceed those used in a number of papers. Additional examples of this method with a light modification are given to establish number of samples in new study areas as well as to estimate number of samples when comparing two (or more) land-uses. Simple and practical procedures like those presented here could estimate the number of samples that adequately represents soil hydraulic properties variability.

**Keywords**: Inceptisols, sampling, variation, water movement.

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## Introduction

Soil hydraulic properties such as infiltration capacity and saturated hydraulic conductivity are important to understand water movement within the soil (Reichardt and Timm, 2012). Such variables have application in

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different areas of soil, agricultural, forestry and environmental sciences such as soil and water conservation (Bertoni and Lombardi Neto, 1990), irrigation (Barreto, 1986), hillslope hydrology (Kirkby, 1978) which, in turn, can help to predict peak flows (Hewlett, 1982).

Infiltration capacity and soil saturated hydraulic conductivity generally present substantial spatial variability (Mesquita and Moraes, 2004; Bonell et al., 2010). Values of such variables can vary up to three orders of magnitude for a given soil type (Salemi et al., 2013; Ghimire et al., 2013; Ghimire et al., 2014). Such variation along with laborious field and laboratory methods make its proper representation a hard task. For example, one single measurement of infiltration took 6 hours using the double ring method (Bono et al., 2012). For this reason, papers that characterized soil hydraulic properties used a quite variable number of samples ranging from 1 to 87 samples (e.g. Elsenbeer et al., 1999; Souza and Alves, 2003; Moraes et al., 2006; Bonell et al., 2010; Salemi et al., 2013; Vilarinho et al., 2013; Ghimire et al., 2013; 2014). Yet, there is a poor discussion on the number of samples necessary to represent such variables that usually vary orders of magnitude in space. In other words, how many sampling units are needed for an accurate assessment?

In this context, the objective of the present paper was to present a simple method used to estimate the number of samples (also known as sample size) to properly characterize the soil saturated hydraulic conductivity.

## Material and Methods

### Study area

The soil saturated hydraulic conductivity (Ksat) measurements of pasture and forest have been obtained from two sites. First, pasture (hereafter in the present paper 'normal data') was a 40-yr old pasture (*Brachiaria decumbens* Stapf.) located in Natividade da Serra – SP (Brazil) (Latitude: 23º 24' 53,9" S Longitude: 45 º 15' 04,0" W). This pasture is sited on steep slopes dominated by medium textured soils classified as cambissolos háplicos distróficos (Brazilian soil classification system by EMBRAPA) or Inceptisols (US Soil Taxonomy). The same soil type was present in Forest (hereafter in the present paper 'non-normal data'). The forest site is located inside the State Park of Serra do Mar in São Luiz do Paraitinga – SP (Brazil) (Latitude: 23º 17' - 23º 24´ S Longitude: 45º03' - 45º11'W). Mean slope for pasture and forest were 37 ± 17% and 28 ± 14% (mean ± standard deviation) respectively. For more details on soil see Salemi et al. (2013).

### Methods

Ksat measurements used in the present paper was measured at 0.15 m soil depth at both sites using a constant head permeameter known as Amoozemeter (Amoozegar, 1992). Twenty five samples have been collected following linear transects from the water divide to approximately 30 meters relative to a first order stream (Salemi et al., 2013). The distance between measurements was ~ 2 meters. We decided to use the observations available in Salemi et al. (2013) for two main reasons: (1) direct access to original observations and (2) a high number of samples (n = 25).

Aiming to estimate an adequate sampling effort, we assumed that the 25 samples used in Salemi et al. (2013) are the best representation of the two sites. For this reason, the statistics calculated with such measurements should be taken as a reference in determining the adequate number of samples. For this, we simulated 10 'new' sampling events for each site. In each simulated sampling, we assumed the 25 samples have been collected randomly as this is a practical and advantageous sampling design compared to others (Hassler et al., 2014). To simulate random sampling, we used a simple on line randomizer (www.randomizer.org). In doing the randomization, mean and standard deviation have been calculated from the first ($x_1$) until the last sample ($x_{25}$) for normal data whereas median and median absolute deviation have been calculated for non-normal data. Thus, 25 measures of central tendency and 24 of variability have been calculated for each of the 10 simulations in each site/data set. Median absolute deviation (MAD) was calculated as follows:

$$MAD = \text{median}\ (|\ xi - \text{median}\ |) \quad (1)$$

Where: *xi* is the observation

Once performed the 10 simulations in each site (data set), a representative number of samples was considered achieved when variability statistics values presented consistently (i.e. for three times consecutively), a maximum of ± 5% of the variation of the statistics obtained from the maximum number of samples (n = 25). Put another way, when standard deviation or median absolute deviation of a given number of samples met such criterion for three times in row, we admitted a representative number of samples had been achieved. This method is an adaptation of the one ecologists use when determining the need for additional samples to define species richness in a given ecosystem (see, for example, Gotelli and Chao, 2013).

**Analysis**

Aiming to demonstrate graphically the effect of increasing number of samples on data variability, we arbitrarily selected 3 of the 10 simulations (randomization 2, 4 and 6) for both data sets ('normal' and 'non-normal').

The basis for the comparison of variability statistics is that when one increases the number of samples (also known as 'sample size'), it is possible to obtain statistics closer to population parameters. In the present paper, we assumed that the best representation of the soil had been achieved with a Ksat sample of 25 originally available in Salemi et al. (2013).

## Results

The statistics for the high number of samples (n = 25) were 29.30 ± 17.09 mm $hr^{-1}$ (mean ± standard deviation) and 60.97 ± 44.24 mm $hr^{-1}$ (median ± median absolute deviation) for normal and non-normal data respectively. In the case of normal data, 17 ± 5 samples had to be collected to reach the criterion (i.e. 5% of the standard deviation of the maximum sampling effort). Number of samples varied from 9 to 23 (Table 1).

Table 1. Number of samples, mean, standard deviation and their absolute difference when compared to the maximum sample size for normal data. All statistics are presented in mm $hr^{-1}$.

| Simulation | Number of Samples | Mean | Standard Deviation | Deviation when n = 25 | |
|---|---|---|---|---|---|
| | | | | Mean | Standard Deviation |
| 1 | 19 | 27.57 | 17.01 | 1.73 | 0.07 |
| 2 | 12 | 30.52 | 17.65 | -1.22 | -0.57 |
| 3 | 19 | 30.39 | 17.71 | -1.09 | -0.63 |
| 4 | 13 | 30.25 | 17.76 | -0.95 | -0.68 |
| 5 | 10 | 29.56 | 17.54 | -0.26 | -0.46 |
| 6 | 9 | 27.05 | 16.51 | 2.25 | 0.57 |
| 7 | 12 | 36.46 | 17.61 | -7.16 | -0.53 |
| 8 | 19 | 29.41 | 17.75 | -0.11 | -0.67 |
| 9 | 18 | 27.01 | 16.63 | 2.29 | 0.45 |
| 10 | 23 | 29.64 | 17.41 | -0.34 | -0.33 |

*Negative values indicate mean and/or standard deviation were higher than those obtained compared to the maximum sample size (n = 25).

As for non-normal data, 20 ± 5 samples had to be collected. Number of samples varied from 7 to 25 (Table 2). In normal and non-normal data sets, there was a relatively low absolute deviation of the variability statistics compared to the one of the maximum number of samples (Table 1 and 2).

Table 2. Number of samples, median, median absolute deviation and their absolute difference when compared to the maximum number of samples for non-normal data. All statistics are presented in mm $hr^{-1}$.

| Simulation | Number of Samples | Median | Median Absolute Deviation | Median | Deviation when n = 25 |
|---|---|---|---|---|---|
| | | | | | Median Absolute Deviation |
| 1 | 24 | 60.97 | 42.44 | 0 | 1.8 |
| 2 | 24 | 60.97 | 42.44 | 0 | 1.8 |
| 3 | 15 | 50.81 | 43.16 | 10.16 | 1.08 |
| 4 | 21 | 50.81 | 40.65 | 10.16 | 3.59 |
| 5 | 20 | 60.97 | 42.44 | 0 | 1.8 |
| 6 | 25 | 60.97 | 42.44 | 0 | 1.8 |
| 7 | 24 | 60.97 | 42.44 | 0 | 1.8 |
| 8 | 24 | 60.97 | 44.86 | 0 | -0.62 |
| 9 | 7 | 60.97 | 16.63 | 0 | -1.25 |
| 10 | 21 | 60.97 | 17.41 | 0 | 0 |

*Negative values indicate median and/or median absolute deviation were higher than those obtained compared to the maximum sample size (n = 25).

For normal data, the simulations 2, 4 and 6 reached the criterion at 12, 8 and 9 samples respectively (Figure 1). As for non-normal data, simulations 3, 4 and 6 reached at 15, 21 and 25 samples respectively (Figure 2).

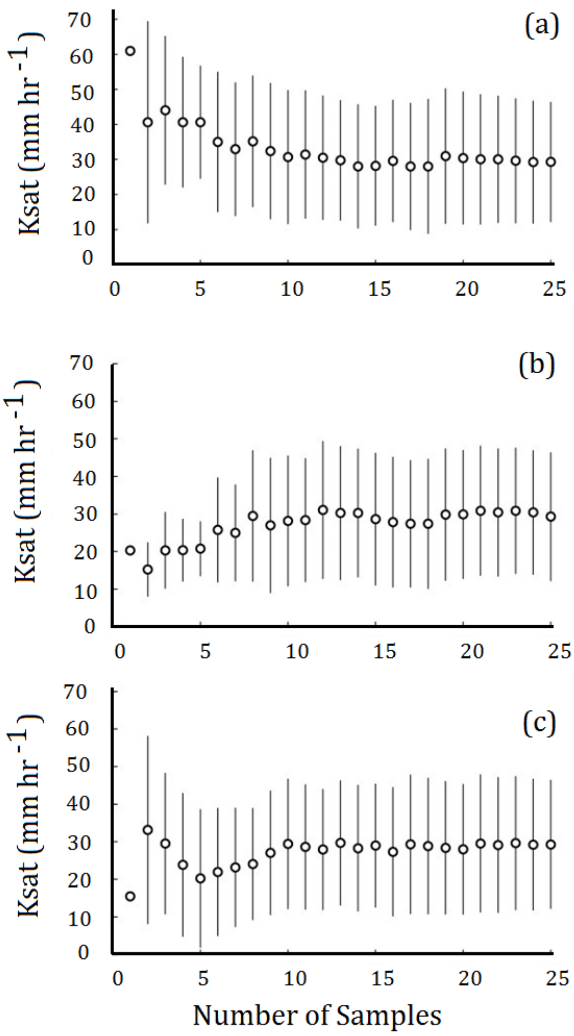


Figure 1. *Normal* data statistics. Circles indicate *mean* whereas bars represent *standard deviation* of the soil saturated hydraulic conductivity (Ksat) for randomizations 2 (a), 4 (b) e 6 (c) as a function of number of samples (x axis)

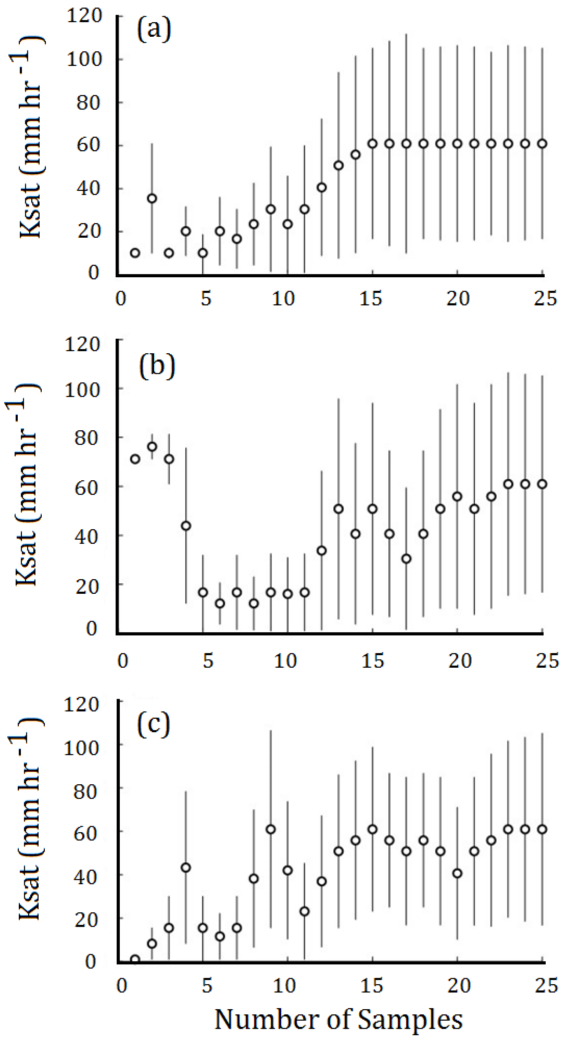


Figure 2. *Non-normal* data statistics. Circles indicate *median* whereas bars represent *median absolute deviation* of the soil saturated hydraulic conductivity (Ksat) for randomizations 3 (a), 4 (b) e 6 (c) as a function of number of samples (x axis).

## Discussion

The criterion to reach a representative sampling were, on average, 17 and 20 samples for normal and non-normal data, respectively. In other words, after collecting these numbers of samples, there was no substantial modification in the variability statistics when adding an additional sample. Such number of samples are higher than the ones used in a number of papers (e.g. Silva and Kato, 1998; Beutler et al., 2001, Araújo et al., 2007; Borges et al., 2009; Bono et al., 2012;). In case our Ksat variation presented for inceptisols also represent other soil types (oxisols, ultisols and others), there have been probably a misrepresentation of such variable in the referred studies. For this reason, such papers probably over or underestimate the actual Ksat variability. As a matter of the fact, there were lower (Figure 1b) and higher (Figure 1a,c) standard deviation when using number of samples equal or lower than 5 which was substantially lower compared to the one indicated by the present approach (n=17). Number of samples lower than 5 have been used in many papers.

The same rationale just described applies to the case for non-normal data. That is to say, low number of samples (i.e. n = 5 or lower) generated variability statistics that do not approached the 'actual' population variability (Figure 2).

Regarding normal data, number of samples equivalent to 17 or even 22 (that is, the mean, 17, plus 5, the higher end of standard deviation) and in the case of non-normal data 20 or even 25 provided reasonable substance to accept that number of samples (n = 21) used by Elsenbeer et al. (1999) and Moraes et al. (2006) as well as the one used by Bonell et al. (2010), which varied from 22 to 87, could probably be considered a well-represented sample, though no explanation on the basis of the number of samples is provided in all these papers and other including Salemi et al. (2013).

We acknowledge that in doing the procedure shown here with maximum number of samples higher than 25, it is possible to obtain different results. This means that, as one increases the number of samples, there is an approximation between the statistics (estimates based on samples) and parameters (actual numbers regarding the population). Thus, increasing the number of samples leads to a more representative sample. That is specially the case when one gets samples varying from more than 2 orders of magnitude which are not uncommon in studies dealing with soil hydraulic properties under certain land-uses (e.g. Moraes et al., 2006; Scheffler et al., 2011; Hassler et al., 2012; Ghimire et al., 2013; Salemi et al., 2013; Ghimire et al., 2014). For instance, inceptisols and luvisols (Ghimire et al., 2013, Salemi et al., 2013; Ghimire et al., 2014), as well as plinthic soils (Moraes et al., 2006) presented Ksat varying 3 orders of magnitude.

The procedure presented here could also be utilized for verifying the number of samples when sampling soil hydraulic properties in a new study area (that is, there is no previous information on soil hydraulic properties of the area). In this case, a slightly different manner is proposed, that is, when collecting samples, if the addition of new samples do not produce substantial variation on the variability statistics for, at least, 3 subsequent additions of new samples, an adequate number of samples can be considered met. Furthermore, the procedure could also be applied in case a comparison between land-uses is the goal as it was the case of many studies (see, for example, Zimmermann et al., 2006; Scheffler et al., 2011; Salemi et al., 2013). The procedure used here could point to a single number of samples that should be collected in the two (or more) land-uses being compared. To exemplify such case, we performed calculations with pasture data ('normal data') using the median and median absolute deviation (the statistics used for non-normal data, that is, forest). In doing so, pasture median absolute deviation stabilized only at 25 samples whereas forest stabilized at 20 samples. Thus, in this case, 25 samples was the standard number of samples that have to be collected in order to have a balanced comparison between land-uses.

Though the criterion (5% around variability statistics) used here is, to some extent, arbitrary, it seems reasonable to assume that no substantial modification of variability indicated a proper representation of soil hydraulic property variation. In addition, such accuracy is well within the limits of accuracy that are required to estimate hydraulic properties in the field (Reynolds and Elrick, 1990).

Lastly, the idea behind such method is not entirely new. Ecologists use similar criterion when deciding the need for additional samples to determine species richness in a given ecosystem (Gotelli and Chao, 2013). In this case, when species samplings do not add new species in the area, the number of species of the ecosystem is considered met.

## Conclusion

A simple and practical procedure to examine number of samples has been provided using variation stability as the main criterion. When sample variability stabilized, it indicated that sample variation probably approached population variability generating an adequate representation. Though the results presented here might be site-specific, the demonstrated procedure can be utilised for estimating number of samples in other areas in future studies.

## Acknowledgements

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# Assessment of land suitability for the production of major crops in Ayrancı district of Karaman province located at arid terrestrial ecosystem

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## Abstract

Land evaluation based on human, economic and physical resources is an important tool for attaining proper land use planning of various agro-ecological zones especially in arid terrestrial ecosystem condition area to ensure that land is not degraded and that it is used according to its capacity to satisfy human needs for present and future generation. The aim of this research was to assess land suitability for the production of major crops in arid terrestrial ecosystem. The study area was carried out Ayrancı district of Karaman province is about 4760 km$^2$ and located between 577076 m - 596768 m east and 41541331 m – 4174001 m north coordination. Elevation of the study area locates between 991 m and 1774 m from sea level and long term annual average precipitation and temperature are 330.8 mm and 12 $^oC$. According to Newhall simulation model, it was determined that soil temperature regime is mesic and moisture regime is weak aridic. The land mapping units were primarily described and land characteristics and qualities were determined using 1:5.000 scaled soil maps of the study area. Land use types to be considered were described and their land requirements were determined. The land requirement of the land use types were compared with the land characteristics and land qualities of land mapping units. The results of the matching process combined with those of assessment and produced a classification showed the suitability of each land mapping unit for each relevant land use type. The agricultural suitability maps prepared revealed that only 8.4 % of the study area soils was not suitable for agricultural uses, 57.2 % of the soils was best suitable for agricultural uses. In addition, 70515.8 ha of the total study area was not suitable for horticulture cultivation whereas, 9859.1 ha was not suitable for field crop cultivation due to the unfavorable land and soil conditions. Moreover, about 35.4% of the total area was found non suitable for vegetable crops in the study area.

## Article Info

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**Keywords**: Arid land, land use type, land characteristics and qualities, land suitability classification.



## Introduction

Undoubtedly, some researchers indicated that one of the ways to provide food is to increase production in area and to use the land with respect to its potentiality in an appropriate way (Dengiz and Başkan, 2009; Ahmed et al., 2015). FAO (2014) recognizes that the adoption of sustainable land-use and land management practices is important for achieving sustainability in its Strategic Objective as "Producers and natural resource managers adopt practices that increase and improve the provision of goods and services in agricultural sector production systems in a sustainable manner". In this sense, land evaluation analysis is a prerequisite to achieving optimum utilization of the available land resources. Lack of knowledge on best combination of factors that suit production of yields has contributed to the low production (Dengiz and Usul, 2018). The term "Land suitability assessment" refers to assessment of land performance to derive maximum

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benefits with minimum degradation when used for a specific purpose. This assessment involves many biophysical factors that directly or indirectly control the ability of this part of land to host the land use under investigation. Performing land suitability evaluation and generating maps of land suitability for agricultural or non-agricultural uses will facilitate to reach sustainable agriculture (FAO, 1976; Vargahan et al., 2011; Rabia and Terribile, 2013). Dengiz et al. (2003) stated that studies of land evaluation are of great importance in guiding decision on land uses in terms of their potential and conserving natural resources for feature generations. Therefore, suitability is a function of land use requirements and land characteristics (Mustafa et al., 2011). That's why, suitability is a measure of how well the qualities of a land unit match the requirements of a particular form of land use (FAO, 1976).

Many methods generally divided into hierarchic and parametric approaches by take into consideration of limitations have been developed for the assessment of land suitability (Dengiz and Sarıoğlu, 2013; Karimi et al., 2018). Simple limitation, regarding number and intensity of limitations, Storie, and square root (Khiddir, 1986) methods are the most widely used (Sys et al., 1991; Dengiz, 2002; Rabia and Terribile, 2013). Comparative evaluations of the different land suitability methods have been presented by Hopkins (1977) and Anderson (1987). Although results of different land suitability methods are generally similar, the parametric methods frequently underestimate the potential of investigated lands (Rabia and Terribile 2013). Sarvari and Mahmoodi (2001), Dengiz et al. (2005) and Jafarzadeh et al. (2008), and demonstrated more realistic results for agricultural land suitability using the square root method evaluation.

The majority of both limitation and parametric methods use the FAO (1976) framework for land suitability classification. In this framework, lands are classified into five classes ranging from highly suitable to permanently not suitable considering the existing limitations for a specific use (FAO, 1976). In addition to the aforementioned methods, new spatial technologies such as geographic information systems (GIS) and remote sensing. GIS technology enables users to integrate multiple geospatial and attribute data with high precision and flexibility and hence improves land suitability evaluation (Bagherzadeh and Mansouri, 2011; Mendas and Delali 2012; Dengiz, 2013; Hamerlinck and Lieske, 2015). Furthermore, GIS facilitates spatiotemporal analysis of various crop production practices (Laingen, 2015; Flynn, 2016).

To combat land degradation and desertification, harmonizing the often-conflicting objectives of intensified human needs and socio-economic development, while maintaining and enhancing the ecology life support functions of land resources is an obligation (Girma et al., 2015). Therefore, land suitability evaluation is very important to provide information on the constraints and opportunities for the use of the land and therefore guides decisions on optimal utilizations of the resources (Dengiz et al., 2010). Land evaluation based on human, economic and physical resources is an important tool for attaining proper land use planning of various agro-ecological zones especially in arid terrestrial ecosystem condition area to ensure that land is not degraded and that it is used according to its capacity to satisfy human needs for present and future generation. In this present study, it was amid to assess land suitability for the production of major crops in arid terrestrial ecosystem.

## Material and Methods

This research was carried out in Ayancık district of Karaman province located in Central Anatolia of Turkey and covers about 4760 km$^2$ (Figure 1). In addition, the study area coordinated at 577076 - 596768 East and 41541331 – 4174001 North (Zone 36, WGS84, UTMm).

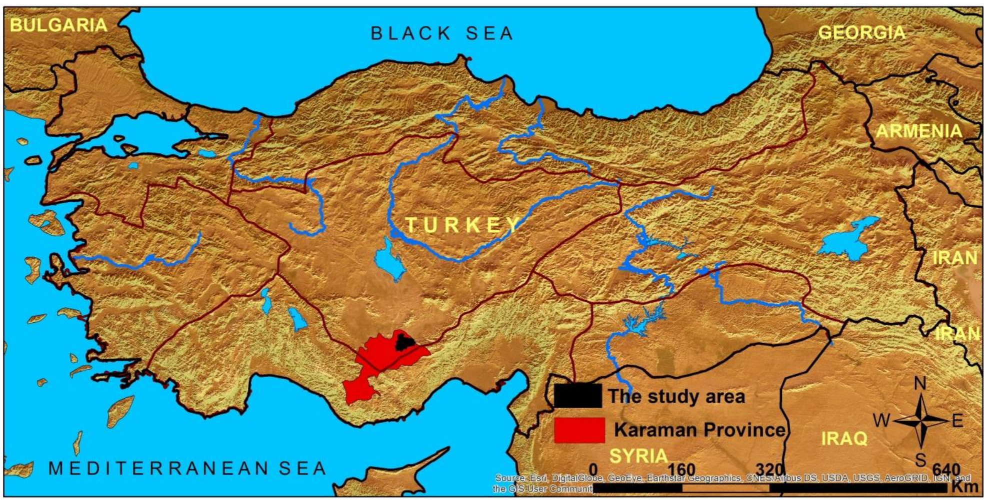


Figure 1. Location map of the study area

The elevation of the study site from sea level varies between 991 m and 1774 m. In addition, mountain and hilly topographic features have located at eastern part of the study area while, northwestern and southwestern parts of the study area have flat area. Therefore, steep slope (more than 30%) distributes mostly eastern direction of the study area (Figure 2).

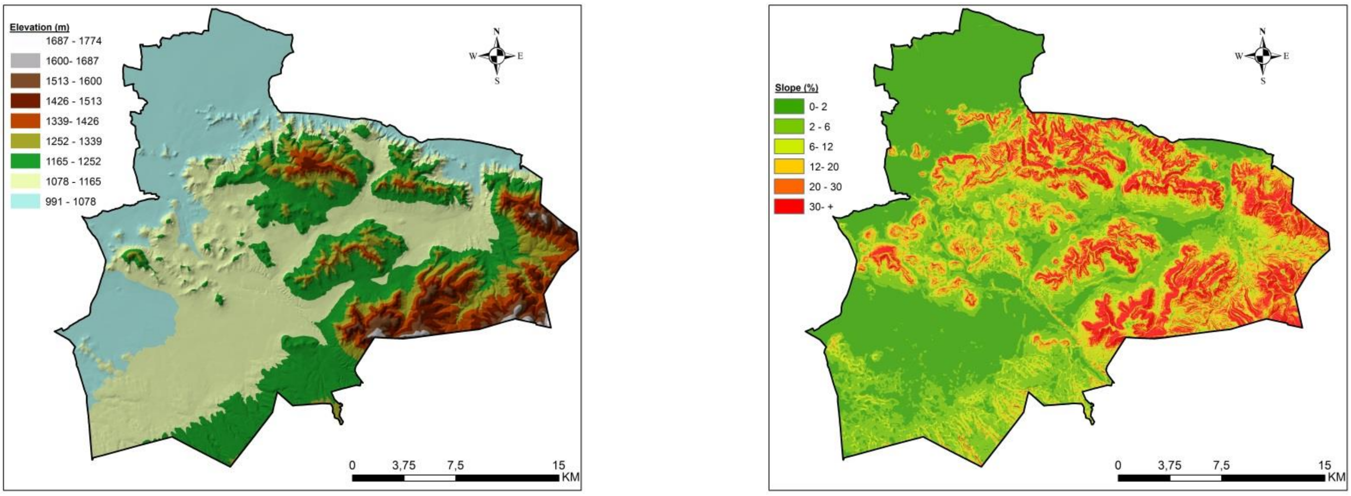


Figure 2. Elevation and slope maps of the study area

In order to reveal the climatic features of the study area, long period data (1960–2015) from the meteorological station of Karaman province has been used. The average annual temperature and precipitation are 12.0 °C and 330.8 mm, respectively. Kurşun and Dengiz (2018) determined soil temperature and moisture rejime as mesic and weak aridic using Newhall simulation model (Newhall, 1972; Van Wambeke, 2000) (Figure 3).

