2017

Volume : 6
Issue : 1
Page : 1 - 91

e-ISSN : 2147-4249

Eurasian Journal of Soil Science

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EURASIAN JOURNAL OF SOIL SCIENCE

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ABSTRACTING AND INDEXING: CABI, EBSCOhost, ULAKBIM-Dergipark, ProQuest, DOAJ, OAJI, CrossRef, CiteFactor, etc.

Year: 2017, Volume: 6, Issue: 1, Page: 1 - 91 **e-ISSN 2147-4249**

EURASIAN JOURNAL OF SOIL SCIENCE

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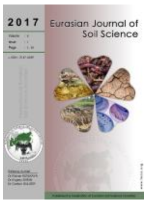

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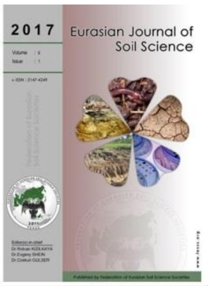
Eurasian Journal of Soil Science

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



Tropical chemical weathering of a garnet rich micaschist in the rainforest zone of Cameroon

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Article Info

Received : 22.03.2016
Accepted : 17.05.2016

Abstract

Soils developed on garnet-rich micaschist in the Southern Cameroon plateau were investigated. Morphologically, two weathering materials constituted the study profile, fine earth and nodules. Each material has a singular evolution from the coarse saprolite to the upper set of clayey and loose horizons. There is Al_2O_3 enrichment in the fine earth concomitantly to Fe_2O_3, Na_2O and K_2O enrichment in nodules in major element–Al_2O_3 variation diagrams. A–CN–K and A–CNK–FM diagrams show a progressive depletion of Al in nodules concomitantly to an enrichment of this element in the fine earth. Three pedogenetic processes emerge from the evolution of weathering products. There is a ferruginization process whose importance increases from the coarse saprolite to the upper set of clayey and loose horizons, giving rise to the formation of dense nodules composed of hematite, goethite and gibbsite. This ferruginization occurs concomitantly with a desaluminization process, which causes Al_2O_3 depletion in nodules. These nodules are formed by the process of induration where the hydrated amorphous hydroxide and oxides are dehydrated to their crystalline oxide form, due to condensation. In addition, there is aluminization, which occurs in the fine earth, leading to the development of a red clayey material composed of kaolinite and gibbsite.

Keywords: Laterite, ferruginization, desaluminization, aluminization, Cameroon.

Introduction

Enormous volumes of rocks are involved in the biogeochemical weathering that affects continental surfaces. Among this, about tens of meters of thickness over about one third of all emerged lands are today undergoing lateritization (Nahon, 2003). Lateritization processes homogenize the weathering products through intense leaching of alkaline, alkaline-earth elements and some silica of the parent rock, and lead to a mineralogical reorganization of silica, alumina and iron oxides (Davy and El Ansary, 1986; Nahon, 1991; Tardy, 1993). These processes lead to the formation of laterites, which are the main constituents of weathering mantles in the tropical zone (McFarlane, 1976). They are complex materials derived from the weathering of various rock types (Tardy, 1993; Thomas, 1994; Beauvais, 2009; Ndjigui et al., 2008; 2013; Tsozué et al., 2011; 2012; Wouatong et al., 2013). Their profiles result from intense chemical weathering in intertropical zones and have commonly developed over several millions of years (Tardy, 1993; Tardy and Roquin, 1998). A remarkable amount of literature exits on the mechanism of chemical weathering under different geomorphic and paleoclimatic conditions (Wouatong et al., 2005; Deepthy and Balakrishnan, 2005; Nguetnkam et al., 2008; Kamgang et al., 2009). Weathering is the alteration and breakdown of rock and soil

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284259

materials at and near the earth's surface by physical, chemical and biological processes. Some of the mineral elements may be released, forming secondary minerals, particularly clay minerals. Chemical weathering in tropical regions favours extensive lateritization which is the cementation of sesquioxide-rich soil horizons (Helgren and Butzer, 1977; Aristizábal et al., 2005) and formation of deeply weathered profiles (Irfan, 1996; Voicu and Bardoux, 2002). The main chemical factors that usually control the weathering of rocks include solution pH, parent material composition and crystallinity, microenvironment, oxidation-reduction potentials, temperature and ionic strength (Wouatong et al., 2013).

Chemical weathering indices based on quantitative measurements based on whole-rock chemical analyses are commonly used to characterize the intensity and mechanisms of weathering (Nesbitt and Young, 1982; Irfan, 1996, 1999; Ng et al., 2001; Gupta and Rao, 2001; Voicu and Bardoux, 2002; Aristizábal et al., 2005; Wouatong et al., 2013). Recent works have shown that weathering indices based on the ratio of a group of mobile elements to one or more immobile elements are useful parameters for characterizing changes induced by weathering (Duzgoren-Aydin et al., 2002; Aristizábal et al., 2005; Wouatong et al., 2013). The elements more mobile during weathering are generally used to quantify the effects of chemical weathering on heterogeneous weathering residua (Price and Velbel, 2003; Aristizábal et al., 2005; Wouatong et al., 2013). Nesbitt and Young (1982, 1984, 1989) and Nesbitt et al. (1996) used ternary A–CN–K and A–CNK–FM diagrams to deduce weathering trends. These authors demonstrated that the bulk compositions of diverse rocks composition follow simple trends that are largely unaffected by the climatic conditions under which weathering took place (Aristizábal et al., 2005; Wouatong et al., 2013). In addition to providing a method of visualizing the degree of weathering, the A–CN– K system permits the evaluation of the weathering trends from fresh rock compositions through their weathering products (Fedo et al., 1995; Aristizábal et al., 2005; Wouatong et al., 2013).

The intensity of chemical weathering is determined by factors like climate, parent material, topography and vegetation. It is generally accepted that chemical weathering is more developed in tropical areas. This is even more important in areas with dense vegetation and a smooth topography, leading thus to the decomposition and/or transformation of original minerals in the bedrocks. Recent characterization of soils developed on garnet rich micaschist in the rainforest zone of Cameroon have shown that nodules observed in the nodular horizon have been formed in situ, directly from the original garnet grains in the bedrock (Tsozué et al., 2011). They are fundamentally different from degradation and aggradation nodules commonly described in the tropical zone (Tardy, 1993). The garnet rich micaschist might undergo differential weathering where garnet minerals exhibit a completely different evolution from that of the other minerals which constitute the bedrock.

The main objective of this study is to investigate weathering trends and intensity, chemical behavior of major elements, improve the understanding of the different weathering processes occurring during the decomposition and/or the transformation of the garnet rich micaschist into a thick weathering mantle under the tropical rainforest of the Southern Cameroon in Central Africa.

Material and Methods

Study site

The study site is located in the Southern Cameroon plateau, approximately between longitudes 13°23'30''E to 13°24'30'' E and latitudes 3°43'33''N to 3°44'45''N (Figure 1). The Southern Cameroon plateau belongs to the African 1 Surface, with altitude between 600 and 800 m a.s.l., which is observed in addition to Cameroon, in Central Africa Republic (CAR), Equatorial Guinea (EG), Gabon and Congo (Figure 1). The study site emerges from the whole Southern Cameroon plateau by its altitude of about 840 m a.sl. The climate is an equatorial type with two dry seasons alternating with two wet ones and a mean annual rainfall of 1640 mm, a mean annual temperature of 23°C and an average annual relative humidity of 80% (Suchel, 1987), favourable for the development of a dense evergreen forest which is strongly degraded by human activities around the villages (Letouzey, 1985). Such climatic conditions are suitable for supergene weathering leading to the formation of red ferrallitic soils (Yongué-Fouateu et al., 2006). The slopes are gentle (6-10%), separated from each other by narrow and outstretched valleys. The bedrock is a massive garnet-rich micaschist. In addition to garnet mineral, there are muscovite, biotite, feldspar and quartz. Microchemical analyses reveal that garnets are grossularite-rich almandine type.

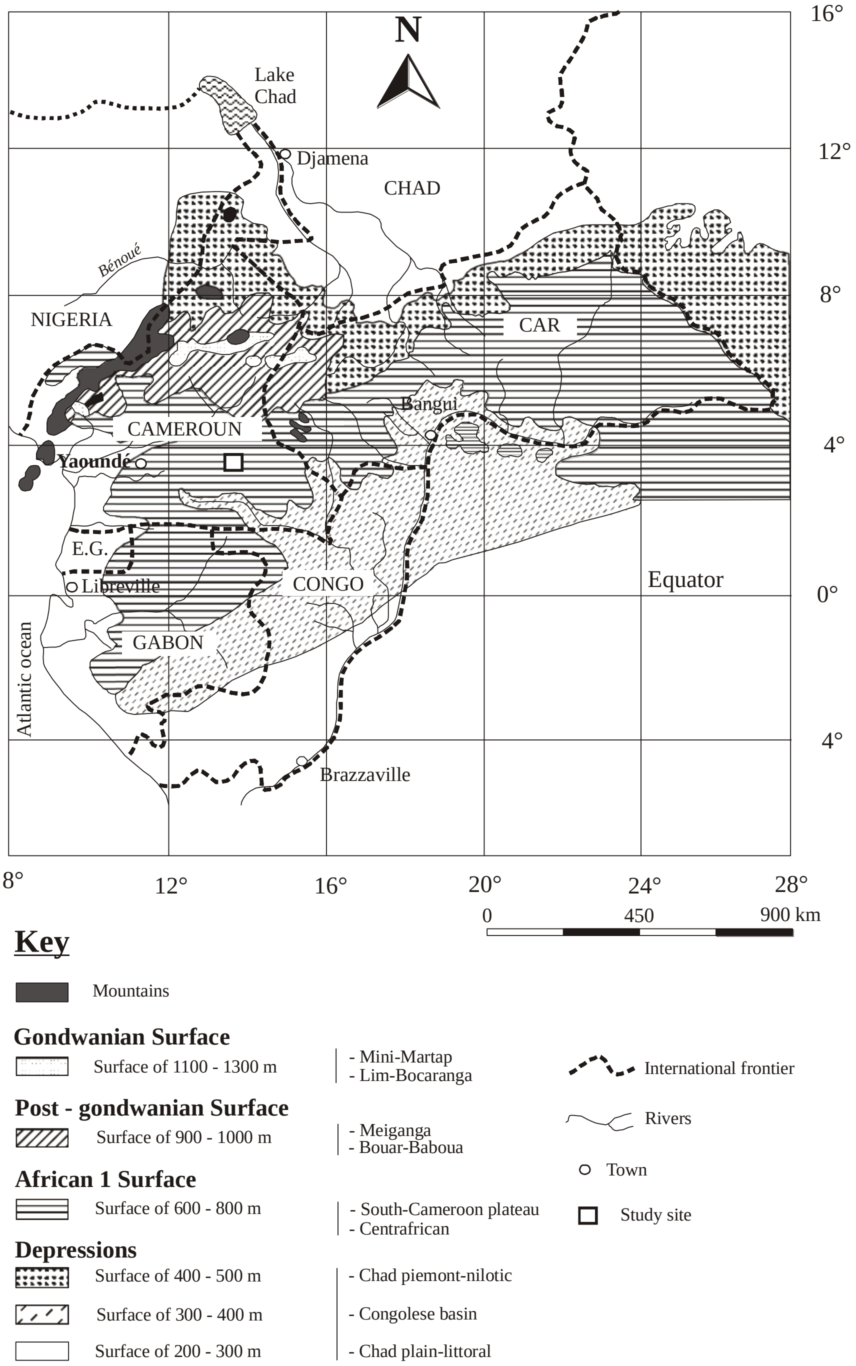

Figure 1. Location of the study area (modified after Temgoua (2001)).

Experimental design

An unweathered garnet-rich micaschiste sample was collected on outcrops in the valley near the studied interfluves, together with soil samples in the studied profile.

In the laboratory, three main types of analyses were conducted. They are microscopic, mineralogical and geochemical analyses. Microscopic analyses consisted of observations of fifteen soil and two rock thin sections under the polarizing microscope. Soil thin sections were obtained after impregnation with resin and then hardening in the air. Soil thin sections were described using the terminology proposed by Stoops (2003). Mineralogical analyses were done by X-ray diffraction (XRD) on total sample powders, using a Philips PW2400 XRD spectrometer with copper anode and equipped with a xenon detector, whose characteristics are: wavelength $\lambda = 1,54x10^{-10}\,m$, energy E = 40 kV. For samples containing goethite, percentage substitution rates in moles of AlOOH were calculated by Thiel (1963) method, based on Vegard's law and reflecting the proportionality between the distance lattice and the substitution rate. Loss on ignition

(LOI) was determined by ignition of samples at 1050°C for two hours. Geochemical analyses were made by X-ray fluorescence on total samples powder. They were performed using a Philips PW 1404 WD XRF spectrometer. The detection limit was 0.01%.

The behaviour of chemical elements, throughout the profile was approached by calculating elements mass balance during weathering. These mass balances were done following the calculated 'mass balance method' (Brimhall and Dietrich, 1987; Brimhall et al., 1988; Colin et al., 1992) by considering titanium as an immobile element (Anderson et al., 2002). It is based on the residual enrichment in closed systems and supergene enrichment in open systems, which previously need the determination of horizon deformation rates. This method enables to estimate the quantity of each element which is depleted or accumulated (Colin et al., 1993). Horizon deformation rate (ε), element mobilization rate (**τ**) and total mass of mobilized elements (m) in each horizon were calculated according to the following equations:

$$\varepsilon_a = \frac{C_{i,p}.d_p}{C_{i,a}.d_a} - 1 \quad ; \tau_{j,a} = \frac{d_a}{d_p}\frac{C_{j,a}}{C_{j,p}}(\varepsilon_a + 1) - 1 \quad ; \quad m_{j,p} = \left(\frac{C_{j,p}}{100}.dp.vp\right)\tau_{j,p}$$

In these, Ci,p and Ci,a are the concentrations of an invariant element i (in this case, Ti) respectively in the parent rock p and the horizon a; Cj,p and Cj,a are concentrations of any common element j, respectively, in the parent rock p and the horizon a; dp and da are, respectively, the bulk density of the parent rock p and the horizon a; vp is the parent rock volume which corresponds to 1 cm^3 (Brimhall et al., 1985).

Results

Morphological, mineralogical and geochemical characterization of the studied profile

The studied profile is about 10 m thick and made up of four horizons, from bottom to top (Figure 2, Table 1):

- a coarse saprolite (10 to 8.25 m), which is gray yellow with a well preserved bedrock structure and the presence of numerous pink globular garnet crystals. Mineralogically, the horizon is dominated by muscovite, goethite, quartz, gibbsite and kaolinite, with an addition of hematite and traces of anatase in the "ghost"of unweathered garnets (Table 2). The loose material is mainly composed of SiO_2 (62.60%), with a small amount of Al, Fe, K, Na, Ca and Mg (Table 3). In the "ghost" of garnet, Si contents are low meanwhile Al and Mg contents are high (Table 3);

- a fine saprolite (8.25 to 6.20 m), red, with many isalteritic relicts, ferruginized friable quartz blocks and nodules, embedded in a clayey matrix with a very weakly developed blocky structure. Microscopically, it is characterized by a weakly birefringent micromass with a locally undifferentiated b-fabric, but sometimes with a stipple speckled b-fabric. Coarse materials represent about 30% of the red loose clay matrix, with double spaced porphyric c/f related distribution patterns. This assemblage is constituted by muscovite, quartz, kaolinite, gibbsite, goethite, hematite and traces of anatase (Table 2). SiO_2 contents decrease, Al_2O_3 contents increase in the matrix and Fe_2O_3 contents increase slightly in nodules, whereas other oxide contents are almost constant (Table 3);

- a nodular horizon (6.20 to 4.60 m), composed of about 40% of nodules embedded in a red clayey matrix with fine blocky structure. Nodules show a groundmass consisting of an orange-brown birefringent micromass (goethitic) or a darker and undifferentiated micromass (hematitic). The mineral composition is muscovite, kaolinite gibbsite, goethite, hematite, quartz and traces of anatase, with high expression of gibbsite in nodules (Table 2). Si, Al and Fe are the most abundant elements both in the matrix (57.38% SiO_2, 15.03 Al_2O_3, 5.62% Fe_2O_3) and in the nodules (47.23% SiO_2, 15.83% Al_2O_3, 8.12% Fe_2O_3) (Table 1). K_2O, MgO, Na_2O and CaO contents remain almost constant but well represented here as in the other horizons (Table 3);

- a set of red clayey and loose horizons (4.60 to 0 m), subdivided from bottom to top into a dense deep horizon (4.60 to 3.30), an aliatic horizon (3.30 to 1.50), a compact horizon (1.50 to 0.08 m), identical to the matrix described in the nodular horizon, and a very thin surficial humiferous horizon (0.08 to 0 m). The groundmass has a moderately to highly separated microstructure. It contains a few quantities of nodules, less than or equal to 3 mm in diameter. Coarse material represents 10 to 20% of the groundmass, with double spaced porphyric to open porphyric c/f related distribution patterns. The mineral assemblage is composed of kaolinite, quartz, gibbsite, hematite and traces of muscovite (Table 2). Si, Al and Fe are the most abundant elements (52.04% SiO_2, 20.12% Al_2O_3, 6.23% Fe_2O_3) (Table 3). They are followed by K (4.02% K_2O), Na (1.32% Na_2O), Ca (1.92% CaO) and Mg (2.70% MgO) which remain present here as in the other horizons (Table 3).

Table 1. Morphological and physical characteristics of soils.

Soil characteristics										
Horizons	Depth (m)	pH		Colour	Texture	Structure	Boundary	Nodules or rock fragments	Consistency	
									Dry	Wet
Humiferous horizon	0-0.08	4.7		10R2.5/2	clay-sandy	vf&wl	g	n	h	s & p
Compact upper red horizon	0.08-1.50	4.6		10R4/4	clayey	vf&mabk	g	n	h	s & p
Red aliatic horizon	1.50-3.30	4.5		10R4/4	clayey	Vf&wg	g	v	h	s & p
Dense deep red horizon	3.30-4.60	4.5		10R4/4	clayey	vf&wabk	a	c	h	s & p
Nodular horizon	4.60-6.20	Nodule	5.2	10R4/6	clayey	vf&wabk	g	a	h	s & p
		Fine earth	4.6							
Fine saprolite	6.20-8.25	Nodule	4.4	2.5YR4/6	clayey	Vf&sbk	g	a	h	s & p
		Fine earth	4.4							
Coarse saprolite	8.25-9		5.2	7.5YR 6/0	sandy-loamy	sc	/	m	h	s & p

Soil parameters					
Structure			Consistency	Rock fragments	Transition
Size	Type	Grade			
vf = very fine (G5 mm) f = fine (5–10 mm) m = medium (10–20 mm) c = coarse (20–50mm) vc = very coarse (>50 mm)	g = granular abk = angular blocky sbk = subangular blocky l=lumpy ma=massive sc=schistose	w = weak (peds barely observable) m = moderate (peds observable) s = strong (peds clearly observable)	Dry: l = loose s = soft h = hard Wet: s = sticky p = plastic	n = none (0%) m = many (15%–40%) v = very few (0%–2%) a = abundant (40%–80%) c = common (5%–15%) d = dominant (>80%)	a = abrupt c = clear g= gradual d = diffuse

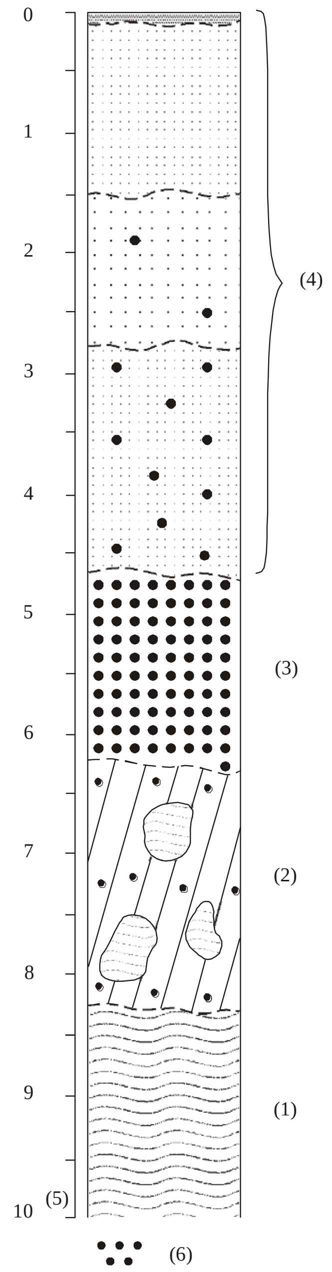

Figure 2. Macroscopic organization of the studied weathering profile: 1. coarse saprolite; 2. fine saprolite; 3. nodular horizon; 4. set of clayey and loose horizons; 5. depth (m); 6. nodules.

Table 2. Mineralogical composition of soils

Horizons	Depth (m)	M	K	Gi	Goe	He	Q	A	% moles of AlOOH in goethite
Set of clayey and loose horizons	(1.25 m)	+	+++	++	/	+	++++	/	/
Nodular horizon	Nodules (5.5 m)	+	/	++++	++	++	+++	/	9
	Fine earth (5.5 m)	++	++	++	/	+	++++	+	/
Fine saprolite	Nodules (8 m)	+	+	+++	++	+	+++	+	8
	Fine earth (8 m)	++	++	++	/	+	++++	+	/
Coarse saprolite	"ghost" of garnet (9 m)	++	+	+++	++	+	++	+	9
	Fine earth (9 m)	+++	+	++	+++	/	+++	/	10

/: non identified ; + : traces ; ++: very deficient ; +++: deficient ; ++++: abundant

M: muscovite ; K: kaolinite ; Gi: gibbsite ; Goe: goethite ; Q: quartz ; He: hematite ; A: anatase

Table 3. Chemical composition of soils and parent rock.

Horizons /Saprolites	Depth (m)	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	K_2O %	Na_2O %	CaO %	MgO %	P_2O_5 %	Total %	$\frac{Si}{Al}$	CIA %	MIA %	LOI %	pH	SOC %
Set of clayey and loose horizons	(1.25 m)	52.04	20.12	6.23	0.66	4.02	1.32	1.92	2.70	0.09	99.80	2.32	70.67	41.34	10.70	4.7	26.35
Nodular horizon	Nodules (5.5 m)	47.23	15.83	8.12	1.11	3.08	3.24	2.40	2.11	0.24	99.91	2.67	52.38	4.76	16,55	5.2	23.95
	Fine earth (5.5 m)	57.38	15.03	5.62	0.79	3.12	2.20	3.13	2.13	0.27	100.03	3.42	64.34	28.68	10.36	4.6	20.65
Fine saprolite	Nodules (8 m)	42.98	18.34	7.31	1.08	2.42	3.36	2.96	3.01	0.31	99.30	2.10	56.97	13.94	17.53	4.4	25.65
	Fine earth (8 m)	50.68	20.34	6.02	0.99	4.01	2.10	2.01	3.12	0.26	99.50	2.23	69.04	38.08	9.97	4.4	26.36
Coarse saprolite	"ghost" of garnet (9 m)	44.23	19.82	5.65	1.21	1.38	2.23	2.20	4.34	0.12	99.70	2.00	62.92	25.84	18.53	/	25.47
	Fine earth (9 m)	62.60	14.03	6.12	0.56	3.23	3.11	2.43	1.98	0.31	101.12	4.00	60.00	20.00	6.75	5.2	20.15
Bedrock	Garnet grains*	34.79	19.34	31.16	0.06	0.00	0.00	8.07	0.56	0.16	94.14	/	70.56	41.12	/	/	50.50
	Total rock	64.01	14.40	6.91	0.71	2.08	2.50	3.01	4.20	0.15	100.34	/	65.48	30.96	2.37	/	21.31

*: results obtained from microchemical analysis

Morphological evolution of weathering products

Morphologically, the study profile is composed of two weathering materials: fine earth and nodules. Each material has a singular evolution from the coarse saprolite to the upper set of clayey and loose horizons.

The loose material or fine earth in the coarse saprolite is polychrome, sandy-loamy, characterized by a preserved bedrock structure and the presence of unweathered muscovite observed under polarized microscope (Figure 3). This material is transformed into a red clayey matrix with a very weakly developed blocky structure in the fine saprolite and a red clayey matrix with a fine blocky structure in the nodular horizon. In the set of red clayey and loose horizons, the fine earth is generalised and constitutes the essential part of the set of horizons (Figure 3). This set is characterized by a weakly expressed blocky structure at the bottom, a fluffy consistency symbolized by high matrix porosity in the median part and a fine blocky structure, and a dark red and shiny clay skins on some aggregates in the upper part, confirmed by typic coatings observed under the microscope (Figure 3). These three horizons are overlapped by a very dark red humiferous horizon with clay-sandy texture and weakly expressed lumpy structure.

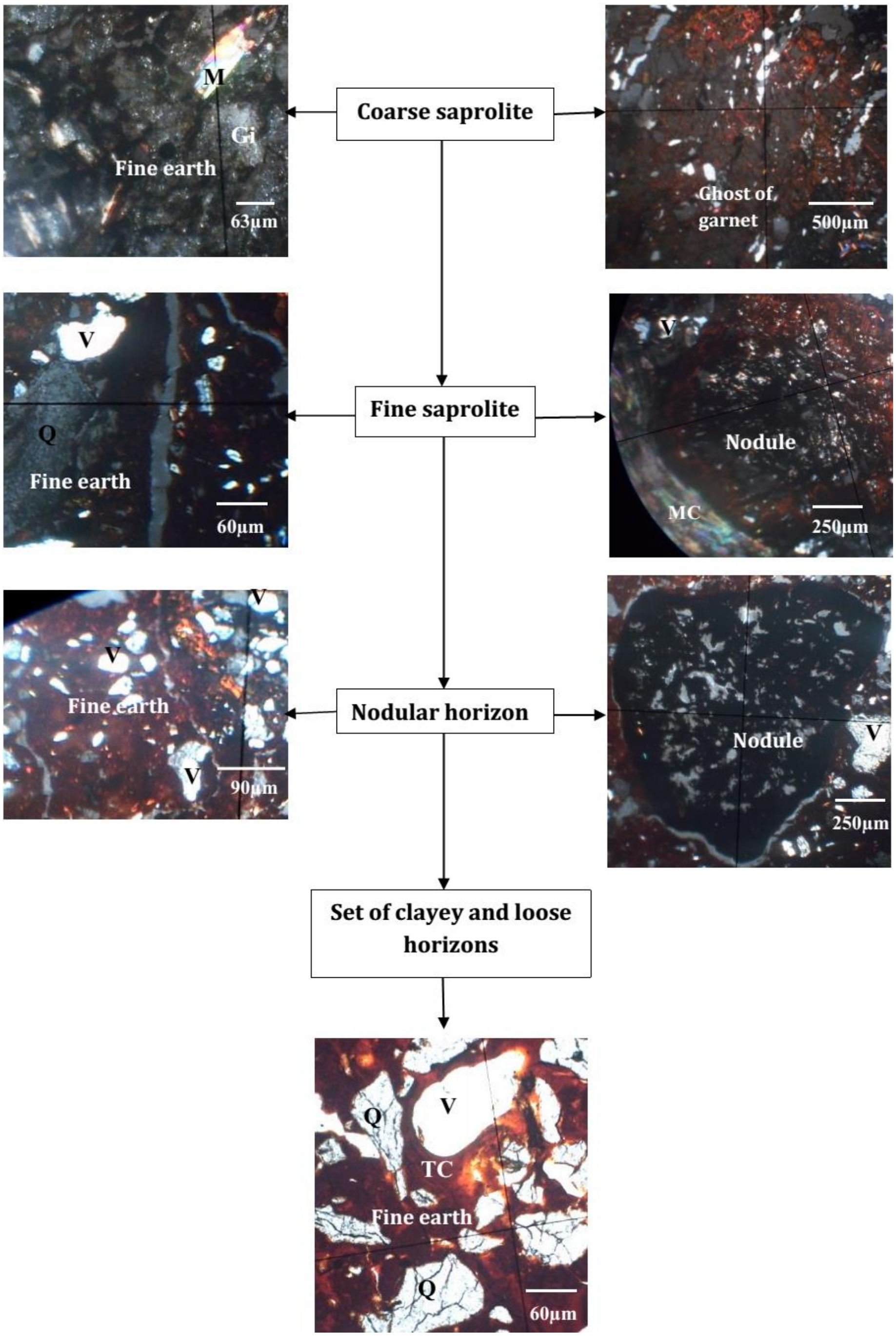

Figure 3. Microscopic observation of materials evolution in the studied profile
(Q: quartz; M: muscovite; MC: micaceous cortex ; V : void; Gi: gibbsite; TC: typic coatings).

On the other hand, there are numerous brown pink globular garnet crystals in the coarse saprolite characterized by a compartmentalized structure under the microscope, structure always noted in this mineral (Figure 3). Garnets are fractured and contain quartz and muscovite inclusions, and gibbsite crystallizations in microcraks and voids. They become slightly hardened in the fine saprolite and with a dark brown fracture and yellowish lining. This fracture shows a micaceous cortex visible under polarized microscope (Figure 3). Nodules become harder and have globally smooth and dark brown fractures, sometimes with whitish lining (Figure 3). Some fissures partially isolate those nodules from the micromass in the nodular horizon (Figure 3). They disappear progressively in the upper set.

Bulk compositions of the studied soils and bedrock

Selected major element–Al_2O_3 variation diagrams plotted on an anhydrous basis are given for each group in Figure 4. The elements plotted are the mobile species CaO, Na_2O, and K_2O, along with Fe_2O_3 (total iron as Fe_2O_3), as a representative of a less mobile element, although Fe abundances may also be influenced by sesquioxide development. Two weathering trends are noted from the bedrock to the set of clayey and loose horizons (Figure 4). In fact, there is enrichment in Al_2O_3 in the fine earth concomitantly to enrichment in Fe_2O_3, Na_2O and K_2O in nodules (Figure 4). Globally, Na_2O, K_2O, CaO and Fe_2O_3 contents exhibit very weak correlations with Al_2O_3 (Figure 4). In detail, from the coarse saprolite to the upper set of red clayey and loose horizons, these elements are well correlated in nodules, confirming the two weathering trends noted. Abundances of these elements are in most cases much upper than in "fresh" rock indicating a weak substantial loss during weathering.

