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PHOSPHORUS FORMS IN CALCAREOUS SOIL AS AFFECTED BY IRRIGATION WATER SALINITY

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Abstract: This study was carried out on five calcareous soils of Egypt characterized by different content (%) of calcium carbonate ($CaCO_3$) and other physical and chemical properties to study their content of different forms of phosphorus and its affected by soil properties and irrigation water salinity. The tested calcareous soils were used in a greenhouse experiment, where these soils were planted by barley and irrigated by tap water and four sources of artificial saline water. The artificial saline water were prepared at 1000 and 2500 mg TSS/l (A1 and A2). Each level of TSS (total soluble salts) have one values (B1 or B2) of sodium adsorption ratio (SAR) of 6.31 and 23.26 for A1 and 9.97 and 36.11 for A2. Plants were harvested at harvesting stage. The dry matter yield of the harvested plants was measured and also its content of P was determined. Some chemical properties of the studied calcareous soils and the content of different P forms .i.e. total, available, organic, inorganic, calcium, aluminum and iron phosphate (T-P,A-P, O-P, I-P, Ca-P, Al-P and Fe-P) were determined. Chemical properties .i.e. pH , EC and the content of soluble ions were increased with the increase of irrigation water salinity and sodicity . The found changes in these properties were varied from soil to another. Dry matter yield of barley plants (straw and grains) and its content of P were clearly decreased with the increase of soil content of $CaCO_3$ and increase of irrigation water salinity and sodicity .The level of this negative effect on grains was high than that found with straw. Generally the studied calcareous soils characterized by low content of P. Most of this content was found in I- P form (>90% of T-P). The major fraction of I-P was Ca-P followed by Al-P. The content of different P-forms was related with the studied soil properties. Irrigation water salinity and sodicity have a clear effect on calcareous soils content of P-forms especially O-P, Al-P and Ca-P. The conclusion of this study is : under similar conditions some sources of saline water may be used in irrigation especially at the short-term of the earlier periods of calcareous soils reclamation.
Key Words: Calcareous soils, Salinity, Sodicity, Phosphorus, Barley

1. INTRODUCTION

Calcareous soils cover more 30% of the earth's surface and their $CaCO_3$ content varies from a few percent to 95% (Marschnen, 1995). Calcareous soils occur naturally in arid and semi-arid zones as well as humid and semi-humid zones particularly where their parent material is rich in $CaCO_3$ (Brady and Weil, 1999). In Egypt the newly reclaimed soils at Nubaria and Borg El-Arab regions cover more than 900.000 fed. of which 290.000 fed. are calcareous soils (Moursy, 2002). These soils are distributed to graduates, beneficiaries and private sector for agricultural utilization . Also, these soils are mainly characterized by slightly alkaline reaction, poor fertility, low organic matter content and poor physical properties.

Since barley is a major cereal crop in such soils for human and animal feeding as well as in many industries. Therefore, more efforts and studies are necessary to improve its productivity.

Surface irrigation with water from shallow wells is utilized on approximately about 30% of irrigated land in Egypt. The quality of the well water is variable with some areas using water with high sodium and total electrolyte concentrations. However, the impact of the water quality on the soil structure, infiltration function and irrigation performance is not always recognized and the quality of the water used for irrigation is not always reported. Hence, few workers have been able to distinguish the physio-chemical impacts associated with the quality of the water applied (El_Sheikh 2000).Phosphorus is very important element to plant and plays a role in metabolic process such as the conversion of sugar into starch and cellulose. As a result, phosphorus deficiency causes stunting delayed maturity and shriveled seed (Basak, 2006).

This study was carried out on some calcareous soils of Egypt varied widely in their properties to evaluate its content of different P forms. Also, effect of irrigation water quality on: 1)Soil chemical properties, 2) The content of different P forms and 3) Plant growth were studied.

2. MATERIAL AND METHODS

2.1. Soil Sampling

In this study, five surface (0-20 cm) samples of different soils represent calcareous soils of Egypt were selected from different five locations i.e. 1- El-Bostan (Behara Governorate); 2-Terat El-Nasr (Alexandria Governorate); 3-Kilo 52 Cairo-Alexandria Desert Road (El-Giza Governorate); 4-El-Nobariya (Behara Governorate); and 5- Borg El-Arab (Alexandria Governorate),. The collected soil samples of each locations were air dried, good mixed and ground to pass through a 2mm sieve. Fine soils(<2mm) were kept and analyzed for some physical and chemical properties and the content of different P forms according to Black(1965) Cottenie et al. (1982) and Page et al (1982) . The obtained data were recorded Table (1).

2.2. Irrigation Water

Five solutions (Tap water or Nile water and four of artifices solutions) varied in their salinity and sodicity and also in their content of Na^+, Ca^{2+} and Mg^{2+} were used in this study. The chemical composition of these solution was recorded in Tables 2 and 3.

2.3. Greenhouse Experiment

This experiment was carried out to study the effect of salinity and sodicity irrigation water on some soil properties P-forms and plant growth. Plastic pots (75 pot) with 20 cm in diameter and 18 cm depth were used in this study. The pots were divided into five main groups (15 pot for each group). Five kg of one soil were placed in each pot of these groups. All pots were fertilized by super phosphate (15.5 % P_2O_5) at application rate of 1.50g super phosphate /pot(300kg fed^{-1}). After that, the pots of each main group were divided into five sub groups (3 pots for each sub group) which represent treatments of the used irrigation solutions. The pots were arranged in split design with three replicates. Each pot was planted with ten seeds of barley and irrigated with tap water to about 60% of water holding capacity of each soil. After 15 days from sown, the plants were thinned to five plants for each pot. Each pot was fertilized with ammonium nitrate (33.5% N) at 0.75 g NH_4NO_3 /pot (equivalent to 50.25 Kg N fed^{-1}) and potassium sulphate (48-50% K_2O) at 0.3g K_2SO_4/pot(equivalent to about 29.4 Kg K_2O fed^{-1}). After that, the pots were irrigation with the tested irrigation solutions. The pots were irrigated every three days by alteration between artificial saline solution and tap water or Nile water by 2:1. The moisture content of pots must be still at 60% of water holding capacity of each soil. The plants were harvested above the soil surface and the spikes were separated from straw. Also, the grains were separated from the spikes. The separated straw and grains were air-dried, oven dried at 70° C until their weights became constant, weighted and kept for the content of P.

2.4. Plant Analysis

0.2 g of the ground oven dry plant sample was digested with 5 ml of concentrated H_2SO_4 on sandy hot plate. Repeatedly small quantities of concentrated $HClO_4$ were added until the digest became clear and uncolored. The digest was diluted to 50 ml with distilled water (Cottenie, et al, 1982). Phosphorus (P) was determined in the digest using the ascorbic acid method of Murphy and Riley (1962).

Table 1. Some physical and chemical properties of the studied calcareous soils

Soil properties.	Soil number				
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Particle size distribution*, (%)					
Coarse sand	67.0	39.8	51.6	43.5	19.4
Fine sand	24.5	29.0	14.8	5.6	22.1
Silt	3.5	10.0	13.1	19.3	12.1
Clay	1.2	9.8	1.1	2.2	4.2
Texture. class	Sand	Sand- loamy	loamy-sand	sand - loam	sand – loam
Total Ca CO_3%	3.80	11.40	19.40	29.40	42.20
Active $CaCO_3$,%	1.00	4.60	10.00	14.00	18.80
W.H.C,%	25.70	27.40	30.70	33.40	40.50
O. M,%	0.30	0.40	0.90	1.76	1.87
pH **	7.87	7.88	7.92	8.10	8.01
E C***,dSm^{-1}	1.61	2.83	12.65	8.20	7.22
Soluble ions, meq/100g					
CO_3^{2-}	0.00	0.00	0.00	0.00	0.00
HCO_3^-	1.56	1.56	2.25	1.30	1.82
Cl^-	6.93	11.88	82.67	60.30	43.46
SO_4^{2-}	7.68	14.85	41.58	20.43	26.99
Ca^{2+}	6.42	10.16	31.27	19.02	23.00
Mg^{2+}	2.85	6.83	22.90	11.46	19.54
Na^+	6.50	10.40	69.62	50.42	28.43
K^+	0.40	0.90	2.71	1.10	1.30
Phosphorus (P) forms (mg/kg)					
T-P	24.77	73.45	92.10	76.37	33.71
A-P	0.21	0.62	0.72	0.57	0.22
O-P	2.97	7.45	10.96	9.96	4.39
I-P	21.59	65.39	80.42	65.84	29.10
Ca-P	14.68	45.10	56.86	49.10	22.58
Al-P	2.42	7.32	8.80	7.15	3.00
Fe-P	0.15	0.44	0.52	0.42	0.18
Res-P	4.33	12.53	12.24	9.17	3.33

* = With Ca CO_3 removal , ** = In 1:2.5 (soil : water) susp. , *** = In soil saturated extract

2.5. Soil Analysis

After plant harvesting, the soil of each pot was token, air-Aried ground and seined through a 2mm sieve. The fine soils were analyzed for some chemical properties according to Cottenie et al. (1982) and Page et al (1982) . Also, the content of different P forms was determined as follows.

Determination of P concentration in different forms was performed according to the methods described by Olsen and Sommers, (1982) and (Editorial Committee for Methods of Soil Environmental Analysis, 1997).

Total P concentration was determined after dissolution with Na_2CO_3 extracted by 0.5N sodium bicarbonate according to Olsen et al., (1954) and determined colorimetrically by ascorbic acid according to Murphy and Riley (1962).

Available –P was extracted by 0.5N sodium bicarbonate according to Olsen et al. (1954) and determined colorimetrically by ascorbic acid according to Murphy and Riley (1962).

Organic P concentration was calculated by subtracting the concentration of inorganic P from that of total P.

Fractionation of inorganic P was subjected to the methods proposed by Editorial Committee for Methods of Soil Nutrients Analysis, (1970). In this fraction no occluded Ca-bound P (Ca-P), Al-bound (Al-P), and Fe-bound (Fe-P) were sequentially extracted with 2.5% CH_3COOH, 1M NH_4 F, and 0.1 M NaOH, respectively. The amount of P in the extracted solution was determined colorimetrically. The concentration of occluded P was calculated by subtracting the concentration of total Ca-P, Al-P and Fe-P from that of inorganic P.

3. RESULTS AND DISCUSSION

3.1. Soil Chemical Properties

The chemical properties (soil pH, EC and soluble ions) of the studied calcareous soils as affected by irrigation water content of total soluble salts (TSS) as EC and Na^+ and values of SAR were recorded in Table(4). These data show that, the soil pH was increased by different treatments of irrigation . Generally the obtained data of pH indicate that, the studied soils takes the order : soil 4 > soil 5 > soil 3 > soil 2 > soil 1. This results are in agreement with the results obtained by (Al- Busaid and Cookson 2003) .The relationships between soil pH and TSS , Na^+ and SAR were by the straight linear equations as follows:

$y = 2E\text{-}08 (TSS)^2 + 3E\text{-}05\ TSS + 7.8516$

(r=0.94) ……..(1)

where y: pH value , TSS =total soluble salts. (mgl^{-1})

$y= -0.0002(SAR)^2 + 0.0152\ SAR + 7.8087$

(r=0.88)……………………………………...….(2)

where y: pH value , SAR =sodium adsorption ratio.

$y = -2E\text{-}08(Na^+)^2 + 0.0001\ Na^+ + 7.8304$

(r=0.90)……………………………..………...(3)

where y: pH value , Na^+= concentrations Na^+ (mgl^{-1})

The increase in total soluble salts, Na^+ concentrations, and SAR of water led to an increase in soil EC (Table, 4). In this respect Abou Hussien et al (2009) and Shalaby, et al (2009) obtained on similar results. To explain the relation between the three properties of the used irrigation water and soil EC , may be ploted the data of three properties against soil EC and derived the equation described these relations .These equations revealed that all found relationships were positive and highly significance. These relations were:

$y = -2E\text{-}06(TSS)^2 + 0.0071x + 1.5407$

(r = 0.74) ……………………………………….(4)

where y: EC value(dSm^{-1}) , TSS =total soluble salts. (mgl^{-1})

$y = -0.0114(SAR)^2 + 0.5144x + 2.2523$

(r = 0.80) …………………………………..……(5)

where y: EC value(dSm^{-1}) , SAR =sodium adsorption ratio.

$y= -3E\text{-}06(Na^+)^2 + 0.0082x + 2.1261$

(r = 079)…………………………………………..(6)

where y: EC value(dSm^{-1}) , Na^+= concentrations Na^+ (mgl^{-1})

Table 2. Chemical analysis of tap or Nile water (Co)

pH	EC dSm^{-1}	Soluble ions ($meql^{-1}$)								SAR
		Cations				Anions				
		Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	
7.80	0.37	1.14	1.21	1.15	0.20	0.00	1.81	0.94	0.95	1.06

Table 3. Chemical composition of the artificial saline solutions

Artificial saline solutions	Na Cl		$CaCl_2$		$MgCl_2$		SAR	TSS mgl^{-1}	Na+ Conc. meq/l
	$mg1^{-l}$	$meql^{-1}$	mgl^{-1}	$meql^{-1}$	$mg1^{-l}$	$meql^{-1}$			
A1B1	666.6	11.39	166.7	3	166.7	3.51	6.31	1000	666.6
A2B2	950	16.23	25	0.45	25	0.52	23.26	1000	950
A2B1	1666.6	28.48	416.7	7.5	416.7	8.77	9.97	2500	1666.6
A2B1	2375	40.52	62.5	1.12	62.5	1.36	36.11	2500	2375

Similar results were obtained by Ragab et al (2008) and Fayed (2009). The studied calcareous soils could be arranged based on their EC values in the following order: soil4>soil5~soil3>soil2>soil1. The effect of irrigation water properties on the studied calcareous soils content (meql^{-1}) of soluble ions (cations and anions) are shown in Table (4). The obtained data show that, increasing total soluble salts , Na^+ ions and SAR of irrigation water, increase the content of soluble ions in the studied soil solutions. These results are in agreement with those obtained by Abou Hussien et al. (2009) and Shalaby et al (2009).

3.2. Phosphorus Forms (P-forms)

The presented data in Table (5) show, the studied calcareous soils content (mg kg^{-1}) of P-forms under study was dissimilar where this content varied from soil to another and also was related with salinity and sodicity levels of irrigation water. The arrangement of the soils according to their content (mg kg^{-1}) of total – P (T-P) was soil3>soil4> soil2>soil5> soil1. This order was in relation with studied soil properties especially their content (%) of total and active $CaCO_3$, clay and O.M and EC values(dSm^{-1}). The content of T-P was increased with the increase of soil content of $CaCO_3$, clay and OM. This positive effect was resulted from the effect of these factors on the decrease of rate of decomposition processes of P compounds. Similar findings were reported by (Abd Alla et al , 2007 and Alshahri, 2008).

The recorded data in Table (5) show increase of irrigation water salinity and sodicity resulted in a decrease of calcareous soils content of T-P. The obtained decrease resulted from the increase of irrigation water sodicity level was higher than that found as a result of increase of salinity level.

This decrease was resulted from the dissolved effect of salinity and sodicity water for some P compounds especially which namely by organic P compounds (Basak, 2006). These results were in agreement with those obtained by Shaban (2005).

Regarding to the calcareous soils content (mg kg^{-1}) of available P (A-P) as recorded in Table (5) it may be noticed that, these soils characterized by low content of A-P where this content was lower than 0.60 mg/kg and also its represent lower than 0.7% of T-P. The low content of A-P resulted from the high content of $CaCO_3$ which converted soil P to un available form (fixed or precipitate) as premonition by Basak (2006).The arrangement of the studied soils according to their content (mg kg^{-1}) of A-P was soil3> soil 2> soil 4> soil 5> soil 1. Similar results were found by Khalil (2000). Also, the calcareous soils content of A-P was in relations with many properties of the studied soils.

The salinity and sodicity levels of irrigation water have a greater and positive effect on calcareous soils content (mg kg^{-1}) of A-P. This positive effect was resulted from the dissolved effect of saline and alkaline solution for organic P compounds. The increase of A-P content associated the increase of water sodicity was higher than that found with the increase of water salinity level. Similar results were obtained by Egashira et al. (2003) and Fayed (2009).

The second main form of P in the studied calcareous soils was a organic form (O-P) where this content represent less than 12% of T-P (Table,5). The high content (mg kg^{-1}) of O-P was found in soil 3 and the lowest one was found in soil1 under different treatments of irrigation water. The content of O-P was in agreement with these soils content of OM. On the other hand, the relationships between the soils content of O-P and either of soil pH or soil content (%) of $CaCO_3$ were negative. (Basak, 2006 and Alshahri, 2008).

Increase of irrigation water salinity or sodicity resulted in a decrease of soil content (mg kg^{-1}) of O-P. The obtained decrease of the content of O-P resulted from increase of irrigation water sodicity was higher than that associated the increase of irrigation water salinity. This decrease resulted from dissolved effect of the used irrigation water of soil O-P compounds (Khalil, 2000 and Egabira et al, 2003).

The main form of P in the studied calcareous soils was inorganic P(I-P) where its represent more than 87% of T-P(Table,5). The calcareous soils content (mg kg^{-1}) of I-P was varied widely from soil to another depending on the soils properties and the treatments of irrigation water where the arrangement of these soils according to their content of I-P was soil 5> soil 4> soil 3> soil 2> soil 1. The high percentages of I-P (% of T-P) revealed to the high content of $CaCO_3$ (%) in these soils (Basak, 2006 and Elshahri, 2008). Similar results were obtained by Ebrahim et al.(2007). Calcareous soils content of I-P was decreased with increase of water salinity and sodicity. This effect may be reviewed to its effect on the studied soils properties and its effect on soil P transformation and solublility (Bayoumi et al., 1997).

3.3. Inorganic-P Fractions

Data in Table (6) show that calcium-P (Ca-P) represent a main fraction of I-P where the content of this fraction represent more than 70% of I-P. These high percentages resulted from the high content (%) of $CaCO_3$ in the studied soils which played a important role in this respect by reaction with P and transferred to un available calcium phosphate (Basak, 2006). So, and based on the prementioned the studied soils takes the following order according to their content (mg kg^{-1}) of Ca-P soil 3> soil 4> soil 2> soil 5> soil 1. This order was related with the studied soils properties (Ebrahim et al, 2007). Increasing water salinity and sodicity, leeds to an increase the content of Ca-P which may be resulted from its effect on dissolving other P forms especially O-P. This positive effect was also found by Bayoumi et al. (1997).

Table 4. Some chemical properties of the studied calcareous soils as affected by saline irrigation water

Studied soils	Irrigation water	pH 1:2.5	EC dSm^{-1}	Soluble ions ($meql^{-1}$)						
				Cations				Anions		
				Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}
Soil1	Co	7.87	2.31	5.92	5.29	10.59	1.30	1.04	8.08	13.98
	A1B1	7.86	2.34	5.70	5.30	11.90	1.40	1.21	14.31	8.78
	A1B2	7.89	2.51	6.86	2.34	14.48	1.42	1.34	16.85	6.91
	A2B1	7.87	3.07	8.35	5.61	15.23	1.51	1.60	15.63	13.47
	A2B2	7.80	3.80	8.81	2.43	25.16	1.60	1.65	18.22	18.13
Soil2	Co	7.88	3.62	9.70	6.53	18.23	1.74	1.66	23.00	11.54
	A1B1	7.88	4.13	12.80	10.19	16.29	2.02	1.77	23.30	16.23
	A1B2	7.90	4.18	12.53	10.40	17.30	1.57	1.84	22.37	17.59
	A2B1	7.88	4.89	18.23	11.32	18.11	1.24	1.86	13.73	33.31
	A2B2	7.91	4.97	21.16	11.27	15.40	1.87	1.94	13.98	33.78
Soil3	Co	7.92	7.78	16.80	11.18	48.64	1.18	2.07	27.01	48.72
	A1B1	7.91	8.22	23.17	12.23	44.73	2.07	2.21	45.66	34.33
	A1B2	7.92	8.37	24.76	13.11	43.80	2.03	2.33	41.15	40.22
	A2B1	7.93	10.13	25.20	19.87	54.02	2.21	2.50	47.60	51.20
	A2B2	7.91	10.56	25.92	20.55	56.80	2.33	2.67	49.80	53.13
Soil4	Co	8.10	6.09	17.78	4.47	37.00	1.65	2.66	39.66	18.58
	A1B1	8.10	6.61	24.48	9.67	29.80	2.15	2.72	38.25	25.13
	A1B2	8.11	6.70	24.72	9.80	30.23	2.25	3.03	32.21	31.76
	A2B1	8.11	7.83	27.15	9.72	38.88	2.55	3.09	40.21	35.00
	A2B2	8.15	7.92	27.36	12.02	37.50	2.32	3.72	38.29	37.19
Soil5	Co	8.01	6.33	18.25	12.42	30.71	1.92	3.64	30.41	29.25
	A1B1	8.01	6.61	22.84	11.65	30.20	1.41	3.67	29.18	33.25
	A1B2	8.02	6.75	22.21	12.23	31.03	2.03	3.71	31.60	32.19
	A2B1	8.01	7.35	28.25	12.42	30.71	2.12	3.86	38.90	30.74
	A2B2	8.05	7.45	29.25	11.31	32.11	1.83	3.92	40.12	30.46

,Calcareous soils content of aluminum-P (Al-P) as mg kg^{-1} or as a percentage of I-P as presented in Table (6) show that, this fraction represent a third main group of I-P, where this fraction represent about 7 to 10% of I-P. Soil properties played an important role on their content of Al-P which decreased with the increase of $CaCO_3$ content. The high content of AL-P (mg kg^{-1}) was found in soil 3 follwed by soil 2 where the lowest one was found in soil 1. Little decrease of soil content of Al-P was found with the increase of irrigation water salinity and sodicity. Ebrahim et al. (2007) obtained on similar results.

Regarding to the studied soils content of iron-P (Fe-P) as mg kg^{-1} and % of I-P, the data of Table (6) show that, the calcareous soils characterized by very low content of Fe-P where its was lower than 1 mg kg^{-1} (lower than 1% of I-P). The content of Fe-P was found in soil 3 folloed by soil 2 and the lowest one was found in soil 1. The low content of Fe-P in the soils under study resulted from low content of these soils of free iron compounds. Little decrease of Fe-P content was found as a result of irrigation by saline and sodic water. The obtained decrease resulted from the effect of the used irrigation water on the properties of calcareous soils especially soil pH and the content of both total and active $CaCO_3$ (El_Sheikh , 2000).

Table 5. The studied calcareous soils content (mgkg-1) of different P forms and its percentages(%) of T-P as affected by soil propertiesand irrigation watersalinity and sodicity

P-form	Irrigation water	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5
		mgkg-1	%of T-P	mgkg-1	%of T-P	mgkg-1	%of T-P	mgkg-1	%of T-P	mgkg-1
T-P	Co	24.12		73.32		89.67		74.11		32.85
	A1B1	22.25		71.35		87.13		72.17		29.83
	A1B2	22.83		71.92		87.72		72.66		30.50
	A2B1	23.11		72.63		88.50		73.15		30.95
	A2B2	23.55		72.75		88.85		73.71		31.60
A-P	Co	0.12	0.51	0.37	0.50	0.40	0.45	0.32	0.43	0.13
	A1B1	0.12	0.55	0.39	0.54	0.44	0.51	0.35	0.48	0.13
	A1B2	0.13	0.57	0.40	0.55	0.46	0.52	0.36	0.50	0.14
	A2B1	0.13	0.58	0.41	0.56	0.47	0.53	0.37	0.51	0.15
	A2B2	0.14	0.61	0.43	0.59	0.51	0.57	0.41	0.56	0.16
O-P	Co	2.53	10.50	7.93	10.82	9.25	10.32	8.27	11.16	3.75
	A1B1	2.33	10.48	7.58	10.63	8.88	10.19	7.83	10.85	3.32
	A1B2	2.32	10.15	7.49	10.42	8.77	10.00	7.83	10.78	3.37
	A2B1	2.32	10.03	7.39	10.17	8.81	9.96	7.71	10.54	3.34
	A2B2	2.31	9.80	7.24	9.95	8.57	9.65	7.50	10.18	3.27
I-P	Co	21.59	89.50	65.39	89.18	80.42	89.68	65.84	88.84	29.10
	A1B1	19.92	89.52	63.77	89.37	78.25	89.81	64.34	89.15	26.51
	A1B2	20.51	89.85	64.43	89.58	78.95	90.00	64.83	89.22	27.13
	A2B1	20.79	89.97	65.24	89.83	79.69	90.04	65.44	89.46	27.61
	A2B2	21.24	90.20	65.51	90.05	80.28	90.35	66.21	89.82	28.33

Table 6. The studied calcareous soils content (mgkg-1) of different I-P fractions and percentages(%) of I-P as affected bysoil propertiesand irrigation, water salinity and sodicity

P-form	Irrigation water	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5	
		mgkg-1	%of I-P	mgkg-1	%of I-P	mgkg-1	%of I-P	mgkg-1	%of I-P	mgkg-1	%of I-P
Ca-P	Co	14.68	60.87	45.10	61.51	56.86	63.41	49.10	66.25	22.58	68.75
	A1B1	13.57	61.00	44.42	62.25	56.92	65.33	48.53	67.25	20.93	70.15
	A1B2	14.39	63.05	46.51	64.67	59.61	67.95	49.96	68.76	21.73	71.23
	A2B1	14.80	64.05	47.85	65.88	61.55	69.55	51.40	70.26	22.65	73.18
	A2B2	15.36	65.22	49.00	67.35	63.06	70.97	53.11	72.05	23.70	75.00
Al-P	Co	2.42	10.05	7.32	9.98	8.80	9.81	7.15	9.65	3.00	9.13
	A1B1	2.21	9.95	6.99	9.80	8.43	9.67	6.73	9.32	2.66	8.93
	A1B2	2.19	9.60	6.77	9.41	8.09	9.22	6.65	9.15	2.68	8.79
	A2B1	2.13	9.20	6.54	9.01	7.94	8.97	6.52	8.91	2.66	8.60
	A2B2	2.12	9.00	6.48	8.91	7.76	8.73	6.35	8.61	2.68	8.48
Fe-P	Co	0.15	0.61	0.44	0.60	0.52	0.58	0.42	0.57	0.18	0.55
	A1B1	0.14	0.61	0.42	0.59	0.50	0.57	0.40	0.56	0.16	0.54
	A1B2	0.13	0.55	0.39	0.54	0.46	0.53	0.37	0.51	0.15	0.50
	A2B1	0.13	0.55	0.38	0.53	0.46	0.52	0.37	0.50	0.15	0.49
	A2B2	0.11	0.48	0.33	0.46	0.40	0.45	0.32	0.43	0.13	0.42
R-P	Co	4.33	20.06	12.53	19.16	14.24	17.71	9.17	13.93	3.33	11.45
	A1B1	4.00	20.08	11.94	18.72	12.41	15.86	8.67	13.48	2.76	10.41
	A1B2	3.80	18.53	10.76	16.70	10.79	13.67	7.85	12.11	2.56	9.44
	A2B1	3.74	17.99	10.47	16.05	9.74	12.22	7.16	10.94	2.15	7.79
	A2B2	3.65	17.18	9.70	14.81	9.06	11.29	6.43	9.71	1.81	6.39

3.4. Dry Matter Yield of Barley Plant

The present data in Table (7) show that, the obtained dry ,matter yield (g pot^{-1}) of barley plants (straw and grains) were greatly affected by soil properties especially the content of $CaCO_3$ where the obtained dry matter yield was decreased with the increase of soils content of $CaCO_3$. So, the high yield of dry matter was found with the plants grown on soil 1 fillowed by that on soil 2. Also, these results reviewed to un suitable conditions in high calcareous soils (high content of $CaCo_3$) to plant growth especially that related with the nutrients availability and water relationships (Khalil, 2000). Barley straw and grains dry matter yield was greater decreased with the increase salinity and sodicity levels of irrigation water. This negative effect was supported from the calculated negative values of relative change (RC,%) which recorded in Table (7). This negative effect was increased with the increase level of irrigation water salinity and sodicity. Also, the negative effect associated the increase in sodicity level was more clear compared with that resulted from the increase of salinity level. Similar results were obtained by Abuo Hassien and Barasoum (2002) and Alshahri (2008).

3.5. Plant Content Of Phosphorus

These data in Tables (8) show that, P uptake (mg pot^{-1}) was decreased with the increase soil content of $CaCO_3$. Thus the high content of P was found in the plants grown on soil 1 followed by that grown on soil 2. Also P uptake by straw were lower than those of grains. Generally, the obtained values of P content were low which resulted from presence high content of $CaCO_3$ which transferred soil P to un available forms (Basak, 2006). With different soils and under the treatments of irrigation water, the obtained values of RC(%) in Table (8)were negative. The negative effect was increased with the increase of irrigation water salinity and sodicity. Also, this effect was become more clear in the soils have high content (%) of $CaCO_3$ Khalil (2000) and Alshabry (2008) obtained an similar results.

$$RC(\%)= \frac{\text{Dry mater yieald of trated plants - Dry matter of untreated plants}}{\text{Dry mater yieald of trated plants}} X100 \qquad ......(7)$$

$$RC(\%)= \frac{\text{P uptake by plants irrigated by salnity water - P uptake by plants irrigated by tap water}}{\text{P uptake by plants irrigated by tap water}} X100 \quad ....(8)$$

Table 7. Dry matter yield (g/pot) of barley plants (straw and grains) and its relative change (RC,%) as affected by thestudied calcareous soils and irrigation water salinity and sodicity

Irrigation water	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5	
	g/pot	RC %	g/pot	RC %	g/pot	RC %	g/pot	RC %	g/pot	RC %
	Straw									
Co	11.32	0.00	10.22	0.00	9.28	0.00	8.33	0.00	7.78	0.00
A1B1	11.07	-2.21	10.15	-0.68	8.95	-2.84	7.74	-7.08	7.62	-2.06
A1B2	10.96	-3.18	10.08	-1.37	8.86	-5.68	7.63	-8.40	7.51	-3.47
A2B1	10.25	-9.45	8.53	-16.54	8.01	-11.14	7.49	-10.08	7.37	-5.27
A2B2	9.38	-17.14	8.49	-16.93	7.98	-23.36	7.47	-10.32	7.29	-6.30
	Grains									
Co	3.89	0.00	3.00	0.00	2.78	0.00	2.56	0.00	2.27	0.00
A1B1	3.64	-6.43	2.99	-0.33	2.69	-3.24	2.38	-7.03	2.22	-2.20
A1B2	3.33	-14.40	2.97	-1.00	2.66	-4.32	2.34	-8.59	2.15	-5.29
A2B1	3.11	-20.05	2.51	-16.33	2.41	-13.31	2.31	-9.77	2.12	-6.61
A2B2	2.84	-26.99	2.49	-17.00	2.40	-13.67	2.30	-10.16	2.11	-7.05

Table 8. P uptake (mg/kg) and its relative change (RC, %) by barley plants (straw and grains) as affected by the studied calcareous soils properties and irrigation water salinity and sodicity

Irrigation water	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5	
	$mgkg^{-1}$	RC %	$mgkg^{-1}$	RC %	$mgkg^{-1}$	RC %	$mgkg^{-1}$	RC %	$mgkg^{-1}$	RC %
Straw										
Co	61.13	0.00	30.66	0.00	13.74	0.00	23.32	0.00	10.11	0.00
A1B1	54.24	-11.26	26.39	-13.93	9.35	-31.95	15.48	-33.63	7.62	-24.66
A1B2	49.32	-19.32	26.21	-14.52	8.21	-40.25	13.73	-41.12	6.01	-40.60
A2B1	37.93	-37.96	15.35	-49.92	6.11	-55.53	10.49	-55.04	4.42	-56.28
A2B2	31.89	-47.83	13.58	-55.69	4.56	-66.81	9.71	-58.36	3.65	-63.96
Grains										
Co	28.40	0.00	18.60	0.00	8.52	0.00	12.29	0.00	9.76	0.00
A1B1	22.20	-21.81	17.94	-3.55	7.12	-16.43	9.52	-22.55	8.66	-11.30
A1B2	18.98	-33.16	16.63	-10.58	5.72	-32.86	8.89	-27.64	6.88	-29.52
A2B1	14.93	-47.43	10.29	-44.67	4.75	-44.25	6.93	-43.60	5.94	-39.19
A2B2	10.22	-64.00	8.96	-51.81	0.00	-100.00	6.67	-45.72	4.64	-52.44

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Research
Araştırma

APPLICATION OF GIS MODEL IN PHYSICAL LAND EVALUATION SUITABILITY FOR RICE CULTIVATION

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Abstract: The objective of this study was to establish spatial model in land evaluation for rice cultivation using GIS in Bafra Plain found in the Kızılırmak Delta and located in the central Black Sea region of Turkey. The study area covers about 4823.7 ha. A land unit resulted from the overlay process of the selected theme layers has unique information of land qualities for which the suitability is based on. The selected theme layers of rice include topographic factor (slope), soil physical factors (soil depth, soil texture, drainage, stoniness, hydraulic conductivity) and soil chemical factors (pH, electrical conductivity, $CaCO_3$ and soil fertility). These theme layers were collected from existing information. Spatial information of soil physical and soil chemical factors were formulated using soil map database. Slope layer of the study area was prepared from DEM. Each land characteristics is also considered as a thematic layer in the GIS. In addition, each of land quality layers with associated attribute data is digitally encoded in a GIS database. After combination of these layers, a resultant map was produced. Land suitability rating model applied to the resultant polygonal layer provided the suitability classes for field crops. Results showed that 79% of the study area is highly and moderately suitable for field crops, whereas 21% of the study area is low and non suitable for rice cultivation due to soil and land conditions. The resultant suitability classes were also checked with field experiment study. 12 rice species were used in experiments. ANOVA was done for grain yield and $LSD_{0.05}$ test was implemented for comparison of mean values in the TARIST statistics package. According to ANOVA results, it was found significantly positive relationship between land suitability classes and grain yield values. The grain yield values were affected at level of $P<0.001$ by land suitability class. In general, the highest grain yield was obtained from rice plots located in S1 class, S2 and S3 classes followed it as well. As for $LSD_{0.05}$ test results, the highest yield values were determined Halil Bey (789.9[a]), Osmancık-97 (760.5[ab]) and Durağan (751.0[b]) in 12 rice species for S1 class while, the highest yield values were found Osmancık-97 (696.1[a]), Şumnu (688.8[ab]) and Neğiş (654.1[bc]) in 12 rice species for S3 class.
Key Words: Land suitability, Soil map, GIS, Rice cultivation

1. INTRODUCTION

Rice is not only the staple food for nearly half of the World's population relying on rice as the major daily source of calories and protein, but also a key source of employment and income for the rural people (FAO, 2003). It ranks as second the main agricultural production in most of Asian countries. Rice is grown in 156 million hectares and the production is 660 million tons in the World (Gençtan, 2009). Rice is also an important cereal crop for Turkey. Rice is grown in every part of Turkey, however, Marmara especially Europe part of Marmara (Thrace) and Black Sea region are the main rice production areas respectively. Turkey has approximately 27.5 million ha total cultivable area only, very small part of it (about 80,000 ha) has been cultivated with rice and total production is about 156.000 tons (Gençtan, 2009). Although most regions in Turkey ecologically are suitable for rice cultivation, this area and rice production in Turkey are not enough for domestic consumption (Sürek, 1998). Rice imports have therefore increased in the last decades. To cope with this problem, it should be increased cultivated rice area.Efficient management of natural resources is essential for ensuring food supplies and sustainability in agricultural development. The task of meeting the demands of man without affecting the ecological assets for the future generations is being given top priority by both scientists and planners. It is indicated that there is an urgent need to match the land resource and the land use in the most possible and logical way to continue sustainable production and to meet the needs of society while conserving fragile ecosystem FAO (1993). The management and analysis of large volumes of spatial data requires computer based systems called Geographical Information System (GIS) which can be used for solving complex geographical and hydrological problems (Garg, 1991). Geographical information system is defined as a system of computer hardware and software designed to allow users to collect, manage, analyse, and retrieve large volumes of spatially referenced data collected from variety of sources (Aronoff, 1991). However, traditional management ability has generally been limited for two reasons: the difficulty in acquiring useful information over vast areas and the lack of a means for effective process and analyse the acquired data (Champbell, 1987). Due to many factors that are associated with each feature under study, analysis, manipulation, and using manual methods cost too much. Besides, they consume too much time or practically impossible. Today advanced computer programs including decision support systems (Geographic Information System and Remote Sensing) contribute to the speed and efficiency of the overall planning process and allow access to large amounts of useful information quickly. Especially during the last decade, GIS and RS have received much attention in application related to resources at large spatial scales (Green, 1995; Hinton, 1996). Therefore, GIS is a powerful tool for management and analysis of data required for any land developmental activity. Therefore, systematic approach to produce information on the suitability is needed.Perera et al. (1993) studied that GIS based research has been carried out to extract new land for rice cultivation in south Sri Lanka with special concern on environmental conservation. The locations of the worth considering lands and impractical lands for paddy cultivation were analyzed and merged with the GIS data base by a specially arranged point system. According to their study, more than 72% of the selected land was classified as highly suitable or suitable for rice cultivation. In addition, Mongkolsawat and others (2002) who studied to establish spatial model in land evaluation for rice using GIS in the lower Namphong watershed located in Northeast Thailand determined the highly suitable land cover an area of about 208.3 km^2 and some 17.7 % of the watershed is unsuitable area for rice which corresponds to the slope land. The resultant suitability class were checked against the rice yield which collected by the Department of Agriculture Extension and they found that it was to be satisfactory.The main objectives of this study are to identify the most suitable areas for rice cultivation while conserving the environment and to establish spatial model in land evaluation for rice cultivation which is based on GIS and digital mapping.