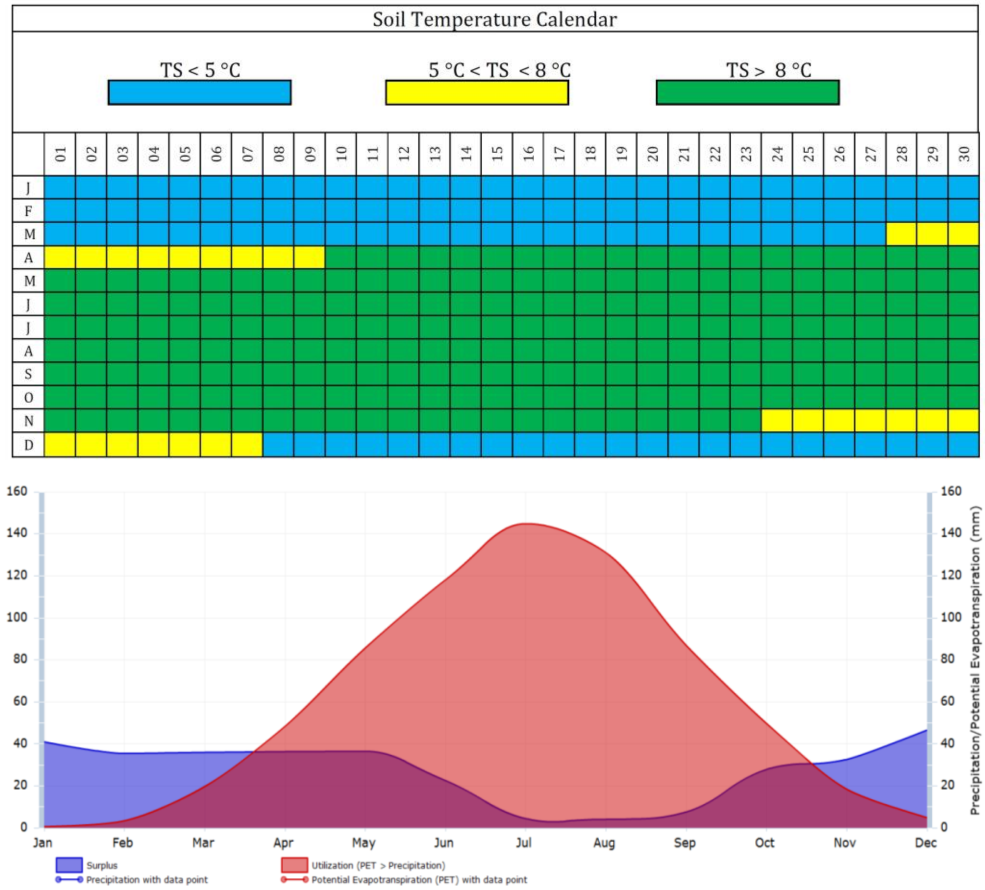


Figure 3. Soil moisture and temperature regime diagrams of the study area's soil

General geological pattern of the study area are marl, lime stone parent materials which are lacustrine origin and kolluvial and alluvial deposits (Murat ve Temur, 1995). According to CORINE-2012 land use land cover classification, the study area has been mostly used as dry farming and pasture lands. Moreover, barren and stoniness lands locate on southern and northern west parts of the study area (Figure 4).

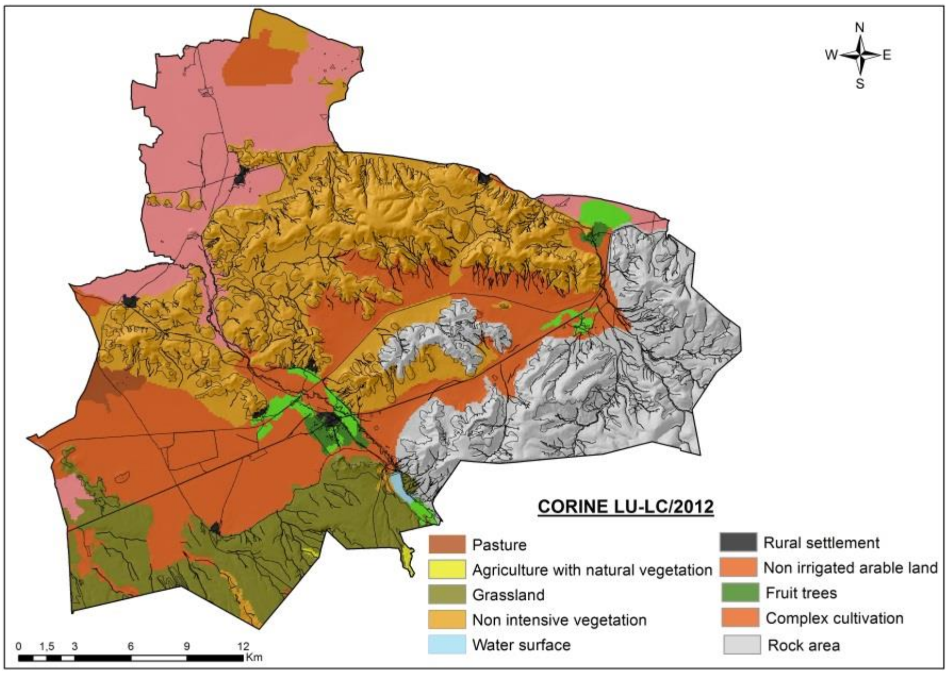


Figure 4. Land use and land cover map of the Study area

**Method**

Land suitability model based on the quantitative assessment of the agro-ecological evaluation in the study area for the land use types (LUTs) of rainfed agriculture, irrigated agriculture, range land, and non-agricultural area was developed by General Directory of Agricultural Reform in the light of the FAO (1976) and Senol (1994) principles. A digital soil database scaled 1:10.000 was prepared by Kurşun and Dengiz (2018) entering the diagnostic physical and chemical characteristics for each land mapping unit (LMUs). A total of 2951 LMUs were described from digital soil data base. In addition 151 different LUTs were distinguished and their land use requirements (LURs) were determined by using related information and available data. Land suitability (LS) is a function of a set of LURs determined for LUTs ($LURs_{LUTs}$) and a set of land characteristics (LCs) measured for LMUs ($LCs_{LMUs}$) as follows:

$$LS_{LMUs\ for\ LUTs} = f\ \{LCs_{LMUs}, LURs_{LUTS}\}$$

The land suitability index (LSI) of the LMUs for each LUT was calculated using the multiplicative combination of suitability rating index (SRI) as follows:

$$LSI_{LMUx\_LUTy} = \prod_{i=1}^{n} SRILCix\_LMUx\_LUTy\ ,$$

$LCi \in [0. . . . 1]$

Where; LSI values show the degree to which the requirements of the LUTs matched each LMU. LSI values were also expressed according to a rating scale of suitability classification for each LUT. At the same time, all LCs were standardized according to the common scale [0. . . .1] where the least beneficial value of LC is 0 and the most beneficial value of LC is 1. In other words, the limiting nature of each LC is taken into account by its effect in reducing productivity. During agronomic analysis, the higher SRI values represented the greater suitability of LMUs for each LUT, namely, the suitability of each identified LMU and LUT was assessed using the model to generate a Land Suitability Index (LSI) and suitability class for LUTs presented in Table 1.

Table 1. Land suitability index (LSI) and suitability class for LUTs

| LSI | Symbol | Suitability classes |
|---|---|---|
| 1.00–0.90 | S1 | Highly suitable |
| 0.89–0.75 | S2 | Moderately suitable |
| 0.74–0.50 | S3 | Marginally suitable |
| 0.49–0.25 | N2 | Currently not suitable |
| 0.24–0.00 | N2 | Permanently not suitable |

All of the LUTs were automatically distributed to land use groups using the model for each type of LMU to determine Potential Land Use Groups (PLUG). Furthermore, the input data of digital soil map databases were examined using model for suitability ratings for agricultural uses (Table 2)

Table 2. Suitability class for agricultural use

| Relative LMU index | Symbol | Classes |
|---|---|---|
| 1.00–0.90 | S1 | Best |
| 0.89–0.75 | S2 | Relatively good |
| 0.74–0.50 | S3 | Problematic |
| 0.49–0.20 | N2 | Restricted |
| 0.19–0.00 | N2 | Non-agriculture |

In the final process of land evaluation, a suitability map for agricultural use was obtained. Thus, the results were added to the soil database for each LMU. The values were also used to generate a rain fed agriculture suitability map, an irrigated agriculture suitability map, non-agricultural use suitability map, a potential land use group's map, and suitability map for agricultural uses of the study area using GIS.

## Results and Discussion

Land use groups which are horticulture groups (B), field groups (T), vegetable groups (S) were generated using the model for each type of LMU to determine Potential Land Use Groups (PLUG) which was given in Table 3, 4, 5 and Figure 5, 6 and 7. In this study, land evaluation is expected to be the prediction of land potential for productive LUTs, and generally the comparison or match of the requirements of each potential land use through the characteristics of each type of land. Therefore, it is essential to assess the cultivated area in order to select or determine the best land use types. All of LUTs were determined by taking into account the prevailing physical, ecological, economic, and social conditions of the region. Eighteen LUTs were determined in horticulture groups which are vineyard, poplar, almond, walnut, apple, plum, apricot, quince, berry, cherry, nectarine, peach, sour cherry, rose hip, blackberry, medlar and cranberry. Distribution of the horticulture suitability classes showed that 14.8% of the study area soils were not suitable for any type of horticulture agricultural applications (B0). About one-third of the study (33%) area is suitable plum, apricot, vineyard, almond, walnut, apple, pear, poplar, quince and berry. Only 0.5 % of the study area soils were suitable for all of the horticulture agriculture land use types (B17).

Table 3. Horticulture land use groups

| Code | LUTs | ha | % |
|---|---|---|---|
| B0 | not suitable for this classification | 70515,8 | 14,8 |
| B1 | vineyard, | 23124,0 | 4,9 |
| B2 | vineyard, poplar | 37,1 | 0,0 |
| B3 | vineyard, almond, walnut, | 33297,2 | 7,0 |
| B4 | vineyard, almond, walnut, apple, | 42413,1 | 8,9 |
| B5 | plum, apricot, vineyard, almond, walnut, apple, poplar, | 31816,5 | 6,7 |
| B6 | plum, apricot, vineyard, almond, walnut, apple, pear, poplar, | 1547,3 | 0,3 |
| B7 | plum, Apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince | 2322,0 | 0,5 |
| B8 | plum, Apricot, vineyard, almond, walnut, apple, Pear, poplar, quince, Berry, | 156765,2 | 32,9 |
| B9 | plum, Apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Berry, cherry | 3985,4 | 0,8 |
| B10 | plum, Apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Berry, Nectarine, | 707,0 | 0,1 |
| B11 | plum, Peach, Apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Berry, Cherry, | 7,0 | 0,0 |
| B12 | plum, Peach, Apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Berry, Nectarine | 47,4 | 0,0 |
| B13 | plum, Peach, apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Cherry, Nectarine, | 34,1 | 0,0 |
| B14 | plum, Peach, Apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Berry, Sour cherry, Cherry, Nectarine, | 996,1 | 0,2 |
| B15 | Erik, Apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Berry, Sour cherry, Cherry, Nectarine, Rose hip, Backberry, | 397,5 | 0,1 |
| B16 | plum, Peach, Apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Berry, Sour cherry, Cherry, Nectarine, Rose hip, Backberry, Cranberry | 105401,7 | 22,1 |
| B17 | plum, Peach, apricot, vineyard, almond, walnut, apple, Pear, poplar, Quince, Berry, Sour cherry, Cherry, Nectarine, Rose hip, Backberry, Medlar, Cranberry, | 2594,5 | 0,5 |
| Total | | 476008,8 | 100,0 |

Twenty LUTs were determined in field crop groups which are rise, sugar beet, wheat, barley, vetch, sunflower, safflower, cole, anasone, hash, corn, avena, rey, tiritikale, alfalfa, trefoil, tare, linen, cannabis and sorghum. Distribution of the field crop suitability classes showed that 20.7% of the study area soils were not suitable for any type of field crop agricultural applications (T0). On the other hand about 34% of the study area is suitable for T17 including safflower, sunflower, cole, anasone, hash, sugar beet, corn, wheat, barley, avena, rey, alfalfa, tare, vetch and trefoil.

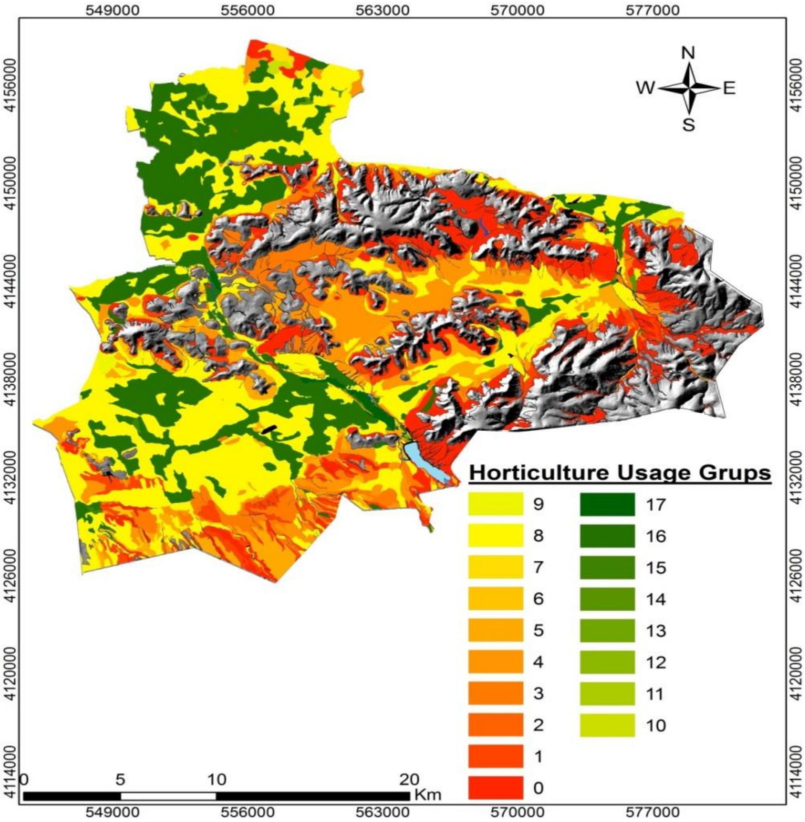


Figure 5. Distribution of the horticulture suitability class map of the study area

Table 4. Field crop land use groups

| Code | LUTs | ha | % |
|---|---|---|---|
| T0 | not suitable for this classification | 9859,1 | 20,7 |
| T1 | Rice, | 9,1 | 0,0 |
| T2 | Sugar beet, | 101,7 | 0,2 |
| T3 | Wheat, Barley, | 3006,6 | 6,3 |
| T4 | Wheat, Barley, Vetch, | 133,4 | 0,3 |
| T5 | Sunflower, Suger beet, Wheat, Barley, | 13,2 | 0,0 |
| T6 | Safflower, Cole, Wheat, Barley, Vetch, | 176,9 | 0,4 |
| T7 | Cole, Anasone, Hash, Sugar beet, Wheat, Barley, Vetch, | 58,6 | 0,1 |
| T8 | Cole, Anasone, Hash, Sugar beet, Corn, Wheat, Barley, Vetch, | 31,9 | 0,1 |
| T9 | Sunflower, Cole, Anasone, Hash, Sugar beet, Corn, Wheat, Barley, Vetch, | 1851,5 | 3,9 |
| T10 | Cole, Anasone, Hash, Wheat, Barley, Avena, Rey, Alfalfa, Trefoil, Vetch, | 9,5 | 0,0 |
| T11 | Cole, Anasone, Hash, Rice, Wheat, Barley, Avena, Rey, Alfalfa, Vetch, | 3,4 | 0,0 |
| T12 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn, Wheat, Barley, Vetch, | 3835,5 | 8,1 |
| T13 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn,Wheat, Barley, Avena, Rey, Alfalfa, Vetch, | 1908,9 | 4,0 |
| T14 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn, Wheat, Barley, Avena, Rey, Alfalfa, Tare, Vetch, | 81,9 | 0,2 |
| T15 | Safflower, Sunflower, Cole, Anasone, Hash, Suger beet, Corn,Wheat, Barley, Avena, Rey, Alfalfa, Vetch, Trefoil, | 96,2 | 0,2 |
| T16 | Safflower, Cole, Anasone, Hash, Suger beet, Corn, Rice, Wheat, Barley, Avena, Rey, Alfalfa, Tare, Trefoil, Vetch, | 0,1 | 0,0 |
| T17 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn,Wheat, Barley, Avena, Rey, Alfalfa, Tare, Vetch, Trefoil, | 15987,6 | 33,6 |
| T18 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn, Rice, Wheat, Barley, Avena, Rey, Alfalfa, Tare, Trefoil, Vetch, | 22,4 | 0,0 |
| T19 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn, Wheat, Barley, Avena, Rey, Alfalfa, Tare, Vetch, Trefoil, Sorghum | 10127,8 | 21,3 |
| T20 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn, Rice, Linen, Cannabis, Wheat, Barley, Avena, Rey, Alfalfa,Tare, Trefoil, Vetch, | 19,7 | 0,0 |
| T21 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn, Rice, Linen, Cannabis, Wheat, Barley, Avena, Rey, Alfalfa, Tare, Trefoil, Vetch, Trefoil, | 148,7 | 0,3 |
| T22 | Safflower, Sunflower, Cole, Anasone, Hash, Sugar beet, Corn, Rice, Linen, Cannabis, Wheat, Barley, Avena, Rey, Alfalfa, Tare, Trefoil, Vetch, Trefoil, Sorghum, | 117,4 | 0,2 |
| Total | | 47600,9 | 100,0 |

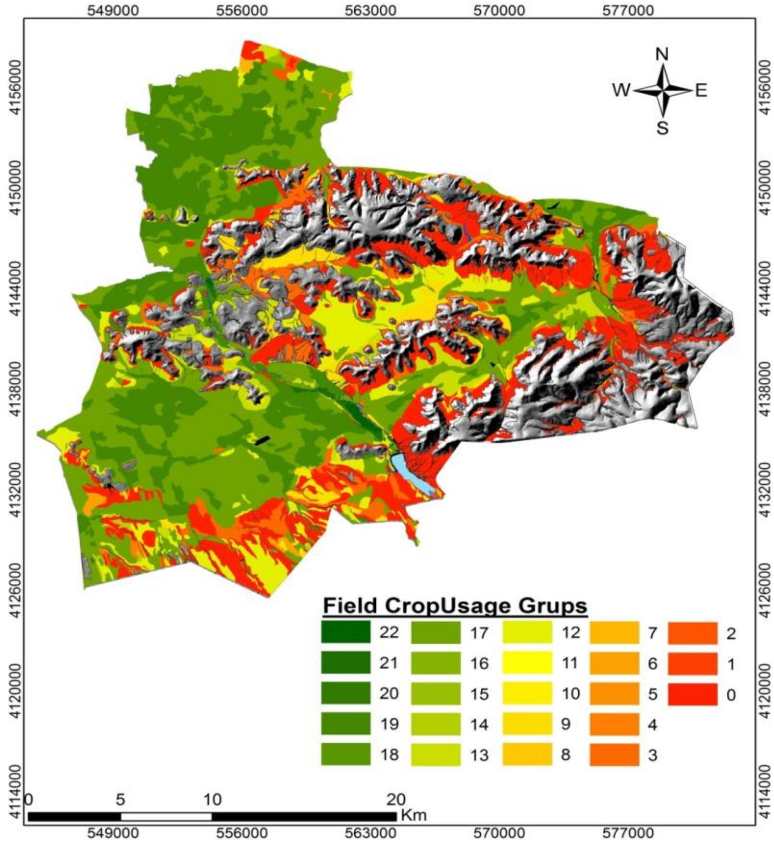


Figure 6. Distribution of the field crop suitability class map of the study area

Thirty-two LUTs were determined in field crop groups which are tomato, melon, water melon, onion, eggplant, pepper, cucumber, bean, reddish shell bean, strawberry, cabbage, gherkin, potato, garlic, lettuce, broad bean, okra, leek, cauli, spinach, parsley, radish, carrot, sunroot, mint, pepperwort, thyme, pea, kind of watercress, rutabaga and broccoli. Distribution of the field crop suitability classes showed that 35.4% of the study area soils were not suitable for any type of field crop agricultural applications (S0). Only 0.5 % of the study area soils were suitable for almost all of the vegetable crop agriculture land use types (S24).

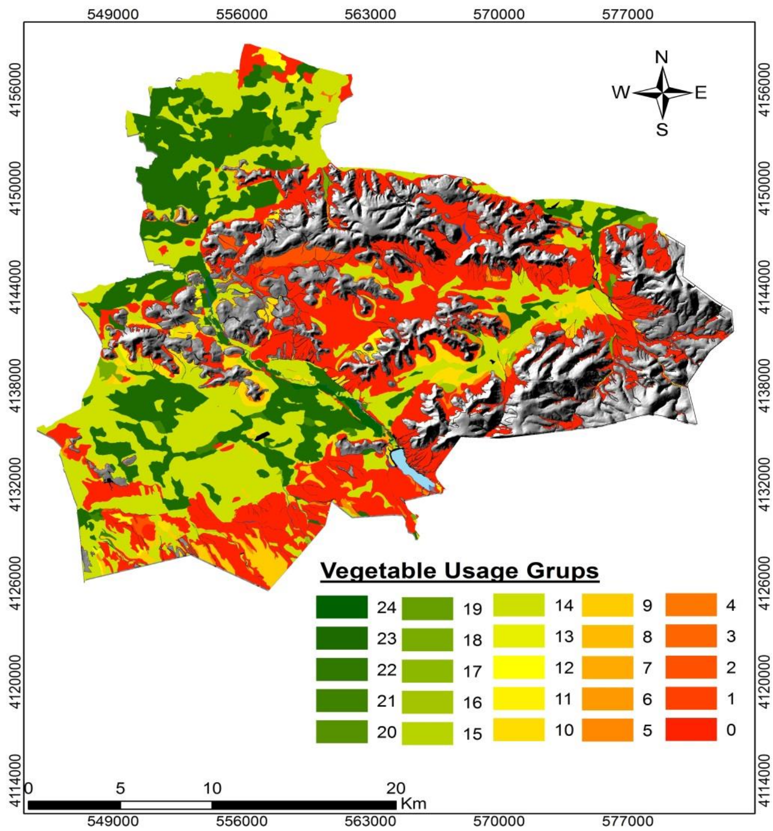


Figure 7. Distribution of the vegetable crop suitability class map of the study area

Table 5. Vegetable crop land use groups

| Code | LUTs | ha | % |
|---|---|---|---|
| S0 | Not suitable for this classification | 16831,3 | 35,4 |
| S1 | Tomato, | 1,16 | 0,0 |
| S2 | Melon, Water melon, | 592,98 | 1,2 |
| S3 | Tomato, Onion, | 13,17 | 0,0 |
| S4 | Melon, Water melon, Tomato, Eggplant, Pepper, | 30,88 | 0,1 |
| S5 | Melon, Water melon, Tomato, Eggplant, Pepper, Onion, Cucumber, Bean, Reddish shell bean, | 453,37 | 1,0 |
| S6 | Strawberry, Melon, Tomato, Eggplant, Pepper, Cucumber, Gherkin, Bean, Reddish shell bean, Potato, | 0,29 | 0,0 |
| S7 | Strawberry, Melon, Water melon, Tomato, Eggplant, Pepper, Onion, Garlic, Cucumber, Bean, Reddish shell bean, | 193,30 | 0,4 |
| S8 | Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Cucumber, Lettuce, Potato, Broad bean, | 3,71 | 0,0 |
| S9 | Strawberry, Melon, Water melon, Tomato, Eggplant, Pepper, Onion, Garlic, Cucumber, Bean, Reddish shell bean, Potato, | 970,01 | 2,0 |
| S10 | Strawberry, Melon, Water melon, Tomato, Eggplant, Pepper, Onion, Garlic, Cucumber, Gherkin, Bean, Reddish shell bean, Potato, | 1492,40 | 3,1 |
| S11 | Strawberry, Melon, Water melon, Tomato, Eggplant, Pepper, Onion, Garlic, Cucumber, Gherkin, Okra, Bean, Reddish shell bean, Potato, | 392,95 | 0,8 |
| S12 | Strawberry, Melon, Water melon, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Leek, Lettuce, Bean, Reddish shell bean, Cauli, Potato, | 47,59 | 0,1 |
| S13 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Leek, Lettuce, Bean, Reddish shell bean, Cauli, Potato, | 7,87 | 0,0 |
| S14 | Strawberry, Melon, Water melon, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Leek, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, | 15176,4 | 31,9 |
| S15 | Strawberry, Melon, Water melon, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Leek, Radish, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, | 9,17 | 0,0 |
| S16 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Leek, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, | 97,71 | 0,2 |
| S17 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Leek, Radish, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, | 4,74 | 0,0 |
| S18 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Carrot, Leek, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, | 366,66 | 0,8 |
| S19 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Carrot, Leek, Radish, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, | 0,81 | 0,0 |
| S20 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Carrot, Leek, Radish, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, | 33,12 | 0,1 |
| S21 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Carrot, Leek, Radish, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, Broad bean, | 478,66 | 1,0 |
| S22 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Carrot, Leek, Radish, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, Sunroot, Broad bean, Mint, Thyme, Kind of watercress, | 6,67 | 0,0 |
| S23 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Carrot, Leek, Radish, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Potato, Sunroot, Broad bean, Mint, Thyme, Kind of watercress, Pepperwort, | 10136,46 | 21,3 |
| S24 | Strawberry, Melon, Water melon, Cabbage, Tomato, Eggplant, Pepper, Onion, Garlic, Cabbage, Cucumber, Gherkin, Okra, Spinach, Carrot, Leek, Radish, Lettuce, Bean, Parsley, Reddish shell bean, Cauli, Broccoli, Potato, Sunroot, Broad bean, Rutabaga, Mint, Thyme, Pea, Kind of watercress, Pepperwort, | 259,45 | 0,5 |
| Total | | 47600,9 | 100,0 |

The distribution of land suitability for agricultural uses showed that 72.7% of the study area soils were classified as best (S1) and relatively good (S2). The distribution of the problematic (S3) and restricted (C4) lands was 12.5% and 6.4% (Figure 8). Finally, only 8.4% of the study area soils were not suitable for agricultural uses (Table 6).

Table 6. Suitability classes for agricultural use

| Description | Class | ha | % |
|---|---|---|---|
| Best | S1: 1-5 | 27243,9 | 57,2 |
| Relatively good | S2: 6 | 7379,0 | 15,5 |
| Problematic | S3: 7 | 5944,1 | 12,5 |
| Restricted | N1: 8 | 3050,7 | 6,4 |
| Non-agriculture | N2: 9-10 | 3983,1 | 8,4 |
| Total | | 47600,9 | 100,0 |

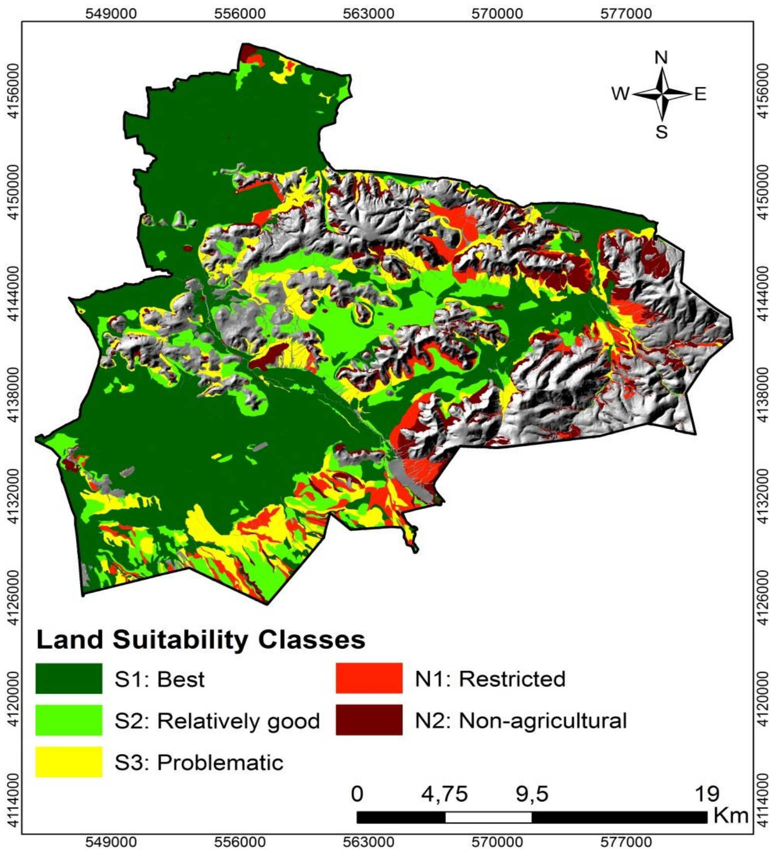


Figure 8. Suitability classes for agricultural use map of the study area

# Conclusion

This current study was performed in Ayancık district of Karaman province located in arid and semiarid environmental ecosystem in order to present an example of alternative agricultural use by considering environmental conditions, because all land can be used for almost all purposes if sufficient inputs are supplied. Each land unit has its own potentialities and limitations, and each land use has its own biophysical requirements. It was found that 8.4% of the study area was not suitable for agricultural activities. In addition, this study confirms the capability of GIS to integrate spatial and attribute data and to offer a quick and reliable method of land suitability assessment with high accuracy. On the other hand, while GIS has been a powerful tool to handle spatial data in land-use analysis, application of this tool alone could not overcome the issue of inconsistency in expert opinion when trying to judge and assign relative importance to each of many criteria considered in a suitability analysis. In conclusion, this research gives suggestions for some alternative applications for the use of land and soil resources and the improvement of agriculture by taking into account the importance of natural values.