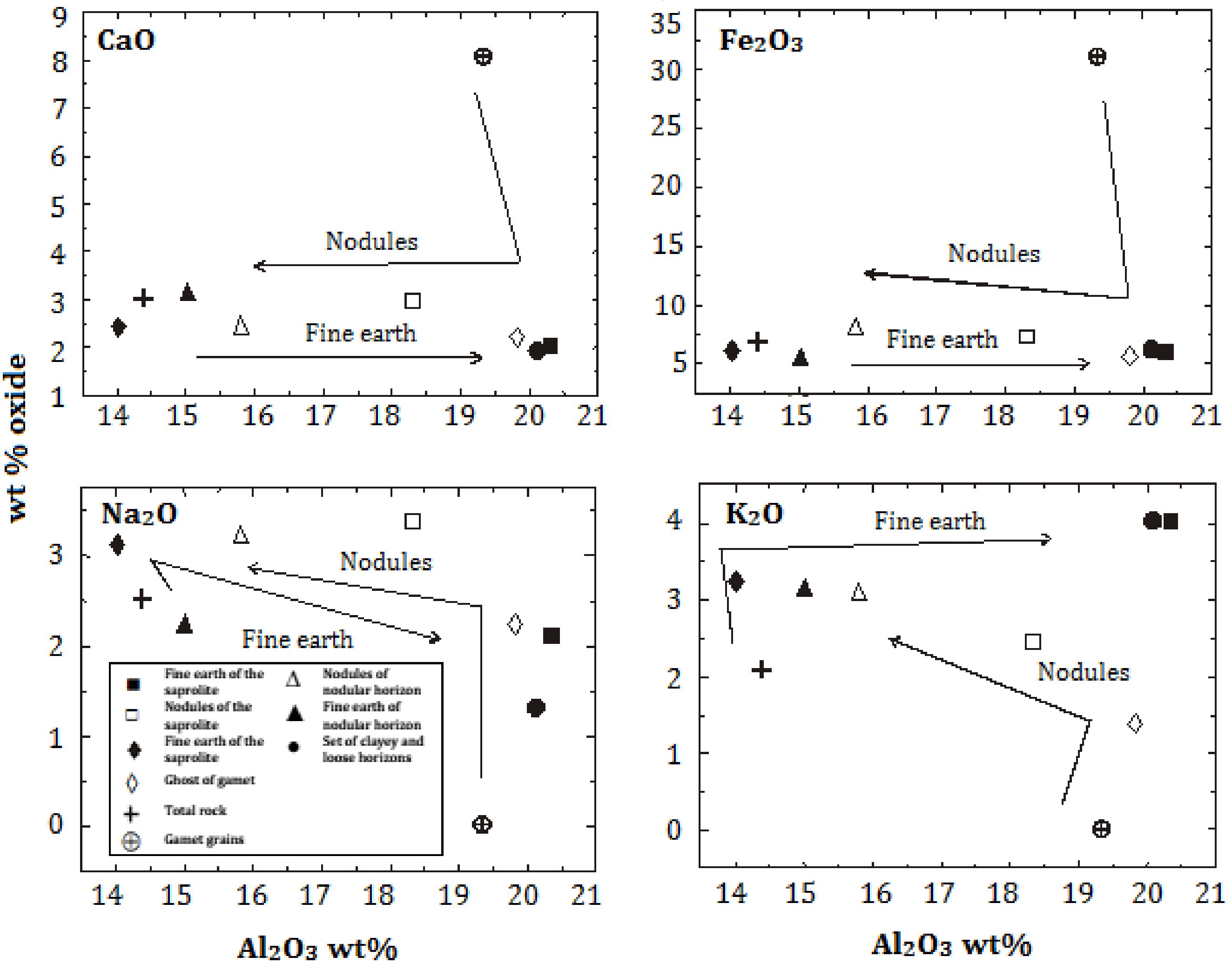

Figure 4. Major element–Al_2O_3 variation diagrams (anhydrous basis) for samples collected in the studied profile.

Evaluation of weathering trend

Degradation of feldspar and concomitant formation of clay minerals is the dominant process during chemical weathering of the upper crust. Calcium, sodium and potassium are generally removed from feldspars, increasing the proportion of alumina to alkalis in the weathered product (Nesbitt and Young, 1982).

The ternary A–CN–K system is useful for evaluating the compositions of fresh plagioclase- and K-feldspar-rich rocks and examining their weathering trends and their weathering products (clay minerals) (Nesbitt and Young, 1984, 1989; Fedo et al., 1995). The most intensely weathered samples plot in the top corner of the diagram, reflecting preponderance of Al-silicates. As plagioclase is more susceptible to weathering than K-feldspar, and hence Ca and Na are leached preferentially over K, the slopes of the trends should lie subparallel to the A–CN boundary as described in Nesbitt and Young (1989). Such trends intersect the A–K boundary once all plagioclase has been destroyed, and then trend toward the A apex because K is extracted from the residues in preference to Al (Aristizabal et al., 2005).

Rock samples and weathered samples plot globally far away from the feldspar join. They lie near the A-CN join, mostly toward the A apex, reflecting high concentrations of Al-bearing minerals (Figure 5). Two weathering trends are noted, materialized by two arrows which correspond to nodules and fine earth (Figure 5). The evolution of nodules from the garnet grain in the bedrock to the nodular horizon shows a progressively depletion in Al, opposite to that observed in the fine earth.

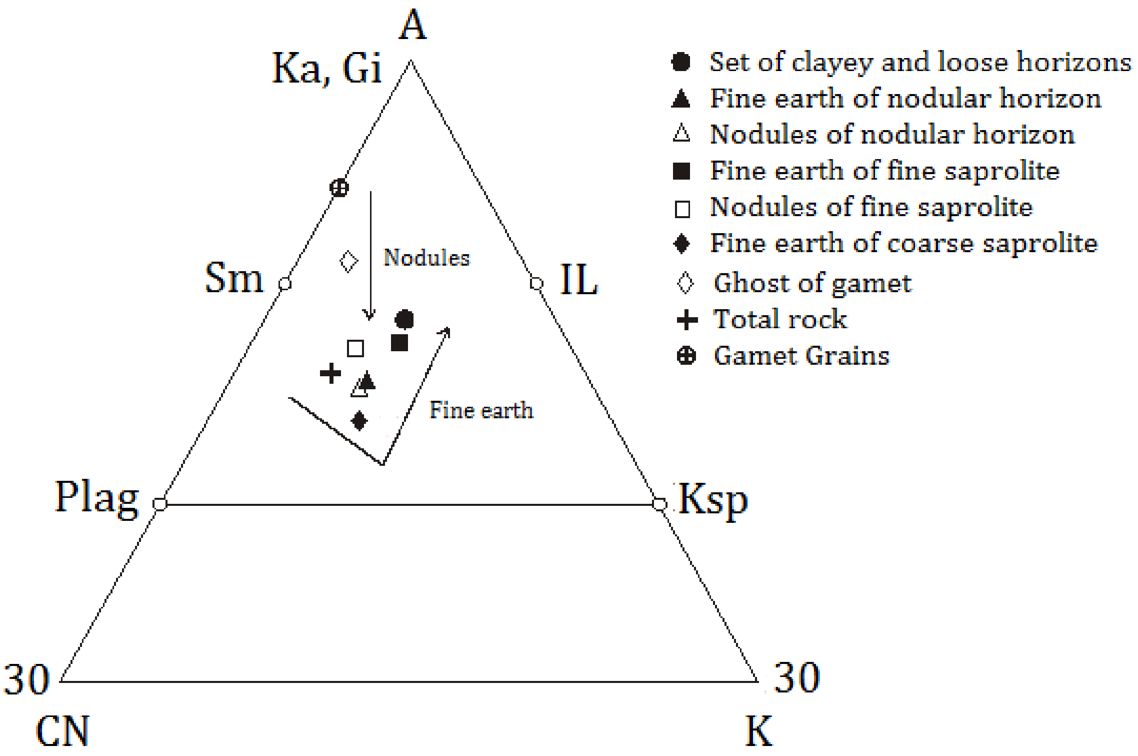

Figure 5. A–CN–K diagram illustrating the weathering trends of the studied soils.
A: Al_2O_3; K: K_2O; CN: CaO^*+Na_2O; Plag: plagioclase; Ksp : K-feldspar; Sm: smectite; IL: illite; Ka: kaolinite; Gi: gibbsite (Nesbitt and Young, 1984; 1989).

Because Mg and Fe are potentially mobile in tropical environments, it is essential to also evaluate the chemical behaviour of these minerals in the weathering profiles (Nesbitt and Young, 1989). All samples plot on the tie line between feldspar (Fel) and the FM apex, lying globally parallel to A-CNK, both for nodules and fine earth. From the coarse saprolite to the upper set of clayey and loose horizons, there is a progressive depletion of Al in nodules concomitantly to an enrichment of this element in the fine earth (Figure 6).

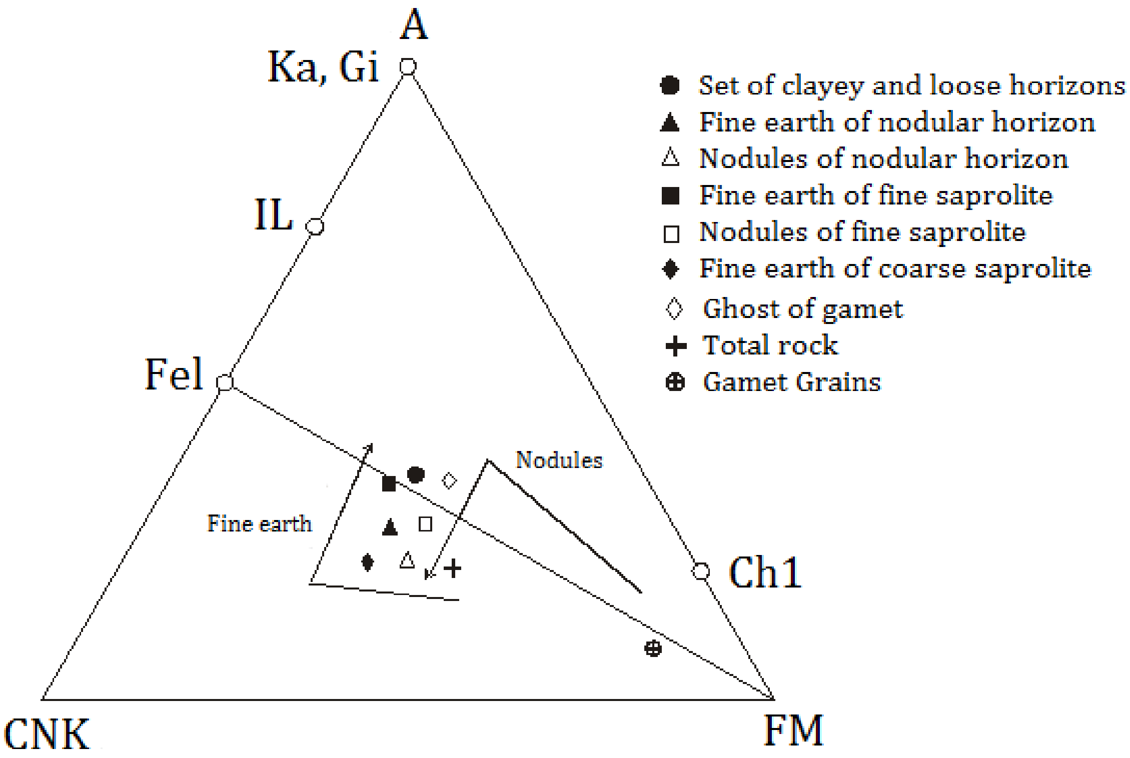

Figure 6. A-CNK-FM diagram illustrating the weathering trends of the studied soils.
A: Al_2O_3; CNK: $CaO^*+Na_2O+K_2O$; FM: FeO^*(total FeO)+MgO; Fel: feldspar; Chl: chlorite; IL: illite; Ka: kaolinite; Gi: gibbsite (Nesbitt and Young, 1989; 1996).

Evaluation of weathering intensity

Many chemical indices are commonly used to evaluate the weathering intensity. Among them, there are pH, loss on ignition (LOI), sesquioxide content (SOC), chemical index of alteration (CIA) and mineralogical index of alteration (MIA).

The chemical alteration index (CAI or CIA) is considered to be a good measure for the degree of weathering (Nesbitt and Young, 1982). Its calculation is based on molecular proportions:

$$CIA= Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)x100$$

In the equations, CaO^* is associated with the silicate fraction and corrected for inputs from carbonate and apatite (Ozaytekin and Uzun, 2012). Since Al is much more immobile than the alkali elements (Na^+ and K^+) and Ca^{2+}, changes in CIA reflect changes in the proportions of feldspar and the various clay minerals developed in the soil profiles. The CIA values are directly represented on the A-CN edge of the A-CN-K triangle (Figure 7) as the elements involving this edge are the same as needed for the calculation of CIA. High CIA values reflect the removal of labile cations relative to stable residual constituents during weathering, and low CIA values indicate the near absence of chemical alteration (Nesbitt and Young, 1982). Chemical Index Alteration (CIA) values are directly represented on the A–CN–K triangle. The CIA corresponds to the horizontal projection on a vertical scale ranging from 0 (A–CN join) to 100 (A apex), where the fresh feldspar join has a value of 50.

As indicated on figure 7, the samples can be subdivided into different weathering states according to their CIA values: residual soil, weathered/disintegrated material and rock discoloured by weathering to fresh rock. Globally, all samples are weathered (Figure 7). Around 50% of material decomposed and/or disintegrated to soil, except for garnet grains and fine earth of coarse saprolite which position in the diagram might be due to absence of K_2O and Na_2O and high Al_2O_3 contents in garnet grains and the presence of muscovite in the fine earth of coarse saprolite (Figure 7). Globally, there are disparities between fine earth and nodules. CIA values in nodules increase from the nodular horizon to the bedrock (Table 3 and Figure 7). Nodules of the nodular horizon are less weathered than other nodules and garnet grain in the bedrock in line with observations already made by Tsozué et al. (2011). They are formed in situ and are stable in this environment of the humid tropical zone.

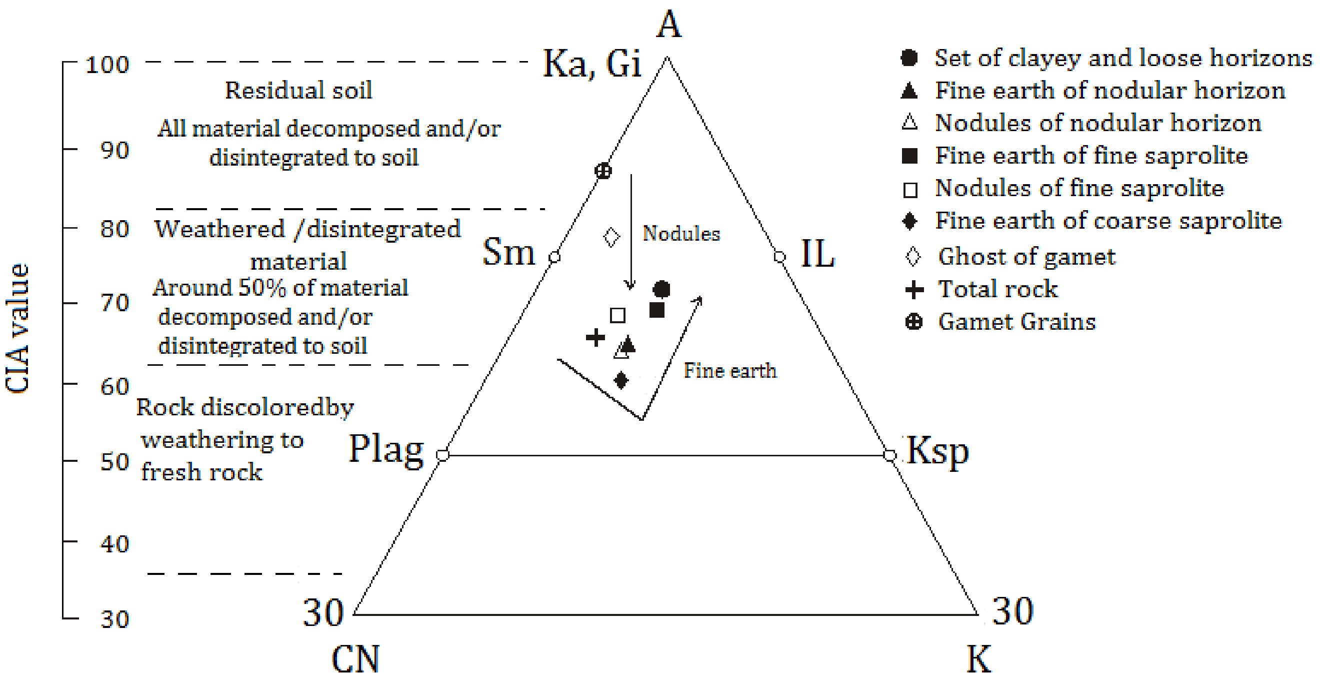

Figure 7. A-CN-K diagram illustrating weathering intensity (CIA values) of all samples collected from the studied profile. The CIA scale is divided into the simplified typical weathering profile described by the Geological Society of London in Lambe (1996).

As indicated on figure 7, the samples can be subdivided into different weathering states according to their CIA values: residual soil, weathered/disintegrated material and rock discoloured by weathering to fresh rock. Globally, all samples are weathered (Figure 7). Around 50% of material decomposed and/or disintegrated to soil, except for garnet grains and fine earth of coarse saprolite which position in the diagram might be due to absence of K_2O and Na_2O and high Al_2O_3 contents in garnet grains and the presence of muscovite in the fine earth of coarse saprolite (Figure 7). Globally, there are disparities between fine earth and nodules. CIA values in nodules increase from the nodular horizon to the bedrock (Table 3 and Figure 7). Nodules of the nodular horizon are less weathered than other nodules and garnet grain in the bedrock in line with observations already made by Tsozué et al. (2011). They are formed in situ and are stable in this environment of the humid tropical zone.

The mineralogical index of alteration MIA evaluates the degree of mineralogical weathering. It is linked to CIA by the following relation:

$$MIA=2.(CIA-50)$$ (Voicu et al., 1996).

MIA values obtained in the studied soil are between 0 and 41.34%, indicating that they are incipient (0-20%) to weak (20-40%) and slightly moderately weathered (40-60%), in line with the high presence of muscovites and micaceous cortex noted respectively in mineralogical analysis and under polarized microscope.

The sesquioxide content (SOC) reflects the Fe_2O_3 and Al_2O_3 content in a sample which are insoluble oxides (Irfan, 1996). An increase of SOC indicates either a higher intensity of leaching or oxidation resulting from the enrichment of ferric iron from the oxidation of ferrous iron (Ng et al., 2001). SOC values vary globally from 20 to 26% in the fine earth and from 23.95 to 25.65% in the nodules (Table 3). These values are highly influence by Fe_2O_3 content in the bedrock (31.16% Fe_2O_3 in the garnet grains) (Table 3). The pH of the studied samples ranged from 4.4 to 5.2, indicating the very acid nature of the environment, favourable to the mobilization of basic cations.

Sueoka et al. (1985) proposed loss on ignition (LOI) as a good indicator of the degree of chemical weathering. In general, LOI increases as the intensity of weathering increases (Aristizábal et al., 2005). LOI values vary from 2.37% in the bedrock to 18.53% in the “ghost” of garnets of the coarse saprolite (Table 3). In detail, LOI values vary from 16.55% in the nodules of the nodular horizon to 18.53% in the ghost of garnet of the coarse saprolite, and in the opposite direction, from 2.37% in bedrock to 10.70% in the set of clayey and loose horizons (Table 3). LOI is less in fine earth and the total bedrock than in nodules (Table 3). As shown in figure 8, there is a very weak correlation between CIA and LOI in all the studied samples (R^2=0.23, Figure 8A). But in detail, there is a good correlation between CIA and LOI in the bedrock and fine earth of different horizons (R^2= 0.70, Figure 8B) and in nodules from the coarse saprolite to the nodular horizon (R^2= 0.99, Figure 8C).

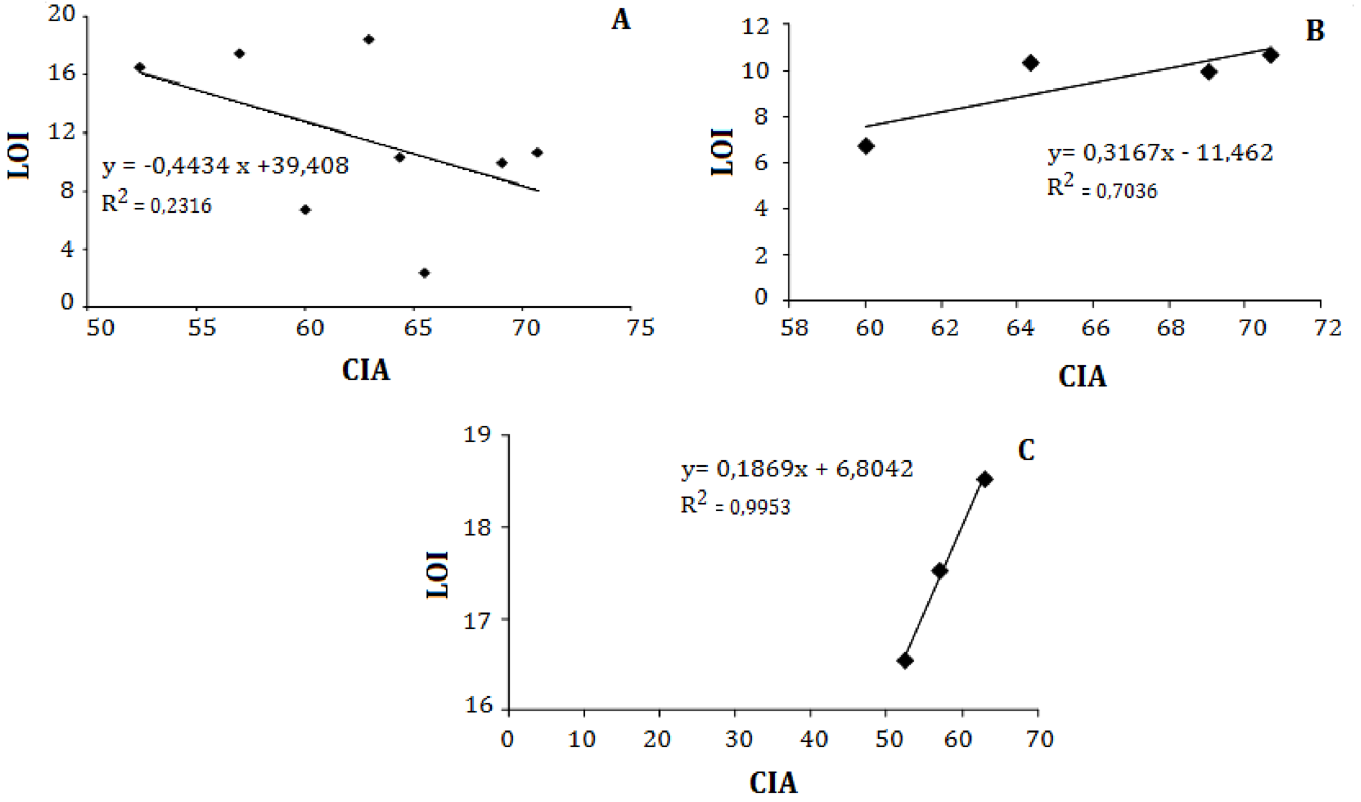

Figure 8. CIA-LOI graph
(A: whole rock and weathering products; B- fine earth of loose horizons; C: nodules of loose horizons).

Mass balance

In the fine earth, Si and Fe are depleted out of the profile. Their mobilization rates fluctuated respectively, from -43% in the fine saprolite to 24% in the coarse saprolite and from -38% in the set of clayey and loose horizons to 12% in the coarse saprolite. The mean values are -13% for Si and -14% for Fe, which correspond respectively, to a total mobilized mass of -0.812 and -0.095 g/cm^3 (Tables 4 and 5). Al, on the other hand, is imported in the fine earth of the studied profile. Its mobilization rate varies between -6% in the nodular horizon and 51% in the set of clayey and loose horizons (Table 4), thus a mean value of 18.5% corresponding to a total mobilized mass of 0.247 g/cm^3 (Table 5). This accumulation of Al in the fine earth already noted in major element–Al_2O_3 variation diagrams corresponds to an "aluminization" process.

Table 4. Bulk density and element mobilization ratios in the fine earth of the studied soils.

Db, ε, τ Horizons	da (g/cm^3)	ε -Ti	τ Si	τ Al	τ Fe
Set of clayey and loose horizons	1,5	0,79	-0,12	0,51	-0,03
Nodular horizon	0,85	1,63	-0,20	-0,06	-0,27
Fine saprolite	0,87	1,05	-0,43	0,01	-0,38
Coarse saprolite	1,4	1,25	0,24	0,23	0,12
Bedrock	2,49	0	0	0	0

Db: bulk density; ε -Ti: deformation ratio at Ti constant; τ: relative enrichment ratio of an element in comparison with the bedrock.

Table 5. Mobilized mass (m) of elements in the fine earth of the studied soils (g/cm^3).

Elements Horizons	mSi	mAl	mFe
Set of clayey and loose horizons	-0,191	0,183	-0,005
Nodular horizon	-0,319	-0,022	-0,046
Fine saprolite	-0,685	0,004	-0,065
Coarse saprolite	0,383	0,082	0,021
Sum	-0,812	0,247	-0,095

In the nodules, all the three elements are depleted out of the profile. Their mobilization rates vary from -30 to 17% for Si, -38 to -13% for Al and -13 to 57% for Fe (Table 6), thus mean values of -6.50% for Si, -25.5% for Al and 22% for Fe (Table 6). These correspond respectively, to a total mobilized mass of -0.253, -0.444 and 0.109 g/cm^3 (Table 7). The depletion of Al corresponds to a "desaluminization" process. The higher depletion rate of Fe is mostly from the bedrock to the coarse saprolite. Here, Fe_2O_3 contents decrease from 31.16% in the garnet of the bedrock to 5.65% in the "ghost" of garnet of the coarse saprolite (Table 3). From the coarse saprolite to the nodular horizon, this content increases from 5.65% to 8.12% (Table 3), corresponding to an accumulation rate of 22%, thus, leading to the densification and the formation of nodules with dark undifferentiated micromass of hematitic nature in their inner part in the nodular horizon (Figure 3), characteristic of a ferruginization process.

Table 6. Bulk density and element mobilization ratios in the nodules of the studied soils.

Db, ε, τ Horizons	Db (g/cm^3)	ε -Ti	τ Si	τ Al	τ Fe
Nodular horizon	2,36	1,03	0,17	-0,13	0,57
Fine saprolite	3,18	-0,07	-0,30	-0,38	-0,13
Coarse saprolite	4,39	0	0	0	0

Db: bulk density; **ε -Ti**: deformation ratio at Ti constant; **τ**: relative enrichment ratio of an element in comparison with the bedrock.

Table 7. Mobilized mass (m) of elements in the nodules of the studied soils (g/cm^3).

Elements Horizons	mSi	mAl	mFe
Nodular horizon	0,330	-0,113	0,141
Fine saprolite	-0,583	-0,331	-0,032
Sum	-0,253	-0,444	0,109

Discussion

Tropical chemical weathering in the studied soil leads to the decomposition of the entire primary mineral except muscovite and quartz, promoting the development of a very thick soil profile (>10 m) composed of kaolinite, gibbsite, aluminous goethite, hematite and traces of anatase. The first stage of garnet-rich micaschist weathering corresponds to a more or less isovolumentric process, with preservation of the overall fabric of the rock. This suggests in situ replacement of primary minerals by kaolinite and gibbsite, confirmed by microscopic observations. The presence of kaolinite in the saprolite characterizes the more advanced stages of weathering, and the intensive tropical weathering is reflected in the formation of iron and aluminum sesquioxides, goethite and gibbsite (Aristizábal et al., 2005).

Garnet minerals specifically, undergo congruent dissolution, leading progressively to replacement of garnet grains by goethite-gibbsite pseudomorphs in the fine saprolite, and the formation of alteromorph nodules described by Stoops (2003). These alteromorph nodules are characterized by the total absence of relicts of original garnet grains, the presence of ferruginous yellowish brown and very birefringent intragranular fracture coatings, essentially of goethite nature, and the maintenance of discontinuous "micaceous cortex" which marks the original flow structures of the original bedrock. Nodules observed in fine saprolite show no etch pits and their surfaces are regular, evidence of well preservation in this environment of the rainforest zone of Southern Cameroon. Ultimately, in the nodular horizon, nodules are pseudomorphosed completely by iron oxides, with however a presence of gibbsite. They show a dark undifferentiated micromass of haematitic nature in their inner part, and globally, there is a development of fissures which partially isolate those nodules from the micromass. This evolution of nodules from the coarse saprolite to the nodular horizon is concomitant to a high depletion of Al_2O_3 and an increase in Fe_2O_3 contents from the coarse saprolite to nodular horizon, meaning that conditions are favourable to the stabilisation of iron oxides, corresponding to the ferruginization process already described by Beauvais and Collin (1993). This stabilisation and accumulation of iron under acid environment was also reported by Marquez et al. (2004) in Brazilian Cerrado soils. This ferruginization process might be due to accumulation of hematite in the small pores in a pre-existing kaolinite accumulation (Tardy and Nahon, 1985; Beauvais, 1999), resulting from a decrease of water activity and of atmospheric relative humidity, and from a temperature increase (Tardy et al., 1991). The formation of nodules obtained here is similar to that of the “first generation nodules” studied by Yongue-Fouateu (1986) in the soil profile of Ekoumdoum developed on garnet-rich migmatitic gneiss in the Yaoundé region, situated at 740 m a.s.l. The author noted the disappearance of gibbsite and the increase of iron contents in the lithorelictual intragranular groundmass of garnet pseudomorphs. The stability of garnet pseudomorph and their individualization in the form of nodules was also reported by Embrechts and Stoops (1982) in Cameroon (Yaoundé) and Parisot et al. (1983) in Brazil. The formation process of the studied nodules is fundamentally different from that of the “second generation nodules” frequently studied by authors in the humid tropical zone, which derive from the degradation of iron duricrust (Beauvais and colin, 1993; Beauvais and Tardy, 1993; Beauvais, 2009; Tsozué et al., 2012). Contrary to the studied soils, the two generations of nodules are present in the Ekoumdoum soil profile, developed on garnet-rich migmatitic gneiss (Figure 9). However, “second generation” nodules are more frequent in humid tropical zone (Tardy, 1993; Beauvais and colin, 1993; Beauvais and Tardy, 1993; Temgoua et al., 2002; Bitom et al., 2004; Beauvais, 2009; Tsozué et al., 2012).

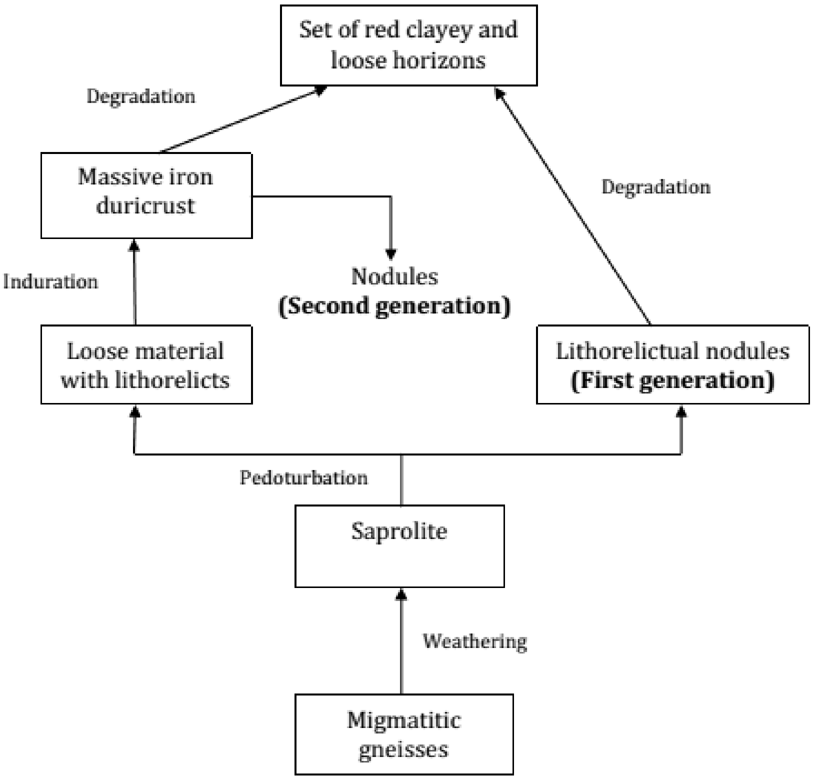

Figure 9. Filiations in the soil profile of Ekoumdoum (Yongue-Fouateu, 1986).