2. MATERIALS AND METHODS

2.1. Description of The Study Areas

This study was carried out in the Bafra Plain found in the Kızılırmak Delta and located in the central Black Sea region of Turkey (Figure 1). The study area (around the Doğanca village) is far 10 km from north of the Samsun-Bafra district (4615-4615 km N- 243-250 km UTM), It covers 4823.7 ha and its lies at an elevation from sea level 1-3 m. The current climate in the region is semi-humid. The summers are warmer than winters (the average temperature in July is 22.2 and in January is 6.9 °C). The mean annual temperature, rainfall and evaporation are 13.6 ºC, 764.3 mm and 726.7 mm respectively. According to Soil Taxonomy (1999), the study site has mesic soil temperature regime and ustic moisture regime. These areas are mainly flat and slightly sloped (0-2 %). The majority of soils were Vertisol, Inceptisol and Entisol in Soil Taxonomy (1999). Top soil texture is heavy (31-60 % clay), while sub soil texture is different due to alluvial deposit in the study area. Soil organic matter content ranges from 1.70 % to 5.92. EC and pH values of soils are changing 0.61-2.79 dS m^{-1} and 7.28- 8.01. The study area has been under intensive agricultural activities. Rice, maize, pepper, watermelon, cucumber and tomato with sprinkler and furrow irrigations in the summer, and cabbage and leek in the winter have been produced in the study area.

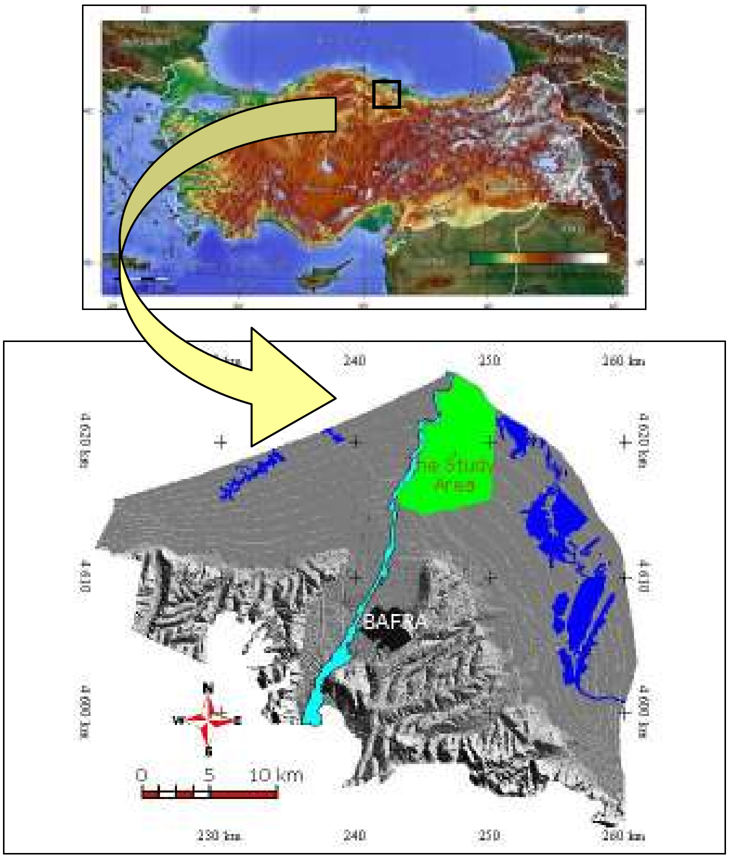

Figure 1. Location of the study area

2.2. Methods

Land utilization types were described by a set of land-use requirements or land quality parameters, which are the land conditions necessary for successful farming, while land map units were described by a set of land characteristics, which are land attributes that influence their suitability for given land utilization types (Van Diepen et al., 1991). Land utilization type is rice in this study. Land-use requirement of rice, in terms of topographic and soil physico-chemical criteria were reviewed from FAO (1983 and 1985), Sys et al (1993), Mongkolsawat et al. (2002), Bunting (1981), Yamada et al. (1995), Sönmez (2003) ve Özcan (2004). These criteria are commonly implemented in physical land evaluation using Table 1.

In order to develop a set of themes for evaluation and ultimately to produce a suitability map for rice, soil and topographic data were taken from digital soil map of the study area. In addition, results obtained from experimental reports and regional experiences were adopted to identify land quality as related to rice ecological conditions. The land qualities used for this evaluation include two main indexes; Nutrient Availability Index (NAI) and Soil Quality Index (SQI). NAI were calculated using the following formulas

$$NAI = N \times P \times K \times Zn$$

Table 1. Factor rating of land quality parameters for rice

Land quality parameters			Factor rating			
	Diagnostic Factor	Unit	1.0	0.8	0.5	0.2
			> □0.60	0.40-0.60	0.10-0.40	< 0.10
I. Nutrient Availability Index (NAI)	NAI= N*P*K*Zn					
	N P K Zn	% ppm ppm ppm	>0.2 >25 >60 >0.7	0.1-0.2 10-25 30-60 0.7-0.5	<0.1 <10 <30 <0.5	- - - -
II. Soil Quality Index (SQI)	SQI = R*T*D*F*Y*P*G* S*K*H					
Derange (R)		-	Very Poor	Poor	Moderately good	Good/excessive
Texture (T)		%	CL, SiCL, SiL, C, SC	L, SCL, SiC	Si,SL, fSL	G, S, LS
Depth (D)		cm	> 50	25-50	15-25	< 15
Topography (F)	Landform and slope	-	Flood plain or 0-2%	Low terrace or 2-4%	Middle terrace or 4-6%	High terrace/ mountain or >6%
Surface Stoniness (Y)	> 2 mm	%	< 20	20-35	35-55	> 55
Hard Pan (P)		cm	> 90	90-50	50-20	< 20
Hydraulic conductivity (G)		cm/h	< 0.5	0.5-2.0	2.0-6.25	> 6.25
Salinity hazard (S) or ESP		dS/m (%)	0-3.1 10	3.2-4 10-20	4.1-5 > 20	> 5.1 > 20
Lime (K)		%	0-5	5-15	15-20	> 20
Soil reaction (H)	pH	-	5.5-7.3	7.4-7.8 5.1-5.5	7.9-8.4 4.0-5.0	> 8.4 < 4.0

Second formulation is SQI given as follow;

SQI = R*T*D*F*Y*P*G* S*K*H

Spatial information on each diagnostic characteristic of NAI and SQI was obtained from land mapping units. Each of land characteristics or factors with associated attributed data was digitally encoded in a GIS database to eventually form two thematic layers. The diagnostic properties of each thematic layer were assigned values of factor rating an identified in Table 1. The evaluation model is defined using the value of factor rating as follows;

SI = NAI * SQI

Where; SI: Suitability Index, NAI: Nutrient Availability Index, and SQI: Soil Quality Index

These two layers were then spatially overlaid to generate a land suitability map. Application of the model to the resultant layer yields a suitability map with four classes according to the resultant values proposed in Table 2.

Schematic chart of the spatial overlay showing the land characteristics and model is illustrated in Figure 2.

2.3. Statistical Analysis

To assess the reliability of the methodology developed, the suitability classes were checked against the rice yield. For this purpose, statistical analyses were performed by using TARIST (1994) statistics package. ANOVA and $LSD_{0.05}$ were done for grain yield values. Field experiment was settled in each suitability class according to randomized block design with three replicates. 12 rice types (Şumnu, Osmancık-97, Gönen, Beşer, Durağan, Halilbey, 7721, Karadeniz, Kızılırmak, Koral, Neğiş and Aromatik-I) were planted in each block.

Table 2. Suitability evaluation of rice

Definition	Suitability Class	Index Value
Highly Suitable	S1	1.00-0.250
Moderate Suitable	S2	0.250-0.100
Marginally Suitable	S3	0.100-0.025
Unsuitable	N	< 0.025

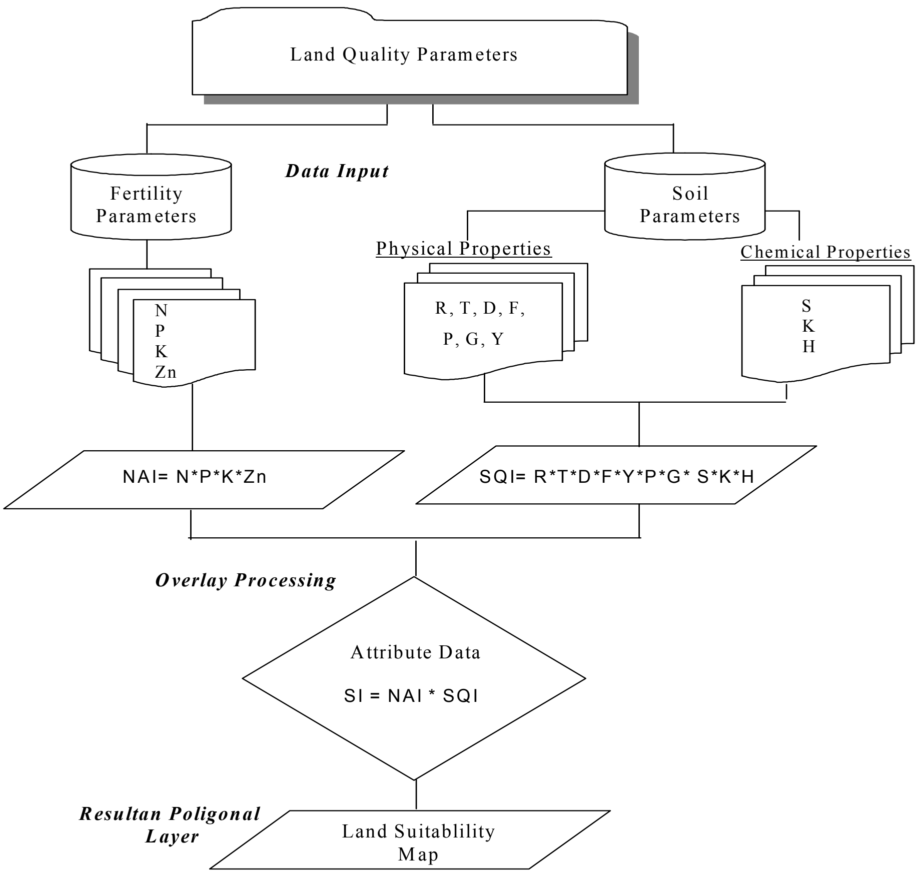

Figure 2. Schematic chart of GIS application to land suitability for rice

3. RESULTS AND DISCUSSION

Land mapping units are adopted as a basis for physical land evaluation in this study. These units are based on combinations of depth, drainage, texture, hydraulic conductivity, surface stoniness, had pan, pH, salinity hazard and lime content There are 20 soil mapping units which are identified in soil map. The description and extent of land mapping units are shown in Figure 3.

Land suitability classification involves the comparison of the land qualities of a land mapping unit or the values of the diagnostic factors for a land mapping unit with the requirements of a land utilization type (expressed in terms of factor ratings). This comparison is part of matching process. This partial suitability for separate land qualities must be combined to come the overall suitability of the land mapping unit for land utilization type (rice). The suitability map resulting from the spatial overlay of factors in the study area is presented in Figure 4. The area of suitability evolution is shown in Table 3. The study provides an approach to identify parametric values in modeling the land suitability for rice. The theme layers to be input in the modeling are assigned the rating value as attribute data. Overall insight into the factors affecting the suitability of land can be provided spatially and quantitatively. The result indicated that the highly and moderately suitable land cover an area of about 3811.6 ha (79 %). 10.8 % of the study area is unsuitable area for rice which corresponds to soil physical and chemical properties.

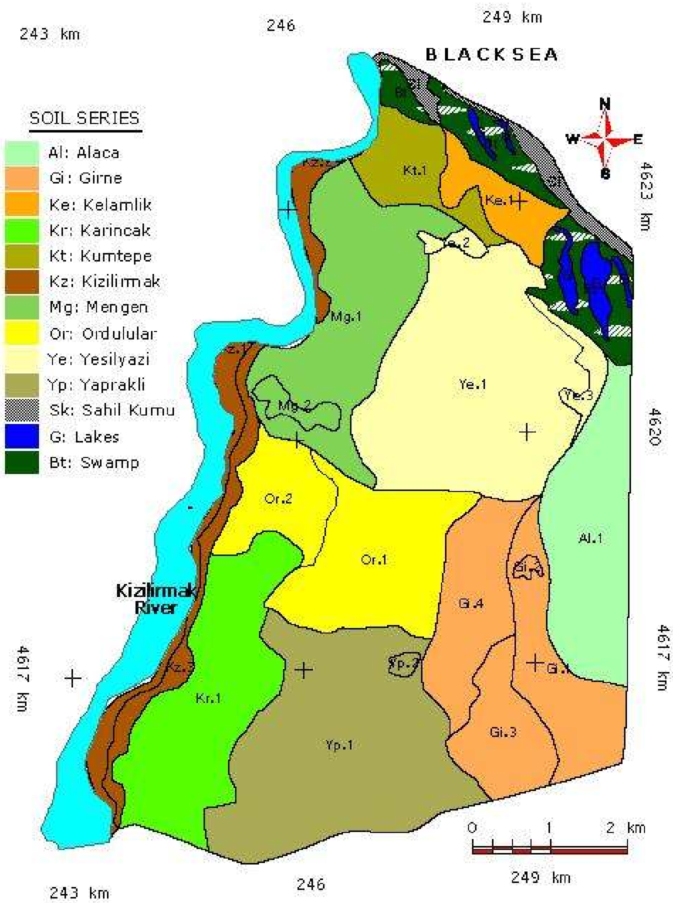

Figure 3. Soil map and land mapping units of the study area

Table 3. Distribution of land suitability class of the study area

Suitability Class	Area (ha)	Ratio (%)
S1: Highly Suitable	2039,2	42,3
S2: Moderate Suitable	1772,4	36,7
S3: Marginally Suitable	492,9	10,2
N: Unsuitable	519,2	10,8
Total	4823,7	100,0

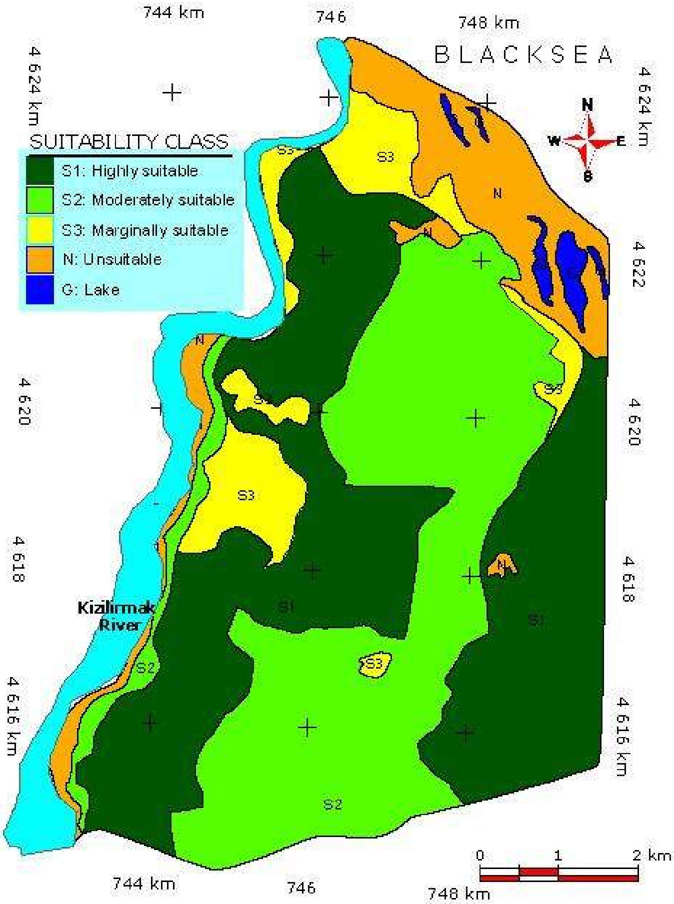

Figure 4. Land suitability map of the study are

To assess the reliability of the methodology developed, the suitability classes were checked against the rice yield. For this purpose, statistical analyses were performed by using TARIST (1994) statistics package. ANOVA and $LSD_{0.05}$ were done for grain yield values. Field experiment was settled in each suitability class according to randomized block design with three replicates. 12 rice species (Şumnu, Osmancık-97, Gönen, Beşer, Durağan, Halilbey, 7721, Karadeniz, Kızılırmak, Koral, Neğiş and Aromatik-I) were planted in each block. Experimental areas were selected according to land suitability classes. In this study, we found that grain yields of all species were affected from location of field experiment (Figure 5). Mean grain yield of the S1, S2 and S3 locations were found at 722.2, 593.9 and 563.3 kg da^{-1}, respectively. There is a discrepancy of 158.9 kg ha^{-1} between S1 and S3 classes. The highest grain yield value of 789.9 kg da^{-1} was obtained for Halil Bey in S1 location. The lowest grain yield value of 432.0 kg da^{-1} was determined for Koral in S3 location (Table 4). ANOVA results indicated that grain yield values were significantly affected by the land suitability class ($P<0.001$). The effect of each land suitability class was also different for different species. Details on the $LSD_{0.05}$ comparison test were given in Table 4. For the S1 class, the ranking of rice species increasing grain yield was found as Halilbey>Osmancık-97>Durağan> Şumnu> 7721> Kızılırmak>Karadeniz>Gönen>Koral>Neğiş>Aromatik-I>Beşer. Similarly, for S2 and S3, the ranking of rice species increasing grain yield Şumnu > Osmancık- 97 > Gönen > Beşer > Durağan > Halilbey > 7721 > Karadeniz > Kızılırmak > Koral >Neğiş > Aromatik-I and Şumnu > Osmancık-97 > Neğiş> Halilbey > Durağan > 7721> Kızılırmak > Karadeniz > Beşer > Aromatik-I > Gönen > Koral, respectively. According to grain yield, Osmancık-97, Halil Bey, Durağan and Şumnu species are the four best species, whereas Aromatik-I, Koral and Neğiş were the three worst species.

From these results, we conclude that S1 is the most suitable location in increasing grain yield, S2 and S3 classes followed it as well. Halil Bey and Osmancık-97 seem to perform best in increasing grain yield in S1 area. We attribute the differences in efficiency of the different locations to their different suitability class for rice.

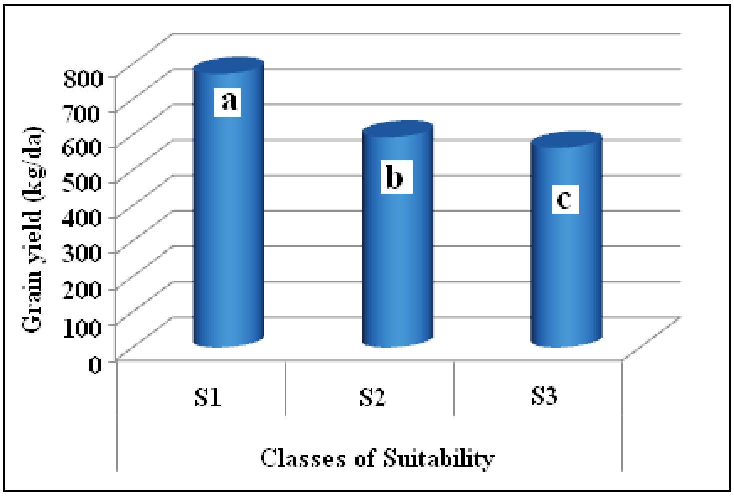

Figure 5. Comparison for general mean grain yield values among land suitability classes of the study area ($LSD_{0.05}$= 11.0)

Table 4. Grain yield values (kg da^{-1}) of rice species growing in Bafra ($LSD_{0.05}$= 53.6)

Class of Suitability	Species	Max.	Min.	SD	Mean
S1	Halil Bey	827.7	771.0	32.7	789.9^{a}
	Osmancık-97	766.0	757.4	5.4	760.5^{ab}
	Durağan	752.3	748.5	2.2	751.0^{b}
	Şumnu	795.0	716.0	45.6	742.3^{bc}
	7721	738.6	733.5	2.9	736.9^{bc}
	Kızılırmak	755.7	722.4	19.2	733.5^{bc}
	Karadeniz	766.7	654.0	65.1	729.1^{bcd}
	Gönen	728.1	701.4	15.4	710.3^{cde}
	Koral	729.3	675.4	31.1	693.4^{def}
	Aromatik-1	701.0	684.5	9.5	690.7^{ef}
	Neğiş	701.0	638.8	31.1	670.5^{f}
	Beşer	674.8	626.3	28.0	658.6^{f}
S2	Osmancık	705.2	680.2	14.4	696.9^{a}
	Şumnu	702.6	668.3	17.7	682.8^{a}
	Gönen	677.8	651.7	14.1	661.6^{ab}
	Beşer	644.2	623.5	12.0	637.3^{b}
	Durağan	644.2	614.9	16.9	634.4^{b}
	Halil Bey	663.6	562.5	58.4	629.9^{b}
	Karadeniz	587.9	563.4	14.1	579.7^{c}
	7721	579.6	561.3	9.2	569.7^{c}
	Kızılırmak	565.4	558.7	3.5	561.5^{c}
	Koral	567.9	520.3	23.8	544.7^{c}
	Neğiş	490.5	477.9	6.4	483.7^{d}
	Aromatik-1	457.3	430.2	13.7	444.9^{e}
S3	Osmancık-97	702.5	688.9	6.8	696.1^{a}
	Şumnu	695.6	685.0	6.1	688.8^{ab}
	Neğiş	660.5	650.9	5.5	654.1^{bc}
	Halil Bey	662.3	629.2	19.1	640.2^{cd}
	Durağan	614.8	613.0	1.0	613.6^{d}
	7721	560.3	546.8	6.9	552.8^{e}
	Kızılırmak	532.6	514.8	10.3	520.7^{ef}
	Beşer	517.9	505.0	6.6	$512.2f^{g}$
	Karadeniz	528.3	503.6	14.3	$511.8f^{g}$
	Aromatik-1	477.3	476.0	0.8	476.4^{gh}
	Koral	445.0	438.0	4.0	440.3^{hi}
	Gönen	470.0	413.0	32.9	432.0^{i}

4. CONCLUSION

The study thus confirms the capability of GIS to integrate spatial and attribute data and offers a quick and reliable method of land suitability with higher accuracy. The spatial relationship between different geographically referenced data can be established using a GIS. In addition, the modeling provided an approach to the improvement of rice yield by enhancing the component of modeling input. In the present study soil database and topographic map has been used as vital tools to generate land suitability map. The result presented shows the potentialities and constraints of a region with regard to its land resources and will also be a useful tool for rice cultivation planning.In conclusion, with analysis of spatial modeling it is possible to assess the land suitability with higher accuracy. In addition the modeling provided an approach to the improvement of rice yield by enhancing the component of modeling input.

5. ACKNOWLEDGEMENT

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Research
Araştırma

RAPID PREDICTION OF AVAILABLE K CONTENT IN SOIL USING NEAR-INFRARED SPECTROSCOPY

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Abstract: Soil NPK testing has been widely used for fertilizer recommendation of annual crops. Soil analyses of available K content by chemical methods are sufficiently accurate, but they are expensive, time consuming and labour intensive. Recently, fertilization recommendation to the farmers is based on reduced number of soil samples due to high price of analyses. For this reason a rapid and cost-effective soil analysis is needed for soil quality assessment. Near infrared spectroscopy (NIRS) could provide a possible alternative. The objective of this study was to investigate the possibilities of NIRS for prediction of available potassium content in different soil units. A total 191 samples from four soil type- Chernozems, Vertisols, Luvisols and Fluvisols were analyzed for available K by conventional chemical method. NIR spectra of all samples were obtained by using an InfraAlayzer 450 spectrophotometer within the range 1445-2348 nm and portable FQA-NIRGun scanning spectrophotometer in shortwave NIR range from 600 to 1100 nm. SIMCA- soft independent modeling of class analogy was performed to classify samples, according to soil type. MLR and PLS regression were used for calibration models development for available K determination. The best model was obtained for samples of Chernozems with correlation coefficient R=0,94, standard error of calibration SEC=2,30 mg/100g, and the ratio of the standard variation of the reference data to the SEC, indicating the performance of the calibration RPD=3,1. Accuracy of determination of K content for models for separated soil units, developed by spectral data in short-wave NIR region, was better to accuracy of models, based on filter-type instrument in classical NIR region. Correlation coefficients for the global calibrations containing the samples of all soil units' decrease and SEC or SEP increase compared to calibrations for separate soil units. The values of R were between 0,76 and 0,79 and RPD were between 1,5-1,7 for the both calibration and test set. Calibration models for each soil type increase accuracy of determination of available potassium content.
Key Words: Near infrared spectroscopy, Available potassium, Quantitative determination

1. INTRODUCTION

Soil nitrogen, phosphorus, and potassium (NPK) testing has been widely used for fertilizer recommendation of annual crops. Soil analyses of available potassium content by chemical methods are sufficiently accurate, but they are expensive, time consuming and labour intensive. Recently, fertilization recommendation to the farmers is based on reduced number of soil samples due to high price of analyses. For this reason a rapid and cost-effective soil analysis is needed for soil quality assessment. For more than 20 years, near infrared spectroscopy (NIRS) has been proved and utilized as a non-destructive, rapid low cost and environmentally-friendly quality alalysis technique for many agricultural products. NIRS could provide a possible alternative for soil analysis. Additional advantage of NIRS was its field portability, making it most amenable to qualitative or directional decision making in on-the-go site-specific management practices.

Recently, successful application of near infrared spectroscopy for measuring soil properties, such as organic carbon, total nitrogen and clay content have been reported (Viscarra Rossel et al, 2006). Reported results for determination of total and available potassium in the soil by NIRS are comparatively small and controversial.

Successful determination of available K by NIR spectroscopy reported Daniel et al,(2003). The authors reported coefficient of determination R^2 = 0.80 between soil available potassium content and predicted by NIRS method. Li et al, (2007) used partial least squares PLS and artificial neural network ANN techniques as calibration methods to relate NIR spectral data to the concentrations of available K. Reported coefficient of determination, based on calibration of PLS was 0.73 and the mean relative errors of PLS model was 7.40 %. Results of model based on ANN was R^2 = 0.95, and mean relative errors 7.87%, respectively.

Contrary results reported Yong et al, (2005) and Song and Yong, (2005) - an weak correlation (R =0,68-0,69) between predicted soil available K and actual soil K, with high SEP - 25,05 $mg.kg^{-1}$.

The objective of this study was to investigate the possibilities of NIRS for prediction of available potassium content in different soil units.

2. MATERIAL AND METHODS

2.1. Soil Samples

A total of 191 samples from the surface and subsurface horizon were collected from different part of Bulgaria during April - October, 2007. Soil types were Calcic Chernozems and Haplic Chernozems from North Bulgaria, Calcic Vertisols and Eutric Vertisols, Chromic Luvisols and Calcic Fluvisols (FAO, 1998) from South Bulgaria. These soil units are representative for soils in Bulgaria and are the most widespread soil units used in agriculture sector. The samples were analyzed for available potassium (K_2O) content by the Egner-Riem method.

2.2. Spectral Analysis

The spectral data of all air-dry samples were measured using two spectrometers: InfraAlyzer 450 - filter-type spectrophotometer within the range of 1445-2348 nm and portable scanning NIR instrument

FQA-NIRGun, (FANTEC, Japan) within a spectral range of 600-1100 nm. Two or three measurements were carried out for each soil sample using independent sampler cell fillings and then averaged to give one spectrum per sample. The absorbance was recorded as a log 1/R, where R is diffuse reflectance.

SIMCA- soft independent modeling of class analogy was performed to classify samples, according to soil types. SIMCA develops models for each class based on principal components analysis (PCA). PCA transforms the original data to a new coordinate system such that the greatest variance by any projection of the data comes to lie on the first coordinate (called the first principal component), the second greatest variance on the second coosrdinate, and so on. Once each class has its own model, new samples could be classified to one or another classes according to their spectra.

Multiple linear regression (MLR) was used for develop calibration models for available K content based on NIR spectra of samples obtained via InfraAlyzer 450 and partial least-square regression (PLS) for spectral data from FQA-NIRGun, respectively. Separate calibration equations were obtained for determination of available potassium (K_2O) for different sets of soil units. Additionally, global calibration equation was developed using two-third of all samples as calibration set and remaining samples as independent test set.

PLS regression and SIMCA modeling were carried out by Unscrambler 9.7 (CAMO Software AS, Norway).

3. RESULTS AND DISCUSSION

3.1. Quantitative Determination of K Content

Descriptive statistics and distribution of soil available potassium content for each soil type are shown in Figure 1. The range of K content varied from 6 to 58 mg/100g, depending on soil units. The range was the widest for Fluvisols and narrow for Luvisols samples. The average value of available potassium content was higher for Luvisols samples. Distribution of the samples according to available potassium content was not even. The samples with high available potassium content were a few for Vertisols, Chernozems and Fluvisols. There was relatively even distribution only for Luvisols.

The results of the quantitative determination of K_2O, mg/100 g content in different soil units by MLR and PLS are presented in Table 1. The obtained correlation coefficients between the measured and predicted values for available potassium were between 0,74 and 0,96. Models, based on InfraAlyzer 450 spectral data for Chernozems, Luvisols and Fluvisols showed R between 0,85 and 0,93 and RPD between 2,4 and 2,6 and could be classified as good models according to Rossel (2007). Models for same soil units, based on short-wave NIR region and PLS regression with R more than 0.94 and RPD were more than 3,0 could be classified as excellent. The statistical data of Vertisols' calibration equations in the both spectral regions showed- low correlation coefficient - 0,74 and 0,76, and RPD values - 2,2 and 2,4 could be classified as a good models.

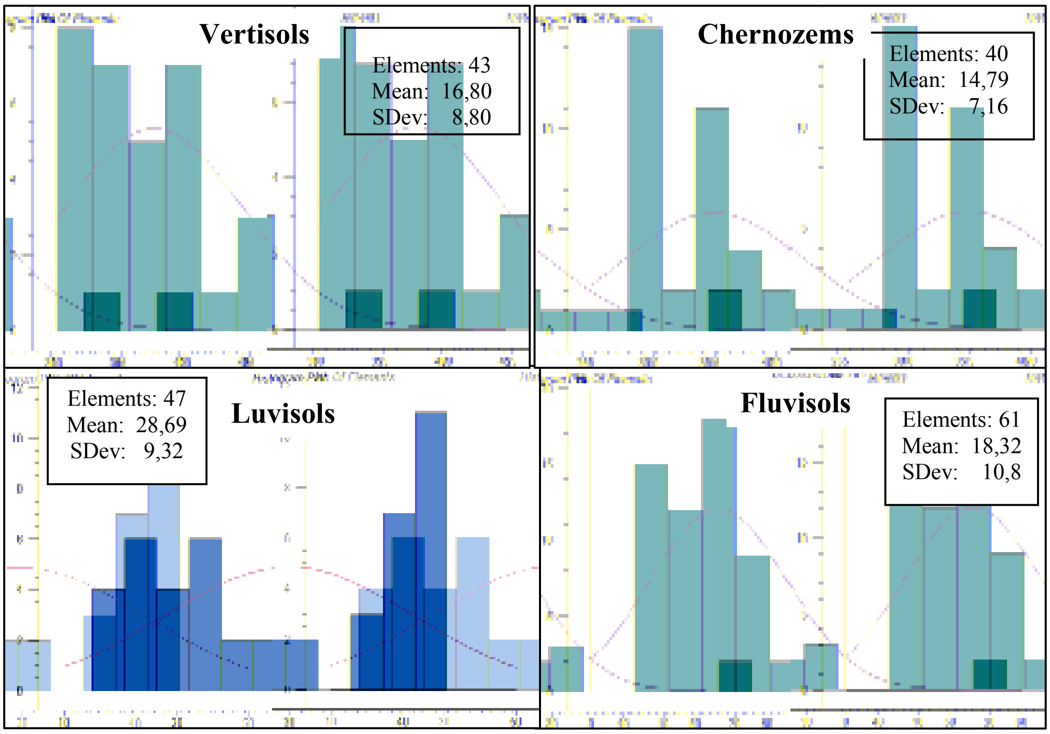

Figure 1. Histogram, mean and standard deviation (SD) of K_2O, mg/100 g content, in different soil units and data set

Table 1. Statistical parameters of the calibration equations for NIRS prediction of K_2O, mg/100 g in different soil units

	InfraAlyzer 450 MLR			FQA-NIRGun PLS		
Soil units	SEC	R	RPD	SEC	R	RPD
Vertisols	4,07	0,74	2,2	3.7	0.76	2,4
Chernozems	2,76	0,85	2,6	2,3	0,94	3,1
Luvisols	3,66	0,93	2,5	3,1	0,96	3,0
Fluvisols	4,41	0,89	2,4	3,4	0,94	3,2

SEC – standard error of calibration, SEP – standard error of prediction,
R – coefficient of multiple correlation, RPD – ratio between SD and SEC

Accuracy of determination of available potassium in all soil units for models, developed by spectral data obtained using FQA-NIRGun instrument in short-wave NIR region, was better compared to an accuracy of models, based on InfraAlyzer 450 spectral data.The reason for obtained better accuracy of determination using short-wave NIR region was probably much more spectral information, available and used for developing of calibration models by PLS, in comparison with spectral information at 6 or 7 wavelengths from total 19, included in models based on InfraAlyzer 450 data. Figure 2 and 3 graphically illustrate the relationships between determined and NIR spectroscopy predicted values of available potassium in Chernozems and Luvisols samples.

Correlation coefficients for the global calibrations for all soil units' decrease and SEC or SEP increase compared to calibrations for separate soil units. (Table 2) The values of R were between 0,76 and 0,79 and RPD were between 1,5-1,7 for the both calibration and test set. Separate calibration models for each soil type increase accuracy of determination of available potassium content.

The most important spectral information for determination of available potassium content in soil samples in short-wave NIR region were found to be at 748 nm, in the region 791-800 nm, at 977, 987, from 1030 to 1040 nm, and 1070 nm. The most often used spectral data in calibration equation, based on InfraAlyzer 450 data were at 1680, 1940, 2230, 2270, 2310, 2336 and 2348 nm.

Soil potassium exists in solution, exchangeable and nonexchangeable forms that are in dynamic equilibrium with each other. Exchangeable K^+ held on the negatively charged sites clay minerals in the soil. The most prevalent clay minerals are the layered aluminosilicates. Their crystals are composed of two basic structural units, namely: a tetrahedron of oxygen atoms surrounding a central cation, usually $Si^{4+,}$ and an octahedron of oxygen atoms or hydroxyl groups surrounding a larger cation usually Al^{3+} or Mg^{2+}. The tetrahedral are joined at their basal corners and the octahedral are joined along their edges by means of shared oxygen atoms.

In regression equations for determination of available potassium content in soil predominated spectral information, connected with absorption of O-H and metals-OH groups. Absorption at 748 nm, 977 nm, 987 nm and from 1030 to 1040 nm is corresponding to overtones of O-H vibrations. The NIR absorption at 1940 nm due to the combinations of the H-O-H bend with the O-H stretches vibrations is typical for a water-rich mineral, like montmorillonite-$AL_2O_32SiO_2nH_2O$, $MgOAl_2O_34SiO_2H_20$. (Clark et al, 1990; Popova,1990). According to Gaydon et al, (2009), absorption in the region from 2170 to 2230 nm is associated with Al-OH group, and at 2240 nm possibly indicated the presence of Si-OH. The NIR absorption at 2270 nm and 2310 nm could be connected with the combination Al-OH bend plus O-H stretch vibrations. Metals–OH bend plus O-H sretch combination near 2200 nm and 2300 nm are diagnostic absorption features in clay mineral identification (Clark et al, 1990).

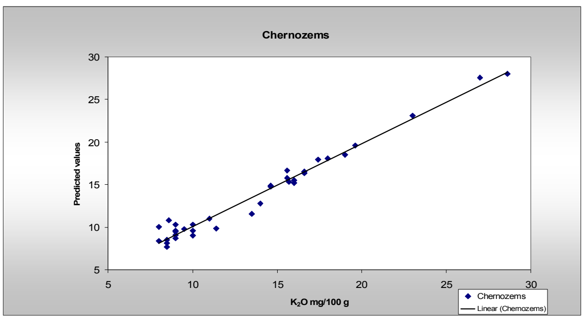

Figure 2. Relation between actual and NIRS predicted values of available potassium in Chernozems samples

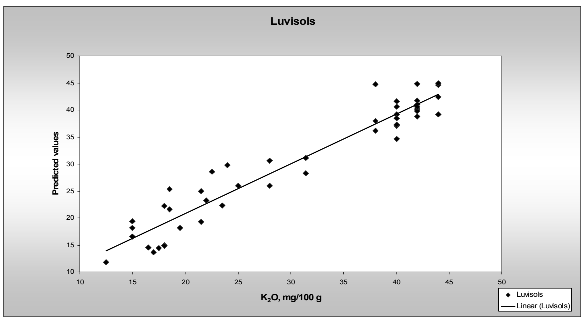

Figure 3. Relation between actual and NIRS predicted values of available potassium in Luvisols samples

Table 2. Statistical data of the calibration equations and validation statistics for NIRS prediction of K_2O mg/100 g in all examined samples

	InfraAlyzer 450 MLR			FQA-NIRGun PLS		
All soil samples	SEC/SEP	R/r	RPD	SEC/SEP	R/r	RPD
Calibration set	5.9	0.79	1.7	6.3	0.78	1.6
Test set	6.5	0.76	1.5	6.2	0.78	1.6

SEC – standard error of calibration, SEP – standard error of prediction, R – coefficient of multiple correlation, r - correlation coefficient between actual and NIRS predicted values, RPD – ratio between SD and SEC or SEP

The spectral information in calibration equations for determination of available K confirmed that determination of potassium in soil was indirect and based on relationship between potassium and clay minerals in soils.

3.2. Classification of Soil Samples According To Soil Units

Four classes were formed according to soil units as follow: Chernozems class, Flivisols class, Luvisols class and Vertisols class. Spectral data obtained by analysis of tested soil samples by FQA-NIRGun were used for classification. Spectra of ten samples from each class were used as validation data set. The remaining samples were used as calibration data set for development of SIMCA models. Obtained SIMCA models with included 10 principal components correct classified all samples from calibration data set. Interclass distance between soil classes varied between 3.08 and 25.15. Greater the distance between 2 classes the greater is the difference in composition of samples belonging to those classes. As a rule of thumb, a distance of over 3 indicates that the samples are well separated. The highest interclass distance was found between class Fluvisols and class Chernozems – 25.15 and between class Fluvisols and class Luvisols – 13.24, respectively. Obtained results showed that specific differences exist between spectral data of soils from different soil units in short-wave NIR region.