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# Assessing soil nutrient change under long-term application of mineral fertilizer micro-dosing to pearl millet [*Pennisetum glaucum* (L.) R. Br.] on a sahelian sandy soil

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## Abstract

In the Sahel, mineral fertilizer micro-dosing technique is known for its benefits to provide higher nutrient uptake and higher crop yields. A study was set up at ICRISAT research station at Sadoré in Niger, which aims at evaluating the sustainability of the technology in the long-term with emphasis on soil nutrients dynamics. The study has started since 2008 and was laid-out in a randomized complete block design that involved two pearl millet varieties, three planting densities, and four nutrients management options. For this study, a sub-set of the treatments from this long-term experiment was used. The nutrient management factor, which includes 4 levels was considered. The most important findings obtained indicated that the change in soil nutrient was markedly different on the planting hills and that from between hill. The change in soil pH-$H_2O$ values on the planting was -7.06 % for the control plots and -9.57 % for the plots applied with NPK. The total nitrogen content has dropped in the two different plots. The amplitude of drop has lowered with the application of NPK micro-dosing on the planting hills with respectively -5.11 % and -12.45 % in the control plots and the micro-dose plots. Positive change in available P was significantly observed ($P \leq 0.05$) in soil between hill with 1.08% in the control plots and 15.97 % in the amended plots. Both grain yield and total dry matter showed similar trend in which decreased yield was obvious over the time. In 2008, an average grain yield of 732 kg. $ha^{-1}$ and 989 kg. $ha^{-1}$ was obtained respectively for the control plots and 6g per hill of NPK plots. Whereas in 2016, 146 kg. $ha^{-1}$ and 218 kg. $ha^{-1}$ were produced respectively for the control plots and the mineral fertilizer micro-dosing plots. These findings indicated that in the Sahel low-input based millet cropping systems, for the mineral fertilizer micro-dosing technology to be sustainable in the long term, the improvement and maintenance of soil fertility should be considered as the cornerstone.

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## Introduction

In the Sahel, one of the most striking constraints that impede crop productivity is low soil fertility (Bationo et al., 2012; Bielders, 2015). Soil nutrient depletion is a major concern in the same part of the Sahel where low-input small-scale farming systems are predominant (Ibrahim et al., 2016). Reports from Sommer et al. (2013) showed that soil nutrient mining is widespread, with a combined average depletion rate of N, phosphorus (P) and potassium (K) of 54 kg per hectare per year in sub-Saharan Africa (SSA). Earlier findings

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from the study conducted in the long term experiment at Sadore Sahelian Centre of International Crop Research Institute for the Semi-Arid Tropics (ICRISAT) have indicated that N and P nutrients significantly affect the grain yield and total dry matter of pearl millet (Akponikpè, 2008; Suzuki et al., 2016). The technology of fertilizer micro-dosing application, which consists of placing small amounts of fertilizer at the hill of plants (ICRISAT, 2009), is widely recognized as a strategy of nutrient management in integrated manner so as to sustain agronomic productivity (Tabo et al., 2005; Idrissa, 2010; Housseini, 2013; Ibrahim et al., 2015a,b). Recent reports from (Akponikpè et al., 2014; Ibrahim et al., 2015b; Suzuki et al., 2017) confirmed that the use of mineral fertilizer in combination with manure resulted in high crop yields in the Sahel. The benefit in the short term of yields increase and income as result of applying mineral fertilizer micro-dosing has been considerably demonstrated across the Sahel region (Hayashi et al., 2008; Twomlow et al., 2008 ; Aune and Ousman, 2011; Bagayoko et al., 2011 ; Sime and Aune, 2014 ; Ibrahim et al., 2015a,b). However, regardless of the increase in crop yields induced by mineral fertilizer micro-dosing technology, Adams et al. (2016), Camara et al. (2013) and Ibrahim et al. (2016) pointed out the fact that such technology leads to an increase of risk of high nutrient export in low-input millet based cropping system and consequently decreased soil fertility. Ibrahim et al. (2015b) have confirmed that a combined application of fertilizer micro-dosing with cattle manure was unable to balance nutrients exported by the obtained yields. On the other hand, Ibrahim et al. (2015a), showed that an increase of fertilizer application depth ranging from 5-10 cm gave a significant increase in terms of the root length density while higher depth of the application of fertilizer has given an increase of high yields. Fewer studies if indeed any exists have been carried out in order to determine the sustainability of that technology. It appears that crop roots are mainly concentrated where nutrients are located but lateral root development is also observed. Hence between hill spaces that in the context of micro-dosing does not receive input, which is expected to provide nutrients to crops. Therefore, to have a better understanding of the sustainability of the technology, the best approach would be to study nutrient dynamics at hill level.

For the current study, the general hypothesis drawn is that as result of hill application of the mineral fertilizer micro-dosing, soil nutrients dynamics on the planting hill will be better and different from that of the soil between the planting hills. The objective of the current study was (i), to evaluate the change with respect to nutrients dynamics from the long-term application of mineral fertilizer micro-dosing and thus determining the level of contribution of planting hill focused and between hills focused nutrients dynamics to soil fertility sustainability of the technology; (ii) to evaluate the effect of mineral fertilizer micro-dosing on crop yield over the years.

# Material and Methods

## Experimental site description

The experiment was conducted at the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) Research Station, Sadoré, Niger (between longitude 13°02'12'' N to longitude 13°15'00'' N, and Latitude 2°16'01''E to latitude 2°17' 00''E). The climatic conditions are characterized by a long and hot dry season (November to May) followed by a very short rainy season between June and September. A highly variable rainfall with an annual average of 550 mm and average temperature is 29 $^{0}$C (ICRISAT database 1984-2016). The field trial is a long-term experiment of a combination of pearl millet and mineral fertilizer micro-dosing started since 2008. The soil type in Sadoré is classified as a sandy Arenosol (West et al., 1984). The field experiment had a sandy soil. The soil organic carbon and extractable P contents were very low with 0.22% and 2.7 mg kg$^{-1}$ respectively. The total Nitrogen (N) content was low with 179 mg kg$^{-1}$ and soil pH ($H_2O$) was strongly acidic (Table1).

## Experimental set-up

Data used in the current study derived from a long-term experiment set since 2008 at International Crops Research Institute for the Semi-Arid Tropics (ICRISAT). This experiment was arranged in a randomized complete block design (RCBD) with three replications. The treatments consisted of a factorial combination of (i) four different nutrient management options (control, 3g of NPK, 6g of NPK and 2g of DAP + 1 g of Urea), (ii) two genotypes of pearl millet (Sadoré local and HKP variety), (iii) three planting densities (Density 1= 5000 hills/ ha); spacing = 1.5 m x1 m; Density2 = 10 000 hills/ ha); spacing = 1 m x 1 m and Density 3 = 15 000 hills/ ha); spacing = 0.8 m x 0.8 m). Plot dimensions were 6 m x 6 m and the gross dimension of the experiment was 64 m x 55 m = 3569 m$^2$. Then, between row spacing was 1 m whereas between replication spacing was 2m and the useful plot size is 25 m$^2$.

To achieve the objective of the current study, two treatments were considered (control, without input) and 6 g hill$^{-1}$ of NPK (15-15-15) with one millet variety (local Sadoré) dibbled at spacing of 1 m x 1 m were used in the present study.

**Soil sampling and analysis**

For initial characterization of the experimental field, soil samples were collected before treatments application in 2008. A total of 36 composite soil samples were collected i.e. 12 samples per replication. To evaluate the change in soil chemical characteristics from initial soil status, the soil samples were collected from the plots. In the present study conducted in June 2017, in addition to 4 composite samples collected between the planting hills, 4 planting hills were also selected randomly on which the same core of samples were collected so as to achieve the objectives of the current study. For the samples collection, a graduated aluminum tube was adapted and used as soil sampling auger. In total, 36 soil samples were collected and three cores samples were considered: 0 – 10 cm; 10 – 20 cm and 20 – 40 cm.

Each sample was analysed for pH-$H_2O$ (soil/water ratio of 1:2.5), soil organic carbon was determined with the method described by Walkley and Black (1934), total N by Kjeldahl method (Houba et al., 1995), exchangeable $K^+$ and extractable phosphorus were determined respectively by using the extraction method described by van Reeuwijk (2002) and the Bray 1 method (van Reeuwijk, 2002).

**Calculation of change in soil nutrient dynamics and statistical analysis**

After the laboratory analysis of the samples, data were processed using Excel. The change in soil nutrients was calculated as follows:

$$\text{Change in N, P, K} = \frac{(\text{ASNC} - \text{ISNC})}{\text{ISNC}} \times 100 \quad (1)$$

where ASNC is the actual soil nutrients content of the experimental field and ISNC is the initial soil nutrients content of the experimental field.

Thereafter, statistical analysis was done with GENSTAT v.9.2 (Trust, 2007) where analysis of variance (ANOVA) was hence performed by using a general treatment structure (in Randomize Blocks). Least Significance Difference (LSD) was used to compare the means. Hence, differences between treatments were considered at error probabilities ≤ 0.05.

# Results

**Initial soil properties of the long-term experimental field**

The initial physical and chemical properties of the soil of the experimental site surveyed in 2008 are presented in Table 1.

Table 1. Initial soil properties of the long-term experiment site in 2008

| Parameters | Soil depths (m) | | |
|---|---|---|---|
| | 0.1 | 0.2 | 0.4 |
| Soil texture | | | |
| Sand (%) | 94.60 ± 0.20 | 76.50 ± 4.40 | 73.20 ± 4.80 |
| Silt (%) | 2.40 ± 0.10 | 8.30 ± 2.00 | 8.30 ± 1.20 |
| Clay (%) | 3.00 ± 0.20 | 15.20 ± 2.80 | 18.50 ± 3.90 |
| Textural class | Sandy | Sandy loam | Sandy loam |
| Soil Chemical properties | | | |
| pH-$H_2O$ (1:2.5) | 5.10 ± 0.03 | 5.20 ± 0.08 | 5.10 ± 0.06 |
| Organic carbon (%) | 0.33 ± 0.04 | 0.19 ± 0.01 | 0.14 ± 0.05 |
| Total-N (mg kg$^{-1}$) | 280.00 ± 13.00 | 153.00 ± 5.00 | 105.00 ± 3.00 |
| Available P (mg kg$^{-1}$) | 3.70 ± 0.30 | 2.30 ± 0.10 | 2.10 ± 0.20 |
| Exchangeable K (mg kg$^{-1}$) | 107.00 ± 40.00 | 43.00 ± 6.00 | 33.00 ± 5.00 |

±Standard error of mean.

The soil texture was sandy with only 3% of clay. 6. The Soil Organic Carbon (SOC) content and extractable P (P-Bray) were all very low with 0.22 % and 2.7 mg.kg$^{-1}$ respectively. The total Nitrogen (N) content was low with 179 mg.kg$^{-1}$ and soil pH ($H_2O$) was strongly acidic. These soil characteristics are representative of the soils in Niger that are characterized by sandy texture and lower level of nutrients and organic matter (Ibrahim et al., 2015b).

## Current soil nutrient measurements of the experiment site

Table 2 illustrates the current soil nutrient content of the experiment site. It is observed that pH values have decreased compared with the initial values. On the plots applied with NPK as micro-dose, the soil pH value was identic (Table 2) while the mean of pH before trial layout in 2008 was 5.1 (Table1). This indicates that the soil is getting acidic despite the application of the mineral fertilizer micro-dosing. The trend is similar concerning the SOC which remains constant (0.2%) as average although crop residues are every year left in to the experiment site. It is concluded that this may be due to the production of biomass, which export much nutrient instead of sequestering into the soil. Nevertheless, the dose of available P has increased over time with application of mineral fertilizer micro-dosing with respectively 3.1 $mg.kg^{-1}$ and 6.1 $mg.kg^{-1}$ for the between hills and the planting hills. It is observed an increase of available P at the planting hills compared with between hills. This could be due to the P accumulation of P into the soil over time.

Table 2. Current soil chemical properties of the experiment site

| | Sampling position | pH-H2O | P Bray1 ($mg.kg^{-1}$) | Total N ($mg.kg^{-1}$) | OC ($g.kg^{-1}$) | $K^+$ ($mg.kg^{-1}$) |
|---|---|---|---|---|---|---|
| Control | Between hill | 4.70 ± 0.13 | 2.70 ± 0.10 | 141.60 ± 5.09 | 1.00 ± 0.01 | 45.30 ± 4.16 |
| Control | Under hill | 4.80 ± 0.09 | 2.50 ± 0.08 | 157.30 ± 10.13 | 2.00 ± 0.02 | 62.80 ± 5.90 |
| NPK(6g.hill) | Between hill | 4.60 ± 0.04 | 3.10 ± 0.25 | 151.60 ± 10.66 | 2.00 ± 0.01 | 44.00 ± 4.50 |
| NPK(6g/hill) | Under hill | 4.60 ± 0.06 | 6.10 ± 0.10 | 170.50 ± 11.44 | 2.00 ± 0.01 | 72.80 ± 0.53 |

±Standard error of mean.

## Changes in soil nutrients content of the experimental field

### Change in soil pH-$H_2O$ of the experimental site

Figure 1 shows that after 9 seasons of cropping, soil pH-$H_2O$ decreased in both the control plot and that applied with 6g of NPK (15-15-15) as micro-dose. In the control plot as well as in the fertilized plots, the amplitude of the change in pH-$H_2O$ was similar whether the sample was collected between the planting hills or on the hills. When compared with the control plots, soil acidity has increased significantly more on the planting hill than between the hill ($p \leq 0.05$). Change in soil pH was -7.06% for the control plot and -9.57% for the plots applied with NPK. The higher negative percentage of this change indicated that a possible acidification of the soil experiment occurred.

### Changes in total nitrogen

Results concerning change in total N occurred in the experimental field are presented in Figure 2. Soil total nitrogen content has dropped over the year of cropping in both the control plot and the plot receiving NPK as micro-dose. This negative change in total Nitrogen was more important with respect to between the hills than to the planting hills regardless of the treatment received. The amplitude of nitrogen content drop was lower in the plot applied with NPK than in the control plots. Application of 6 g of NPK has lowered the amplitude of nitrogen content drop on the planting hill (-5.11 %) compared with the control plot (-12.45 %) indicating partial replenishment compared with the between hills space and the control. Therefore, micro-dosing option significantly ($p \leq 0.005$) affected Nitrogen content. The negative change might be due to the mobile character of N into the soil and to the soil nutrient export from biomass production of pearl millet.

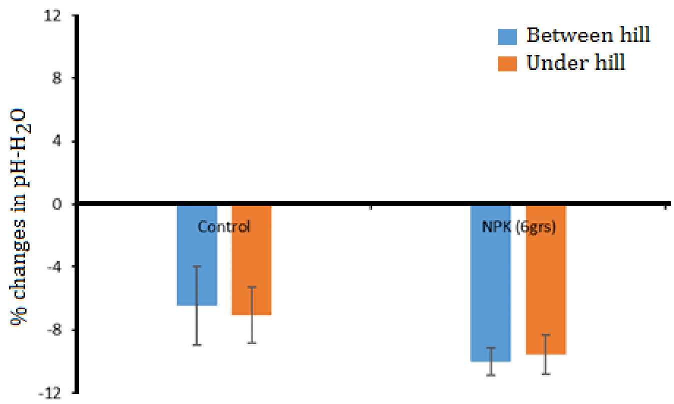


Figure 1. Change in the pH ($H_2O$) values from 2008 to 2017of the experiment site as affected by treatments

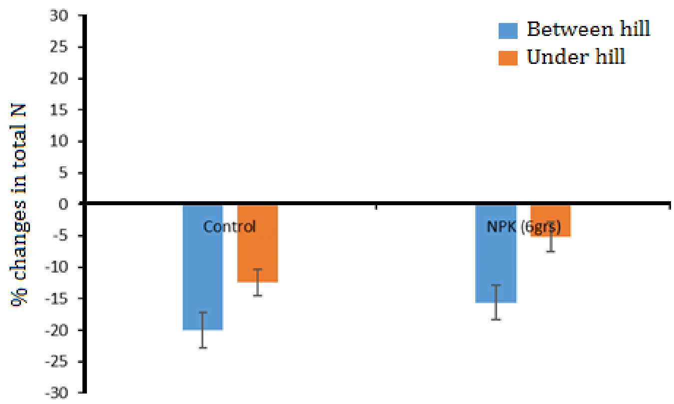


Figure 2. Change in total nitrogen content of the soil as affected by treatments

### Changes in extractable phosphorus (P-Bray1)

Figure 3 presents the change in extractable phosphorus content of the experimental soil from 2008 to 2017. Higher and positive change was observed in plots applied with NPK compared with the control particularly on the planting hills (88.19 % vs -6.27 %). In both the control and the fertilized plot, positive change was observed in available P in soil between the planting hills. This is an indication that even though P export through biomass production has occurred in both treatments, P accumulation has occurred in the plot applied with NPK. Presumably P mobilization from the soil pool have occurred that was more important on the planting hills.

### Change in exchangeable $K^+$

Figure 4 indicates the change in exchangeable $K^+$ of the experimental field. The results showed a positive change on the planting hill and it is significantly higher in plots amended with NPK (6 g) on planting hill than in the control plots with 19.64 % and 3.18 % respectively in micro-dosing plots and the control plots. Difference between soil sampling positions is significantly different ($p \leq 0.05$). The change is however negative in between hills with respectively -34.6 % and -25.59 % in fertilizer micro-dosing plots and the control plots respectively. The positive change in exchangeable $K^+$ means that this nutrient is gradually stocked in the soil with the application of 6 g of NPK per hill over time. Nevertheless, the positive change was also observed in the control plots. Thus, this indicates that the accumulation of exchangeable $K^+$ is not only from the nutrients applied.

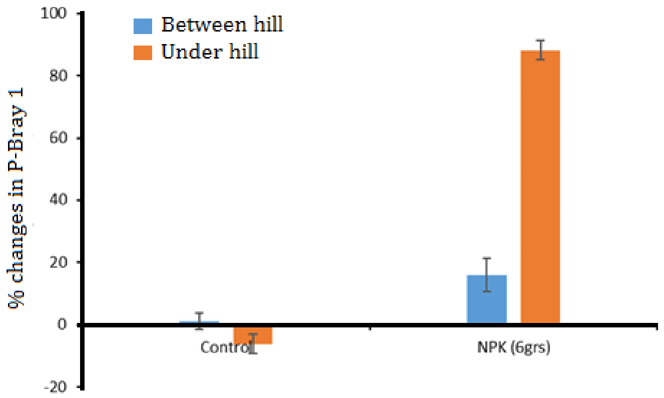


Figure 3. Change in extractable Phosphorus content of the experimental soil as affected by treatments

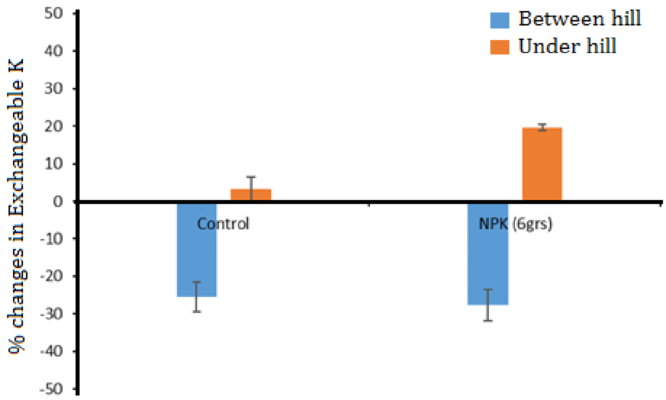


Figure 4. Change in exchangeable K+ content of the experimental soil as affected by treatments

### Changes in soil organic carbon

Results of the changes in organic Carbon of the experimental soil are presented in figure 5. The proportion of changes in organic Carbon was negative both on planting hill and in between hills space. The trend observed is similar to that of soil pH (Figure1). Results showed that the change was a little bit lower in the fertilized plots compared with the control plots with respectively -21.85 % and -26.71 % of change in organic Carbon. The same applies to the between hill where the change was negatively greater in the control plots (-34.46 %) compared to the micro-dosing plots (-25.29 %). However, there was no significant difference ($p \leq 0.05$) among treatments and soil sampling position as well.

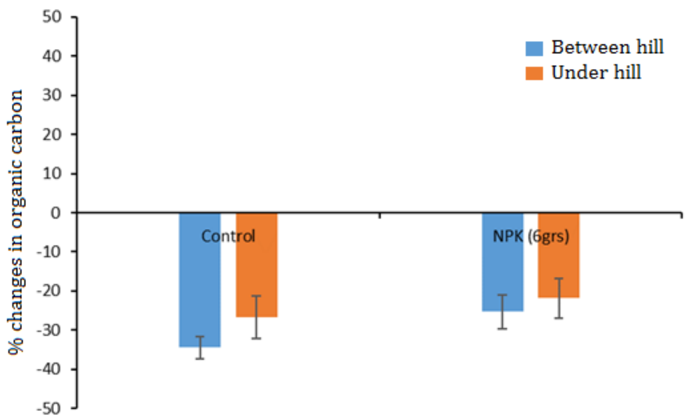


Figure 5. Change in the of organic Carbon content of the experimental soil as affected by treatments

**Effect of mineral fertilizer micro-dosing on pearl millet yield over the two years**

Grain yield and total dry matter of the two years of cropping systems were presented in the Table 3 to illustrate the effect of the mineral fertilizer micro-dosing application. In 2008, mineral fertilizer micro-dosing technology resulted in increased grain yield and total dry matter production. With respect to grain yield in 2008, the control plots produced 732 kg.ha$^{-1}$ while the mineral fertilizer micro-dosing plots produced 989 kg.ha$^{-1}$. However, in the 2016; grain yield as well as total dry matter dropped both in the control plots and in the plots treated with 6g per hill of NPK with respectively 1196 kg.ha$^{-1}$ 2987 kg.ha$^{-1}$ whereas in 2008 the control plots and the plots treated with the 6g per hill of NPK produced respectively 4118 kg. ha$^{-1}$ and 6870 kg. ha$^{-1}$. From the observed trend; grain yield and total dry matter have dropped over time in both the plots amended with micro-dosing and the control plots. This explains that a lone application of mineral fertilizer micro-dosing could not maintain crop yield over time in low-input millet based cropping systems.

Table 3. Millet yields and harvest index

| | Grain yield (kg ha$^{-1}$) | | Total dry matter (kg ha$^{-1}$) | | HI | |
|---|---|---|---|---|---|---|
| | 2008 | 2016 | 2008 | 2016 | 2008 | 2016 |
| Control | 732±124 | 146±22 | 4118±419 | 11960±204 | 0.15±0.01 | 0.12±0.01 |
| Microdose | 989±132 | 218±42 | 6870±445 | 2987±412 | 0.14±0.01 | 0.07±0.01 |
| Probability values | | | | | | |
| Year (Y) | < 0.001 | | < 0.001 | | 0.003 | |
| Treatment (T) | 0.117 | | < 0.001 | | 0.037 | |
| Y x T | 0.341 | | 0.072 | | 0.053 | |
| CV (%) | 29.8 | | 22.7 | | 13.7 | |

±Standard error of mean.

## Discussion

The soil type of the study area was a Sahelian sandy soil which is inherently fragile and infertile (Bationo et al., 1998). The results of the study were similar to the findings obtained by Housseini (2013) that showed a variation of soil pH-$H_2O$ value of about -0,45 after applying 1g of NPK on the planting hill of sesame farm in Kollo (Niger). These results are in line with the work of Bandoum (2005) where he showed that mineral fertilizer micro-dosing caused nutrient export initially present in the soils. These results also agreed the findings obtained by Ibrahim et al. (2016) who found that fertilizer micro-dosing with (2 g DAP and 6 g NPK) had a negative effect on both partial and full nutrient balance in pearl millet field. Added to that, the work of Housseini (2013) confirmed that total dry matter of sesame local variety seriously exported partial nutrient balance with about 21.9 g/kg N with application of NPK at hill. Therefore, it is concluded that mineral fertilizer micro-dosing has led to a negative contribution with regard to partial and full soil nutrient balances instead of increasing such nutrient balances. However, Ibrahim et al. (2016) reported that a combined use of fertilizer micro-dosing along with manure had a positive partial nutrient balance. This indicates that pearl millet used significantly much more nutrients from the native soil nutrients. On the other hand, the highest percentage of change observed between hills may be due to the lateral root development of pearl millet that permit to the plant to look for nutrients far from the hill. This is a strategy of pearl millet adopted so as to benefit from nutrients where they are concentrated (Ibrahim et al. 2015b). With such nutrient mining character of fertilizer micro-dosing, cropping system could not be quite sustainable meaning that the technology cannot sustain the nutrient requirements of pearl millet over time. Research has shown that pH, Fe, Al and Ca concentration as well as soil texture and organic matter significantly affect P availability for the plant (Mkhabelaa and Warman, 2005). In acidic soils and particularly with sandy structure like the one of our experiment with up to 47 % aluminium saturation (Fatondji et al., 2006), it is expected that P immobilization occurs at pH lower than 5. In the sampled plots, soil pH has dropped from 5 to 4.8 (Figure1). Some studies (Bationo et al., 2003, 2011) revealed that the accumulation of $K^+$ in the soil is that the native Sahelian soils in Sadoré contains a high percentage of exchangeable cations such as $K^+$, $Ca^{2+}$. Ibrahim et al. (2016) observed that nutrient depletion is the great consequence of the export of nutrients of crop residue. Though crop residues are usually left in the experimental field over the years, we realize that the change in organic Carbon was relatively negative. First, this may be due to the rapid mineralization of organic matter over time of the soil as it is a Sahelian sandy soil which is fragile and inherently infertile and hence its organic matter rate is very low (<1%). Most importantly, lack of application of organic manure over time in the experimental field can exacerbate the drastic decrease of organic Carbon in the long term. Ibrahim et al. (2015b) indicated that a combination of organic manure with fertilizer micro-dosing is necessary in the long term so as to increase and sustain pearl millet yield as well as efficient use of limited nutrients such as soil organic Carbon in Sahelian cropping systems.

Yield reduction observed over time shown in the experiment is in line with the work of Adams et al. (2016), who demonstrated negative yield trends of fertilizer micro-dosing treatments indicating that mineral fertilizer alone is unstainable at Sadoré. However, crop residue or manure addition at a certain level buffered pH by 0.3 and increased pearl millet yield. A combined application of manure and mineral fertilizer enhances increased grain yield in Sahel (de Rouw and Rajot 2004; Ibrahim et al., 2015a; Suzuki et al., 2016). Earlier manure application is favourable for root system development (Michels and Bielders, 2006) and allows faster initial leaf growth, thereby increasing water use efficiency and crop productivity (Shapiro and Sanders, 1997; Bationo et al., 1998). Similarly, in Sahelian cropping system, many studies have shown the importance of crop residue in the Sahel Region. Buerket et al. (2000) reported that 73% of millet grain yield increase was due to application of 2 $t.ha^{-1}$ of millet residue. Many studies have reported increased soil permeability and aggregate stability as well as increased water infiltration and water holding capacity, increased soil organic matter (SOM), pH, CEC and nutrient availability which can lead to sustainable yield and sustained soil fertility over time (Bationo and Mokwunye, 1991; Buerkert and Hiernaux, 1998).

Overall, this yield reduction over time might be attributed to fast nutrient release and organic matter decomposition reported for Sahelian conditions (Bationo et al., 2005; Manyame, 2006). In addition to soil fertility decline, other environmental factors such as dry spell periods might be bringing about a drop of total biomass production over time. On the other hand, recurrent dry spell periods observed in Sadoré over the years coinciding with critical peal millet growth in this season including the grasshopper attack which has led to a replanting of the whole field (Sani, 2018).