Beside the garnet grain, other primary minerals exhibit an opposite evolution. Intensive tropical weathering leads to their complete decomposition into fine earth. The evolution of the groundmass of this fine earth from the saprolite to the set of clayey and loose horizons is mainly structural, through the reorganization of the reddish clayey ferruginous micromass (Yongue-Fouateu, 1986). In relation with this reorganization, the porosity increase, giving rise to clayey ferruginous typic coating deposit noted in the upper part of the set of clayey and loose horizons. The set of red clayey and loose horizons observed here on top of the nodular horizon might derive from the generalization of the internodular red clayey matrix, in addition to the fine earth generated by the degradation of nodules. The fine earth is composed of kaolinite, gibbsite, goethite, hematite, anatase, muscovite and quartz. The formation of kaolinite may derive from the late weathering of micas if the water activity in matrix pores is ≤0.9 (Beauvais, 2009), but hematite could remain stable (Trolard and Tardy, 1987). Both micas and kaolinite may however transform into gibbsite if the water activity is > 0.9 (Tardy, 1993), and the hematite is dissolved and partly transformed into goethite at the base of the studied profile (Trolard and Tardy, 1987). Globally, there is Al_2O_3 enrichment in the fine earth concomitantly to Fe_2O_3 depletion. In fact, within the studied profile, biological activity might provide more reducing conditions (Beauvais and Tardy, 1993; Beauvais, 2009). At the upper part of the profiles, within the humic layer, the weathering solutions are loaded with reducing anions such as SO_4^{2-}, NO_3^{-}, PO_4^{3-} and Cl^{-}, which decrease Eh and pH and thus lead to iron leaching (Beauvais and Tardy, 1993), and consequently to a progressive accumulation of Al_2O_3 in the fine earth.

Three pedogenetic processes emerge from the evolution of weathering products derived from the studied garnet-rich micaschist. There is a ferruginization process whose intensity increases from the coarse saprolite to the upper set of clayey and loose horizons, giving rise to the formation of dense nodules with dark undifferentiated micromass, composed of hematite, goethite and gibbsite. This ferruginization occurs concomitantly to a desaluminization process, which cause a high depletion of Al_2O_3 in nodules, with a mobilization mass of -0.444 g/cm^3. These nodules are formed by the process of induration in which the hydrated amorphous hydroxide and oxides are dehydrated to their crystalline oxide form, due to condensation, leading thus to the development of stable inert aggregate units in the soil, containing hematite and gibbsite minerals (Sherman et al., 1969). In addition, there is an aluminization process, which occurs in the fine earth, leading to the development of a red clayey material constituted of kaolinite and gibbsite. These processes which occurs in opposite direction, materialized by two trends in major element-Al_2O_3, A–CN–K and A–CNK–FM diagrams, operate continuously under acidic conditions in the humid tropical rainforest of Southern Cameroon. The acidic conditions are maintained perhaps by high organic activity (Jayant et al., 2007), leading thus to the development and the differentiation of the studied soils.

Conclusion

The main objective of this study was to investigate weathering trends and weathering intensity, chemical behavior of major elements and improve the understanding of the different weathering processes occurring during the decomposition and/or the transformation of the garnet-rich micaschist in Southern Cameroon. Morphologically, two weathering materials constituted the studied profile. They are fine earth and nodules. Each material has a singular evolution from the coarse saprolite to the upper set of clayey and loose horizons. Around 50% of material decomposed and/or disintegrated to soil, except for garnet grains and fine earth of coarse saprolite which might be due to absence of K_2O and Na_2O and high Al_2O_3 contents in garnet grains and the presence of muscovite in the fine earth of coarse saprolite. CIA values in nodules increase from the nodular horizon to the bedrock. Nodules of the nodular horizon are less weathered than other nodules and garnet grain in the bedrock. SOC values vary globally from 20 to 26% in the fine earth and from 23.95 to 25.65% in the nodules. The pH of the studied samples ranged from 4.4 to 5.2, indicating the very acid nature of the environment, favourable to the mobilization of basic cations. LOI values vary from 2.37% in the bedrock to 18.53% in the “ghost” of garnets of the coarse saprolite. In detail, LOI values vary from 16.55% in the nodules of the nodular horizon to 18.53% in the ghost of garnet of the coarse saprolite, and in the opposite direction, from 2.37% in bedrock to 10.70% in the set of clayey and loose horizons, in the fine earth. The evolution of nodules from the coarse saprolite to the nodular horizon is concomitantly to a high Al_2O_3 depletion and an increase in Fe_2O_3 contents from the coarse saprolite to nodular horizon, characteristic of desaluminization process. This process occurs together with ferruginization process, giving rise to the formation of nodules with dark haematitic undifferentiated micromass in the nodular horizon. On the other hand, there is an aluminization process which occurs in the fine earth, leading to the development of a red clayey material constituted of kaolinite and gibbsite. These three processes occur together, leading to the weathering of the garnet-rich micaschist and the development and the differentiation of the studied soils.

Acknowledgements

The authors thank Dr Azinwi Tamful Primus for his critical comments and suggestions on this paper. We are also glad for the comments and suggestions of the anonymous referees who have substantially improved the quality of this paper.

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Eurasian J Soil Sci 2017, 6 (1) 20 - 27

Eurasian Journal of Soil Science

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

Fractal approach in characterization of spatial pattern of soil properties

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Abstract

The objective of the study was to characterize spatial pattern of soil properties ($CaCO_3$, soil organic carbon, P_2O_5, K_2O, and clay content) using fractal concept. Total of 141 top-soil samples (0-30 cm) were collected on 1850 ha in karst polje (Petrovo polje, Croatia) and analyzed for listed soil properties. The semi-variogram method was used to estimate fractal dimension (D) value which was performed from both of isotropic and anisotropic perspective. The D value of soil properties ranged between 1.76 to 1.97, showing a domination of the short-range variations. The SOC and K_2O fractal D values 1.79 and 1.76 respectively, exhibited a spatial continuity at the entire analysed range of the scale. The D value for P_2O_5 (1.97) showed a nearly total absence of the spatial structure at all scales. The $CaCO_3$ and clay content indicated a multifractal behavior mainly attributed to effects of alluviation, differences in geology and its spatial changes and transitions. The results of anisotropic analysis of soil properties pattern have showed strong relations with directions and partial self-similarity over limited ranges of scales defined by scale-break. Finally, our results showed that fractal analysis can be used as a appropriate tool for the characterization of spatial pattern irregularities of soil properties and detection of soil forming factors that cause it.

Keywords: Fractal dimension, scale independency, self-similarity, semi-variogram.

Article Info

Received : 16.03.2016
Accepted : 23.05.2016

Introduction

Spatial distribution of soil properties is strongly connected to soil forming factors and processes which operate over different spatial (and temporal) scales (Beckett and Webster 1971; Burrough, 1983a). The scale dependent nature of measurements and natural processes has been observed by many researchers (Burrough, 1981; Burrough, 1983a; Klinkenberg, 1992; Mark and Aronson, 1984; Peitgen and Saupe, 1988). Since the measurements are scale dependent the problem arises when representing the properties at the scale different from the one at which the measurements are made.

Fractal theory offers the possibility of analysing and quantifying soil variability measurements at different spatial scales. The term „fractal" was introduced by Mandelbrot (1967), as a infinitely complex patterns that are self-similar across all spatial scales. Fractal (Hausdorff-Besicovitch) dimension (D) is generally a measurement of the irregularity of the object and a statistical indicator of the complexity of the fractal pattern that compares how the detail changes with scale. In fractal theory the concept of self-similarity means that fractal dimension (D) is a constant parameter at all scales implying that the form or pattern of the spatial phenomenon remains unchanged throughout all scales.

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284260

Numerous empirical studies have shown that this kind of true or mathematical fractals with strict self-similarity do not exist. Burrough (1981) has shown that many environmental variables are fractals and that the D values would be useful for separating scales of variation. The consequence is a variation of fractal dimension constant present only within specific ranges of scales. For this reason, natural features often show fractal self-similarity in many scales and a distinct fractal dimension for an each particular scale. Rather than using D in the strict sense Burrough (1981) suggested that Mandelbrot's D value can be used as an useful indicator of variation over many scales for natural phenomena. This phenomena (Burrough, 1983a; Klinkenberg and Goodchild, 1992) can be explained by a large number of various natural independent processes operating at own discrete scales separated by distinct scale breaks. Fractal dimension of landforms and linear natural phenomena are typically in the range of 1.1-1.3 (Mandelbrot, 1977), indicating domination of large-scale factors.

The fractal dimension (D) of a curve is a continuous function with range 1 to 2. D=1 implies a continous curve, while D=2 signifies a curve so „noisy" and complex that it effectively takes up the whole of a two-dimensional space. Large *D* values (close to 2) indicate the importance of short-range variation, while small *D* values reflect the importance of long-range variation (Burrough, 1981; Burrough, 1983a). Fractal dimensions of soils usually have a much higher proportion of short-range variation then other environmental variables (Burrough, 1981; Culling and Datko, 1987; Burrough, 1983a; Burrough, 1984). Fractal D values of soil properties almost always exceed 1.5, and many are greater than 1.8 (Burrough, 1981), suggesting that short-range effects prevail over long-range ones.

Many researchers (e.g. Burrough, 1981; Burrough, 1983a; Burrough, 1983b; Armstrong, 1986; Culling, 1986; Anderson et al., 1998; Bartoli et al, 1995) used fractal dimension (D) as a measure of relative ratio between short-range and long-range sources of variation.

In this study we calculated fractal dimension (D) for analysed soil properties for maximum point-pair distances and for linear portion of experimental log–log variogram defined with scale break. The objectives of the study were to establish fractal dimensions of the next soil properties: $CaCO_3$, SOC, P_2O_5, K_2O, and clay content and characterize its spatial pattern.

Material and Methods

Study area

The study area is located in Petrovo polje in the middle Dalmatia, Croatia, centred on 43°51'05" N; 16°12'45" W (Figure 1). The climate of the researched location belongs to Mediterranean temperate humid climate with hot summer. Hydrology of this typical karst polje is characterized by excessive wetting and occasional flooding in wet period of the year and water deficit in hot season. Petrovo polje is a large flat depression with a slope 0-2º (slopes <0.5° prevail), and intersected by the Čikola river and its tributary torrent Mahnitaš. Alluvial sediments cover most of the area (Ivanović et al., 1972), with occasional interbeds of Permian volcanic rocks (spilite and diabase) and Permian/Triassic clastic sediments (sandstones and breccias). The variety of soil forming factors and processes and their complex interactions resulted in a great diversity of soil types in Petrovo polje (Miloš, 1987). Investigated soils are identified as Calcaric Gleyic Fluvisols (Loamic) and Mollic Eutric Gleysols (Clayic, Humic, Vertic), (IUSS Working Group WRB, 2014). Study area is dominated by complex cultivation patterns (ploughed land, meadows and pastures) and vineyards.

Soil data set and laboratory analyses

Total of 141 top-soil samples (0-30 cm) were collected on the area of 1850 ha using grid sampling scheme with distance of 350 m. Soil samples were analysed by following methods: SOC content (Kotzman method, JDPZa, 1966), total carbonates content (Scheibler method, JDPZa, 1966), available phosphorus and potassium content (AL method, JDPZa, 1966) and soil particle size distribution (International B pipette method, JDPZb, 1966).

Measurement of fractal dimension

The variogram method was used in the estimation of fractal dimension (*D*). The semivariance is defined by equation:

$$\gamma\,(\mathrm{h}) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} (z_{x+h} - z_x)^2$$

where, h is the lag distance (distance between succesive points), γ (h) is the semivariance at lag distance „h“, $Z_{(x)}$ and $Z_{(x+h)}$ – values of the variable at location x_i and x_{i+h}, respectively and $N(h)$ is the number of pairs considered.

Fractal distributions are characterized by a variogram model of the following form:

$$2\gamma_h = h^\beta$$

where, D = 2 - β/2 (Hausdorff-Besicovitch statistic – fractal dimension, β = 4-2D (the slope of the log-log plot variogram).

Fractal dimensions were calculated for the isotropic and anisotropic perspectives for four main directions of h (0°: N–S, 45°: NE–SW, 90°: E–W and 135°: SE–NW) which were set with an angular tolerance of 22.5°.

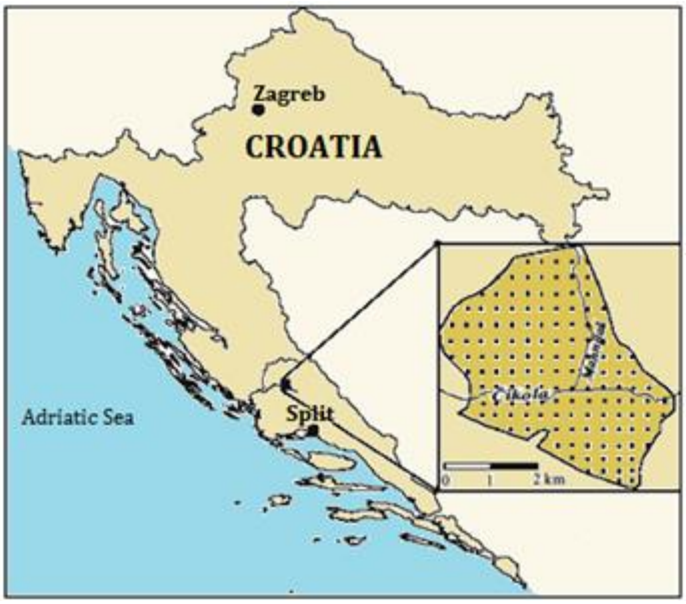

Figure 1. Location of the study area and sampling points

Determination of scale breaks

The fractal dimension was estimated from a slope of log-log variogram. The changes of the slope are continuously from one linear segment to another. When break in the slope of the double log variogram plot was observed the break distance or scale-break was determined, as the distance within which the log-log variogram can be fitted by a line provided that the coefficient of determination as a goodness-of-fit measure $R^2>0.90$ (Klinkenberg, 1992). The next requirement for determining the break distance was minimum of 100 point pairs at a distance with goodness-of-fit measure $R^2>0.90$. The additional fractal parameter was gamma (γ) defined as the intercept of the best-fitting line with the ordinate (Klinkenberg and Goodchild, 1992).

Results and Discussion

Descriptive statistics of the soil properties

Statistical parameters of the top-soil horizon attributes of Petrovo polje are given in Table 1. The $CaCO_3$ content has a wide range, a high coefficient of variation (CV) and slightly right-skewed distribution with a more rounded peak near the mean with shorter thinner tails. The wide range of $CaCO_3$ is caused by great differences in geology and characteristics of alluvial deposits. Due to this soils vary from non-calcareous to strongly calcareous, in average are moderately calcareous. The top-soil SOC content varies from very low to medium, in average is low. The distribution of SOC content is asymmetrically, highly right skewed with a long tail to the right. Positive kurtosis indicates a sharper peak around the mean with longer, fatter tails. The clay content is characterized with a high mean value, wide range, low coefficient of the variation and near normal distribution. The variation of clay content is related to differences in parent material and alluviation.

The mean P_2O_5 and K_2O content show that the top-soil horizon is very low supplied with available phosphorus and sufficient with available potassium. The P_2O_5 content has high coefficient of variation and substantially right-skewed distribution with a long tail to the right and high peak around the mean with longer, fatter tails. The K_2O content has a lower coefficient of variation and considerably weaker expressed asymmetry than P_2O_5.

Table 1. Descriptive statistics for $CaCO_3$, SOC, K_2O, P_2O_5 and clay content

Property	Mean	Min.	Max.	#S.D.	&CV %	Skewness	Kurtosis
$CaCO_3$ (%)	16.66	0.00	53.30	13.74	82.5	0.45	-0.91
SOC (g C kg^{-1})	19.26	9.88	49.59	7.09	36.8	1.16	1.85
Clay <0.002 mm(%)	38.95	24.70	6.60	8.60	22.1	0.40	-0.39
K_2O mg/100g	21.10	5.50	55.60	8.99	42.6	0.94	0.84
P_2O_5 mg/100 g	2.81	0.10	10.50	2.32	82.7	1.52	1.78

#S.D., standard deviation. &CV (%), coefficient of variation (%).

Fractal parameters of the soil properties

Estimated log-log variograms of the soil properties (Figure 2 and Figure 3) are complex functions characterized with different forms. We recognized a few fractal log-log plot forms. The SOC and, in particular, K_2O log-log isotropic variogram forms show small discontinuity at origin and gradually oscillating increase with separation with distance at all scale. These variogram shapes show a spatial continuity at the entire analysed range of the scale. The high D values of 1.76 (K_2O) and 1.79 (SOC) indicate dominance of short-range effects of spatial variations (Table 2). The results of anisotropic analyses for SOC indicate a low spatial continuity (domination of irregular and largely uncorrelated variations) for all directions except N-S, which shows elements of a slight smoothly variation (Figure 2b and Table 2). This spatial structure is probably related to the alluviation and topography position which are the most obviously changing in this direction.

The results of anisotropic analyses for K_2O show how its self-simarity varies with direction (Figure 2d and Table 2). The higher R^2, lower intercept gamma (γ) and standard error (SE) and, consequently lower D value have SE-NW and E-W directions. This indicates the presence of smoothly variations of K_2O in these directions. These directions correspond to the direction of the most distinctive changes of intensity of fertilization.

The log-log isotropic variogram plot for P_2O_5 (Figure 2e) shows a great discontinuity at origin and irregular form that effectively takes up the whole of a two-dimensional topological space. This form approximated by a straight line is characterized with great intercept gamma (γ), small slope of the regression line, very high standard error and consequently a very high fractal D value (Table 2). These results show dominance of ultra short-range effects spatial variation indicating an almost totally random data and nearly absence of the spatial structure. Very high fractal D values for soil phosforus (D=2.0) and lower D for soil potassium (D=1.6) found Burrough (1981) using data from earlier soil research of Webster and Butler (1976).

Table 2. The fractal dimension (D), gamma (γ), coefficient of determination (R^2) and standard error (SE) of soil organic carbon (SOC), K_2O and P_2O_5 for isotropic and anisotropic perspective

Soil property	Statistic parameters	Isotropic		Anisotropic (All lag h)		
		All lag h	N-S	NE-SW	E-W	SE-NW
SOC C g kg^{-1}	D	1.79	1.76	1.82	1.84	1.81
	gamma (γ)	0.28	0.09	0.40	0.31	0.62
	R^2	0.92	0.91	0.53	0.68	0.84
	SE	0.138	0.14	0.43	0.32	0.22
K_2O mg/100 g	D	1.76	1.82	1.89	1.70	1.66
	gamma (γ)	0.26	0.51	1.02	-0.12	-0.31
	R^2	0.89	0.51	0.27	0.81	0.97
	SE	0.19	0.39	0.86	0.21	0.07
P_2O_5 mg/100 g	D	1.97	1.86	1.98	1.84	1.90
	gamma (γ)	0.35	1.33	0.49	-0.19	-0.16
	R^2	0.23	-0.64	0.02	0.88	0.83
	SE	0.86	0.36	3.73	0.18	0.22

The anisotropic log-log variogram shapes for P_2O_5 indicate almost totaly absence of the spatial structure in the N-S and NE-SW directions (Table 2 and Figure 2f). Contrary, P_2O_5 log-log shapes appear to be homogeneous in the E-W and SE-NW directions. It is interesting to note that P_2O_5 as well as K_2O shows the highest self-similarity in E-W and SE-NW directions in which anthropogenic impact (fertilization) is the most intense changing.

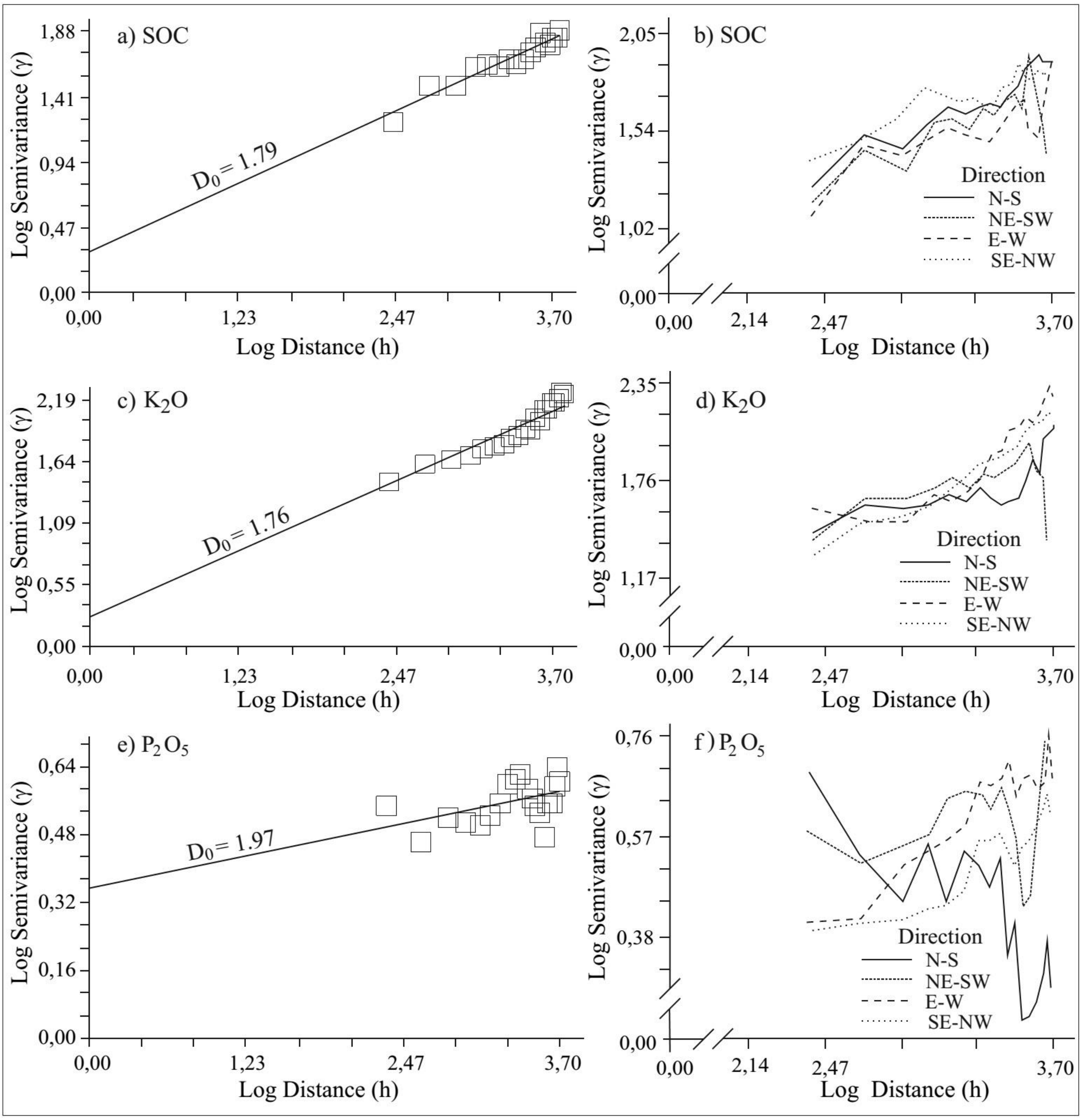

Figure 2. Log-log plot of isotropic variograms with fractal dimension (D_0) for SOC (a), K_2O (c), P_2O_5 (e); anisotropic variograms for SOC (b), K_2O (d), P_2O_5 (f) for four main directions of h (N–S, NE–SW, E–W and SE–NW)

The fractal parameters for $CaCO_3$ and clay content are performed from both an isotropic and anisotropic perspective (Figure 3 and Table 3). The double log isotropic variograms show a great discontinuity at origin, non-monotonic increase with separation and having achieved sill, then it decreases (Figure 3a and 3c). Approximation of this variogram forms with straight line resulted in a low coefficient of determination (R^2), the high associated SE and consequently high fractal D value (Table 3). Burrough (1981) has found similar high fractal dimension (D = 1.8) for top-soil silt + clay at 1 km lag distance. The soil properties often exhibit a great spatial variation at short distances. The high variability at short distance of soil properties has been reported in many studies (Becket and Webster, 1971; Webster and Butler, 1976; Burgess and Webster, 1980; McBratney and Webster, 1981; Burrough, 1983a). The high dicontinuity of the soil properties at origin and its often highly dependence on sampling directions are in accordance with previous geostatistical research of the soil variability in Petrovo polje (Miloš, 2000).

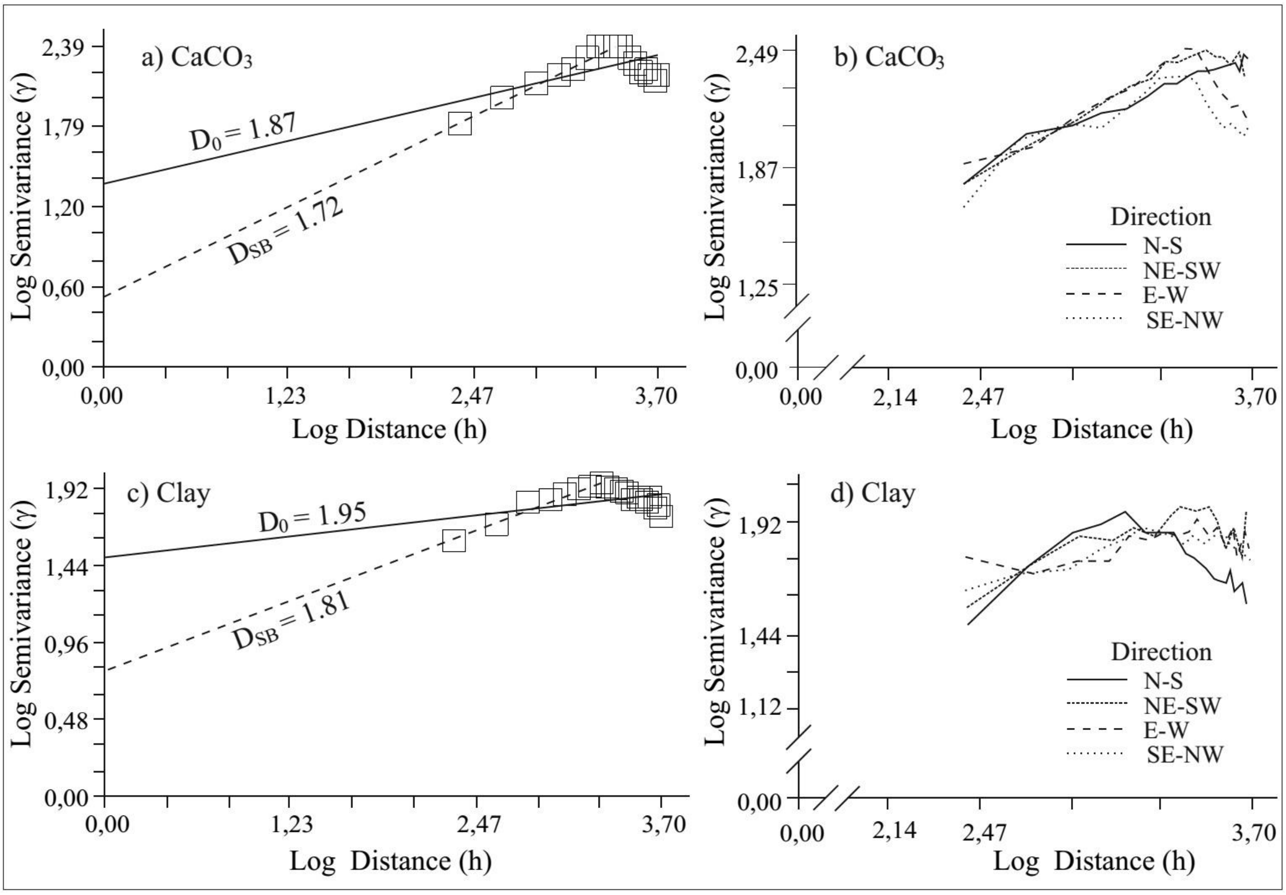

Figure 3. Log-log plot of isotropic variogram with fractal dimension (D_0) of the regression line for the all lag h; D_{SB} - fractal dimension of the first regression segment separated with the scale-break for $CaCO_3$ (a) and clay content (c); anisotropic variograms for $CaCO_3$ (b) and clay content (d) for four main directions of h (N–S, NE–SW, E–W and SE–NW)

Table 3. The fractal dimension (D), gamma (γ), coefficient of determination (R^2), standard error (SE) and scale-break (SB) for $CaCO_3$ and clay content for isotropic and anisotropic perspective

Soil property	Statistic parameters	Isotropic		Anisotropic (All lag h)			
		All lag h	Scale-break	N-S	NE-SW	E-W	SE-NW
$CaCO_3$ (%)	D	1,87	1.72	1.76	1.73	1.90	1.89
	gamma (γ)	1.36	0.53	0.59	0.54	1.53	1.42
	R^2	0.40	0.98	0.97	0.90	0.22	0.24
	SE	0.59	0.06	0.09	0.16	0.93	0.87
	SB (m)	-	3150	5250	3500	3150	2800
Clay <0.002 mm (%)	D	1,95	1.81	1.98	1.89	1.95	1.94
	gamma (γ)	1.51	0.77	1.93	1.20	1.49	1.42
	R^2	0.21	0.93	0.01	0.48	0.42	0.40
	SE	0.98	0.21	4.69	0.54	0.60	0.62
	SB (m)	-	2450	1750	2800	3500	2100

The $CaCO_3$ and clay content showed a multifractal behavior in the isotropic and anisotropic perspective characterized with hole effect and partial self-similarity over limited ranges of scales defined by scale-break (Figure 3). Over the analyzed scale of 5250 m we found a scale break at the distance of 3150 m for the $CaCO_3$ and 2450 m for the clay content for isotropic perspective. These results show that $CaCO_3$ and clay content point values are scale independent or self-similar over the scale of 3150 m and 2450 m, respectively. An estimated very high D values indicated high proportion of short-range variation and the closeness of scales of variation of factors that can cause abrupt transitions (Figure 3a and Figure 3c and Table 3). These results are consistent with research of Burrough (1981 and 1983a) and Culling (1986) who reported on the high fractal values of the individual properties of the soil.

The results of anisotropic analysis for $CaCO_3$ and clay content show strong effect of direction on the distance within which its values are spatially correlated. In the N-S direction $CaCO_3$ content is scale independent at all lag h (5250 m). Other three main directions have shorter break-distance and a higher D values (Table 3 and Figure 3b).

The anisotropic analysis of clay content shows domination of short-range variations and strong relations between directions and its spatial continuity. The double log variogram shape for N-S (Figure 3d), as well as E-W and SE-NW directions for $CaCO_3$ (Figure 3b) exhibit the hole effect indicating a multifractal behavior that is mainly attributed to effects of various soil-forming factors which operate simultaneously at different scales. Estimated fractal parameters (Table 3) indicated high proportion of short-range variations and the closeness of scales of variations of factors that can cause abrupt transitions.

The causes of high fractal D values of analysed soil properties and consequently a short-range effect are numerous. The spatial pattern of $CaCO_3$ and clay content are mainly attributed to effects of various soil-forming factors and processes, first of all, by alluviation, differences in geology and its spatial changes and transitions.

In order to compare our results to classical geostatistical approach we conducted (semi)variogram analysis. The parameters of experimental semivariograms: nugget (discontinuity at the origin), sill (structured variance), nugget/sill ratio (nugget effect), range (lag distance at which the semivariogram reaches the sill value) and fitted models were calculated for isotropic perspective (Table 4). The K_2O and SOC content are the best fitted with Gaussian and Exponential model and characterized with small nugget effects of 15.0% and 19.3%, respectively. The ranges for these models (9650 m for K_2O and 9050 m for SOC) exhibited a spatial continuity at the entire analysed scale. The experimental semivariograms for $CaCO_3$ and clay content are fitted with spherical model and characterized with shorter range than distance of the analyzed scale (5250 m). The nugget effect represents 25.6 % of the spatial variation for $CaCO_3$ and 32.3 % for clay content. The P_2O_5 semivariogram have a great nugget effect (42.5 %) and range smaller than the sampling interval. Comparison of estimated nugget effects and ranges in Table 4 shows that higher nugget effect imply shorter range.

Table 4. Geostatistical parameters of experimental semivariogram for soil properties

Soil property	Nugget (Co)	Sill (Co +C)	Nugget/sill ratio Co/(Co+C) x 100 (%)	Range (m)	Model
$CaCO_3$ (%)	48.3	188.9	25.6	2150	Spherical
SOC (g C kg^{-1})	16.5	85.35	19.3	9050	Exponential
Clay <0.002 mm (%)	23.3	72.17	32.3	1250	Spherical
K_2O, mg/100 g	37.6	250.5	15.0	9650	Gaussian
P_2O_5, mg/100 g	1.55	3.65	42.5	100	Gaussian

By comparing the results of variogram analysis and fractal approach, especially in term of range variation, we can see agreement in the fitted ranges of the experimental semivariograms and ranges defined with scale break for all selected soil properties.