Obtained models were tested using spectra of samples from validation set and results were presented in table 3. At the 5% significance level the most of the samples from validation set were recognized by their type correct class. Only two Vertisols samples were not recognized as belong to any soil class.

The discriminating power is a measure of variable importance, in this case spectral data, which contribute to the development of classification models. A value close to 0 indicated low discrimination ability in a variable, while a value much larger than 1 implied high discrimination power. The most significant spectral data for discrimination between investigated classes by SIMCA models were found to be at wavelengths 600, 626, 706, 752, 787, 961, 1024 and 1080 nm. Probably the differences in the visible region around at 600, 626 and 706 nm were caused from colour differences in soil units. Absorption at 753, 961 and 1080 nm is corresponding to overtones of O-H vibrations. Another important wavelength in discriminating power plot at 787 could be associated with absorption of N-H stretch vibration, third overtone and at 1024 nm with N-H primary aromatic amine bands, respectively. These finding showed that discrimination between classes was based on differences in soil composition, mainly clay and organic matter content.

Results from classification procedure showed possibilities of near-infrared spectroscopy in combination with multivariate chemometrics technique such as SIMCA for fast classification of soil samples according to their types. That will allow choosing the most suitable calibration equation and will increase an accuracy of determination of available potassium content in soil.

4. CONCLUSION

The results in the present study demonstrate potential of near infrared spectroscopy for developing a fast and cost-effective analysis of available potassium soil content. Accuracy of available potassium content determination depends on soil types, spectral region and available spectral information. Dividing the samples into groups according to their soil types improved accuracy of NIR prediction of available K content. Accuracy of determination of available K in all soil units for models, developed by spectral data in short-wave NIR region, was better compared to accuracy of models, based on filter-type instrument in classical NIR region. Near infrared spectroscopy in combination with multivariate chemometrics technique offers an alternative approach to traditional methods with large potentials for a rapid and reliable soil analysis.

Table 3. Results for SIMCA models, validation set.

Soil units	Chemozems class	Fluvisol class	Luvisol class	Vertisol class	No match
Chernozems	**10**	0	0	0	0
Fluvisols	0	**10**	0	0	0
Luvisols	0	0	**10**	0	0
Vertisols	0	0	0	**8**	2

5. ACKNOWLEDGEMENT

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Research
Araştırma

PEDOLOGICAL DEVELOPMENT ON FOUR DIFFERENT PARENT MATERIALS

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Abstract: The influence of parent materials on soil properties has long been recognized. Early pedologists and soil geographers based their concepts of soils largely on its presumed parent material. Later, parent material was viewed simply as a factor that influences soil development-an influence that diminishes in importance with time. The main objective of this study is to research the influence of four different soil parent materials on some soil physical, chemical, mineralogical and morphological properties of the study area located in the Southeast Anatolia Region of Turkey. Four soil profiles were investigated. Soil samples were analyzed using standard procedures. The results show that basalt and lime stone-marn derived soils have relatively deeper profiles, lower bulk density, higher clay content, organic matter, exchangeable bases, micronutrients and weatherable minerals. They are also higher in their CEC and base saturation percentage while available water capacity, hydraulic conductivity and natural water content are more adequate in them. The parent materials of around soils are basalt, lime stone-marn, sand stone materials and alluvium materials. It was observed that soil pedons formed on lime stone-marn and basalt parent materials were well developed while; pedons formed on sand stone and alluvial deposit have weak pedogenesis process. Development of B horizons (Bw, Bss and Bk) and carbonate accumulation were main pedogenic processes in subsurface horizons and vertic and orhric epipedon were developed on top surface. The most abundant clay mineral was smectite, followed by and illite and kaolinite. Four soil pedons were classified as Entisol, Vertisol and Aridisol according to Soil Taxonomy.
Key Words: Soil parent materials, Soil properties, Soil classification

1. INTRODUCTION

The influence of parent materials on soil properties has long been recognized. Early pedologists and soil geographers based their concepts of soils largely on its presumed parent material. Jenny (1941) stated that parent material is one of the five main factors. Later, parent material was viewed simply as a factor that influences soil development-an influence that diminishes in importance with time (Schaetzl and Anderson, 2007). Besides, soils develop as various pedogenic, geomorphic and biologic processes act on initial materials changing in to a soil that location in time. Parent material is the framework for the developing soil profile. There have been many studies on examining morphologic, physical, chemical and mineralogical properties of soils developed on different parent materials. For instance, chemical and mineralogical composition of the parent material can have effect on soil texture that may have influence on movement of fine soil particles and plant nutrients together with water within the soil profile, on weathering, on types of vegetation growing and organisms living in the soil (Jacobs, 1998). Another study carried out in Nigeria indicated that soils derived from basalt parent material with volcanic ash were the best agricultural soils compared to soils of granite parent material (Olowolafe, 2002). In addition, Gökbudak and Özcan (2008), in their study they investigated to compare some selected hydro-physical properties of soils developed from different parent materials were selected in the northeast part of Turkey and to present significant differences in the soil characteristics. According to their results all properties studied except for saturation capacity and particle density of soils differed significantly with respect to the parent materials. Compared to other soil types developed from the parent materials, granite formed soils with greater sand and lower silt contents, numerically greater porosity, and significantly higher dispersion ratio and organic matter. On the other hand, soils formed on arkose parent materials had the lowest pH value, numerically the greatest available water content and saturation capacity and organic matter percentage.

The main objective of this study is to research the influence of four different soil parent materials on some selected soil physico-chemical, mineralogical and morphological properties of the study area located in the Southeast Anatolia Region of Turkey.

2. MATERIAL AND METHODS

2.1. Site Characteristics

The study area is located between 675005-4224686 E and 706779-4181675 N coordinates (UTM) (Figure 1) in Batman province of the Southeast Anatolia Region of Turkey. It ranges in elevation from 475m to 987 m above mean sea level. Site topography is generally flat and gently flat and some part of it hilly. The underlying bedrocks within the study area consist of lime stone-marn, basalt, sand stone and alluvium materials.This area is characterized by arid and semiarid climate. The average amount of annual rainfall is 479 mm. Total evaporation is 1581 mm. The mean annual air temperature is 16.6 ^{o}C. According to the Soil Taxonomy (1999) criteria, the soil moisture regime is aridic the soil temperature regime is thermic (Figure 2 and Table 1).

2.2. Methods

Morphological properties of these four profiles in the field were identified and sampled by genetic horizons and classified according to Soil Survey Staff (1993 and 1999). Soil samples were taken to investigate for their physical and chemical properties at the laboratory.

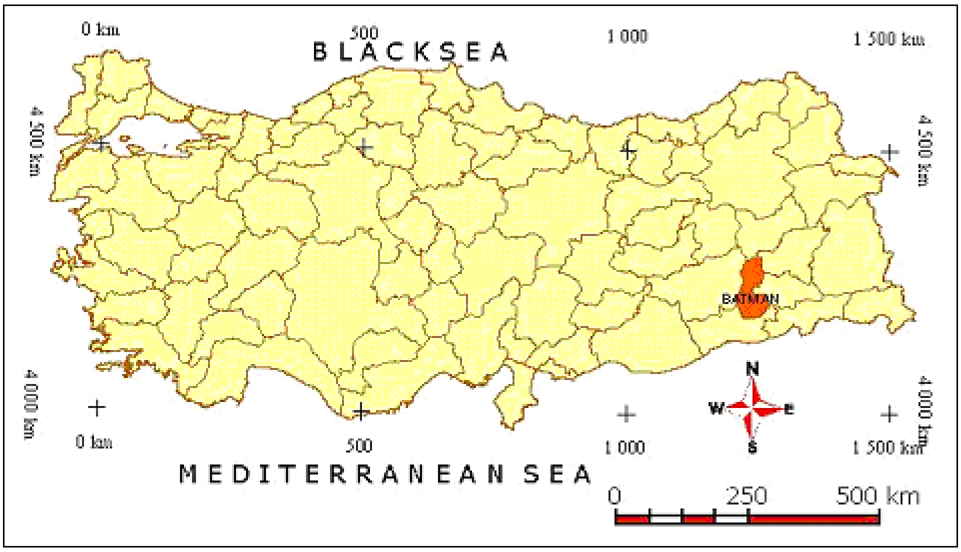


Figure 1. Location of the study area

Table 1. Meteorological data of the study area

Month	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**Annual**
T °C	3,40	5,20	9,60	15,10	20,10	26,80	31,30	30,30	25,10	17,80	10,10	4,60	16,62
P, mm	56,20	67,60	81,80	69,40	40,70	7,60	0,30	0,40	2,60	26,70	54,50	72,10	479,90
PE, mm	0,54	1,77	12,65	49,18	124,34	284,79	447,00	381,38	198,13	68,62	11,92	1,25	1581,58
P-PE	55,66	65,83	69,15	20,22	-83,64	-277,19	-446,70	-380,98	-195,53	-41,92	42,58	70,85	
W, mm	100	100	100	100	16	0	0	0	0	0	42,58	100,00	
R, mm											42,58	57,42	100,00
S, mm	55,66	65,83	69,15	20,22								13,43	224,29
U, mm					83,64								83,64
D, mm						277,19	446,7	380,98	195,53	41,42			1341,82

T: Temperature P: Precipitation R: recharge water S: surplus water U: Utilized water D: Deficit water

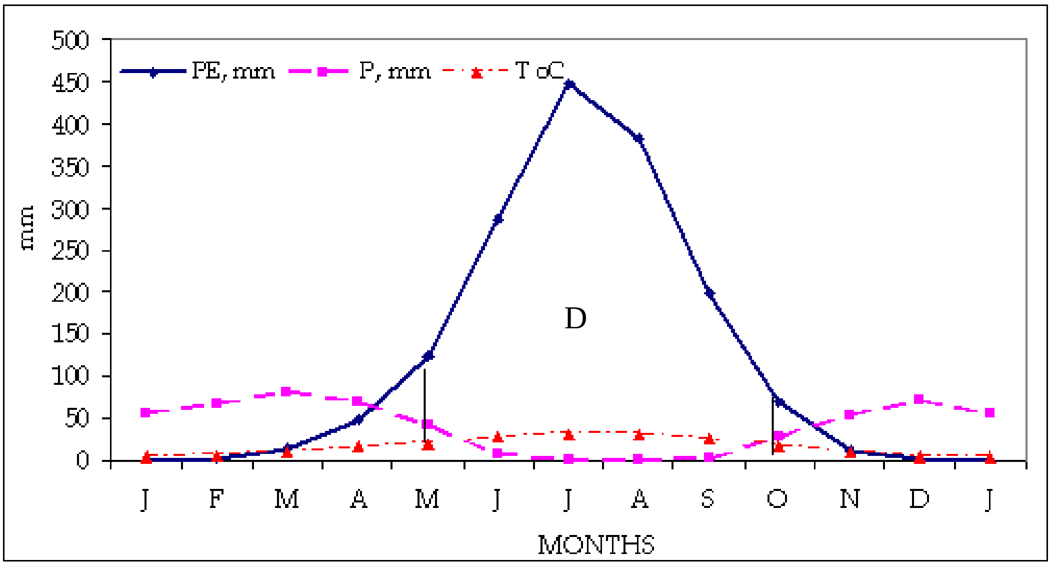


Figure 2. Soil water budge chart of the study area

Disturbed soil samples were then air-dried and passed through a 2 mm sieve to prepare for laboratory analysis. After soil samples were then air-dried and passed through a 2 mm sieve, particle size distribution was determined by the hydrometer method (Bouyoucos, 1951) after removal of organic matter with 30 % H_2O_2, of sulphate by leaching salts with distilled water, of carbonates with 1 M NaOAC at pH 5, and dispersion by agitating the sample in 10 ml of 40 % sodium hexametaphosphate (calcon) (Gee and Bauder, 1986). Bulk density (Blacke and Hartge, 1986) and water retention (field capacity-FC and permanent wilting point-PWP) (Klute, 1986) were determined from undisturbed samples. Available water capacity (AWC) was calculated from taking difference between FC and PWP. Hydraulic conductivity measurement was determined by saturated soil condition (Oosterbaan, 1994). Organic matter was determined in air-dry samples using the Walkley-Black wet digestion method (Nelson and Sommers, 1982). pH, EC-electrical conductivity (of the saturation) by method of the (Soil Survey Labrotory, 1992). Lime content by Scheibler calsimeter (Soil Survey Staff, 1993). Exchangeble cations and cation exchange capacities (CEC) were measured using a 1 N NH_4OAC (pH 7) method (Soil Survey Labrotory, 1992). Pearson correlation coefficients were estimated to investigate the relationships among the soil properties.

3. RESULTS AND DISCUSSIONS

Different parent materials affect the morphology, mineralogical and physico-chemical characteristics of soils under the same conditions such as biosphere, topography and climate especially in arid and semiarid regions. Therefore, differences in these properties of soils are related primarily to parent material (Washer and Collins, 1988).

3.1. Soil Physical and Morphological Properties

Soil physical and morphological properties that have been taken into consideration in this study showed variability as a result of dynamic interactions among natural environmental factors such as parent material under the same climate. Parent material, through its impacts on texture and surface area, also affects rates of pedogenesis. Leopold and Miller, 1956, Graf, 1982 and Alexander et al., 1999 indicated that alluvial lands and floodplains formed under ephemeral flow regimes, especially in arid and semiarid regions, lack many of the same relationships between hydrology, sedimentology, and morphology that obtain in perennial rivers. According to these authors, the concept of pedogenic maturity is used to infer sediment accumulation rates at different locations in ancient floodplain environments: weak soil development is assumed where sedimentation rates are rapid and strong development is presumed where sediment accumulation is slow. The same results were also observed in the study area. The major physical and morphological properties of the soils are presented in Table 1 and Figure 3. There is an abrupt textural transition in Profile 1 that contains silty loam and loam textures. This changing has also effect on structural development owing to loss of organic matter and fine texture, structural developing of Typic Torrifluvent is moderate and weak, fine and very fine granular. Sub surface soil texture of Lithic Torriorthent has also silty loam however; slope contributes to greater runoff, as well as to greater translocation of surface materials down slope through surface erosion and movement of fine soil. Typic Haplotorrert has the highest clay content (64%) while, Typic Torrifluvent has the highest sand content. This high clay content also causes slickensides features in Typic Haplotorrert. All soil profiles color is 10 YR except Typic Haplotorrert that has more reddish due to iron oxidation derived from basaltic parent material. In addition, soil color of Typic Haplocambid becomes lighter from top surface to sub surface horizons. Top surface of it is 10 YR 4/3 while, due to carbonate accumulation in depth color was change to 10 YR 7/3 in sub surface horizons. Bulk densities of the soils formed on four different parent materials ranged from 1.10 to 1.48 g/cm^3 and they were significantly different each other. Soils from basaltic parent material had the lowest while those from alluvial soil had the greatest bulk densities due to the soil textural variety. Typic Haplotorrert has the highest aggregate stability while, due to low clay and organic matter content aggregate stability is low in Typic Torrifluvent.

3.2. Soil chemical properties

Soil chemical properties considered in this study are pH, Electrical Conductivity (EC), Organic Matter (OM), Cation Exchange Capacity (CEC), exchangeable cations, calcium carbonate and macro and micro nutrients. Soil chemical properties on parent material were significantly affected by the degree of soil development and leaching processing (Table 3 and Table 4). In this study, it was found that pH values of soils developed from four different parent materials changed between 7.40 and 7.89 and a very high base saturation. Soil pH is generally greater at depth than at the soil surface whereas, EC values increased in top surface soil. However, there is no problem about salt accumulation for al pedons. Organic matter levels in soils of basalt, sand stone and alluvial areas are below 2.0% except lime stone-marn that has slightly higher than 2%. This is due to high temperature in most period of the year, leading to high rates of decomposition, mineralization and disappearance of organic materials, thereby preventing appreciable accumulation of organic carbon in the soils. Calcium carbonate content of the soils was found to be high. The calcium carbonate content was even much more higher in the horizons with carbonate accumulation (i.e. calcic horizons) (Table 3). The low amount of $CaCO_3$ in Typic Torrifluvent and Lithic Torriorthent can be explained by leaching of $CaCO_3$ in the profiles. High CaCO3 content in the other soils was a result of basalt and lime stone parent materials with rich carbonate content. Soil total cation varied between 8.6 to 45.8 cmol kg^{-1}. The soil with the highest total cation was Typic Haplotorrert with high clay content, while the lowest value was determined in in Typic Torrifluvent soil. Concerning exchangeable cations, Ca and Mg are the dominant cations at the exchange sites of basalt soils. Compared to these two, K and Na levels are not as high. According to Loue (1968) and Lindsay ve Norvell (1978), the two groups of soils (Lithic Torriorthent and Typic Haplotorrert) are low in their total nitrogen contents. Rapid mineralization due to high temperature of the arid region must have contributed to low levels of total N. Concerning soil available makro and micronutrient elements, particularly P, B and Zn, deficiencies exist in all soils perhaps because of the relatively low organic matter content of the soils and low levels of these elements in the parent rocks (Table 3). However, available Cu is found in sufficient quantities in soils derived from basalt and so do not constitute limitation to crop production. In addition, soils derived from basalt appear to be relatively higher in total iron than the other soils. There is no problem in terms of heavy metal concentration (Cd and Ni).

Coordinate: 679 509 E - 419 40 66 N
Parent Material: Alluvial deposit

Horizon Definition

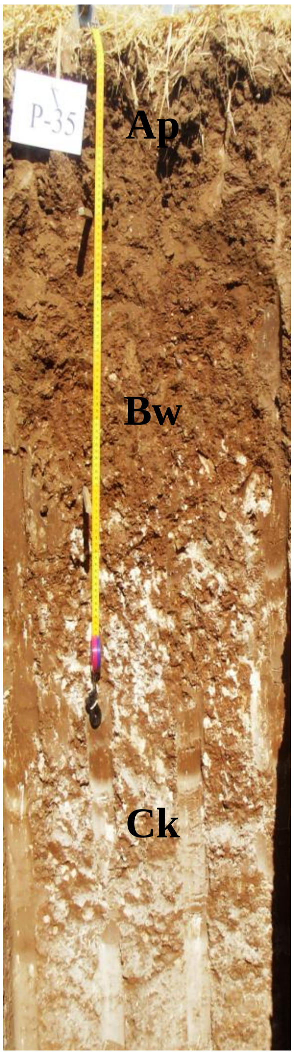
Pale brown (10 YR 6/3, dry), yellowish brown (10 YR 5/4, moist); silty loam; medium, medium granular structure; slight hard in dry, hard in moist; sticky when very moist; very lime; no-rock; medium common secondary roots; marked smooth border.

Pale brown (10 YR 6/3, moist); loam sandy; massive structure; loose in dry, individual in wet, no sticky when very moist; very lime; no-rock; medium common secondary roots; marked smooth border, sand band.

Brown (10 YR 4/3, moist); loam; massive structure; hard in dry; slight sticky and slight plastic in very moist; very lime; no-rock; medium common secondary roots; marked smooth border, oxidation spot started

Brown (10 YR 4/3, moist); loam; massive structure; tight when moist; slight sticky and slight plastic when very moist; very lime; no-rock; medium common secondary roots; humidity started.

Coordinate: 690 724 E - 419 38 41 N
Parent Material: Lime stone-Marn



Horizon Definition

Brown (10 YR 4/3, dry); dark brown (10 YR 3/3, moist); clay medium, medium, granular structure; hard when dry, tight when moist, sticky when very moist; very lime; thin common secondary roots; marked smooth border.

Yellowish brown (10 YR 5/4, dry), brown (10 YR 5/3, moist); clay; medium, medium subangular blocky structure; very hard when dry, very tight when moist, sticky when very moist; very lime; low rocky; very thin very loose secondary calcium carbonate nodules, marked smooth border

Very pale brown (10 YR 7/3, dry), very pale brown (10 YR 7/3, moist); clay; massive structure; very hard when dry, very tight when moist; sticky when very moist; high lime content ; low rocky; marked smooth border, secondary calcium carbonate nodules

Figure 3. Morphological description of the soil profiles

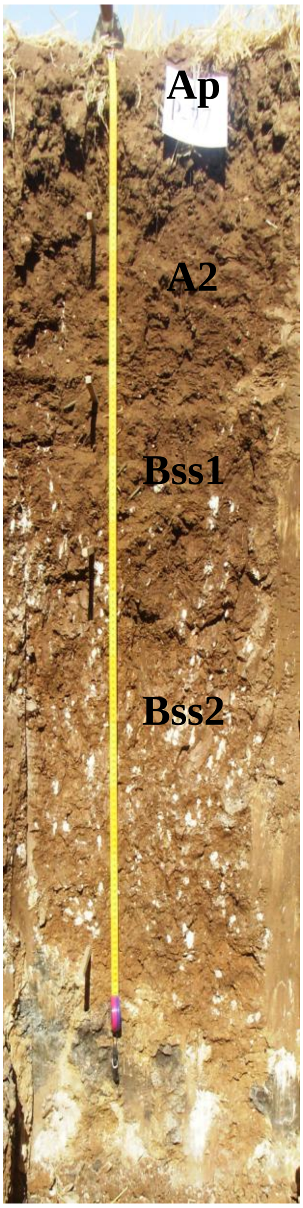
Coordinate: 692 013 E - 421 06 74 N
Parent Material: Sand stone

Horizon Definition

Yellowish brown (10 YR 5/4, dry), dark yellowish brown (10 YR 4/4, moist); silt loam; medium, small, granule structure; hard when dry, tight when moist, sticky when very moist; very lime; no-rock; thin, common secondary roots; marked wavy border.

Sand stone

Coordinate: 700 718 E - 419 63 33 N
Parent Material: Basalt



Horizon Definition

Dark brown (7,5 YR 3/3, dry), dark brown (7,5 YR 3/3, moist); clay; medium, medium, granule structure; hard when dry, tight when moist, sticky when very moist; very lime; no-rock; thin, common secondary roots, marked smooth border

Dark brown (7,5 YR 3/3, dry), dark brown (7,5 YR 3/3, moist); clay; medium, medium, subangular blocky structure hard when dry, tight when moist, sticky when very moist; very lime; no-rock; thin, very loose secondary roots, marked wavy border

Dark brown (7,5 YR 3/3, dry), dark brown (7,5 YR 3/3, moist); clay; medium, medium, subangular blocky structure hard when dry, tight when moist, sticky when very moist; very lime; no-rock; thin, very loose secondary roots, slicken sides marked wavy border

Dark brown (7,5 YR 3/3, dry), dark brown (7,5 YR 3/3, moist); clay; massive structure; very hard when dry; very tight when moist, very plastic when very moist; very lime;no-rock; very thin, very loose secondary roots; marked wavy border; small slicken sides and $CaCO_3$ nodules by 0.5 cm.

Figure 3. continue.

Table 2. Selected physical properties for four representative profiles

Horizon	Depth (cm)	Color (Dry, wet)	Particle size Clay (%)	Silt (%)	Sand (%)	Texture class	Aggregate stability (%)	Bulk Density (g m^{-3})	*Clay minerals
Profile 1. Typic Torrifluvent									
Ap	0-26	10 YR6/3 10 YR5/4	16	52	32	SiL	21.03	1.24	I-S-K
C1	26-50	10 YR7/3 10 YR6/3	6	16	77	LS	21.26	1.49	I-S-K
C2	50-86	10 YR5/3 10 YR4/3	16	46	37	L	21.35	1.23	K-I-S
C3	86-154	10 YR5/3 10 YR4/3	8	46	46	L	21.48	1.29	I-K-S
Profile 2. Typic Haplocambid									
Ap	0-30	10 YR 4/3 10 YR 3/3	42	34	24	C	58.31	1.14	S-I-K
Bw	30-71	10 YR 5/4 10 YR 5/3	48	22	30	C	59.15	1.10	S-K-I
Ck	71 +	10 YR 7/3 10 YR 7/3	44	22	34	C	58.01	1.19	S-K-I
Profile 3. Lithic Torriorthent									
Ap	0-21	10 YR 5/4 10 YR 4/4	24	52	24	SiL	63.58	1.19	S-K-I
Cr	21+	-	-	-	-	-	-	-	-
Profile 4. Typic Haplotorrerts									
Ap	0-26	7,5 YR 3/3 7,5 YR 3/3	64	16	20	C	72.16	1.11	S-I-K
A2	26-51	7,5 YR 3/3 7,5 YR 3/3	64	18	18	C	71.54	1.10	S-I-K
Bss1	51-73	7,5 YR 3/3 7,5 YR 3/3	58	26	16	C	70.36	1.12	S-I-K
Bss2	73-135	7,5 YR 3/3 7,5 YR 3/3	52	30	18	C	71.94	1.17	S-I

*S: smectite, I: illite K: kaolinite L: Loam, C: Clay, SiL: Silty Clay, LS: Loamy sand

Table 3. Selected chemical properties for four representative profiles

Horizon	Depth (cm)	pH	EC (dS m^{-1})	O.M (%)	Calcium Carbonate (%)	Exchangeable cations (cmol kg^{-1}) Ca+Mg	Na	K
Typic Torrifluvent								
Ap	0-26	7.40	1.21	1.42	9.48	20.1	1.2	2.1
C1	26-50	7.75	0.42	0.38	8.69	7.3	0.8	0.5
C2	50-86	7.72	0.74	0.57	9.95	19.5	1.4	1.1
C3	86-154	7.89	0.26	0.26	5.53	8.1	1.1	1.0
Typic Haplocambid								
Ap	0-30	7.65	0.81	2.04	15.96	32.1	0.5	11.4
Bw	30-71	7.67	0.79	1.72	21.33	29.5	2.0	8.3
Ck	71 +	7.76	0.78	0.38	21.96	30.2	1.0	4.5
Lithic Torriorthent								
Ap	0-21	7.51	0.29	0.96	9.32	23.05	1.1	4.8
Cr	21 +	-	-	-	-	-	-	-
Typic Haplotorrerts								
Ap	0-26	7.55	0.47	1.12	6.64	25.2	0.5	20.1
A2	26-51	7.79	0.39	0.66	9.64	26.7	0.5	14.3
Bss1	51-73	7.64	0.38	0.98	22.36	28.4	0.5	8.3
Bss2	73-135	7.65	0.41	0.47	15.88	22.1	0.5	7.6

Table 4. Macro and micro nutrient elements of the four representative profiles

Horizon	Total N (%)	P mg kg^{-1}	B mg kg^{-1}	Total Fe %	Zn mg kg^{-1}	Cu mg kg^{-1}	Ni mg kg^{-1}	Cd mg kg^{-1}
Typic Torrifluvent								
Ap	0.14	4.50	0.478	1.688	0.271	0.713	0.412	0.004
C1	0.02	6.00	0.033	1.184	0.266	0.946	0.685	0.005
C2	0.03	5.10	0.057	1.349	0.342	0.318	0.784	<0.001
C3	0.01	4.10	0.019	1.411	0.120	0.635	0.452	<0.001
Typic Haplocambid								
Ap	0.11	7.70	1.035	1,209	0.315	0.203	0.691	<0.001
Bw	0.10	3.80	0.036	1,523	0.195	0.367	0.560	0.003
Ck	0.02	2.80	0.055	1,718	0.288	0.216	0.548	0.003
Lithic Torriorthent								
Ap	0.05	5.00	0.072	1,849	0.256	0.299	0.453	0.004
Cr	-	-	-	-	-	-	-	-
Typic Haplotorrerts								
Ap	0.06	2.43	0.186	1,939	0.291	0.242	0.327	<0.001
A2	0.04	7.45	0.026	1,876	0.518	1,152	0.741	0.005
Bss1	0.05	9.50	0.088	2,073	0.362	0.062	0.446	0.004
Bss2	0.02	8.00	0.355	2,961	0.322	0.922	0.207	<0.001

4. CONCLUSION

After comparing the soils formed on four different parent materials it can be concluded that physico-chemical, mineralogical and morphological properties of soils examined varied each other depending on type of parent material. This relationship has been especially well illustrated by a comprehensive review of by Dahlgren et al (2004). This review highlights the fact that soils derived from volcanic and carbonate rocks that possess distinctive physical, chemical and mineralogical characteristics that are usually not found in soils developed in each other (Wilson, 2006). In addition, it is widely recognized that parent material may be responsible for the origin of some unusual chemical soil properties such as the high exchangeable Mg/Ca ratio or heavy metal content of their. However, parent material can not be said to be major criterion for soil development. For most systems, soil type is based on a number of different criteria related to pedogenesis, stressing particularly the nature and intensity of the process, as controlled largely by combinations of the other soil-forming factors, namely climate, topography, biota and time.

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PHYTOEXTRACTION OF HEAVY METALS FROM MINE SOILS USING HYPERACCUMULATOR PLANTS

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Abstract: Phytoextraction is an environmental-friendly and cost-effective technology that uses metal hyperaccumulator plants to remove heavy metals from soils. The metals are absorbed by the roots, transported and accumulated in the aerial parts of the plants, which can be harvested and eliminated. The aim of this work was to study some hyperaccumulator species that could be useful to decontaminate mine soils and also to investigate the bioavailability and uptake of these metals by plants with the addition of organic amendments. Pot experiments were performed with soil samples collected from two mining areas in the north of Madrid, where there was an intense mining activity more than 50 years ago. Three species (*Thlaspi arvense*, *Brassica juncea* and *Atriplex halimus*) were grown under controlled conditions in pots filled with contaminated soils mixed with 0 Mg, 30 Mg and 60 Mg per hectare of two different organic amendments: a commercial compost made of pine bark, peat and wood fiber and other made of horse and sheep manure and wood fiber. Plants were harvested at the end of their crop cycle and were digested in order to measure metal concentration (Zn, Cu and Cd) in roots and shoots. Highest plant metal concentration was observed in pots treated with pine bark amendment and with pure soil due to an increase in metal bioavailability with decreasing pH. Also in those treatments the total plant biomass was lower, even some plants could not germinate. On the contrary, there was a lower metal concentration in plant tissues of pots with manure because its higher pH whereas plant growth was significantly larger so there was an incresing amount of metals removed from soil by plants. Comparing the three species results indicate a higher total metal uptake in *A. halimus* than *B. juncea* and *T. arvense*. In conclusion, results show that pH affects metal bioavailability and uptake by hyperaccumulator plants. Addition of organic amendments could be a successful technique for stabilization of metals in contaminated soils.
Key Words: Hyperaccumulator, Phytoextraction, Mine soil, Organic amendment, *Thlaspi arvense, Brassica juncea*

1. INTRODUCTION

Metal mining and smelting activities are important sources of heavy metals in the environment, resulting in considerable soil contamination. The accumulation of these metals in soil can result in a decrease in soil microbial activity, biodiversity and soil fertility, crop yield losses, and even damage on animal and human health through the food chain. Various *in situ* and *ex situ* techniques have been employed to remediate soils but most of them are expensive or unsuitable.

Phytoremediation, defined as the use of green plants to remediate contaminated soils or waters, is a cost-effective and environmental-friendly strategy, which can compliment or replace conventional approaches. There are several specific subsets of metal phytoremediation being developed. One of them is phytoextraction, in which high biomass metal-accumulating plants and appropriate soil amendments are used to transport and concentrate metals from the soil into the above-ground shoots, which are harvested with conventional agricultural methods (Raskin et al., 1997). One approach for phytoextraction is to use hyperaccumulator plants, which are plants capable of accumulating more than 100 times larger concentrations of metals than normal plants (Brooks et al., 1977).

Several studies have been made using Indian mustard (*Brassica juncea*), an oilseed crop tolerant of the Mediterranean climate and capable of substantial heavy metal accumulation in its above-ground parts (Kumar et al., 1995; Blaylock et al., 1997). On the other hand, species belonging to the genus *Atriplex* may be of special interest because of their high biomass production associated with a deep root system able to cope with the poor structure and xeric characteristics of several polluted substrates. In this study Mediterranean saltbush (*Atriplex halimus*) was used, which is present as a natural invading shrub in several mining areas of Northern Africa and Sothern Europe. Also a non-accumulator species was used to compare results, *Thlaspi arvense*, a Brassicaceae related to *Thlaspi caerulescens*, another known hyperaccumulator.

Disadvantages of hyperaccumulator plants are that they have a small biomass, usually are only tolerant to one or two metals and are sensitive to climate conditions. A low-cost option could be stabilization using organic matter. Organic amendments can decrease the bioavailability of heavy metals in soil by adsorption and by forming stable complexes with humic substances (Shuman, 1999), thus permitting the re-establishment of vegetation on contaminated sites. This organic matter can re-distribute heavy metals from soluble and exchangeable forms to fractions associated with organic matter or carbonates and the residual fraction. Also, the use of organic wastes as source of organic matter for agricultural or ecological benefit is a way of recycling them. Effects of organic matter on metal fractionation in soil are pH-dependant. Walker et al. (2004) suggested that changes in soil pH and the presence of phosphorous and inorganic salts in organic amendments could contribute more to the change in metal fractionation in soil when such amendments were applied than the nature and the humification degree of the organic matter.

The objectives of this study were to investigate the effect of two organic amendments (pine bark compost and manure compost) on metal concentration in plants and on fractionation of metals in an acid and sandy mine soil from Madrid through pot experiments. Several hyperaccumulator species were grown and compared evaluating such plants performance in relation with the different chemical fractions of metals.

2. MATERIAL AND METHODS

Two heavy metal contaminated soils from the north of Madrid (Spain) were selected for this study. The first one ("Garganta") is situated at the village Garganta de los Montes close to an abandoned copper mine. The second ("Cuadron") is situated in El Cuadron where there is an old blend mine. Soils were collected from the top 20 cm and samples were air-dried and sieved to < 2 mm for analysis. In the samples different properties were determined (Table 1). pH and Electric Conductivity (EC) in distilled water (1:2.5), Total Organic Carbon (TOC) by Loss On Ignition method, Water soluble Carbon (WSC) by Ciavatta et al. (1991) and Benito (2002), Cation Exchange Capacity (CEC) by barium chloride method, total heavy metal content (Cu, Zn and Cd) extracted in aqua regia and texture. These two soils are acid, sandy and poor in organic matter. Two organic amendments were added to these soils: a compost made of sheep and horse manure with wood fiber ("Manure"), and a compost of pine bark, wood fiber and peat ("Pine bark"). Main properties of these amendments are also shown in Table 1. Ten different treatments were prepared with mixtures of each soil with one of the amendments and the doses applied were 0, 30 and 60 Mg ha^{-1} of dry organic matter. Thus, treatments with Garganta soil were: soil not amended (G0), soil with 30 Mg ha^{-1} of manure compost (G30M), soil with 60 Mg ha^{-1} of manure (G60M), soil with 30 Mg ha^{-1} of pine bark compost (G30P) and soil with 60 Mg ha^{-1} of manure (G60P); and treatments with Cuadron soils were: C0, C30M, C60M, C30P and C60P.

In this study three species were used: *Brassica juncea*, *Atriplex halimus* and *Thlaspi arvense*. Plants were grown in 0,7 L polyethylene pots filled with 700 g of soil and amendment mixtures mentioned above. The base of the pots was covered with a metallic mesh and with a 2-3 cm layer of gravel. Pots were placed at a greenhouse with four replicates per treatment and for each species one control treatment with pine bark, wood fiber and peat but without contaminated soil was used. A total of 44 pots per species were prepared.

B. juncea and *T. arvense* seeds were stored 12 days at 3±2ºC and 7 days at 10-25ºC. *B. juncea* seeds were scarified in order to promote its germination. Eight seeds of these species were sown in the pots and plants were harvested 110 days after sowing. Seedlings of *A. halimus* were prepared in root boxes with perlite and environmental control and later one seedling was transplanted into each pot. *A. halimus* plants were harvested 393 days after transplanting.

Plants were watered with a nutrient solution containing 17 g L^{-1} $Ca(NO_3)_2$; 0,50 g L^{-1} KNO_3; 0,16 g L^{-1} $H_2PO_4NH_4$ and 0,20 g L^{-1} NH_4NO_3. This solution was added manually every one or two days (30-60 ml) to keep the water content near to field capacity but avoiding leaching. Temperature and insolation were also controlled at the greenhouse.

Table 1. Physical and chemical properties of soils, amendments and different mixtures

		pH	EC ($dS\ m^{-1}$)	TOC (%)	WSC ($g\ kg^{-1}$)	CEC ($cmol_+\ kg^{-1}$)	Total Cu ($mg\ kg^{-1}$)	Total Zn ($mg\ kg^{-1}$)	Total Cd ($mg\ kg^{-1}$)	Texture USDA
Garganta	G0	6.2	0.08	1.52	1.41	4.74	801.2	238.4	6.5	Sand
	G30M	6.5	0.51	1.88	8.78	5.28	879.9	315.8	7.6	
	G60M	6.8	0.94	2.53	18.61	5.99	939.9	336.4	8.2	
	G30P	5.9	0.11	1.92	3.51	5.30	1130.9	363.3	8.6	
	G60P	5.6	0.17	2.61	4.61	5.68	957.4	325.1	8.5	
Cuadron	C0	5.5	0.10	2.39	2.51	4.79	251.4	146.2	3.0	Sand
	C30M	5.8	0.58	2.73	1.64	5.67	264.5	156.6	3.3	
	C60M	6.1	0.99	3.29	2.29	6.16	290.0	167.0	3.2	
	C30P	5.4	0.16	2.81	5.68	4.87	252.9	141.8	3.2	
	C60P	5.3	0.16	2.80	6.78	5.89	268.5	157.2	3.3	
Manure		9.4	4.95	46.95						
Pine bark		5.7	0.40	78.96						

After harvest plants were cut at ground level and stems, leaves and inflorescences of each plant were separated and weighed for fresh weight determination. Also plant height and inflorescence height were measured. Roots were rinsed with deionised water and roots and aerial organs were dried in an oven at 65ºC for 48h. Dry weight was measured and material was ground gathering together stems, leaves and inflorescences.

For each vegetable sample, digestion of ground dry matter was accomplished by a dry ashing procedure (Tüzen, 2003) at 450ºC for 4h and dissolving ashes in HNO_3 (25 % v/v) in order to measure metal concentration in plant tissues (shoots and roots).

A sequential extractions procedure was applied to fractionate Zn, Cu and Cd presented in pots after plant harvest, following the methodology of Tessier et al. (1979) and Lena and Rao (1997), designed to separate heavy metals into six operationally defined fractions: Water Soluble, Exchangeable, Carbonate-bound, Fe-Mn Oxides-bound, Organic-bound and residual. Water Soluble and Exchangeable were summed and data was presented as Water Soluble + Exchangeable.