## Conclusion

The change in soil nutrients obtained in this study showed that fertilizer micro-dosing stimulates the export of soil nutrients that are initially into the soil which consequently encourages the soil impoverishment. Thus, fertilizer micro-dosing significantly affects soil nutrients in the long term. It is concluded that the trend of the change in soil pH-$H_2O$ as well as in soil organic carbon, and in total nitrogen content were negative. However, only Phosphorus and exchangeable K+ have presented positive change. The change in soil nutrients dynamics is better on the planting hills than that from between hills space. Further, pearl millet yield dropped over time regardless of the treatments applied with mineral fertilizer micro-dosing. Hence, we concluded that crop yield was not only affected by micro-dosing options but also environmental factors were included. Similarly, the study concluded that the hill placement character greatly influences soil nutrients dynamics in long-term application of micro-dosing. Further research should be implemented in order to thoroughly assess the sustainability of that technology.

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# Changing dynamics of micronutrients in piedmont soil of Bangladesh

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## Abstract

A study was aimed to delineate the micronutrient status, their change directive with time and relationship with other soil variables in piedmont soils of Bangladesh. Northern and Eastern Piedmont Plains (AEZ 22) is one of the 30 agro-ecological zones (AEZs) of the country whose bench mark status of soil micronutrient has been used for comparing with the present status. There is an indication of zinc (Zn) and boron (B) depletion to some extent after a decade of time whereas the very high fertility status of copper (Cu), manganese (Mn) and iron (Fe) prevails as it was in the previous status. In general view, the micronutrient content of surface soil (0-15 cm) was higher than those of sub-surface soils (15-30 cm). In surface soil clay content showed significant correlation with soil Zn (r=0.403**), Cu (r=0.752**), Fe (r=0.501**) and Mn (r=0.340**). Cu content of soil exhibited positive relationship with all the soil parameters except soil pH and P content; there existed highly significant negative correlation of Cu with soil pH (r=-0.578**) and P (r=-0.420**). The availability of Fe in soil was strongly related with soil clay content (r=0.501**), soil pH (r=-0.686**) and organic matter content (r=0.527**). In surface soil, Fe content influenced significantly with the content of Zn, Cu and Mn. Accordingly in sub-surface soil, positive significant interaction of Zn-Fe, Cu-Fe, Cu-Mn and Fe-Mn was observed. The message revealed from this study concerning nutrient depletion, and interactions among different soil parameters and nutrient elements will pave the way for efficient use of soil resources in a sustainable way.

**Keywords**: Change directive, interaction, micronutrient, piedmont soil, status.



## Introduction

Once upon Bangladesh was a land of fertile soils; now it is in the eve of loosing its glory. Over the last 2-3 decades, enormous pressure has been exerted on its soil resources to produce more food for the ever increasing population of the country. Soil degradation has far reaching consequences particularly in relation to crop production and environmental stability (Lal and Stewart, 1992). Declining productivity in Bangladesh due to the decrease of soil fertility has been cited by many authors (Islam, 1990; Saunders, 1990, 1991; Ali, 1991; Saheed, 1991, 1994). Intensification of agricultural land use has increased remarkably, along with increasing use of modern crop varieties, which in turn has resulted in deterioration of soil fertility with emergence of new nutrient deficiencies. In 1983-84, the cropping intensity of the country was 171% whereas it was 194% in 2015-16 (BBS, 2017). Accordingly, coverage of HYVs and hybrid varieties of only rice increased from 2631 thousand ha in 1983-84 to 9685 thousand ha in 2015-16 (BBS, 2017; BBS, 2018). As a consequence, soil fertility is declining day by day (Islam, 2008; SRDI, 2010a,b). Hence, chronologically N, P, K, S, Zn and B deficiency have arisen in this country's soils (Jahiruddin and Satter, 2010). On the other hand, cropping systems have undergone some drastic changes since 1973 due to the adoption of high

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yielding varieties along with increased use of irrigation and fertilizer (Huq et al., 1990). Natural disasters (e.g. floods, cyclones, drought etc.), human interference (Farakka barrage etc.), over intensification due to population pressure, deforestation, low supply of recyclable organic matter and other types of agricultural mismanagement might exert adverse long-term effects on the soils of Bangladesh. Among the agro-ecological zones (AEZs) of the country, Northern and Eastern Piedmont Plains (AEZ 22) is an important one considering land coverage of 4,03,758 ha as well as crop cultivation (BARC, 2012).

Zinc deficiencies in rice were observed in early 1980s in Bangladesh. Among the crops maize and rice have been found to be more sensetive to zinc deficiency (Akhter et al., 1990; Islam et al., 1997; Alam et al., 2000). Boron deficiency of some crops is reported in early 1990's. Sporadic information of Cu and Mn deficiencies in crops has been reported (Bhuiyan et al., 1998; Khanam et al., 2000; Ferdoush et al., 2003). Among the micronutrients Fe and Cl deficiencies are not yet reported in Bangladesh. The Zn deficiency in rice was first identified at Bangladesh Rice Research Institute (BRRI) and concurrently at Bangladesh Agricultural University (BAU) (Bhuiya et al., 1981; Jahiruddin et al., 1981). Thereafter, the status of Zn in soils and crop plants, and areas prone to Zn deficiency in rice were identified through the "FAO-BARC Coordinated Programme on Zn and S Deficiencies of Bangladesh Soils", with the participation of several institutes viz. Bangladesh Rice Research Institute (BRRI), Bangladesh Agricultural Research Institute (BARI), Bangladesh Institute of Nuclear Agriculture (BINA) and Bangladesh Agricultural University (BAU) (Islam, 1984). Considering the above aspects, deficient micronutrient along with it deficient zones in the country should be identified. In addition to that it is essential to know about the depleting trend of those nutrients and interacting factors related to the issue. Hence, the present study was undertaken to avail the information related to the change in soil micronutrients, their depleting mode and the influencing factors act on them in the aforesaid AEZ.

## Material and Methods

### Previous soil data collection

Soil Resource Development Institute, a leading soil research institute in Bangladesh generated the previous soil fertility status of AEZ 22 through respective Upazila Nirdeshika (Adorsho Sadar and Burichong upazila of Cumilla district. Previous soil analytical data were collected from those Upazila Nirdeshika.

### Collection of soil samples

Soil sampling was done from the representative sites of the study area to delineate the the present fertility status. The sampling sites were selected based on the existing cropping pattern, land type and soil series. The corresponding previous sampling spots, cited in the respective Upazila Nirdeshikas were also in consideration. The highest efforts were given for selecting the same/closer spots to the previous sampling spots maintaining the above mentioned criteria. GPS reading was recorded for each site. Fifty sampling sites were selected, and from each site two samples were collected at two soil depths (0-15 cm and 15-30 cm). The collected soil samples were spread on brown paper in the laboratory for air-drying. After removing the plant roots and other debris the air-dried soil was ground and passed through a 2-mm sieve. The processed samples were kept in polyethylene bags.

### Chemical analysis of processed soil samples

Subsequently, the soil samples have been analyzed for basic soil properties (pH, organic matter and texture), macronutrient (N, P, K, S, Ca and Mg) and micronutrient (Cu, Fe, Mn, Zn and B) status following standard methodology as described in Table 1.

### Processing and statistical analysis of soil analytical data

The analytical results of soil samples have been categorized into very low, low, medium, high and very high status. Similarly, the status of basic soil parameters also used in such categorization (BARC, 2012). Relationship between each nutrient and other soil characteristics were examined by correlation analysis (Gomez and Gomez, 1984). A comparative feature was developed using the analytical data derived from collected soil samples and the previous available data from respective Upazila Nirdeshika (SRDI, 1999, 2000, 2006). The analytical results derived from collected soil samples and Upazila Nirdeshika is denoted in this manuscript as present and previous status, respectively. Standard statistical tools were used in comparing the data by using Microsoft Excel (Gomez and Gomez, 1984).

Table 1. Methods for analysis 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 wet oxidation method (Nelson and Sommers, 1996), the soil organic matter was oxidized by 1N potassium dichromate and the amount of organic carbon in the aliquot was determined by titration against 0.5 N ferrous sulphate hepta-hydrate solution. The amount of 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 soil was determined by 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's, 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 wave length |
| Exchangeable Ca, Mg, K | These elements were extracted from soil by 1M $CH_3COONH_4$ with a 1:10 soil-extractant ratio and the extractable amount was determined by flame AAS for Ca & Mg and by flame photometer for K (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 wave length (Fox et al., 1964; Jones et al., 1972) |
| Available Zn, Cu, Mn, Fe | These micronutrients were 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) |

# Results

## Present status of soil micronutrient and its deviation from respective previous one

Different data as mean, maximum, minimum and standard deviation for each micronutrient derived from chemical analysis of soil is summerized in Table 2. Previous status of the micronutrients is also presented in the same table for comparing both statuses. Comparison was done between present statuses of each micronutrient with their corresponding previous one, as recorded in Upazila Nirdeshika. The soil samples incorporated in those Upazila Nirdeshika were collected from field during 1996-2003. Hence, almost a decade of time gap between present and previous soil analytical results. Comparison between present and previous status of different micronutrients are graphically shown in Figures 1-5.

Table 2.Summary of zinc, boron, copper, iron and manganese levels (mg $kg^{-1}$) of soils at two depths (n=50)

a) Present status

| Micronutrients | 0-15 cm soil depth | | | | 15-30 cm soil depth | | | |
|---|---|---|---|---|---|---|---|---|
| | Min. ( µg $g^{-1}$) | Max. (µg $g^{-1}$) | Mean (µg $g^{-1}$) | SD | Min. ( µg $g^{-1}$) | Max. (µg $g^{-1}$) | Mean (µg $g^{-1}$) | SD |
| Zn | 0.54 | 3.28 | 1.681 | 0.789 | 0.45 | 4.49 | 1.21 | 0.77 |
| B | 0.10 | 0.50 | 0.27 | 0.10 | 0.08 | 0.33 | 0.18 | 0.08 |
| Cu | 0.98 | 7.58 | 3.49 | 1.67 | 0.64 | 8.67 | 2.83 | 1.75 |
| Fe | 43.0 | 397 | 217 | 79 | 19.0 | 200 | 91.0 | 48.47 |
| Mn | 17.0 | 91.0 | 45.1 | 20.7 | 9.6 | 67.4 | 28.8 | 14.81 |

b) Previous status

| Micronutrients | 0-15 cm soil depth | | | |
|---|---|---|---|---|
| | Min. ( µg $g^{-1}$) | Max. (µg $g^{-1}$) | Mean (µg $g^{-1}$) | SD |
| Zn | 0.30 | 3.90 | 2.62 | 0.856 |
| B | 0.11 | 0.54 | 0.33 | 0.130 |
| Cu | 0.50 | 9.40 | 4.12 | 1.810 |
| Fe | 12.00 | 475 | 195 | 114 |
| Mn | 4.00 | 171 | 44.60 | 36.60 |

### Status of plant available zinc

After almost a decade of time, a clear depletion was observed in soil Zn status of the study area (Figure 1). The available Zn ranged in surface soil (0-15 cm depth) from 0.30 to 3.90 and 0.54 to 3.28 µg $g^{-1}$ with the averages of 2.62 and 1.68 mg $kg^{-1}$ in previous and present investigations, respectively. On the other hand, present sub-surface soil had available Zn status varied from 0.45 to 4.49 µg $g^{-1}$. Previously, surface soil Zn status was 2% very low, 2% low, 10% medium, 8% optimum, 14% high and 64% very high, and in present situation it is 16% low, 30% medium, 24% optimum, 6% high and 24% very high.

### Status of plant available boron

Available B in surface soil varied from 0.11 to 0.54 and 0.10 to 0.50 µg $g^{-1}$ having the averages 0.33 and 0.27µg $g^{-1}$ in previous and present status, respectively. Again, it ranged from 0.08 to 0.33 µg $g^{-1}$ with an average value 0.18 µg $g^{-1}$ in present sub-surface soil. Among the soil samples studied, 20% hold very low, 33% low, 37% medium and 10% optimum B in previous status, while it was 10% very low, 40% low, 46% medium and 4% optimum in present data (Figure 2).

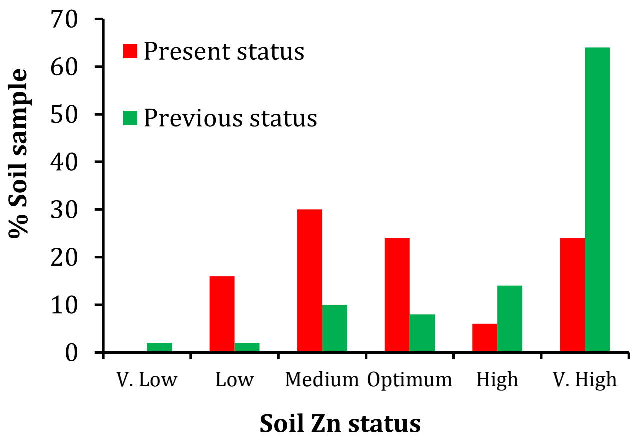


Figure 1. Changing trend of soil available Zn status over time in AEZ 22

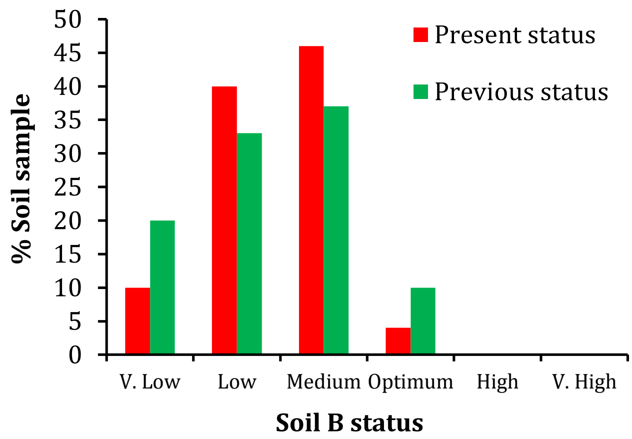


Figure 2. Changing trend of soil available B status over time in AEZ 22

### Status of plant available copper

The available Cu status in surface soil ranged from 0.50 to 9.40 and 0.98 to 7.58 µg $g^{-1}$ having the averages 4.12 and 3.49 µg $g^{-1}$ in previous and present fertility, respectively. On the other hand, it was from 0.64 to 8.67 µg $g^{-1}$ in present sub-surface soil where the average value was 2.83 µg $g^{-1}$. In both previous and present surface soil, very high status of available Cu was reported (Figure 3).

### Status of plant available iron

The soil status of available Fe was very high in both previous and present fertility (Figure 4). It varied from 12.0 to 475 and 43 to 397 µg $g^{-1}$ having the average values of 195 and 217 µg $g^{-1}$ in previous and present data, respectively. Again in present sub-surface soil, it was from 19 to 200 µg $g^{-1}$ with an average of 91 µg $g^{-1}$.

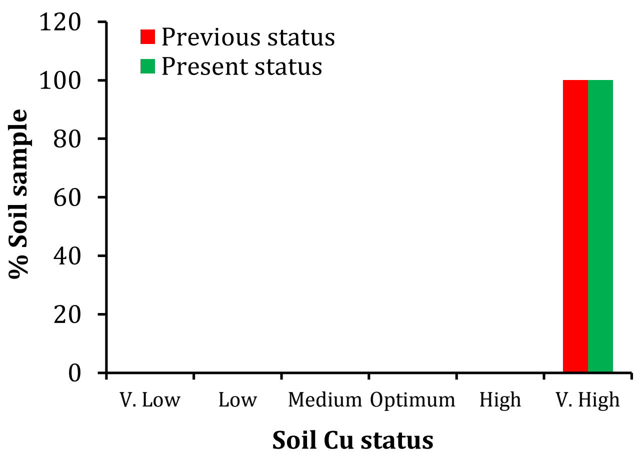


Figure 3. Changing trend of soil available Cu status over time in AEZ 22

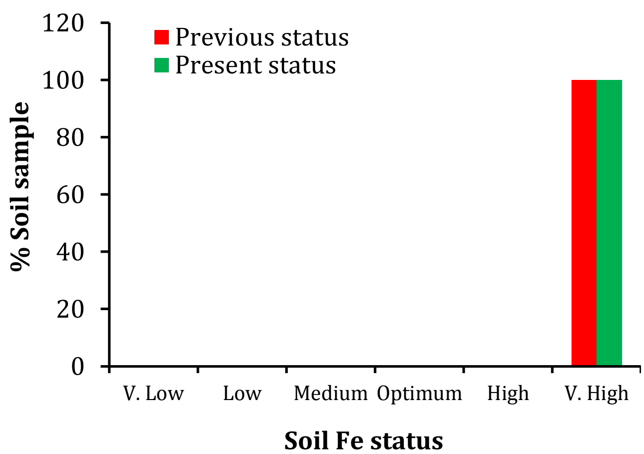


Figure 4. Changing trend of soil available Fe status over time in AEZ 22

### Status of plant available manganese

In all cases, the soil status of available Mn categorized as very high in both previous and present status, and it ranged from 4.0 to 171 and 17.0 to 91.0 μg $g^{-1}$ with an average of 44.6 and 45.1 μg $g^{-1}$ in previous and present data, respectively (Figure 5). Again, the range was 9.6 to 67.4 μg $g^{-1}$ in present sub-surface soil where the average content was 28.8 μg $g^{-1}$.

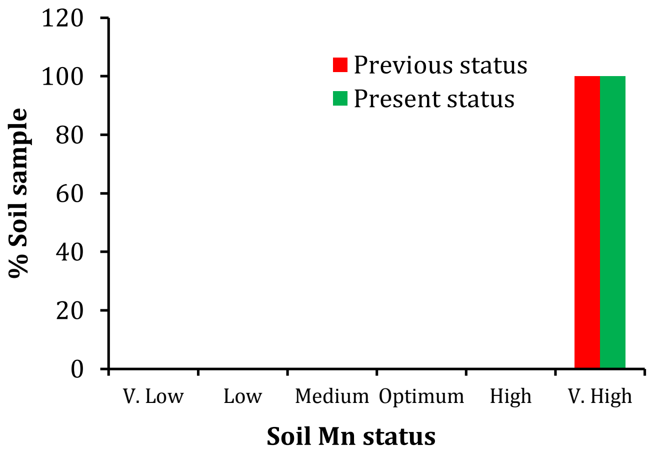


Figure 5. Changing trend of soil available Mn status over time in AEZ 22

## Relationship of micronutrients status with other soil variables

Correlation statistics was performed to examine the relationship of micronutrients with other soil variables and to see the interrelationship among the micronutrients. This statistics was done separately for surface and sub-surface soils (Tables 3 and 4). The number of soil samples i.e. observations for both cases were 50.

Table 3. Correlation matrix of soil variables (soil collection at 0-15 cm depth)

a) Relationship of micronutrients with other soil variables (n=50)

| Micronutrients | Clay | pH | OM | N | P | K | Ca | Mg | S |
|---|---|---|---|---|---|---|---|---|---|
| Zn | 0.403** | -0.192ns | 0.048ns | -0.045ns | 0.368** | 0.366** | 0.077ns | -0.015ns | 0.177ns |
| B | -0.202ns | -0.008ns | -0.191ns | -0.129ns | 0.205ns | -0.052ns | -0.181ns | -0.137ns | 0.052ns |
| Cu | 0.752** | -0.578** | 0.565** | 0.509** | -0.420** | 0.650** | 0.770** | 0.629** | 0.497** |
| Fe | 0.501** | -0.686** | 0.527** | 0.480** | -0.082ns | 0.520** | 0.435** | 0.243ns | 0.540** |
| Mn | 0.340* | -0.255ns | 0.299* | 0.420** | -0.290* | 0.430** | 0.309* | 0.232ns | 0.397** |

b) Interrelationship among micronutrients in soils (n=50)

| Micronutrients | Zn | B | Cu | Fe |
|---|---|---|---|---|
| Zn | - | | | |
| B | -0.004ns | - | | |
| Cu | 0.178ns | -0.198ns | - | |
| Fe | 0.293* | 0.025ns | 0.563** | - |
| Mn | 0.083ns | -0.055ns | 0.154ns | 0.359** |

* = Significant at 5% level, ** = Significant at 1% level, ns = Not significant

Table 4. Correlation matrix of soil variables (soil collection at 15-30 cm depth)

a) Relationship of micronutrients with other soil variables (n=50)

| Micronutrients | Clay | pH | OM | N | P | K | Ca | Mg | S |
|---|---|---|---|---|---|---|---|---|---|
| Zn | 0.080ns | -0.437** | 0.167ns | 0.036ns | 0.719** | 0.291* | -0.156ns | -0.182ns | 0.113ns |
| B | -0.134ns | 0.178ns | -0.129ns | -0.255* | 0.119ns | -0.051ns | -0.045ns | -0.035ns | 0.187ns |
| Cu | 0.713** | -0.305* | 0.654** | 0.557** | -0.219ns | 0.601** | 0.545** | 0.399** | 0.259* |
| Fe | 0.344* | -0.666** | 0.593** | 0.368** | 0.237ns | 0.300* | 0.123ns | -0.063ns | 0.374** |
| Mn | 0.388** | -0.254ns | 0.247ns | 0.163ns | -0.153ns | 0.345** | 0.267* | 0.287* | 0.327* |

b) Interrelationship among micronutrients in soils (n=50)

| Micronutrients | Zn | B | Cu | Fe |
|---|---|---|---|---|
| Zn | - | | | |
| B | 0.047ns | - | | |
| Cu | 0.221ns | -0.200ns | - | |
| Fe | 0.415** | 0.029ns | 0.573** | – |
| Mn | 0.173ns | 0.060ns | 0.479** | 0.456** |

* = Significant at 5% level, ** = Significant at 1% level, ns = Not significant

**Characteristics of surface soil (0-15 cm soil depth)**

Clay content of soil showed significant correlation with soil Zn (r=0.403**), Cu (r=0.752**), Fe (r=0.501**) and Mn (r=0.340**) (Table 3). The Zn content showed significant relationship with available P (r=0.368**) and exchangeable K (r=0.366**) content of soil. Among the micronutrients under study, the soil B content exhibited positive but non-significant relationship with soil P (r=0.205) and weak relation with S content (r=0.052); while it showed negative relation with all other soil characteristics under study. The Cu availability in soil was influenced by many soil variables. Cu content of soil exhibited positive relationship with all the soil parameters except soil pH and P content; there existed highly significant negative correlation of Cu with soil pH (r= -0.578**) and P content (r= -0.420**). The availability of Fe in soil was highly related with soil clay content (r=0.501**), soil pH (r= -0.686**), organic matter (r=0.527**), total N (r=0.480**), K (r=0.520), Ca (r=0.435**), Mg (r=0.243) and S content (r=0.540**). Accordingly, the soil Mn level showed significant relationship with clay content, organic matter (r=0.299*), total N (r=0.420**), P (r=0.290*), K (r=0.430**), Ca (r=0.309**) and S content (r=0.397**). Incase of interrelationship among soil micronutrients, soil Cu content showed non-significant positive interaction with soil Zn content (r=0.178) and negative interaction with soil B content (r= -0.198). Soil Fe content influenced signicantly by Zn (r=0.293*), Cu (r=0.563**) and Mn content (r=0.359**).

**Characteristics of sub-suface soil (15-30 cm soil depth)**

Like surface soils, availability of Zn, Cu, Fe and Mn in sub-surface soils was markedly influenced by many other soil variables (Table 4). Other than soil B, all the micronutrient contents were negatively correlated with soil pH indicating that micronutrient availability decreases as soil pH increases and vice-versa. This point is very important for soil fertility concern. Cu, Fe and Mn content were significantly correlated with clay content (r=0.713*, r=0.344** and r=0.388**, respectively). Significant positive relationship of soil organic matter with soil Cu (r=0.654**) and Fe (r=0.593**) was observed. The Cu and Fe content in soil was positively correlated with soil N content, r values being 0.557** and 0.368**, respectively, while B content was negatively related (r= -0.255*) with N content. Soil P content was associated only with Zn content (r=0.719*). K content significantly correlated with soil Zn (r=0.291*), Cu (r=0.601**), Fe (r=0.300*) and Mn (r=0.345**) content. The contents of other basic cations viz. Ca and Mg were found positively associated with Cu and Mn contents in soil. Soil S content was also positively affected micronutrient availability in soil. There was significant positive interaction of Zn-Fe (r=0.415**), Cu-Fe (r=0.573**), Cu-Mn (r=0.479**) and Fe-Mn (r=0.456**) in soil. The other interactions were not significant.

## Discussion

Comparing both present and previous statuses of Zn, it is observed that lower statuses have improved to some extent over time. According to BARC (2012), low to medium and very low to low status of Zn and B, respectively, prevailed in soils of AEZ 22. An indication of depleting trend was observed in soil zinc and boron status of the study area after almost a decade of time. For such negative changes, high cropping intensity along with cultivation of modern varieties of crop might be contributed a lot. Depleting trend of soil Zn and B in some areas of Bangladesh was reported by some researchers (Siddique et al., 2014). The most B deficient areas are Dinajpur, Rangpur, Bogra, Sirajganj, Cumilla and Sylhet (SRDI, 2010b). Considering available Cu, Mn and Fe, very high status of each was prevailed as it was in previous status. There was an observation of higher micronutrient content in surface soils than the sub-surface soil in the present study. The reason could be attributed to addition of fertilizers and manures to surface soil during farming practices. In addition to that, other probable reasons for higher micronutrient content in surface soil could be due to the accumulation of biomass in the surface layer leading to higher organic matter and increased clay content in the surface soils. Similar observation was found by different authors (Vijayakumar et al., 2011; Singh and Shukla, 1985; Bassirani et al., 2011). Typical profile distribution of soil micronutrient is likely a result of higher decomposition of organic matter and crop residues that contribute to nutrient especially micronutrient accumulation to the top layers of soil. Again, root distributions and rooting depth have some impact on micronutrient profiles as nutrients taken up by deep roots are transported into the top soil layers and redeposited there through different mechanisms like stem flow (Garcia et al., 2014; Jiang et al., 2009; Franzluebbers et al., 1996).

Studied micronutrients except B had significant positive relation with clay content in surface soil while in sub-surface soil, only Cu, Fe and Mn had significant positive relation. This might be due to the availability of binding sites for different cations on the clay particles. Increased total content of Zn, Cu, Fe and Mn was observed with an increase in soil clay content Sharma et al. (2004). Significant positive relation between soil Zn and clay content was also reported by some other scientists (Sarker et al., 2018; Mustapha and Fagam, 2007). Soil available B was negatively correlated with clay content where the relation was non-significant. A good number of researchers found negative significant correlation between soil B and clay content. Worku et al. (2016) also found negative significant correlation between soil B and clay content (r = -0.46**) which has conformity with Sharma et al. (2003) and Kumar and Babel (2010). Worku et al. (2016) also found negatively association (r= -0.16) between Cu and pH values. Other than B, the micronutrients under study negatively correlated with soil pH in both surface and sub-surface soils which has conformity with some other researchers (Mustapha and Fagam, 2007; Mahashabde and Patel, 2012; Njukeng et al., 2013; Yadav, 2011). Available Cu, Fe and Mn had strong association with soil organic matter content in surface soil.

In sub-surface soil only Cu and Fe had highly significant positive association with organic matter while positive but non-significant relation existed between Mn and organic matter content. The result of this study is in agreement with those reported by different authors (Goldberg et al., 2002; Wesley, 2004; Jacob and Joseph, 2008; Elbordiny et al., 2008; Vijayakumar et al., 2011; Mahashabde and Patel, 2012; Nath, 2013; Worku et al., 2016).

## Conclusion

The depleting tendency of zinc (Zn) and boron (B) as revealed from the study is an awareness message for the agricultural research personnel as well as policy makers. The key findings of this study related to interactions and interrelationships among different soil parameters and nutrient elements will be helpful in planning soil management practices that will ensure the efficient use of soil resources in a sustainable manner.

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# The relation between yield indices of maize plant and soil physicochemical characteristics

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## Abstract

The aim of this study was to set regression models based on correlation between yield parameters of maize plant (height, thousand seed weight and yield) and physical and chemical characteristics of soils and to determine applicability of obtained models in estimation of plant yield grown in soils of Çarşamba Plain. Regression coefficient (R), root mean square error (RMSE), index of agreement ($d$), model efficiency (ME) were evaluated to determine the validity of regression models between the yield components and physical and chemical characteristics of 40 soil samples taken from root zone of cultivated farms. Model associated with the relation between (i) plant height and bulk density (BD), field capacity (FC), clay and sand content wasn't statistical significant ($R$= 0.53, $p$>0.05); (ii) thousand seed weight and soil electrical conductivity (EC), organic matter (OM), lime ($CaCO_3$), nitrogen (N), phosphorus (P), potassium (K), Ca + Mg was characterized with a moderate $R$ ($R$=0.79, $p$ < 0.05), and (iii) seed yield and OM, N, P, K, copper (Cu), cation exchange capacity (CEC), $CaCO_3$ indices has the highest R ($R$ = 0.87; $p$ <0.01). In general, statistical parameters were within the validity limits. The established regression models can be applied for the predicting of yield parameters of maize plant grown in the farmed areas of the region.