Our results showed that fractal approach can provide appropriate tool for the characterization of spatial pattern irregularities of soil properties and identification of soil forming factors that drive spatial heterogeneity.

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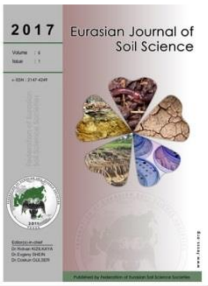
Eurasian Journal of Soil Science

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



Influence of the artisanal gold mining on soil contamination with heavy metals: A case study from Dar-Mali locality, North of Atbara, River Nile State, Sudan

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Abstract

Twenty soil samples were collected from North of Atbara (Dar-Mali locality),River Nile State, Sudan (17.82289 to 17.82389N and 33.99974 to 34.02127E) inside and outside gold mining area in order to assess the influence of the gold mining on the concentrations of selected heavy metals (Co, Cu, Fe, Mn, Ni, Pb, Zn, Hg) in study area. The soil contamination by heavy metals of study area was studied using two parameters; (i) Comparison of the heavy metals concentrations with mean concentrations in most world soils, (ii) Enrichment Factor (EF). Results revealed that the concentrations of heavy metals were varying in the study area, the highest concentrations were obtained at the center of mining area particularly inside the mining basins of gold extraction. The concentrations of Cu, Fe, Mn, Zn, Co, Ni, and Pb were ranged from (4.85 to 34.65 mg kg^{-1} soil), (6,355 to 14,635 mg kg^{-1} soil), (37.35 to 655 mg kg^{-1} soil), (11.85 to 42.7 mg kg^{-1} soil), (0 to 16.5 mg kg^{-1} soil,) (2.5 to 47.3 mg kg^{-1} soil) and (2.65 to 823.5 mg kg^{-1} soil), respectively. The results also indicated that the soil samples which collected from inside mining basins have a highest EF for most heavy metals particularly Pb, which showed EF value of (676.3), suggesting that the Pb may be derived from anthropogenic source. This study recommends regular monitoring of heavy metals in the soils around the Artisanal gold Mining for conservation and protection from pollution.

Article Info

Received : 03.03.2016
Accepted : 25.05.2016

Keywords: Sudan, River Nile State, gold mining, enrichment factor, mining basins.

Introduction

The development in the world in various fields such as industry, agriculture and other technology led to contamination the surrounding environment. The most important of these contaminants are heavy metals contamination such as lead, arsenic, cadmium, and mercury which using in extraction of gold in the most mining areas worldwide (Mandal et al., 2011).

Mining has been identified as one of the human activities which can have a negative impact on the quality of the environment (Donkor et al., 2005). It causes the destruction of natural ecosystems through removal soil and vegetation and burial beneath waste disposal sites funeral (Cooke and Johnson, 2002). Mining waste can

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284261

be divided into two categories: (i) mine tailings, generated during processing of the ore, and (ii) waste rock produced when uncovering the ore body (Ledin and Pederse, 1996).

Anthropogenic sources not only lead to increasing heavy metals concentrations in the environment, but also it can cause an unnatural enrichment, leading to metal pollution of the surface soils. The soil enriched with heavy metals can significantly cause an adverse impact on the population via inhalation, ingestion and dermal contact. The soil-accumulated heavy metals can also pose potential long-term hazards to plants and animals as well as humans that consume these plants (Singh and Kumar, 2006).

To our knowledge, in Sudan (especially at the gold mining areas), there is no research on soil contamination with heavy metals derived as a result of anthropogenic activities (gold mining activities) and its impacts. Thus, there is a need for proper assessment of heavy metals in the soils to ensure environmental sustainability. Therefore, the main objectives of the present study are to assess the influence of mining industry on the concentrations of soil heavy metals in the Dar-Mali locality, North of Atbara city, River Nile State, Sudan and to study the effect of vicinity and distance from mining zone on concentration of heavy metals in the study area.

Material and Methods

Site description and soil sampling

The study area is located at North of Atbara city, River Nile State, Sudan, with an altitude of (336-358 meters) above sea level. The study area covered about 8.0 km^{2}and it is located within coordinates of17.82289 to 17.82389 N and 33.99974 to 34.02127 E. The study area falls within the arid climatic zone (Van der Kevie, 1973). The average annual rainfall varies from 0 to 100 mm. Mean maximum temperature of the hottest months (May and June) is 43˚C. Mean minimum temperature of the coldest month (January) is less than 13˚C. The mean annual relative humidity ranges between 15 to 21% (January to February), and less than 15% (March to June). The predominant natural vegetation consists of the following species;Tundub (*Capparis decidua*), Seyal (*Acacia tortilis*), Usher, Musket (*Prosopischilensis*), Heglig (*Balanitesaegypiaca*) and Seder (*Zizyphusspina-christi*). The calculated soil temperature regime is hyperthermic and soil moisture regime is aridic. The soils of the study area belong within Entisols and Aridisols orders (Soil Survey Staff, 2014a).

Twenty soil samples were collected from three different Nile river terraces (Table 1). At each site, approximately 5kg of soil sample was collected from the depth of 0-30cm using an auger and kept in a plastic bag. The study area completely descends towards the river Nile. Highest elevation was recorded at the instructional farm for Agricultural College (358 masl) and lowest elevation recorded at recent Nile River terrace (349 m asl), which may increase the possibility of pollutants transition from mining area towards the river Nile (especially at raining season) or via wind through transition and sedimentation processes. The descriptive and geographical locations with the textural classes of samples sitesare presented in (Table 1). The soil texture ranged from sandy loam at the first terrace, silt loam at the second Instructional (Nile Valley University). By contrasting to that, the soil texture for samples at the Agricultural College farm was sand. This could be due to the fact that these soils fall in the mining area are truncated soils.

Determination of soil properties

In the laboratory, soil samples were air-dried (25± 2°C) and passed through 2 mm mesh sieve to obtain the fine earth fraction. The particles-size distribution of the soil samples was determined using particle size analyzer model (Mastersizer 2000, Malvern) and the textural class was obtained by using the USDA textural triangle according to (Soil Survey Staff, 2014b). Soil chemical properties were measured according to standard methods (Sparks et al., 1996). Soil pH was measured in 1:5 soil suspensions using a digital pH meter Jenway Model 3510 (U.S. Salinity Lab. Staff, 1954), and the results were compared according to the classification of Horneck et al. (2011). The electrical conductivity (EC dS/m at 25˚C) was determined in 1:5 soil extract using a conductivity meter Jenway (Model 4510), and the results were compared according to the classification of Rhoades (1996). Calcium carbonate percent was estimated by calcimeter. The samples were treated with 0.1N HCl; the volume of CO_2 from pure calcium carbonate and samples were recorded. The percent of calcium carbonate was then calculated according to (Horváth et al., 2005). Ion Chromatography Model (Dionex 5000) was used to determine the soluble cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and anions (F^-, Cl^-, SO_4^{2-} and PO_4^{3-}) in the extracted solutions.

Table 1. Description of the studied samplesand sites within the study area

Sample Site No.	Descriptive Locations	Geographical coordinates		Elevation (m asl)
		N	E	
1	Instructional farm (Nile Valley University)	17.82289	34.02127	356
2	Instructional farm, Nile Valley University	17.82283	34.02044	354
3	Instructional farm, Nile Valley University	17.82062	34.0203	351
4	Instructional farm, Nile Valley University	17.82044	34.02142	353
5	near wells of the instructional farm	17.82214	34.02237	358
6	Farm near mining mills	17.82503	34.01473	354
7	Outside the farm in the mining zone	17.82503	34.01473	354
8	Outside the mills in mining zone	17.82578	34.01468	356
9	Outside washing basin and the gold extraction	17.82288	34.01498	352
10	Outside washing basin and the gold extraction	17.82288	34.01498	352
11	Outside washing basin (red color)	17.82145	34.01407	351
12	Inside washing basin (red color)	17.82145	34.01407	351
13	middle of mining zone	17.82167	34.01612	357
14	Farm near mining zone	17.82483	34.00957	351
15	recent Nile River terrace	17.81779	33.99229	349
16	recent Nile River terrace	17.81779	33.99229	349
17	Inside Residential zone	17.81763	33.99478	351
18	Inside Residential zone	17.82344	33.99523	352
19	Inside Agric. College (Nile Valley Uni.)	17.82389	33.99974	356
20	Inside Agric. College (Nile Valley Uni.)	17.82389	33.99974	356

Determination of heavy metals in the soil samples

Microwave digestion oven model (CEM Mars 5) was used to digest soil samples to estimate the heavy metals, 0.5 gram of air-dried soil was used after a well-milled, and then placed in a microwave oven pipes. 10 ml of nitric acid was added to each pipe containing soil sample and well closed, then introduced into the microwave oven, and digested using (EPA-3051A) method described by (Link et al., 1998). After samples digestion, extracted samples were transferred quantitatively into 50 ml volumetric flask and the volume was completed by deionized water to the mark. All digested samples filtered using filter paper (Whatman No. 42) and then transferred to (ICP-Optima 4300 DV) in order to estimate the heavy metals (Mn, Cu, Pb, Cd, Zn, Fe, Ni, Hg).

Assessment of heavy metal pollution levels in the soil samples

In order to verify the quantity of heavy metal pollution levels in the soil samples; the enrichment factor (EF) has been applied. The EF was calculated by using the equation described by Sutherland (2000), as follows:

$$\mathrm{EF}m = \frac{\mathrm{Cm(sediment)/CFe\ (sediment)}}{\mathrm{Cm\ (earth\ crust)/CFe(earth\ crust)}}$$

Where: C_m (sediment) is the metal concentration in the sediment sample; C_{Fe} (sediment) is the concentration of the reference metal (Fe) in the sediment sample; C_m (earth crust) is the metal concentration in the earth crust; and C_{Fe} (earth crust) is the concentration of the referenced metal (Fe) in the earth crust. The EF values are classified into five categories: deficiency to minimal (EF<2), moderate (2<EF<5), significant (5<EF<20), very high (20<EF<40), and extremely high enrichment (EF>40).

Statistical analysis

The values of maximum, minimum, and means were calculated, and Tukey significant difference was tested for means separation (*P*< 0.05). All statistical analyses were performed by using statistical package for social science software SPSS Statistics version 16.0 (IBM Corp., 2012).

Results and Discussion

Physico-chemical properties of soil samples

Data in Table 2 presents maximum, minimum, and average of some physico-chemical properties of the studied soil samples.The soil reaction varied from alkaline to strongly alkaline (Horneck et al., 2011), with a pH values ranged from 7.46 to 8.8. The composite sample (Figure 1) taken from outside washing basin showed least value of soil reaction (pH 7.46). This could be due to the washing of soil bases through mining process and their later removal during gold extraction. The EC values ranged from 0.13 to 20.9 dS m^{-1}, suggesting non-saline to extremely saline conditions at the different sites (Rhoades, 1996). The content of the calcium carbonate ($CaCO_3$) varied in the soil samples from non calcareous to moderately calcareous (FAO, 2006) at different sites and the $CaCO_3$ranged from 2.58 to 10.32%. By contrast, the $CaCO_3$ was disappeared in the samples taken from inside washing basin. This could be due to possibility of $CaCO_3$ dissolution and transported inside soil depths via washing water. The texture of the studied samples at different sites is dominantly by sand fraction and ranged from 5.61 to 87.99 %.

Table 2. Some physico-chemical soil properties

Sampling sites		Characteristics						
		pH	EC (dSm^{-1})	$CaCO_3$ %	Sand %	Silt %	Clay %	Textural Class
Instructional farm (Nile Valley University)	Max	8.73	4.57	7.4	52.57	61.14	6.66	SL
	Min	7.86	0.15	2.75	32.61	41.57	5.49	SL
	Average	8.26	1.06	4.78	39.44	54.61	5.95	SL
Agricultural College (Nile Valley University)	Max	8.8	0.57	3.44	87.99	12.13	1.75	S
	Min	8.35	0.46	2.58	86.12	11.78	0.23	S
	Average	8.58	0.51	3.01	87.06	11.96	0.99	S
Inside Residential zone	Max	8.8	4.64	4.64	58.07	37.78	12.0	SL
	Min	8.15	2.58	2.58	56.0	32.0	4.16	SL
	Average	8.48	3.61	3.61	57.04	34.89	8.08	SL
Mining zone	Max	8.68	0.19	10.32	86.79	49.96	64.33	S
	Min	8.19	0.09	3.44	7.32	13.24	5.74	S
	Average	8.48	0.13	5.59	52.38	30.87	20.95	S
Recent Nile River terrace	Max	8.42	0.25	5.5	48.38	62.98	31.41	SCL
	Min	8.01	0.23	4.47	5.61	47.77	3.85	SCL
	Average	8.22	0.24	4.98	26.99	55.38	17.63	SCL
Outside washing basin	Max	8.76	20.9	6.02	77.8	37.21	9.85	SL
	Min	7.46	0.14	2.58	57.21	20.53	1.66	SL
	Average	8.15	7.43	4.3	62.65	31.55	5.8	SL
Inside washing basin	Max	8.11	0.41	ND	81.48	18.28	0.24	S
	Min	-	-	ND	ND	ND	ND	ND
	Average	-	-	ND	ND	ND	ND	ND

ND not detectable

Soil heavy metals concentrations of the study area

Data in Table 3 present the maximum, minimum, and mean of heavy metals (Cu, Fe, Mn, Zn, Co, Ni, and Pb) concentrations (mg kg^{-1} soil) in the soils of the study area. Among all heavy metals, the concentration of Cd was detected only in one sample at inside washing basin, and Hg was not detected in all studied soil samples. Results revealed that concentrations of heavy metals were varying in the study area, and highest concentrations were obtained in the mining area particularly inside washing basin and gold extraction. The concentrations of Cu, Fe, Mn, Zn, Co, Ni, and Pb were ranged from (3.65 to 33.55 mg kg^{-1} soil), (6,355 to 14,635 mg kg^{-1} soil), (42 to 655 mg kg^{-1} soil), (11.85 to 40.85 mg kg^{-1} soil), (2.8 to 16.15 mg kg^{-1} soil), (2.5 to 44.95 mg kg^{-1} soil) and (2.65 to 823.5 mg kg^{-1} soil) respectively. Overall, the heavy metals in the study area were rated as to following sequences: Fe>Mn>Zn>Ni>Cu>Co>Pb>Cd>Hg.

Figure 1. Composite sample represents contaminated soil after extraction of gold.

Table 3. Maximum, minimum and mean concentrations of heavy metals in the soil samples of the study area

Sampling sites		Heavy metals concentrations (mg kg^{-1}soil)								
		Cu	Fe	Mn	Zn	Co	Ni	Pb	Cd	Hg
Instructional farm (Nile Valley University)	Max	18.100	10995	345.50	40.15	8.500	23.35	4.200	ND	ND
	Min	14.350	9485.0	302.25	17.10	6.300	18.15	2.650	ND	ND
	Mean	16.390	9820.0	319.35	23.95	7.350	20.63	3.360	ND	ND
Agricultural College (Nile Valley University)	Max	22.050	11885	396.10	28.65	9.100	25.00	7.050	ND	ND
	Min	11.800	8335.0	242.20	18.50	5.700	15.90	4.550	ND	ND
	Mean	16.925	10110	319.15	23.575	7.400	20.45	5.800	ND	ND
Inside Residential zone	Max	15.850	9755.0	345.10	29.15	7.100	20.65	8.250	ND	ND
	Min	15.400	8930.0	330.35	29.05	6.500	20.15	4.050	ND	ND
	Mean	15.625	9342.5	337.73	29.10	6.800	20.40	6.150	ND	ND
Mining zone	Max	31.750	9985.0	350.10	28.75	8.600	22.95	39.65	ND	ND
	Min	4.8500	6355.0	42.000	ND	ND	2.150	ND	ND	ND
	Mean	19.000	8473.0	238.11	20.85	5.200	15.33	12.46	ND	ND
Recent Nile River terrace	Max	3.6500	14635	655.00	42.70	16.50	47.30	6.150	ND	ND
	Min	32.500	14390	454.50	39.00	15.80	44.60	5.000	ND	ND
	Mean	33.550	14513	554.75	40.85	16.15	45.95	5.575	ND	ND
Outside washing basin	Max	21.650	9485.0	221.35	77.70	6.250	18.10	823.5	ND	ND
	Min	17.95	3566	37.35	18.45	-	2.5	14.4	ND	ND
	Mean	20.23	7262.00	149.37	39.07	3.88	11.78	285.00	ND	ND
Inside washing basin	Max	21.15	8135	203.65	11.85	2.8	8.45	3.55	0.521	ND
	Min	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Mean	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND not detectable

Comparison of soil heavy metals concentrations with common concentrations in most world soils

Comparing the heavy metals concentrations with most world soils concentrations (Table 4), we obtained that the Cd concentration inside washing basin (0.521 mg kg^{-1} soil) as shown in Table 3 was nearly to its maximum concentration in most world's soil (0.7 mg kg^{-1} soil), and this may increase the possibility to exceeds its maximum when using same washing basin more times. Pb concentration at outside washing basin (823.5 mg kg^{-1} soil) exceed 4 times the concentration in most world's soils, and Zn atsamesite (77mg kg^{-1} soil) exceed one half times the concentration in most world's soils. Likewise, Pb concentrations in all sites were in their concentrations limits in soil except outside washing basin (Riley et al., 1992). Similarly, the same sitealso exceeded the regulatory limits (NIDEP, 2012) and intervention value (DPR-EGASPIN, 2002) which means, Pb seriously contaminates this site (Outside washing basin of gold extraction). Furthermore, according to Dutch standard same sample exceeded the target and intervention values.Cu concentration exceeds the average concentration in all studied sites. According to DPR-EGASPIN (2002) Cu concentrations exceeded the intervention value in all studied sites, except for recent Nile River terrace (Table 3) which means these soils are seriously contaminated so theyneed to be remediated in order to be suitable for sustainability for human, animals and plants life. On the other hand, Ni, Co and Mn concentrations were obtained at their average concentrations in most tested sites, except for Ni concentration in recent Nile Riverterrace site (mean of 45.95 mg kg^{-1} soil) which was exceeded the target value according to Dutch standard. Mn concentrations in recent Nile River terracesite (mean of 554.75 mg kg^{-1} soil) exceeded the average limits of worldwide. This could be due to intensive utilization of mineral fertilizers enriched in these heavy metals as impurities. Contrasting, Hg was disappeared in all samples detected by ICP despite for its intensive utilization in gold extraction (Figure 2). This could be due to its evaporation during exposed to the ICP plasma heat when its estimation. This finding in agreement with Almasoud et al. (2015).

Table 4. Heavy metals concentrations in most world soils (Lindsay, 1979).

Element	Common rang in soils (mg kg^{-1} soil)		
	Max	Min	Average
Cd	0.7	0.01	0.06
Co	40	1	8
Cu	100	2	30
Fe	55000	7000	38000
Mn	3000	20	600
Ni	500	5	40
Pb	200	2	10
Zn	300	10	50

Figure 2. Utilization of Hg in gold extraction processes in the mining area.

Use of Enrichment factor (EF) to assess the soil contamination in the study area

The EF is appropriate measure of geochemical trends and is applied for contemplating on lithogenic or anthropogenic origin of heavy metals (Sutherland, 2000; Ye et al., 2011). The results of EF values for different heavy metals in the study area are presented in Table 5. Results revealed that EF for cobalt (Co) according to (Sutherland, 2000) was in its minimum limit for all sites; except recent Nile terrace site was in medium concentrations with EF of 2.35 and 2.21 respectively. EF for Cu showed medium concentrations in mining zone sites, outside and inside washing basin (3.3, 4.98 and 2.13, respectively). In contrast, EF for Mn and Ni were obtained at the minimum limits. In addition, EF for Pb showed that Agricultural College, Residential zone, mining zone and out washing basin sites were polluted. Nevertheless, EF value was least in sites 17 and 19. This could be due to transition of pollutants via wind (northeast) from mining area to nearest areas especially southwest areas at same wind direction (Figure 3). Contrary to all studied sites, site No.10 (from inside washing basin and gold extraction) showed highest EF (676.3). Reason for this may due to combustion of the fuel used in gold extraction mills in the study area. This infrared confirmed that washing basins and gold extractions were severe polluted in Pb, which may increase dramatically with frequent use. Based on our results all tested sites were polluted with Zn except for site No. 8. However, samples No. 7 (mining zone) and 11 (outside washing basin) showed highest EF values (137.36 and 6312.11 respectively), which means these sites could be described as highly concentrated with contaminated element (Zn), and this confirmed that the washing basins were severe dangerous.

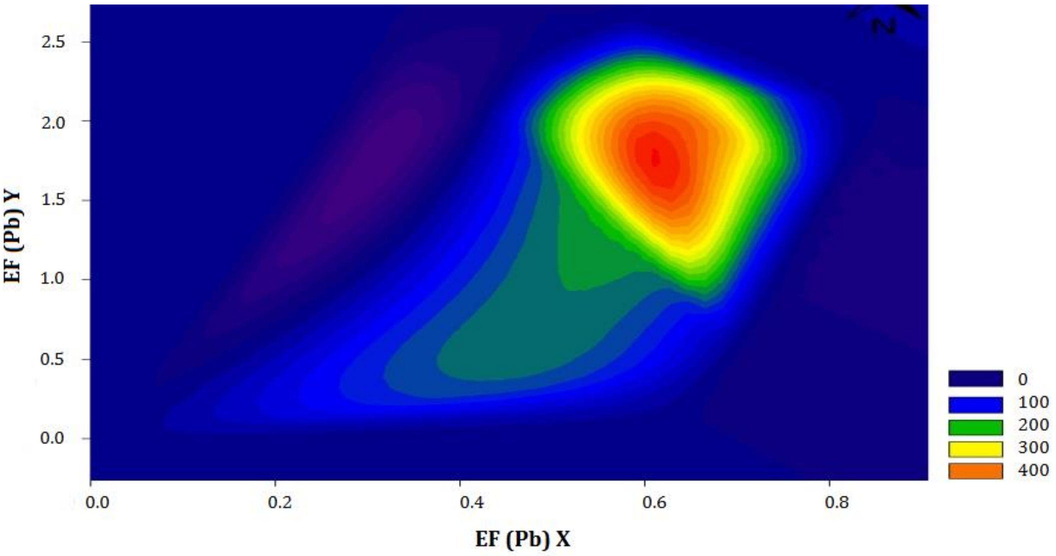

Figure 3. Distribution of Pb pollution in the study area based on EF values (red color is the center of mining area)

In order to facilitate comparison between enrichment values for various zones in our study, we selected the recent Nile River terrace site as control site due to the fact that it's receives seasonally deposits from Ethiopian Plateau and for its distance from the mining area. EF values for heavy metals more than 2 considered as major concern contaminant as suggested by some researchers (e.g. Yongming et al., 2006; Ye et al., 2011). In this context as shown in Table 5, the EF values for Co and Cu (in 90% of sites), Mn and Ni (in all sites) and Pb (in 65% of sites) were less than two, suggesting that their contaminations may be not a major concern. By contrast, the EF values for Zn (in 65% of sites) ranged from 5-20. In contrast, around 15% of sitesreached very high enrichment (20<EF<40) and 20% of sites had EF values >40 for Zn, which indicate a severe degree of Zn contamination may possible in the study area.

Table 5. Enrichment values for heavy metals in the study area

Sites	Co	Cu	Mn	Ni	Pb	Zn
1	1.70	1.45	0.13	1.17	0.94	8.81
2	1.47	1.34	0.15	1.06	0.88	8.25
3	1.51	1.30	0.13	1.03	0.95	8.83
4	1.51	1.40	0.14	1.07	1.28	11.95
5	1.46	1.36	0.16	1.05	0.96	8.93
6	1.77	1.70	0.15	1.18	2.04	19.03
7	1.14	3.30	0.14	0.90	14.72	137.36
8	0.00	0.63	0.03	0.17	ND	ND
9	1.27	1.98	0.11	0.87	5.73	53.51
10	0.00	4.98	0.05	0.36	676.30	6312.11
11	1.35	1.55	0.09	0.98	4.45	41.50
12	0.71	2.13	0.11	0.53	1.28	11.93
13	1.51	1.84	0.14	1.10	4.21	39.25
14	1.43	1.59	0.12	1.03	0.97	9.05
15	2.35	1.85	0.14	1.68	1.02	9.50
16	2.21	1.94	0.19	1.56	1.23	11.49
17	1.49	1.46	0.16	1.16	2.71	25.25
18	1.49	1.29	0.15	1.08	1.22	11.35
19	1.40	1.16	0.13	0.98	2.48	23.12
20	1.57	1.52	0.14	1.08	1.12	10.46

According to (Hernandez et al., 2003), EF≤2 indicates that the heavy metals may be as resulting from crustal materials or as product of natural weathering processes. However, EF ≥2 indicate that a major proportion of the heavy metals are mainly due to anthropogenic inputs. Therefore, the heavy metals of Co, Cu, Mn, and Ni in most sites having EF values less than 2, suggesting that these heavy metals may be as a result of crustal materials or natural weathering processes. While, the heavy metals of Pb (in 40% of sites) and Zn (in all investigated soil samples) having EF higher than 2, indicating that these heavy metals may be enriched as a result of anthropogenic inputs (especially mining activities). Overall, it was observed that the mean EF values of Co and Ni in the soil samples atthe inside washing basin and the mining zones were lower when compared tothe recent Nile River terrace (Figure 4). This may be due to the fact that the soils at recent Nile River terrace are used for agricultural purposes which mean these heavy metals were added during fertilization with trace elements as impurities. In addition, the mean EF of Zn at mining site were lower compared to the recent Nile River terrace (control zone). The same previous justificationmay occur. By contrast, the EF of Cu, Mn and Pb in all sites were higherthan those at the recent Nile River terrace (Figure 4). This suggests that the sites located far away from the Nile River and near the activities of mining may have probability to enrich soil with some heavy metals (Almasoud et al., 2015).

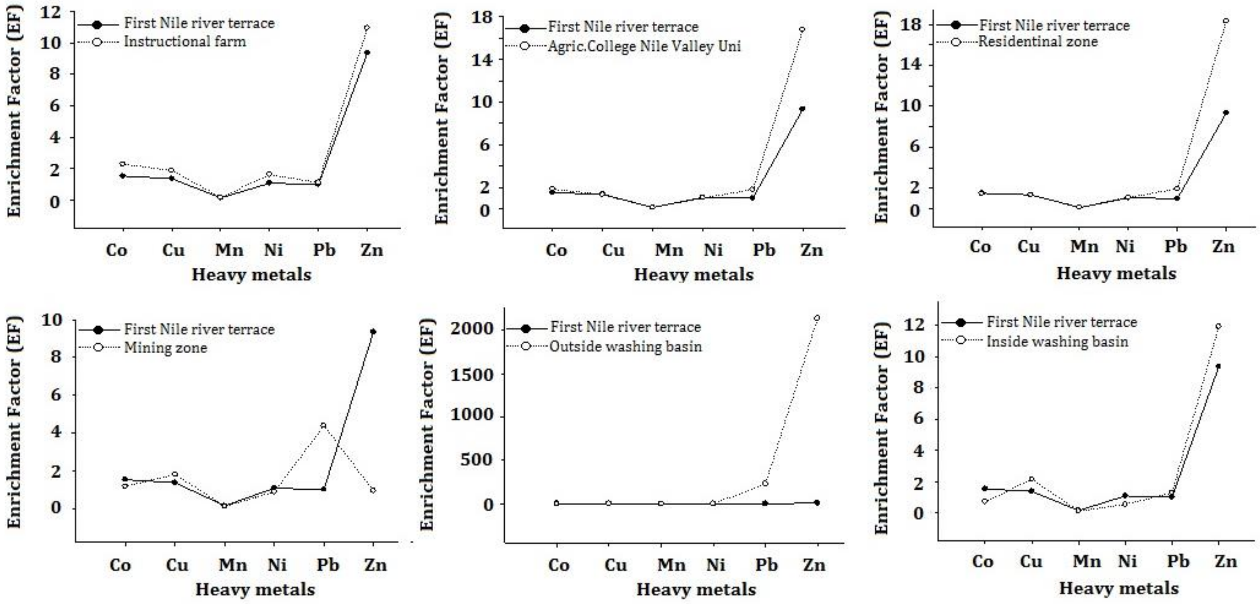

Figure 4. Enrichment values for heavy metals at different studied sites.

Conclusion

After studied the influence of artisanal gold mining on heavy metals concentration at Dar-Mali locality, we concluded that the heavy metals concentration in study area were obtained according to the following sequence; Fe>Mn>Zn>Ni>Cu>Co>Pb>Cd. In addition to that, mining zone was clearly affected by high concentration of heavy metals, particularly Pb inside mining basins; indicate that the latter was more prevalent in study area with wind direction. Applying of EF indicated that, cobalt (Co) was in its minimum limit in most studied sites; Cu showed medium concentrations in mining zone sites, outside and inside washing basin, Mn and Ni were obtained at the minimum limits, and Pb showed that Agric. College, Residential zone, mining zone, and out washing basin sites were polluted.

Acknowledgements

The authors are greatly indebted to dean of Agriculture College and general manager of Educational Farm - Nile Valley University, and Special thanks to the head of soil sciences department, King Saud University, Riyadh, Saudi Arabia, for availing their laboratories facilities and for their technical advice.

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Eurasian Journal of Soil Science

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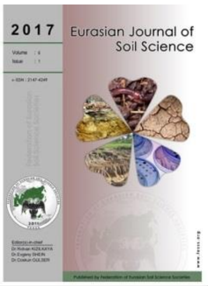

Enzyme activity of Chromic Luvisols under different degree of erosion and land use

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Abstract

Soil erosion is a serious environmental problem and a threat to the sustainable agriculture production. Little information is available on enzyme activities of eroded soils in Bulgaria, especially on their relations to the degree of erosion and soil properties. In this work, slightly, moderately and severely eroded Chromic Luvisols under different land use (pasture, crop field and virgin) were studied. Enzyme activities (invertase, catalase and phosphatase), total nitrogen, total carbon, available phosphorus contents and soil particle distribution were determined and possible relations between them were examined. Data showed that enzyme activities tended to lower with increasing the degree of erosion. This was better pronounced for invertase and phosphatase in pasture and virgin soils. Depending on land use, all enzyme activities decreased in the order pasture > virgin > crop field soils, showing positive impact of soil cover and negative effect of cultivation practices. Soil invertase and phosphatase activities were in close relations with soil carbon content. The activities of catalase and phosphatase correlated positively with soil clay. Invertase only was in positive relation with soil silt and in negative relation with the sand content. Data obtained are intended to contribute to development of biological indicators of eroded soils.

Article Info

Received : 14.03.2016
Accepted : 06.06.2016

Keywords: Enzymes, eroded soils, degree of erosion, land use, soil properties.

Introduction

Soil erosion is a threat to the environment and sustainable agriculture development. Due to loss of top soil the structure, air and water regime of soils are getting worse and nutrients are lost. As a result, the fertility and productivity of eroded soils often decline (Lal, 2006).

Soil enzymes play essential role in maintaining soil fertility. They catalyze biochemical reactions involved in organic matter decomposition, nutrient cycling and element transformation thus releasing plant available nutrients. They respond quickly and sensibly to changes in soil environment. Enzyme activities are considered in monitoring and assessing the soil status and quality. They are proposed as suitable biological indicators for evaluation of soil alterations in natural and agro-ecosystems (Trasar-Cepeda et al., 2000; Puglisi et al. 2006; Acosta-Martinez et al., 2007).