Heavy metal concentration in solutions was measured by Atomic Absorption Spectrophotometry (AAS). All reagents used were of analytical grade or better. Double deionised water was used for all dilutions and all the plastic and glassware were cleaned by soaking in dilute HNO_3.

Statistical treatment of experimental data was performed using SPSS 14.0. Means were compared by a one-way analysis of variance (ANOVA) with Duncan's test ($P \leq 0.05$) and in order to assess relationships between metal fractions and metal concentration in plant tissues Pearson's correlation coefficients (r) were obtained by a two-tailed test. Standard deviations were calculated to determine means variability between replicates.

3. RESULTS AND DISCUSSION

Plant growth presented different values in the applied treatments as indicates shoot and root dry weight (figure 1), and in all cases was lower than growth obtained in control pots. Plants grown in pine bark mixtures and in not amended soils did not result in a high biomass production. Even, all *T. arvense* plants (G0, G30P, G60P, C0, C30P and G60P) and some of *B. juncea* (C30P and almost every pot of G30P) did not germinate in such treatments or died few days after the germination. However, manure treatments reached higher yields and every plant of *B. juncea* and some of *T. arvense* (only in Garganta treatments) presented flowering at the end of the crop. The higher growth was probably due to a lower metal bioavailability and therefore a low metal stress, specially for the non-accumulator *T. arvense*, and also because the improvement of soil fertility with these amendments. Wu et al. (2004) observed that N and P application produced a increasing yield in *B. juncea* that resulted in a higher Cu uptake, in spite of a decrease in Cu concentration.

A.halimus developed more biomass production in all treatments than *B. juncea* and *T. Arvense*. The last was the species that presented the lowest growth, specially in Garganta treatments where the high Cu content of this soil probably induced Cu stress in this plant. In all cases dry weight of root material was much less than the weight of aerial parts but in most cases both followed the same pattern.

The metal concentration in different parts of the plants was related to the amendment applied as it is shown in figure 2, 3 and 4. Highest plant metal concentration (Zn, Cu) was observed in pots treated with pine bark amendment and with pure soil. On the contrary, there was a lower metal concentration in plant tissues of pots with manure due to a decrease in metal bioavailability caused by an increasing pH with the addition of an alkaline amendment such as horse and sheep manure (pH 9.4) to an acid soil. The lower concentration is emphasized with an increasing dose of manure amendment. Organic matter contributed by this amendment and increasing pH affects the adsorption sites of soils and reduce metal uptake by plants. On the other hand, metal concentration was not significantly different with the addition of pine bark amendment compared to not amended soils.

Cu concentration in plant tissues was higher with Garganta soil (copper mine) while there was more Zn content in plants with Cuadron soil (zinc blende mine), except in G60P where Zn concentration in roots of *B. juncea* (14429 mg kg^{-1}) was extremely high.

Cu concentration in roots was generally higher than the concentration in aerial organs of the plants, whereas Zn in shoots was much higher than root concentration in some treatments of *A. halimus* (C0 and C30P) and *T. arvense* (G30M and G60M).

Generally there was a greater Zn concentration in shoots and roots of *B. juncea* and *T. arvense* than *A. halimus* but this last had a higher shoot Cu concentration. Ebbs and Kochian (1997) showed that *Brassica* spp. were more effective at removing Zn from a nutrient solution than Cu and that the removal of each metal was reduced in presence of both.

Cd concentration in plant tissues was also measured but it was in most cases below detection limits (< 0,02 mg L^{-1}).

In spite of the higher concentration of metals in plants grown in pine bark amendment and in pure soil the total uptake by plants (Figure 2, 3 and 4) was in most cases lower in these treatments due to the lesser growth reached. Results suggest that manure amendments not only stabilize metals in mine soils but also allow more plant growth and consequentially an increasing amount of metals removed from soil.

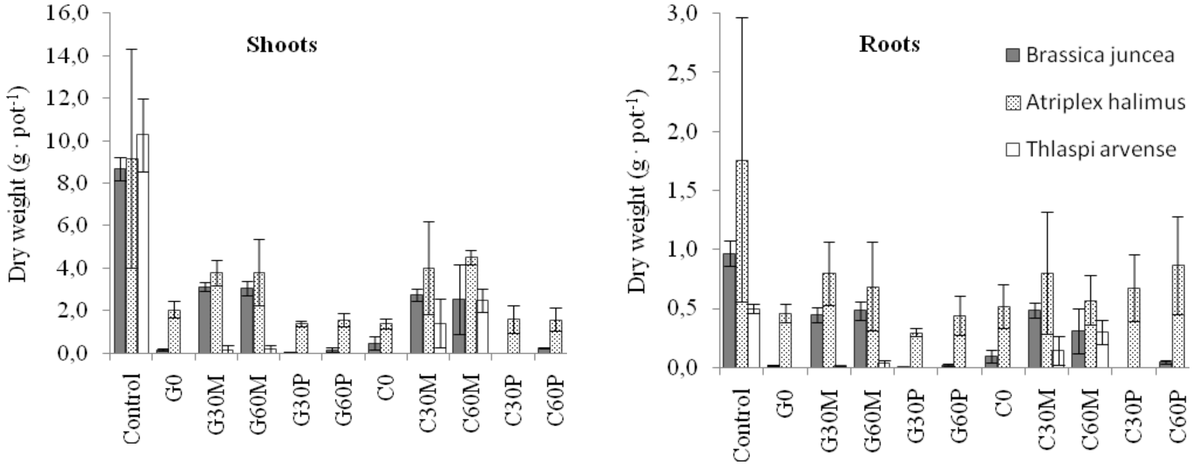

Figure 1. Shoot and root dry weight after harvest of each crop in different soils and amendments (Error bars represent standard deviation)

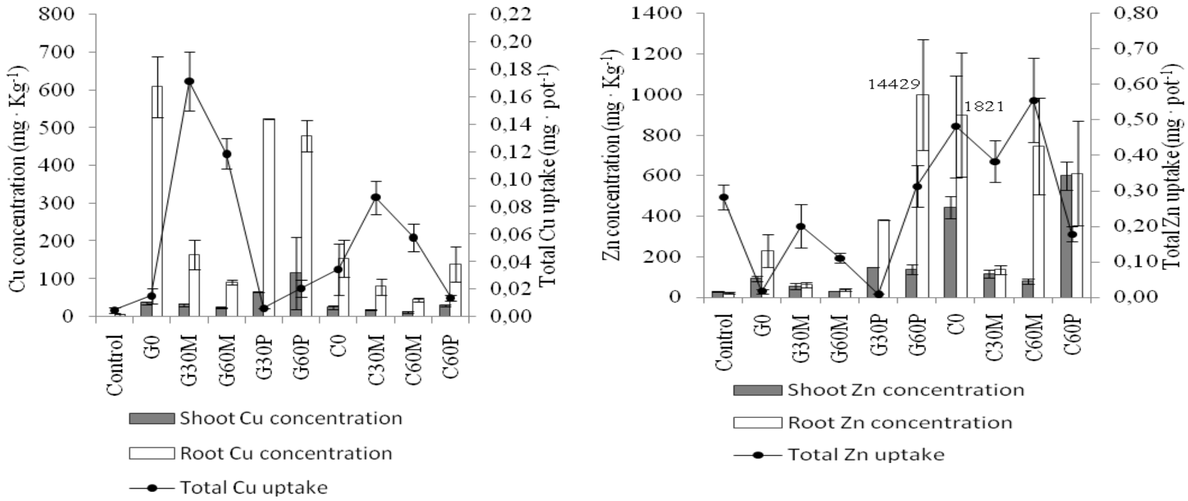

Figure 2. Metal concentration in shoot and root and total metal uptake by *B. juncea* in different soils and amendments (Error bars represent standard deviation. Bars of G60P and G0 of Zn concentration were reduced in order to maintain the graphic scale. Their total values are shown on the top of the bar and error bars were proportionally reduced)

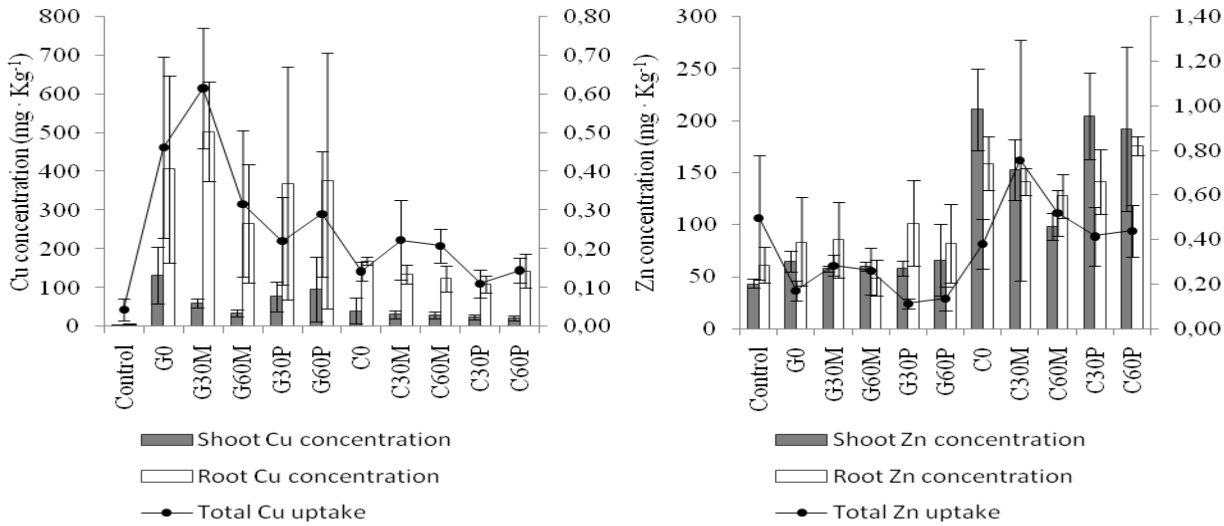

Figure 3. Metal concentration in shoot and root and total metal uptake by *A. halimus* in different soils and amendments (Error bars represent standard deviation)

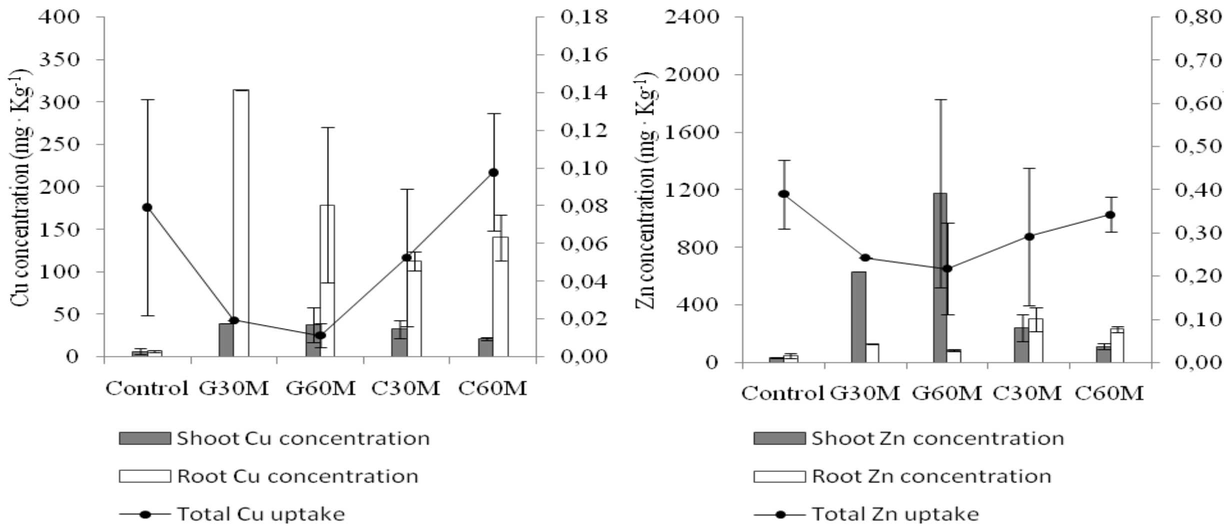

Figure 4. Metal concentration in shoot and root and total metal uptake by *T. arvense* in different soils and amendments (Error bars represent standard deviation)

A sequential extractions procedure (Tessier et al., 1979) was carried out in order to observe the different chemical fractions of Zn and Cu (

Figure 5). Residual fraction was not measured because its little influence on metal bioavailability. Results show that a high amount of Zn was bounded to Fe-Mn oxides because it is strongly associated with oxides whereas a considerable amount of Cu, which has a high affinity for carboxylic and phenolic groups, was associated to organic matter. Also the water soluble + exchangeable fraction of Zn was high, specially in Cuadron treatments.

Althought *A. halimus* presented a lower Zn concentration it was the species that achieved the greatest metal uptake (Cu and Zn) because its greater growth, with the highest accumulation in aerial organs and therefore suitable for phytoextraction techniques. Lutts et al. (2004) observed that *A. halimus* accumulates Zn and Cd in aerial organs without showing any significant decrease in biomass production during 3 weeks in nutrient solution. On the contrary, *T. arvense* had the lowest metal uptake.

The most labile fraction of Cu and Zn (water soluble + exchangeable) decreased while carbonate fraction increased when manure amendments were added to soils. Xian and In Shokohifard (1989) found that the proportion of Zn in the exchangeable fraction increased and that Zn in the carbonate fraction decreased when soil pH was lowered. This loss in soluble + exchangeable fraction was balanced with an increasing organic-bounded Cu or Zn bounded to Fe-Mn oxides. These changes were due to the increasing pH of manure amendments that affected the variable charge of organic compounds and Fe-Mn oxides. The two soils followed the same pattern but Cuadron treatments presented more Cu and Zn bioavailability whereas in Garganta treatments the sum of Cu recovered across the four fractions was considerable higher.

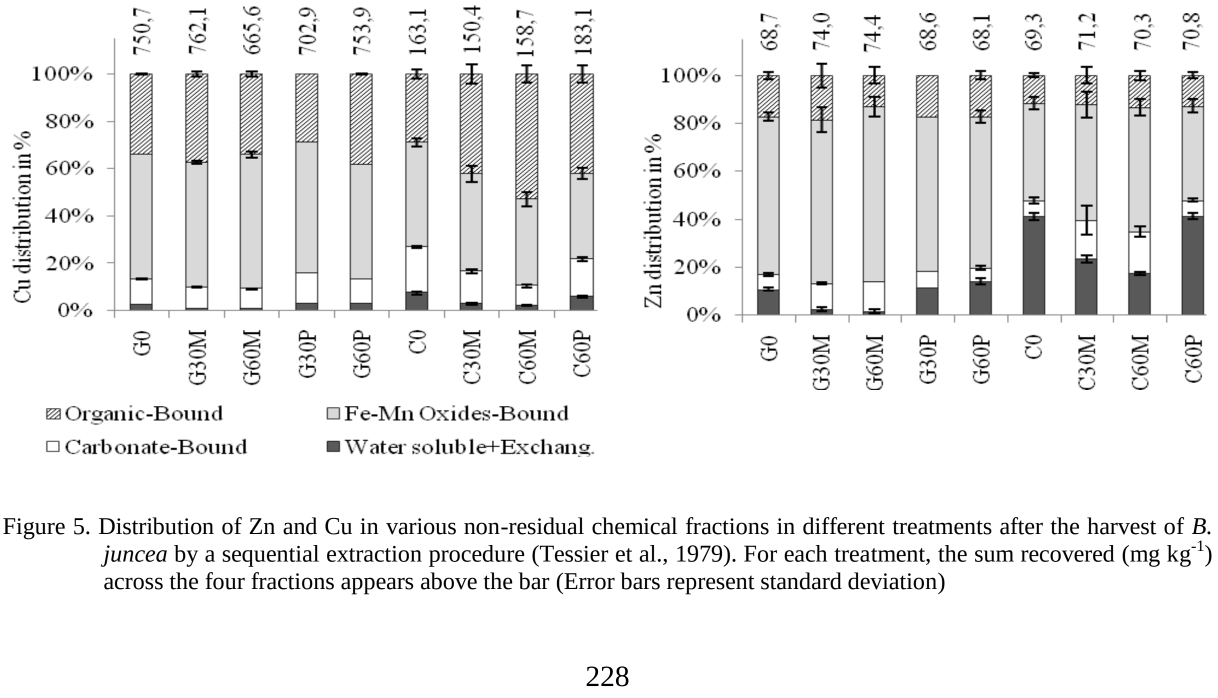

Figure 5. Distribution of Zn and Cu in various non-residual chemical fractions in different treatments after the harvest of *B. juncea* by a sequential extraction procedure (Tessier et al., 1979). For each treatment, the sum recovered (mg kg^{-1}) across the four fractions appears above the bar (Error bars represent standard deviation)

Table 2. Pearson's correlation coefficients (r) between metal uptake and concentration in plant organs (shoots and roots) of *B. juncea* and metal concentration in the different fractions by the Tessier et al. (1979) procedure

Correlation coefficient (r)		I.Water soluble+ exch.	II.Carbonate	III.Fe-Mn oxides	IV.Organic	Sum of I+II
Zn	Shoot	0.90**	-0.29	-0.36*	-0.27	0.77**
	Root	0.06	-0.29	0.07	0.11	-0.04
	Total uptake	0.40*	0.33	-0.42*	-0.38*	0.48**
Cu	Shoot	0.62**	0.48**	0.41*	0.49**	0.54**
	Root	0.89**	0.80**	0.63**	0.66**	0.86**
	Total uptake	-0.40*	0.24	0.42*	0.30	0.10

** Significant at probability level $P < 0.01$; and * Significant at probability level $P < 0.05$

Table 2 shows correlation coefficients between metal concentration in plants and total uptake by *B. juncea* and concentration of the different non-residual fractions in soils. The strong correlation between water soluble + exchangeable fraction and Zn shoot (r = 0,90) and Cu root (r = 0.89) concentration stands out and this fraction is also good correlated with Cu shoot concentration. Therefore, metal concentration in plant tissues increased in response of a higher soluble and exchangeable metal content in soil. There was also a good correlation between carbonate fraction and Cu in roots and less with this metal in shoots, whereas Zn concentration did not present such relation. If the sum of these two first and most available fractions is considered these results are consistent with Xian (1989) who found that the sum of exchangeable and the carbonate-bound forms were strongly correlated with Zn uptake by *Brassica oleracea*.

4. CONCLUSION

The addition of manure compost to metal contaminated soils resulted in a higher biomass production and a lower Cu and Zn concentration in plant tissues. This was probably due to a low metal bioavailability caused by an increasing pH and the contribution of organic matter that not only reduced metal phytotoxicity but was also a source of nutrients for plants. Moreover, a larger amount of metal was removed from soils when adding this amendment given the higher plant growth. Addition of this type of organic amendment could be effective for stabilization of metals in contaminated soils. In contrast, pine bark amendments did not achieve such results.

It was observed that *A. halimus* developed a considerable growth in spite of metal stress conditions and achieved the greatest Cu and Zn uptake making it suitable for phytoextraction purposes. The sequential extractions procedure of Tessier et al. (1979) was designed to separate Zn and Cu in different fractions showing that the most labile fractions decreased with the application of manure amendment increasing the proportion of metals associated to more unavailable chemical forms. This decrease was reflected in a lower metal concentration in plant tissues of *B. juncea*.

5. ACKNOWLEDGEMENT

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Research
Araştırma

DECOMPOSITION RATES OF INTERCROPPED GREEN MANURE CROPS IN OAXACA, MEXICO

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Abstract: In the Central Valleys of Oaxaca, México, crop production is seriously limited by soil moisture and fertility, as well as by land scarcity. To try to alleviate these constraints, an experiment to evaluate the feasibility of producing green manure crops intercropped with maize (*Zea mays*), residue decomposition rates and nitrogen content at full bloom was conducted. The mung beans (*Vigna radiata*) and dolichos beans (*Dolichus lablab*), planted as single crops, out yielded widely the other species evaluated, but decreased significantly their dry matter production when intercropped with maize, particularly mung beans. Maize production was also affected by the intercrops, especially crop grain yields when grew associated with crotalaria (*Crotalaria juncea*). On average, biomass production of intercropped legumes decreased 31.3 %, with extreme values of 22.1 % for crotalaria and of 37.4 % for mung beans. Using the methodology of burying residues contained in mesh bags, it was found that mung and dolichos beans showed the highest decomposition rates (8.8 and 9.1 g ha^{-1} per day, respectively), while crotalaria and common beans reached values of 4.1 and 5.7 g ha^{-1} per day, respectively. Decomposition rates were significantly related to soil temperature and water content, as well as to C/N ratios of the residues. Given its characteristics of high drought tolerance and rate of height increase when intercropped, crotalaria is a species suitable for intercropping with maize in more marginal areas. Because of its growth habit and long life cycle, which minimizes competence with maize during its critical stages, dolichos bean has a good potential to grow well in association with maize in deep soils under rain-fed conditions.

Key Words: Crotalaria, Dolichus, Vigna, Phaseolus, Poor soils, Peasant agriculture

1. INTRODUCTION

In the region of the Central Valleys of Oaxaca there are serious limitations for the production of maize, the staple food crop of most Mexicans. Among the main problems are mid summer drought and low soil fertility are included (Ruiz and Silva, 1999).

A possible alternative to solve the problems of low fertility and variability of crop production is the association of maize with legumes. The maize-bean intercrop, where the beans are an early variety, is more likely to produce, given the greater precocity of beans (Herrera and Ruiz 1994, Ruiz and Loaeza, 2004). The problems of low soil nitrogen and variable rainfall, can be alleviated with the association of maize with drought-tolerant legumes (Graham and Ruiz, 1996).

Sangakkara *et al*. (2004) found that the addition of green manure for three years was reflected in an improvement of the physical properties of soils, as well as increased amounts of available N, P and K. Incorporation of Crotalaria, with higher nitrogen content, promoted plant growth, while Tithonia favored the development of the root system of maize. In a previous study (Ruiz and Loaeza, 2003), we investigated the possibility of producing green manure crops in association with maize under rainfed conditions in the Central Valleys of Oaxaca, but the humidity conditions could be limiting for decomposition of the plant material, as well as for nutrient mineralization. In Tabasco, Mexico, it was found that temperature and high humidity favored the decomposition of Mucuna pruriens residues, but under excessive moisture decomposition rates decreased by about 50% (Jerome *et al*., 2002). Other factors affecting the rate of decomposition are the C / N ratio, which is determined by the nitrogen content of crop residues and soil. Ellis *et al*. (2003) reported that the amount of N mineralized was higher in alfalfa residues than in grass residues, given the lower C/N ratio in the legume. In this area, nitrogen (N) is the major constraint to maize production, therefore the N derived from symbiotic fixation is an important component of soil fertility and is required to know more accurately the contribution of symbiotic N to soil reserves. The precise quantification of total nitrogen of the plant is difficult due to the difficulty to include the rootlets and rhizosphere fractions of root systems (Kuskopf *et al*., 2003). The nitrogen content in the roots, which is proportional to its dry weight varies between 28 and 52% of total N accumulated per plant (Rochester *et al*., 1998, Khan *et al*., 2002).

The proportion of nitrogen in the root and aerial parts is differentially affected by water stress according to the species of legume. Ludlow (1989) reported that the decrease of soil moisture reduced the amount of N in both root and aerial parts of the two legumes. However, mung bean maintained a nearly constant proportion (35 to 40%) of N in the roots, while the peanut increased its value from 24 to 44%.

This study was aimed to assess the rates of decomposition of crops that can serve as a green manure, planted in monoculture and also associated with maize under rain-fed conditions, as well as the potential contribution of organic matter from aboveground and belowground structures.

2. MATERIAL AND METHODS

The experiment was planted June 15, 2001 in Santa Cruz Xoxocotlan, Oax., Mexico in a deep sandy loam soil of fluvial origin, but low in organic matter (0.70%) and with medium levels of phosphorus and potassium (9.40 mg kg^{-1} and 1.72.cmol (+) kg^{-1}, respectively).

Santa Cruz Xoxocotlan is located at 17 º 03 'N and 96 º 43' W, at an altitude of 1552 m. It has an average annual temperature of 21.5 º C, with average monthly maximum of 36.4 º C in May and minimum of 5.8 º C in January. Average annual rainfall is 660 mm, concentrated in the months of June to September; in this period, the monthly maximum temperatures range between 31 and 33 º C while the monthly minimum temperatures range between 11 and 13 ºC.

The experimental treatments consisted of four legumes planted in monoculture and associated with maize (*Zea mays*) var. "Criollo Bolita". The legumes were common bean (*Phaseolus vulgaris*) var. thin black, mung bean (*Vigna radiata*) var. Texas, Dolichos bean (*Lablab purpureous*) var. Brown and Crotalaria (*Crotalaria juncea*). The maize planting density was maintained at 40 000 plants ha^{-1}, while legumes were seeded at a density of 66% of the planting rates used in their monocultures.

During the growing season data on crop growth, rainfall and temperature were collected. Plant heights and development were measured in 10 plants per plot every 15 days using the Fehr *et al.* (1971) system for legumes and Ritchie *et al.* (1992) for corn. When legumes reached full bloom (R2) we estimated dry matter production at the roots and shoots from a sample of 10 plants per treatment and repetition. The plants were pulled out from the soil, which had a good moisture content, the root and shoots were separated and placed to dry for 48 hours in an oven at 70 ºC.

The proportion of dry matter present in the roots (PPR) was estimated using the following formula:
PPR = (root weight / (root weight + weight aerial part)) x 100.

To estimate the rates of decomposition, we buried 15x20 cm mesh bags in two replications per treatment, at a depth of 15 cm. Each bag contained 10 g of fresh material from the aerial part of Crotalaria, Dolichos bean, mung and common bean. This amount was equivalent to 986.6, 916.5, 1086.4 and 1016.3 kg ha^{-1} of dry matter according to the moisture present in each species. The determination of the N percentage of crop residues was by the Kjeldahl method (AOAC, 1999).

The bags were removed at three, six and nine weeks after placement, and thus obtained 2 remaining weight values, for a total of 6 per species. During this period were quantified minimum and maximum temperatures of soil (7-8 and 14-15 h) to 15 cm deep (glass thermometer mod Taylor brand. 6332), and its moisture content by gravimetric method.

Also were generated linear models (SAS, 2002) to relate the decay rates of residues with average soil temperature and moisture.

3. RESULTS AND DISCUSSION

3.1. Plant Height and Dry Matter Production

Under conditions of monoculture, maize was the dominant crop, followed by crotalaria. The latter one showed greater height under association than in monoculture at all dates. The common and mung beans showed very low rates, but were not significantly affected by competition with corn until 48 days after planting (dap). At 61 dap, the height of the latter crop was significantly lower in association, while the Crotalaria and dolichos beans in policulture tended to exceed the height observed in monoculture.

Competition between crops under policulture starts from the time of emergency. Effects of high competition between tall corn varieties and legumes have been reported. Parra (1989) found that hybrid corn was not suitable to be associated with common bean or mung bean given its height. In this study, mung beans were more affected than the common bean when associated with maize.

Jeranyama *et al*. (2000) found that two green manure species associated with maize responded differently according to their growth habit. *Vigna ungiculata* showed less growth than *Crotalaria juncea* because the latter has an upright growth habit which allows crotalaria to intercept more solar radiation.

Regarding the time of coexistence between crops, corn stopped growing at 65 dap, while dolichos beans continued to grow up to 130 dap. Thus, the critical stages occur in very different dates, and a high interspecific competition was not observed.

In another study, associations of jack beans-maize and jack beans-sorghum were compared and found that the intensity of interspecific competition was greater in the first association, as the corn plants were higher than those of sorghum, as well as the coexistence time (Contreras *et al*., 1989).

In this study, Dolichos and mung beans grown in monoculture surpassed all other species tested, but also decreased significantly their productivity when associated with corn, especially mung beans. On average, the biomass yield of associated legumes decreased 31.3%, with extreme values of 22.1% to 37.4% for crotalaria and common beans, respectively. These results are similar to those reported by Ruiz and Loaeza (2003), who found average declines of 28.5% in soybeans and chickpeas when they were associated with maize in the same region. However, for the common bean *Phaseolus vulgaris* reductions of up to 45% have been observed when associated with maize (Clark and Francis, 1985).

Apparently the root / shoot ratio (R/S) of beans is highly influenced by soil fertility. Thus, Bernal *et al*. (2007) reported values of 33 % of roots in cv. C60 in a soil fertilized with diammonium phosphate, whereas without fertilization there were values close to 50 %. Also Avilán and Louis (1976) reported that the proportion of roots in beans cv "Carioca" varied between 18.0 and 25.2 %, the highest value was found in a very low soil P.

In another study, dry matter yields for Crotalaria were from 0.9 to 2.9 t ha^{-1} (Jeranyama *et al*., 2000), while for eight varieties of beans planted in monoculture at high densities values from 0.7 to 1.8 ton ha^{-1} were obtained at full bloom (Araujo *et al*., 2000).

For dolichos beans, the production of the aerial part, evaluated at 19 weeks after planting, was 1.8 to

2.0 ton ha^{-1} of dry matter (Carsky *et al*., 1999). The yield of green manure of mung beans has been estimated between 1.1 (Thonnissen *et al*., 2000) and 2.3 ton ha-1 dry matter (Leyva *et al*., 2003).

Table 1 shows the values of R/S for different crops. The maximum values of R/S were observed for Crotalaria both in monoculture and in association. These values seem low, especially when compared to figures reported by Stoffella (1979), who estimated that the amount of dry matter remaining in the roots of common beans can be up to 58%. In an evaluation of 13 species of leguminous cover crops, which included the Dolichos bean, it was found that root weight represented about 1 / 3 of the total weight of the plant (Tian and Kang, 1998).

Crotalaria and mung beans showed the highest values of R/S both in monoculture (25.3 and 21.8%) and in association (22.7 and 18.6%); also they were the least affected in terms of R/S when associated with corn (10.2 and 14.7 %). Islam *et al*. (2007) reported variations from 15.7 to 21.2% in the R/S of 530 genotypes of mungbean. Rajendira and Ramanujam (2004) reported values of dry weight of roots and shoots of 4.9 and 24.9 g / plant, respectively, for the cultivation of mung beans var KM-2, resulting in a R/S = 19.6%.

Maize yields were also affected, especially grain production, when associated with crotalaria. This is a legume with a high growth rate, which allowed it to compete effectively with corn for light in the vegetative growth stage.

3.2. Decomposition Rates and Nitrogen Supply

Maximum decomposition rates were observed in mung beans and Dolichos (8.8 and 9.1 g ha^{-1} per day, respectively) at the maximum values temperature and moisture contents experienced (24.5 º C and 12.6 %). This means that in four weeks with adequate conditions of humidity and temperature, around 250 kg ha^{-1} would decompose when these green manures are incorporated into the soil, which was equivalent to 23% of mungbean residues and to 35% of dolichos bean residues. These values of decomposition are lower than those reported by Njunie *et al*. (2004), whom, in a more humid environment, found that the percentage of residues remaining in dolichos beans was 54, 35, and 25% after 2, 4 and 8 weeks of incorporation. In another study, Dolichos beans with a C/N ratio of 11:1, lost 63% of their initial weight after four weeks (Ibewiro *et al*., 2000).

The crotalaria and beans showed the lowest decay rates, reaching 4.1.y 5.7 g / day, respectively, under the maximum conditions of temperature and humidity shown above. We know that these rates were also conditioned by the C/N ratio, in addition to the soil nitrogen content (Ryan *et al*., 2003). Table 5 shows that these two species had high values of C/N.

Abreau (1996), found that the rate of decomposition of crop residues evaluated during the rainy season, varied with the crop species, noting a slower decomposition in *Crotalaria juncea*, followed by *Cajanus cajan, Phaseolus lunatus* and *Canavalia ensiformis*. After 32 days, *C . juncea* had lost 26.8% of its initial dry weight, whereas *C. ensiformis* had lost 69.3 %. The C/N ratio was higher in *C. juncea*. Table 2 shows the percentages of nitrogen for the four species in both above and below ground plant parts, as well as the C/N ratios. Dolichos and mung beans showed higher contents and contributed the largest total amount (35-62 kg ha^{-1}).

Dolichos and mung beans can contribute up to 80-106 kg ha $^{-1}$ N (Cherr *et al*. 2006; Shah *et al*. 2004), while crotalaria is characterized by its high fiber content in the stem and a low leaves/stem ratios; while it's C/N ratio is close to 40 (Yano *et al*., 1994;), its N supply capacity was estimated at 53 kg ha^{-1} (Jeranyama *et al*. 2000). Beans are characterized by their low capacity for symbiotic N fixation, which coupled with its low biomass production, resulted in a contribution of only 19-28 kg N ha-1 (Araujo *et al*., 2000; Ojiem *et. al.*, 2007).

Table 1. Dry matter yields and root/shoot ratios of mono and intercropped green manure species

Crop or policulture	Residues (kg ha^{-1})	Roots (kg ha^{-1})	Root/shoot ratio (%)
Common beans (CB)	1219 c †	248 bc †	16.9 c †
Mung beans	1955 b	546 a	21.8 b
Dolichos beans	2865 a	666 a	18.8 c
Crotalaria	1731 b	587 a	25.3 a
Maize-CB	763 d	111 c	12.7 d
M.- mung beans	1290 c	296 b	18.6 c
M.- dolichos beans	1951 b	324 b	14.2 d
M.-crotalaria	1347 c	396 b	22.7 ab

† Values with the same letter are not statically different according to Duncan (P< 0.05) test

Table 2. Nitrogen content, C/N ratio and total N content of four species of green manure crops associated with maize

Crop under policulture	N content (%)	C/N ratio	Total N content (kg ha^{-1})
Common beans	2.32	18.75 b	17.70 c †
Crotalaria	1.94	22.42 a	34.21 b
Mungo beans	2.76	15.76 c	35.60 b
Dolichos beans	3.21	13.55 c	62.63 a

† Values with the same letter are not statically different according to Duncan (P< 0.05) test

4. CONCLUSION

The crotalaria considerable height growth rates, especially when planted in association. Given its high drought tolerance, is a species with high potential for cultivation as green manure in association with maize in areas with thin soils and low or ill-distributed rainfall.

Another promising species for policulture is the dolichos bean, since it's growth habit and life cycle avoid competition for resources in the critical stages of corn, therefore it is recommended in association with corn for deep soils in rain-fed areas.

Decomposition rates were highly conditioned by air temperatures and soil moisture, as well as the C /N of the crop residues.

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Research
Araştırma

NUTRIENT ACCUMULATION IN STREET GREENERY OF RIGA (LATVIA) IN INCREASED SALINITY CONDITIONS, 2005 AND 2007

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Abstract: One of the most widespread tree species of street greenery in Central, Northern and Eastern Europe, int. al. in Riga (Latvia) located in the boreo-nemoral zone, is lime tree *Tilia x vulgaris* H. A topical problem in the boreo-nemoral zone is using of de-icing material in winter to prevent ice formation on roads and salt accumulation in greenery. The aim of the research was to find out the macronutrient status in the street greenery of Riga to reveal the effect of de-icing salt accumulation on the element supply and the vitality of *T. x vulgaris*. The concentrations of K, Ca, Mg and Na, Cl^- were estimated in lime leaf and soil samples collected from 27 study sites (5 streets or 8 objects) in Riga from March 2005 to August 2007, but the concentrations of N, P and S in samples from June and August 2007. Additional three sites in a park area were chosen for the background level. A bioindication research on the vitality of the street greenery carried out in August of 2005 and 2007 revealed mainly damaged status of lime trees. The damages to the deciduous trees typically appeared as leaf necrosis and dead branches. Ordination with principal component analysis (PCA) of results showed a high heterogeneity of the soil and lime leaf chemical composition. A negative medium close correlation was found between the concentration of Na and K in the leaf samples in July and August 2005 and August 2007, as well as between Na and Mg in June 2005. Our research did not reveal a statistically significant correlation between the content of Cl^- and its antagonists (N, S, P) concentrations in lime leaf and soil samples, as exception – there was a negative medium close correlation between the Cl^- and Ca in lime leaves of August 2007. The main problems of the mineral nutrition of the street greenery in Riga during 2005 and 2007 were elevated concentration of Ca, Mg and P, decreased concentration of N, S and, especially, K in soil, which could be promoted by Na and Cl^- regular accumulation in soil, as well as other factors. Whereas insufficient amount of K and in several sites S, Mg and P, was stated in lime leaves in 2005 and 2007. Probably, it could be facilitated by Na^+ and Cl^- antagonism in the street greenery of Riga.

Key Words: Elements, De-icing salt, Street trees, Soil, Lime leaves

1. INTRODUCTION

Plant supply with mineral nutrients, which functions can not be replaced by other chemical elements, is an important factor for normal plant growth and development. In the boreo-nemoral zone street trees are subjected by many negative factors, int. al., imbalanced plant supply with nutrients, as well as de-icing salt accumulation in greenery soil. Our previous works on chestnut and lime in Riga (Latvia), located in the boreo-nemoral zone, showed a regular and intensive accumulation of Na^+ and Cl^- in street greenery snow, soil and tree leaves reaching toxic amounts (Cekstere et al., 2008). Both Na^+ and Cl^- have antagonistic effect on plant nutrient uptake (Marschner, 1995; Neuman et al., 1996). An inadequate supply with biogenous elements and regular accumulation of de-icing salts in street greenery is a very serious problem causing disturbances in different plant physiological processes, decreasing tree tolerance to unfavourable factors, therefore influencing greenery ecological functions. According to Mertens et al. (2007) there are differences in nutrient accumulation between plant species growing in the same soils, as well as differences due to regional variations, sampling time, pollution etc. Results of different urban soil studies are also difficult to compare due to differences in soil extraction. One of the most widespread tree species of street greenery in Central, Northern (Sæbø et al., 2003) and Eastern Europe, int. al., Riga (Latvia) is lime tree - *Tilia x vulgaris* H. Thereby, nutrient supply for *T. x vulgaris* in the street greenery based on soil and plant chemical analysis in conditions of increased salinity has not been investigated sufficiently. The object of the research was to find out the macronutrient status in the street greenery of Riga to reveal the effect of de-icing salts on the element supply and the vitality of street trees *T. x vulgaris*.