**Keywords**: Soil physicochemical properties, plant height, regression models, seed yield.



## Introduction

In order to meet the nutritional needs of the growing world population with the existing agricultural lands, the need to obtain higher yields from the unit agricultural land has emerged, increasing and estimating the productivity is one of the current and research priority issues. It depends on the physical, chemical and biological properties of the soil along with management, environmental and genetic factors for high yield. For this reason, the researchers (Carena et al., 1987; Ekberli and Dengiz, 2016; Kars and Ekberli, 2019a) tried to establish the relationship between soil characteristics and yield parameters of various plants, since it was emphasized as a necessary step to access methods for protection, estimation and increase of productivity. In many studies, plant height, thousand seed weight and seed yield, are reported to vary significantly and depending on factors such as soil properties, plant genotype and sowing frequency, and environmental conditions (Whitman et al., 1985; Dotlacil and Toma, 1991; Peterson et al., 1992; Maiti and Wesche-Ebeling, 1998).

In the Çarşamba Plain, which has the most important agricultural potential in the Black Sea region of Turkey, the most recent cultivation area of the maize plant is 4038 ha, the production is 27021 tons and the yield is 706 kg da$^{-1}$ (Anonymous, 2019). Maize has a higher benefit from sunlight than other cultivated plants (cotton, wheat, rice). This leads to the formation of more dry matter and better utilization of the nutrients present in the maize plant soil, resulting in higher yields per unit area (Çolakoğlu, 1985). It has been

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reported, that thousand seed weight of maize plant is positively correlated to its yield and thousand seed weight decreases when yield decreases (Angelov, 1994).

Regression models have wide applications in the fields of ecology, hydrology and agriculture as well as in soil and plant sciences, where parallel to the accumulation of sufficient level of soil and plant data, such models have been used appropriately. Making and using regression models in soil and plant ecosystem are expressed more easily and practical than theoretical model wth partial differential equations (Bayraklı et al., 1999; Overman and Scholtz, 2002; Gülser, 2004; Huang et al., 2014; Dorsey and Hardy, 2018; Thiéry et al., 2018; Kars and Ekberli, 2019b). Using both experimental (regression) and theoretical models may accept several assumptions and similar contribution of the used parameters (Bouma and van Lanen, 1987; Pachepsky and Rawls, 2004). With the help of regression models, quantitative relationships between yield parameters (biomass or height, thousand seed weight, seed yield) of various plants and easily determined physical and chemical properties of soil associated with soil quality and management can be explained (Vereecken et al., 2010; Gülser et al., 2016; Dengiz and Ekberli, 2017). The use of different statistical parameters to determine the validity of regression models is one of the important and necessary stages in model creation. Applicability of regression models mostly determined by the statistical parameters such as the root mean square error (RMSE), index of agreement ($d$), maximum relative error (MRE), mean of absolute error (MAE), coefficient of determination (R) (Alexandrov and Hoogenboom, 2000; Budka et al., 2015).

This resarch was carried out to determine the correlation between some physical and chemical properties of cultivated soils with traditional tillage method and yield parameters of maize plant in Çarşamba Plain, Samsun, and to establish regression models among these properties, and to determine the applicability of the obtained models in the estimation of plant yield.

## Material and Methods

The research was carried out in the territory of 20 villages representing the Çarşamba Plain of Samsun province in 2013-2014. In each year 20 soil samples were taken from 0-20 cm depth of the cultivated farm fields. The method shown in Anonymous (2018) was used to collect plant samples from the same areas. The locations where soil and plant samples taken were shown in Figure 1.

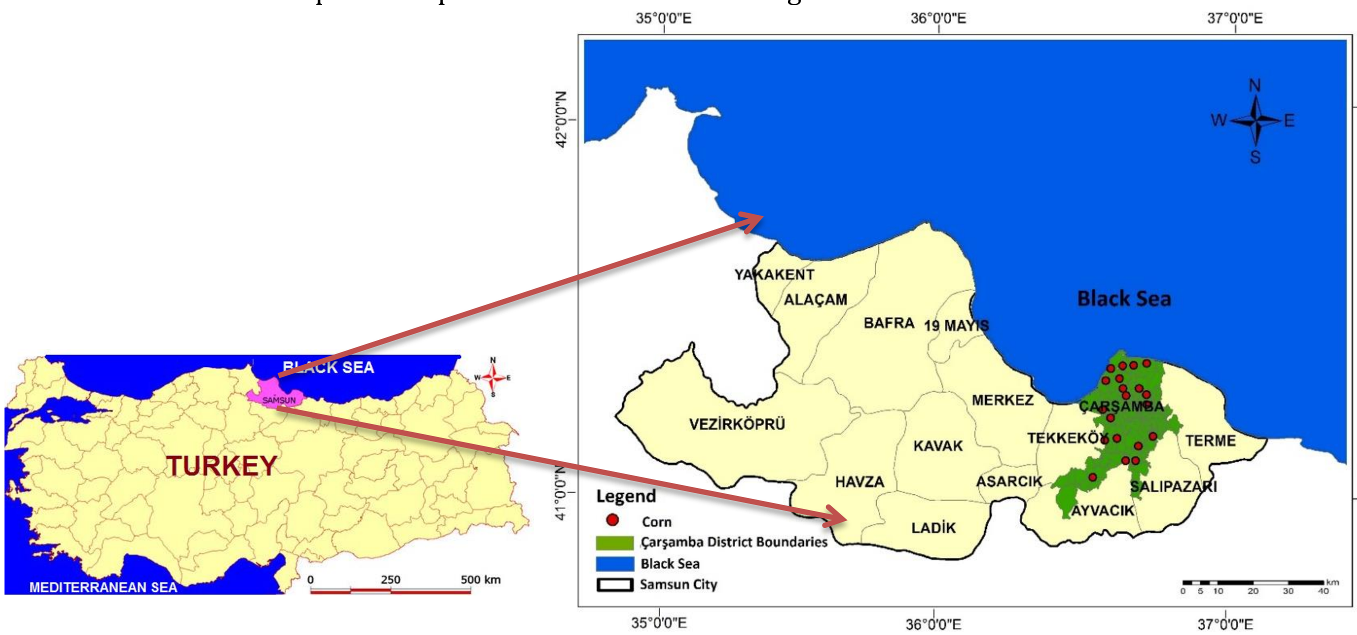


Figure 1. Locations where soil and plant samples were taken

Soil samples were air dried and sieved from a screen with 2 mm opening size to prepare for analysis. Sand, silt, clay contents of the soil samples were determined by hydrometer method (Bouyoucos, 1962). Bulk density (BD) values were determined by soil core method (Demiralay, 1993). Soil pH values were measured in soil suspension (1:1 w:v) by glass electrode pH meter, and EC values were determined in the same soil suspension (1:1 w:v) by EC meter (Rowell, 1994). Soil organic matter (OM) contents were determined by modified Walkley-Black method, (Walkley and Black, 1934). Determination of soil chemical properties was conducted by the following approach: lime ($CaCO_3$) contents by Scheibler calcimeter according to Nelson (1982), and total nitrogen (N) contents by Kjeldahl method (Kacar, 1994), exchangeable cations (Ca, Mg, K, Na) by ammonium acetate extraction (Kacar, 1994), available phosphorus by Olsen's method (Olsen et al., 1954), DTPA extractable heavy metals (Fe, Mn, Zn, Cu) according to Lindsay and Norvel (1978), cation exchange capacity (CEC) by Bower method (US Salinity Laboratory Staff, 1954). Moisture contents in field capacity (FC) and permanent wilting point (PWP) were measured at a pressure plate apparatus under 1/3 and 15 atm pressure after soils reached a hydraulic balance state, available water content (AWC) was determined by calculating the difference between FC and PWP (Black, 1965). Plant height (PH), thousand seed weight (TSW) and seed yield (SY) measurements in maize plant were determined within the principles reported by Anonymous (2018).

### Statistical analysis

Descriptive statistics of soil and plant analysis results and correlations between soil properties and plant yield parameters were calculated in SPSS 17.0 package program, and regression models formed between yield parameters and soil properties were created in Minitab 17.0 package program. The indices of the statistical analysis, the root mean square error (RMSE), the index of agreement (d), the model efficiency (ME) were calculated using the following expressions, respectively:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left(x_i - y_i\right)^2} \quad (1)$$

where, $n$ - is the number of data, if $n$<30 $m = n$-1, if $n > 30$ $m = n$; $x_i$ - measured values; $y_i$ - estimaded values.

$$d = 1 - \frac{\sum_{i=1}^{n} \left(x_i - y_i\right)^2}{\sum_{i=1}^{n} \left(\left|x_i - \bar{y}\right| + \left|y_i - \bar{y}\right|\right)^2} \quad (2)$$

where, $\bar{y}$ is the mean measured values.

$$ME = 1 - \frac{\sum_{i=1}^{n} \left(x_i - y_i\right)^2}{\sum_{i=1}^{n} \left(y_i - \bar{y}\right)^2} \quad (3)$$

The root mean squares erorr is the standard deviation of the estimation errors. The index of agreement ($d$) is an indicator of the validity of the model and the $d$ is close to 1 indicates the applicability of the model. In a study of the experimental hydrological model by Krause et al. (2005), ME values were shown to vary between 1 and ∞, and if the ME was smaller than zero, the measured mean value was more effective than the calculated value. Comparison of analytical expressions of $d$ and ME showed greater $d$ value than ME (Willmott and Matsuura, 2005; Willmott et al., 2012; Kumar et al., 2015; Wang et al., 2016).

## Results and Discussion

### Distribution of maize plant yield parameters

Results of the descriptive statistics of some yield parameters of maize plant grown in the research area were given in Table 1.

Table 1. Some descriptive statistics of some yield parameters of maize plant (n=40)

| Parameters | Minimum | Maximum | Mean | SD | *CV*, % | Skewness |
|---|---|---|---|---|---|---|
| PH, cm | 172.33 | 351.22 | 294.16 | 32.85 | 11.16 | -1.639 |
| TSW, g | 167.54 | 450.75 | 345.19 | 63.59 | 18.42 | -0.274 |
| SY, kg da$^{-1}$ | 833.58 | 1584.37 | 1293.53 | 173.05 | 13.37 | -0.621 |

PH: Plant height; TSW: Thousand seed weight; SY: Seed yield; SD: Standard deviation; *CV*: variation coefficient

The values of the yield indices of maize plant, namely PH, TSW and SY varied between 172.33-351.22 cm, 167.54-450.75 g and 833.58-1584.37 kg da$^{-1}$ respectively, and their average values were 294.16 cm, 345.19 g and 1293.37 kg da$^{-1}$, acordingly (Table 1). Statistical indicators vary within valid limits. Being the skewness values close to zero from the right and left, indicates that the distribution is close to normal. The SY had more than 2-5 times a higher standard deviation than that of PH or TSW, which could be associated with the wide range of seed yield and soil properties.

**Relationship between some yield parameters and some physical and chemical properties of soil**

Correlation coefficients (r) of maize plant yield parameters and some physical and chemical parameters of soil were given in Table 2. A significant positive correlation (0.54, *p<0.01*) was found between thousand seed weight and seed yield. There was a significant correlation between SY value of maize plant and OM, Cu and N contents of soils, as well as between SY value and EC, P, K, Na and Zn contents (r > 0.3-0.4) of the soil. There was no statistically significant correlations between the agronomic characteristics of the maize plant and the other physical and chemical parameters of the soil. Angelov (1994) also reported the significant and high correlation between seed yield and ripening time, plant height, number of leaves in the plant, first cob height. Karabulut and Ünver (2012) found a positive correlation between the parameters of clay and K, OM, N, CEC (*p<0.05*), and negative correlation between sand and these properties in a study conducted in the farmer's field where maize was cultivated, reveling that plant yield is highly linked as soil properties as well as management.

Table 2. Correlation matrix for some yield parameters of maize plant and chemical and physical properties of soil

| Parameters | PH, cm | TSW, g | SY, kg $da^{-1}$ |
|---|---|---|---|
| PH, cm | 1 | | |
| TSW, g | -0.137 | 1 | |
| SY, kg $da^{-1}$ | -0.053 | 0.542** | 1 |
| Clay, % | -0.235 | 0.085 | 0.006 |
| Silt, % | 0.123 | -0.225 | -0.197 |
| Sand, % | 0.147 | 0.055 | 0.112 |
| BD, g $cm^{-3}$ | 0.207 | 0.032 | -0.116 |
| FC, % | -0.332 | 0.344 | 0.212 |
| PWP, % | -0.322 | 0.361 | 0.287 |
| AWC, % | -0.276 | 0.247 | 0.051 |
| pH, (1:1) | 0.020 | 0.255 | 0.117 |
| EC, dS $m^{-1}$ (1:1) | -0.112 | 0.431* | 0.384* |
| $CaCO_3$,% | 0.068 | -0.029 | 0.236 |
| OM, % | -0.135 | 0.378* | 0.518** |
| N, % | -0.236 | 0.637** | 0.655** |
| P, ppm | -0.051 | 0.024 | 0.377* |
| K, cmol $kg^{-1}$ | -0.198 | 0.233 | 0.421* |
| Ca+Mg, cmol $kg^{-1}$ | -0.148 | 0.284 | 0.192 |
| Na, cmol $kg^{-1}$ | 0.095 | -0.006 | 0.403* |
| CEC, cmol $kg^{-1}$ | -0.146 | 0.285 | 0.221 |
| Fe, ppm | -0.125 | -0.152 | -0.104 |
| Mn, ppm | -0.010 | -0.231 | -0.168 |
| Cu, ppm | -0.194 | 0.403* | 0.556** |
| Zn, ppm | -0.074 | 0.220 | 0.409* |

** P<0.05, * P<0.01

**Regression models between yield parameters and some physical characteristics properties of soils**

Regression models between maize PH, TSW and SY and some physical characteristics of soils were given in Table 3. Results of the correlation analysis (Table 2) between yield parameters and soil physical characteristics were taken into consideration in the creation of regression models (Table 3).

Table 3. Regression models between maize plant height, thousand seed weight, seed yield and some physical characteristics of soils

| | Models | R | F | p |
|---|---|---|---|---|
| 1. | PH = 436-4.83 Clay - 80 BD + 3.70 (BD×Clay) - 0.26 PWP - 0.87 FC | 0.451 | 1.12 | 0.378 |
| 2. | PH = 1002-8.53 Sand - 507 BD – 13.4 Clay + 6.15 (BD×Sand) + 10.3 (BD×Clay) + 2.17 (BD×PWP) – 0.070 $(PWP)^2$ - 1.71 FC | 0.504 | 0.81 | 0.603 |
| 3. | PH = 1034+4.4 Clay - 284 BD - 114 $\sqrt{Clay}$ - 20.5 $\sqrt{Sand}$ + 7.17 (BD×Clay) - 2.40 FC + 1.12 PWP+30 $(BD)^2$ + 0.32 (BD×Sand) - 0.062 $(Clay)^2$ | 0.533 | 0.67 | 0.734 |
| 4. | TSW = - 65+266 BD + 9.27 Clay + 1.39 AWC + 2.86 PWP - 7.35 (BD×Clay) | 0.425 | 0.97 | 0.455 |
| 5. | TSW = 842-75 BD + 0.0435 $(Clay)^2$ + 1.02 (BD×Clay) – 24.8 $\sqrt{Sand}$ - 3.40 FC - 69.0 $\sqrt{Clay}$ +6.10 (BD×PWP) | 0.510 | 1.10 | 0.402 |
| 6. | TSW = - 178+1700 BD-45 $\sqrt{Clay}$ -70.2 $\sqrt{Sand}$ -740 $(BD)^2$ +1.49 (BD×Clay)-3.98 FC+ 5.84 (BD×PWP)+0.0075 $(Clay)^2$ + 3.20 (BD×Sand) | 0.600 | 0.88 | 0.559 |
| 7. | SY = 1675 - 393 BD+2.51 Sand + 23.1 PWP - 9.5 FC | 0.435 | 1.35 | 0.281 |
| 8. | SY = 1766 - 449 BD+18.5 Sand - 11.8 (Db× Sand) + 26.1 (BD×PWP) - 15.4 FC | 0.529 | 1.71 | 0.174 |
| 9. | SY = - 43 + 4315 BD – 2.06 Silt - 10.1 FC - 155 PWP + 136 (BD×PWP) - 2480 $(BD)^2$ | 0.682 | 3.04 | 0.027 |

PH: Plant height; TSW: Thousand seed weight; SY: Seed yield.

Coefficients of determination was varied between 0.45 and 0.53 in the regression models expressed by various polynomial functions between maize plant height and soil clay, sand, BD, FC, PWP characteristics (Table 3). The F value, used to determine whether interaction and major factors are significant, increased as the p value decreased. The regression coefficient was the highest (R = 0.53) in the model number three, which was formed by clay, BD, sand, FC, PWP parameters and the lowest (R = 0.45) in the model number one containing clay, BD, PWP and FC parameters (Table 3). However there was no statistically significant difference according to p values. For the models formed between the TSW and some physical properties of soils, the regression coefficients varied from 0.42 to 0.60, and F values from 0.88 to 1.10, and p values from 0.402 to 0.559. Regression coefficient (R = 0.60) was found to be moderate in model number 6, although there was no statistically significant difference between maize TSW and physical properties of soils (Table 3). Research shows that the expression of regression models with polynomials covering the square, square root and product of soil properties increases the regression coefficient and also the significance of the estimation (Kosheleva et al., 2002; Gülser and Candemir, 2014). In the models created between the physical properties properties of soils such as BD, sand, silt, PWP, FC and SY, the regression coefficients were between 0.43 and 0.68, F values were between 1.35 and 3.11, and p values were between 0.027 and 0.281 (Table 3). The highest statistically significant regression coefficient (R = 0.68, $p <0.05$) were found in model 9 which included silt, bulk density, PWP and FC parameters. In the regression equations created by Malone et al. (2007) to estimate seed yield in maize and soybean plants, the coefficients of determination were reported to be 0.85-0.87.

**Regression models between yield parameters and some chemical characteristics of soils**

Table 4. Regression models between maize plant height, thousand seed weight, seed yield and some chemical characteristics of soils

| | Models | R | F | p |
|---|---|---|---|---|
| 1. | $PH=393+2.10\ (OM)^2+135(EC)^2-111\sqrt{EC}-278N-0.202\ P-46.0\ K+2.77\ (N\times P\times K)-0.00270\ (CEC)^2$ | 0.358 | 0.35 | 0.935 |
| 2. | $PH = 322-3.54\ (CaCO_3)^2+4.06\ (OM)^2+5.7\ (EC)^2-0.00247\ (CEC)^2-429\ N-10.1\ K-4.95\ Cu+28.9\ CaCO_3$ | 0.372 | 0.38 | 0.916 |
| 3. | $PH = -3-2.27\ (CaCO_3)^2+17.0\ (OM)^2+32\ (EC)^2-3296\ N+19.3\ CaCO_3-0.214\ Ca+Mg-70.1\ OM+2256\sqrt{N}$ | 0.433 | 0.46 | 0.881 |
| 4. | $TSW = 66+21.3\ pH+188\ EC-10.6\ CaCO_3+26.3\ OM$ | 0.578 | 2.88 | 0.045 |
| 5. | $TSW = 148+3.6\ pH+131\ EC-7.19\ CaCO_3-5.3\ OM+995\ N$ | 0.680 | 3.79 | 0.013 |
| 6. | $TSW = -760+56\ EC+16.4\ CaCO_3+60\ OM-7397\ N+0.4548\ (Ca+Mg)-204\sqrt{OM}-106\sqrt{CaCO_3}-0.0298\ (N\times P\times K)^2+6442\sqrt{N}$ | 0.785 | 3.22 | 0.017 |
| 7. | $SY = 820+142\ EC+13.8\ OM+2929\ N+2.63\ P-112\ K$ | 0.697 | 4.15 | 0.008 |
| 8. | $SY = 670+78\ EC-128\ OM+4058\ N+3.56\ P-237\ K+4.01(Ca+Mg)+13.9\ Cu+67.7\ Zn+88.9\ Na$ | 0.807 | 3.73 | 0.008 |
| 9. | $SY = -3355-831\ EC+141\ OM-32480\ N+4.46\ P-42\ K-28.4\ Cu+100\ Na+713\ (EC)^2+0.0229\ (CEC)^2+26682\sqrt{N}-557\sqrt{OM}-3.96\ (CaCO_3)^2$ | 0.866 | 3.75 | 0.009 |

PH: Plant height; TSW: Thousand seed weight; SY: Seed yield.

The regression models were formed by taking into consideration the results of the correlation analysis (Table 2) between the TSW and soil properties. As seen from regression models numbered (1)-(3) between maize PH and soil chemical parameters such as EC, OM, CEC, $CaCO_3$, N, P, K, Cu, Ca+Mg, regression coefficients were low and not significant (p > 0.1), and ranged between 0.36 and 0.43 (Table 4). In model 6 including EC, $CaCO_3$, OM, N, P, K, Ca+Mg parameters and square, product and square root of some parameters, improved the model anf regression coefficient was found to be the highest among the models 1-6, and significant (R = 0.79, $p <0.05$). Models (7)-(9) formed between maize SY and some chemical properties of soils, the regression coefficients of the models were higher and varied between 0.70 and 0.87, with p values were between 0.008 and 0.009, i.e. showed high statistical significance (p <0.01) (Table 4). The highest regression coefficient (R=0.87) was obtained in the (9) model including EC, OM, CEC, $CaCO_3$, N, P, K, Cu, Na parameters. Analogously, Jin et al. (2017) established regression models for wheat SY estimation, and reported the high and significant R ($R^2$= 0.42, $p< 0.01$).

**The validity of regression models formed between the yield parameters and some soil properties**

In order to determine the validity of the used regression models (obtained from the experimental data) it should applied for the data other than the values used in the creation of the models or from the values in the data bank (Wang et al., 2016). Statistical parameters of the validity of the regression models between the maize of PH, TSW, SY and physical and chemical characteristics of the soils were given in Table 5.

Table 5. Some statistical parameters of regression models of maize plant height, thousand seed weight and seed yield

| Models (No) | R | RMSE | *d* | ME |
|---|---|---|---|---|
| PH (3) (P) | 0.533 | 14.580 | 0.984 | 0.160 |
| PH (3) (C) | 0.433 | 49.601 | 0.972 | -0.515 |
| TSW (3) (P) | 0.600 | 32.243 | 0.983 | -0.293 |
| TSW (3) (C) | 0.785 | 49.355 | 0.993 | 0.162 |
| SY (3) (P) | 0.682 | 38.171 | 0.997 | 0.869 |
| SY (3) (C) | 0.866 | 48.402 | 0.998 | 0.884 |

PH: Plant height; TSW: thousand seed weight; SY: Seed yield; R: Regression coefficient; RMSE: Root mean square error; *d*: index of agreement; ME: Model efficiency; P: physical properties of soils; C: chemical characteristics of soils

As shown in Table 5, descriptive statistics of regression models were generally within the validity limits. Karadavut et al. (2010), using three different models in a study that predicted dry matter accumulation in maize varieties, determined ME values betweeen 83 and. In a study conducted by Usowicz et al. (2013), RMSE value of the model used in the estimation of soil thermal conductivity was determined as 0.104.

The comparison of calculated and measured PH, TSW, SY values according to third models was given in Figure 2. The r values of linear relations calculated and measured according to the regression models between PH, TSW, SY and physical properties of the soils were 0.53, 0.55 and 0.78, respectively, and were statistically significant at 0.01 level, showing that current approach could be used for such prediction.

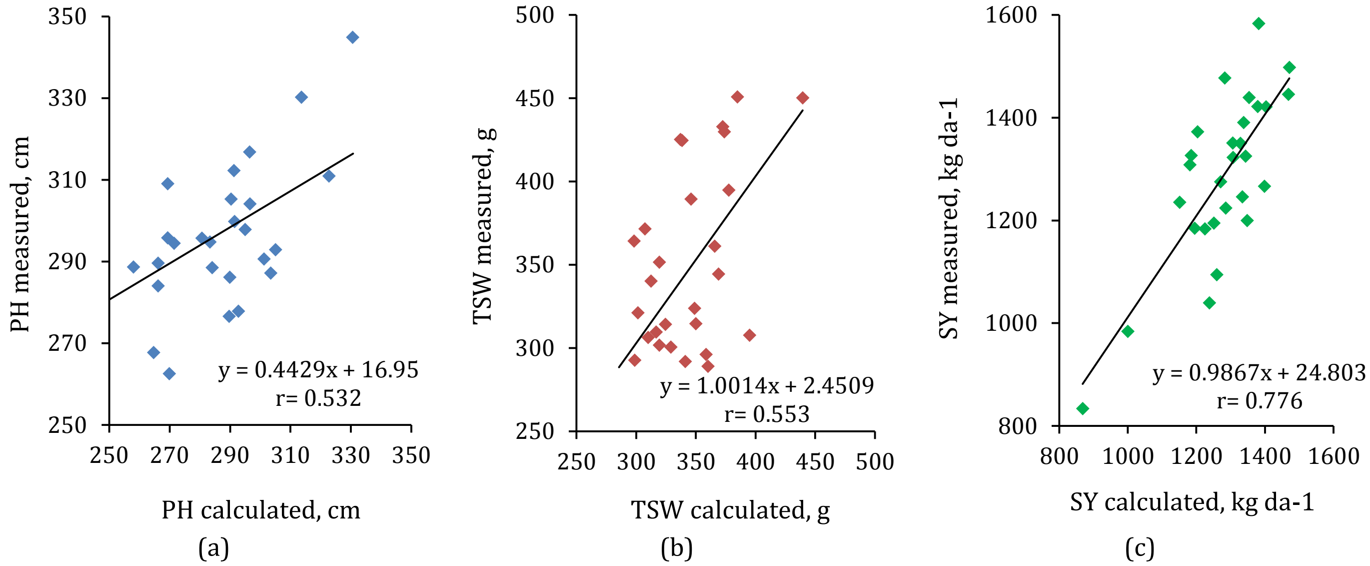


Figure 2. The relationship between calculated and measured plant height (A), thousand seed weight (B), seed yield (C) and physical properties of the soil according to regression models

## Conclusion

It is important to determine the experimental relations between soil properties and yield parameters of agricultural land where different agricultural plants are grown, in evaluation and estimation of yield potential. Experimental relationships can evaluate quantitatively the interaction between yield and soil properties at the various scale (from field to watershed). Regression models have been established between some physical and chemical properties of agricultural soils, cultivated using traditional soil tillage methods and yield parameters of the maize, the main crop grown in Çarşamba Plain. In the formation of regression models, soil and plant parameters with significant and high correlation were taken as basis. The performance of the models including plant yield components (PH, TSW and SY) and square, product and square root of the soil parameters were found to be higher. The comparison of the measured and calculated yield values using regression models showed that the models obtained by evaluating statistical parameters were applicable to the estimation of yield parameters in maize grown soils of the region. Factors such as failure of regular agricultural operations (fertilization, irrigation, etc.) by the farmers in the study area, changes in climatic conditions, adversely affect the physical and chemical properties and cause soil properties to change over short distances or time intervals, and therefore affects the performance of the regression models between yield parameters and physical and chemical soil properties. For building and applying regression models, it is necessary to create a data bank of soil properties and yield components of different regression models for various plants at local and regional level. In addition, it is necessary to benefit from the data which is not used in the creation of the models to determine the validity of the regression models.