Various aspects of erosion impact on enzyme activities in soils of different type and usage had been investigated. Park et al. (2014) reported that enzyme activities tended to decrease in eroded Alpine grassland soils under intense agricultural activities (grazing and hay harvesting). Enzymes (β –glucosidase,

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284262

N–acetyl glucosamidase, phosphatase and arylsulfatase) correlated positively with soil carbon and nitrogen concentrations.

Studying soils affected by different levels of erosion, Moreno-de las Heras (2009) found that erosion had greatly influenced the processes related to soil physical and biological functionality. Significant decreasing trends in aggregate stability, microbial activity and enzyme activities (phosphatase, β -glucosidase and urease) along the erosion gradient were found. The impact of organic matter and clay content on soil structure formation and microbial and enzymatic activities was proved.

Kizilkaya et al. (2003) found significant correlation between acid phosphatase activity and soil erodibility indices in soils from Black Sea region. Yin et al. (2014) used enzyme activity as one of the indicators of re-vegetation effect on severely eroded red soil. Authors reported that re-vegetation improved soil enzyme activities compared with bare eroded soil. All enzymes studied (β –glucosidase, invertase, cellulase, acid phosphatase, polyphenoloxydase and urease) correlated with soil organic carbon and total nitrogen contents.

Information on enzyme activities of eroded soils in Bulgaria is scarce. Little is known about their relations to soil properties and the degree of erosion. The present work aimed to describe changes in enzyme activities, chemical and physical properties of Chromic Luvisols depending on the degree of erosion and land use, and to find out any relationships between them.

Material and Methods

Soil sampling

Samples from 0-20 cm soil layer of eroded Chromic Luvisols (FAO legend) located in Sofia plane (Bulgaria) were collected. Pasture soils, crop field soils under conventional agriculture and virgin soils, differing in the degree of erosion were included in this study. Sample description and numbering are shown in Table 1. Soils under different degree of erosion within each land use group and between the three groups studied were compared for enzyme activities, chemical and physical properties.

Table 1. Chromic Luvisols sample description

Land use	Sample №, degree of soil erosion, plant cover
Pasture	**1** – slightly eroded, grasses **2** –moderately eroded, grasses
Crop field; conventional agriculture	**3** – non-eroded, stubble **4** – moderately eroded, corn **5** – moderately eroded, wheat
Virgin soils	**6** – slightly eroded, meadow **7** – moderately eroded, meadow **8** – severely eroded, meadow

Enzyme activities and analyses

Three enzymes – invertase, catalase and acid phosphatase, known to participate in important biochemical processes in soil were studied. Soil invertase (EC 3.2.1.26) is involved in the carbon cycle. It plays catalytic function in the hydrolysis of sucrose – one of the most abundant plant soluble sugars. Invertase activity was determined by modified Hoffman's method (Ampova and Paskaleva, 1970) and results were expressed as μg glucose g^{-1} h^{-1}.

Catalase (EC 1.11.1.6) decomposes hydrogen peroxide formed during respiration and organic matter oxidation thus preventing cells from damage caused by molecular oxygen released. Catalase activity was determined by $KMnO_4$ titration according to Stefanic and Dumitru (1970) and data were presented as mg H_2O_2 g^{-1} h^{-1}.

Soil phosphatases (EC 3.1.3) hydrolyze organic phosphorus compounds in soil and release free phosphate ions for plant nutrition. They take part in phosphorus cycling. Phosphatases are among the most commonly studied enzymes as indicators of soil alteration (Puglisi et al., 2006). In this study we measured acid phosphatase (EC 3.1.3.2) activity using the assay of Tabatabai (1994). Results were presented as μmol p-nitrophenol g^{-1} h^{-1}.

Fresh soil samples were stored in refrigerator at 4°C. Before analyzing they were processed through 2-mm sieve and root fragments were removed. Assays were performed in triplicates.

Chemical and physical analyses

Air dried soil was sieved through 2-mm mesh and samples were analyzed for total carbon (C) (method of Tyurin (Arinushkina, 1975)), total nitrogen (N) (Kjeldahl's digestion procedure), and available phosphorus (P) (Ivanov, 1984) contents. Soil reaction (pH) was determined in 1:2.5 soil/water suspension using potentiometer. Mineral particles content - sand (1.0-0.25 mm and 0.25-0.05 mm particle size fractions), silt (0.05-0.01 mm, 0.01-0.005 mm and 0.005-0.001 mm size fractions) and clay (<0.001 mm size-fraction), was determined by wet sieving according to the method of Kachinskiy (1968).

Statistical analyses

Data were processed by ANOVA and mean values were compared by Dunkan's test at $P<0.05$. Relationships between enzyme activities and soil properties were assessed by correlation analysis.

Results

Chromic Luvisols studied were characterized by sandy loam texture, medium acid reaction and medium level of humus content. Among samples, soil properties differed depending on the degree of erosion and land use.

Enzyme activities

Within each land use group of soils, enzyme activities tended to decrease in soils subjected to higher degree of erosion. Soil invertase activity lowered in moderately eroded pasture soil, in moderately eroded crop field soil under corn and in severely eroded virgin soil. Catalase activity decreased in moderately eroded crop field soil under corn. Phosphatase activity decreased in moderately eroded pasture soil, and in moderately and severely eroded virgin soils (Figure 1).

In general, the highest enzyme activities were recorded in pasture soils, followed by virgin and crop field soils which was confirmed for the three enzymes studied.

Soil chemical properties

Total carbon and total nitrogen contents lowered with increasing the degree of soil erosion, as noticed for moderately eroded pasture and crop field soils and for moderately and severely eroded virgin soils (Figure 2). Available phosphorus content showed no changes within pasture and virgin soil groups. Among crop field soils, phosphorus lowered in moderately eroded soil under corn.

Soil pH had little variations among all samples, except the moderately eroded crop field soil under corn where pH noticeably lowered (Figure 2).

Soil texture

In moderately eroded pasture soil, silt content decreased (in 0.01-0.005mm–size and 0.05-0.01mm-size fractions), and in return sand (0.25-0.005 mm-size fraction) and clay contents increased. In moderately eroded crop field soils under wheat and under corn, silt and clay contents decreased, and in response sand content considerably increased. In moderately and severely eroded virgin soils silt content decreased (considerably in 0.01-0.005mm–size fraction), clay content slightly lowered and sand content considerably increased *(*Figure 3).

Relationships

Soil invertase activity correlated positively with soil total carbon and silt contents and negatively with soil sand (Table 2). Catalase activity correlated positively with soil clay content and with invertase and phosphatase activities, as well. Soil phosphatase was in positive correlations with soil total carbon and clay contents. Concerning all soils studied, no correlation between erosion degree and enzyme activities was found (Table 2). In particular, phosphatase correlated negatively with the degree of erosion ($r= -0.847$) in virgin soils group.

Table 2. Correlation coefficients (r) between enzyme activities and properties of the Chromic Luvisols studied

Soil properties	Invertase	Catalase	Phosphatase
pH	0.668	0.502	0.156
C	0.713*	0.549	0.726*
N	0.556	0.410	0.670
P	0.388	0.546	0.152
Sand (1.0-0.25 mm)	-0.830*	-0.663	-0.538
Sand (0.25-0.05 mm)	-0.524	-0.111	-0.212
Silt (0.05-0.01 mm)	0.766*	0.460	0.369
Silt (0.01-0.005 mm)	0.538	0.097	0.255
Silt (0.005-0.001 mm)	0.548	0.148	-0.273
Clay (<0.001 mm)	0.522	0.725*	0.719*
Degree of erosion	-0.094	0.025	-0.105
Invertase		0.792*	0.631
Catalase			0.844**

Significant at: * - $P<0.05$; ** - $P<0.01$

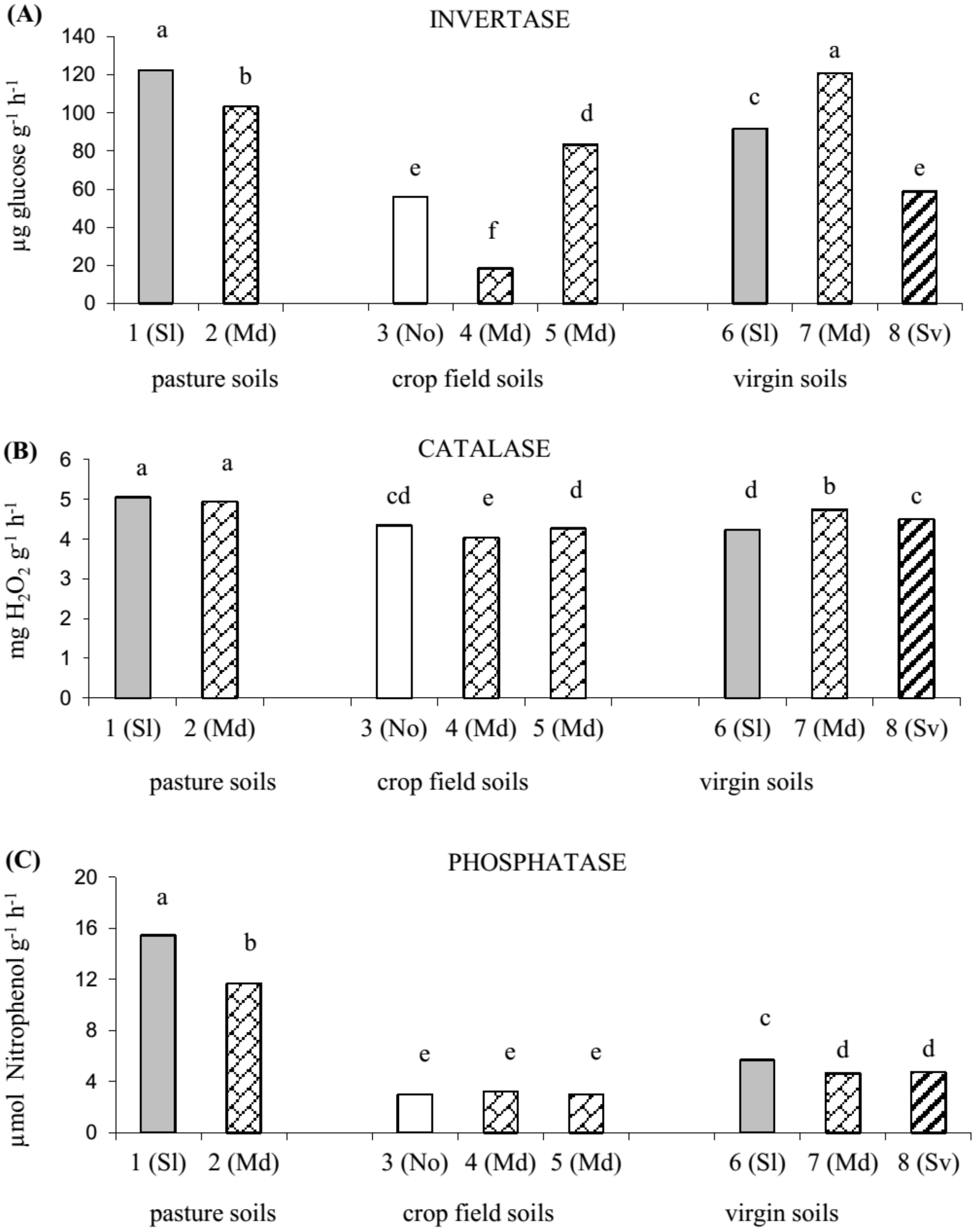

Figure 1. Invertase (A), catalase (B) and phosphatase (C) activities of slightly eroded (Sl), moderately eroded (Md), severely eroded (Sv) and non-eroded (No) Chromic Luvisols under different land use. Different letters above bars show significant differences between values at $P<0.05$

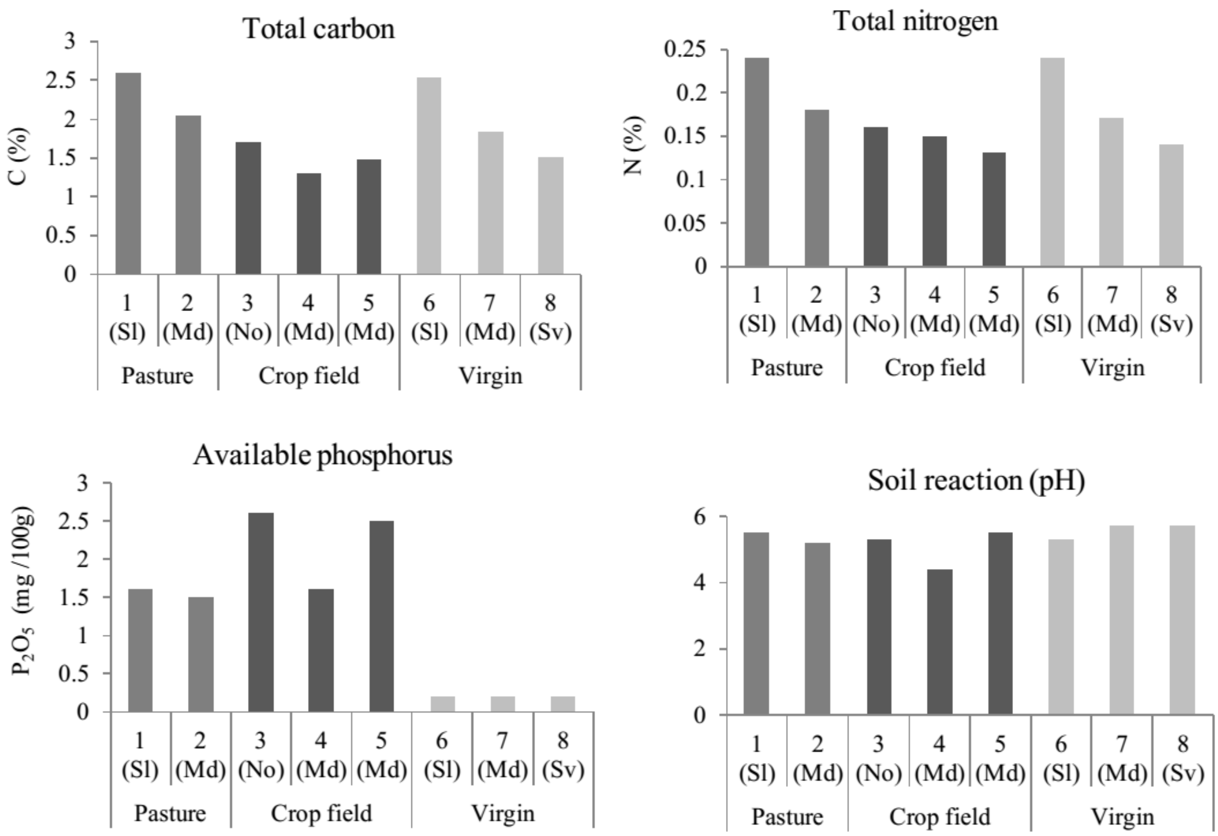

Figure 2. Soil chemical properties of slightly eroded (Sl), moderately eroded (Md), severely eroded (Sv) and non-eroded (No) Chromic Luvisols under different land use

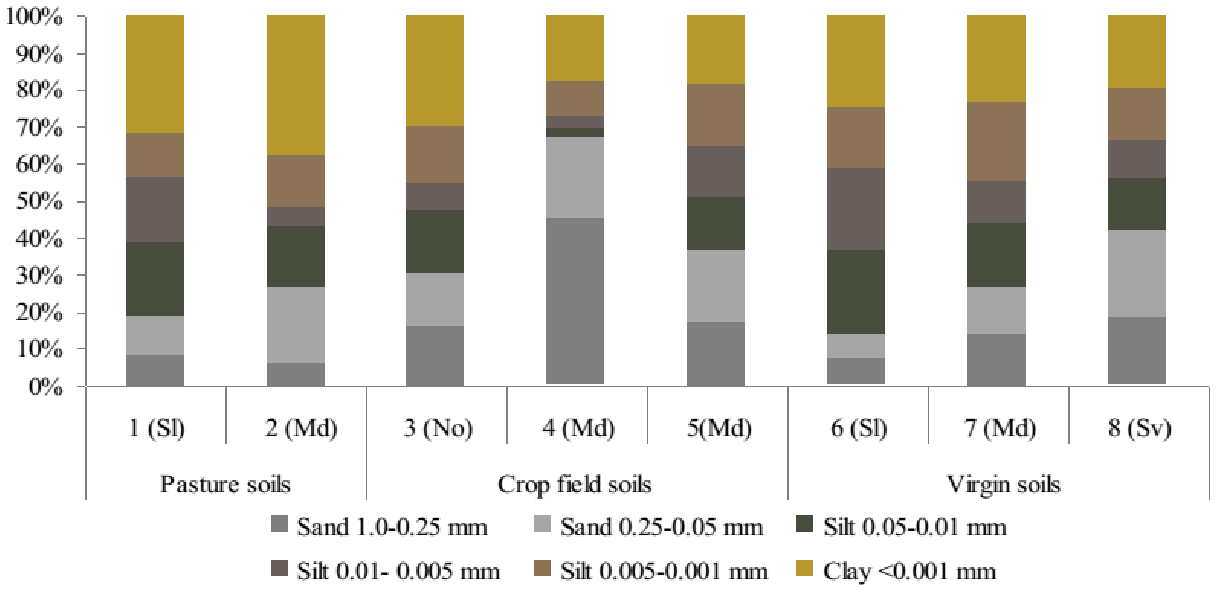

Figure 3. Soil texture of Chromic Luvisols studied: slightly eroded (Sl), moderately eroded (Md), severely eroded (Sv) and non-eroded (No)

Discussion

Enzyme activities of Chromic Luvisols studied varied depending on the degree of erosion and land use type. They tended to lower with increasing the degree of erosion. This was better pronounced for invertase and phosphatase in pasture and virgin soils. In crop field soils, enzymes were influenced by crop plant, as well. Invertase and catalase activities decreased in the soil under corn, but increased in the soil under wheat when the degree of erosion increased.

Depending on the land use type, all enzyme activities decreased in the order pasture > virgin > crop field soils, showing positive impact of plant cover and negative effect of cultivation practices. Similarly, Acosta-Martinez et al. (2007) reported on lower enzyme activity in agriculture comparing to pasture soils (non-eroded ones).

Washing the top soil away, erosion usually causes loss of nutrients. In this study, a tendency of decreasing of total carbon and total nitrogen soil contents with increasing the degree of erosion within each land use soil group was found. The total carbon and nitrogen contents were lower in the non-eroded crop field soil compared to slightly eroded pasture and virgin soils which pointed the negative influence of crop cultivation practices. This also proved the well known protective function of grasses against soil erosion. Such effect of forages in improving aggregate stability and organic carbon content of a clay soil was shown by Gülser (2006). Available phosphorus content differed among the three groups of soils. In general, it was higher in pasture and crop field soils compared to virgin soils which was obviously due to soil amendments. They commonly improve soil nutrient status and structure. Özdemir et al. (2015) reported that organic and inorganic carbon sources improved the structure and decreased erodibility of an acid soil.

Due to erosion fine soil particles are commonly washed what results in increased sand content. In this study, soil texture tended to worsen in soils with higher degree of erosion. In moderately eroded crop field soils, the reduction of silt and clay contents was higher than that in moderately eroded pasture and virgin soils, indicating that crop field soils were more susceptible to erosion. This could be related to soil disturbance by tillage and lower root aggregation effect of crops compared to dense native vegetation.

Some relationships between enzyme activities and Chromic Luvisols properties were found. Soil invertase and phosphatase activities were in close relations with soil carbon. The results are in confirmation with data obtained by other authors. Marx et al. (2005) showed that activities of hydrolases studied positively correlated with organic carbon content in grassland silty clay loam soil. Similar correlations were reported by Park et al. (2014) and Yin et al. (2014), as cited before.

The positive correlations of catalase and phosphatase activities with soil clay and of invertase activity with soil silt we found, confirmed findings by other authors. Studying enzyme activities in soil particle size fractions, Kandeler et al. (1999) reported that invertase activity was mostly located in the silt fraction and that alkaline phosphatase activity was mainly registered in the silt and clay fractions of Haplic Chernozem. Authors showed that enzyme activities in particle-size fractions were mostly affected by the type of tillage. According to the study of Marx et al. (2005) phosphatase had the highest absolute activity in the clay-size fraction of grassland soil.

An effect of erosion gradient on virgin soils properties was noticed in our study. Carbon, nitrogen, silt and clay contents gradually decreased with increasing the degree of erosion, while sand content gradually increased. Particularly, phosphatase activity tended to decrease in virgin soils under higher degree of erosion. In our previous study (Nedyalkova et. al., 2013), negative correlation between phosphatase activity and the degree of erosion in virgin soils was reported.

Conclusion

A clear tendency of nutrients and texture loss with increasing the degree of erosion in crop field, pasture and virgin Chromic Luvisols was found. Negative effect of erosion gradient on virgin soils properties was noticed. Crop field soils were more susceptible to erosion. The protective function of grasses against erosion was shown, as well.

Enzyme activities decreased in the order pasture > virgin > crop field soils. Invertase and phosphatase activities tended to lower with increasing the degree of erosion in pasture and virgin soils.

Relationships with soil properties differed for particular enzymes. Soil invertase and phosphatase activities were in close relations with soil carbon. Catalase and phosphatase positively correlated with soil clay, and invertase with soil silt content.

Results from this study suggested that along with chemical and physical indicators, enzyme activities could be additional indicators of the degree of erosion of Chromic Luvisols. Further studies on different soil types are to be carried out. Data obtained are intended to contribute to development of biological indicators of eroded soils.

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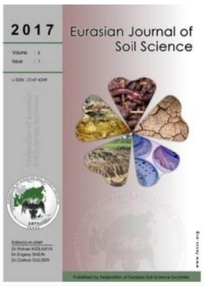

Conductive and steam-diffuse constituents of thermotransfer in different soil moisture contents: case study of the Altai Region's soils

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Abstract

The goal of this study was to determine the conductive and steam-diffusive heat transfer constituents in the soil. Based on the solution of differential equation system of heat and mass transfer, the method to determine the conductive and steam-diffusive heat transfer constituents in wet soils was developed. To measure the thermophysical properties in laboratory setting, a pulse method of a two-dimensional heat source was used. The method takes into account the patterns of temperature field equalization in an unbounded medium after the heat source termination. A feature of this process is the occurrence of peak temperature at the investigated point of the medium at a given instant. In this experiment, the temperature was controlled not only at the investigated point of the medium, but also at the soil-heater interface. The proposed method was used to study the thermophysical indices of the chernozems of the Altai Region's Priobye area (the Ob River area). The chernozem under study is of light-loamy particle-size composition; the illuvial horizon *B* is enriched by a sand fraction. It has been found that the soil conductive thermal diffusivity is reduced with increasing moisture content. The steam-diffusive thermal diffusivity has the extremum at the moisture close to the discontinuous capillary moisture. In humus horizons it plays a smaller role than in the mineral horizons. The thermal diffusivity determined by the steam molecule motion in the pore space of the soil exceeds the conductive thermal diffusivity two or three times. At the same time thermal steam diffusivity is more than ten time lower than the conductive constituent. Eventually, the stem molecules though dramatically accelerating the processes of heat transfer in the soil profile conduct a small amount of heat and make a weak contribution to soil thermal accumulation.

Article Info

Received : 07.08.2015
Accepted : 09.06.2016

Keywords: Soil, thermal capacity, thermal conductivity, thermal diffusivity, thermo-transference in soils, conductive and steam-diffuse constituents.

Introduction

The processes of thermal accumulation and thermal transference in soil profile are a great deal determined by heat capacity, thermo and thermometric conductivity of soil. These qualities depend on mechanical composition, organic matter content, moisture content, density and other soil-physical factors (Nerpin and Chudnovskiy, 1970; Gülser and Ekberli, 2004; Mikayilov and Shein, 2010; Arkhangelskaya, 2014). This predetermines big practical possibilities for directed coercion on the soil climate, and therefore, on the processes and life conditions of plants.

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284264

The chernozem of the Priobye area, formed in the Altai Region, is the most promising in terms of water-and-heating meliorations, causing the raise in productivity. The efficiency of the used agronomic practices should be scientifically substantiated which demands a detailed research of thermo-physical parameters of chernozem.

The heat transfer in moist soil was studied by a number of researchers (Globus, 1983; Globus, 1987; Lunin, 1972; Panfilov and Makarychev, 1981; Philip and De Vries, 1957); their works developed the concept of soil moisture heat transfer. The concept is based on the acknowledgement of the mixed heat-and-moisture mechanism of thermo-moisture transference, which includes conductive thermo-transference through firm and liquid phases and diffuse transference of heat by the streams of steam and liquid moisture. The mixed mechanism nowadays is the most acknowledged in soil thermo-physics. Nevertheless, the development of the theory of the mixed mechanism of thermo-moisture exchange made us introduce, for concordance of theory and experiment, the so-called reinforcement factors (Globus, 1983), based on the row of assumptions (Globus, 1987), not always objectively reflecting real conditions formed in soil.

This leads to some mistakes by the determination of heat-stream components caused by thermo-diffusion of steam and liquid moisture, and also its phase transformations, especially when the moisture content is less or more than the critical one (Globus, 1983). The goal of this study was to determine the conductive and steam-diffusive heat transfer constituents in the soil.

Material and Methods

According to the research goal, the leached chernozem of light-loamy particle-size composition of the Priobskoye Plateau of the Altai Region and quartz sand were studied (Makarychev and Mazirov, 1996; Bolotov and Makarychev, 2015). The samples of undisturbed structures in different soil horizons were studied.

To measure the thermophysical properties in laboratory setting, a pulse method of a two-dimensional heat source was used. The method takes into account the patterns of temperature field equalization in an unbounded medium after the heat source termination. A feature of this process is the occurrence of peak temperature at the investigated point of the medium at a given instant (Chudnovskiy, 1976). The knowledge of this temperature and time enables to determine the soil thermal capacity, thermal conductivity and thermal diffusivity.

Results and Discussion

We made an attempt to find directly the conductive and steam-diffuse constituents of thermotransference on the base of using impulse method of flat heater, when the stream of liquid moisture does not influence the results of the experiment (Lunin, 1972; Tikhonov and Arsenin, 1979). The suggested method is based on the solution of the so-called inverse problem (Anikonov and Bubnov, 1981; Lavrentyev, 1986). We solved the system of differential equations of heat-and-mass transference (Lunin, 1972) for it.

$$C_h\gamma_h\frac{\partial t_h}{\partial \tau}=\lambda_h\frac{\partial^2 t_h}{\partial x^2}+W \qquad (1.1)$$

$$C\gamma\frac{\partial t}{\partial \tau}=\lambda\frac{\partial^2 t}{\partial x^2}+r\cdot I_s \qquad (1.2) \qquad (1)$$

$$C_s\gamma_s\frac{\partial P}{\partial \tau}=\mu\frac{\partial^2 P}{\partial x^2} \qquad (1.3)$$

with initiate $t(0,x)=t_0, x\geq R$ and limited conditions $t(\tau,R)=\varphi(\tau), \tau\geq 0$.

If the temperature on the borderline of the heater and the investigated pattern is measured in the process of experiment, there is no need then to solve the equation (1.1), which characterizes the parameters of the heater.

In this case it is sufficient to consider the following problem:

$$C\gamma \frac{\partial t}{\partial \tau} = \lambda \frac{\partial^2 t}{\partial x^2} + r \cdot I_s \tag{2.1}$$

$$C_s \gamma_s \frac{\partial P}{\partial \tau} = \mu \frac{\partial^2 P}{\partial x^2} \tag{2.2}$$ (2)

$$t(0, x) = t_0, x \geq R \tag{2.3}$$

$$t(\tau, R) = \varphi(\tau), \tau \geq 0 \tag{2.4}$$

Note: C - specific heat of soil, γ - soil density, C - specific heat of steam, γ_s - steam density, $\gamma_s = MP/RT$, $\gamma/P = K$, λ - conductive thermal conduction, μ - coefficient of a team permeability, r - specific heat of vaporization, t - soil temperature, P - pressure of saturated steam in porous space of soil, τ - time, x - distance from the heater, I_s - capacity of conditional heat source caused by steam transference.

As the initial condition (2.3) and limited condition (2.4) are given, then it's defind:

$$P(t(0, x)) = P(t_0) = P_0 \tag{2.5}$$

and

$$P(t(\tau, R)) = \psi(\tau) \tag{2.6}$$

If we look at the equation (2.2) with the conditions (2.5), (2.6), we shall see, that the solution $P(\tau)$ of this mixed problem exists and it is sole.

Substituting the received $\frac{\partial P}{\partial \tau}$ in (2.1) we shall come to equation:

$$C\gamma \frac{\partial t}{\partial \tau} = \lambda \frac{\partial^2 t}{\partial x^2} + kr \frac{\partial P}{\partial \tau} \tag{3.1}$$

with initial $$t(0, x) = t_0, x \geq R \tag{3.2}$$ (2)

and limited conditions: $$t(\tau, R) = \varphi(\tau), \tau \geq R \tag{3.3}$$

Hence it appears that the solution of the system (2) exists and it is sole, because it is correct.

It is necessary to define coefficient μ in the equation (2.2) for direct solution of the system. It will demand additional data, i.e. the measuring of the temperature in the moment of time τ^* in point $x^* + R, \tau^* > 0, x^* > 0$ and $t(\tau^*, x^* + R)$.

Taking it all into consideration, we shall get the problem, including the equation (2.2), conditions (2.5), (2.6) and the condition $P(t(\tau^*, x^* + R)) = \wp(\tau^*)$.

defining $P(t(\tau, x + R)) = U(\tau, x)$, $a^* = \frac{\mu}{C_s \gamma_s}$

we shall have: $$\frac{\partial U}{\partial \tau} = a^* \frac{\partial^2 U}{\partial x^2} \tag{4.1}$$

$$U(0,x)=\varphi(0) \qquad (4.2) \qquad (4)$$

$$U(\tau,x)=\psi(\tau)\,,\ \tau\geq 0 \qquad (4.3)$$

$$U(\tau^*,x^*)=\wp(\tau^*) \qquad (4.4)$$

To find a^*, i.e. to solve the inversed problem, it is necessary to know the temperature on the heater surface $t(\tau,R)$ and on the distance x^* from it $t(\tau^*,x^*+R)$ at the moment of time τ^*.

So, $\varphi(0)=P(t_0)$

$\psi(\tau)=P(t(\tau,R))$

$\wp(\tau^*)=P(t(\tau^*,x^*+R))$ will be given.

Finally, expressing it from equation (2.2) $\Im_s=\mu\dfrac{\partial^2 P}{\partial x^2}$ and substituting the given dependence in (2.1) we shall get:

$$C\gamma\frac{\partial t}{\partial\tau}=\lambda\frac{\partial^2 t}{\partial x^2}+kr\mu\frac{\partial^2 P}{\partial x^2}$$

Calculating: $$\frac{\partial P}{\partial x}=\frac{\partial}{\partial x}\big(P\big(t(\tau,x)\big)\big)=\frac{\partial P}{\partial\tau}\cdot\frac{\partial t(\tau,x)}{\partial x}$$

we shall find: $$\frac{\partial t}{\partial\tau}=\frac{\partial}{\partial x}\left(\left(\frac{\lambda+\dfrac{kr\mu}{C_s\gamma_s}\cdot\dfrac{\partial P}{\partial\tau}}{C\gamma}\right)\frac{\partial t}{\partial x}\right)$$

This is a well-known equation of thermoconductivity-quasi-linear, parabolic; and the coefficient.

$$\lambda+\frac{kr\mu}{C_s\gamma_s}\cdot\frac{\partial P}{\partial t}$$

is the, total thermal conduction of soil, and

$$\frac{kr\mu}{C_s\gamma_s}\cdot\frac{\partial P}{\partial t}$$

is the constituent of thermal conduction, caused by steam-transference.

The direct calculation of thermometric conductivity a^*, caused by phase transformation of moisture on the "warm" and "cold" sides of water cuffs and the movement of steam molecules in the porous space is done with the help of computer program, and the temperature values on the surface of the heater and in the studied point of damp soil at definite moments were used as initiate data.

The values of partial pressure of steam, necessary for calculation, were defined by the known table (Kay and Laby, 1995).