2. MATERIAL AND METHODS

The study was conducted in Riga (a capital of Latvia, Eastern Europe) - situated along the Baltic Sea at the southern part of the Gulf of Riga in the boreo-nemoral zone. The climate of Riga is moderately warm and humid. The mean annual amount of precipitation is 700-720 mm. The average temperature in January is - 4.7^oC, in July - +16.9^oC (Anonymous, 2005). 27 old street trees (8 objects, to ~100-year-old trees) and 3 trees growing in a park (one object - a background level) were selected in the central part of Riga in 2005 (Figure 1), but in 2007 – 26 street trees as one tree was decayed. Each object consisted of 3-4 neighbouring trees located up to 3 m from the edge of the road with intensive traffic.

Soil samples (obtained from three sub-samples) were collected from a tree-rooting zone (roadside) to a depth of 35 cm in March, June and July 2005, June and August 2007. For each plant sample 50 leaves (just reaching maturity and full size) were collected from different branches of trees along roadsides during the vegetation season of 2005 (June, July and August) and 2007 (June and August).

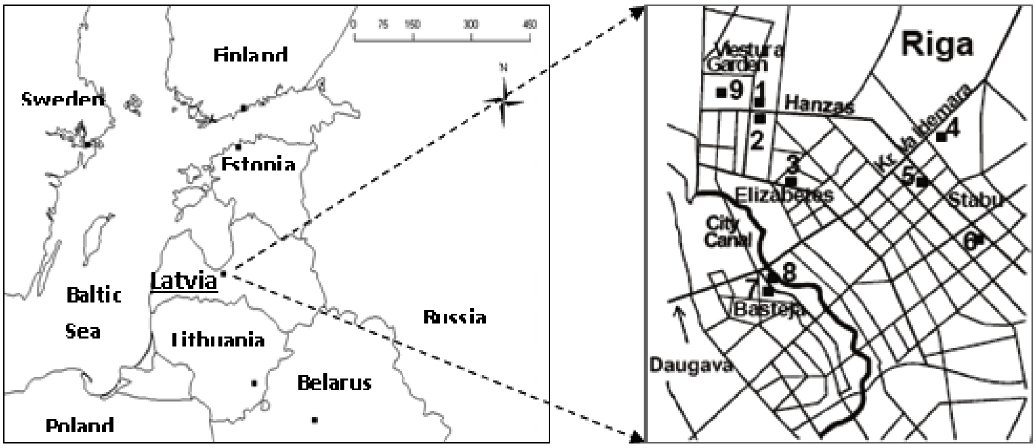

Figure 1. Studied object location in the central part of Riga. (1 – Hanzas 1; 2 – Hanzas 2; 3 – Elizabetes; 4 – Kr. Valdemara; 5 – Stabu 1; 6 – Stabu 2; 7 – Basteja 1; 8 – Basteja 2; 9 – Viestura Garden (park/background level)

After tree crown pruning in winter 2005 leaf sampling was not possible for 6 trees (2 objects) in June 2005. Along with leaf sampling in August an assessment of the physiological status of the street trees (healthy, slightly damaged, medium damaged and severely damaged) was done.

The soil samples were dried at +35°C and sieved <2 mm. To determine the plant available amounts of 6 macronutrients and Na the soil samples were extracted with 1 M HCl solution. The leaf samples were washed with distilled water, dried at +60 °C, ground, then dry-ashed in concentrated HNO_3 vapour, re-dissolved in HCl solution. Ca and Mg were determined by AAS (*Perkin Elmer AAnalyst 700*); K, Na - by flame photometer (*JENWAY PFPJ*); N, P - by colorimetry, S - by turbidimetry, Cl^- - by $AgNO_3$ titration in all samples of 2007 (Rinkis et al., 1987). The level of K, Ca, Mg, Na and Cl^- was estimated in samples collected in 2005.

Statistical analyses of chemical results were done using *SPSS 14.0 version*. The correlation coefficients were classified as follows: r<0.5 week, 0.5<r<0.8 medium close, and r>0.8 close correlation, $p<0.05$. Ordinations with principal component analysis of results were done using *PC-ord5*.

3. RESULTS AND DISCUSSION

The results of the street tree's vitality in Riga (Table 1) revealed mainly seriously damaged status for *Tilia x vulgaris* during the vegetation season of 2005 and 2007 (in 2005: 17.81 % healthy, 7.41 % slightly damaged, 22.22 % medium damaged, 55.56 % severely damaged trees; in 2007: 15.38 % healthy, 3.85 % slightly damaged, 34.62 % medium damaged and 46.15 % severely damaged trees). The main typical damages for trees were: leaf necrosis, crown defoliation and dead branches, as well as insect damages.

Vast ranges of optimal and average concentrations of nutrients have been found in different studies on *Tilia* spp. (Insley et al. 1981; Bergmann 1988; Kopinga, van den Burg 1995; Nollendorfs 2003; Čekstere et al. 2005). Our soil and lime leaf chemical results also revealed a high heterogeneity of macronutrient, as well as Na and Cl^- concentrations in the street greenery (Figures 2 & 3). The lowest element concentration variance in soil and leaf samples was stated for nonmetals S and N, but the highest variance for metals Ca and Mg. There was no close correlation between the concentration of macronutrients, as well as Na and Cl^- in the soil and lime leaves.

The use of de-icing salt (NaCl) caused a considerably increased Na and Cl^- accumulation in the street greenery soil, especially at the end of winter 2005, and lime tree leaves to compare with the park (Figures 2 & 3). In several sites the concentration of Na in soil samples of March 2005 was even more than 1000 mg/kg (max. 1568 mg/kg), which exceeded the background values by up to 51 times. The decrease in Na and Cl^- concentrations from March to July of 2005, as well as from June to August of 2007 was likely due to leaching from upper layer of the soil, percolation deeper into soil and uptake by plants. However the concentrations of Na, unlike Cl^-, in the soil of the street greenery remain still increased during the both vegetation periods. Our results revealed that the concentrations of Cl^- in the street soil samples collected in June 2005 and 2007 on average were not significantly different, while results of Na were significant higher in 2005 to compare with 2007. Such situation could be explained by the winter season of 2006/2007, which was warmer in comparison to 2004/2005 (www.meteo.lv/public). As a result, decreased amounts of de-icing salts were applied on streets and decreased accumulation of ions occurred in the street soil. Besides, Cl^- as anions are more leachable from the soil and more rapid decrease in concentrations to compare with Na^+ occurred. Cl^- usually follow the water and do not take part in chemical reactions, while Na^+ participate in chemical processes in the soil and are to a great extent retained in the upper part of the soil profile (Lundmark, Olofsson, 2007).

Table 1. Description of studied objects in Riga

Object	Distance of tree's stems to street	Status of trees in August 2005 and 2007
1: Hanzas 1 (3 trees)	~2m	2005: severely damaged (*); 2007: severely damaged.
2: Hanzas 2 (3 trees)	~2.15m	2005: medium damaged: 2007: medium damaged.
3: Elizabetes (5 trees)	~0.7m	2005: 1-healthy, 1-slightly damaged, 3- severely damaged; 2007: 1-healthy, 3-severely damaged, 1-dead in 2006.
4: Kr.Valdemara (3 trees)	~0.7m	2005: 1-medium damaged, 2-severely damaged; 2007: medium damaged.
5: Stabu 1 (3 trees)	~0.6m	2005, 2007: 2-medium damaged, 1-severely damaged.
6: Stabu 2 (4 trees)	~0.6m	2005: 1-slightly damaged, 3-severely damaged; 2007: 1-slightly damaged, 1-medium damaged, 2-severely damaged.
7: Basteja 1 (3 trees)	~3.5m	2005, 2007: healthy.
8: Basteja 2 (3 trees)	1.0-1.5m	2005, 2007: severely damaged.
9: Park (3 trees)	>50m	2005, 2007: healthy.

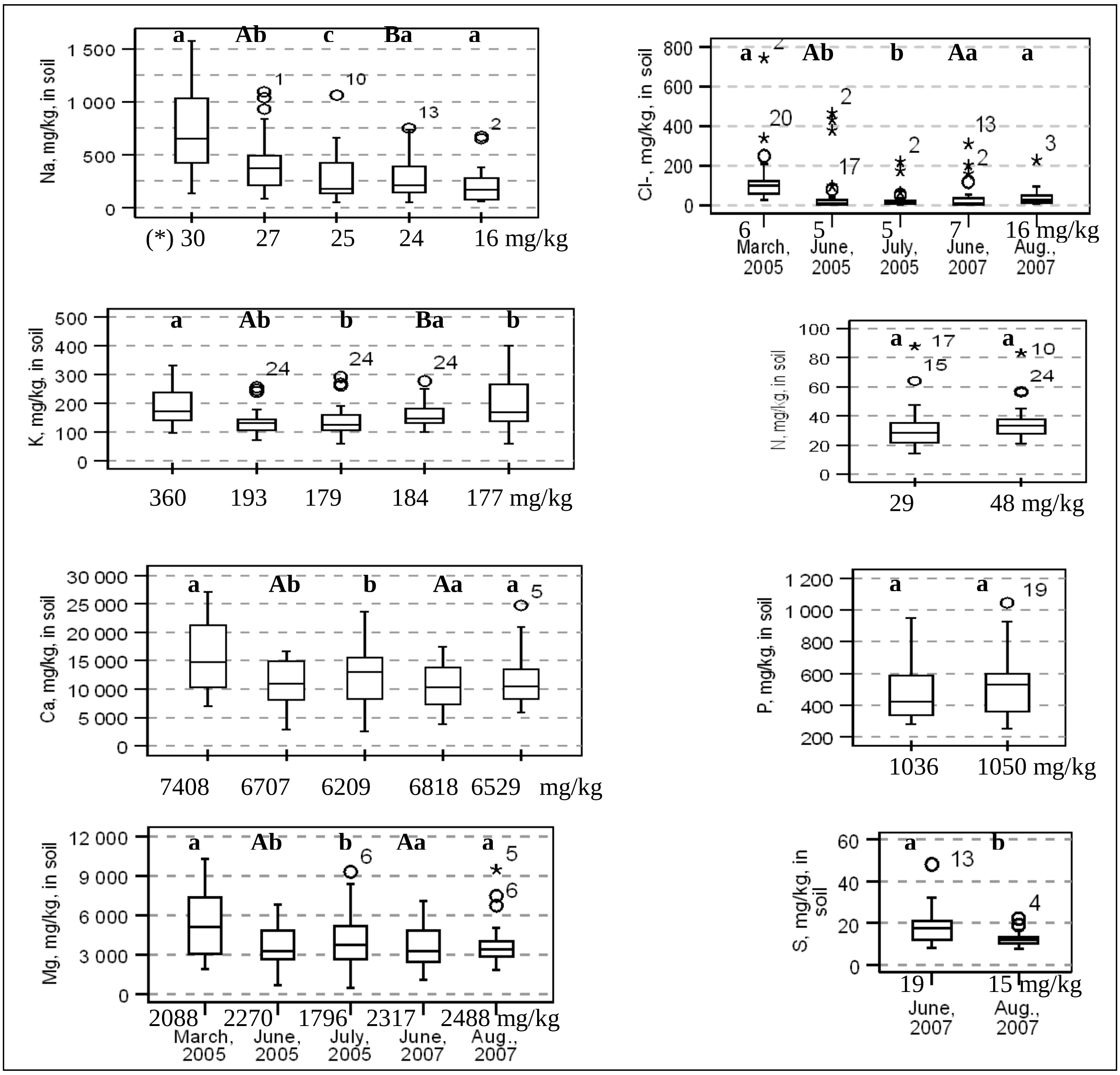

Figure 2. Macronutrient, Na and Cl^- concentration in soil samples in Riga during 2005 and 2007 (* - background level (park) abc – to compare the results between the months during one year AB – to compare the results between the same months of different years)

The analysis of plant material showed that the soil salinity induced increased Na and Cl^- concentrations in lime leaves in sites with higher soil salinity during 2005 and 2007. During the vegetation seasons, Na ranged from 0.01 % in June to 1.93 % in August, which was up to 48 times higher than at the park, but Cl^- concentration ranged from 0.17 % to 3,00 %, and was more than 25 times above the background level. The lowest concentrations of Na and Cl^- in lime leaves were found in sites situated about 3.5 m from the carriageway. These limes were characterized as healthy. In general, the concentrations of Na and Cl^- in tree leaves showed a tendency to increase during the vegetation periods, except Cl^- in summer of 2007. The investigation revealed a significant problem in the street tree supply with K, which is one of the main antagonistic elements to Na (Figure 2). A low level of K was stated for most of the street soil sites at the beginning of spring 2005 (96-200 mg/kg), which continued decreased markedly during the vegetation season (up to 61 mg/kg). Also the concentrations of K in the soil from the vast majority of sampling sites (2005) were lower to compare with the park. It was consistent with other studies in urban areas where soil contented construction and demolition wastes (Meyer, 1978; Čekstere et al., 2005).

The results showed a negative medium close correlation between the level of K in the soil samples of March 2005 and Na in the leaves during summer 2005 (r_{June}=-0.65, n=21, r_{July}=-0.61, $r_{Aug.}$=-0.58, n=27) revealing the great importance of soil chemical composition in early spring. To compare two-year results, the level of K in the street soil samples was statistically significant higher in June 2007, contrary to Na. In most of the studied street sites the level of K in the soil was the same as in the park or even elevated, and showed a tendency to increase from June to August, probably due to application of K containing fertilizers. Less amounts of Na in the street soil, which could displace K in the exchange sites in the soil, resulted in improved the K/Na ratio in 2007. In total, the K/Na ratio in the soil samples from the park ranged from 4.15 to 13.48. In the street soils, for healthy limes, the K/Na ratio was 0.13-6.45, for medium damaged limes - up to 4.82, and for damaged trees - 0.07-2.66. It means that the narrow K/Na ratio in the street soil samples had additive harmful impact on the tree status. Better street trees supply with K and lower Na amounts in soil, resulted in higher concentrations of K in lime leaves collected in 2007 to compare with results of 2005. The smallest K result (0.15%) stated in 2005 was even up to 6.33 times lower to compare with the min. K concentration in lime leaves in the park. The status of tree – damaged. At the same time the highest concentrations of K (max. 3.40%) were also stated in lime leaves with necrosis, which mean that sufficient supply with K could not prevent the appearance of leaf necrosis. In Riga, K concentration in healthy lime leaves without necrosis ranged from 0.76% to 2.42%, which was in good agreement with results generalized by Polevoi (1989). The reduction of K in lime leaves during the summer could be explained by reutilization in plant and antagonistic effect of Na ($r_{Na,K\ Aug.2005}$= -0.68, n=27; $r_{Na,K\ Aug.2007}$= -0.44, n=26).

As the external salt concentration rises, the concentration of Na^+ increases and that of K^+ decreases in the roots and leaves. It appears that Na^+ out-compete K^+ for specific binding sites on the K^+ transport proteins, causing K^+ deficiency (Denny 2002; Subbarao et al. 2003). As the result, the decrease of K/Na ratio from June to August was stated. The K/Na ratio for healthy lime leaves without necrosis in Riga's street greenery ranged from 2.92 to 237 (in park: 24.12-270.83), but for leaves with severe necrosis (>30 %) ranged even from 0.15 to 72.00. In general, the stated K/Na ratio diapasons in Riga were substantially wider to compare with results reported by Czerniawska-Kusza et al. (2004) in Opola for *Tilia cordata* (1.76-15.65). It can be concluded that sufficient K/Na ratio in lime leaves did not have determinant role, if the stated leaf necrosis were caused by Cl^- toxicity, or the Na concentration in leaves reached toxic level.

In general, lime tree supply with P in 2007 and Ca, Mg during the vegetation season of 2005 and 2007 in soil could be characterized as optimal to excessive. Soils of Riga are highly anthropogenic, containing in different amounts brick peaces, building remains, as well as constructional dust etc., which contain Ca and Mg. Accordingly, optimal till abundant levels of the elements were stated in the leaves. Expressed tendency for Ca in lime leaves was stated: concentration of Ca increased during the both vegetation periods, as Ca in plants formed insoluble compounds and was not subjected for reutilization. However, the found Mg content in lime leaves less than 0.20% in some streets, probably, due to element antagonism and hard soluble compounds could be insufficient for normal plant development. Na^+ in soil can replace not only K^+, but also Ca^{++}, Mg^{++}, NH_4^+ and other cations on the soil exchange complex. This could lead to nutrient deficiencies and caused injury (Marschner 1995; Sieghardt et al. 2005). A negative, medium close correlation was found between the elevated concentration of Na in the lime leaves and Ca, Mg content in the leaves, especially for June 2005 ($r_{Na,Ca}$=-0.46, $r_{Na,Mg}$=-0.54, n=21). The results of P concentrations in the street greenery soil are consistent with the studies of Ripa and Petersons (1968) on greenery soils in Riga, where high or toxic levels of P were stated, but differ from those of Meyer (1978), who found decreased levels of P and K in substrates with increased contents of artificial materials with alkaline reaction. This fact in Riga could be explained by possible application of phosphate fertilizers, as well as formation of hard soluble P compounds in the neutral and alkaline greenery soils (Cekstere, Osvalde, 2009).

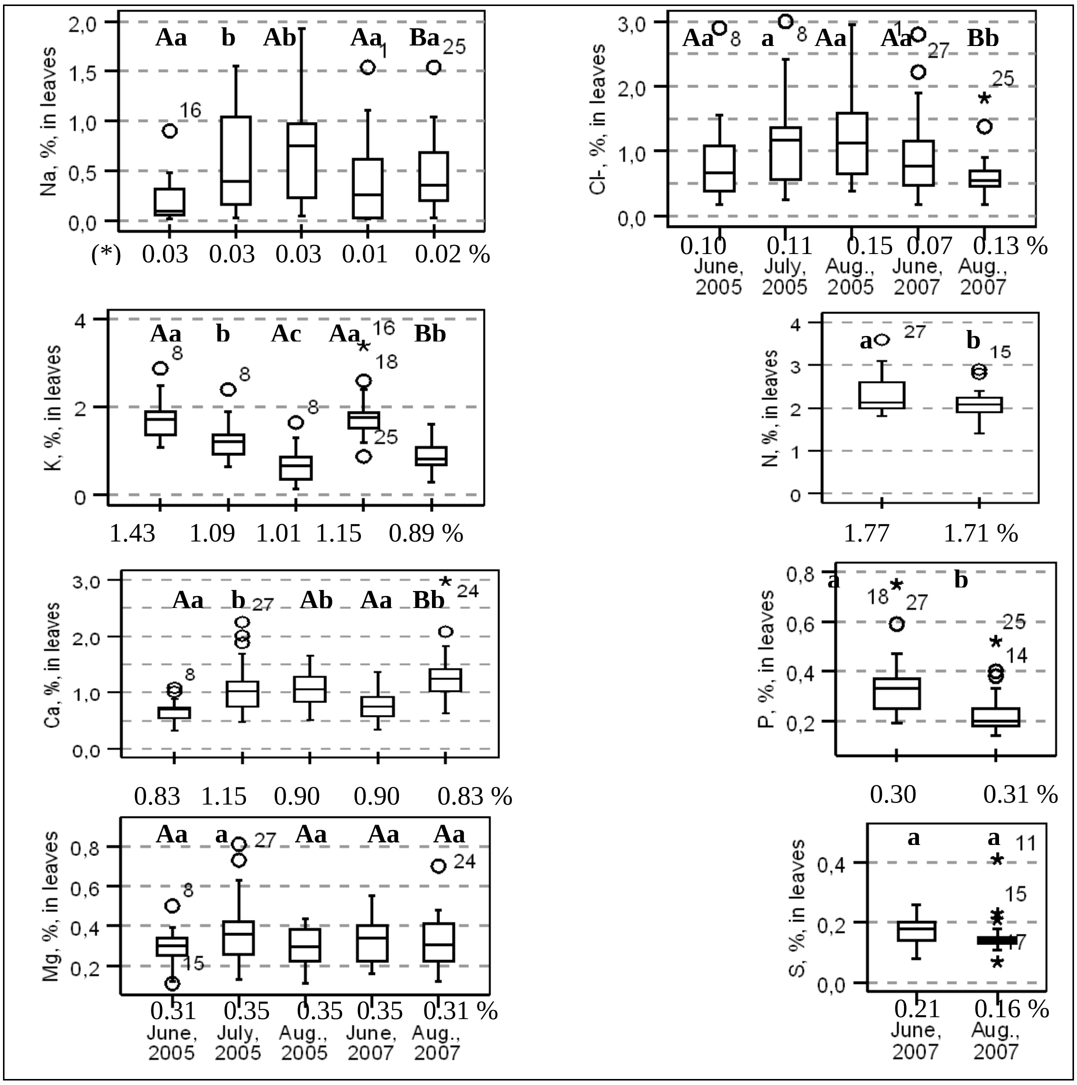

Figure 3. Macronutrient, Na and Cl^- concentration in lime leaf samples in Riga during 2005 and 2007(*) - background level (park) abc – to compare the results between the months during one year. AB – to compare the results between the same months of different years

Thus the stated P concentrations in leaves, mainly in August of 2007, showed insufficient to optimal levels. Our study revealed low levels of N and S in the vast majority of the analyzed soils in June and August of 2007. These results were in a good agreement with other studies in urban areas (Oleksyn et al. 2007).S and N as anions are more leachable from soil to compare with cations. Low levels of S and N in soils of street trees could be due denitrification and desultification processes as the street soils in Riga are highly compact. In highly industrialized areas S requirement of plants is often met to a substantial degree by atmospheric SO_2 pollution. During the last decades industrial SO_2 emissions have been drastically decreased in Western and Northern Europe, int. al. in Latvia and Riga (Jankovska et al. 2008). As the result the low levels of S and N in the soils did not correspond to the optimal demands of plants. Accordingly decreased concentrations of S (in several sites below 0.12 %) were also stated in the lime leaves. Different studies have showed that NaCl is a decisive factor that may be responsible for the decreased level of foliar N via a reduction in NO_3^-, NH_4^+ uptake (Neuman et al. 1996; Oleksyn et al. 2007). In general, almost sufficient level of N in lime leaves (June: 2.34±0.09 %; August: 2.09±0.06 %) could be explained by NO_x uptake from air due to increased air pollution with NO_x during the last decades in Riga (Ļuļko et al. 2008). It is well known that plants can uptake NO_2 through leaf stomata (Manning and Harris 2009). However, the reduction of N and P concentration in the lime leaves during the vegetation season is in a good agreement with other studies on N and P seasonal changes (Chapin, Kedrowski, 1983). In total, our research did not reveal statistically significant correlation between the content of Cl^- and its antagonist (N, S, and P) concentration in lime leaf and soil samples. Exception – there was a negative correlation between the Cl^- and Ca in lime leaves of August 2007 (r=-0.50, n=26). The results of this study confirmed and expanded the data reached in the previous studies on the nutritional status of street trees in Riga. It was found that one of the main negative factors affecting the growth and development of old street trees (limes and chestnuts) was deficiency of N, K and S (Čekstere et al. 2005). Principal component analysis (PCA) of soil results of August 2007 showed 37.44 % variance with Axis 1 and 22.33 % with Axis 2, but PCA of leaf results: 35.27 % and 19.60 % variance, respectively. The spatial distribution of the studied trees according to leaf results showed continuum, but soil results could be characterized as rather structured depending on the street (Figure 4). PCA results of August 2007 revealed some tendencies for the street greenery in Riga: 1) a wide dispersion of the soil and leaf sample chemical composition even in one street; 2) better vitality for trees with lower Na and Cl^- concentration in the soil and leaves, but higher level of Ca, Mg, K and S in the lime leaves; 3) similar chemical composition of detected macronutrients and Na, Cl^- in the soil samples for trees with different level of damages.

4. CONCLUSION

The study revealed a high heterogeneity of macronutrient concentrations in the soil and leaves of the street trees, and mainly medium and severely damaged status for the lime trees in August 2005 and 2007. The main problems of mineral nutrition of the street greenery in Riga during 2005 and 2007 were elevated concentration of P, Ca, Mg and decreased levels of N, S, K, which, probably, could be promoted by Na and Cl^- accumulation in soil. The concentration of K in lime leaves in the most of cases was in insufficient levels and occasionally deficiencies of S, Mg and P was also found. Probably, it could be facilitated by Na^+ and Cl^- antagonistic impact on nutrient uptake in the street greenery of Riga. Our results also suggest that there was no significant improvement during the last five years in the street tree nutritional status.

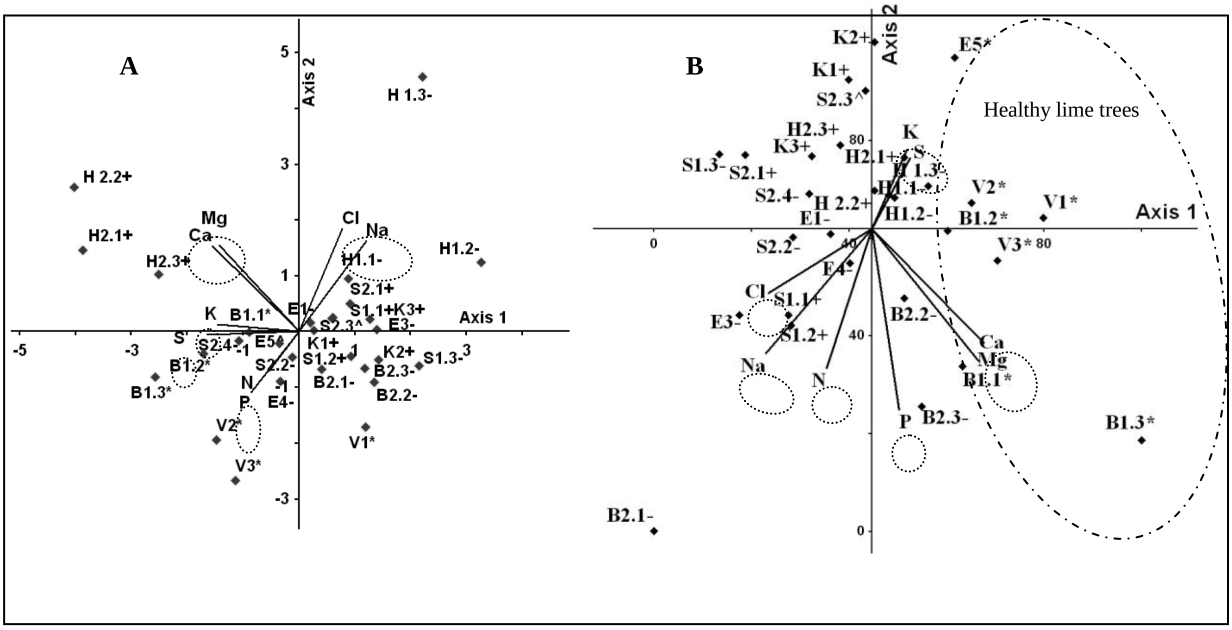

Figure 4. Principal component analysis of soil (A) and lime leaf (B) sample chemical results in Riga, August 2007 (S – the first letter indicates the street; 1 – tree number in the street; * - healthy; ^ - slightly damaged; + - medium damaged; - – severely damaged)

5. ACKNOWLEDGMENT

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Research
Araştırma

TERRESTRIAL ISOPODS DIVERSITY RELATED TO IRRIGATION AND AGRICULTURAL PRACTICES IN NORTH-EAST OF TUNISIA

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Abstract: Environmental factors and land-use affect soil biological communities and their functions. Terrestrial Isopods (woodlice) are detritivorous and reliable bio indicators of habitat quality and soil capacity production. In order to evaluate the effect of different irrigation practices, woodlice richness (S), diversity indices (H' and J') and their relative abundance (A) were studied according to 3 types of irrigation (drip, surface mode and sprinkler) in 16 plots and 9 different types of cultivation: market gardening (artichoke, tomato and melon); vegetable crop (alfafa, sorghum and maize) and fruit-trees (apple, pear and olive) in the Majerda low plain (North-East Tunisia). Pitfalls were used to collect woodlice during 3 weeks (from 22nd August to 09th September 2008). Physico-chemical analyses were performed from soil sampled in each plot. According to the type of irrigation, 7 species of terrestrial Isopods were listed and their richness (S) was very important in the case of sprinkler. The mean relative abundance of *Porcellio laevis* was very important when the surface mode of irrigation was used. For both *Porcellio variabilis* and *Porcellionides sexfasciatus* it was respectively with sprinkler and drip. Both Shannon's diversity and Equitablity indices were higher with the sprinkler mode. According to the type of cultivation, species richness was higher in the alfafa and maize cultivation. *Porcellionides pruinosus, Chaetophiloscia. elongata*, *Armadillidium sulcatum* and *Leptotrichus panzeri* were the less abundant in each type of cultivation. The mean Isopods diversity revealed that their diversity was higher in the sorghum cultivation. Moreover, a relationship between the soil features and a relative abundance of terrestrial Isopods was described.
Key Words: Terrestrial isopods, Irrigation systems, Cultivation types, Soil analyses, Tunisia.

1. INTRODUCTION

The Madjerda Valley is the most important river in Tunisia. In it's a low plain where the agriculture is among the oldest practice in the country (Abbes *et al.*, 2005). In fact, 51% of the population in this site is composed of farmers. The irrigated cultivation is the major component of the evolution of agriculture in Tunisia (40% of total agricultural production). It is also the case of the low plain where most of farmers used the irrigated agriculture (21.317 ha among 29.761 ha of cultivated area) (Report of Wadi project).

In each agroecosystem, soil fauna is an important component to sustain health soil and quality for improved agricultural productions (Moron-Rios 2010). The majorities of this soil fauna are invertebrate members of the decomposer community (Herrick, 2000; Wolter, 2001). Among edaphic organisms, terrestrial Isopods are fundamental representative of soil fauna playing an important role in decomposing leaf litter and in mineralizing organic matter (Hassall & Sutton, 1978; Sutton, 1980) in agroecosystems. But some agricultural activities, such as the drainage, create habitat changes and reduce available leaf litter. Consequently, the species composition, abundance and diversity of beneficial soil species were affected (McLaughlin & Mineau, 1995; Santos *et al.*, 2006; Souty - Grosset *et al.*, 2005). It has been mentioned that the specific diversity and abundance of terrestrial Isopods were influenced by the agriculture practices such as tillage, drainage, fertilizer, pesticides (Paoletti & Hassal, 1999).

The objective of this study was to estimate the biodiversity of terrestrial Isopods related to the type of cultivation and the mode of irrigation in order to assess the effect of these two agricultural practices on their community in the North-East of Tunisia. Thus Isopods were used as bioindicators to improve the soil quality and also in order to sustain soil biodiversity enhancing the agricultural production and the protection of the environment.

2. MATERIAL AND METHODS

2.1. Study Area

The study site is an agricultural area of the Majerda low plain, located in the North-East of Tunisia (Figure 1), between the city of Bizerte and Tunis.

This site belongs to the upper semi-arid region. The climate is Mediterranean. The annual average of precipitation was 433mm, the average of temperature varied between 11 and 27°C and the relative moisture was between 65 and 80 %. The low valley of Majerda has a great economic and social importance and soil fauna was an important component of this agroecosystem. In this site, agricultural practices are not only market guarding -vegetable crop often associated with a dairy breeding- but also fruit trees, olive, cereals and other annual cultivation, particularly vegetables. In this region, the operating system was based on the water with an important activity of the irrigation. The surface system of irrigation is the most common used (Abbes *et al.*, 2005).

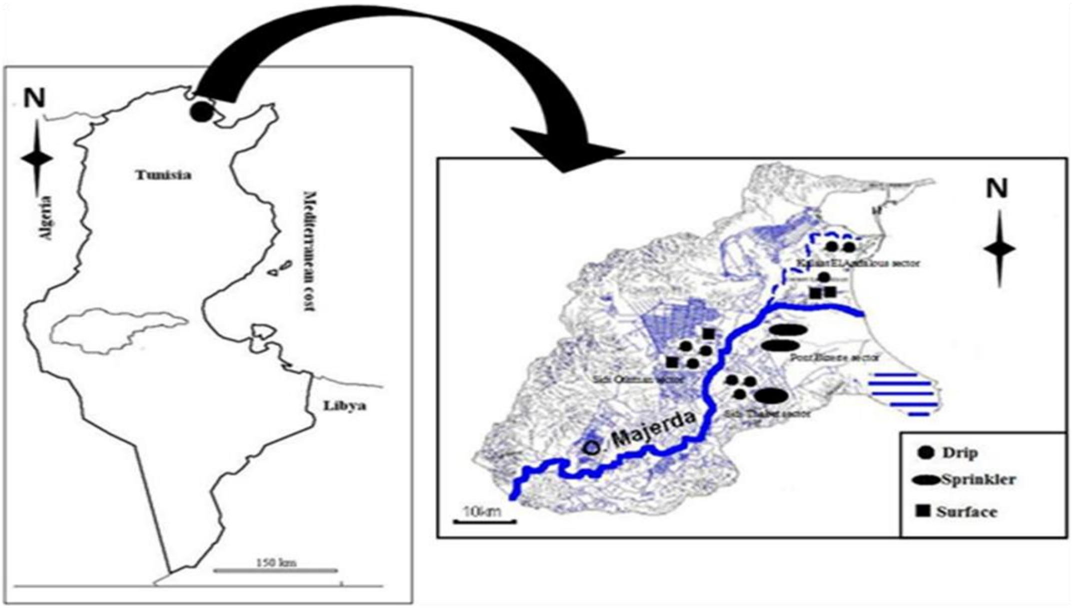

Figure 1. Study site and modes of irrigation

2.2. Methods

Sampling was performed in 16 plots and 9 different types of cultivation which were accounted: market gardening (artichoke, tomato and melon); vegetable crop (alfafa, sorghum and maize) and fruit-trees (apple, pear and olive). In the whole studied plots, 3 modes of irrigation were used: drip, surface and sprinkler mode (Table 1).

Pitfalls traps (plastic cups, 7 cm of height, 5.5 cm of diameter, 1/4 filled with ethylene glycol 70%) (Figure 2) were used to collect woodlice during 3 weeks (from 22nd August to 09th September 2008). This methodology is commonly used as a substitute of true quantitative sampling methods (Duelli *et al.*, 1999; Paoletti & Hassall, 1999; Perner & Schueler, 2004). In fact, this sampling procedure measures epigeic activity of soil-dwelling animals (Santos *et al.*, 2007; Sfenthourakis *et al.*, 2005; Zimmer et *al.*, 2000). This technique has some advantages: it is simple, economic and works continuously through day and night (terrestrial Isopods being nocturnal), allowing many samples to be taken (Lobry de Bruyn, 1999). All trapped individuals were preserved in 70% ethanol, counted and species identified under Leica MS 5 binocular microscope.

Samples of the soil were taken in every statement of the traps and mixed to obtain a composite from each plot. pH water and pH KCl were measured using pH meter EUTEH instruments (pH510). Carbon (C) and nitrogen (N) were analyzed using elemental analyzer. The C/N of soil is important to know the status of mineralization of organic matter.

2.3. Data Analysis

Relative abundance [A (%): number of individual of species i (ni)/total number of woodlice captured (N)] and species richness (S: total number of species) were calculated according to the type of irrigation and cultivation.

Diversity was measured using the Shannon–Wiener index H' and equitability J'

$$H' = -\sum_{i=1}^{S}[ni/N * \text{Ln } ni/N] \quad (1)$$

ni :meaning the number of individuals of the species *i*
N: total number of individuals of all species
S: Total number of species

$$J' = H'/\log_2 S \quad (2)$$

Difference of species richness between different type of cultivation and the different irrigation system was tested using one-way ANOVA analysis.

3. RESULTS AND DISCUSSION

Seven woodlice species belonging to three families (*Armadillidiidae*, *Porcellionidae* and *Philosciidae*) were collected in the 9 types of cultivation examined (Tab. 2A). Clear differences- species richness, abundance and diversity were noted between study plots (Table 2 (A, B) and 3, Figures, 2, 3, 4 and 5). According to the type of cultivation, *Porcellio laevis*, *Porcellio variabilis* and *Porcellionides sexfasciatus* dominanted over 50%. The others species did not exceed 10% (Figure 2).

Terrestrial Isopods in olive tree, alfafa and melon cultivation, were dominated, respectively, by *Porcellio variabilis* (A=84%), *Porcellio laevis* (A=83%) and *Porcellionides sexfasciatus* (A=82%). Whereas *Porcellionides pruinosus, Chaetophiloscia elongata*, *Armadillidium sulcatum* and *Leptotrichus panzeri* were less abundant in each type of cultivation. The highest average species richness was recorded in the alfafa and maize (S= 5 in one plot studied) cultivation (Tab. 3) and the lowest one in the artichoke (S=2.2±0.84). These values were not statistically different. The average diversity indices fluctuated between H'= 0.66±0.48; J'= 0. 66±0.48 in the apple tree (Tab. 3) and H'=1.46; J'=0.73 in the sorghum cultivation (in one plot studied). Differences, observed between different types of cultivation, confirms the results of Cortet *et al.* (2002) who found that some soil arthropods (collembolans) were influenced by the type of cultivation and rotation.

Related to irrigation systems, (Figure 3) the highest mean relative abundance of *P. laevis* was recorded in the surface (A=69%) and drip (A=39%) mode of irrigation. Whereas, in the sprinkler system, *P. variabilis* is the dominant species (A=49%). Mean species richness of woodlice (Figure 4) was more important in sprinkler mode of irrigation (S=4.67±1.33) than in surface (S=2.75±1.04) and drip (S=2.56±0.83) systems. In the sprinkler irrigation, richness species was significantly more important than in drip and surface systems (ANOVA test; $p<0.05$). Diversity index (H') and Evenness (J') were higher in sprinkler mode (H'=1.12±0.29; J'=0.52±0.18) than in surface (H'=0.72±0.33; J'=0.64±0.40) and drip (H'=0.85±0.5; J'=0.61±0.38) systems (Figure 5). Similarly, Moron-Rios *et al.* (2010) indicated the effect of irrigation on decomposers animals such as Oligochaeta, Diplopoda and Isopoda.

The influence of the irrigation system on the woodlice richness was also mentioned in previous investigations (Fraj, 2008 *unpublished*) in some oasis plots of Kebili region (S-W of Tunisia). The traditional mode favored the Isopod richness compared to the modern one. The difference of species richness related to the mode of irrigation could be explained by the fact that, in drip and surface systems, soil moisture exceeded the optimum survival of terrestrial Isopods.