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# Electro-chemical charge characteristics of surface-subsurface region of selected soils in the tropics

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## Abstract

A study was conducted to investigate the relation between soil chemical, mineralogical properties and surface charge characteristics of selected tropical soils in West Bengal, India. The objectives of this study were to analyse the electro-chemical charge characteristics of surface-subsurface soils in accordance with point of zero charge (PZC) and pH-dependent charge. Subsoil's generally have higher PZC than corresponding surface horizons and pH-dependent surface charges are maximum in upper layer than that of other. Relatively lower value of PZC (or $pH_0$) along the depth, mostly affected by organic matter, clay content free Fe and Al oxides. Result shows that PZC (or $pH_0$) values decrease with increasing organic matter content and increase with increase in sesquioxides content. The PZC of the charge-pH curves in Diamond Harbour soil (DH) (0-45cm) was on the acid side of the zero point titration indicate that the samples possess permanent negative charge and in Raigunj soil (RG) (30-45cm) was on basic side possess slight permanent positive charge. Amount of surface charge reduces along the depth (subsurface region) than corresponding surface region except in RG (30-45cm) due to considerable increase in positive charges by presence of various electrolyte or synthetic hematite as $\alpha$-$Fe_2O_3$. PZC has the strong negative correlation with pH-dependent charge (r= -0.85707*) that supports the superiority of the present study. Regression value also supports the strong dependency of electrochemical surface charge on PZC and organic matter content of corresponding soil layers ($R^2$= 0.971474).

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## Introduction

Surface charge properties have an important bearing on the migration of ions in soil, the formation of organo-mineral complexes, soil structure, plant nutrition, and the dispersion, flocculation, swelling, and shrinkage of the soil fractions (Zhang and Zhao, 1997). The surface charge of variable charge constituents depends on the pH and ionic strength of soil solution (van Raij and Peech, 1972; Naidu et al., 1994). Variable surface charge is attributed to the ionisation of functional groups on organic matter, hydrous Fe and Al oxides, and edge sites on kaolin by protonation and deprotonation processes (Phillips and Sheehan, 2005). Surface charge can be positive, negative, or zero depending on conditions of the soil solution. Surface sites of these soil constituents generally have net positive charge under acidic conditions (Qafoku et al. 2004). Moreover, adsorbed organic anions (Xu et al., 2003), phosphate (Naidu et al., 1990), and sulfate on surfaces contribute to negative surface charge (Bolan and Barrow 1984; Fahrenhorst et al., 1999).

Parks and de Bruyn (1962) distinguished two types of electrical double layer on the basis of the mechanism by which free charges are distributed across a solid solution interface; (i) a reversible double layer which exists on surface bearing constant potential, and (ii) a completely polarisable double layer which exists on surfaces bearing constant charge. The constant potential model applies to soil minerals such as Fe and Al oxides, hydroxides while constant charge model applies to layer silicate mineral such as smectite and vermiculite which bear permanent negative surface charges due to isomorphous substitution (van Raij and

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Peech, 1972; Keng and Uehara, 1973). The most suitable phenomenon for predicting the charge dependent fingerprint of oxide minerals is the point of zero charge (PZC). The PZC of an oxide mineral is the pH at which the net surface charge from all sources is zero (Parks, 1967).

Point of zero charge often denoted as $pH_0$ is one of the most important parameters used to describe variable charge surfaces (Barale et al., 2008). The balance of surface charge in a soil is developed from the perspective of coordination chemistry and is employed to derive the conditions under which the zero point of charge is equal either to the crossover point of two proton titration curves or to the point of zero net charge (Sposito, 1981). Uehara and Gillman (1981) indicated that $pH_0$ is the pH where the amounts of negative and positive charge of variable charge components where these are equal. Point of zero charge varies with soil according to the variation of organic matter and sesquioxide/allophane content. Charge characteristics of soil are a function of organic carbon content and mineralogical composition of soil (Khan and Kar, 2018).

The previous studies showed that the $pH_0$ values decrease with increasing organic matter content and increase with increase in sesquioxides (Hou et al., 2007; Anda et al., 2008; Sharami et al., 2010). Interaction among amorphous materials and crystalline minerals in the clay fraction may result in certain modification of the surface and subsurface charge characteristics of the soil system. The constant potential colloids such as Fe and Al oxides play a crucial role in influencing the physical and chemical properties of highly weathered soils in tropics. This paper reports the electrochemical charge characteristics of surface-subsurface region of selected soils in the tropics.

## Material and Methods

### Sampling sites

Six soil samples were collected from Diamond Harbour of South 24 parganas and Raigunj of Uttar Dinajpur district of West Bengal, India. The soils are mostly tropical climate with an annual rainfall of approximately 1250mm and mean temperature of approximately 24.8 $^0$C (Metrological Department, 2018). The sampling sites and classification of the soils in this study are given in Table1. The soil samples are air dried, crushed, and then passed through 2mm sieve for laboratory analysis.

Table 1. Sampling site, Soil order, Vegetation Type, Parent material, Genetic horizon, Texture and Textural class

| Sl.No. | Location | Soil order | Soil Classification | Vegetation type | Parent material | Genetic horizon | Textural Class |
|---|---|---|---|---|---|---|---|
| 1. | Diamond Harbour Soil (DH), West Bengal, India. 22.19° N, 88.20° E | Fluvaquent | Fine-loamy, Aeric Epiaquepts | Rice-rice-rice | Deltaic Alluvium | Ap-Bw-BC | Silty clay loam |
| 2. | Raigunj Soil (RG), West Bengal, India 26.32$^0$N, 89.45$^0$E | Haplaquept | Fine-loamy, Typic Dystrustepts | Tropical decudious forest | Indo-Gangetic Alluvium | A-Bw-BC | Clay loamy |

### Physico-chemical analysis

Soil pH as measured in a 1:1 soil : solution in $H_2O$ and 1M KCl (National Soil Survey Centre, 1996), Organic Carbon (OC) was measured by the Walkley-Black method (Nelson and Sommers, 1996) and used to calculate the amount on Organic matter (OM) (OM= OCx1.742). Cation exchange capacity was determined by $NH_4OAC$ at pH 7.0 and is defined by the some of the exchangeable cations that a soil can absorb (Chapman, 1965). Anion exchange capacity is determined by colorimetric methods (Clarke, 1950). Particle size distribution was analysed by the pipette method (Gee and Bauder, 1986). The ΔpH index was calculated from the difference between $pH_{KCl}$ and pHwater (Mekaru and Uehara, 1972). Calcium and Magnesium estimated by Sparks (1996). Exchangeable Al and Fe were estimated by Bertsch and Bloom, 1996 and Sparks, 1996 respectively. The Fe and Al contents associated with secondary minerals were determined in extracts obtained after boiling both 1g of soil for 30minutes in 20 ml 9(M) $H_2SO_4$. The acid extract were analysed for Al and Fe. Soil fused with alkali and total Fe and Al estimated by atomic absorption spectrometry (AAS) (Sparks, 1996). Mineralogy of synthesized precipitates (Clay) was determined by X-ray powder diffraction analysis.

### Surface charge analysis

### i.Potentiometric titrations

The procedure described by van Raij and Peech (1972) was used. A series of 4g soil samples was equilibrated with known amounts of acid (HCl) and base (KOH) in various concentration of KCl (1, 0.1, 0.01, 0.001N) for 3 days in a closed humidified glass container to prevent evaporation. The pH of supernatant solution was determined using a pH meter with micro glass electrode and a recorder after centrifugation.

The amount of $H^+$ and $OH^-$ ion adsorbed at a given pH value is equal to the amount of HCl and KOH added after correction for the amount of acid or base required to bring the electrolyte solution alone to the corresponding pH value. The surface charge or adsorption density, ($\sum H^+ - \sum OH^-$), is then plotted against the equilibrium pH of the system. The PZC of the soil is taken as the pH value where the charge-pH curves measured in different electrolyte concentrations intersect one another (Parks and de Bruyn, 1962).

**ii.Determination of electric charges**

The procedure involves saturating a series of 4g soil samples with 1N KCl solution, adjusting the pH to desired values with KOH and HCl. After equilibrium is attained, the suspensions were first washed 3 times with 0.2N KCl solution, then 8 times with KCl of desired concentrations (1, 0.1, 0.01, 0.001N) by centrifugation for fine adsorption of ions. The solutions were pre-adjusted to desired pH values. Finally, the $K^+$ and $Cl^-$ were then extracted 5 times with 0.5N $NH_4NO_3$. Correction was made for the entrapped $K^+$ and $Cl^-$ in the equilibrium solution. Potassium was determined on a flame photometer and chloride by potentiometric titration using Beckman chloride electrode.

**Statistical analysis**

Each experiment was treated as a completely randomized design. Because the experiments were performed individually on each soil, comparisons of surface charge of the soils as a function of pH were accomplished by the use of correlation coefficient, were used to determine statistical significance of any differences in the surface charge measurements.

## Results and Discussion

Important soil chemical and physical properties of the soil used in this study are given in Table 2. Where it can be seen that phase wise samples of Raigunj soils (RG) are more acidic (4.82) compare to Diamond Harbour soils (DH) (6.10). Diamond Harbour soils are poor in organic carbon (1.26%) than Raigunj soils (1.85%). Cation exchange capacity (CEC) of the Raigunj soil (46.4 $cmol_c kg^{-1}$) is more compare to native Diamond Harbour soil (28.3 $cmol_c kg^{-1}$) indicates the highest ion exchange property of that soil. All these experimental soils had ΔpH less than zero, which indicate they present negative net surface charge (Mekaru and Uehara, 1972). In both soils, production of negative charge along the depth was decreases due to presence of lower amount of organic matter and higher amount of sesquioxide/allophane content. Li and Xu (2008) reported that the layer silicate clays (2:1 clays) decreased the PZC or $pH_0$ values, while the 1:1 clay minerals as kaolinite increased the $pH_0$. Besides, Uehara and Gillman (1981) reported that the oxides of Fe and Al have high $pH_0$ values (pH 7–9), while silica ($SiO_2$) and organic matter have low $pH_0$ values. Therefore, the low levels of $pH_0$ in the present study were probably related to layer silicate clays (2:1 clays) and high pH in the entire surface-subsurface horizon. Clay as well as organic matter content in Raigunj soil was significantly higher than the Diamond Harbour soil and this is enhances the corresponding cation exchange capacity of soils and also indicated the dominance of layer silicate 2:1 mineral in the clay fraction of this soil.

Table 2. Chemical and physical characteristics of soils

| Soil characteristics | Diamond Harbour Soil (DH) | | | Raigunj Soil (RG) | | |
|---|---|---|---|---|---|---|
| | 0-15 cm | 15-30 cm | 30-45 cm | 0-15 cm | 15-30 cm | 30-45 cm |
| pH in water | 6.10 | 5.92 | 5.87 | 4.82 | 4.65 | 4.62 |
| pH in 1N KCl | 5.88 | 5.74 | 5.70 | 4.17 | 4.14 | 4.11 |
| *ΔpH | -0.22 | -0.18 | -0.17 | -0.65 | -0.51 | -0.51 |
| EC, $mSm^{-1}$ | 0.12 | 0.07 | 0.04 | 0.27 | 0.13 | 0.10 |
| OC, % | 1.26 | 0.97 | 0.72 | 1.85 | 1.21 | 0.98 |
| OM,% | 2.17 | 1.67 | 1.24 | 3.19 | 2.08 | 1.68 |
| CEC, $CmolcKg^{-1}$ | 28.30 | 28.0 | 27.5 | 46.40 | 45.20 | 44.60 |
| Exchangeable Fe, $g.kg^{-1}$ | 0.24 | 0.18 | 0.09 | 0.67 | 0.68 | 0.72 |
| Exchangeable Al $g.kg^{-1}$ | 0.13 | 0.15 | 0.11 | 0.56 | 0.62 | 0.66 |
| Total Fe, $g.kg^{-1}$ | 26.50 | 22.20 | 15.40 | 58.20 | 61.40 | 66.70 |
| Total Al, $g.kg^{-1}$ | 0.34 | 0.25 | 0.13 | 0.95 | 0.96 | 1.02 |
| $Al_2O_3$, $g.kg^{-1}$ | 11.50 | 10.20 | 7.80 | 24.20 | 22.60 | 22.30 |
| Si, $g.kg^{-1}$ | 0.24 | 0.28 | 0.20 | 1.05 | 1.16 | 1.24 |
| $SiO_2$, $g.kg^{-1}$ | 2.36 | 1.87 | 1.04 | 17.20 | 17.60 | 16.50 |
| $SiO_2$, $g.kg^{-1}$ | 5.02 | 3.98 | 2.21 | 36.60 | 37.40 | 35.10 |
| Clay, % | 28.00 | 24.00 | 18.00 | 37.00 | 28.00 | 27.00 |
| Minerals | Hydrated & Disordered Kaolinite | | | Hydrated Kaolinite/halloysite,vermiculite with chlorite | | |

**Surface charge-pH Curves**

The surface charge-pH curves for all soil samples measured in the four KCl concentrations (1, 0.1, 0.01 and 0.001N) intersect one another in accord with the constant potential model for soil colloids (Figure 1). The point of zero charge or $pH_0$ values ranged from pH 1.5 to 3.4 (Table 3). With increasing the percent of organic matter and clay content point of zero charge reduces. In present study a significant relationship observed between PZC and content of soil organic matter and clay (r=-0.97147* and -0.96692* respectively). The result can be ascribed the positive correlation between clay and organic matter contents with pH-dependent surface charge (r= 0.950988** and 0.871071** respectively). Regression value also supports the strong dependency of electrochemical surface charge on PZC and organic matter content of corresponding soil layers ($R^2$= 0.971474).

Table 3. PZC, pH-dependent charge and their relation with various chemical characters

| | Diamond Harbour Soil (DH) | | | Raigunj Soil (RG) | | |
|---|---|---|---|---|---|---|
| | 0-15 cm | 15-30 cm | 30-45 cm | 0-15 cm | 15-30 cm | 30-45 cm |
| PZC* | 2.60 | 3.10 | 3.40 | 1.60 | 2.50 | 2.70 |
| pH-dependent charge ($cmol_c kg^{-1}$) | 2.50 | 1.80 | 1.10 | 3.20 | 2.10 | 2.50 |
| Correlation Coefficients (r) values | | | | | | |
| Between PZC & pH-dependent charge | -0.857070 | | | | | |
| Between soil pH & PZC | 0.576696 | | | | | |
| Between PZC & Ex. Fe | -0.702170 | | | | | |
| Between Ex. Fe & pH-dependent charge | 0.666889 | | | | | |
| Between PZC & Ex. Al | -0.610720 | | | | | |
| Between Ex. Al & pH-dependent charge | 0.551042 | | | | | |
| Regression value (PZC & OM) ($R^2$) | 0.971474 | | | | | |

In all cases, the PZC or $pH_0$ occurred below the natural pH value of the soil indicating that the soil colloids bear net negative charges under natural conditions. This is also in agreement with negative delta pH values, ($\Delta pH= pH_{KCl}-pH_{water}$), of the soils (Table 2). The PZC of the charge-pH curves was on the acid side of the zero point titration has been attributed to the presence of permanent negative charge (van Raij and Peech, 1972). The relative low PZC values of the surface soils in both the Diamond Harbour (DH) and Raigunj soils (RG) may be attributed to the large amounts of silicate clay minerals and $SiO_2$ present in the soil in addition to the effect of the organic matter. The PZC of kaolinite and $SiO_2$ occurs at pH 3.5 (3.4) and 2 (1.6) respectively (Parks, 1967) that supports the present investigation (Table 3). Presence of small amounts of specifically adsorbed Si, Fe and Al oxides may also contribute to low PZC and higher pH-dependent surface charge of the soils used in this study.

In all cases, the PZC values were on the acid side of the zero point titration except in RG (30-45cm), may due to presence of specifically adsorbed sulphate ions that increases the positive charges on the soil colloid (Figure 1f). The magnitude of both positive and negative charges as measured by $K^+$ and $Cl^-$ retention as a function of pH and electrolyte concentration is in good agreement with the charge-pH curves of both the soils (Figures 1).

The source of permanent negative charges is apparently due to structural substitutions in 1:1 type layer silicate and Fe oxides since the subsurface soil samples do not contain any detectable amount of smectite type layer silicates (Gallez et al., 1975). Evidence has also been reported indicating the presence of permanent positive charges in soils due to structural substitution of $Ti^{4+}$ for $Fe^{3+}$ in Fe oxide (Sumner and Davidtz, 1965). However, soils used in this study contain negligible amount of permanent positive charge as indicated by $Cl^-$ adsorption (Figure 1f).

## Conclusion

This result indicates that for the topsoil's, OM contributes substantially to pH-dependent CEC. The positive charge of the soil increased due to removal of OM, possibly due to adsorbed OM complexes being removed from the surface of Fe and Al oxides and kaolin exposing more variable positive charge sites. The charge characteristics of these two highly weathered soils indicate that clay, mineral layer silicate and Fe oxides provides permanent negative surface charges and sesquioxide/allophane gives the permanent positive charges that play an important role on net surface charge. Point of zero charge varies with soil according to the variation of organic carbon and Fe, Al and Si content. The present study draws the information about the electrochemical charge characteristics of various surface subsurface soils in tropics.

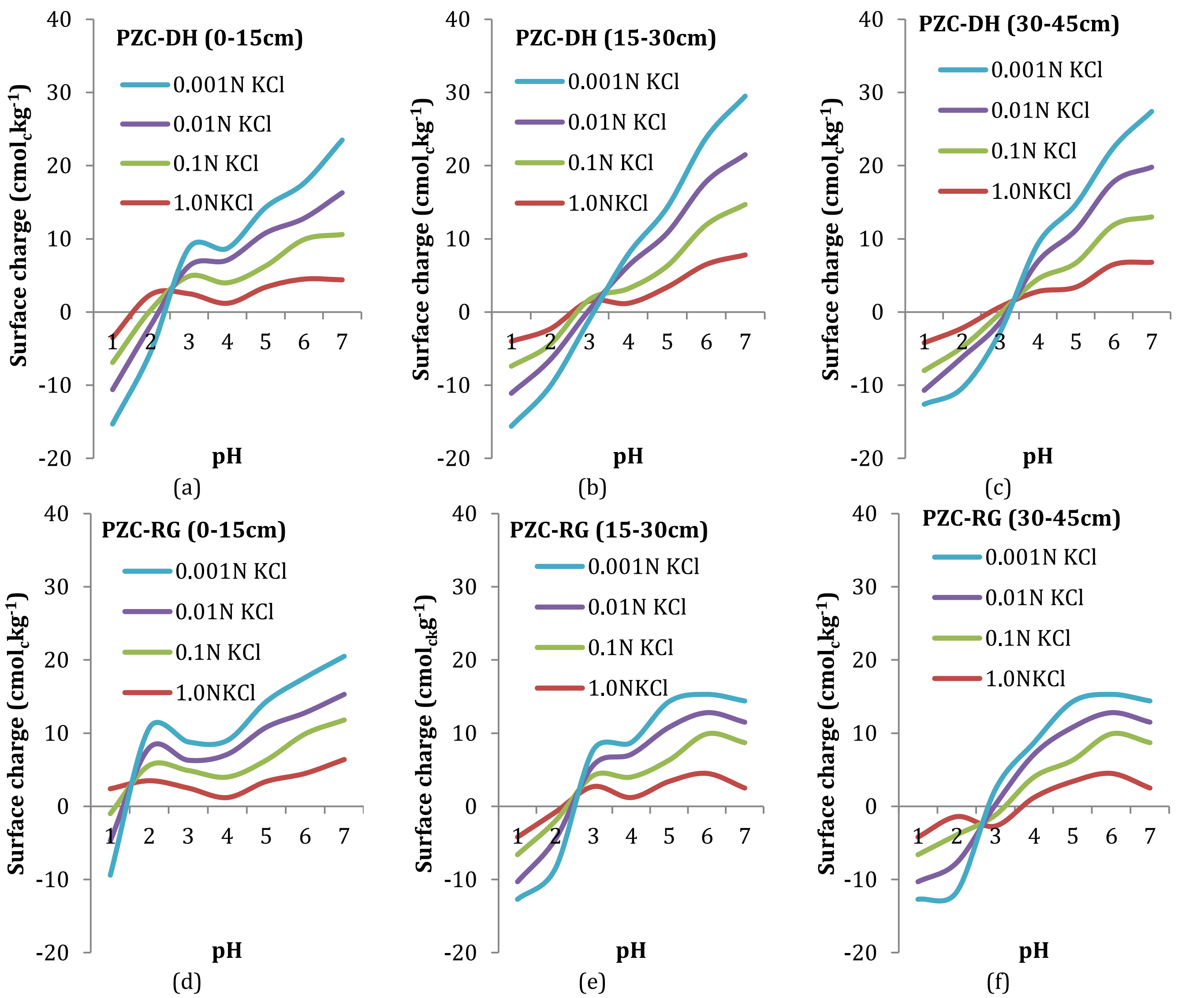


Figure 1. Surface charge-pH curves of soils determined in KCl

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# Responses of salt-stressed citrus plants to foliar-applied proline

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## Abstract

In this study, one-year old grapefruit trees grafted onto sour Orange (SO) and C22 rootstocks were exposed to NaCl-induced salinity (approx. 6 dS $m^{-1}$) in pot culture for two months under greenhouse conditions. The experiment was laid out in a randomized block design with eight replicates. The trees were irrigated with saline solution containing 0.1% liquid fertilizer "Miracle-Gro Liqua Feed 9-4-9" ($N$-$P_2O_5$-$K_2O$) enriched with micronutrients. The experimental treatments consisted of three levels (4 mM, 8 mM, 12 mM) of foliar applied proline along with control application. Distilled water served as the control. During the experiment the seedlings were sprayed totally five times with ten days intervals. At the end of the treatment physiologically mature leaves, free of damage or defects, were sampled. Dried and ground leaf samples were used for chemical (Na and Cl) and biochemical (DPPH scavenging activity, reducing power, total phenolic content, proline) analysis. Spesific leaf area, leaf water relations and leaf gas exchange of the plants were also determined. Foliar PRO application decreased Na and Cl concentrations of the leaves, and improved spesific leaf area in the final dose. Water leaf relations, photosynthetic activity and biochemical parameters were affected positively even though some differences were determined between the cultivars.

## Article Info

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**Keywords**: Salinity, proline, NaCl, C22, SO.



## Introduction

Citrus is one of the important horticultural crops worldwide and is relatively salt sensitive. In many of its growing regions, such as Texas in the US and Turkey in the Mediterranean Basin, drought and salinity are the most limiting abiotic factors for the production.

Compatible solutes, such as proline (PRO) is known to play a role in the process of osmotic adjustment in many crops and to accumulate under conditions of environmental stresses (Rhodes and Hanson, 1993). Their main role is probably to insulate plant cells against the ravages of salt by preserving the osmotic balance, by stabilizing the structure of key proteins such as Rubisco, by protecting the photosynthetic apparatus and by functioning as oxygen radical scavengers. In general, many plant species accumulate these organic osmolytes to overcome abiotic stress factors such as salinity and drought. Therefore, exogenous application of these compounds has been suggested as an alternative/additional approach to genetic engineering to improve crop productivity under stress conditions (Itai and Paleg, 1982). In recent years, foliar application of PRO has been proven useful to reduce the negative effects of abiotic stress factors in different perennial plants. The purpose of this study was to provide additional information on foliar application of PRO and its ability to counteract salt inhibitory effects in citrus.

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## Material and Methods

The research was carried out in a greenhouse at Texas A&M University-Kingsville Citrus Center, located in Weslaco, TX (USA) during July 11, 2013 -September 21, 2013. Approximately 1 year-old Sour Orange (SO) and C22 cultivars' seedlings were grown in 10 cm x 10 cm x 36 cm tall pots.

After planting the seedlings were started to irrigate with an amount of water accounting for a leaching factor of 50-55% and fertilized with 0.1% liquid fertilizer "Miracle-Gro Liqua Feed 9-4-9" ($N-P_2O_5-K_2O$) enriched with micronutrients. Average water applied per pot was about 1000 ml during the experiment.

In order to create salt stress on plants the seedlings were exposed to NaCl-induced salinity (approx. 6 $dSm^{-1}$) during the experiment. Salinity level was adjusted by the addition of appropriate amounts of NaCl to the applied nutrient solution and increased gradually in order to prevent any possible shock effect of salinity on experimental plants. Average EC of leachate was measured about 5.23 dS $m^{-1}$ during the experiment.

Experimental treatments consisted of 3 levels (4 mM, 8 mM, 12 mM) of foliar–applied PRO. Distilled water served as the control application. Twenty days after the first salt solution application to the pots the seedlings were sprayed with PRO solutions for 5 times with 10 days intervals. Applications were performed between 6.30 am-7.30 am and approximately 500 ml of PRO solution was used for each replication (8 plants in total).

At the end of the experiment physiologically mature leaves, free of damage or defects, were sampled. In order to eliminate surface contamination, leaves were carefully washed with tap water and rinsed 2 times with deionized water. For chemical and biochemical analysis, the samples were placed in paper bags and dried in a forced-air oven at 70°C for 72 hours. The dried leaf samples were then ground in a stainless steel mill (IKA A 11 Basic, Staufen, Germany).

### Chemical analysis

For Na determination the ground leaf samples were wet digested in a mixture of nitric/perchloric acid ($HNO_3/HClO_4$) (4/1, v/v) solution. Sodium contents in the digest were determined using flame photometer (Jenway PFP7, Staffordshire, UK) (Westerman, 1990). Chloride was extracted from 0.1 g of ground sample by shaking the mixture with 10 ml of deionized water for 2 h. Chloride concentrations of the extracts were measured by chloridometer (Jenway PCLM3, Staffordshire, UK) (Brown and Jackson, 1955).

### Physiological analysis

Leaf dry matter percentage (DMP) was calculated based on leaf fresh weight (FW) and dry weight (obtained after 48 h at+80 °C, DW). DMP was calculated by using (DMP=100×(FW−DW)/(FW) equation.

Spesific leaf area (SLA) was determined by using total leaf area and leaf dry weight values measured at the end of the experiment. SLA was calculated by using (leaf area ($cm^2$)/ leaf DW (g)) equation.

### Biochemical analysis

Proline (PRO) analysis was performed on dried leaf samples according to Bates et al. (1973). In order to determine total phenolic contents (TPC), reducing power (RP) and DPPH radical scavenging activity a plant extract was prepared. Distilled water were employed for the preparation of plant extracts. In brief, 0.25 g of ground leaf was mixed with 5 mL of water and the mixture was shaken for 2 h in a shaker (Heidolph Promax 2020, Schwabach, Germany). The filtrate was then used for analysis immediately. Total phenolic content (TPC) of the extracts was assayed according to the Folin-Ciocalteu method (Singleton et al., 1999). Reducing power (RP) of the extracts was measured according to the method of Oyaizu (Oyaizu, 1986). Radical scavenging activity of the plant extracts against the DPPH radical was determined spectrophotometrically according to Brand-Williams et al. (1995).

### Leaf water relations

During the experiment leaf water status were determined 3 times, July 30, 2013 (4 leaves of each PRO application); August 21, 2013 (4 leaves of each PRO application); and September 20, 2013 (5 leaves of each PRO application). For this purpose a Scholander-type pressure chamber (PMS Instrument Co., Albany, OR) (Scholander et al., 1965) was used. The leaves were previously introduced in plastic bags covered with duct tape that avoided light penetration, minimized transpiration and equilibrated leaf water potential. Measurements were taken at least 2 h after leaves were covered, normally starting at 13:00 h. In order to determine the osmotic potential of the leaves an osmometer (Wescor Vapro 5600- Wescor Inc. Logan, UT) was used.

### Chlorophyll fluorescence system and leaf gas exchange

Chlorophyll fluorescence measurements were performed on intact leaves with a portable Opti-Sciences OS1p fluorometer on 4 plants per PRO application totally 32 plants in August 21, 2013 between 16 pm and

16.30 pm. Leaf $CO_2$ gas exchange measurements were performed on 6 plants per PRO application totally 48 plants in September 20, 2013 between 10 am and 12 am. For this purpose Licor 6400 photosynthesis system was used.

**Experimental design and statistical analysis**

The experiment was laid out in a randomized block design with 8 replicates and 1 plant per pot. Regression analyses were carried out according to Little and Hills (1978) for the investigation of the relationship between PRO and the experimental data.

## Results

Sodium concentrations of C22 and SO leaves increased up to 8 mM and 4 mM respectively, and then decreased. In terms of leaf Cl concentrations; increasing PRO doses decreased leaf Cl concentrations of the cultivars linearly (Table 1).

Leaves' DMP of the cultivars increased up to 8 mM PRO application then decreased (Table 2). Specific leaf area and leaf PRO content of the cultivars showed a fluctuation with the increasing PRO application doses (Table 2 and Table 3).