The suggested method of getting steam-diffuse parameters of thermotransference was used while making an experimental research in leached chernozem with light-loamy mechanical structure of the Priobskoye Platean on the Altai Region, and for comparison, of quartz sand. According to the data of the Department of Soil Science of the Altai Agricultural Institute, the chernozem under study is of light-loamy particle-size composition (Table 1); illuvial horizon *B* is enriched by sand fraction.

The volume weight of the upper humus-accumulating layers varies from 1200 to 1160 kg/m^3, rising in the horizon *B* to 1330 kg/m^3. Correspondingly, the total porosity is lower there, just as the porosity of aeration by the field moisture capacity (*FC*) is the lowest in the arable layer.

The minimum moisture-capacity of genetic horizons of chernozem decreases with the depth. The capillary bond breaking moisture (*CBB*) changes analogically.

Down the profile the number of organic matter decreases very much (from 5.2 per cent to 0.5 per cent correspondingly in the horizons *A* and *B*).

Table 1. Physical-mechanical and hydro-physical characteristics of leached chernozem

Soil Horizon	Porosity		Fractions		Hydroconstants		
	Total	Aeration	Clay	Sand	*WP*	*CBB*	*FC*
	%				% from weight		
A	52.2	15.6	29.0	34.9	6.9	23.1	30.3
AB	54.0	22.5	26.5	29.5	6.9	20.6	27.2
B	48.4	20.7	26.2	52.3	7.0	17.0	20.8

WP – wilting point

The investigated quartz sand with predominating 2 mm faction has volume weight 1580 kg/m^3, total porosity 40.3 percent. Because of field moisture capacity (only 6 percent of total weight) the porosity of aeration reaches 53 percent of volume of porous space. Some results of thermophysical research are represented in Table 2. The data of Table 2 shows that the conductive thermometric conductivity of genetic horizons of leached chernozem and quartz sand has the tendency to decrease with the rise of moisture content. One can see it especially in the sand and in the illuvial horizon *B*, containing a little amount of humus. Conductive thermometric conductivity in them lowers from 0.4 x 10^{-6} to 0.16 x 10^{-6} m^2/s and from 0.36 x 10^{-6} to 0.17 x 10^{-6} m^2/s, respectively.

Table 2. Conductive (numerator) and steam-diffuse (denominator) thermometric conductivity of chernozem and quartz sand by different degrees of moistening (a; a^*x10^{-6} m^2/s)

		Leached chernozem		
Soil Horizon	Absolutely dry			
A	0.36	$\frac{0,35}{0,13}$	$\frac{0,33}{0,16}$	$\frac{0,30}{0,13}$
AB	0.40	$\frac{0,33}{0,19}$	$\frac{0,32}{0,29}$	$\frac{0,32}{0,24}$
B	0.36	$\frac{0,16}{0,33}$	$\frac{0,17}{0,39}$	$\frac{0,16}{0,36}$
		Quartz Sand		
Moisture, %	0.0	2.5	7.5	15.0
	0.40	$\frac{0,24}{0,86}$	$\frac{0,22}{1,03}$	$\frac{0,20}{0,88}$

Such change is caused by the fact, that a well thermometric conductive soil air is substituted by water, which thermometric conductivity is much less. In humus horizons this process becomes even more complicated. Under the influence of substantial sorbing power the moisture is absorbed into organic and mineral earth fractions, filling their micropores and reducing the number of heat contacts, which causes the increase of conductive thermometric conductivity. As a result, with the growth of moisture it decreases slower than in mineral horizons or in the sand.

The thermometric conductivity, caused by steam transference (a^*) for the investigated samples of chernozem is characterized by extreme values, referring to moisture content close to CBB, and in the quartz sand – to capillary moisture content. This is the degree of soil-moistening which provides the best conditions for thermal and steam conduction, when the concentration of steam molecules is high enough and there is the possibility for their free movement in a porous space.

At the same time, the presence of water cuffs does not make the obstructions for thermotransference, i.e. while dissolving on the “warm” side of the cuff, the steam molecules, moving in an airy pore, condense on the “cold” border of the next water pellicle, accelerating the process of heat transference owing to phase transformations of soil moisture.

It is necessary to point out that the steam-diffuse constituent in humus horizons of the chernozem plays the less role, than in lower mineral ones, and much less in the quartz sand in comparison with conductive constituent. It shows once again the high mobility of steam molecules in the systems, where the energy of connection of liquid and firm phases is not great. So, in the *B* horizon of leached chernozem by *CBB* the thermometric conductivity, caused by steam-transference, is twice larger than the conductive one. In the quartz sand, where the dispersion degree is much less, this exceeding can reach 4 and more times.

Figure 1 presents the interdependence of equivalent (total) and thermometric conductivity, caused by the steam molecules movement, as well as the coefficient of thermal-and-steam conductivity of chernozem and quartz sand depending on the moisture content. The picture shows that the curves of thermal-and-steam conductivity also have extreme values. This proves the existence of the conditions, optimum for thermo-transference, arisen by the definite hydrological constant, depending on the dispersion degree.

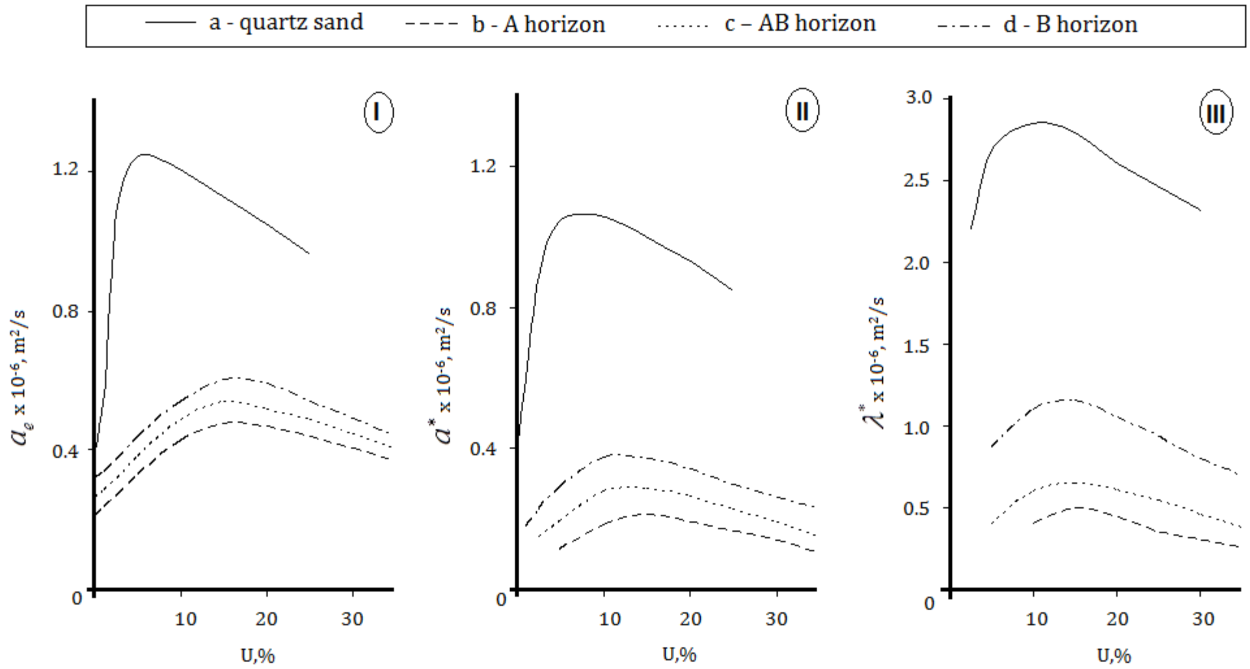

Figure 1. The interdependence of equivalent (total) (I- a_e) and thermometric conductivity (II- a^*), caused by the steam molecules movement, as well as the coefficient of thermal-and-steam conductivity (III- λ^*) of chernozem and quartz sand depending on moisture content (*U*): *a* - quartz sand, *b* - *A* horizon, *c* – *AB* horizon, *d* - *B* horizon.

At the same time the coefficient of thermal condition, caused by steam-transference, is many times lower than of the conductive one, which by moistening from absolutely dry condition to (*HB*) undergoes a change for different horizons of chernozem in the range (0.3 – 1.4) W / (m K)

Therefore, the steam molecules, dramatically accelerating the process of thermal conditions in the soil profile, especially in mineral horizons, transfer some heat, promoting a little thermal accumulation in the soil. This was reported by Globus (1983).

Conclusion

- The solution of system of differential equations lets work out the method of determination of steam-diffuse constituents of the complex mechanism of thermal transference based on the use of impulse method of flat heat source.
- It was shown that the part of thermometric conductivity caused by the steam molecule movement is very substantial in heat-exchange, especially in mineral horizons of chernozem. It also depends very much on the dispersion degree of firm phase of soil. Conductive thermometric conductivity, with the increase of soil moisture content has the tendency to lower because of moisture-substituted soil air.
- The amount of heat transferred by steam is not large, because the thermal-and-steam conduction is many times less than conductive thermal conduction, caused by firm and liquid phases of soil.

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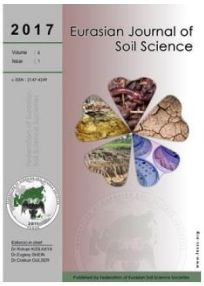

Using microbiological leaching method to remove heavy metals from sludge

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Abstract

Microbial leaching is one of the most effective methods to remove heavy metals from sludge. In the conducted researches, the sludge samples were processed with *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* obtained via cultivation, extraction and purification processes. Heavy metals such as Pb, Cd, Cu and Ni were leached from sludge by *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* within different substrate concentration and pH value conditions. It is defined that from the point of view of economy and efficiency the optimal concentration of $FeSO_4.7H_2O$ and sulfur for bio-leaching process was 0.2 g. The leaching rates of heavy metals such as Pb, Cd, Cu and Ni of the same concentration were 74.72%, 81.54%, 70.46% and 77.35% respectively. However, no significant differences depending on the pH value among the leaching rates were defined, even for the pH value of 1.5. Along with the removal of heavy metals from sludge, the organic matter, N, P, K were also leached to some extent. The losing rate of phosphorus was the highest and reached 38.44%. However, the content of organic matter, N, P, K in the processed sludge were higher in comparison with level I of the National Soil Quality Standards of China. Ecological risk of heavy metals in sludge before and after leaching was assessed by Index of Geo-accumulation (I_{geo}) and comprehensive potential risk (RI). The results of research defined that the content of heavy metals in sludge meets the level of low ecological risk after leaching and their contents is lower in comparison with the National Agricultural Sludge Standard of China. Sludge leached by biological methods is possible to use for treatment for increasing soil fertility.

Article Info

Received : 13.05.2016
Accepted : 11.07.2016

Keywords: pH value, sludge, microbiological leaching, substrate concentration, heavy metals.

Introduction

Urban sewage and industrial wasted water became one of the main ecological problems in cities of China, along with the growing economy and expanding population. Therefore, proper sanitization of sewage sludge is a critical task for wasted water plants. Sludge contains large quantity of nutrient substance such as organic matter, nitrogen, phosphorus and potassium. 50-80% heavy metals in sewage sludge (Lester et al., 1983; Brown et al., 1979) discharged from wasted water without proper disposal is the main secondary pollutant

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284265

source of the environment. Currently, the mostly applied methods used in wasted water plants in China were incineration, throwing to sea, landfill and land application (Wang et al., 2014; Liu, 2014). The land application has been considered as the most efficient disposal method in the future, as it brought positive inclinations in the soil-plant-sewage-sludge system. However, heavy metals in sludge provide environmental risk with their poisonous, long-latency and accumulative characteristics (Dai et al., 2012; Shen et al., 2007). Chemical, electro-chemical and bio-leaching methods are widely used in removing heavy metals in sludge (Jakobsen et al., 2004; Shi et al., 2013; Babel et al., 2006). Bio-leaching is mostly implemented due to low acid waste utilization and high extract efficiency (Pathak et al., 2009a).

Bio-leaching is the method based on extracting heavy metals in infusible solid form by using functions of natural micro-organism such as oxidation, reduction, complexion and dissolution (Pathak et al., 2009b; Peng et al., 2011; Zhu et al., 2013). Heavy metals in liquid wasted water are usually removed by chemical and electrochemical methods (Kaminari et al., 2007; Hunsom et al., 2005). *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* are the common micro-organisms used in bio-leaching methods. Those bacteria in $FeSO_4.7H_2O$ and sulfur substrates perform well in removing heavy metals in sludge and their implementing is not expensive (Sreekrishnan and Tyagi, 1996). The majority of studies on bio-leaching of heavy metals in sludge focused only on the removal efficiency, but the nutrient matters questions in sludge were often omitted. The aim of our researches is to define changing in the nutrient matters under the bio-leaching of heavy metals in sludge with *Thiobacillus ferrooxidans* (T.f.) and *Thiobacillus thiooxidans* (T.t.), and decide the appropriate substrate ($FeSO_4.7H_2O$ and sulfur) condition and pH value suitable for maintaining nutrients content and removing heavy metals.

Material and Methods

Sample collection and treatment

Sludge samples were isolated form the Hedong wasted water treatment plant in Urumqi in May, 2014. Sewage contains in average 15g L^{-1} sludge. After air drying sludge was pulverized with mortar and pestle after and separated with 100 mesh sieve. Powder sample was stored in fridge at 4°C in plastic bottle. Physical and chemical properties of sludge were measured with standard methods (Pansu et al., 2006).

Table 1. Physical and chemical properties of sludge ($mg \cdot kg^{-1}$ of heavy metals, $g \cdot kg^{-1}$ of nutrients)

Sample	Pb	Cd	Cu	Ni	Organic Matter	N_{total}	P_{total}	K_{total}
Sludge	45.00	8.00	95.57	158.35	435.61	11.49	13.24	4.8
National Agricultural Sludge Quality Standard of China pH<6.5	300	5	250	100	-	-	-	-
National Agricultural Sludge Quality Standard of China GB4282-84 pH≥6.5	1000	20	500	200	-	-	-	-

Source and cultivation of microorganisms

Thiobacillus strains were obtained from sewer mud in the campus of Xinjiang Agricultural University in Urumqi, and some mud samples were stored in sterile water.

Thiobacillus ferrooxidans (T.f.) cultivation

10 mL bacteria sample was placed in Erlenmeyer flasks, that contained 100 ml 9 k standard growth medium, and the medium was incubated at 30 °C and 160 rpm min^{-1} for 5 days. Clear part was extracted from red brown liquid and incubated repeatedly, then separated and purified in 9 k solid medium. Reddish colony appeared in 9 k solid medium after 7 days. Selected colony was expanded in liquid medium to get T.f. bacteria (Lombardi et al., 2002).

Thiobacillus thiooxidans (T.t.) cultivation

10 mL bacteria sample was incubated in an Erlenmeyer flask containing 100 ml of the Starkey-S medium at 30 °C and 160 rpm min^{-1}. The medium became turbid and elemental sulfur precipitated that causes the decline of pH (about 1) after 7-10 days. Then bacteria was separated and purified in sodium thiosulfate culture medium. Then after 6 days, white colony that appeared in medium was selected to amplify in Starkey-S culture medium, and quite pure T.t was obtained (González et al., 1995).

Heavy metal leaching methods for different substrates

1. Bio-leaching of sludge with different substrates: 0.4 g sulfur, 5 mL T.t. and 5 mL T.f. were added into 150 mL sludge in 300 ml Erlenmeyer flask, then 0.1, 0.2, 0.3, and 0.4 g of $FeSO_4 \cdot 7H_2O$ were added to maintain pH of 6.0.
2. Bio-leaching of sludge with different sulfur treatments: $FeSO_4 \cdot 7H_2O$ with optimal concentration obtained by method (1) , 5 mL T.t. and 5 mL T.f. were added to 150 mL sludge in 300 mL flask. The pH values of each solution were about 6.0 and 0.1, 0.2, 0.3, and 0.4 g and sulfur powder were added into the solutions.
3. Solution of the optimal substrate concentration obtained by method (2) was divided into four groups with pH values of 6.0, 5.0, 4.0, 3.0, and 2.0 before cultivation. Each substrate was performed in three replications and incubated in the rotatory shaker apparatus at 160 rpm min^{-1} and 30 °C for 10 days. The water lost with evaporation during the cultivation period was supplemented with sterile water.

Analysis methods

The pH values of the solution were measured with pHS-3C pH meter every day. Sludge in heating oven was dissolved with aqua regia + $HClO_4$, then rinsed with 0.1mol L^{-1} HCl before filtration and diluted to constant volume. Heavy metal content was measured with atomic adsorption spectrometry (TAS 990, Pgeneral Beijing). Chemical compounds of heavy metals before and after leaching were analyzed with Tessier sequential extraction method (Tessier et al., 1979) for assessment of potential ecological risk. Total content of nitrogen, phosphorus, potassium and organic matter were measured with standard methods (Pansu et al., 2006).

Assessment methods

Two methods were used to assess the heavy metal pollution caused by sludge application.

(1) *Indexes of geoaccumulation* (Muller, 1969) were used to assess the value of the pollution level and the value of level I (GB15618-1995）that was taken as the background for assessment. Assessment formula:

$$I_{geo}=\log_2 (C_n/1.5B_n) \tag{1}$$

C_n - concentration of the metal pollutant ($mg.kg^{-1}$);
Bn - geochemical background concentration of the pollutant in sediment ($mg.kg^{-1}$)
1.5 - background matrix correction factor caused by lithogenic effect.
I_{geo} consists of seven grades ranging from unpolluted to very highly polluted (Table 2).

Table 2. Indexes of geo-accumulation and RI and the pollution grades of heavy metal

Index of geo-accumulation			Potential ecological risk index			
I_{geo}	Grade	Assessment	single metal risk factor grade		Integrated RI grade	
0	0	Uncontaminated				
0-1	1	Uncontaminated to moderately contaminated	$E_i \le 40$	I low	$RI \le 150$	A low
1-2	2	Moderately contaminated				
2-3	3	Moderately contaminated to highly contaminated	$40 < E_i \le 80$	II middle	$150 < RI \le 300$	B middle
3-4	4	Highly contaminated	$80 < E_i \le 160$	III appreciable	$300 < RI \le 600$	C appreciable
4-5	5	Highly to very highly contaminated	$160 < E_i \le 320$	IV high	$RI > 600$	D high
>5	6	Very highly contaminated	$E_i > 320$	V much high		

(2) *Potential ecological risk index* (Yu et al., 2010)

RI method assesses the pollution by toxicity coefficients of a single and multiple metal pollutants. The index is represented as:

$$E_i=T_i \times C_n/B_n \tag{2}$$

$$RI=\sum E_i \tag{3}$$

Both C_n and B_n were identical to formula (1);
E_i - potential ecological risk index of metal i ;
T_i - toxicity coefficients of Pb, Cd, Cu, and Ni are 5, 30, 5, and 5, respectively (Hakanson, 1980; Liu et al., 2014). The pollution level graded by E_i and RI is shown in Table 2.

Results and Discussion

Impact of $FeSO_4$ concentration on the efficiency of bio-leaching

Two strains of *Thiobacillus* oxidized Fe^{2+} and sulfur to Fe^{3+} and sulfuric acid. In the result, pH slightly decreased (Chao et al., 2008). At the beginning, T.f. populated massively, H^+ was generated during the oxidation of Fe^{2+} to Fe^{3+}. When pH declined to 4, T.f. began to propagate and oxidized elemental sulfur to sulfuric acid. Finally pH declined to about 1.5 (Wang, 2004).

During the first 2 days, pH value rose slightly and reached to 6.51, and then pH value declined. This result defined that the bacteria need about 2 days to start their propagation. After 8 days, pH value in variants with amount $FeSO_4.7H_2O$ ≥0.2 g tended to balance and pH value in variants with amount $FeSO_4.7H_2O$ = 0.1g came to balance in 10 days. At the 8th day, pH values of the solution were 2.42, 1.61, 1.52, and 1.43, respectively. Overall, increasing the $FeSO_4.7H_2O$ amount forced acid generating in solution and the earlier balance of the oxidation process. After 10 days the reaction stopped (Figure 1).

The leaching of mixed bacteria was quite inefficient while treatment with 0.1g $FeSO_4.7H_2O$ and began to be efficient with 0.2 g $FeSO_4.7H_2O$. The leaching rate of Pb, Cd, Cu and Ni were 76.53%, 80.54%, 72.10%, and 75.38%, respectively. The leaching effect became significant in case $FeSO_4$ $7H_2O$ amount exceeded 0.2 g and the minimum amount of $FeSO_4.7H_2O$ in bio-leaching must be 0.2 g. The growth of T.f. was suppressed by the rising of Fe^{3+} concentration (Zhou et al., 2002) that prevented leaching. In case of industrial application the concentration of iron compound has to be maintaining at the level of about 5 % (Shen et al., 2005) for enhancing the leaching efficiency (Figure 2).

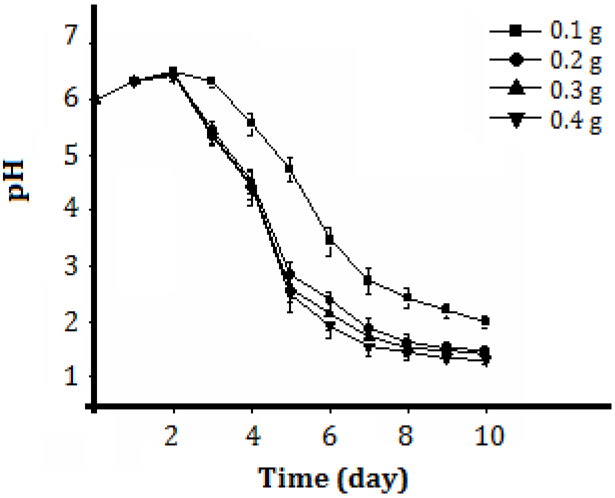

Figure 1. Effect of $FeSO_4$ $.7H_2O$ implementing on pH of leaching solutions

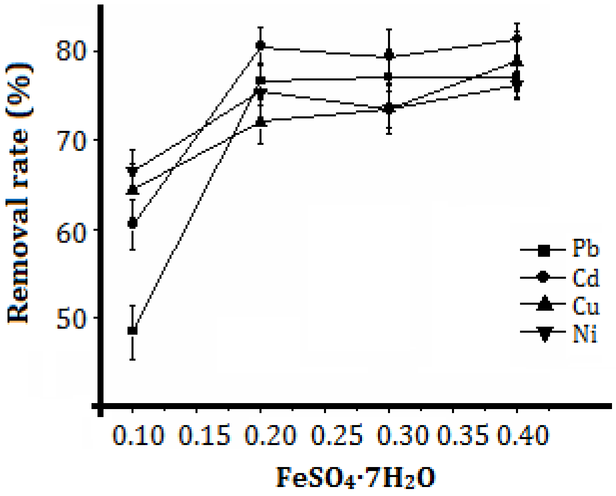

Figure 2. Effect of $FeSO_4 \cdot 7H_2O$ concentration on the leaching efficiency of heavy metals

Effect of sulfur concentration on the leaching efficiency of mixed bacteria

Changing the pH value of leaching solution under different sulfur concentrations along with the same $FeSO_4.7H_2O$ amount (0.2 g) is defined (Figure 3). During the first 2 days, the pH value increased slightly and reached the maximum value of 6.79 at the end of the second day. Then pH began to decrease significantly along with the increment of sulfur concentration. It is explained by influence of sulfur content on bacteria propagation. The acidity became higher along with increasing the sulfur concentration in leaching solution. All the solutions tended the balance after 8 days. The pH value of the solutions after 10 days depending on sulfur concentration (0.1; 0.2; 0.3; 0.4 g) were 2.15, 1.47, 1.44 and 1.43 respectively.

The leaching effect of mixed bacteria was the most significant in variant with sulfur concentration of 0.2 g. The leaching rates of heavy metals such as Pb, Cd, Cu and Ni of the same concentration were 74.72%, 81.54%, 70.46%, and 77.35% respectively. There was no significant increase in leaching rates of heavy metals when sulfur concentration exceeded 0.2 g. The leaching rates of Ni declined slightly. The result indicated in variants with $FeSO_4.7H_2O$ and sulfur concentration of 0.2 g the leaching effect of T.f. and T.t. in mixed condition may be quite significant and economic, and the heavy metal contents meet with the National agricultural standards (Figure 4).

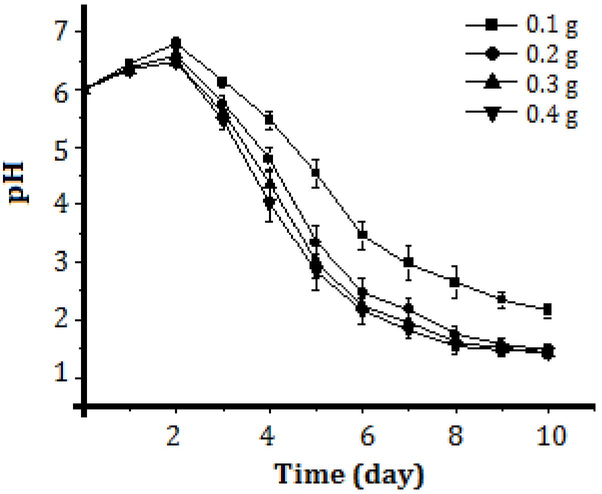

Figure 3. Effect of sulfur concentration on pH of leaching solutions

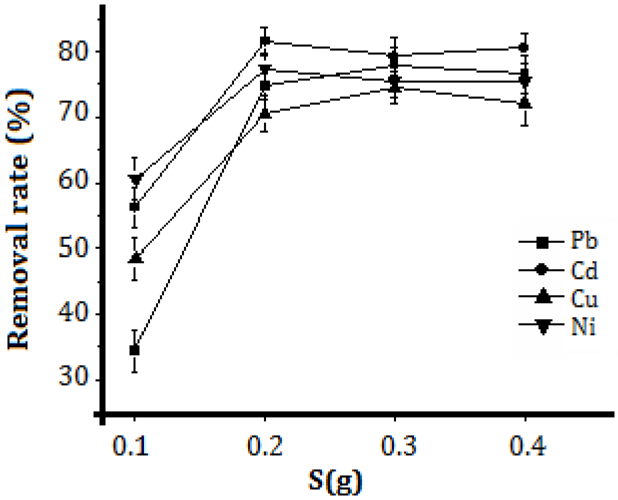

Figure 4. Effect of sulfur concentration on the leaching efficiency of heavy metals

Effect of different pH conditions on the leaching efficiency of mixed bacteria

At the beginning, the pH value of all solutions increased in small rate then decreased significantly up to the minimum pH value of about 1.5 (Figure 5). In case the pH value exceeded 2.0 the leaching rates of heavy metals were relatively high. However, in case the pH value was lower than 2.0 the bio-chemical reaction was suppressed by increased content of acids, and bio-leaching process was absent. When the initial pH values were 6.0, 5.0, 4.0 and 3.0, there were no significant differences between the leaching rates of heavy metals. The result indicated that the pH value of bio-leaching solution should not be rather high as the bio-leaching process generated acid and increased content of acid in the initial stage may facilitate the bio-leaching reaction. The pH value declined to 1.5 at the end of the process. Most of heavy metals separated out of solid sludge into the solution and concentrated in solid-liquid fraction (Figure 6).

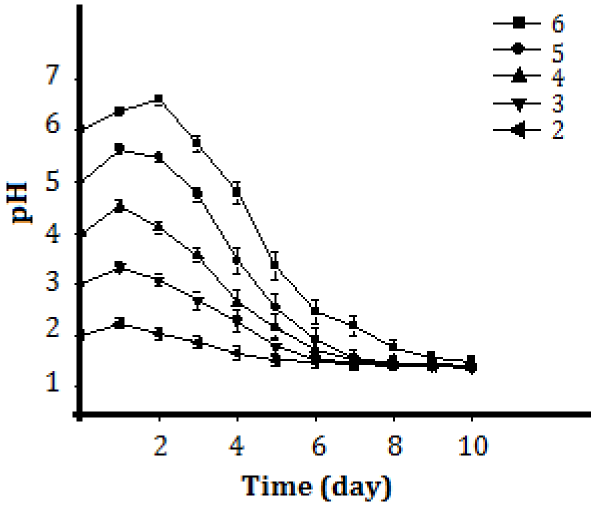

Figure 5. Effect of pH value on the leaching solutions

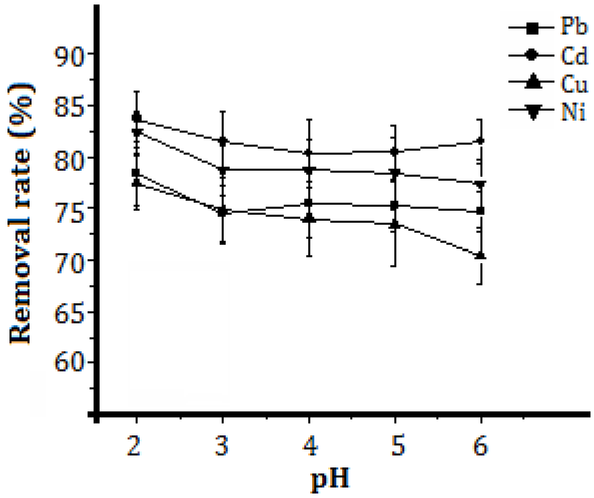

Figure 6. Effect of initial pH on the leaching efficiency of heavy metals

Changes in nutrient matters content while bio-leaching process

Leaching process generated acids and the pH value declined to low parameters. Some nutrient matters in sludge dissolved into solution along with heavy metals. The nutrient matters are absorbed by T.f. and T.t. from the sludge during their propagation that resulted as the nutrient matters losses. Moreover, some nutrient matters losses connected with microbial nitrification that is restricted in acidity condition and some heterotrophic microorganism denitrified nitrogen into NH_4^+-N (Benmoussa et al., 1998). After 10 days the losses of nitrogen was 1.77 g kg^{-1}, and the_rate of losses was 15.40% (Table 3).

Table 3. Content of nutrient matters in sludge (g kg^{-1})

Sludge	Organic Matter	N_{total}	P_{total}	K_{total}
Before Leach	435.61	11.49	13.24	4.8
After Leach	396.92	9.72	8.15	4.13
National Primary Standard of China	＞40	＞2.0	＞1.0	-

As to the losses of phosphorus in leaching solution, phosphates in not dissolvable stage and some phosphorus compounds were changed into free phosphate ions under acid condition. Relevant researches showed that epicyte protein of T.t. cells needed more phosphorus than other microorganisms (Varela et al., 1998). After 10 days the losses of phosphorus was 5.09 g.kg^{-1}, and the rate of losses was 38.44%.

The losses of potassium were not so high. Most potassium compounds were soluble so potassium in sludge was not affected in such rate by the leaching process. And potassium in solid sludge is not solved within low pH condition that resulted low rate of losses during bio-leaching process. After 10 days the losses of potassium was 0.67 g.kg^{-1}, and the rate of losses was 13.96%.

The losses of organic matter during the leaching were also not so high. In the experiment, two types of autotrophic organisms conducted the bio-leaching process. Therefore, the losses of organic matter during the leaching process connected with another heterotrophic microorganism. The results showed that humic substance combined with bivalent heavy metals and transferred from sludge to bio-leaching liquid under acidic condition (Fournier et al., 1998). After 10 days the losses of organic matter was 38.69 g.kg^{-1} and the rate of losses was 8.88%.

According to the secondary report on soil characteristics in China, N, P, K and organic matter contents exceeded the standards: the organic matter, N, and P contents were 10, 5 and 8 times higher in comparison with the standards, respectively. Furthermore, the heavy metal contents within the National Primary Standard of China. Therefore, bio-leaching of sludge is the possible_agricultural treatment for increasing the value of the land with low content of the nutrients.