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Table 1. Characteristics of studied plots

Number	Locations	Code plots	Latitude/Longitude	Cultivation	area (ha)	Irrigation
1	Kalaat El Andalous	Art KA1	N37°06'4.26'' E010°09'16.9''	Artichoke	0,75 ha	Drip
2	Kalaat El Andalous	Art KA2		Artichoke	1ha	Drip
5	Kalaat El Andalous	Art KA3	N37°04'42.4'' E 010°07'50.4''	Artichoke	1ha	Drip
6	Kalaat El Andalous	Pea KA4		Pear tree	2,5ha	Surface
7	Kalaat El Andalous	App KA5		Apple tree	2,5ha	Surface
8	Sidi Thabet	Alf ST1	N36°56'07.6'' E 010°02'35.1''	Alfafa	1 ha	Sprinkler
9	Sidi Thabet	Art ST2	N36°57'07.7'' E010°01'46.6''	Artichoke	1,5ha	Drip
10	Sidi Thabet	Mel ST3		Melon	3ha	Drip
11	Sidi Thabet	Tom ST4		Tomato	1,5ha	Drip
12	Sidi Othman	Art SO1	N36°56'04.0'' E 009°53'59.3''	Artichoke	15ha	Drip
13	Sidi Othman	App SO2		Apple tree	5ha	Surface
14	Sidi Othman	Oli SO3		Olive tree	6ha	Drip
15	Sidi Othman	Pea SO4		Pear tree	3ha	Surface
16	Sidi Othman	Tom SO5		Tomato	7ha	Drip
15	Pont Bizerte	Sor PB1	N36°58'58.4'' E 10°03'53.6''	Sorghum	3ha	Sprinkler
16	Pont Bizerte	Mai PB2		Maize	1ha	Sprinkler

Table 2. The relationship between pH, C/N soil and relative abundance of terrestrial Isopods

		Art KA1	Art KA2	Art KA3	Pea KA4	App KA5	Alf ST1	Art ST2	Mel ST3	Tom ST4	Art SO1	App SO2	Oli SO3	Pea SO4	Tom SO5	Sor PB1	Mai PB2
(A)	*P. laev*	98%	100%	50%	40%	94%	83%	25%	8%	0%	16%	50%	0%	90%	50%	23%	8%
	P. vari	0%	0%	0%	0%	0%	3%	17%	8%	25%	76%	50%	84%	7%	50%	63%	82%
	Ps. prui	0%	0%	0%	0%	0%	1%	0%	0%	25%	0%	0%	2%	1%	0%	0%	6%
	Ps. Sexf	2%	0%	50%	60%	6%	10%	58%	83%	50%	8%	0%	10%	1%	0%	10%	2%
	C. elon	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	5%	2%
	A. sulc	0%	0%	0%	0%	0%	3%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	L. panz	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	4%	1%	0%	0%	0%
(B)	pH water	7,68	7,96	7,92	7,9	7,68	7,67	7,74	7,9	7,84	7,75	7,85	7,73	7,9	7,87	7,67	8,01
	pH KCl	7,29	7,46	7,58	7,58	7,53	7,4	7,61	7,52	7,75	7,67	7,65	7,58	7,63	7,61	7,58	7,38
	C/N	0,00	7,35	9,39	7,87	8,06	7,87	8,14	12,21	7,77	8,78	9,12	0,00	8,13	10,38	8,02	7,73

A: Average of relative abundance of terrestrial Isopods
B: pH water, pH KCl and C/N of soil

Table 3. Average species richness (S), diversity (H') and evenness (J') related to the type of cultivation, (± standard deviation)

	S	H'	J'
	2,2±0,84	0,70±0,61	0,52±0,44
Artichoke	3,5±1,24	0,77±0,44	0,61±0,37
Pear tree	2,5±0,7	1,25±0,35	0,97±0,97
Tomato	2	0,66±0,48	0,66±0,48
Apple tree	4	0,84	0,42
Olive tree	5	0,92	0,40
Alfafa	4	1,46	0,73
Sorghum	5	0,99	0,43
Maize	3	0,82	0,52

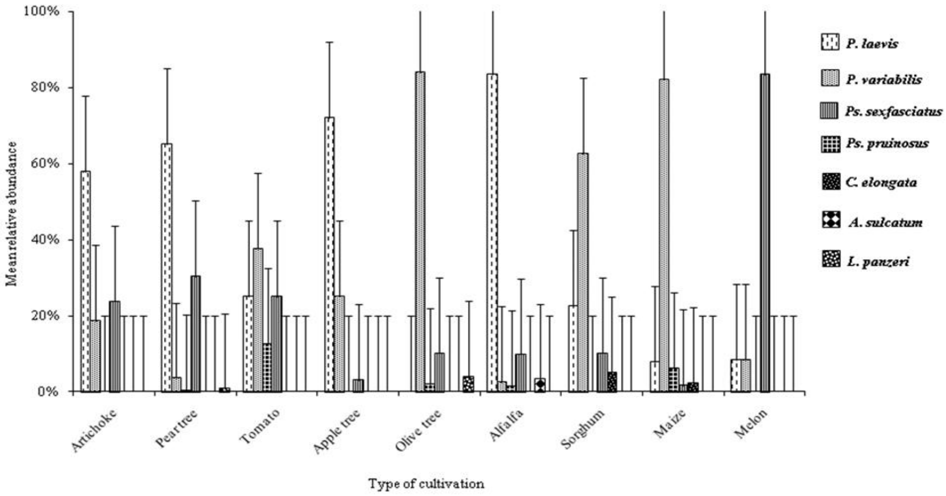

Figure 2. Mean relative abundance of terrestrial Isopods related to cultivation type

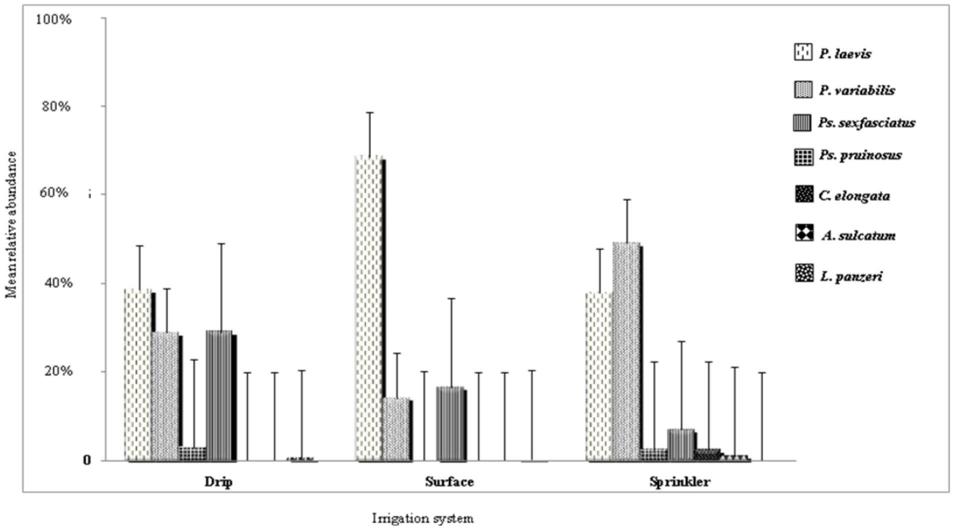

Figure 3. Mean relative abundance related to irrigation system

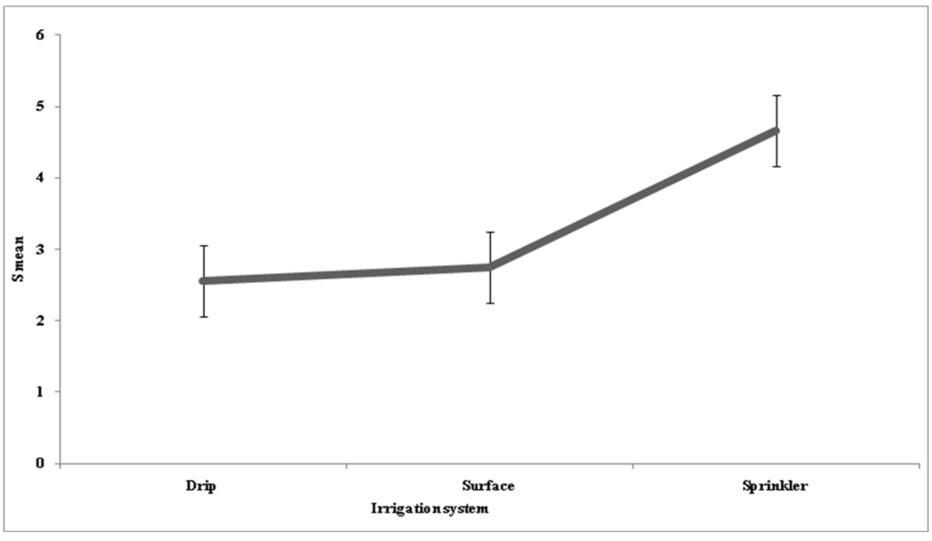

Figure 4. Mean species richness related to irrigation system

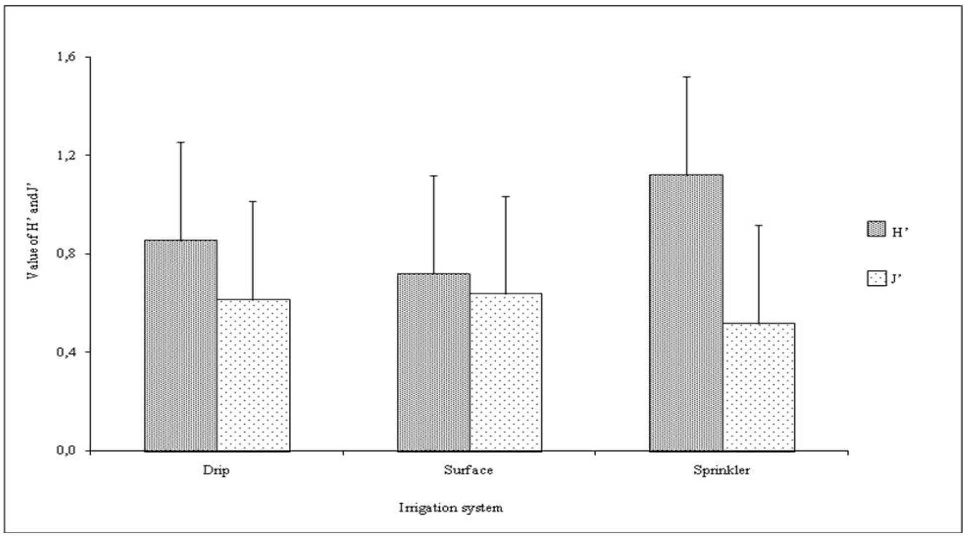

Figure 5. Shannon and equitability indices related to irrigation system

Moreover, the nature and the physicochemical properties of soil were also very important factors. Hassall *et al.* (2006) indicated that pH of soil was the only environmental variable for which the number of terrestrial Isopods per plot was relatively significant. In the present study, a relationship between the soil features and a relative abundance of terrestrial Isopods was detected. pH water and pH KCl varied within studied plots. *P. variablis* was a very abundant species in maize (Maize PB1: pH water=8.01) and artichoke (Art SO1: pH KCl=7.67) (Tab. 2B). Compared to *Oniscus asellus*, which is an acidophil species (Van Straalen & Verhoef, 1997), *P. variabilis* will be considered as an alkaline species. *P. laevis* was the most abundant species in the Alf ST1 and Sor PB1 plots with low values of pH water (7.67) and pH KCl (7.29). Contrary to Carabidae, Isopods have been shown to react to variations in pH water and pH KCl (Souty- Grosset *et al.*, 2005).

Our results showed that *Ps. sexfasciatus* was the most abundant species in the plot with the highest value of C/N (Mel ST3: 12.21). However, *P. laevis* and *P. variabilis* were abundant in the soil with C/N equal to 0. For cultivated soil, the C/N was about 9 when the mineralization was good. But, for a report value equal or greater than 12, mineralization process was bad (Baize, 2000). In the melon cultivation where *Ps. sexfasciatus* was very abundant, the mineralization process was very bad. In the artichoke and olive cultivation, the C/N reveals good mineralization. According to these preliminary results, the two species, *P. laevis* and *P. variabilis* will be considered as bioindicators and a useful tool to determine the soil quality.

4. CONCLUSION

Our results showed that agricultural practices influenced diversity of terrestrial Isopods in the Madjerda low plain. The mode of irrigation has an effect on the abundance and distribution of woodlice at different types of cultivation. The sprinkler irrigation may be considered a good system to Isopods diversity conservation. Thus, our study also shows that cultivation type affected woodlice community. Indeed, differences in Isopods richness, abundance and diversity were observed between market gardening, vegetable crop and fruit-trees cultivation. This study underscores that woodlice community of agricultural area constitutes a useful tool to sustain the soil health and quality. These data provide to the scientists the necessary information to evaluate the impact of some agricultural activities on soil fauna and will aid farmers to adapt the appropriate practices inducing a more sustainable agricultural production. In order to confirm these results, works are in progress by studying other types of cultivation and other systems of irrigation.

5. ACKNOWLEDGEMENT

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Research
Araştırma

HYDRAULIC CONDUCTIVITY AT AND NEAR SATURATION OF AN ORTHIC LUVISOL AFTER 15 YEARS OF DIFFERENT SOIL MANAGEMENT PRACTICES

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Abstract: Soil tillage is one of the key soil management practices in agricultural land use. The farming concepts are based on understanding of soil physical and hydrological characteristics under different tillage treatments. Hydraulic conductivity of the surface layer determines water infiltration into the soil profile and possible runoff formation. The treatment of the surface layer affects the soil pore system (distribution and connectivity of macroscopic cracks, voids, holes, etc.). The aim of this study was to evaluate the changes in hydraulic conductivity at and near saturation under the field conditions for soil with different tillage treatments (reduced tillage – RT, no tillage – NT, and conventional tillage – CT). The field experiments were carried out in four phases (June 2008, September 2008, April 2009, and July 2009) in order to characterise also the seasonal changes in hydraulic conductivity of the soil. Pressure ring infiltrometer (Matula and Kozáková, 1997) was employed to carry out the infiltration tests to determine hydraulic conductivity at saturation, K_s. The infiltration time was allowed long enough to obtain steady state infiltration data, which were analysed based on the equations formulated by Philip (1985) and Reynolds and Elrick (1990). To determine hydraulic conductivity near saturation *K(h)*, Mini Disk infiltrometer (Decagon Devices, Inc.) was used. The transient infiltration data obtained from Mini Disk infiltrometer were analysed by HYDRUS 2D software (Šimůnek et al., 1999). Analysis of variance identified significantly lower K_s values for NT plots, while CT and RT plots did not differ from each other. When comparing the *K(h)* values measured at three consecutive water pressure heads (-5, -3, and -1 cm) the statistically significant differences were found between all three treatments (CT > RT > NT). The seasonal changes in hydraulic conductivity were reflecting the changes in structure of the surface layer (caused for example by tillage operation, winter frost, and wetting and drying circles). In contrast to some published studies, this study showed no improvement in soil structure of soil under NT after certain time period, resulting in significantly lower values of hydraulic conductivity during each of the experimental phase.
Key Words: Hydraulic conductivity, Tillage treatment, Pressure ring infiltrometer, Mini disk infiltrometer

1. INTRODUCTION

Hydraulic conductivity controls water and solute transport within the soil profile. Davis et al. (1999) reported saturated hydraulic conductivity K_s as one of the most sensitive input parameters for hydrological models, which is very difficult to measure accurately and thus disputing the model results. Sobieraj et al. (2004) concluded that predictability of K_s is very little, if the soil does not have a course structure. Tillage of the topsoil layers changes the soil structure and thus its hydrophysical properties. It is important to characterise its changes in time with regard to the different tillage management practices. It was found that long-term tillage effects on hydraulic conductivity at saturation vary; Arshad et al. (1999), and Coutadeur et al. (2002) reported higher infiltration rates for soils under no-tillage when compared to the conventional tillage, Blanco-Canqui et al. (2004), Gregorich et al. (1993), and Karlen et al. (1994) reported similar values, while Lampurlanés and Cantero-Martínez (2006), Moret and Arrúe (2007a), and Kribaa et al. (2001) reported smaller infiltration rates. The effects of tillage were found to be strongly time-dependant (Xu and Mermoud 2001). Tillage operations lead to soil loosening accompanying by an increase in number of active macropores and disruption of macropores continuity. The amount of macropores and mesopores can be calculated based on the measured infiltration rates for certain water pressure heads (tensions) near saturation. Park and Smucker (2005) reported tillage as a factor decreasing aggregate stability due to increased mineralisation of organic matter, which is enhanced by rain-drops impact. Osunbitan et al. (2005), and Kribaa et al. (2001) reported that hydraulic conductivity at saturation decreases with time (weeks) after soil cultivation due to soil reconsolidation and compacting effects of rainfall.

The aim of this study was to evaluate changes in hydraulic conductivity at and near saturation for a silty clay loam under three different tillage treatments (conventional tillage, reduced (non-inversion) tillage and no-tillage) measured at four phases within approximately one year period (from June 2008 to July 2009).

2. MATERIAL AND METHODS

The experimental site (Figure 1& 2) is located in the area of Crop Research Institute in Praha- Ruzyně (sugar beet production area; altitude 340 m a. s. l.; latitude 50°05’ N; longitude 14°20’ E; annual precipitation 472 mm; annual average temperature 7.9°C). The soil being tested was classified according to FAO system as Orthic Luvisol. The experimental site was established in 1994. Since then, three different tillage practices, each one on the particular plot were applied. The tillage systems were as follows: i) conventional tillage CT (ploughed to 25 cm); ii) reduced tillage RT (non-inversion treatment of a surface soil layer to 10 cm); iii) no-tillage NT (direct drilling). The measurements were carried out in four phases: in June 2008 before the harvesting of the preceding crop (*Triticum aestivum*), in September 2008, 2 weeks after planting of the main crop (*Brassica napus subsp. napus*), in April 2009 during the flowering period and in July 2009 just before harvesting.

Pressure ring infiltrometer (Matula and Kozáková, 1997) was used for the infiltration experiments to determine hydraulic conductivity at saturation K_s. Three replicates in 1 m distance were performed for each tillage treatment at each experimental phase (36 infiltration tests in total). The infiltrometer consists of a large Mariotte type water reservoir (app. 10 litres) which is placed on an iron metal ring driven into the soil up to 8 – 10 cm. The inner diameter of the iron ring is 15 cm. A wide range of water pressure can be applied on the soil surface inside the infiltration ring by adjusting a movable air tube inside the infiltrometer water reservoir. The scheme with basic dimensions of the infiltrometer together with the field application is presented in Figure 3.

The infiltration time was allowed at least 60 min to ensure steady water flow. To determine the hydraulic conductivity at saturation K_s equations formulated by Philip (1985), Reynolds and Elrick (1990), Reynolds and Elrick (1991) and Elrick and Reynolds (1992) can be applied on the steady-state infiltration data. Matula (2003) presented a final formula for K_s determination from the pressure ring infiltrometer measurements:

$$K_s = \frac{q_\infty \, G}{\left(a\,H + a^2\,G\,\pi + \dfrac{a}{\alpha} \right)} \tag{1}$$

where K_s (L T^{-1}) is saturated hydraulic conductivity, q_∞ (L^3 T^{-1}) is steady state infiltration rate, H (L) is positive hydrostatic head, α (L^{-1}) is the alpha parameter, a (L) inner radius of the infiltration ring, G is a dimensionless geometry factor defined by Reynolds and Elrick (1990) for the pressure ring infiltrometer:

$$G = 0.316\,(d/a) + 0.184$$

where d (L) is the depth of the iron ring insertion.

The Mini Disk infiltrometer (Figure 4) was used to determine the hydraulic conductivity near saturation *K(h)*. It is a handy manually operated device to measure hydraulic conductivity near saturation at pressure head between -0.5 cm and -6 cm. It consists of two chambers, which are filled with water. The upper chamber (bubble chamber) controls the pressure head. Water for infiltration is stored in the lower chamber. There is a porous sintered stainless steel disk at the bottom of the lower chamber. The disk is 0.3 cm thick and has a diameter of 4.5 cm. Disk with such a small parameter is relatively easy to set up in the field on the soil surface, which needs to be smooth and levelled. However, the measurement site might be quite small with respect to the heterogeneity of the soil. The amount of water, which can be infiltrated, is approximately 100 cm^3. The Mini Disk infiltrometer was applied directly on the soil surface, no contact material was used. Three consecutive pressure heads h were set during one infiltration measurement (-5 cm, -3 cm, -1 cm). Each tension was allowed at least for 20 min (conventionally tilled soil), in some experiments even more than 45 minutes (plots with no-tillage). 33 sets of infiltration tests for each pressure head were carried out during the experimental period.

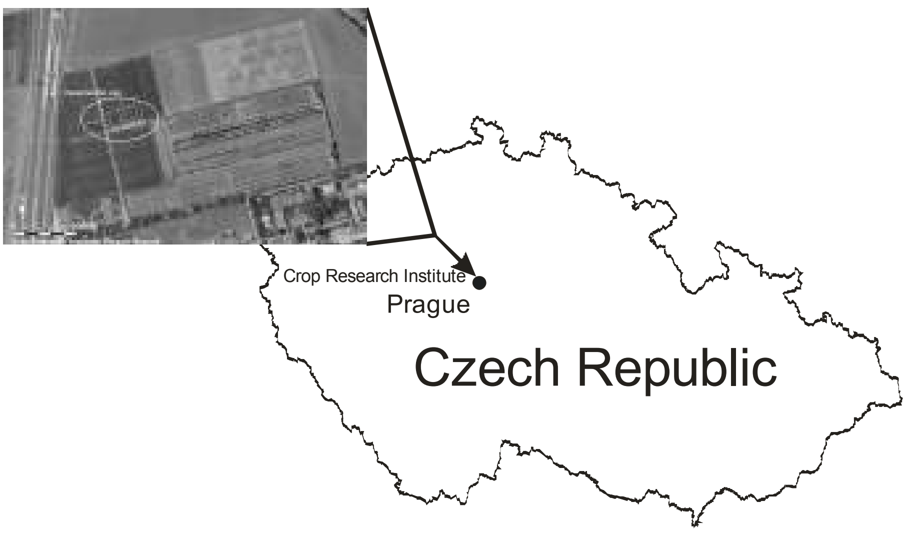


Figure 1. Experimental plots of the field in Crop Research Institute in Praha - Ruzyně
(map background: GEODIS, available on-line: http://www.mapy.cz)

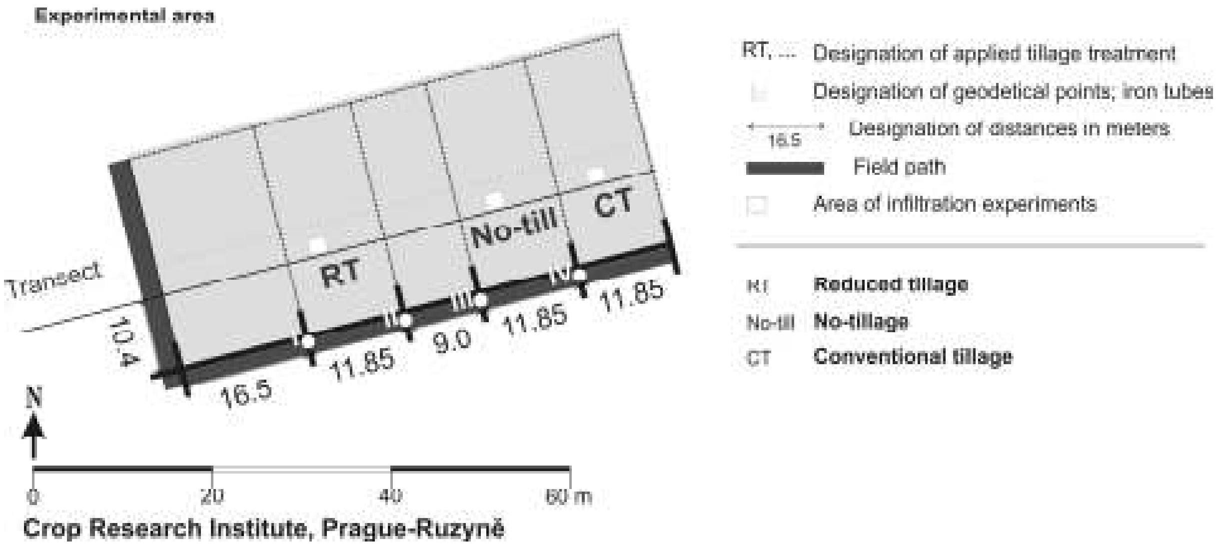
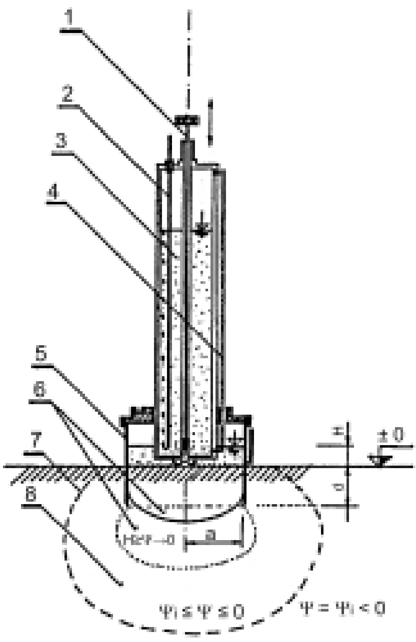


Figure 2. Detailed scheme of the experimental plots of the field in Crop Research Institute in Praha - Ruzyně



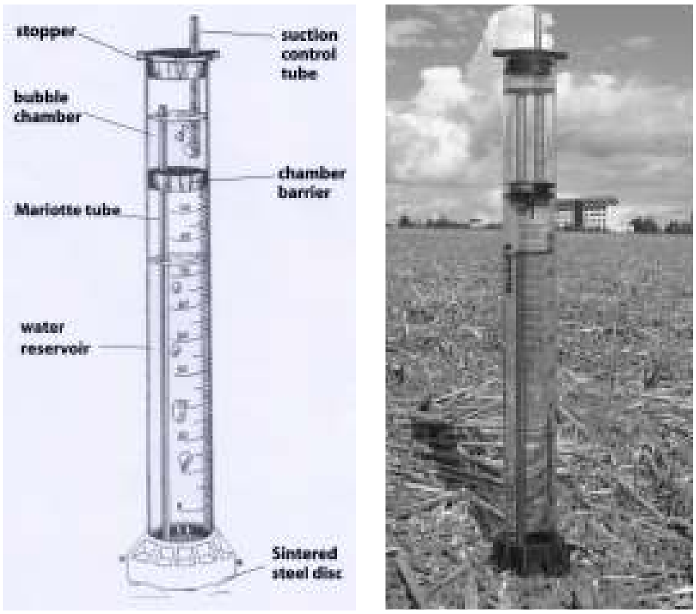
a)

b)

Figure 3. Pressure ring infiltrometer by Matula and Kozáková (1997)

a) Pressure ring infiltrometer scheme:
- 1-Piston valve to open or close the water outlet
- 2-Moveable air tube to set the applied water pressure *H* on infiltrating surface
- 3-Marriote type water reservoir
- 4-Plexiglass tube of a small diameter to enable accurate fading of the water level
- 5-Iron ring with a radius of a driven into the soil to the depth d
- 6-Bulb of field saturated soil
- 7-Wetting front
- 8-Wetted zone;

b) Pressure ring infiltrometer applied in the field



a) b)

Figure 4. The Mini Disk infiltrometer

a) Scheme of the infiltrometer (User's manual, Decagon Devices, Inc., 2006)
b) Application of the infiltrometer in the experimental field

To determine the unsaturated hydraulic conductivity for the applied pressure heads, a method proposed by Zhang (1997a) was applied. Cumulative infiltration vs. time was measured and then fitted with the following equation (Philip, 1957):

$$I = C_1 + C_2\sqrt{t} \tag{2}$$

where: C_1 (L T^{-1}) and C_2 (L $T^{-1/2}$) are parameters related to hydraulic conductivity and soil sorptivity respectively, I (L) is the cumulative infiltration, and t (T) the time.

The hydraulic conductivity of the soil K at the particular applied pressure head h is then calculated as follows:

$$K(h) = \frac{C_1}{A} \tag{3}$$

where: C_1 is the slope of the curve of the cumulative infiltration vs. the square root of time, and A is a value relating the van Genuchten parameters (van Genuchten, 1980) for 12 soil texture classes to the radius of the disk and applied pressure head. The A parameter was determined based on the data reported in the User's manual (Decagon Devices, Inc., 2006); for silty clay loam is A equal to 10.1 for pressure head -5 cm, 9.1 for pressure head -3 cm, and 8.3 for pressure head -1 cm.

Šimůnek and van Genuchten (1996, 1997), and Šimůnek et al. (1998) proposed an inverse numerical method to estimate the parameters of the hydraulic conductivity function and the soil water retention curve from transient infiltration data from disc infiltrometers. The determination of soil hydraulic parameters from inverse modelling requires a numerical solution of the Richards' equation (Richards, 1931) for given initial and boundary conditions and the optimisation of the parameters in assumed forms of the soil hydraulic functions. Software HYDRUS 2D (Šimůnek et al, 1999) was used for the numerical solution; an axisymetrical vertical flow of water was modelled on a generally described domain discretised into 1111 2D elements with 599 nodes. The hydraulic parameters for the inverse solution were set as follows: saturated moisture content θ_s was determined as an averaged value for each tillage treatment at each experimental phase; θ_r was set as a constant at a value of 0.08 cm^3 cm^{-3}; parameter l was set to 0.5; all other parameters α, n, and K_s were optimised during the calculation procedure. An additional value of final moisture content θ_{final} was used to improve the optimisation procedure.

Calculated $K(h)$ and K_s values were transformed (logarithm to the base of 10) and than statistically assessed by analysis of variance on a significance level $\alpha = 0.05$ (Statgraphics Centurion XV software).

The accessibility to the field was governed by the soil moisture content at the particular period. Averaged daily temperatures and amount of daily precipitation (sum) during the whole experimental period is displayed in Figure 5.

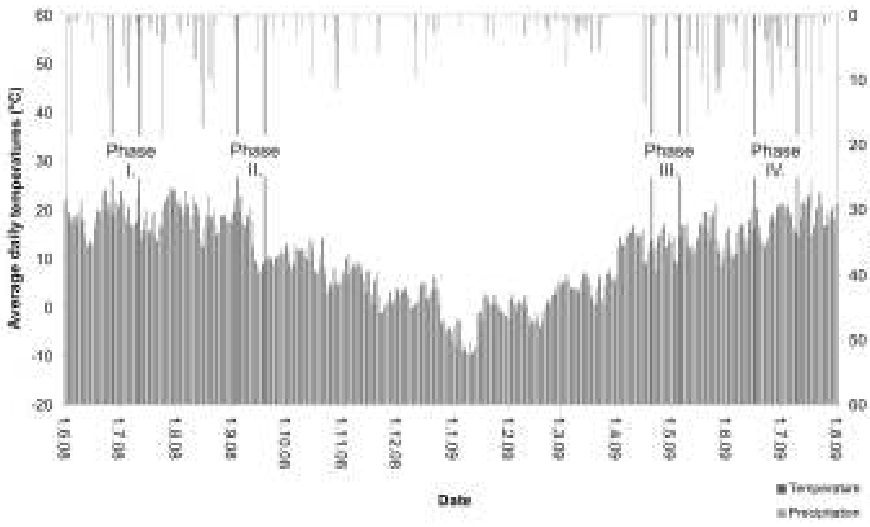


Figure 5. Average daily temperatures and amount of daily precipitation (sum) for the whole experimental period (Crop Research Institute, data taken from: http://www.vurv.cz/meteo)

3. RESULTS AND DISCUSSION

An overview of averaged initial and final conditions together with the averaged values of an *n* resulting from the inverse solution in HYDRUS 2D and averaged values of hydraulic conductivity for each soil treatment and experimental phase is presented in Tab.1.

3.1. Effect of Time

The changes of hydraulic conductivity near saturation *K(h)* in time are displayed in Figure 6a. Statistically significant increase in *K(h)* was observed after the soil treatment carried out just before the measurement at the second experimental phase. Further decrease in *K(h)* was observed during the third and fourth experimental phases. To observe the changes in *K(h)* in time for each soil treatment, an interaction effect of soil treatment and measurement phase was studied (Figure 6b). The increase in hydraulic conductivity at the second experimental phase was observed for all treatments, CT, RT, and NT. The largest increase was observed for RT and NT, while for CT the increase was statistically insignificant.

Significantly smaller values of K_s (Figure 7a) were measured in June 2008 (the first experimental phase) before harvesting the preceding crop (*Triticum aestivum*) for all tillage treatments. After the tillage and seeding operations of the main crop (*Brassica napus subsp. napus*) the K_s increased significantly for all treatments. The increase in K_s measured on NT plot was relatively smaller when compared to the other two tillage systems (CT and RT). There was another increase in hydraulic conductivity in the following experimental phase in April 2009. This was probably caused by the improving effects of winter frost, wetting and drying periods and developing root system of the main crop. During the last measurement phase in July 2009 a decrease in K_s was observed on RT and NT plots. However, the K_s on plot with conventional tillage were increasing very mildly during the rest of the experimental period after tillage operations. The changes of K_s in time for the different tillage treatments are displayed in the interaction plot in Figure 7b.

The results are in correspondence with the findings of other published studies. Moret and Arrúe (2007a) observed short-term changes of hydrophysical properties of plots under CT, RT and NT; they reported a significant increase in K_s and *K(h)* as a result of an increase in number of water-conductive macropores, which was followed by decline in hydraulic conductivity due to soil reconsolidation by post-tillage rains and associated wetting and drying circles. Xu and Mermoud (2001) observed a significant decrease in *K(h)* with time during the growing season on soils with CT, RT, NT and subsoiling tillage. Such a significant decrease in K_s was not observed, probably because of the improving effect of the roots of the main crop.

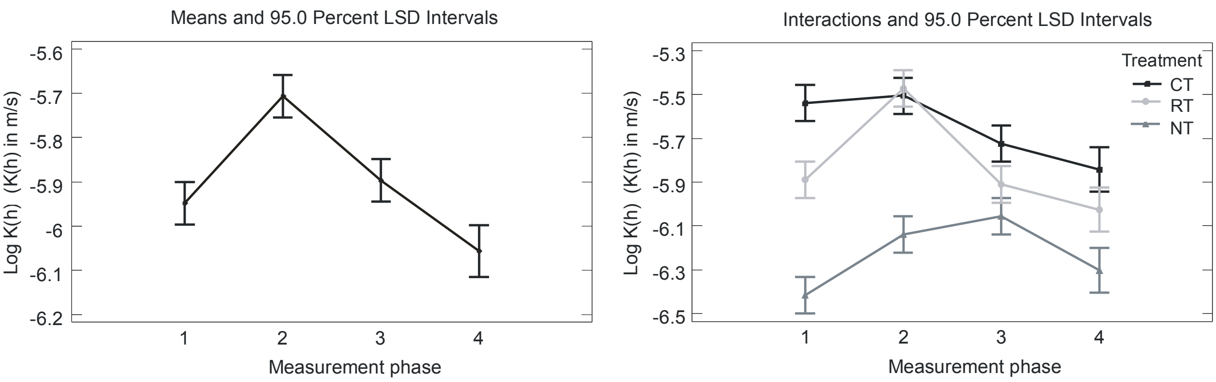
3.2. Effect of Tillage

Analysis of variance identified a significant effect of tillage treatment on the resulting *K(h)* values (Figure 8a). Significant differences were found between all three treatments. The highest values of *K(h)* were determined on CT plot, lower values on RT plot and the smallest values on NT plot. Changes in *K(h)* for plots with different tillage treatments at each of the experimental phase are displayed in the interaction plot in Figure 8b. A significant increase in *K(h)* at the second experimental phase was followed with a decrease in *K(h)* at the third and fourth measurement phase on CT and RT plots. On NT plot the *K(h)* values increased at the second and also at the third experimental phase, and than at the fourth phase decreased almost to the level at the beginning of the experimental period.