RP increased with increasing PRO application doses (Table 3). TPC content increased up to 8 mM PRO application dose and then decreased in C22. On the other hand a fluctation was observed in SO (Table 4). Increasing foliar PRO doses decreased leaf DPPH scavenging activity of SO up to 8 mM PRO and then increased. A fluctation was observed in C22 (Table 4). Compared to control application; increasing PRO application doses decreased pressure potential of the C22 leaves at first and then increased it in the 8 mM and 12 mM PRO application doses. Increasing PRO application doses increased pressure potential of SO leaves up to 8 mM PRO and then decreased in 12 mM PRO (Table 5).

Compared to control application; osmotic potential of the C22 leaves increased initially and then decreased after 8 mM and 12 mM PRO applications. Osmotic potential of the SO leaves increased constantly (Table 5). Increasing foliar applied PRO increased the leaves' water potential of the cultivars up to 8 mM. In the highest PRO application dose (12 mM) leaf water potentials of the cultivars stayed stable in C22 and decreased in the SO (Table 6).

In terms of photosynthesis, stomatal conductance and leaf transpiration rate; the cultivars showed similar response to the increasing PRO application doses. All the parameters given above decreased with the increasing PRO application up to 8 mM then increased. On the other hand; increased PRO doses affected water use efficiency (WUE) of the cultivars in different ways. WUE of the cultivar C22 increased in the first application dose (4 mM) and then decreased. However, WUE of the cultivar SO stayed stable up to the last application dose ( 12 mM) and then increased. Ci/Ca of the cultivar C22 increased with the increase in PRO doses, while Ci/Ca of the cultivar SO was decreased (Tables 6-8).

## Discussion

Foliar application of PRO offers a valuable tool for studying mechanisms of salt tolerance. One of these mechanisms depends on the capacity for osmotic adjustment which allows growth to continue under saline conditions. It is generally accepted that under salt stress, this process is mainly achieved by uptake and accumulation of inorganic ions, mainly $Na^+$ and $Cl^-$ and partly by synthesis and accumulation of organic compatible compounds (Demiral et al., 2011; Flowers et al., 1977). Increasing PRO application doses decreased Na concentration of the leaves in the final doses. Chloride concentrations of the leaves decreased steadily with the increasing PRO application doses (Table 1). It might be concluded that exposure of the plants to saline nutrient solution increased the levels of Na in the leaves. As reported, there is a relationship between the PRO content and the osmotic adjustment in plants under salt stress (Rhodes and Hanson, 1993). Depicted in Table 1, Na concentration of the cultivars' leaves was decreased in the highest PRO application dose. On the other hand PRO did not affect Cl accumulation of the leaves. This process might also be related to decrease uptake capacity of the plants' roots. According to Lin and Kao (2001) exogenous application of PRO markedly inhibited root growth of rice. Hence decreasing Na and Cl concentrations of the leaves under increasing PRO applications might be related to decreasing uptake potential of the roots.

The DMP and SLA of the cultivars' leaves increased up to 8 mM application dose and then decreased (Table 2). This might be accomplished by adjusting the osmotic potentials of the cells in the leaves through the organic and/or inorganic solutes. According to Tester and Davenport (2003), the exposure of plants to salinity commonly results in a water deficit in plant cells, and maintaining osmotic homeostatis requires an adjustment in osmotica, either by the uptake of soil solutes or by the synthesis of metabolically compatible compounds. Probably changes in the Na concentrations of the cultivars' leaves support this tendency (Table 1).

Table 1. Na and Cl concentration of the cultivars under increasing PRO application doses

| | Plant Parameters | | | |
|---|---|---|---|---|
| | Na (%) | | Cl (%) | |
| | Cultivars | | | |
| PRO (mM) | C22 | SO | C22 | SO |
| Control | 0.47 | 0.40 | 0.64 | 0.72 |
| 4 | 0.50 | 0.44 | 0.64 | 0.62 |
| 8 | 0.53 | 0.44 | 0.62 | 0.59 |
| 12 | 0.41 | 0.37 | 0.62 | 0.55 |
| Regression Equation | $y = -0{,}0023x^2 + 0{,}0244x + 0{,}4625$ | $y = -0{,}0011x^2 + 0{,}0099x + 0{,}4045$ | $y = -0{,}002x + 0{,}642$ | $y = -0{,}0135x + 0{,}701$ |
| Determination coefficient ($R^2$) | 85.7 | 83.6 | 80.0 | 92.2 |
| Correlation Coefficient (r) | ns | ns | ns | * |

*Values are means of 8 replications. (n=2) *, ** Significant at P <0.05 and 0.01 espectively. ns: nonsignificant

Table 2. Dry matter and spesific leaf area of the cultivars under increasing PRO application doses

| | Plant Parameters | | | |
|---|---|---|---|---|
| | DM (%) | | SLA ($cm^2$ $g^{-1}$) | |
| | Cultivars | | | |
| PRO (mM) | C22 | SO | C22 | SO |
| Control | 65.74 | 66.64 | 89.26 | 94.17 |
| 4 | 66.06 | 67.45 | 89.87 | 102.10 |
| 8 | 68.03 | 67.57 | 89.34 | 96.21 |
| 12 | 67.30 | 67.35 | 100.04 | 98.26 |
| Regression Equation | $y = -0{,}0165x^2 + 0{,}3641x + 65{,}519$ | $y = -0{,}016x^2 + 0{,}2482x + 66{,}659$ | $y = 0{,}1576x^2 - 1{,}0953x + 89{,}876$ | $y = -0{,}0917x^2 + 1{,}2606x + 95{,}259$ |
| Determination coefficient ($R^2$) | 72.3 | 98.9 | 90.9 | 31.0 |
| Correlation Coefficient (r) | ns | ** | * | ns |

*Values are means of 8 replications. (n=2) *, ** Significant at P <0.05 and 0.01 espectively. ns: nonsignificant

Table 3. Proline and RP of the cultivars under increasing PRO application doses

| | Plant Parameters | | | |
|---|---|---|---|---|
| | PRO (μg $g^{-1}$ DW) | | RP (%) | |
| | Cultivars | | | |
| PRO (mM) | C22 | SO | C22 | SO |
| Control | 7203.79 | 10878.79 | 11.55 | 12.25 |
| 4 | 7260.86 | 7975.00 | 14.85 | 13.24 |
| 8 | 7225.97 | 10270.45 | 17.03 | 14.28 |
| 12 | 7687.63 | 11470.71 | 16.99 | 15.86 |
| Regression Equation | $y = 101{,}15x^2 - 161{,}77x + 7233{,}2$ | $y = 1026x^2 - 2670{,}9x + 10564$ | $y = 0{,}4627x + 12{,}331$ | $y = 0{,}2966x + 12{,}129$ |
| Determination coefficient ($R^2$) | 89.1 | 71.7 | 85.7 | 98.5 |
| Correlation Coefficient (r) | ns | ns | ns | ** |

*Values are means of 8 replications. (n=2) *, ** Significant at P <0.05 and 0.01 espectively. ns: nonsignificant

Table 4. TPC and DPPH radical scavenging activity of the cultivars under increasing PRO application doses

| | Plant Parameters | | | |
|---|---|---|---|---|
| | TPC (mg GAE $g^{-1}$ DW) | | DPPH radical scavenging activity (IC50, µg DW $mL^{-1}$) | |
| | Cultivars | | | |
| PRO (mM) | C22 | SO | C22 | SO |
| Control | 44.65 | 37.99 | 80.17 | 106.41 |
| 4 | 54.15 | 39.85 | 84.27 | 122.92 |
| 8 | 70.20 | 35.78 | 82.50 | 124.74 |
| 12 | 64.10 | 38.04 | 90.90 | 99.42 |
| Regression Equation | $y = 1{,}8599x + 47{,}115$ | $y = -0{,}098x + 38{,}5$ | $y = 1{,}0768x^2 - 0{,}1863x + 80{,}968$ | $y = -10{,}456x^2 + 29{,}453x + 105{,}79$ |
| Determination coefficient ($R^2$) | 73.1 | 09.2 | 79.8 | 98.3 |
| Correlation Coefficient (r) | ns | ns | ns | ** |

*Values are means of 8 replications. (n=2) *, ** Significant at P <0.05 and 0.01 espectively. ns: nonsignificant

Table 5. Pressure potential and osmotic potential of the cultivars under increasing PRO application doses

| | Plant Parameters | | | |
|---|---|---|---|---|
| | Pressure Potential (Mpa) | | Osmotic Potential (Mpa) | |
| | Cultivars | | | |
| PRO (mM) | C22 | SO | C22 | SO |
| Control | 0.35 | 0.20 | -1.20 | -0.83 |
| 4 | 0.27 | 0.62 | -0.97 | -1.21 |
| 8 | 0.32 | 0.68 | -1.01 | -1.20 |
| 12 | 0.42 | 0.59 | -1.11 | -1.43 |
| Regression Equation | $y = 0{,}0028x^2 - 0{,}0273x + 0{,}346$ | $y = -0{,}008x^2 + 0{,}1264x + 0{,}2105$ | $y = -0{,}0052x^2 + 0{,}0676x - 1{,}1895$ | $y = 0{,}0023x^2 - 0{,}0729x - 0{,}8615$ |
| Determination coefficient ($R^2$) | 97.2 | 98.4 | 93.1 | 89.3 |
| Correlation Coefficient (r) | * | ** | * | ns |

*Values are means of 8 replications. (n=2) *, ** Significant at P <0.05 and 0.01 espectively. ns: nonsignificant

Table 6. Water potential and photosynthesis of the cultivars under increasing PRO application doses

| | Plant Parameters | | | |
|---|---|---|---|---|
| | Water Potential (Mpa) | | Photosynthesis (µmol $CO_2$ $m^{-2}$ $s^{-1}$) | |
| | Cultivars | | | |
| PRO (mM) | C22 | SO | C22 | SO |
| Control | -0.85 | -0.64 | 6.11 | 4.75 |
| 4 | -0.70 | -0.59 | 5.54 | 4.64 |
| 8 | -0.69 | -0.53 | 4.21 | 3.19 |
| 12 | -0.69 | -0.84 | 4.78 | 5.38 |
| Regression Equation | $y = -0{,}0023x^2 + 0{,}0404x - 0{,}8435$ | $y = -0{,}0056x^2 + 0{,}054x - 0{,}659$ | $y = 0{,}0178x^2 - 0{,}3468x + 6{,}243$ | $y = 0{,}0359x^2 - 0{,}4202x + 4{,}999$ |
| Determination coefficient ($R^2$) | 95.4 | 86.6 | 85.7 | 51.7 |
| Correlation Coefficient (r) | * | ns | ns | ns |

*Values are means of 8 replications. (n=2) *, ** Significant at P <0.05 and 0.01 espectively. ns: nonsignificant

Table 7. Stomatal conductance and leaf transpiration of the cultivars under increasing PRO application doses

| | | Plant Parameters | | | |
|---|---|---|---|---|---|
| | | Stomatal Conductance (mol $H_2O$ $m^{-2}$ $s^{-1}$) | | Leaf Transpiration (mmol $H_2O$ $m^{-2}$ $s^{-1}$) | |
| | | Cultivars | | | |
| | PRO (mM) | C22 | SO | C22 | SO |
| | Control | 0.15 | 0.11 | 3.56 | 2.83 |
| | 4 | 0.13 | 0.11 | 3.13 | 2.91 |
| | 8 | 0.10 | 0.07 | 2.66 | 1.98 |
| | 12 | 0.12 | 0.12 | 3.10 | 2.99 |
| Regression Equation | | $y = 0,0006x^2 - 0,0105x + 0,153$ | $y = 0,0008x^2 - 0,0096x + 0,1165$ | $0,0136x^2 - 0,2094x + 3,6075$ | $y = 0,0145x^2 - 0,1856x + 2,9775$ |
| Determination coefficient ($R^2$) | | 86.1 | 42.7 | 88.8 | 34.2 |
| Correlation Coefficient (r) | | ns | ns | ns | ns |

*Values are means of 8 replications. (n=2) *, ** Significant at P <0.05 and 0.01 espectively. ns: nonsignificant

Table 8. Water use efficiency and Ci/Ca of the cultivars under increasing PRO application doses

| | | Plant Parameters | | | |
|---|---|---|---|---|---|
| | | WUE | | Cİ/Ca | |
| | | Cultivars | | | |
| | PRO (mM) | C22 | SO | C22 | SO |
| | Control | 0.17 | 0.16 | 0.78 | 0.79 |
| | 4 | 0.18 | 0.16 | 0.78 | 0.79 |
| | 8 | 0.15 | 0.16 | 0.79 | 0.77 |
| | 12 | 0.15 | 0.18 | 0.80 | 0.76 |
| Regression Equation | | $y = -0,0023x + 0,176$ | $y = 0,0015x + 0,156$ | $y = 0,0018x + 0,777$ | $y = -0,0028x + 0,794$ |
| Determination coefficient ($R^2$) | | 60.0 | 60.0 | 89.0 | 89.6 |
| Correlation Coefficient (r) | | ns | ns | ns | ns |

*Values are means of 8 replications. (n=2) *, ** Significant at P <0.05 and 0.01 espectively. ns: nonsignificant

But it is clear that Cl does not contribute to the process (Table 1). Although there is a slight fluctuation in 8 mM PRO application dose, constant increase in PRO accumulation of the cultivar C22 leaves support this process (Table 3). Change in tendency of TPC in the cultivar C22 also seem to support this process (Table 4).

Cultivar SO exhibited different responses compared the C22 in terms of PRO and TPC accumulation in its leaves. Highest PRO accumulation value was found in the leaves of the control plants (Table 3). PRO accumulation dropped dramatically after the first application dose (4 mM PRO) and then increased constantly with the increasing doses. The greater accumulation of PRO in control plants' leaves of cultivar SO cultivar may result from high endogenous production under salinity. There are some inconsistent results about the probable reasons of PRO accumulation in plants under stress. According to Ramajulu and Sudhakar (2000) PRO accumulation is one of the results of the adaptation of plants to salinity. Some authors did not observe any appreciable increase in PRO content (Jain et al., 1987, Mousa, 2010) while others consider an enhanced PRO level merely as a stress effect (Moftah and Michel, 1987). It has been reported that PRO accumulation appears to be a reaction to salt-stress damage (de Lacerda et al., 2003) or a symptom of salt-susceptibility (Chen et al., 2007) and not a plant response associated with salt tolerance.

TPC accumulation of the SO cultivar was found nonsignificant with the lowest "determination coefficient ($R^2$)" value of the study which means that the related "regression equation" explaines only 9.2 percent of the change in the TPC accumulation under increasing PRO doses (Table 4). Many researchers stated that the synthesis and accumulation of phenolic compounds is generally stimulated in response to biotic and abiotic stresses in plants (Dixon and Paiva, 1995; Naczk and Shahidi, 2004). However different findings have also been published by other researchers. For instance, according to Ksouri et al. (2007) salinity reduced the TPC of *Cakile maritima* (cv Tabarka) leaves. The authors stated that relationship between salinity and TPC of the leaves is possibly related to the salinity tolerance level of the plants. As reported by Agastian et al. (2000) TPC and PRO contents of different mulberry genotypes increased at low salinity levels (1-2 dS $m^{-1}$) and decreased at high salinity levels (8-12 dS $m^{-1}$). Phenolic compounds belong to the category of natural antioxidants and their abundance is positively and directly related to the antioxidant capacity of plants (Boskou and Visioli, 2003). Therefore it may be concluded that increasing foliar PRO application doses contributed significantly to the osmotic adjustment in the cells of the plants.

According to Demiral et al. (2011) DPPH scavenging activity expressed as $IC_{50}$ was greatly affected by salinity and the scavenging activities of water extracts decreased at higher salinity levels. Although there are small differences, increasing PRO doses stimulated DPPH scavenging activity of the cultivars in the study. DPPH scavenging activity of cultivar C22 leaves fluctated while DPPH scavenging activity of cultivar SO leaves' decreased up to 8 mM PRO application dose and then increased in the final dose (Table 4). It is known that a lower $IC_{50}$ value reflects improved DPPH radical scavenging activity (Molyneux, 2004). Hence, it might be concluded that increasing PRO doses did not affect DPPH radical scavenging activity positively except the highest PRO dose (12 mM PRO) applied to the SO cultivar (Table 4).

RP of the cultivars increased steadily with the increasing foliar PRO application doses (Table 3). As reported by Demiral et al. (2011) increased salinity led to a general decrease in PR in olive plant. Hence it may be speculated that increasing PRO doses stimulated the production of metabolites responsible for the reducing mechanism of the plants under salt stress.

In terms of leaf water relation parameters (pressure, osmotic and water potentials); the cultivars showed similar responses to the increasing PRO doses. All the parameters changed direction in 8 mM PRO application dose (Table 5, Table 6).

Increasing foliar PRO application doses clearly affected water potentials of the test plants' leaves (Table 6). As expected, increasing PRO doses affected pressure and water potentials in positive ways. This positive effect continued up to 8 mM PRO dose and then changed direction, but the pressure potential of the cultivar C22 did not obey this tendency. This parameter was quite high in control plants, then decreased in the first application dose and increased constantly again (Table 5). If the pressure potential result of cultivar C22 is ignored, it can be said that PRO application contributed to water balance of the plant cells under salinity up to 8 mM PRO level. These parameters decreased in the highest application dose (12 mM PRO). Osmotic potentials of the test plants also support this tendency. These results suggest that the conclusive effect of foliar PRO may be attributed to two factors; the toxicity of the PRO molecule itself and the stimulation of salt uptake. Exogenous PRO interfered with the normal process of osmotic adjustment based on the accumulation of ions such as Na and Cl. Increasing PRO doses stimulated water absorption and/or hindered uptake of ions such as $Na^+$ and $Cl^-$ by the roots.

A nonsignificant effect of foliar PRO application was observed on WUE of the cultivars (Table 8). However the cultivars differed in terms of CI/Ca. CI/Ca of cultivar C22 decreased under increasing foliar PRO application (Table 8). Leaf transpiration, stomatal conductance and photosynthesis of the test plants' leaves showed more or less similar patterns between the cultivars. In all these parameters control plants gave slightly higher values than that of 4 mM and 8 mM PRO application doses. These results suggest that using of distilled water as control application decreased the stress level of the test plants under salt stress more than expected. Hence the effects of PRO applications on the test plants under salinity became uncertain.

A number of studies show that plant growth is positively associated with photosynthetic capacity, and decline in plant growth due to salt stress is often attibuted to suppression in photosynthesis (Lawlor, 2002; Jamil et al., 2007; Noreen et al., 2010). However, considerable salt-induced reduction in photosynthesis rate is attributed to reduced optimum concentration of photoassimilates required for better growth (Maas and Nieman, 1978), reduced leaf area (Marcelis and Hoojdonk, 1999), and inbalance in water status (Ashraf, 2004). According to da Silva Sa et al. (2016), exogenous application of PRO on the leaves reduced stomatal conductance and consequently affected the transpiration of bell pepper plants irrigated with water of low salinity (Table 7). It should be pointed out that the reduction in stomatal conductivity in plants under controlled application (distilled water) reached higher levels, compared to the plants treated with various PRO doses. These results denote the efficiency of exogenous application of PRO in the stomatal regulation of test plants, promoting higher transpiration without any damage to photosynthetic activity and with gains in water use efficiency (Table 6, Table 8).

These responses may be related to the osmotic adjustment promoted by the exogenous application of PRO on the leaves, so that transpiration guaranteed the occurrence of absorption and transport of water inside the plant, maintaining its water relationships active, through stomatal regulation. Thus, the increase in transportation is an indication of the efficiency of exogenous application of PRO in the osmotic regulation of the test plants, especially because there was an increase in the WUE of these plants.

Based on the results obtained in this experiment we conclude that foliar PRO application decreased Na, Cl concentrations of the leaves and improved spesific leaf area in the final dose. Water leaf relations, photosynthetic activity and biochemical parameters were affected positively even though some differences were determined between the cultivars. However, more studies have to be carried out in near future to determine optimal concentrations of PRO that provide beneficial effects in citrus plant grown in different development stages.

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# Agronomic zinc biofortification of wheat to improve accumulation, bioavailability, productivity and use efficiency

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## Abstract

Zinc (Zn) deficiency causes low crop production and malnutrition in human. Agronomic biofortification of food crops can resolve the issues of global food security and human nutrition on sustainable basis. Field experiments were conducted to improve Zn bioavailability, growth and yield of wheat in response to varying Zn application rates for two consecutive years (2016-17 & 2017-18). Significant increase in grain yield was recorded with the application of Zn. Highest grain yield (5.41 t $ha^{-1}$) was recorded with the application of 5.00 kg Zn $ha^{-1}$. Human available Zn fraction was also improved in response to Zn application. Zn application resulted in lowering phytate/Zn molar ration in wheat grains. Higher Zn accumulation (338.72 g $ha^{-1}$) was observed by applying 7.5 kg Zn $ha^{-1}$. Zinc application was found critical to meet internal (36.53 µg $g^{-1}$) and external (4.48 kg Zn $ha^{-1}$) Zn requirements to achieve near maximum yield of wheat. The results reinforced the concept of Zn fertilization to achieve better productivity and quality.

**Keywords**: Biofortification, cereals, food security, nutrition.



## Introduction

Wheat is important crop for our food security and human nutrition. It is staple food for 35% of world population (Poursarebani et al., 2014). It is inherently low in Zn and consuming large proportion of wheat based food products can lead to the Zn deficiency in human (Bouis and Welch, 2010). Its deficiency can affect human health by impairing growth, immune functions, mental health and sexual maturation (Andreini et al., 2006; Krężel and Maret, 2016).

In plants Zn deficiency causes disruption in enzymatic functions, protein synthesis and hampers plant growth (Akram et al., 2017). Moreover, Crops cultivated on the Zn deficient medium is more prone to biotic and abiotic stresses (Cakmak and Kutman, 2018). Breeding wheat varieties with high Zn accumulation potential can resolve the prevalent Zn deficiencies in human and crop plants on sustainable basis (Bouis and Saltzman, 2017). However, this is a long and tedious process. Therefore, scientists are more inclined to agronomic Zn biofortification of food crops to enhance Zn bioavailability to human and sustaining crop yield because this type of biofortification have more adaptability and access to rural population (Cakmak, 2008).

To achieve the goal of biofortification plant should be able to translocate Zn from vegetative parts to grains (Gibson, 2012; Gupta et al., 2016). Increasing Zn accumulation in edible parts of the crop is not the only challenge for biofortication efforts but the availability of bio-accumulated Zn to the consumer is another challenge. Cereals constitute major fraction of daily human diet, yet they do not provide sufficient concentrations of essential metals to fulfill their daily body requirements due to high phytic acid contents (Juliano, 1993). Phytic acid is indigestible inositol phosphorus stored in grains (Raboy, 2000). It has net negative charge and chelates positively charged mineral ions and render them insoluble in human digestive system due to absence of phytase enzymes (Marounek et al., 2010). Nonetheless, protein absorption in

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human stomach and small intestine is also affected by phytate. Therefore, development of high yielding food crops with greater mineral bioavailability have become prime research goal of scientific community to achieve global food security in both quantitative and qualitative terms (Bouis and Saltzman, 2017).

Crop genotypes with better yield and high micronutrient concentrations in grains are suitable to address food security and human micronutrient deficiencies (Cakmak and Kutman, 2018). However, high grain yield and high nutrient concentrations are usually achieved by consuming costly inputs at high doses, which often affects nutrient use efficiency (Farooq et al., 2018). Therefore, determination of Critical internal and external Zn requirements of crops is important to sustain their yield and quality of crop (Kanwal et al., 2009). The critical internal Zn concentration delineates the quantity or intensity faction of nutrient in the plant, associated with the near to maximum yield of the crop. Whereas, the intensity/quantity of the nutrient in the soil equilibrated with the soil solution concentration, associated with the near maximum crop yield is called as external requirement (Sarfraz et al., 2008). The present study was conducted to evaluate wheat grain yield, Zn concentration, accumulation, bio-availability, Zn use efficiency and critical internal and external Zn requirement in response to Zn application.

## Material and Methods

A field experiment was conducted at Research Farms of Nuclear Institute of Agriculture (NIA), Tando Jam, Sindh-Pakistan for the two consecutive years 2016-17 and 2017-18. The crop was sown on fixed layout in the months of November and was harvested in the end of April in during both growing seasons. The site was located at latitude of 25°41’30.22” North and longitude of 68°51’78.09” East. The experimental site has arid climate (Figure 1) and average high and low temperatures in the growing seasons were 26.5.1°C and 14.7°C, respectively (NAMC, 2018). Before sowing soil samples were collected from the field at depth of 0-15cm and 15-30cm and were analyzed for various physio-chemical properties of soil (Table 1). Five treatments of Zn (0, 1.25, 2.5, 5.0 and 7.5 kg Zn ha$^{-1}$ from $ZnSO_4.H_2O$) were randomly allotted to fifteen experimental units each of dimension 4m x 4m so that each treatment was repeated thrice. Wheat genotype “SD-1013” was sown by using manual hand drill and row to row distance of 30 cm was maintained.

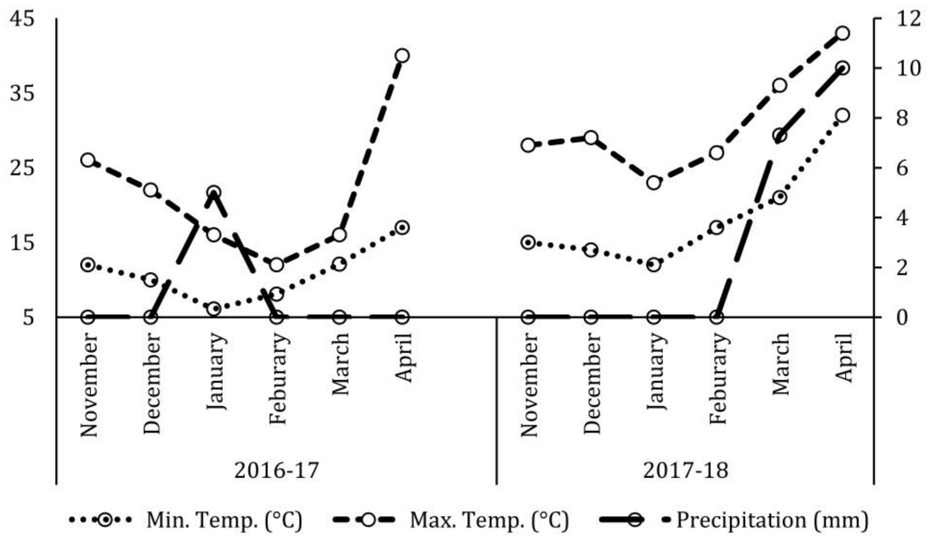


Figure 1. Agro-meteorological conditions during Rabi 2016-17 and 2017-18

Table 1. Physico-chemical properties of soil at experimental site

| Soil properties | Unit | Value | | Reference/method |
|---|---|---|---|---|
| | | 2016-17 | 2017-18 | |
| Textural class | -- | Silt loam | Silt loam | Bouyoucos (1962) |
| EC (1:2.5) | dS m$^{-1}$ | 0.32 | 0.35 | Anderson and Ingram (1993) |
| pH (1:2.5) | -- | 8.1 | 8.0 | Anderson and Ingram (1993) |
| Organic matter | % | 0.53 | 0.59 | Nelson and Sommers (1982) |
| Kjeldhal nitrogen | % | 0.03 | 0.03 | Jackson (1962) |
| AB-DTPA extractable phosphorus | mg kg$^{-1}$ | 5.86 | 6.01 | Soltanpour and Workman (1979) |
| AB-DTPA extractable zinc | mg kg$^{-1}$ | 0.51 | 0.57 | Soltanpour and Workman (1979) |
| AB-DTPA extractable potassium | mg kg$^{-1}$ | 160 | 150 | Soltanpour and Workman (1979) |

AB-DTPA = Ammonium bicarbonate-diethylene triamine penta acetic acid

Di-Ammonium Phosphate (90 kg $P_2O_5$ ha$^{-1}$) and Sulfate of Potash (60 kg $K_2O$ ha$^{-1}$) were applied at the time of sowing to supplement Phosphorus (P) and Potassium (K) to the crop. Whereas, Nitrogen (150 kg N ha$^{-1}$) was supplemented in the form of urea in three equal splits *viz.,* at the time of sowing, tillering, and panicle initiation. Zn was applied at tillering stage alongwith nitrogen. Four irrigations of canal water were applied to the crop at critical growth stages. Chemical and manual eradication of weeds was performed as per requirement. At maturity attributes related to plant growth, yield and Zn concentrations and Zn accumulation were recorded.