Concentration of heavy metals depending on bio-leaching process

The concentration of all heavy metals in sludge declined after bio-leaching process. Residual form (T5) was defined in sludge in high concentration due to its chemical stability. The sum of T1 and T2 forms for defining the mobility and the sum of T1, T2 and T3 forms for ecological availability assessment of heavy metals were used. The percentages of T1, T2 and T3 forms of Pb, Cd, Cu and Ni were 28.12%, 23.65%, 23.13% and 24.34%, respectively. The above results point to their weak mobility and low availability that suggests low potential ecological risk (Table 4).

Table 4. Content of heavy metals in sludge depending on bio-leaching process（mg kg^{-1}）

Heavy metals	Pb		Cd		Cu		Ni	
	before bio-leaching	after bio-leaching	before bio-leaching	after bio-leaching	before bio-leaching	after bio-leaching	before bio-leaching	after bio-leaching
Exchangeable form (T1)	2.10	1.03	0.90	0.19	2.78	2.85	25.81	4.26
Carbonate bound form (T2)	6.20	0.72	1.80	—	8.69	1.31	17.49	1.94
Oxidable form (T3)	9.01	1.45	1.70	0.16	1.47	2.37	30.26	2.53
Organic bound form (T4)	6.89	0.82	1.0	0.16	45.31	1.17	18.37	4.47
Residual form (T5)	20.80	7.36	2.60	0.97	37.32	20.53	66.42	22.67
Total	45.00	11.38	8.00	1.48	95.57	28.23	158.35	35.87

Ecological risk assessment of heavy metals concentration in sludge

The sum of T1, T2, T3 and T4 forms equals to measured value that is the assessment basis for Index of Geo-accumulation (I_{geo}) and Potential Ecological Risk Index (E_i). Before implementing bio-leaching, pollution with Cd was assessed as I_{geo}=5 in comparison with I_{geo} =4.17 that meant high potential ecological risk. Nevertheless, the pollution with other heavy metals did not cause any potential risk. However, the potential ecological risk caused by pollution with Cd diminished to moderate grade of contamination after implementing bio-leaching as 1, while the I_{geo} of other heavy metals declined to uncontaminated stage (I_{geo}<1).

Table 5. Geo-Accumulation Index and Potential Ecological Risk Index of heavy metals in sludge

Metals	Before bio-leaching		After bio-leaching		Metals	Before bio- leaching		After bio- leaching	
	I_{geo}	grades	I_{geo}	grades		E_i	Risk	E_i	Risk
Pb	-1.12	0	-3.71	0	Pb	3.46	Low	0.57	Low
Cd	4.17	5	0.77	1	Cd	810	High	76.5	Middle
Cu	0.15	1	-2.77	0	Cu	8.32	Low	1.1	Low
Ni	0.62	1	-2.18	0	Ni	11.49	Low	1.65	Low
					RI	833.27	High	79.82	Low

The toxicity coefficient (T_i) of heavy metals is used to evaluate their harmful effect on humans and ecological environment, and is characterized by T1, T2, T3 and T4 parameters. Potential Ecological Risk Index is calculated based on T_i and reflects the sensitivity of biological organism to heavy metals. Therefore, for assessment comprehensive potential risk (RI) is used as well (Liu et al., 2009). RI assessment also defined that the level of pollution with Cd was very high (E_i=810) while the pollution with other heavy metals was assessed by low risk parameters. After bio-leaching RI parameter was reduced to 76.5 and assessed as middle potential ecological risk index. The comprehensive potential risk reduced to the grade of low potential risk that confirmed the significant reduction of ecological risk. After bio-leaching, the concentration of all heavy metals in sludge meets with the National Agricultural Sludge Quality Standard of China (GB4284-1984).

Conclusion

- From the point of view of economy and efficiency the optimal concentration of $FeSO_4 \cdot 7H_2O$ and sulfur for bio-leaching process was 0.2 g. The leaching rates of heavy metals such as Pb, Cd, Cu and Ni of the same concentration were 74.72%, 81.54%, 70.46%, and 77.35% respectively. The heavy metal contents were within the National Agricultural Sludge Quality Standard of China (GB4284-1984).
- The high pH value facilitated the bio-leaching process. The eosin-bacteria *Thiobacillus ferrooxidans* (T.f) and *Thiobacillus thiooxidans* (T.t) acidified the leaching solution by metabolism activity and decreased pH value to 1.5.
- The content of N, P, K and organic matter in sludge after bio-leaching exceeded the National Primary Standard of China that points to using the bio-leached sludge for increasing soil fertility.
- After bio-leaching, the potential ecological risk of heavy metals in sludge on the basis of parameters of geo-accumulation index and potential ecological risk index was reduced from the grades of high and middle to low risk.

Acknowledgments

This work was supported by the Project № 948 of the Ministry of Agriculture of China (No. 2013-Z73) and Fundamental Researches Fund of the Russian Federation No. 414611048. We appreciate assistance of Mr. Gangliang Tang to the experiment.

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Eurasian J Soil Sci 2017, 6 (1) 59 - 64

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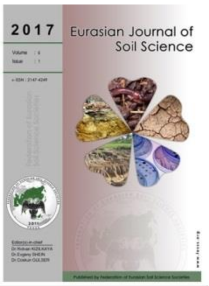

Contamination of soils with Cu, Na and Hg due to the highway and railway transport

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Abstract

Contamination of soils with three metals due to the highway and railway transport was studied. Copper was selected as a suitable indicator for both kinds of transportation. Sodium served to assess the level of contamination resulting from the road salting in winter. Mercury was determined in samples taken close to the railway in order to test its release from impregnated wooden ties. All analytes were determined using the methods of the trace element analysis; values are expressed as dry matter. The highest concentrations of copper, sodium and total mercury in soil samples were 52.7 mg/kg, 770 mg/kg and 0.181 mg/kg respectively. The highest copper content was observed in soils taken close to the railroad and the highway. Elevated sodium levels originated from winter road salting – the highest winter value was 770 mg/kg as compared with maximal summer value of 416 mg/kg. The concentration of total mercury in soils depended on the type of railway ties used – the highest values for location with wooden and concrete ties were 0.181 mg/kg and 0.145 mg/kg, respectively. Wooden railroad ties are considered as a potential source of mercury because of impregnation with antifungal mercury compounds.

Article Info

Received : 09.05.2016
Accepted : 20.07.2016

Keywords: Copper, environment protection, mercury, salting of roads, trace element analysis.

Introduction

Soil is the basis of all agroecosystems; it is an important part of the Earth. Most of soils are endangered with various types of erosion and pollution. Heavy metals and hazardous elements play a significant role among the pollutants. The aim of the present study is to quantitatively characterise the contamination of soils taken close to the major highway and railway in South Bohemia with selected metals: copper, sodium and mercury. Copper was determined in samples taken close to the highway and railway as well. Sodium served as an indicator of the road salting. Mercury concentrations in soils were measured in order to test the possible release of this heavy metal from impregnated wooden railway ties. The study should assess the risk of the highway and railway transportation for the environment and for the agricultural production.

All observed metals occur in soil in their natural forms. Copper is a microelement essential for many organisms. It is present in soil in form of ions, organic compounds, complexes, chalcopyrite ($CuFeS_2$) and other sulphide ores. Sodium is a ubiquitous element, mainly present as a free ion Na^+ in capillary water, or bound into salts. In contrast, mercury is present in soil only in trace amounts and is considered as a polluting element with toxic effect on all organisms. Mercury is the volatile element; its ability to form toxic alkyl-mercury derivatives is well-known (Harley et al., 2015; King et al., 2002).

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284266

The pollution of soils with metals due to the aerial transportation is a worldwide issue. Metals are released during various processes, such as combustion or component wearing. Lead, copper, zinc and cadmium are considered as major inorganic pollutants. Previous studies revealed that the highway traffic increased copper levels in soil close to the road up to 20 times. Copper concentration at the studied locations was usually higher in surface layers; it reached 565 mg kg^{-1} and decreased along with depth (Kluge and Wessolek, 2012). Brakes and sidings wear contribute to the total copper release in road runoff water more than by two thirds, most of it comes to nearby soils (Davis et al., 2001).

Concerning the railroad transport, the pollution depends on an engine type. Diesel locomotives use fuel combustion. Similarly to the road vehicles, they also release polycyclic aromatic hydrocarbons (Wiłkomirski et al., 2011). In contrary, electric locomotives are considered as environmentally friendly, however, the presence of the railroad itself could significantly increase metal concentrations in nearby soils (Zhang et al., 2012; 2013). In addition, particle abrasion from wheels, tracks and pantographs can get metals into aerosols and pollute the wider railway surroundings (Bukowiecki et al., 2007). Cleaning bays and railway sidings are also heavily polluted areas; concentrations of Pb, Cu, Zn, Fe, Cr and Hg in soils could be several times higher than at relatively clean control areas outside study sites (Malawska and Wiłkomirski, 2001).

The main anthropogenic sources of sodium are road salting and fertiliser usage. Concentration of sodium in road runoff water varied from 25 mg L^{-1} up to 10400 mg L^{-1} after consistent application of de-icing salt (Helmreich et al., 2010). Road salt helps to melt the snow and ice on the road surface; it is composed mainly of sodium chloride (NaCl), often with addition of calcium chloride ($CaCl_2$). Alternative compounds were used, for instance calcium-magnesium acetate (CMA), but the cost/efficiency ratio was not optimal in this case (Vitaliano, 1992). High sodium and chloride concentration originating from de-icing salt usage during winter could also increase the mobility of the mentioned metals (Tromp et al., 2012). Intensive use of road salt and consecutive excess of sodium in soil can also cause an ion imbalance and adverse effects on many plants (Moťková et al., 2014).

Material and Methods

Study sites

Soils were taken from two sampling sites. One site was situated 25km north-east from České Budějovice (South Bohemia, Czech Republic) near the České Budějovice – Prague highway "E55" (49°15'97.825"N, 14°64'29.089"E). The daily traffic density ranged between 7.000 and 10.000 vehicles in 2010 (Czech Traffic Survey, 2010). A meadow is located next to the road; the grass is usually mown up to six times per year. Five sampling points were designated at this sampling site in distances of 0, 5, 10, 80 and 100 m from the road. Six soil samples were taken at each point (three surface samples from the depth of 0-15 cm and three from the depth of 15-30 cm) three times in 2014 (April 4, August 8 and November 17). An additional sampling was conducted on February 15, 2015 in order to determine sodium in soil taken near the highway and to investigate the effect of road salting. Second sampling site was situated a few kilometres north-east (49°12'27.622"N, 14°45'6.194"E). It was located near the railway that connects České Budějovice and Brno cities. Four sampling points were designated at this site (at distances of 1.5, 3, 10 and 25 m from the railroad). Samples were taken three times throughout 2014 (April 29, August 10 and October 30) in 2-, 10-, 20- and 30-cm depths. There are two different types of railway ties used at this site: concrete and wooden. The wooden ties can be a potential source of mercury contamination due to their impregnation. Therefore, two batches of soil samples were taken: in the vicinity of concrete and wooden railway ties, respectively. The only possible pollution sources are traffic and agriculture. The sampling sites have not been industrially active.

Sampling and sample pre-treatment

All collected samples were transported to the laboratory, where larger particles, stones and roots were removed. Samples were further processed with slightly modified treatment according to Borůvka et al. (1996) and Száková et al. (2010). The soil was air-dried for 6 hours at 100 °C. From each sample, 8 g of dried soil was mixed with 40 ml of 2M nitric acid (Merck, Darmstadt, Germany) and shaken thoroughly for 24 hours. Mixtures were filtered through Whatman glass microfibre filters (pores size of 1.2 µm) and the extracts were diluted with deionised water to 50 ml volume. Samples were analysed by flame atomic absorption spectrometry (FAAS) and flame photometry in the case of copper and sodium, respectively. A fraction of each raw sample taken at the railway sampling site was dried at room temperature for 7 days. Samples treated in this way were used for direct total mercury determination by an advanced mercury analyser (AMA-254).

Instrumental and determination of analyses

Ultrapure (deionised) water was obtained from a Milli-Q® Gradient A 10 system (Millipore, Billerica, USA). All chemicals used were either of analytical reagent grade or of higher purity. Stock standard solutions (1000 mg/l) of individual metals (Merck, Darmstadt, Germany) were used to prepare calibrating solutions and validate the analytical methods. Quantitative data were obtained based on the calibration curve method. Two certified reference materials [Light Sandy Soil 7001 (Analytika, Prague, Czech Republic) and SPS-WW2 (Spectrapure standards, Oslo, Norway)] were used to determine the accuracy. Precision is expressed as repeatability. Limits of detection (LOD) and quantification (LOQ) were determined on the basis of 3σ and 10σ criteria, respectively. All characteristics of the analytical methods are summarised in Table 1.

Table 1. Characteristics of analytical methods used for determination of individual analytes

Characteristic	Cu	Na	Hg
Accuracy	105.2 %	99.1 %	96.6 %
Repeatability	0.36 %	0.26 %	1.95 %
Linear dynamic range	0.18–10.00 mg dm^{-3}	0.08–2.00 mg dm^{-3}	1.20–200.00 µg kg^{-1}
Limit of detection	0.054 mg dm^{-3}	0.024 mg dm^{-3}	0.360 µg kg^{-1}
Limit of quantification	0.182 mg dm^{-3}	0.080 mg dm^{-3}	1.200 µg kg^{-1}
Sensitivity	0.0540 dm^{-3} mg	0.4910 dm^{-3} mg	0.0022 kg µg^{-1}
Correlation coefficient	0.9994	0.9988	0.9975
Characteristic conc.	0.08 mg dm^{-3}	N/A	2.30 µg kg^{-1}

The analytical methods were always properly optimised and validated. A Thermo Scientific iCE 3500 spectrometer (Thermo Fisher Scientific, Cambridge, United Kingdom) was used for sodium and copper determination. It was operated in the flame atomic absorption spectrometry (an acetylene/air flame) and the flame photometry modes for Cu and Na determination, respectively. Mercury was determined using an advanced mercury analyser (AMA 254, Altec, Prague, Czech Republic).

Results and Discussion

Stagnosol (pseudogley) soil group dominates on the sampling site. The geochemical background concentrations in topsoils vary from 8.7 to 17.5 mg kg^{-1} for copper and from 0.05 to 0.09 mg kg^{-1} for mercury, according to the Geochemical Atlas of Europe. We measured somewhat lower values (20-100m from the highway and railway), because of the dissolving in nitric acid. The total content of metals and their availability heavily depend on many physical and chemical characteristics of soils (soil type, pH, redox potential, amount of minerals, organic material and water). pH of the soil is very important, it is well known that most metals are less available and less mobile in basic soils. And conversely, along with possible acidification of soils and thus with decreasing pH the mobility of metals increases. Measured pH (H_2O) values of our soil samples ranged from 6.48 to 8.46 with average value 7.56, they are not affected with acidification. All samples were dried before analytes determination, the content of water varied from 10.6 % to 14.1 %, Slightly wetter soil samples were found on the second sampling site, but the difference compared to the first sampling site is negligible just as the effect on availability of the Cu, Na and Hg. Different amounts of organic compounds affect the migration of metals and their solubility in water (Smičiklas et al., 2015). Some other studies mentioned positive correlation between organic matter and the sorption of metal cations (Kluge and Wessolek, 2012). Total organic carbon (TOC) determined in our samples was 1.35 ± 0.26 %. Measured values are usual for this soil type.

Determination of copper

All values mentioned in results are expressed as dry matter. The results obtained for copper in soil samples taken close to the highway are given in Figure 1 and 2. Individual lines in these figures show the concentrations obtained for respective sampling dates. The concentration changes in the course of the year bring significant information (the effect of the road salting), therefore mean values were not calculated in this case. According to the Ministry of the Environment of the Czech Republic (1994), the concentration limit of copper in agricultural soils is 50 mg kg^{-1}. The determined values did not exceed the limit. As expected, the highest content of copper was found near the road, most likely due to the traffic. Other authors obtained similar or even higher concentration of copper, especially near very frequent highways, and reported the same conclusions (Zehetner et al., 2009; Kluge and Wessolek, 2012; Zhang et al., 2012). The friction of brakes and moving engine parts as well as other vehicular components could release copper (Davis et al., 2001). The concentration of copper falled down rapidly with the distance from the highway. Back from the road (more than 5 meters), the determined content of copper varied between 4 and 8 mg kg^{-1}. Similar concentration levels were published in other studies as well (Sabiene et al., 2004; Zhang et al., 2012).

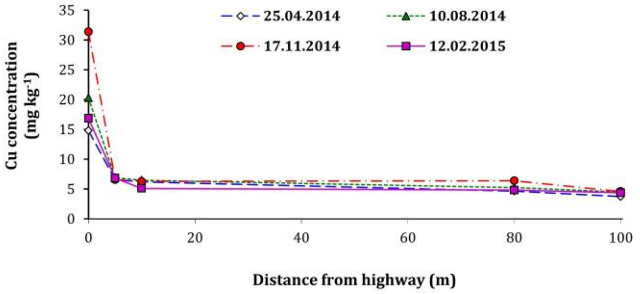

Figure 1. The influence of the distance from the highway on copper concentration in soil (surface samples).

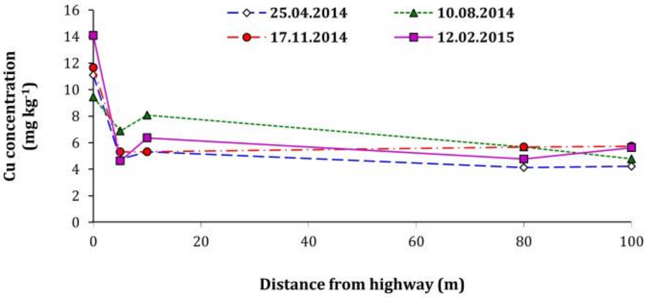

Figure 2. The influence of the distance from the highway on copper concentration in soil (samples from the depth of 15–30cm).

As it is evident from Figure 2, copper also migrates into the deeper (15-30 cm) layer of soil, however, its peak concentration is lower than in the respective surface layer. It supports the presumption that highway traffic has been the source of pollution. Copper content in soil samples taken near the railway reached 52.7 mg kg^{-1} and 25.0 mg kg^{-1} at locations with wooden and concrete ties, respectively. The determined concentrations were up to ten times higher in comparison with a background concentration value (the samples taken farthest from the railroad) and the difference between the highest and the lowest copper concentration measured was more than 50 mg kg^{-1}. The trend is similar to the results obtained for the first location: the concentration of copper decreased sharply with the distance from the railway (Figure 3 and 4). Individual lines in these figures show the average concentrations obtained for respective sampling depths in this case. Significantly higher copper concentration obtained for soil samples taken at the site with wooden ties can be explained as a consequence of the wood impregnation using copper compounds (Reinprecht, 2010).

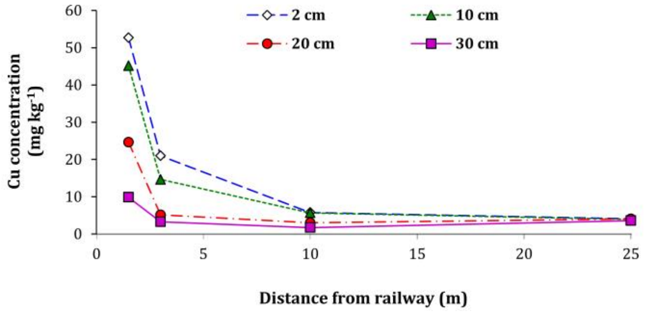

Figure 3. The influence of the distance from the railway on copper concentration (wooden ties used).

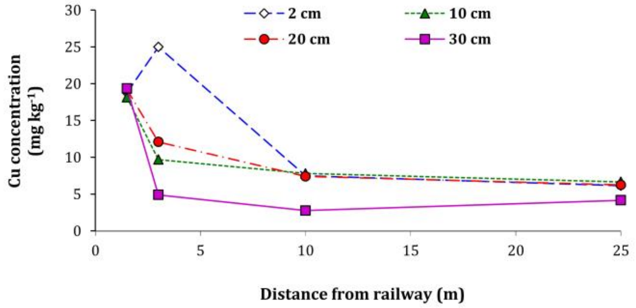

Figure 4. The influence of the distance from the railway on copper concentration (concrete ties used).

Determination of sodium

Sodium concentrations were also significantly higher in soil sampled close to the highway, as shown in Figure 5 and 6. The highest concentration was 770 mg kg^{-1}. The extraction efficiency depends on used extraction agent in the case of sodium as reported by Zehetner et al. (2009), who used the solution of NH_4NO_3 in order to extract sodium from soil sampled near the highway and obtained the maximum concentration of 48 mg/kg only. During winter months, the salt (NaCl) was applied in order to lower melting point of ice and to prevent ice forming on the road surface. Therefore, the sodium concentration in both soil layers was higher in winter and also in spring. During severe winters with extremely low temperatures, snowfalls and ice formation, elevated sodium level could be expected in soils close to the roads due to the extensive road salting. High concentration of sodium results in decreased bioavailability of potassium, calcium and magnesium for plants (Moťková et al., 2014). Sodium content in soils more distant from the road was lower, the determined values ranged from 28.5 to 165.0 mg kg^{-1}. According to the Czech Hydrometeorological Institute (CHMI), the precipitation during the winter period was below average (Czech Hydrometeorological Institute Data, 2014). It can be assumed that more sodium would be found in deeper soil layers in the case of more intensive precipitation. Sodium content in soil samples taken near the railroad was not determined since there is no salting effect in the vicinity of railroad.

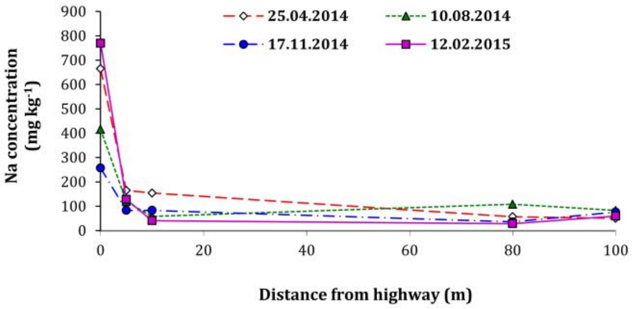

Figure 5. The influence of the distance from the highway on sodium concentration in soil (surface samples).

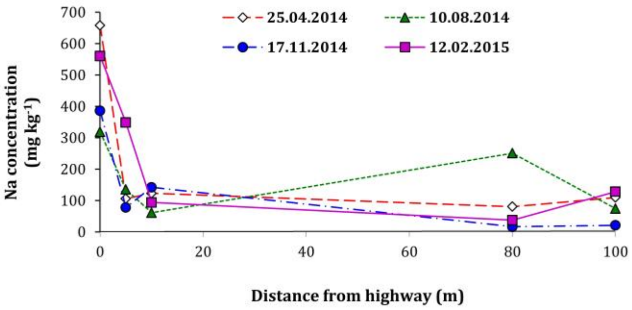

Figure 6. The influence of the distance from the highway on sodium concentration in soil (samples from the depth of 15–30cm)

Determination of mercury

Total mercury concentrations were determined in soil samples taken from the railroad location only. The results obtained for the sampling site situated close to the railway are shown in Figure 7. There is an evident correlation between distance from the railway and total content of mercury in soil. The highest Hg concentration reached 0.181 mg kg^{-1} at distance of 1.5 m from the railway, in the surface sample near the wooden ties. High concentrations of mercury near the railroad indicate that the track bed could be the source of pollution. It is known that railway wooden ties were impregnated using the mercury compounds in order to prevent fungal degradation (Reinprecht, 2010). The lowest mercury concentration (0.017 mg kg^{-1}) was found in the distance of 10 meters from railway, in the depth of 30 cm. The different results were obtained for the location with concrete railway ties (Figure 8). The concentration of mercury slowly increased with the distance from the railway with the highest value of 0.145 mg kg^{-1}. This supports the assumption that the main source of pollution is impregnation of wooden ties (Reinprecht, 2010).

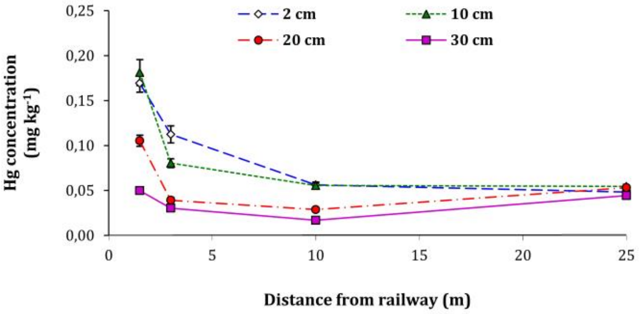

Figure 7. The influence of the distance from the railway on total mercury concentration (wooden ties used).

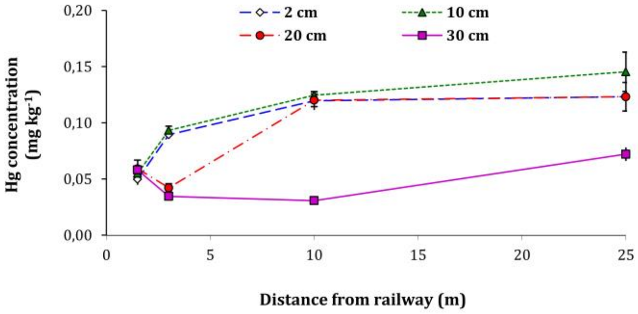

Figure 8. The influence of the distance from the railway on total mercury concentration (concrete ties used).

Conclusion

There is still a lack of available information dealing with concentration of metals in soils near highways and especially near railroads. This study revealed that the wooden railroad ties could be a source of mercury and copper in soils near older railroads since their wooden ties were impregnated with mercury and copper compounds. Another significant aspect of the study is the elucidation of the road salting effect on nearby soils. Along with the strong rise of traffic and road transport, surrounding soils are potentially endangered by increasing salinity. The level of copper concentration in soil depends on the distance of nearby railway or highway as trains, cars and trucks release copper into the environment as well. However, the relatively fast decrease in concentrations of individual contaminants with increasing distance from the highway and railway indicates that the safe distance, e.g. for agricultural production, is approximately 10 m from the source of pollution.

Acknowledgments

The authors are much obliged to Prof. Pavel Kalač for the English revision.

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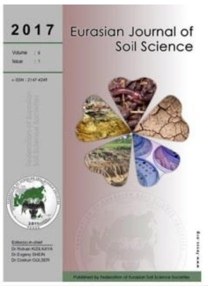

Soil organic matter content and composition in different pedoclimatic zones of Bulgaria

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Abstract

The present paper focused on content, quality and composition of soil organic matter in different pedoclimatic zones of Bulgaria. The country has temperate continental climate with Mediterranean influence. There are six combinations of soil temperature and moisture regimes over the territory of Bulgaria, such as Thermic-Xeric, Mesic-Xeric, Mesic-Ustic, Mesic-Udic, Cryic-Udic and Pergelic – Udic. Typical soil types for Bulgaria are Chernozems, Luvisols. Vertisols, Cambisols, Phaeozems, Leptosols, Regosols, Planosols, Umbrisols and etc. Fifteen soil profiles were studied which are representative for the area. The content and composition of organic matter were determined according to the method of Kononova-Belchikova. The purpose of this study is to determine the influence of pedoclimatic conditions over soil organic matter content and composition of various areas with different soil cover, vegetation, management and etc. Grouping soil types in different soil temperature and moisture regimes shows that there are similarities in soil carbon content and composition. Soils developed under cooler and moister conditions accumulate more organic carbon. In such areas the content of organic carbon can reach about 255 t.ha^{-1} in a surface horizon and the type of humus is predominantly Fulvic. Respectively, soils developed under dry and warmer conditions have lower organic carbon content and the type of humus is usually Humic.

Keywords: Soil organic matter, soil carbon, pedoclimate, soil temperature, moisture regimes

Article Info

Received : 13.05.2016
Accepted : 02.08.2016

Introduction

Soils of Bulgaria are developed in different climatic conditions. The country lies between the strongly contrasting temperate continental and Mediterranean climatic zones. Bulgarian mountains and valleys act as barriers or channels for air masses, causing sharp contrasts in weather over relatively short distances. The continental zone is predominant, because continental air masses flow easily into the unobstructed Danubian plain.

Mediterranean influence is spread manly over south parts of the country (Geography of Bulgaria, 2002). Bulgaria is a country with alternation of contrasting seasons. Soils have an annual heating cycle, becoming warm during the summer and then cool to freezing during the winter. The effect on soil is determined by the rates of chemical and biological reactions and evaporation (Shishkov et al., 2014). Climatic conditions have the main impact on vegetation and crop management, which also has influence over soil organic matter content. Soils have the potential to store carbon, in grassland and forest, and particularly in peatlands, through the removal of carbon dioxide during photosynthesis. Soils contain a stock of carbon that is about

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284267

twice as large as that in the atmosphere and about three times that in vegetation (Smith et al., 2008). The content of organic carbon in soils is increasingly important topic in recent years in relation to climate change, greenhouse gas emissions associated with carbon emissions into the atmosphere.

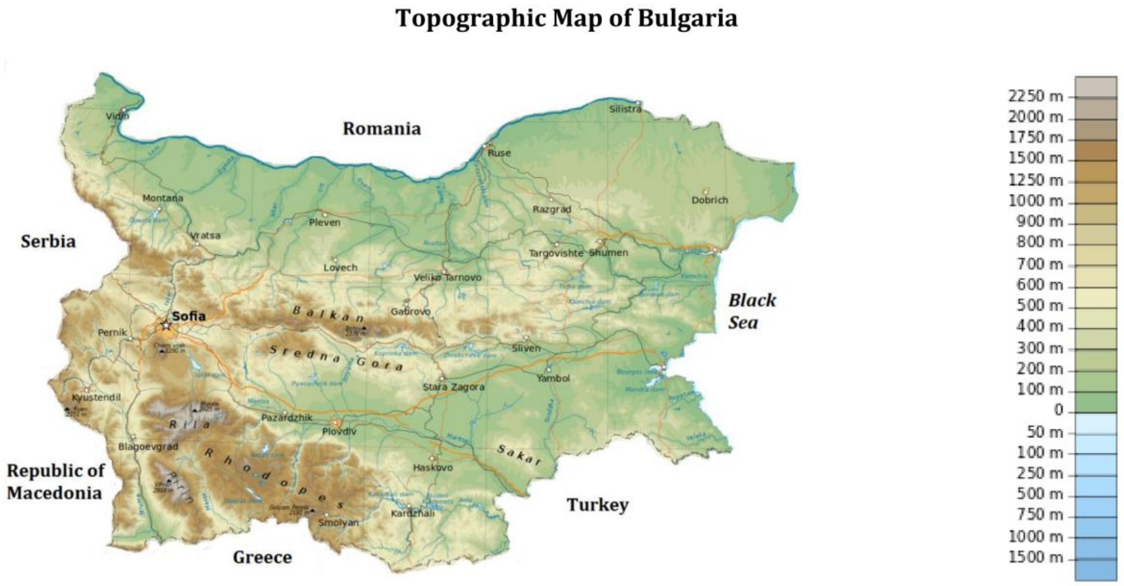

Figure 1. Topographic map of Bulgaria
(https://commons.wikimedia.org/wiki/User:Ikonact)

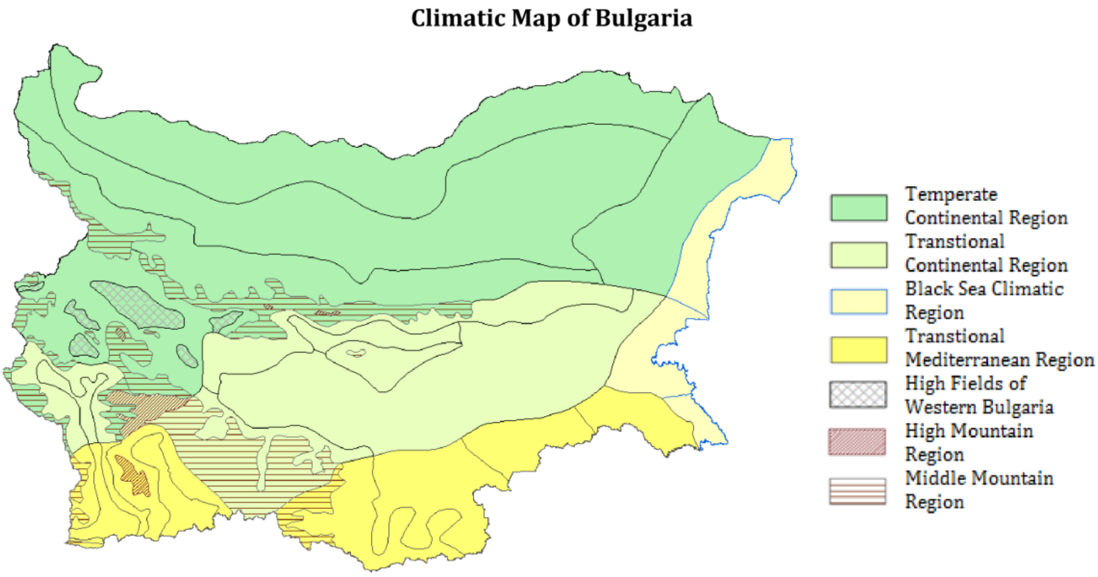

Figure 2. Climatic map of Bulgaria. (Subev et al. (1963) digitized by Dimitrov (2014))

Now we are talking about sequestration of carbon from the atmosphere and holding in the soil to avoid the negative consequences of climate change. The climate is one of the major driving force of soil formation and accumulation of organic carbon (Constatini et al., 2013). Soil climate regimes, expressed via soil moisture and soil temperature regimes, are important in a wide range of applications as soil quality, farming, and ecosystem management. Soils themselves may respond to climate change, leading to both positive and negative effects. Organic carbon in soils is also sensitive to climate change, because this is an interaction between vegetation, climate and parent materials. Soil organic matter is one open dynamic system which is permanently renovated and humus is always in thermodynamic equilibrium with the environmental conditions (Schnitzer and Khan, 1972; Stevenson 1994; Orlov, 1985; Krastanov et al., 2003; Filcheva, 2015). The amounts of soil organic C depend on the relative temperature sensitivities of productivity and soil organic matter decomposition rate. Equations for the temperature dependence of net primary productivity have been widely used, but the temperature dependence of decomposition rate is less clear (Kirschbaum, 1995).