Table 1. Averaged initial and final conditions together with the averaged values resulting from the inverse solution in HYDRUS 2D and averaged values of K_s for each soil treatment and experimental phase determined by Mini Disk and Pressure ring infiltrometers

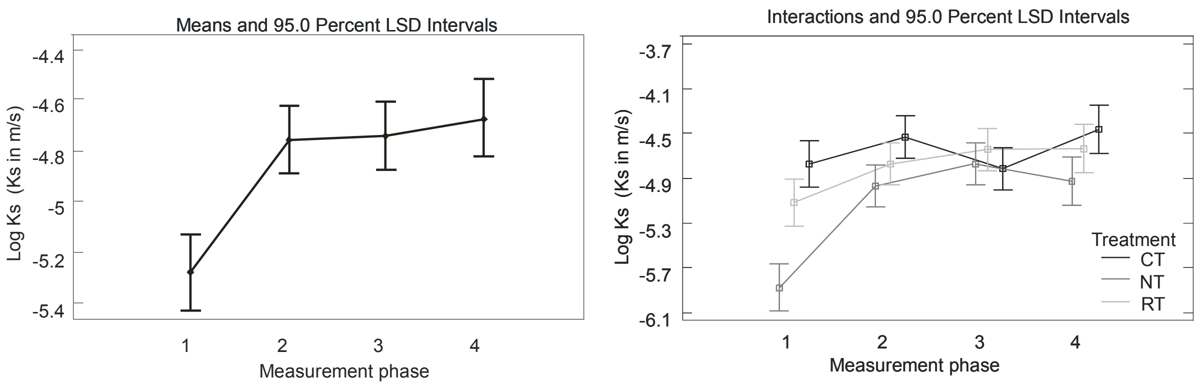
Treat-ment	Mini Disk infiltrometer Input data □ *initial* (cm^3 cm^{-3})	□ *final* (cm^{3}cm^{-3})	HYDRUS 2D results □□ (cm^{-1})	*n* (-)	K_s (cm min^{-1})	Coefficient of determination R^2	Pressure ring infiltrometer results K_s (cm min^{-1})
Exp. phase I.							
CT	0.125	0.338	0.1397	2.1004	0.04673	0.9986	0.09827
RT	0.139	0.345	0.1999	1.8178	0.02938	0.9983	0.05171
NT	0.151	0.339	0.2052	1.8914	0.00733	0.9950	0.01278
Exp. phase II.							
CT	0.187	0.323	0.2190	1.8829	0.07704	0.9985	0.49662
RT	0.188	0.339	0.2512	1.5753	0.14546	0.9983	0.06906
NT	0.222	0.347	0.6050	1.2316	0.36237	0.9963	0.03265
Exp. phase III.							
CT	0.126	0.321	0.1627	1.5842	0.04123	0.9987	0.58626
RT	0.155	0.338	0.5247	1.3931	0.32927	0.9967	0.47732
NT	0.173	0.323	0.8524	1.4240	0.70469	0.9928	0.06954
Exp. phase IV.							
CT	0.234	0.385	0.5129	1.2359	0.43622	0.9982	0.66826
RT	0.271	0.399	0.5083	1.1973	0.47263	0.9969	0.27466
NT	0.303	0.387	0.5865	1.1526	0.51410	0.9940	0.16642

Analysis of variance identified also a significant effect of tillage treatment on the resulting K_s values (Figure 9). Significantly lower values of hydraulic conductivity were measured on NT plot, while CT and RT plots did not significantly differ within the whole experimental period. The effect of used infiltrometer was also tested in order to compare the ability of the Mini Disk infiltrometer to determine the K_s values. If the infiltration data were analysed according to the manual, the resulting K_s values were significantly lower than those measured by the Pressure ring infiltrometer (Matula and Kozáková, 1997). The interaction plot (Figure 9b) shows that the Mini Disk infiltrometer was systematically underestimating K_s for all plots, because of the underestimation of macropores (only small underestimation of K_s for NT plot). However, the estimates for the plots with smaller amount of macropores (RT, NT) were not statistically different.



a) b)

Figure 6. ANOVA results for an effect of time
a) Changes in hydraulic conductivity near saturation *K(h)* for the four experimental phases between June 2008 and July 2009;
b) Interaction plot describing the changes in hydraulic conductivity near saturation *K(h)* for each plot with different soil treatment at each experimental phase



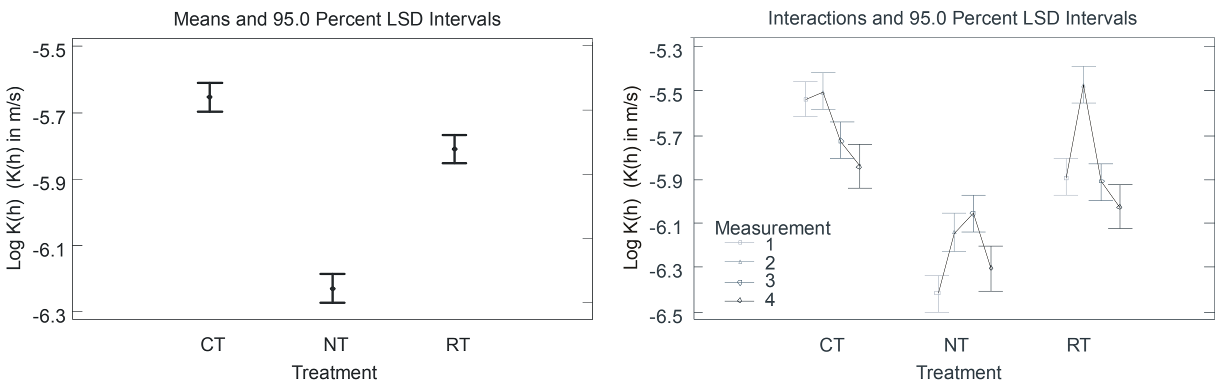
a) b)

Figure 7. ANOVA results for effect of time
a) Means and 95% LSD intervals describing seasonal changes in K_s for all tillage treatments (the first phase in June 2008 - before tillage; and the second phase in September 2008 – after tillage);
b) Interaction plot describing the changes in K_s for each plot with different soil treatment at each experimental phase

The inverse solution in HYDRUS 2D provided statistically comparable results, but when the results were specified for the particular soil treatment, the results were significantly different. In practice, it means that if the value of K_s is required with good accuracy, it needs to be measured individually with the device designed for its determination. Similar effect, enhanced infiltration rates on soils with conventional tillage when compared to reduced and no-tillage operation, were also reported by Cully et al. (1987), Zachmann et al. (1987), and Moret and Arrúe (2007b) who measured lower *K(h)* in soils under no-tillage management, when compared to reduced and conventional tillage. However, the results characterising the effect of tillage on soil hydraulic properties differ. Logsdon et al. (1993), Benjamin (1993), Cameira et al. (2003), and Buczko et al. (2006) observed the opposite effect; and Ankeny et al. (1990), Starr (1990), Blanco-Canqui et al. (2004) and Gregorich et al. (1993) observed no significant differences in hydraulic properties of soils under different tillage treatments.

4. CONCLUSION

The temporal changes in K_s with time after tillage operation were found to be in agreement with other published studies. The effect of tillage operations significantly increasing the infiltration rates for CT and RT plots was observed at each of the experimental phase. After 15 years of the soil under NT does not tend to improve its structure to ensure comparable infiltration rates with CT and RT plots. Based on the above discussed papers with opposite observations, the relevance of different tillage treatments with respect to the soil structure and soil hydraulic properties needs to be always addressed to the particular area of interest (soil type, crop-plant, climate, etc.).



a) b)

Figure 8. ANOVA results for effect of tillage treatment
a) means and 95% LSD intervals describing differences in hydraulic conductivity *K(h)* between plots with different tillage treatments for all experimental phases together;
b) Interaction plot describing differences in *K(h)* between the tillage treatments at each of the experimental phase

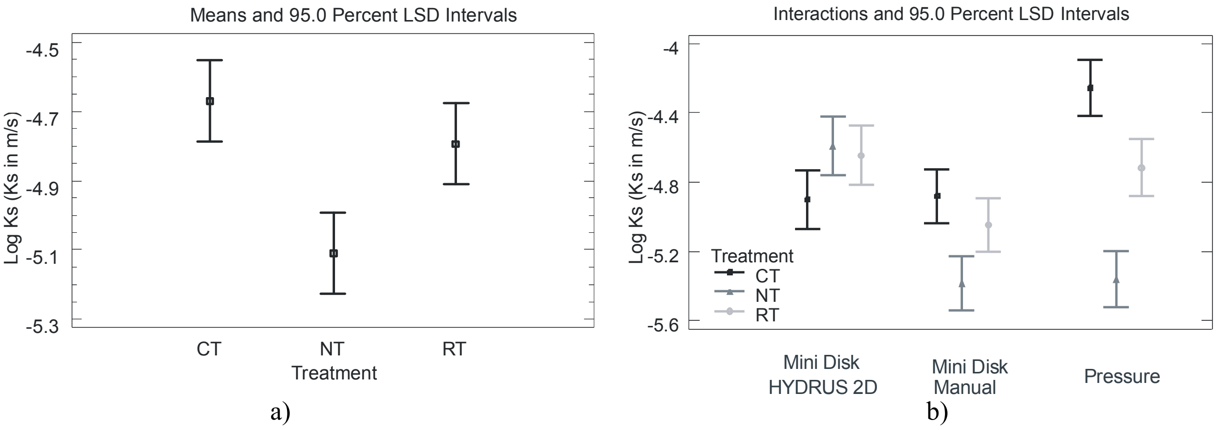


Figure 9. ANOVA results for effect of tillage treatment
a) Means and 95% LSD intervals describing differences in saturated hydraulic conductivity K_s between plots with different tillage treatments for all experimental phases together;
b) Interaction plot describing differences in K_s determined by using different types of infiltrometers

5. ACKNOWLEDGEMENT

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Research
Araştırma

MODELING CONVECTIVE WATER FLOW IN REPACKED SAND COLUMNS BY BREAKTHROUGH CURVES OF CHLORIDE

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Abstract: This paper describes a novel theory for modeling water flow in porous media, such as soils, using breakthrough curves of nonreactive chemicals. Miscible displacement tests of chloride were conducted in repacked sand columns (30.0 cm length and 8.0 cm id.) that were prepared using washed sand particles with diameters of 2.0-1.0, 1.0-0.5, 0.5-0.25, and <0.25 mm. Sands with different particle-size were used to evaluate the theory in different water flow regimes. The resultant BTCs of Cl were used to model the hydraulic conductivity as a function of mobile water content ($K(\theta_m)$) of the sand columns. Laboratory measured and modeled values of saturated hydraulic conductivity (K_s) were compared to validate the model developed. Correlation analysis of the measured and approximated K_s values resulted in a correlation coefficient of r = 0.91 (P<0.001), suggesting that the model developed successfully utilized the data in BTCs to quantify the water flow in the sand columns evaluated in this study.
Key Words: Mobile water content, Hydraulic conductivity, Breakthrough curve, Chloride, Porous media, Water flow

1. INTRODUCTION

Water flow in a porous medium is a combined function of many variables and parameters inherent to the medium and fluid. The fluid properties are its viscosity and density, while pore geometry (size distribution of the pores, topology of pore space, and connectivity of the water phase) is the primary characteristic that defines the porous medium (Klute and Dirksen, 1986; Vogel and Roth, 1998). In natural porous systems, such as soils, the intricate nature of porosity makes it impossible to formulate the exact relationship between soil pore characteristics and hydraulic conductivity (Tuli, 2002).

Several methods have been developed to express hydraulic conductivity (*K*) in porous media as a function of porosity. For example, Henry Darcy first showed that water flux through sand filter beds was proportional to the gradient of the hydraulic head. This relationship, which is known as Darcy's law, has become one of the most important achievements in water flow theory. Indeed, numerous studies have since been conducted using analytical derivations of Darcy's equation (Gardner 1986; Stephens, 1996). One such equation is the Buckingham-Darcy Equation, which was developed in 1907, in which hydraulic conductivity is used instead of permeability and water pressure is replaced by matric head (Gardner, 1986).

J.L. Poiseuille and G.H.L. Hagen independently derived an equation for water flux in capillary tubes that was a function of the tube radius, pressure gradient, and viscosity of the fluid (Gardner, 1986). This equation, which is known as the Hagen-Poiseuille equation, is based on Newton's law of viscosity and has since been applied to flow through other cross sections. The Hagen-Poiseuille equation expresses the same relationship as the Darcy equation; however, the conductivity is given in terms of the measurable quantities of radius and viscosity in the Hagen-Poiseuille equation, adding meaning to the expression (Gardner, 1986).

Kozeny (1927) derived an equation to describe the relationship between water velocity and the properties of porous media. He assumed that pore space is composed of a bundle of capillary tubes with an average cross-sectional area. Later, Carman (1948, 1956) incorporated tourtousity effects into the Kozeny equation, resulting in the Kozeny-Carman equation. The Kozeny-Carman equation, which states that the permeability of a porous material is directly proportional to the cube of the porosity and inversely proportional to the square of soil particle surface area, is probably the best known and most often quoted equation relating porosity to permeability (Boersma et al., 1972).

Miscible displacement tests have long been used to evaluate the chemical transport properties of porous media (Nielsen and Biggar, 1961; Biggar and Nielsen, 1962; Nielsen and Biggar, 1962, 1963; van Genuchten and Wierenga, 1977; Ersahin et al., 2002; Kamra and Lennartz, 2005; and many others). In most of these studies, the shape of the breakthrough curve (BTC) was interpreted to assess features of the soil macropores and the extent of preferential flow, while the measured and fitted parameters of the BTC were used to quantitatively characterize the soils as transmitting media. In addition, a few of these studies attempted to characterize the pore water velocity variation quantitatively.

Many studies (Radulovich et al., 1989; Kung et al., 2005) of water and chemical breakthrough have been conducted in an attempt to characterize the pore size distribution and corresponding water flow characteristics of soil macropores. Such studies have used the functional relationship between the time needed for a tracer to travel through a soil column with a known length and the radii of pores through which the displacing solution flows. Deeks et al. (1999) used observed changes in solute concentration following miscible displacement of a 250 mg L^{-1} Cl solution to characterize the size-distribution of large soil conduits. In their study, they determined the values for the volume of discharging fluid in a specified time from the observed rate of movement of tracer within the soil to calculate the pore-radius using Poiseuille's equation.

The majority of miscible displacement studies have shown that one of the most important physical features of porous media is the magnitude of the volume of water not readily displaced, which is often termed the immobile water content of the porous system. Therefore, it has been suggested that the amount of mobile water needed to transport a given amount of a tracer within a specified time can be calculated. Using the approximated amounts of mobile water together with their corresponding arrival time in Darcy's equation can allow water flow to be modeled as a function of mobile water content in a system.Thus, this study was conducted to develop a theory to model water flow distribution in natural porous media, such as soils, as a function of mobile water content using displacement data for a nonreactive tracer. The theory and principles developed here were applied to the BTCs of chloride from small columns (30 cm length and 8 cm id) of uniform sand.

2. THEORETICAL

The capillary bundle model may be extended to develop a simple model of water flow in soils (Jury et al., 1991). The capillary bundle model is based on the idea that porous medium is composed of a number of capillary tubes with the same lengths, but different cross-sectional areas. The radius of the capillary bundle governs the rate of flow through the medium. In addition, it is assumed that all of the capillary tubes are continuous, with no dead ends or stagnant regions, although they may be twisted or tortuous. Finally, the model presumes that laminar flow prevails in each of the capillary tubes (Jury et al., 1991). The total flow of the porous medium is equal to the sum of the volume flow rates out of each tube divided by the cross-sectional area of the medium (i.e., soil column). The volume flow rate in a single capillary with a radius, r, is defined by Poiseuille's law (Jury et al. 1991; Deeks et al., 1999):

$$Q = \frac{\Pi r^4}{8\eta} \rho_w g \frac{\Delta H}{\Delta L}, \quad (1)$$

where, Q is the flow rate ($L^3 T^{-1}$), η is the coefficient of viscosity ($ML^{-3}T^{-1}$), ρ_w is the density of water (ML^{-3}), g is the acceleration due to gravity (LT^{-2}) and $\Delta H/\Delta L$ is the hydraulic gradient. The mean velocity over the cross-sectional area is (Hillel, 1980):

$$q = \frac{r^2}{8\eta} \frac{\Delta H}{\Delta L}. \quad (2)$$

2.1. Relating the Capillary Bundle Model to a BTC

In the absence of longitudinal dispersion and diffusion of the tracer, such as in the case of piston flow, the resultant BTC will be identical to the one shown in Figure 1a. However, natural porous systems (e.g. soil) are composed of numerous capillaries, each having a particular size, shape, tourtousity, and connectivity to others. Additionally, the flow in a single capillary is not spatially uniform; rather, the highest velocities occur at the pore center and the slowest velocities occur in regions adjacent to the pore walls. Furthermore, the tracer has a tendency to move from areas with higher concentrations to those with lower concentrations via diffusion. These effects all result in the formation of a BTC similar to the one illustrated in the Figure 1b.

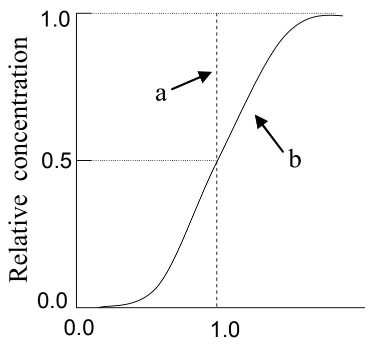

Figure 1. Hypothetical breakthrough curves for different displacement conditions a) piston flow and b) flow contributed by convection and hydrodynamic dispersion

When a nonreactive chemical is subjected to relatively rapid transport, the shape and location of the resultant BTCs are the outcome of the pore geometry (pore-size distribution, tortuosity, connectivity, shape, etc.) in a porous system. When compared to other components (shape, tortuosity, etc.) of the pore geometry, the pore-size distribution is the most important determinant of the shape of a BTC since the conductivity of an effective pore is largely dependent on its size. Assuming that the properties of convective transport are simply a function of pore-size, the BTC can be related to the size-distribution of the effective pores in the system. Supposing, for convenience, that the shape of a BTC of Cl is determined by the velocity distribution in the system, the following assumptions can be made:

In a miscible displacement test of a nonreactive chemical (i.e. chloride) conducted in a column repacked with an inert porous material (glass beads, washed sands, etc.), if the original solution at the inlet of the transmitting pores appears in the outlet of the column, the volume of effluent, ΔQ, needed to transport the mass of the chemical (tracer) between times t_i and t_{i+1} can be calculated as:

$$\Delta Q = \frac{\Delta M \Delta V}{M} . \quad (3)$$

where, M is the concentration (in molar) of tracer at the inlet of the column (stock solution), ΔM is the difference in the concentration of the tracer at the outlet between times t_i and t_{i+1}, and ΔV (L^3) is the volume of effluent collected between t_i and t_{i+1}.

Applied to a BTC, the above formula gives Eq. (4);

$$\Delta P = \Delta C_r x \Delta P_r . \quad (4)$$

where, ΔC_r is the change in relative concentration C_r ($C_r=C/C_0$), ΔP_r is the change in relative dimensionless pore volume ($P_r=V/P_0$, where V is the cumulative volume of effluent (L^3) and P_0 is the volume of water (L^3)) in the column determined by oven drying at 105 ^oC, and ΔP is the dimensionless pore volume needed to transport the mass of the tracer corresponding to ΔC_r. The value for ΔQ can then be calculated as:

$$\Delta Q = \Delta P x P_0 \quad (5)$$

Knowing ΔQ allows us to calculate the hydraulic conductivity using Darcy's equation by:

$$K(C_{ri}) = \frac{\Delta Q_i}{\Delta A_i t_c} \frac{\Delta z}{\Delta H} , \quad (6)$$

where, ΔA_i is the fraction of cross-sectional area of the soil column supporting the particular sized capillaries discharging ΔQ_i, t_c is the cumulative time that has elapsed since the beginning of the test, $\Delta z/\Delta H$ is the gradient of soil water head, which can be taken as unity for a miscible displacement test conducted under a pressure potential of zero. Hereafter, $\Delta z/\Delta H$ will be taken as unity, and, for brevity, will not be included in subsequent equations. The value for ΔA_i can be approximated by;

$$\frac{\Delta A_i}{A} = \frac{\Delta Q_i}{\Delta P_i x P_0} . \quad (7)$$

Here it was presumed that the ratio of ΔQ_i to $\Delta P_{ri} x P_0$ was identical to the ratio of ΔA_i to A, where A is the cross sectional area of the column. Combining Eqs. (6) and (7) yields Eq. (8);

$$K(C_{ri}) = \frac{\Delta Q_i}{\frac{\Delta Q_i}{\Delta P_i x P_0} t_i} . \quad (8)$$

2.2. Accounting for the Hydrodynamic Dispersion Effect

The variable, ΔQ_i, in Eq. (8) is calculated without accounting for the hydrodynamic dispersion effect, D_s. If there were no hydrodynamic dispersion in the column, one pore volume would be sufficient to displace the water inside the column using the stock solution (pulse). That is, without D_s, the resultant BTC would be identical to the one shown in the Figure1a, where C_r= 1.0 at P_r=1.0. In this case, the convective flow would be the only means by which the tracer was transported. However, D_s is known to make contributions to solute transport that vary depending on the characteristics of the porous media. Therefore, in the presence of D_s, more than one pore volume of pulse would be needed to displace one pore volume of water inside the column. Eq. (9) was proposed to account for the hydrodynamic dispersion effect on the transport of the tracer:

$$\Delta Q_{ci} = \frac{\Delta Q_i}{P_{r(Cr=1.0)}} , \quad (9)$$

where, ΔQ_{ci} is the volume of effluent corresponding to convective flow and $P_{r(Cr=1.0)}$ is the dimensionless pore volume of effluent collected at C_r=1. Finally, combining Eq. (8) with Eq. (9) yields Eq. (10);

$$K(C_{ri}) = \frac{\Delta Q_{ci}}{\frac{\Delta Q_{ci}}{\Delta P_i x P_0} t_i} . \quad (10)$$

Eq (10) can be used to quantify the distribution of water flow rate using BTCs of nonreactive chemicals such as chloride and bromide.

2.3. Approximating Hydraulic Conductivity for a Specified Mobile Water Content, θ_m

The hydraulic conductivity at a specified soil mobile water content, θ_m (or matric head corresponding to the θ_m), is the function of all of the water filled effective pores. Therefore, the conductivity of the system for θ_m can be calculated as a cumulative function of Eq. (10) as follows:

$$K(\theta_{mi}) = \sum_{i=1}^{n} K(C_r)_i . \quad (11)$$

where, i=1 corresponds to the hydraulic conductivity, $K(C_r)$, corresponding to the narrowest effective pore class in the system (calculated against a dimensionless concentration of 1.0 ($C_r=C/C_0$=1.0), and n corresponds to any prescribed value for θ_{mi}, which can be calculated as;

$$\theta_{mi}(\Delta Q) = \sum_{i=1}^{n} \Delta Q_i . \quad (12)$$

The variable $K(\theta_m)$ calculated by Eq. (11) can be interrelated to the matric pressure of mobile water by solving Eq.(2) and then Eq. (13):

$$h = \frac{2\sigma}{r} , \quad (13)$$

where r (L) is the radius of the pore, and σ (FL^{-1}) is the surface tension of the soil water.

3. MATERIAL AND METHODS

The theory and methodology proposed in the theoretical section were applied to experimental breakthrough curves (BTCs) of chloride obtained using sand columns (30 cm length and 8.0 cm id) repacked with well-sorted washed sand grains. These sand columns were preferred to minimize the interactions between the chloride and the porous medium.

The sand columns were packed with sand screened sand with sieves with mesh sizes of 2, 1, 0.50 and 0.25

mm. To achieve an adequate packing, the bottom of the columns was gently tapped on the laboratory bench during packing.

3.1. Miscible Displacement Tests

Prior to conducting the miscible displacement experiment, both ends of the sand column were supported with a fabric. The core was then gradually saturated with 0.01 M KBr solution from the bottom of the column (van Genuchten and Wierenga, 1977). Upon saturation, the core was positioned on an upright stand, after which the inlet at the top of the column was connected to a disc infiltrometer with a base of 8 cm id (Figure 2).

After steady state flow was established under zero tension, approximately 6.0 pore volumes of tracer solution of 0.05 $CaCl_2$ in 0.01 M KBr solution were introduced into the column under zero tension using a disc infiltrometer. The effluent was then collected by a fraction collector and analyzed for chloride with a chloride specific electrode.

Following the miscible displacement tests, the sand column was removed and placed in an oven with a constant temperature of 105 ^oC to determine the bulk density and total porosity *f*. The total porosity was calculated by;

$$f = 1 - \frac{D_b}{D_p}, \qquad (14)$$

where, D_b is the bulk density (ML^{-3}) of the column and D_p is the density of particles (ML^{-3}), which was assumed to be 2.65 Mgm^{-3}. The saturated water content of the column was deemed to be equal to the volume of pores in the oven dried sand column.

Dimensionless concentrations of chloride were calculated by dividing the concentration of chloride in the effluent, measured with a chloride sensitive electrode, by the concentration of the stock solution measured using the same electrode.

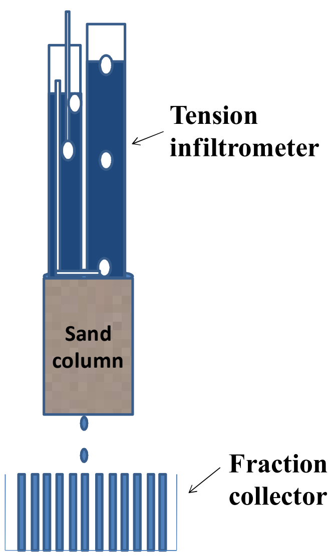

Figure 2. Apparatus used to conduct miscible displacement tests

3.2. Calculation of K(C_r)

Initial and boundary conditions:

Initial conditions: $t=0,\ C = 0$ and $t = t_s>0$, C>0 at the inlet of the column.

$C=0,\ V=0$ and $C>0,\ V>0$ at the outlet of the column

Boundary conditions: $t=t_{max},\ P_r=P_{rmax},\ C_r = 1.0$.

The following step-by-step procedure was applied using the above specified initial and boundary conditions:

1. Experimental BTCs for chloride were obtained by plotting the dimensionless concentration of chloride, C_r, against the dimensionless volume of effluent collected, P_r ($P_r = V/P_0$, where V is the cumulative volume of effluent collected and P_0 is the volume of water held in the saturated column, and $C_r = C/C_0$, where C is the concentration of chloride in the outlet and C_0 is the concentration in the inlet).
2. The property ΔP in Eq. (7) was calculated by multiplying P_r by its counterpart, C_r.
3. The value for P_0 was calculated by multiplying *f* in Eq. (14) by 100 cm^3 (the volume for each sand column), after which the values for ΔQ in Eq. (5) were calculated.
4. The value for ΔQ obtained during stage 4 above was divided by P_{rmax} (the value for P_r at Cr=1.0) to account for the hydrodynamic dispersion effect. This gave the value for ΔQ_c in Eq. (9).
5. The value of ΔQ_{ci} was divided by the corresponding value for P_{ri} (the value of P_r calculated in step i), which gave the value for $(\Delta A/A)_i$ in Eq. (10).
6. The value for the cumulative time elapsed (t) was determined as t_i-t_s, where t_i is the cumulative time elapsed for step i and t_s is the time (starting time) at which the first pulse infiltrated the column.
7. The values calculated for ΔQ_c, t, and ΔP were used in Eq. (10) to calculate K_i against the corresponding relative concentration, C_{ri}.
8. The calculations were repeated for about 30 points in each BTC to cover the range of C_r from C_r=C_{rmin} (where C_{rmin} is the C_r at the first breakthrough of tracer) to C_r = 1.0. The calculations were conducted using a spreadsheet program prepared in MS-Excel.

3.3. Calculation of $K(\theta_m)$ by $K(C_r)$

The values of $K(C_r)$ were approximated by Eq. (11) for hydraulic conductivity against the mobile water content θ_{mi}, which was calculated by Eq. (12). For example, to calculate K_s ($K(\theta_m)$ at saturated water content) all of the $K(C_r)$-values were summed.

4. RESULTS AND DISCUSSION

The characteristics of the sand columns used to determine the miscible displacement of chloride are given in Table 1. As expected, the lowest bulk density D_b occurred when the particle size was smallest. The pore water velocity, ν (cm s^{-1}), decreased gradually as the particle-size of the sand in the columns decreased.

Table 1. Properties of repacked sand columns used in the miscible displacement tests. Each column has 30 cm length and 8 cm id.

Column ID	PS mm	D_b grcm^{-3}	f	K cms^{-1}	θ_s cm^{3}cm^{-3}	P_o cm^3
a	2-1	1.60	0.39	0.46	0.39	588.1
b	1-0.5	1.67	0.37	0.03	0.37	557.9
c	0.50-0.25	1.59	0.40	0.0073	0.40	603.2
d	<0.25	1.56	0.41	0.0064	0.41	618.3

PS: particle size, D_b: bulk density, f: total porosity, K: hydraulic conductivity, θ_s: volumetric water content at saturation, P_o: pore volume at saturation

The breakthrough curves of chloride for the sand columns are presented in Figure 3. Columns packed with different sized sand materials yielded different shaped BTCs. In general, the BTCs gradually shifted right in response to decreasing pore water velocity in response to the lower mean particle-size of the sand used to pack the columns. This shift was attributed to the smaller particles being arranged more closely, which resulted in stagnant regions that harbored larger amounts of Cl that was not readily displaced. Nielsen and Biggar (1961) attributed a right shift to soil texture and aggregation, with sand having the least amount of water not readily displaced and clays having the greatest amount of water that was not easily displaced.

The $K(\theta_m)$ was calculated from BTCs seen in Figure 3 and the results were shown in Figure 4. A sharp decrease in K versus θ_m is noticeable at the beginning for all the cases. Expectedly, the change in K against θ_m decreased more slowly after then.

The validity of the calculations was assessed, comparing saturated hydraulic conductivity measured K_{sm} with that calculated K_{sc} (Figure 5). As Figure 5 shows, the model over predicted for the column d (the column packed with <0.25 mm particle size, see Table 1). The correlation analysis between measured and calculated values for saturated hydraulic conductivity resulted in a correlation coefficient (r) of 0.91. This suggested that, in overall, the model developed proved to be useful at least in the experimental conditions set in this study. More data are needed to evaluate model in diverse porous media such as soils.

Number of studies conducted to evaluate the relationship of the breakthrough of water and/or chemicals to flow characteristics in porous media is limited. German and Beven (1981) used the Hagen-Poiseuille equation to describe macropore flow, and Radulovic et al. (1989) applied the same equation to evaluate soil macropore distribution from the water breakthrough curves. However, neither of these studies addressed the full range of effective pore-size distribution in soils. Rather, they considered only the macropore segment of the pore-size distribution range. Water flow in soils depends primarily on pore geometry and pore-size distribution, which are controlled by soil structure and soil texture. However, it is quite difficult to quantify the relationship between soil structure and water and solute transport in soils (Deeks et al., 1999). The theory and applications developed here suggest several directions for future research efforts. The development and application of laboratory techniques for the measurement of effective pore-size distribution together with the convective flow of water in soils with a variety of structures may generate a significant breakthrough in understanding water and chemical transport in structured soils.

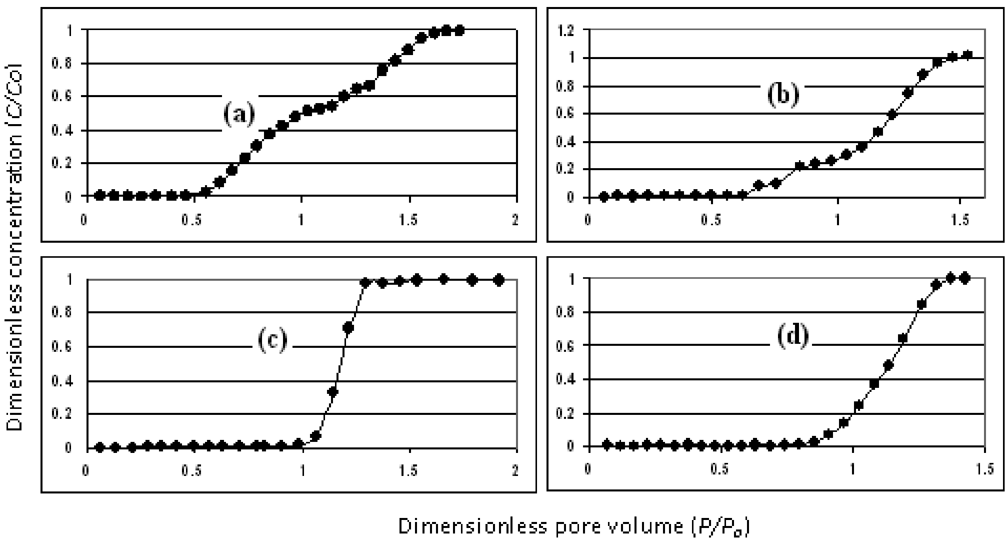

Figure 3. Breakthrough curves of chloride in columns prepared with uniform sand with particle size of a) 2-1, b) 1-0.5, c) 0.50-0.25, and d) <0.25 mm. See Table 1 for details of the columns

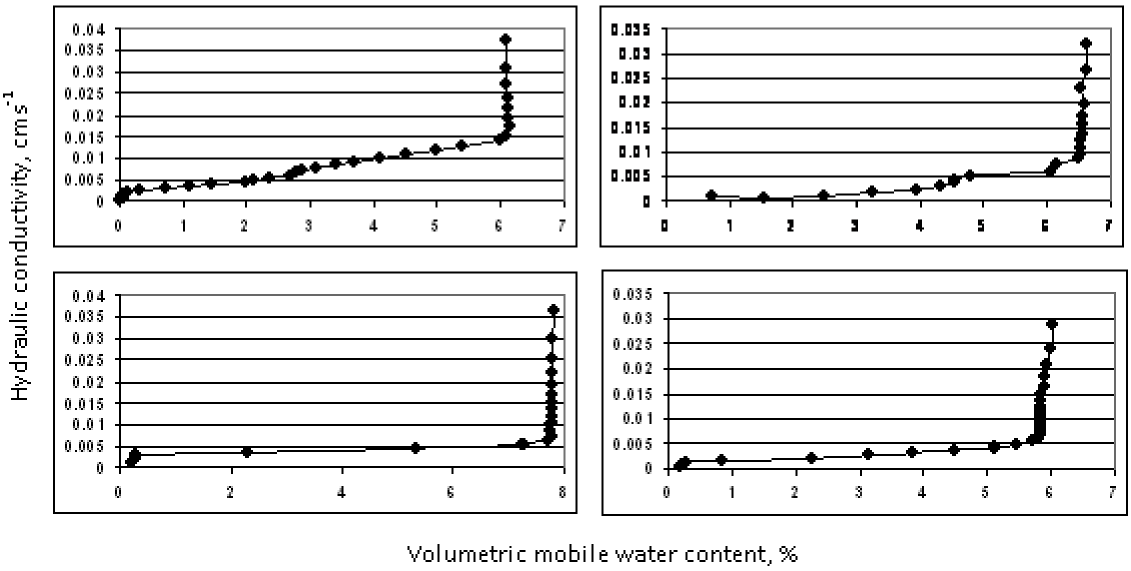

Figure 4. Hydraulic conductivity of the columns packed with uniform sand of particle size a) 2-1 mm, b) 1-0.50 mm, c) 0.50-0.25 mm, and d) <0.25 mm.

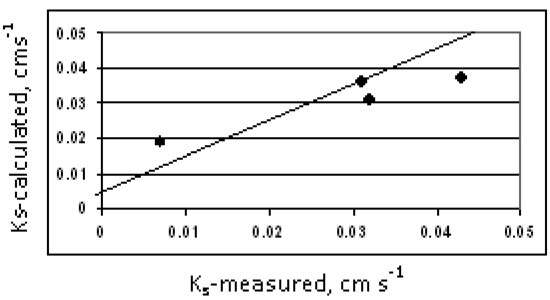

Figure 5. Relationship between measured and calculated values of hydraulic conductivity calculated with BTCs given in Figure 3. The diagonal represents the 1:1 line

5. CONCLUSION

Water flow was modeled in relatively large sand columns (30 cm long and 8 cm wide) packed with washed sands of different particle size. Darcy's equation was combined with the Pouisuille equation to approximate the hydraulic conductivity as a function of mobile water content calculated from breakthrough curves of Cl. The approximated results for the saturated water flow were then compared with measured K_s-values and found to be highly correlated (r=0.91, P<0.01) at all sand size-distributions evaluated. These findings demonstrated the validity of the method developed here for modeling hydraulic conductivity under saturated conditions in.

The theory and model developed in this paper differ from conventional models of water flow, which are based on the relationship of water content to water potential in soils. The model developed in this study is based on the amount of mobile water required to transport a known amount of tracer within a known amount of time. As expected, the particle size of repacked sand and the mobile water content of the columns were related. The theories proposed and the procedures developed in this study worked well in repacked sand columns. However, further research is needed to validate the calculations using intact and repacked soil columns.

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APPENDIX A

List of Symbols

A	Cross-sectional area of the column (L^2)
C	Concentration of the tracer in the discharged effluent (ML^3)
C_0	Concentration of the tracer in the stock solution (ML^3)
C_r	Relative concentration (C/C_0, dimensionless)
C_{rmin}	The minimum value for C_r
D_s	Hydrodynamic dispersion (L^2T^{-1})
D_b	Bulk density (ML^{-3})
D_p	Particle density (ML^{-3})
f	Porosity (dimensionless)
g	Acceleration due to gravity ($L\ T^{-2}$)
H	Soil water head (L)
h	Soil water pressure/matric head (L)
K	Hydraulic conductivity (LT^{-1})
K_s	Saturated hydraulic conductivity (LT^{-1})
M	Concentration of tracer (ML^3)
L	Length (L)
P_0	Pore volume (L^3)
P_r	Relative pore volume (V/P_0, dimensionless)
P_{rmax}	Relative pore volume against C_r=1
Q	Discharge rate in the Poiseuille equation ($L^3\ T^{-1}$)
Q_{ci}	Volume of effluent corresponding to convective flow (L^3)
q	Discharge rate in Darcy's Equation (LT^{-1})
r	Radius (L)
t	Time (T)
t_s	Time at which the first pulse was introduced to the column (T).
t_{max}	Time (T) at C_r=1
V	Cumulative volume of the effluent collected (L^3)
z	Gravitation head (L)
η	Coefficient of viscosity ($ML^{-3}T^{-1}$)
θ	Water content (L^3L^{-3})
θ_m	Mobile water content (L^3L^{-3})
θ_{mc}	Mobile water content contributing to convective flow (L^3L^{-3})
ρ_w	Density of water (ML^{-3})
σ	Surface tension of soil water (FL^{-1})
ν	Pore water velocity (LT^{-1})

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Research
Araştırma

PHYSICAL PROPERTIES OF SODDY- PODZOLIC SOILS UNDER LONG-TERM FIELD EXPERIMENT

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Abstract: The fundamental physical properties of sod-podzolic soils under long-term field experiment were studied. The results showed that these properties have not changed significantly under the influence of nearly 100 years of liming, chemical and organic fertilization. The significant differences of approximation parameters of dependence penetration resistance from soil moisture content indicated that the application of manure increased interparticle contacts within the studied moisture range. This approximation parameters allow to affirm the significant increase interparticle forces by decreasing moisture content in the control and lime treatments compared with the others ones that resulted from the sand fractions increasing in granulometric composition of control treatment soils and aggregation of particles due to the influence of lime (lime treatment).
Key Words: Soil physical properties, Long-term field experiment, Penetration resistance

1. INTRODUCTION

Many soil properties are subjected to changes under conditions of intensive farming. In particular, these changes take place under the impact of mechanical compaction. The creation of a compacted soil layer under the plow horizon affects the soil water regime and the soil aeration. This is accompanied by changes in the soil biota and, often, in the character of the soil organic matter transformation. The application of fertilizers, including organic fertilizers, also affects many soil properties. In particular, relatively stable (conservative) physical properties may be affected, such as the aggregate size distribution, specific surface, etc. (Ditartre and Andreux, 1993; Achmad Rachman et al, 2003).