Grain and straw samples were collected from each treatment replication and were dried at 70°C in oven. Dried plant samples were then grinded and digested in 5:1 di-acid mixture of $HNO_3$ and $HClO_4$ (Rashid, 1986). Digested samples were analyzed for Zn concentration using Atomic Absorption Spectrophotometer (Analytik Jena Nova 400, Germany). Zinc uptake and use efficiency related attributes were calculated using following equations (Farooq et al., 2018).

$$\text{Zinc accumulation (g ha}^{-1}\text{) =Zn concentration} \times \text{yield}$$

$$\text{Agronomic efficiency} \left(\text{kg kg}^{-1}\right)= \left(\frac{GY_f - GY_c}{N_{ap}}\right)$$

$$\text{Physiological efficiency (kg g}^{-1}\text{)}= \left(\frac{BY_f - BY_c}{TAc_f - TAc_c}\right)$$

$$\text{Apparent recovery efficiency (\%)}=\left(\frac{TAc_f - TAc_c}{N_{ap}}\right)\times 100$$

Where:

| | | |
|---|---|---|
| $GY_f$ | = | Grain yield of fertilized plots |
| $GY_c$ | = | Grain yield of control (unfertilized) plots |
| $N_{ap}$ | = | Nutrient applied |
| $BY_f$ | = | Biomass yielded from fertilized plots |
| $BY_c$ | = | Biomass yielded from control |
| $TAc_f$ | = | Total Zn accumulation in fertilized plots |
| $TAc_c$ | = | Total Zn accumulation in control |

To assess the Zn complexation by phytate (PA) the total inositol Phosphorus/phytate was determined according to the method explained by Haug and Lantzsch (1983). Briefly, wheat grains were grinded to flour and extracted with dilute HCl. 0.5 mL extract was mixed with 0.4mM Iron (III) sulfate (dissolved in 0.2N HCl) solution in a caped glass tube. Afterwards, tubes were first heated for 30 minutes in a boiling water bath then cooled for 15 minutes in ice water. Samples were allowed to rest to attain room temperature. Then 2mL of 2, 2'-bi-pyridine solution (prepared by dissolving 5g of 2,2'-bi-pyridine of in 500mL of 1% (*v/v)* thioglycollic acid solution) were added to the mixture. Absorbance of pink Colour produced by the unreacted Fe(III) was measured at 519 nm using UV-Visible Spectrophotometer (U-2900, Hitachi, Japan). Phytate concentration was calculated using standards calibration curve established by running standards prepared from sodium phytate.

To calculate [phytate]: [Zn] in wheat grains their molar concentrations were used. Tivariate model of Zn absorption derived by Miller et al., (2007) was used to estimate the bioavailable Zn. Given below is the model based on Zn homeostasis in human digestive system. Total available Zn was calculated on reference adults consuming 300g wheat flour per day as the only daily Zn source (Rosado et al., 2009).

$$TAZ=0.5\cdot\left(A_{max}+TDZ+K_R\times\left(1+\frac{TDP}{K_P}\right)\right)-\sqrt{\left(A_{max}+TDZ+K_R\times\left(1+\frac{TDP}{K_P}\right)\right)^2-4\times A_{max}\times TDZ}$$

Where:

| | | |
|---|---|---|
| TAZ | = | Total daily absorbed Zn (mg Zn/day) |
| $A_{max}$ | = | maximum Zn absorption |
| TDZ | = | Total daily dietary Zn (mmol Zn/day) |
| $K_R$ | = | Equilibrium dissociation constant of the Zn-receptor binding reaction |
| TDP | = | Total daily dietary PA (mmol PA/day) |
| $K_P$ | = | Equilibrium dissociation constant of the Zn-PA binding reaction |

For Zn homeostasis in human intestine 0.091, 0.680 and 0.033 are the constant values for $A_{max}$, $K_P$ and $K_R$ (Hambidge et al., 2010).

The Zn requirement of wheat crop was determined on the basis of near to maximum crop yield (95% of the maximum attainable crop yield) following Kanwal et al. (2009). The data were analyzed using Microsoft Excel 2010® (Microsoft Cooperation, USA) and Statistix 8.1® (Analytical Software, Tallahassee, USA). Significantly different means were separated using Tukey's HSD test (Steel et al., 1997).

## Results

Plant growth attributes *viz.,* plant height, number of tillers and spike length are presented in Table 2. Plant height and number of tillers per plant increased significantly with the application of Zn. The increments recorded in the parameters with Zn, applied at the rate of 5 kg $ha^{-1}$ were statistically higher than all the treatments with exception to the increments recorded with application of 7.5 kg Zn $ha^{-1}$. Highest plant height of 93.33 cm was observed where 5 kg Zn $ha^{-1}$ was applied. Minimum height of 87.42 cm was recorded in the control. Whereas, highest number of tillers (5.87) were recorded in response to 5 kg Zn $ha^{-1}$ which were statistically at par with the number of tiller recorded in the plants, applied with 7.5 kg Zn $ha^{-1}$. In case of spike length, Zn applications affected the parameter positively but the increases in the spike length were recorded statistically similar to each other at all Zn application rates. Maximum spike length (11.43 cm) was recorded with the application of 2.5 kg Zn $ha^{-1}$. Whereas, minimum (10.83 cm) was recorded in control.

Table 2. Growth attributes of wheat as influenced by Zn application rates

| Treatments, | Plant height, cm | | | Number of tillers, per plant | | | Spike length, cm | | |
|---|---|---|---|---|---|---|---|---|---|
| kg Zn $ha^{-1}$ | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean |
| 0.00 | 87.47 e | 87.37 e | 87.42 C | 4.40 f | 4.47 ef | 4.43 D | 11.20 | 10.47 | 10.83 A |
| 1.25 | 90.13 d | 91.80 bc | 90.97 B | 4.53 d-f | 5.33 b-d | 4.93 C | 11.57 | 10.87 | 11.22 A |
| 2.50 | 91.47 cd | 89.97 d | 90.72 B | 4.87 c-f | 5.27 b-e | 5.07 BC | 11.93 | 10.93 | 11.43 A |
| 5.00 | 93.20 ab | 93.47 a | 93.33 A | 5.53 a-c | 6.20 a | 5.87 A | 11.43 | 11.20 | 11.32 A |
| 7.50 | 93.07 ab | 92.10 a-c | 92.58 A | 5.87 ab | 5.20 b-f | 5.53 AB | 11.33 | 11.37 | 11.35 A |
| Mean | 91.07 A | 90.94 A | | 5.04 B | 5.29 A | | 11.49 A | 10.97 B | |
| Tuckey's HSD $_{(0.05)}$ | | | | | | | | | |
| Zn | | 0.929 | | | 0.479 | | | 1.038 | |
| Yr | | 0.408 | | | 0.211 | | | 0.456 | |
| Zn × Yr | | 1.557 | | | 0.803 | | | 1.739 | |

Means sharing similar letters in a column are statistically similar to each other at $p \leq 0.05$. Data is average of 3 replicates.

The grain yield of wheat responded appreciably to the application of Zinc. Significant increase in the yield was observed with the increasing Zn application rates (Table 3). Average grain yields during 2016-17 and 2017-18 were 5.85 and 4.09 t $ha^{-1}$. The yields obtained with the five Zn rates (0, 1.25, 2.5, 5.0 & 7.5 kg Zn $ha^{-1}$) were 4.12, 5.02, 4.97, 5.41 and 5.34 t $ha^{-1}$, respectively. Maximum increase in grain yield (31.31%) over the control was recorded with the application of 5 kg Zn $ha^{-1}$ but this increase was statistically similar with the grain yield (5.34 t $ha^{-1}$) attained with the application of 7.5 kg Zn $ha^{-1}$. Similarly, straw yield was also affected by the application of Zn. Highest mean straw yield of both years (5.95 t $ha^{-1}$) was observed with the application of 7.5 kg Zn $ha^{-1}$. Whereas, lowest (4.58 t $ha^{-1}$) was in the control. Straw yield increased by 28.82% over the control with the application of 5 kg Zn $ha^{-1}$. Likewise, total biomass of yielded with the application of Zn was appreciably higher than of control. Highest biomass (11.35 t $ha^{-1}$) was yielded with the application of 5 kg Zn $ha^{-1}$ which was statistically comparable with the biomass yielded from experimental units applied with of 1.25, 2.50 and 7.5 kg Zn $ha^{-1}$ (Table 3).

Table 3. Yield attributes of wheat as influenced by Zn application rates

| Treatments | Grain yield, t/ha | | | Straw yield, t/ha | | | Total biomass yield, t/ha | | |
|---|---|---|---|---|---|---|---|---|---|
| kg Zn $ha^{-1}$ | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean |
| 0.00 | 5.21 b | 3.03 e | 4.12 C | 5.94 a-c | 3.22 d | 4.58 B | 11.15 b | 6.25 d | 8.70 B |
| 1.25 | 5.79 a | 4.24 cd | 5.02 B | 6.08 a-c | 5.45 bc | 5.77 A | 11.88 ab | 9.69 c | 10.78 A |
| 2.50 | 5.88 a | 4.06 d | 4.97 B | 6.52 a | 5.73 a-c | 6.13 A | 12.40 a | 9.79 c | 11.09 A |
| 5.00 | 6.21 a | 4.61 c | 5.41 A | 6.31 ab | 5.49 bc | 5.90 A | 12.60 a | 10.10 c | 11.35 A |
| 7.50 | 6.19 a | 4.49 cd | 5.34 A | 6.50 a | 5.41 c | 5.95 A | 12.60 a | 9.90 c | 11.25 A |
| Mean | 5.85 A | 4.09 B | | 6.27 A | 5.06 B | | 12.13 A | 9.15 B | |
| Tuckey's HSD $_{(0.05)}$ | | | | | | | | | |
| Zn | | 0.259 | | | 0.522 | | | 0.604 | |
| Yr | | 0.114 | | | 0.229 | | | 0.266 | |
| Zn × Yr | | 0.434 | | | 0.875 | | | 1.013 | |

Means sharing similar letters in a column are statistically similar to each other at $p \leq 0.05$. Data is average of 3 replicates.

The Zn concentrations in grains and straw increased significantly with different application rates of Zn fertilizer (Table 4). Highest concentrations were recorded in grain (42.12 µg $g^{-1}$) with the application of 7.50 kg Zn $ha^{-1}$. Minimum concentration of 8.57 µg $g^{-1}$ was depicted by the control. Highest input rat of Zn fertilizer depicted 4.91 times higher grain Zn concentration than of control. Straw Zn concentration was also increased in response to the applied Zn. Highest straw Zn 19.54 µg $g^{-1}$ was recorded with the application of 5.00 kg Zn $ha^{-1}$. However, this was statistically similar to the straw Zn concentration (19.43 µg $g^{-1}$) found, with the application of 7.50 kg Zn $ha^{-1}$. The minimum straw Zn was (4.89 µg $g^{-1}$) found in the plants applied with no Zn fertilizer.

Table 4. Zinc concentrations [Zn] in wheat as influenced by Zn application rates

| Treatments, | [Zn] in grains, µg/g | | | [Zn] in straw, µg/g | | |
|---|---|---|---|---|---|---|
| kg Zn $ha^{-1}$ | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean |
| 0.00 | 9.81 f | 7.33 g | 8.57 D | 5.01 f | 4.77 f | 4.89 D |
| 1.25 | 36.51 d | 32.08 e | 34.30 C | 11.18 e | 20.67 c | 15.92 C |
| 2.50 | 37.66 d | 38.06 cd | 37.86 B | 11.40 e | 24.00 a | 17.70 B |
| 5.00 | 39.84 bc | 37.06 d | 38.45 B | 16.69 d | 22.39 b | 19.54 A |
| 7.50 | 41.19 ab | 43.06 a | 42.12 A | 17.59 d | 21.28 bc | 19.43 A |
| Mean | 33.00 A | 31.52 B | | 12.37 B | 18.62 A | |
| Tuckey's HSD $_{(0.05)}$ | | | | | | |
| Zn | | 1.162 | | | 0.739 | |
| Yr | | 0.511 | | | 0.325 | |
| Zn × Yr | | 1.947 | | | 1.239 | |

Means sharing similar letters in a column are statistically similar to each other at *p≤0.05*. Data is average of 3 replicates.

Zn quantity factor (accumulation) was also calculated (Table 5). The results showed that highest Zn accumulation in grains (224.08 g $ha^{-1}$) was with the application of 7.50 kg Zn $ha^{-1}$. Application of 5.00 kg Zn $ha^{-1}$ resulted in second highest Zn accumulation in grain (209.11 g $ha^{-1}$). Lowest grain Zn accumulation of 36.64 g $ha^{-1}$ was recorded in control plots. Accumulation of Zn in straw was also highest (114.64 g $ha^{-1}$) with the application of 7.50 kg Zn $ha^{-1}$ but statistically similar to 114.09 g Zn $ha^{-1}$ accumulated in straw of wheat plants treated with 5.00 kg Zn $ha^{-1}$. Control showed lowest straw Zn accumulation of 22.31 g $ha^{-1}$ among all the treatments. Total Zn accumulated in wheat plant was recorded as highest (338.72 g $ha^{-1}$) with the application of 7.50 kg Zn $ha^{-1}$ while lowest (58.95 g $ha^{-1}$) was recorded in control. Overall, Zn application increased Zn accumulation in wheat plant.

Table 5. Zinc accumulation in wheat as influenced by Zn application rates

| Treatments, | Zn accumulation in grains, g/ha | | | Zn accumulation in straw, g/ha | | | Total Zn accumulation, g/ha | | |
|---|---|---|---|---|---|---|---|---|---|
| kg Zn $ha^{-1}$ | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean |
| 0.00 | 51.06 i | 22.23 j | 36.64 E | 29.24 h | 15.38 i | 22.31 D | 80.30 h | 37.61 i | 58.95 E |
| 1.25 | 211.10d | 136.02h | 173.56D | 68.05 g | 112.62d | 90.33 C | 279.15f | 248.31 g | 263.73D |
| 2.50 | 220.89 c | 154.61 g | 187.75 C | 74.36 f | 137.66 a | 106.01B | 295.25d | 292.27 e | 293.76C |
| 5.00 | 247.29 b | 170.94 f | 209.11 B | 105.31 e | 122.87 b | 114.09 A | 352.60 b | 293.81de | 323.20B |
| 7.50 | 254.85 a | 193.31 e | 224.08 A | 114.20cd | 115.08 c | 114.64 A | 369.05 a | 308.39 c | 338.72A |
| Mean | 197.04 A | 135.42 B | | 78.23 B | 100.72 A | | 275.27 A | 236.08 B | |
| Tuckey's HSD $_{(0.05)}$ | | | | | | | | | |
| Zn | | 1.153 | | | 1.165 | | | 1.475 | |
| Yr | | 0.507 | | | 0.512 | | | 0.649 | |
| Zn × Yr | | 1.933 | | | 1.953 | | | 2.473 | |

Means sharing similar letters in a column are statistically similar to each other at p≤0.05. Data is average of 3 replicates.

The better quality of produce is as important as the quantity factor in order to ensure the availability of nutritious food to the masses. Therefore, the quality traits of the wheat genotype were also recorded (Table 6). The Zn fertilization had minimum effect on the grain PA concentration. Highest grain PA concentration (7.39 mg $g^{-1}$) was recorded where 1.25 kg Zn $ha^{-1}$ was applied but it was statistically similar to the grain PA concentrations (7.454 and 7.06 mg $g^{-1}$) recorded where 2.50 and 5.00 kg Zn $ha^{-1}$ were applied, respectively. Lowest grain PA concentration (6.83 mg $g^{-1}$) was observed in control where no Zn was applied and it was comparable with the concentrations (7.06 and 7.00 mg $g^{-1}$) overserved in response to the application of 5.00 and 7.50 kg Zn $ha^{-1}$.

Higher levels of PA in wheat flour can affect Zn bioavailability of Zn to human. Therefore, PA/Zn ratios were also calculated (Table 6) on the molar concentration basis at each Zn input level. It was observed that the PA/Zn ratio decreased with increasing Zn fertilizer. Higher the input, greater was the grain Zn uptake therefore, lower the PA/Zn ratio was. Lowest PA/Zn ratio (16.51) was recorded where 7.50 kg Zn $ha^{-1}$ was applied. Application of 5 kg Zn $ha^{-1}$ resulted in second lowest PA/Zn ratio (18.23) which was statistically similar to PA/Zn ratio (18.82) recorded in the grain supplied with 2.50 kg Zn $ha^{-1}$. Although, control had lowest PA concentration yet it depicted highest PA/Zn ratio of 81.96.

Table 6. Grain phytate, PA/Zn ratio and estimated Zn bioavailability from wheat as influenced by Zn application rates

| Treatments, | Grain phytate, mg/g | | | Phytate-Zn ratio | | | Estimated Zn bioavailability, mg/300g/day | | |
|---|---|---|---|---|---|---|---|---|---|
| kg Zn $ha^{-1}$ | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean |
| 0.00 | 7.14 bc | 6.53 d | 6.83 C | 75.55 b | 88.37 a | 81.96 A | 0.33 e | 0.27 e | 0.30 D |
| 1.25 | 7.85 a | 6.92 b-d | 7.39 A | 21.38 c | 21.41 c | 21.39 B | 0.97 d | 0.98 d | 0.97 C |
| 2.50 | 7.45 ab | 6.90 b-d | 7.18 AB | 19.64 d | 18.00 e | 18.82 C | 1.04 cd | 1.14 bc | 1.09 B |
| 5.00 | 7.31 a-c | 6.81 cd | 7.06 A-C | 18.23 e | 18.23 e | 18.23 C | 1.11 bc | 1.13 bc | 1.12 B |
| 7.50 | 7.17 bc | 6.83 cd | 7.00 BC | 17.26 e | 15.75 f | 16.51 D | 1.17 b | 1.27 a | 1.22 A |
| Mean | 7.384 A | 6.799 B | | 30.41 B | 32.35 A | | 0.924 B | 0.957 A | |
| Tuckey's HSD $_{(0.05)}$ | | | | | | | | | |
| Zn | | 0.333 | | | 0.748 | | | 0.057 | |
| Yr | | 0.146 | | | 0.329 | | | 0.025 | |
| Zn × Yr | | 0.557 | | | 1.254 | | | 0.096 | |

Means sharing similar letters in a column are statistically similar to each other at *p≤0.05*. Data is average of 3 replicates.

Bioavailability of Zn to human on the basis of trivariate mathematical was also calculated (Table 6). The current study showed that application of had significant role in improving Zn bioavailability to human (Table 6). Highest bioavailable Zn (1.22 mg/300g/day) was recorded with the application of 7.50 kg Zn $ha^{-1}$. Zn bioavailability observed with the application of 2.50 and 5.00 kg Zn $ha^{-1}$ were 1.09 and 1.12 mg/300g, respectively. Lowest bioavailability (0.30 mg/300g) was depicted by control where Zn was not applied.

Better nutrient use efficiency is added quality of contemporary wheat genotypes. Therefore, Zn use efficiency was calculated (Table 7). The results showed that higher input rates have inverse relation with nutrient use efficiency. Higher efficiencies were recorded at lower Zn application rates. Highest Zn recovery efficiency (16.40%) was recorded with the application of 1.25 kg Zn $ha^{-1}$. Whereas, lowest recovery efficiency (4.23%) was found where 7.50 kg Zn $ha^{-1}$ was applied which was statistically comparable to the recovery efficiency (5.14%) found with application of 5.00 kg Zn $ha^{-1}$. Likewise, in case of agronomic efficiency lowest efficiency (162.50 kg $kg^{-1}$) was recorded in the plant treated with 7.50 kg Zn $ha^{-1}$ while highest (716.76 kg $kg^{-1}$) was observed with the application of 1.25 kg Zn $ha^{-1}$. Higher Zn inputs has non-significant effect on physiological efficiency. Lower efficiency (9.24 kg $kg^{-1}$) was recorded with the application of 7.50 kg Zn $ha^{-1}$. Whereas, highest (10.23 kg $kg^{-1}$) was recorded with 5.00 kg Zn $ha^{-1}$.

Table 7. Zinc use efficiency of wheat as influenced by Zn application rates

| Treatments | Recovery efficiency, % | | | Agronomic efficiency, kg $kg^{-1}$ | | | Physiological efficiency, kg $g^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| kg Zn $ha^{-1}$ | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean | 2016-17 | 2017-18 | Mean |
| 0.00 | 15.93 a | 16.86 a | 16.40 A | 466.67 b | 966.67 a | 716.67 A | 3.75 b | 16.31 a | 10.03 A |
| 1.25 | 6.52 c | 10.19 b | 8.35 B | 266.67 e | 412.50 c | 339.58 B | 5.81 b | 13.90 a | 9.85 A |
| 2.50 | 5.16 cd | 5.12 cd | 5.14 C | 200.00 f | 316.67 d | 258.33 C | 5.42 b | 15.04 a | 10.23 A |
| 5.00 | 4.85 d | 3.61 d | 4.23 C | 130.56 g | 194.44 f | 162.50 D | 5.02 b | 13.46 a | 9.24 A |
| 7.50 | 8.115 B | 8.944 A | | 262.97 B | 472.49 A | | 5.00 B | 14.68 A | |
| Mean | 15.93 a | 16.86 a | 16.40 A | 466.67 b | 966.67 a | 716.67 A | 3.75 b | 16.31 a | 10.03 A |
| Tuckey's HSD $_{(0.05)}$ | | | | | | | | | |
| Zn | | 0.941 | | | 8.36 | | | 2.07 | |
| Yr | | 0.491 | | | 4.37 | | | 1.08 | |
| Zn × Yr | | 1.614 | | | 14.35 | | | 3.55 | |

The relative grain yield was plotted against grain Zn concentration and Zn application rates to calculate critical internal and external requirements of Zn to attain near maximum (95%) relative grain yield (Figure 2). The critical internal requirement of wheat for near maximum yield was calculated as 36.53 µg $g^{-1}$. Similarly, critical external Zn requirement to attain near maximum grain yield of wheat was found to be 4.48 kg $ha^{-1}$.

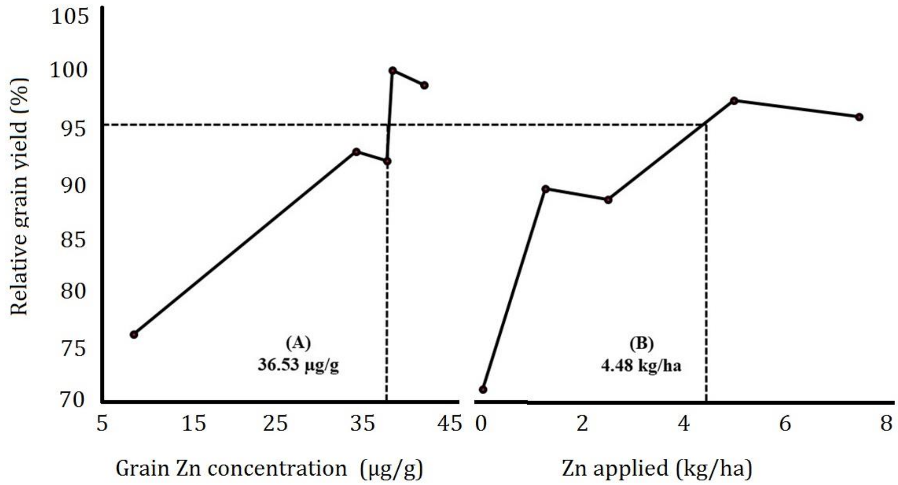


Figure 2. Critical internal (A) and external (B) Zn requirements of wheat to achieve near maximum grain yield

## Discussion

Application of Zn had significant effect of wheat growth and productivity. Zn application enhanced plant height, number of tiller per plant and spike length (Table 2). Likewise, Grain, straw and total biomass yields of wheat were also enhanced (Table 3). Lower average yield during 2017-18 was due to higher temperature (Figure 1) throughout the growing season as compared to 2016-17. Kutman et al. (2011) explained this stimulating effect of Zn to improve plant growth and development. Increased growth and development of plants is attributed to the role of Zn as co-factor of all the six classes of enzymes (Imran et al., 2015). Application of Zn increased the wheat growth and yield, this increment is due to the role of zinc in plant enzymatic functions, pollination and grain development (Kaya and Higgs, 2002). Pedda Babu et al. (2007) reported better grain yield due to increased translocation and synthesis of carbohydrates in grains due to Zn fertilization. Muthukumararaja and Sriramachandrasekharan (2012) also found similar results they reported 80-100% increase in the crop yield with the application of Zn in a pot experiment. While, with the 97% increase in grain yield has been reported by Fageria et al. (2011) in response to Zn application to the rice.

Zn application improved its concentration in wheat grains and straw appreciably (Table 4). In grains the increment was found almost 5 times higher than of control. Similarly, highest Zn concentration in straw was found four times higher than control. Zn accumulation in grains and straw was also improved with Zn application (Table 5). Accumulation in wheat grains supplied was almost eight times higher than control upon application of 7.50 kg Zn $ha^{-1}$. Similar pattern of increase was observed in Zn accumulated in wheat straw where highest accumulation was 6 times higher than control. Chen et al. (2017) explained increased Zn bioavailability to plants through calcareous soils upon application of Zn fertilizer. Cakmak et al. (2010) explained role of improved protein synthesis and activity due to better enzymatic functions in plants, in increasing Zn concentration in vegetative parts and Zn translocation into grains. Kutman et al. (2012), Barunawati et al. (2013), Sperotto et al. (2013) and Akram et al. (2017) also found similar results when Zn was applied to different crops.

Phytic acid is indigestible in human yet, its concentration is important for grain vigor and plant functions. PA acts as cation source, precursor to the cell wall, energy and P storage in seeds/grains. Reduced availability of PA bound micronutrients to human is the only negative effect of high PA concentration in grains (Harland and Morris, 1995). The results showed slight decrease in the phytaic acid concentration in grains with increasing Zn application rate (Table 6). Overall, this decrease was found non-significant. However, Erdal et al. (2002) found appreciable decrease in the PA concentrations in seeds of wheat genotypes with agronomic Zn biofortification. They explained this decrease was due to the dilution effect of increased grain yield of wheat. However, Zhang et al. (2012) reported that application of up to 50 kg $ZnSO_4{\cdot}7H_2O$ $ha^{-1}$ did not affect PA concentration in wheat products. In agreement with the Zhang et al. (2012) the present study showed overall insignificant changes in grain PA concentrations in response to different Zn input levels. Despite of the dilution effect due to increase in the grain yield the change in grain PA concentration was minimal. It suggests that PA concentration was independent of grain Zn concentration. The PA/Zn ratio decreased with increased Zn input (Table 6). This was indicator to attainment of biofortified wheat grains. These results were in agreement with Ma et al. (2005), Morris and Ellis (1989) and Lim et al. (2013). Ryan et al. (2008)

found the lower PA/Zn ratio with increased grain Zn uptake. Hussain et al. (2013) also advocated that lower PA/Zn ratio is more desirable for increased Zn bioavailability to human.

Ideally, 3mg Zn must come from 300g of wheat products to meet daily Zn requirement of an adult (Rosado et al., 2009). In the present study, the Zn bioavailability was lower irrespective of higher Zn concentration in grains. This was due to higher PA concentration in whole grain especially in wheat bran (Liu et al., 2017). According to Ryan et al. (2008) PA/Zn ratio and PA/Ca ratio were found lower in refined flour than whole grain. Moreover, Erdal et al. (2002) and Tang et al. (2008) have reported that among the wheat varieties the Zn and PA concentrations vary significantly.

Zn use efficiency (ZnUE) in wheat was decreased significantly with increasing Zn application levels (Table 7). Also the diminishing response of grain yield to higher input rates explains the low Zn use efficiency with high Zn rates due to poor distribution and formation of insoluble products of Zn applied at high rates (Genc et al., 2002; Figeria et al., 2011).

## Conclusion

The present study reinforces the concept of agronomic biofortification of wheat to achieve higher yield and quality of produce. We can conclude that Zn application affects wheat growth and yield appreciably. Zn fertilization increases Zn concentration in grains and subsequently improves Zn bioavailability to human. Increased Zn accumulation is a direct indicator to higher Zn bioavailability. Higher Zn accumulation lowers the PA/Zn ratio. The Zn use efficiency is also affected by the Zn application rate. Zinc application is very critical to attain near maximum yield potential of wheat.

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