However, in dependence on the particular farming practices, soil properties, and climatic conditions, these changes may be very different. In some cases, they are clearly manifested. In other cases, they can not be diagnosed by the traditional methods. As shown in a number of works, the long-term application of fertilizers may exert negligible effect on the soil texture and bulk density (Munkholm et al, 2002; Ulrich et al, 2004). Many physical properties of soils are relatively stable, and their minor changes can not be properly estimated by the routine methods. In this context, it is important to develop the methods making it possible to judge unambiguously about changes in the physical properties of soils under the impact of the particular agricultural loads. Our work was aimed at studying a wide range of the physical properties of a soddy-podzolic soil and their changes under the impact of mineral fertilizers, lime, and manure.

2. MATERIAL AND METHODS

Field studies were performed on the plots of the long-term experiment of the Timiryazev Agricultural Academy. This experiment was established by Prof. A.G. Doyarenko in 1912 on a gently inclined surface (1^0 toward the northwest) within the southern margin of the Klin–Dmitrov Ridge. The area of 1.5 ha with a light loamy soddy medium podzolic soil was subdivided into two parts; six rectangular fields were established within each of the parts. Continuous crops (winter rye, potatoes, barley, clover, flax, and clean fallow) have been cultivated on the first part. The second part has been used in rotation (clean fallow–winter rye–potatoes–oats (barley) with clover–clover–flax).

Each field within the part with continuous crops was divided into eleven plots of 100 m^2, on which different variants of fertilization have been tested: control (two plots), N, P, K, NP, NK, PK, NPK, manure, and NPK + manure. Since the fall of 1949, regular liming (once per 6 years) has been practiced on a half (50 m^2) of the plots (Kiryushin, Safonov, 2002).

In April 2008, auger samples were obtained from the layers of 0–10, 10–20, 20–30, and 30–40 cm from the plots with continuous crops; the following trials were tested: control, lime, NPK, and NPK + manure. The soil bulk density was determined in the samples taken by a cylindrical auger (Pol'skii's auger).Particle size distribution analysis was performed in two stages. At the first stage, ground soil was sieved through 1mm and 0.25mm screens to separate coarse soil particles (> 0.25 mm). At the second stage, particle size distribution in the fraction <0.25 mm was determined on a FRITSCH Analysette22 laser diffractometer after the ultrasonic pretreatment. Thus, we obtained data on the content of coarse fractions (>0.25 mm) and on the particle size distribution for finer fractions. This was necessary, because the content of coarse fractions in the analyzed soil was significant and hampered the analysis of particle size distribution curves for fractions <0.25 mm. The soil specific surface was determined by the method of desorption equilibrium above saturated salt solutions and by the method of heat desorption of gases (nitrogen). In the first case, the soil samples (3–5 g) were wetted and stored for two weeks in desiccators above water to reach quasiequilibrium saturation. After this, the samples were placed in desiccators with saturated salt solutions ensuring relative vapor pressures of 0.15, 0.332, 0.55, 0.86, and 0.98. The desorption of water from the samples until the equilibrium state continued for about three months. Then, the samples were dried at 105°C, and their water content was determined. The specific surface was calculated according to the BET method (Shein, Karpachevskii, 2007). The specific surface was also determined by the method of the heat desorption of gases (nitrogen) with the help of a SORBTOMETER device (Shein, 2005; Shein, Karpachevskii, 2007). Aggregate size distribution in the upper horizons (0–10 and 10–20 cm) was determined by the method of dry sifting using a RETSCH device (Retsh GmbH, 2005). The organic carbon content was determined on an automatic analyzer (AH7529) at the temperature of 900–1000°C in the flow of purified oxygen (Shein, Karpachevskii, 2007).

The wetting heat (*WH*, cal/g) was determined on an OX12K calorimeter. It was calculated as follows:

$$WH = \frac{K_k \cdot t_n}{P_d}, \qquad (1)$$

where K_k is the heat capacity of the calorimeter, t_n is the real rise in temperature, and P_d is the mass of absolutely dry soil sample (Shein, Karpachevskii, 2007).

The strength of dry aggregates of 3–5 and 5–7 mm in size was determined in 20 replicates with the help of a cone penetrometer developed by P.A. Rebinder:

$$P_m = 1.108 \cdot \frac{F}{h^2}, \qquad (2)$$

where F is the load, kg; h is the depth of the cone penetration, cm; and 1.108 is the coefficient for the cone of 30°. According to this method, the penetration resistance (P_m) is measured in kg/cm^2 (Khaidapova, Pestonova, 2007). It was determined for the samples with different contents of water.

3. RESULTS AND DISCUSSION

Data on the major soil physical properties of studied soils are summarized in Table 1. According to the particle size distribution data, the soil has a medium loamy texture; in the surface horizons of the control plot, the soil texture is light loamy. The coarsening of the soil texture (up to the loamy sandy texture) with the high content of coarse (> 0.25 mm) fractions is also observed in the layer of 30–40 cm from the plot treated with NPK fertilizers. It should be noted that particle size distribution curves with two peaks observed in the experimentare typical of the poorly sorted moraine deposits. The specific surface values obtained by the two methods are relatively low and remain stable within the soil profiles, except for the lower part (30–40 cm) of the soils on the control plot and on the plot with NPK and manure, where this index increases. Also, the specific surface determined by the method of the water vapor desorption increases in the soil of the plot with NPK and manure. This may be due to the increased hydrophilicity of organic substances in the soil of this plot and, probably, due to some change in the mineralogical composition of the low soil horizons (Munkholm et al, 2005).

Table 1. Some physical properties of soddy-podzolic soil

Variants	Depth, cm	Granulometric particles content, %			Soil density, g/cm^3	Aggre-gates 10-0.25 mm, %	$C_{org.}$, %	S_{H2O}, m^2/g	S_{N2}, m^2/g	WH, cal/g	Plastic limit, %	Liquid limit, %
		<0.01 mm	<0.001 mm	>.0.25 mm								
Control	0-10	27,61	3,92	24,64	1,56	71,89	1,04	22,01	2,90	1,68	14,49	19,24
	10-20	28,17	3,90	28,34	1,58	71,71	1,04	20,84	3,26	1,56	15,10	18,16
	20-30	29,27	4,59	34,18	1,80	-	0,65	18,67	3,78	1,37	12,60	15,29
	30-40	34,04	4,98	28,64	1,75	-	0,24	26,20	10,81	1,39	12,33	15,25
Lime	0-10	31,48	4,23	25,30	1,67	76,77	1,20	22,60	2,50	2,18	15,10	19,88
	10-20	29,54	3,95	24,34	1,65	82,58	1,2	21,80	2,50	1,46	15,56	19,43
	20-30	31,34	4,23	25,56	1,88	-	1,05	20,79	2,80	1,46	15,53	20,03
	30-40	25,82	3,41	32,32	1,97	-	0,75	14,10	3,56	1,25	12,61	14,02
NPK	0-10	32,53	4,77	24,88	1,58	72,43	1,16	21,77	3,18	1,44	15,16	19,92
	10-20	31,10	4,26	26,50	1,50	71,92	1,22	17,69	2,92	1,78	14,45	18,96
	20-30	29,13	3,88	35,30	1,67	-	0,67	19,02	3,90	1,47	12,87	16,59
	30-40	17,39	2,42	59,10	1,75	-	0,26	13,75	4,36	0,78	12,95	13,71
NPK +manure	0-10	32,12	4,23	20,26	1,44	81,13	1,77	27,83	2,44	2,20	12,82	26,45
	10-20	31,08	4,20	25,86	1,40	75,10	2,09	31,38	2,44	3,13	21,38	27,22
	20-30	27,42	3,76	29,02	1,75	-	0,57	20,40	3,39	1,23	13,20	17,13
	30-40	35,57	6,55	25,20	1,84	-	0,21	46,66	17,84	2,11	13,30	19,48

Note: $C_{org.}$, - content of soil organic matter, S_{H2O} and S_{N2} – soil specific surface determined by water and nitrogen desorption

An increased water retention capacity of the soil of this plot should also be noted; in particular, this soil is characterized by the increased values of the plastic and liquid limits.It is known that the bulk density determined with the use of Pol'skii's auger is usually somewhat higher, than the bulk density determined with the use of cylindrical rings of Kachinskii. However, the auger method can be applied for comparative assessments of bulk density values in different variants of the experiment. According to our data (Table1), the soil bulk density increases down the soil profile in all the variants. The minimum values are observed in the Ap horizon of the variant with NPK and manure, because the application of manure decreases the soil bulk density in the Ap horizon. The maximum values are observed in the variant with lime application. They are reliably higher than those in the control variant. Increased bulk density values in the variant with lime application were already noted during the survey in 1996–1998; however, it was concluded that the difference between the control variant and the variant with lime were within the experimental error (Kiryushin, Safonov, 2002).The wetting heat varies from 0.78 to 3.13 cal/g; according to this index, the soils are slightly hydrophilic. The maximum values of the wetting heat are in the variant with NPK and manure application, which may be explained by the addition of hydrophilic organic matter. The control variant somewhat differs from other variants by a higher content of coarse particles; the variant with NPK and manure application is characterized by the increased content of the finest particles in the entire profile. The latter circumstance allows us to assume that this phenomenon may be related to the initial textural difference between the plots. However, it is also possible that the increased content of finest particles in this variant is due to the formation of colloidal and fine clay organo-mineral particles in the soil treated with manure.

In general, a comparative analysis of some physical and chemical properties of the upper soil horizons from different variants of the experiment shows that the difference between major physical characteristics of the soil solid phase for different variants is relatively small. The spatial heterogeneity in the distribution of the studied indices within the particular soil profiles and between them is considerable. It can be supposed that a somewhat coarser soil texture at the control variant and an increased content of clay particles in the variant with NPK and manure application are related to the initial heterogeneity in the soil properties rather than to the different agricultural loads on the soils. The degree of changes in the soil physical properties under the impact of different agricultural loads is relatively small. Only the variant with NPK and manure application differs significantly from other variants in a higher content of finest particles and, hence, in a higher water retention capacity at the plastic and liquid limits. Relatively small differences between the major physical properties of soils at different variants of the experiment necessitated the search for other differentiating properties. In particular, the strength of soil aggregates and penetration resistance were studied at different water contents. These characteristics are indicative of the strength of interparticle bonds. As seen from Fig. 2, the strength of airdry aggre gates in the variants with lime and with NPK and manure is higher than that in the control and NPK variants for both studied depths (0–10 and 10–20 cm) and for both aggregate diameter groups (3–5 and 5–7 mm). These data are in agreement with the existing notions about the effect of lime on the mechanical strength of acid soils (Khaidapova, Pestonova, 2007; Khaidapova, Prudnikova, 2002). As for the NPK + manure variant, an increase in the physical strength of the aggregates may be explained by the addition of organic substances. These substances favor the development of coagulation bonds. In the case of soil drying, such bonds may be transformed into stronger mixed and cementing bonds. As a result, the stability of soil micro and macroaggregates in the dry state increases (Boujilla, Gallali, 2008). Thus, the addition of organic fertilizers (manure) not only increased the soil organic matter content (Table 2) but also improved the strength of soil aggregates in the airdry state. Interesting results were also obtained upon penetration resistance (P_w) tests at different soil water contents (W). In this case, the soil is subjected to the compression stress and shear stress. The soil dilatant properties characterizing interaction between the soil particles are clearly manifested. The tests were performed within the soil water range from the liquid limit to the plastic limit.

The results are presented in Fig.1. It is seen that the P_w–W curves for the variant NPK + manure are shifted to the right, i.e., at a given soil water content, the soil resistance to penetration in this variant is higher than in other variants due to the formation of coagulation bonds between the particles. The variant with lime is also characterized by an increased penetration resistance, which is seen from the steep slope of the P_w–W curves. In all the variants, the strength of soil structure (soil resistance to penetration) increases sharply within a relatively narrow range of the soil water contents. This is typical of the soils with an increased content of coarse particles. As seen from Fig. 1, with a decrease in the relative degree of soil moistening, the soil penetration resistance increases most significantly in the variant with lime application; the minimum increase is observed in the variant with NPK and manure application, which is explained by the lubricant action of hydrophilic organic matter in this case. The highest penetration resistance in the limetreated soil is in agreement with earlier published data (Khaidapova, Prudnikova, 2002). The control variant and the variant with NPK occupy an intermediate position. However, the qualitative analysis of the curves does not make it possible to estimate the reliability of the established differences between the soils of different variants. To estimate it, we approximated the obtained curves by the following power equations:

$$P_w = \left(\frac{W}{b2}\right)^{-b1} \tag{3}$$

where P_w is the value of soil resistance to penetration , W is the soil water content, and $b1$ and $b2$ are approximation parameters. The reliability of differences between the approximation parameters obtained for different variants of the experiment was specially evaluated. In this model, parameter $b2$ characterizes the position of the curve relative to the abscissa axis: the higher $b2$, the higher the soil resistance to penetration at the given soil water content (i.e., the stronger interparticle bonds). Parameter $b1$ points to the slope of the curve: the higher $b1$, the steeper the curve, i.e., the more significant changes in the penetration resistance take place with the change in the soil water content. This means that the soil particles come into close contact and display strong internal friction with a decrease in the soil water content.

The results of corresponding calculations and the assessment of reliability of the differences between different variants of the experiment are presented in Table 2.

At all the depths, parameter $b2$ at the variant with NPK and manure is higher than that at other variants, i.e., the corresponding curve lies higher, which is well seen from Fig. 1. Parameter $b1$ is reliably lower for the deep soil layers in this variant, which is seen from the lower steepness of corresponding curves.

Significantly lower values of parameter $b1$ in the variant with NPK and manure point to stronger bonds between the soil particles in this variant and to their relatively small changes within the studied range of soil water contents. This parameter is reliably higher in the control variant and in the variant with lime application, particularly, in the layer of 30–40 cm. This attests to the growing strength of interparticle bonds with a decrease in the soil water content. As noted above, this is typical for the soils with the high content of coarse particles and with the strong aggregation of the particles under the impact of lime application.

Thus, the analysis of the curves showing the dependence of soil physical properties (penetration resistance) on the soil water content makes it possible to obtain information about the reliability of differences in the parameters of the curves and, hence, in the rheological behavior of the soils from different variants of the experiment. Note that routine determinations of the major physical proper ties of the soils did not make it possible to judge about their differences in different variants of the experiment.

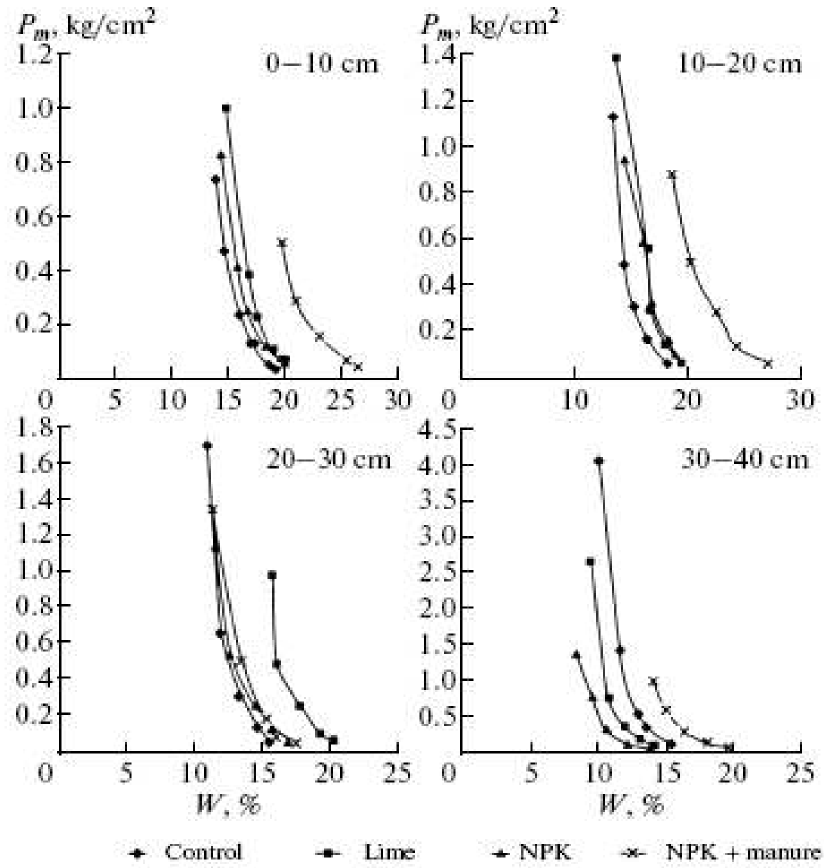

Figure 1. Penetration resistance (P_w, kg/cm^2) as dependent on the soil water content (W,%of dry soil mass) in different experimental variants

Table 2. Assessment of the influence of mineral fertilizers, lime and manure on the changes in soil strength using the power function

Depth 0-10 cm							
Variants		Control		Lime		NPK	
		b1	b2	b1	b2	b1	b2
Lime	b1	8,72					
		9,37					
	b2		13,61*				
			15,04				
NPK	b1	8,72		9,37*			
		8,14		8,14			
	b2		13,61*		15,04*		
			14,23		14,23		
NPK+ manure	b1	8,72		9,37*		8,14	
		7,85		7,85		7,85	
	b2		13,61*		15,04*		14,23*
			18,13		18,13		18,13
Depth 20-30 cm							
Variants		Control		Lime		NPK	
		b1	b2	b1	b2	b1	b2
Lime	b1	10,68					
		13,60					
	b2		11,82*				
			15,57				
NPK	b1	10,68		13,60			
		8,22		8,22			
	b2		11,82		15,57*		
			11,94		11,94		
NPK+ manure	b1	10,68*		13,60		8,22	
		6,93		6,93		6,93	
	b2		11,82*		15,57*		11,94
			12,09		12,09		12,09

Note: Numerators denote the data in columns, and denominators denote the data in rows.
* - Significantly different (with the 0.95 probability) values

4. CONCLUSION

(1) The physical properties of soils, such as particle size distribution, bulk density, specific surface, aggregate size distribution, wetting heat, and penetration resistance as dependent on the soil water content within the range from the liquid limit to the plastic limit were determined in soils of the longterm field experiment at the following plots: control, lime, NPK, and NPK + manure.

(2) It was found that the long-term application of lime, mineral fertilizers, and manure had a minor effect on the main physical properties of the studied soddy-podzolic soils. Only the soil of the plot with NPK and manure application was characterized by a somewhat higher content of finest particles and a higher water retention capacity.

(3) The physico-mechanical properties of the soils (the strength of soil aggregates and the dependence of penetration resistance on the soil water content) were more sensitive and statistically reliable to indicate soil changes under the impact of different treatment systems. These soil properties characterize interparticle bonds and their changes in dependence on the degree of soil moistening, i.e., the rheological behavior of the soils.

(4) The parameters of approximation of the curves showing the dependence of penetration resistance on the soil water content for the NPK + manure variant differed reliably from the analogous parameters for other variants, which pointed to stronger interparticle bonds and their low dependence on the soil water content (within the studied range) in the soil of this variant. Soils of the control variant and the variant with lime application also differed reliably from other soils in the parameter characterizing the increase in the strength of interparticle bonds with a decrease in the soil water content. This can be explained by a some what coarser texture of the soil at the control variant and by a stronger aggregation of the soil particles in the variant with lime application.

5. ACKNOWLEDGEMENT

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Research
Araştırma

BIOREMEDIATION OF SEWAGE SLUDGE FOR LAND APPLICATION AS A FERTILIZER USING BIOLEACHING

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Abstract: Huge amount of sewage sludge is generated worldwide that needs a proper discharge strategy, which retains both future sustainability and present needs. Land application of sewage sludge can be a good solution, whereas it is cost-effective disposal method for treatment plants and also can provide a favorable fertilizer for farm lands. It provides an economical alternative for the final disposal of the sewage sludge, but heavy metals in sewage sludge is always an issue restricting its general use. Therefore, removal of heavy metals prior to land application is likely to be a possible and practical means for reducing metal content in sewage sludge. Bioleaching appear to be a promising technology in removing heavy metals from contaminated sewage sludge. The effect of bioleaching on heavy metals solubilization and also their DTPA-extractable (Diethylene Triamine Pentaacetic Acid) form changes was investigated in this work. The samples of activated sludge were collected from three of most important sewage sludge treatment plant of Tehran. Total metal concentration and DTPA-extractable metal content of samples were determined. Bioleaching using Acidithiobacillus ferrooxidans was carried out in two experiments to study solubilization rate and changes in DTPA-extractable Fe, Cu, Ni and Pb. Results showed that bioleaching could affect metal DTPA-extractable form significantly but, there was no definite behavior for each metal and also each metal in different samples. However, bioleaching can efficiently remove mentioned metals from sewage sludge solid phase. Bioleaching removed approximately 24.73 % of Fe, 83.96 % of Cu, 81.46% of Ni and 38.96 % of Pb from sewage sludge samples. In fact, bioleaching is more efficient and economic than chemical leaching. Indeed Acidithiobacillus ferrooxidans is a powerful bacterium in metals removal and environmental remediation programs.
Key Words: Bioleaching, Heavy metal, Sewage sludge, Bioremediation, Acidithiobacillus ferrooxidans, DTPA-extractable

1. INTRODUCTION

Wastewater treatment plants generate millions of tons of sludge worldwide every year. The management of this sludge is a major part of waste treatment, involving substantial cost and effort (Babel and Dacera, 2005).The basic disposal methods for such large quantities of sludge are land application, land filling, incineration, ocean dumping (Metcalf and Eddy, 2003). Ocean dumping is being phased out, incineration is costly and may contribute to air pollution and landfill space is becoming more and more scarce. One possible long- term solution appears to be recycling of the sludge nutrients and using it for beneficial purposes. Land application of sludge on agricultural lands, forest and disturbed lands represents one of the better options for utilization of this material by recycling plant nutrients and organic matter to soil for crop production (Wong et al., 2004). Agricultural utilization also provides a cost- effective method for sludge disposal (Smith, 1996). In Iran because of terrestrial climate in most regions, soils often have not sufficient organic matter.Therefore, land application of sewage sludge can be a good solution, whereas it has large amount of organic matter. The application of biosolids such as sewage sludge in to land, improves the water- holding capacity and nutritive value of poor soils due to its high content of organic matter and nutrients (Epstein, 1976). Until a few years ago, sewage sludge could be re- used directly in agriculture as fertilizer. Recently, however, there has been an increased concern because of high concentration of heavy metals in sewage sludge (Lue-Hing et al., 1998).The heavy metals therefore must be removed before land application to prevent environmental contamination and health hazards due to the presence of heavy metals in the sludge (Tyagi et al., 1991). Heavy metals removal can be achieved either by chemical or biological methods. Biological leaching referred as bioleaching. It has been proven that bioleaching technique is 80% cheaper than chemical methods (Tyagi et al., 1998). Bioleaching is based on the oxidation of sulfur or iron by chemiolithotrophic bacteria. The most widely used microorganisms in metal leaching are Acidithiobacillus thiooxidans and Acidithiobacillus ferrooxidans (Tyagi et al., 1991; Cho et al., 1999). In this work, we have investigated bioleaching of Cd, Zn, Mn and Co in comparison with chemical solubilization by acidification. This work was carried out to evaluate the ability of Acidithiobacillus ferrooxidans in heavy metal removal from sewage sludge. The effect of pH decrease and microbial activity on metal release was also compared and changes in DTPA-extractable form of metals also were investigated.

2. MATERIAL AND METHODS

2.1. Sample Preparation

The samples of activated sludge were collected from three of most important sewage sludge treatment plant of Tehran, namely Ekbatan, Shahrak-e-Gharb and Shosh. Samples immediately were transferred to the laboratory. The pH value and EC (Electrical Conductivity) were determined immediately by pH meter (Orion 920) and EC meter (Jenway 4230). Then samples of three treatment plant were mixed and finally a uniform sample obtained. To avoid any effect of solid content of sewage sludge on bioleaching rate, samples were dried at room temperature and stored at 4^{o}C until experiments.

2.2. Analysis

Total amount of metals, DTPA- Extractable form and soluble form were determined. To determine total metal concentration in sludge samples, the samples were digested in HNO_3 and $HClO_4$ (Page et al., 1982) and heavy metals were determined by Atomic Absorption Spectroscopy (Shimadzu A-660). In addition, DTPA-extractable amount of metals were determined (Lindsay and Norwell, 1978). DTPA extraction provides a chemical evaluation of the amount of metals that are available for plant uptake (Pretuzzelli, 1989; Su and Wong, 2003). The concentration of heavy metals in terms of soluble form was determined (Table 2) with the proportion of 5:1distilled water and dry sludge (v/w). Some physiochemical properties of sludge samples such as nutrient concentration, solid percentage, and organic C (Walkley and Black, 1934) were also determined and results are shown in Table 1.

2.3. Inoculum Preparation

The type of Acidithiobacillus ferrooxidans was ATCC (American Type Culture Collection) no.16466 that maintained in mineral salt medium which proposed by Tuovinen and Kelley (1973). Appropriate amount of inoculums were obtained through several steps of enrichment. Inoculum was maintained fresh and biologically active until experiment.

2.4. Bioleaching experiment

Two bioleaching experiments were designated; the first was to investigate the effect of microbial leaching on solubilization of heavy metals from sewage sludge solid phase in comparison with artificial acidification. The second was to investigate the effect of microbial activity on DTPA- extractable amount. Each experiment consisted of three treatments, which were triplicated. The treatments are inoculated, pH control and control treatments. At first, sludge samples were mixed with distilled water by proportion of 10:1 distilled water and dry sludge. To evaluate effect of microbial activity and pH decrease separately, another treatment was designated as pH control treatment, which used to add sulfuric acid to correspond the pH value with Inoculated treatment every day during experiment. So, we have two control treatments. pH control treatment which was exposed to pH values exactly same as inoculated treatment. Control treatment which only elemental sulfur was added. Samples were autoclaved (20 min at 121 ^{o}C) and inoculated in septic condition by appropriate inoculum (20% v/v). The experiments were carried out in fifty four 250 ml Erlenmeyer flask with 100 ml mixed sewage sludge and agitated at 120 rpm and 28 ^{o}C for 15 days. The sludge in all flasks also, was mixed with 5% (w/v) elemental sulfur powder as substrate. Determination of pH value for inoculated samples was done in septic condition every day during experiment. The sludge samples were centrifuged at 10000 rpm for 15 min to separate the solid from liquid fraction. The liquid fraction was filtered and stored at 4 ^{o}C prior to determination of heavy metals by Atomic Absorption Spectrometry (AAS). For the second experiment, solid fraction derived from centrifugation mixed with DTPA by the proportion of 1:5 (w/v) of solid fraction of sewage sludge and DTPA (1M). Then the mixture was filtered out by paper filter (Watman no.40). The solution which passed through filter, stored at 4°C until determinations by Atomic Absorption Spectrometry (AAS). All data were analyzed using the SAS statical package. One way ANOVA (Analysis of Variance) was carried out to compare the means of different treatments. Where significant F values were observed, the differences between individual means were tested using Duncan's test (Little and Hills, 1978).

Table 1. Some selected physiochemical properties of sludge samples

selected characteristics			
sludge sample	Ekbatan	Shahrak-e-gharb	Shosh
Solid (%)	1.8	2.0	1.7
pH	6.8	6.8	7.0
EC(ds.m-1)	0.7	1.0	1.3
Kjeldahl N (%) (Kjeldahl, 1883)	5.53	5.87	6.02
Organic Carbon (%)	26.3	26.6	28.5
Olsen(1954) P(mg.kg-1 dry sludge)	5700	16634	6154

Table 2. Heavy metals concentrations (mg.kg-1 dry sludge)

Total heavy metal concentration (mg.kg-1 dry sludge)	
Fe	29352.94
Cu	3808.24
Ni	121.65
Pb	55.52
DTPA-extractable form (mg.kg-1 dry sludge)	
Fe	364.67
Cu	-
Ni	3.52
Pb	18.83

3. RESULTS AND DISCUSSION

3.1. First Experiment

pH changes

As shown in Figures 1 and 2, pH value was decreased gradually during experiments in any of samples. Because of bacterial activity, acid produced and as a result, pH decreases during bioleaching. A.ferrooxidans uses elemental sulfur to produce sulfuric acid. A.ferrooxidans can also use sulfide form of metals as energy source and finally yield sulfuric acid. The addition of elemental sulfur, solely, did not affected pH, as it is shown in control treatment. Figures 1 and 2 show that pH decrease approximately after 4 days, because bacterial activity is not sufficient in initial days after inoculation. When pH begins to decrease, it gradually decreases approximately to value 1-2 and remains constantly to the end of the experiment. Samples from different sewage treatment plants did not different significantly in terms of pH decrease ($p < 0.05$).

Metal solubilization

The amount of Fe in liquid phase increases over time. Then after 10 days, decrease, probably because of production of other chemical forms of Fe, which are less soluble (Figure 3). Cu solubilized during experiment, but the rate of solubilized is different. At first five days, the solubilized rate is slow in comparison to next five days (5-10). The last five days (10-15), the solubilized rate decrease as slow as first days. The amount of soluble Cu increase significantly in inoculated treatment in comparison to the pH control and control treatments (Figure 4). Ni also solubilized in a rate such as that of Cu. All three treatments were significantly different (Figure 5).

Pb solubilized up to 38.96 % of total Pb of solid phase. Soluble Pb rises during experiment in approximately constant rate.Inoculation increased solubilized rate significantly in comparison to control treatments (Both pH control and control treatment). Regarding to significant difference between inoculated treatment and pH control treatment, it can be concluded that, bacterial activity play an important role in solubilization.

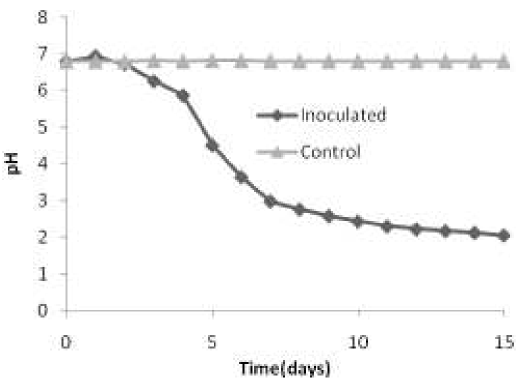

Figure 1. pH changes during first experiment

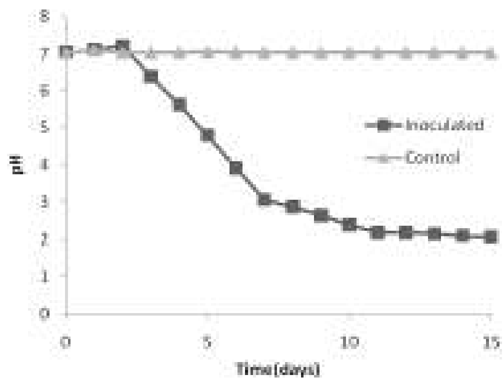

Figure 2. pH changes during second experiment

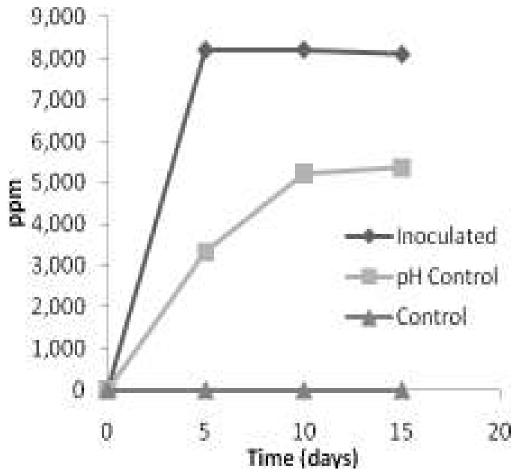

Figure 3. Fe changes in sewage sludge during bioleaching

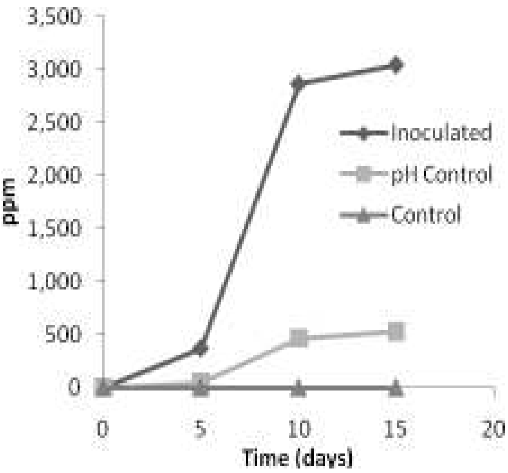

Figure 4. Cu changes in sewage sludge during bioleaching

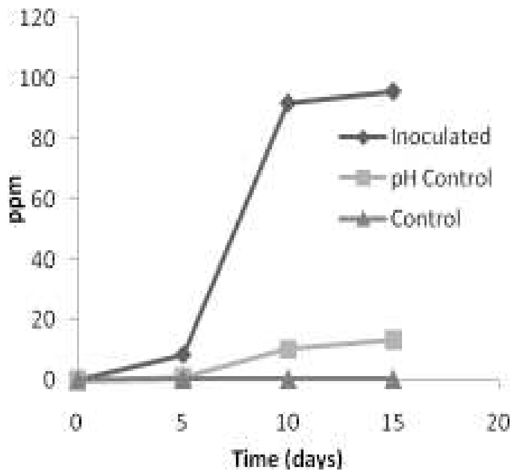

Figure 5. Ni changes in sewage sludge during bioleaching

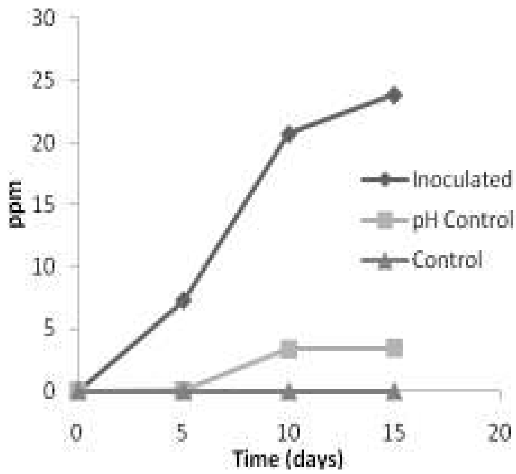

Figure 6. Ni changes in sewage sludge during bioleaching

3.2. Second Experiment

The effect of bioleaching on DTPA-extractable form of metal

In the case of all of four metals in second experiment, it is obvious that bioleaching did not affect DTPA-extractable forms of metals in a definite behavior. However DTPA-extractable forms of metals, change during experiments but it do not increase this form significantly. As we are to use the bioleached sludge as fertilizer, thus, this can be a good characteristic of bioleaching. As mentioned DTPA-extractable form of metals represents the amount of metals that can be uptake by plant roots. Whereas bioleaching decrease metals content of solid phase of sludge and also do not increase the absorbable form of metals, thus it can be recommended as a proper solution for high metal-polluted sludge. Cu can not be extracted with DTPA.

4. CONCLUSION

Results showed that bioleaching is an efficient and powerful tool for removal of heavy metals from sewage sludge. Sewage sludge samples were different in terms of response to bioleaching and consequent metal release likely because of organic matter nature or different forms of metals in sewage sludge. However, different metals are not same in the case of solubilization rate. Bioleaching removed approximately 24.73 % of Fe, 83.96 % of Cu, 81.46% of Ni and 38.96 % of Pb from sewage sludge samples. Generally, it can be concluded that bioleaching is an efficient approach in heavy metals removal form sludge and subsequent land application. In fact, bioleaching is more efficient and economic than chemical leaching. Indeed *Acidithiobacillus ferrooxidans* is a powerful bacterium in metals removal and environmental remediation programs.

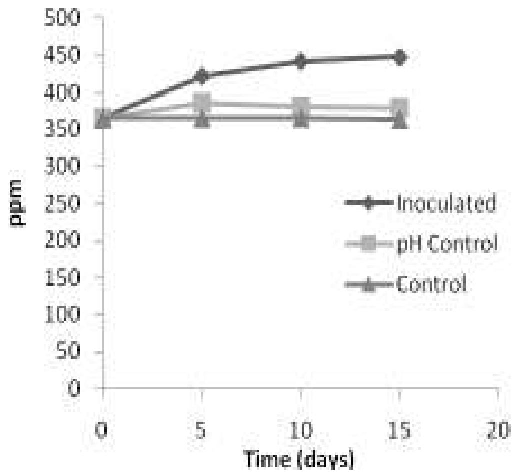

Figure 7. DTPA-extractable Fe changes in sewage sludge during bioleaching

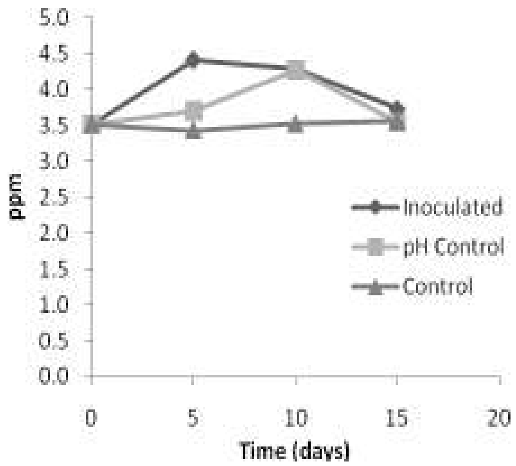

Figure 8. DTPA-extractable Ni changes in sewage sludge during bioleaching

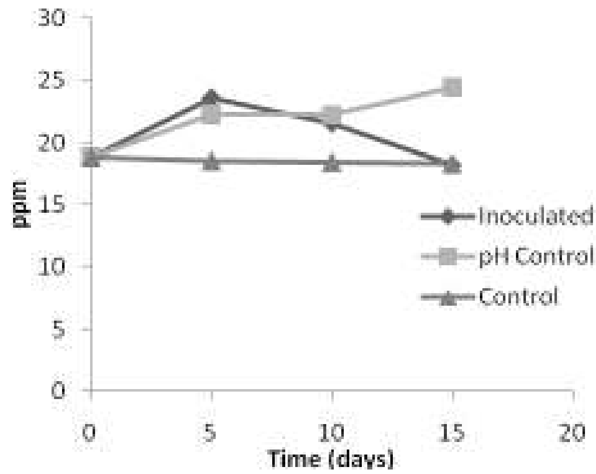

Figure 9. DTPA-extractable Ni changes in sewage sludge during bioleaching

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