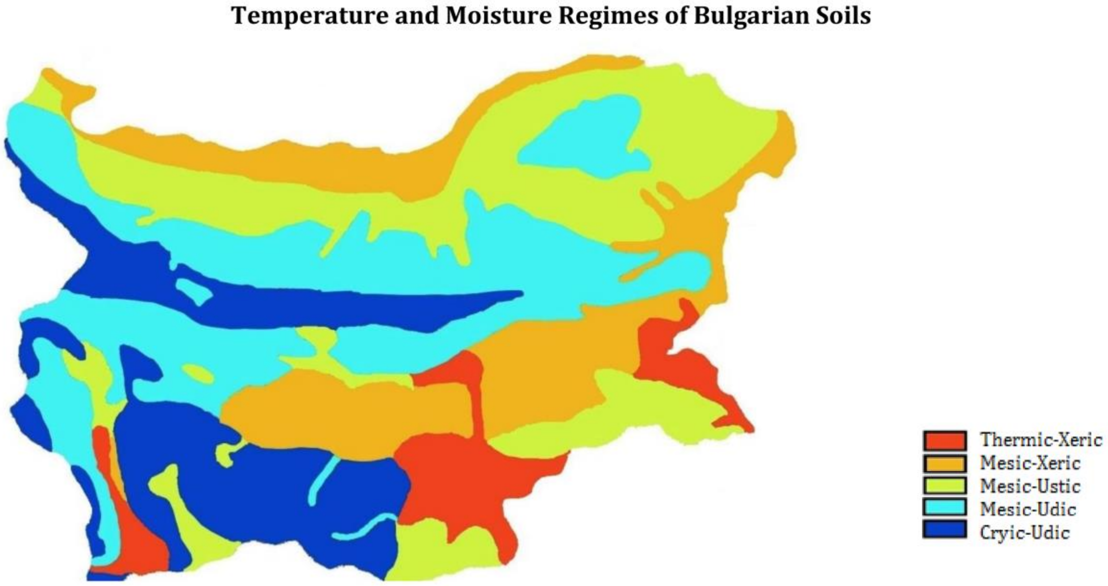

Figure 3. Temperature and moisture regimes of Bulgarian soils. (Boyadjiev, 1989)

The aim of this paper is to focus on influence of different pedoclimatic conditions on soil organic matter content and composition of various areas with different vegetation, management and etc.

Material and Methods

Five climatic regions are typical for the territory of Bulgaria (Figure 2) – Temperate continental, Transitional continental, Transitional Mediterranean, Black Sea coast, and Mountainous (Subev et al, 1963; Dimitrov, 2014). All these climatic regions have influence over soil temperature and moisture regimes as defined in Soil Taxonomy (Soil Survey Staff, 1999, 2010; FAO, 2006). Boyadjiev (1989) applied the model of Newhall (1972) and identified six different combinations of temperature and moisture regimes over the territory of Bulgaria (Figure 3): Thermic-Xeric, Mesic-Xeric, Mesic-Ustic, Mesic-Udic, Cryic-Udic and Pergelic – Udic. The last one Pergelic - Udic is too small and it is united with Cryic - Udic zone, which is spread mainly on mountainous area of Bulgaria. The Mesic – Udic zone is cover the area of fore-mountains, high fields of central and western Bulgaria and the region of "Ludogorie" of North-East Bulgaria. Soils with Mesic – Ustic regime cover also some regions with lower hilly-mountain relief in South and West Bulgaria. Mesic - Xeric and Thermic- Xeric zones are spread over the lowest and most dry places of Bulgaria, the first one covers northern parts the second one is in the south parts of Bulgaria.

In all these pedoclimatic zones of Bulgaria, typical soil profiles data would be given according to specific soil group of WRB (2014).

Soil organic matter composition was determined by the method of Kononova-Belchikova (Kononova, 1966; Filcheva and Tsadilas, 2002).Total humic and fulvic acids (Cextr.) after extraction with mixed solution of 0.1M $Na_4P_2O_7$ and 0.1 M NaOH; "free" and R_2O_3 bounded humic and fulvic acids (C_{NaOH}) after extraction with 0.1 M NaOH and the most dynamic, low molecular fraction of organic matter, so called "aggressive" fulvic acids fraction – 1^a extracted with 0.05 M H_2SO_4, ratio soil:solution=1:20 for the three extractions. Humic and fulvic acids in both extracts C_{extr}. and C_{NaOH} were separated by acidifying the solution with sulfuric acid (0.5 M).

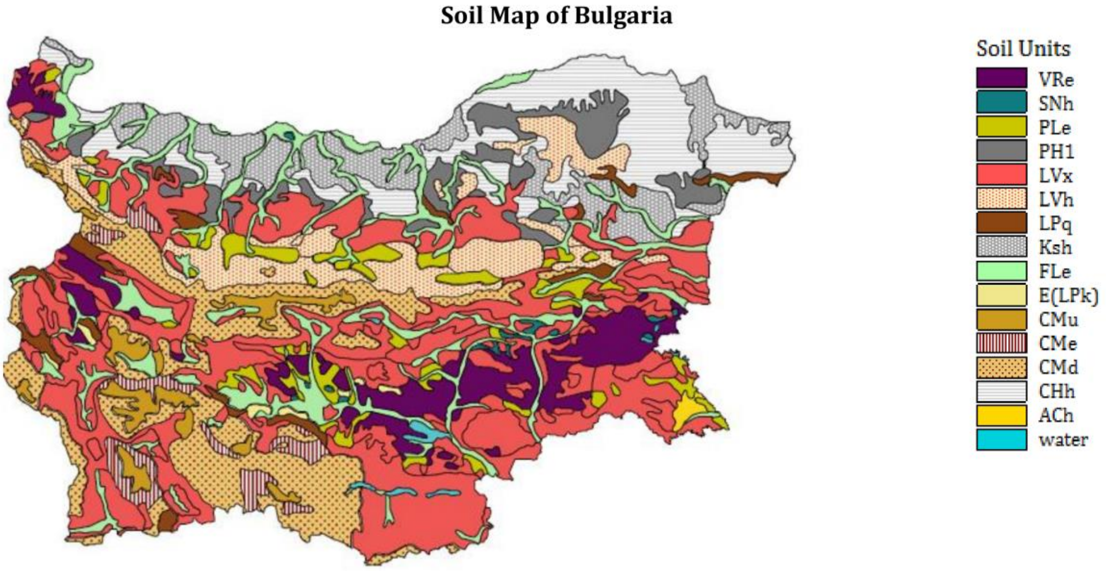

Figure 4. Soil map of Bulgaria. (Kolchakov, 1994), (Soil Units: VRe - Eutric Vertisols; SNh - Haplic Solonetz; PLe - Eutric Planosols; PHl - Luvic Phaeozems; LVx - Chromic Luvisols; LVh - Haplic Luvisols; LPq - Lithic Leptosols; KSh - Haplic Kastanozems; FLe - Eutric Fluvisols ; LPk - Rendzic Leptosols ; CMu - Humic Cambisols; CMe - Eutric Cambisols ; CMd - Dystric Cambisols; CHh - Haplic Chernozems; ACh - Haplic Acrisols)

Results and Discussion

1. Cryic – Udic

About 13 % of the territory of Bulgaria has mountainous relief higher than 1000 m above sea level, which is typical for Balkan region (Geography of Bulgaria, 2002). Cryic – Udic is typical soil temperature and moisture regime for high mountains of Bulgaria, because the temperature is low and soils are almost always wet (Figure 3). Typical soil types here are Umbrisols, Leptosols and Cambisols, according to soil map of Bulgaria (Figure 4). Well known fact is that Umbrisols are soils with a surface accumulation of organic matter with shallow depth, spread in the highest alpine parts of the mountains. The influence of the climate on soil formation is strong because of high humidity, low annual temperature - about 0°C, and annual precipitation sums of about 900 – 1000 mm. The organic matter content is high 8–19 % in surface horizon (Shishkov et al., 2014, Andreeva, 2014). According to Artinova (2014) the area of Leptic Umbrisols is about 140 000 ha and organic matter stocks are about 255 t.ha^{-1} in a surface horizon.

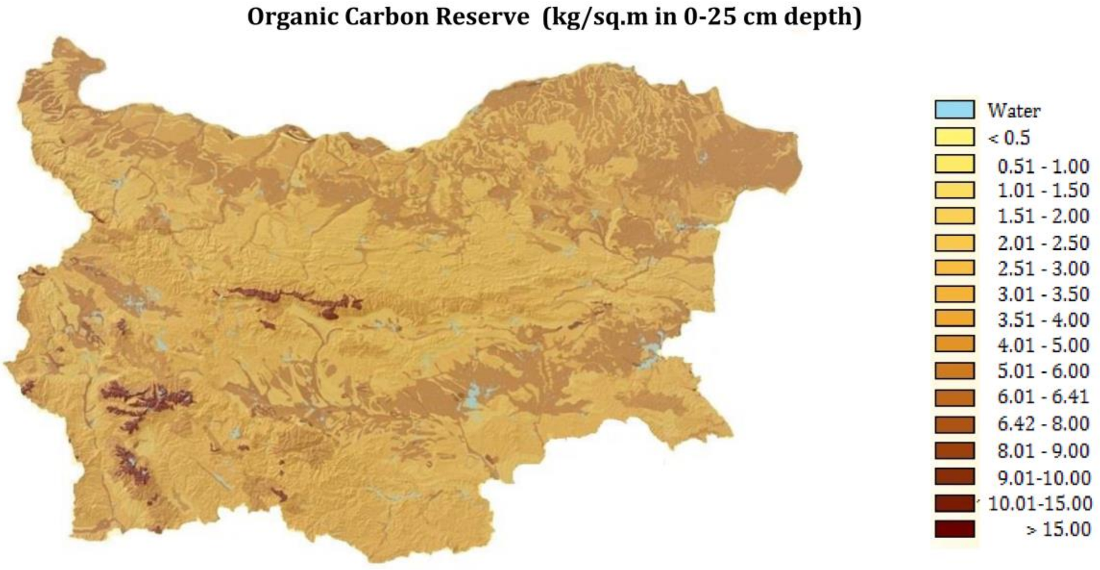

Figure 5. Organic carbon reserve 0 – 25 cm depth of Bulgarian soils. (Filcheva, 2014)

Fulvic acids prevail in the humus composition (Table 1). The type of humus is Fulvic – Humic (Ch/Cf 1 – 1.5) and in the alpine parts is Fulvic (Ch/Cf < 0.5). Fulvic acids are characterized by low molecule condensation. Some amounts of Humic acids may occur at the top of the soil, they are represented by "free" and Humic acids bound with R_2O_3 (Filcheva, 2015). The carbon stocks may exceed 15 kg/m^2 in 0 – 25 cm layer (Figure 6) and the degree of humification is high 20 – 27 % (Artinova, 2014). Other soil types Cambisols and Leptosols have similar properties, especially soils with Umbric horizons, but the organic matter could be lower.

Table 1. Organic matter of Umbrisol, Cambisol and Leptosol with Cryic – Udic regime (* - % of the total organic carbon, **- % of the total HA)

Horizon, Depth cm	Total Carbon (C) %	Org. Carbon% -Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			"Free" Humic acids % or bound with R_2O_3, **	Humic acids % bound with Calcium (Ca^{+2}), **	Ch/Cf
		Total (%), *	Humic acids (%), *	Fulvic acids (%), *			
Profile 1. Haplic Umbrisols – Artinova et al. (1985) (Stara planina- mountain. 1400m.)							
Ah 0-19	9.15	59.25	32.33	26.91	100	0	1.2
A2 19-36	7.22	67.11	38.99	28.32	98.49	1.51	1.37
Profile 2. Umbric Cambisols – Artinova et al. (1985) (Stara planina- mountain, 1400m.)							
Ah 0 – 20	4.33	56.97	21.07	35.89	100	0	0.58
Bw1 20–48	1.85	66.87	9.98	57.63	100	0	0.16
Bw2 48-58	0.94	61.79	6.88	54.91	-	-	0.12
Profile 3. Umbric Leptosols – (M8-1) Andreeva (2014) (Vitosha mountain, 2290m.)							
Ah 0 – 20	10.1	94.06	34.95	59.10	100	0	0.59

2. Mesic – Udic

Mesic – Udic pedoclimatic zone is spread mainly over foremoutain area, high fields of central and western Bulgaria and Ludogorie region. Typical for these regions: they are covered with forest and the relief is hilly-mountainous. The main soil types for that zone are Cambisols, Planosols, Stagnosols, Luvisols, Leptosols and Phaeozems that cover the region of Ludogorie. The area is covered manly with forest, the belt of beech form 800 m to 1500 m and oak forests from 0 – 800 m altitude. Cambisols are the main soil type under forest and on the slope deluvial terrains.

Table 2. Organic matter of Cambisol, Palnosol and Luviosol with Mesic – Udic regime (* - % of the total organic carbon, ** - % of the total HA).

Horizon, Depth cm	Total Carbon (C) %	Org. Carbon% -Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			Free Humic acids % or bound with R_2O_3, **	Humic acids % bound with Calcium (Ca^{+2}), **	Ch/Cf
		Total (%), *	Humic acids (%), *	Fulvic acids (%), *			
Profile 4. Haplic Cambisol –Shishkov et al. (2015) (Sredna gora – mountain, 520 m)							
Ah 0-10	1.83	44.26	19.67	24.59	100.00	0.00	0.80
A2 10 – 30	1.99	35.18	15.07	20.11	70.00	30.00	0.75
Bw1 30– 35	1.21	34.13	15.87	18.26	65.00	35.00	0.87
Bw2 35– 45	0.91	31.87	14.29	17.58	0	100.00	0.81
C1 55-70	0.67	37.31	17.91	19.4	0	100.00	0.92
Profile 5. Luvic Planosol - Hadjiyanakiev et. al. (1981) (village of Zlatosel – 350 m)							
AE 0 – 10	0.70	48.39	20.77	27.65	83.08	16.95	0.75
E 10 – 28	0.28	52.20	18.62	33.92	100.00	0.00	0.56
Btg1 40-55	0.18	53.46	21.76	33.70	13.59	84.41	0.68
Btg1 55-73	0.18	52.22	5.00	44.22	0.00	100	0.1
Btg1 73-96	0.20	46.76	4.83	41.92	0.00	100	0.12
Prfofie 6. Haplic Luvisol - Shishkov et al. (2015) (Hisarya , 350 m)							
Ah 0-20	0.86	36.05	14.44	0.94	0.0	100.0	0.94
Bt1 20 –40	0.48	29.17	25.00	6.00	0.0	100.0	6.00
Bt2 40– 60	0.36	38.89	0	-	0.0	0.00	-
Bt3 60 –80	0.31	32.26	0	-	0.0	0.00	-
BC 80 -100	0.21	38.09	0	-	0.0	0.00	-

Because of forest vegetation biological activity is intensive in the topsoil. Humus accumulation occurs in the horizon beneath the litter. The dark brown color is due to the presence of Fulvic acids and/or brown colored Humic acids (Shishkov et al., 2014). The content of organic matter sharply decreases with the increasing of soil depth (Table 2). Humus content in surface could be very high in pre-alpine area and a few times lower in deciduous forest 400 – 800 m. This is the reason that the organic carbon content varies widely. Typically in soils developed under forest the Fulvic acids prevail over Humic acids (Profile 4), the type of humus is humic-Fulvic and the ratio Ch/Cf is 0.5 – 1. The degree of humification is moderately low and the Humic acids are “free” or bound with R_2O_3 (Filcheva, 2015; Hristov et al., 2016) in the surface horizon.

In the lower parts of the mountains, mainly under deciduous forest Planosols and Luvisols are spread. Planosols have one of the lowest content of organic matter in the country (Artinova, 1978). Soil formation proceeds under the influence of acid plant residues from forests and seasonal waterlogging caused by the surface stagnating waters. Soil formation consisted of some pseudo-gley formation processes as, waterlogging, leaching, and clay formation (Koinov et al., 1998). Average organic matter content is about 1 - 1.5 % in cultivated soils, up to 2 % in forest soils. The organic matter stocks in the one-meter layer do not exceeds 2 t.ha^{-1} in uncultivated lands and 1-1.5 t.ha^{-1} in agricultural areas (Koinov et al., 1998). Fulvic acids (Cf) are presented in significant quantities, which determine the very low Ch/Cf ratio. The humus type is Humic-Fulvic or Fulvic along the soil profile depth (Ch/Cf 1-0.5 or <0.5).

Most wide spread soil type of Bulgaria is Luvisol with area of 33 % from the territory of the state. These soils usually occupy uplands on the plains, elevated sites in the valleys, and the foot slopes of mountains with elevation below 700 m. Luvisols have shallow profile about 90 cm, and typical for them clay enriched luvic horizon. The content of carbon is low in the surface horizon about 0.7 – 1.5 % and decreases sharply in depth. The type of humus is Fulvic – Humic (Ch/Cf 1.5 – 1.0) and under forest usually is Humic – Fulvic (1.0 – 0.5). Dilkova et al. (1998) found that the ratios Ch/Cf of surface waterlogged layers (A, A_1A_2, A_{2l}) of Planosols and Luvisols increase with degree of surface waterlogging of these soils. The degree of humification is high in A horizon (about 25 %) (Filcheva, 2015).

3. Mesic – Ustic regime.

Mesic – Ustic zone covers the middle hilly part of Danubian plain and some high fields, hills, and low mountains in South Bulgaria. Main soil types are Phaeozems and Chernozems in Danubian plain and Luvisols in the south. Phaeozems and Chernozems are the most productive and fertile soil in all over the world. The so called “Corn belt” of Europe is crossing at that longitude.

Table 3. Organic matter of Phaeozem, Haplic Chernozme and Luvisol with Mesic – Ustic regime (* - % of the total organic carbon, ** - % of the total HA).

Horizon, Depth cm	Total Carbon (C) %	Org. Carbon% -Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			Free Humic acids % or bound with R_2O_3, **	Humic acids % bound with Calcium (Ca^{+2}), **	Ch/Cf
		Total (%), *	Humic acids (%), *	Fulvic acids (%), *			
Profile 7 . Luvic Phaeozem - Hadjiyanakiev et. al. (1981) (v. of Grivitza 256m.)							
Ah 0-12	2.62	50.22	20.09	30.12	38.73	61.27	0.66
A2 12 – 35	0.78	61.04	24.05	36.98	12.52	87.48	0.65
ABt 35 – 65	0.8	31.98	10.03	21.95	0	100	0.45
Bt1 65 – 95	0.4	53.54	37.97	21.56	0	100	1.48
Bt2 95 -130	0.25	55.59	20.71	35.28	0	100	0.58
Ck 130 -	0.29	34.53	14.71	19.81	0	100	0.74
Profile 8. Haplic Chernozem – Artinova (1989) (Dobrich, 240m)							
A1 0 – 17	2.28	43.4	23.6	19.8	24.6	75.4	1.2
A2 17 – 37	1.16	40.1	22.4	17.7	0	100	1.3
AB 37 – 60	0.95	47.6	27.0	20.6	0	100	1.3
AB 60 – 83	0.58	49.8	29.0	21.0	0	100	1.4
BC 83-95	0.52	49.2	29.2	20.0	0	100	1.5
Profile 9. Haplic Luvisol - Hadjiyanakiev et. al. (1981) (v. of Bohot 256m.)							
Ah 0 – 15	1.61	48.9	21.8	27.1	75	25	0.8
A1 15 - 40	0.92	43.5	17.1	26.4	75	25	0.65
Bt1 40 - 55	0.49	53.5	12.1	41.4	67	33	0.3

Phaeozems in North Bulgaria occupy about 200 000 ha and they are located on the North-Western part and Ludogorie plateau or approximately 1.79 % of the entire territory of the country. The typical distinguishing features are humus accumulation, deep carbonate leaching (below 120–250 cm), low differentiation of clay, low compaction pronounce, and high biological activity, especially of earthworms (Shishkov et al. 2014).

Usually soil organic matter content in (A) horizon is 2.0–4.5 %. Humic acids prevail over Fulvic acids and they are bounded with calcium whch makes them stable (Table 3, Profile 7). The stocks of organic matter in a 100 cm layer is 200–300 t.ha^{-1}, however, it is about 200–250 t.ha^{-1} in the arable lands (Filcheva et al. 2002). These soils are characterized with high degree of humification and the type of humus in surface horizons is Humic – Fulvic (Ch/Cf 1.0 – 0.5) or even Fulvic (Ch/Cf <0.5) in depth. Manly in (A) horizon there are some "free" and more Humic acids bound with calcium. Other most valuable (fertile) soils in Bulgaria are Chernozems. They are spread over the larger part of the Danubian Plain, Dobrudja and Ludogorie plateau. Chernozems occupy about 2 250 000 ha or 20 % of the territory of the entire country (Koinov et al., 1998). They are formed in climatic zones with annual precipitation of 450–600 mm, with maximum of precipitation in spring and early summer, cold winters, and relatively hot summers. In the colder areas of these climatic zones, natural grass vegetation develops on soil profiles. Carbonates may accumulate below this layer because of limited downward percolation of calcium salts and in Bulgaria they are developed over loess parent material. Chernozems are characterized by a surface layer that is rich in humus and in available calcium ions bound to soil particles, resulting in a well-aggregated structure with abundant natural grass vegetation. In the south part of Danibian plain Leached Chernozems (Haplic Chernozems) are the most typical soil type with territory of about 850 000 ha. The thickness of the Leached Chernozem is 80–120 cm, and the thickness of the humus horizon (A + AB) is 50–80 cm. The organic carbon content is from 2.3 to 0.5 % at the upper part of the humus horizon and gradually decreases downwards (Table 3, Profile 8). Soil organic matter stocks in whole profile are about 200 t.ha^{-1} and 80 t.ha^{-1} in A horizon (Artinova, 2014). The Humic acids prevail over Fulvic acids (Ch/Cf 1.0 – 1.5) and the type of humus is Fulvic-Humic. Usually the Humic acids are bound with calcium.

In the southern part of Danubian plain mainly under forest vegetation Luvisols are also spread.

The Luvisols (Grey forest soils, Koinov et al., 1963; Penkov et al., 1992) from north Bulgaria occupy the area of 1.6 million ha or 14.5 % of the state (Koinov et al., 1998). These soils are formed on loesslike materials, carbonate moraines, and other parent materials that are usually rich in calcium and an elutriate water regime. The movement of humates of potassium from the top horizons to deeper ones and precipitation on the surface of structural partings in the form of humus films are especially typical of gray forest soils. The soil organic matter content is about 1.5 – 2 % in cultivated lands and 2- 3 % in the natural soils. The humus stocks are 180 – 250 t.ha^{-1} in 1 m depth. The type of humus is Humic – Fulvic (Ch/Ch 1. 0 – 0.5) which is typical for Luvisols and 75 – 67 % of the Humic acids are "free" or bound with R_2O_3 (Table 3, Profile 9).

4. Mesic – Xeric regime.

The lower parts of Danubian plain and the bigger part of Upper Thrace Valley have Mesic- Xeric soil temperature and moisture regime. This area is spread over the watersheds of the biggest rivers in Bulgaria, Danube and Maritsa, where the main soil types are Fluvisols, Vertisols and Calcic Chernozems (Kastanozems).

Calcic Chernozems are distributed immediately to the south of the Danube River, mainly in the Lom - Svishtov soil- geographical province on calcareous loess. They occupy about 5 million ha. WRB (2014) has allowed that some soils that have a Mollic horizon can be referred to Kastanozems in semi-arid climate conditions. There is discussion about whether Kastanozens can be morphologically identified where Calcic Chernozems occur (Shishkov, 1998). Compared with other Chernozems generally they are shallow and the organic carbon content is lower (Table 4, Profile 10). Content of humus varies from 2.0 to 4.2 % on the upper part of humus horizon, decreases by 18-20 % compared to uncultivated soils and in recent years is it range from 1.5 to 2.1 %. Organic matter stocks are from 250 to 400 t.ha-^{1} to a depth of 100 cm (Filcheva et al., 2002). The type of humus is Fulvic – Humic or Humic (Ch/Cf 1.0 – 1.5 or >1.5). The Humic acids are stable and 100 % bound with calcium.

Vertisols are distributed mainly in southern Bulgaria and occupies 600 000 ha or about 5.34 % of the entire country's territory (Koinov et al., 1998). They are most commonly formed in warm, subhumid or semi-arid climates, where the natural vegetation is predominantly grass. Two climatic regions are associated with the distribution of Vertisols in Bulgaria. The first is confined to the transitional continental climatic zone with Mediterranean influence in the Thracian Lowland. The second region is confined to the transitional continental zone in Western Bulgaria (Shishkov et al., 2014). Vertisols are usually very dark in color, with widely variable organic matter content (1 – 6 %). They typically form on Calcium and Magnesium rich materials such as limestone, basalt, or in areas of topographic depressions that collect these elements leached from uplands.

Table 4. Organic matter of Calcic Chernozme, Vertisol and Fluvisol with Mesic – Xeric regime (* - % of the total organic carbon, ** - % of the total HA).

Horizon, Depth cm	Total Carbon (C) %	Org. Carbon% -Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			Free Humic acids % or bound with R_2O_3, **	Humic acids % bound with Calcium (Ca+2), **	Ch/Cf
		Total (%), *	Humic acids (%), *	Fulvic acids (%), *			
Profile 10. Calcic Chernozem – Artinova (1989) (dis. V. Turnovo, 150m)							
Ak 0 – 23	1.93	25.1	14.7	10.4	0	100	1.4
Ak2 23 -38	1.21	24.5	15.3	9.2	0	100	1.6
ABk 38 – 60	0.87	30.1	16.4	13.7	0	100	1.2
BCk 60 – 84	0.55	26.7	13.6	13.1	0	100	1.0
Profile 11. Haplic Vertisol – Teoharov et al. (2007) (v. Choba, Plovdiv, 180m)							
Ap 0 – 22	2.44	17.37	13.37	3.99	0	100	3.35
AB 44 - 72	0.73	26.17	24.89	1.28	0	100	19.48
Bk 72 – 105	1.03	16.11	12.61	3.50	0	100	3.6
BCk 105-135	0.48	19.09	10.52	8.56	0	100	1.23
Profile 12. Haplic Fluvisol – Mihailov (1988) (town of Belene, 25 m)							
Ap 0 - 25	0.54	46.3	29.63	16.67	0	100	1.78
C1 25 – 50	0.49	44.9	32.65	12.24	0	100	2.67
C2 50 – 70	0.38	42.11	26.35	15.79	0	100	1.67

Humus stocks for uncultivated lands in surface horizon is about 115 t.ha^{-1} and 313 t.ha^{-1} for whole profile (Artinova, 2014), the type of humus is Humic or Fulvic-Humic (Ch/Cf > 1.5 or 1.0 – 1.5). Humic acids are bound with calcium (100 %) and the degree of humification is very high, with high condensation of aromatic nuclei (Filcheva, 2015).

Fluvisols could be found on alluvial plains, river fans, valleys and tidal marshes on all parts of Bulgaria and in all climatic zones. Under natural conditions periodical flooding is fairly common. In Bulgaria typical areas of occurrence are in the Thracian Lowland and Danubian plain. They are occupy 6.53 % of the state or 730 000 ha. Fluvisols have a clear evidence of stratification. Soil horizons are weakly developed, but a distinct topsoil horizon may be present. These soils exhibit a stratified profile that reflects their depositional history or an irregular layering of humus and mineral sediments in which the content of organic carbon decreases with depth. Fluvisols are characterized by a low stock of nutrient elements (Shishkov et al., 2014). Soils are poor in organic carbon content under 1 % (Profile 12). The type of humus is Humic (Ch/Cf > 1.5). Humic acids are bound with calcium (100 %) and have high condensation of aromatic nuclei and the degree of humification is very high.

5. Thermic – Xeric regime

The driest and warmest pedoclimatic regime in Bulgaria with subtropical influence occupies the south border parts of the state. The climate is formed under the influence of transformed tropical air masses and those of the temperate latitudes. The average annual temperature is 13° C - 13,5° C. Rainfall regime - autumn-winter maximum and summer-minimum - is typical for Mediterranean climate. Dry period is not so long and the maximum and minimum rainfall is less presented. Annual rainfall amounts between 500-600 mm. The main soil types for these regions are Vertisols, Luvisols, Cambisols, Regosols and Leptosols.

Vertisols in that region have similar properties as those with Mesic- Xeric temperature and moisture regime.

Cinnamonic forest soil of South Bulgaria is the main soil type (Koinov et al., 1963). In the geographic distribution, these soils are found in elevated areas, where the level of ground water is of considerable depth. Meadow soil varieties occur near the river valleys and old terraces (Shishkov et al., 2014). According WRB (2014) Cinnamonic forest soil could be classified as Cambisols with cambic horizon, Luvisols if they have argic horizon and even Leptosols when they are shallow. Chromic Cambisols and Chormic Luvisols are spread over calcareous materials and they occupy area about 12 000 ha. The content of organic carbon in A horizon range usually from 0.9 % to 1.35 %. The organic matter stocks vary 72 t.ha^{-1}, in the surface horizon to 144 t.ha^{-1} for the whole profile (Artinova, 2014). The Humic acids in profile 14 totally dominate over Fulvic acids and the type of humus is humic. Expectable the degree of humification is high and Humic acids are 100 % bound with calcium.

Table 5. Organic matter of Vertisols, Cambisols and Regosols with Thermic – Xeric regime (* - % of the total organic carbon, ** - % of the total HA).

Horizon, Depth cm	Total Carbon (C) %	Org. Carbon% -Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			Free Humic acids % or bound with R_2O_3, **	Humic acids % bound with Calcium (Ca^{+2}), **	Ch/Cf
		Total (%), *	Humic acids (%), *	Fulvic acids (%), *			
Profile 13. Haplic Vertisol – Artinova (2014), (v. Yastrebovo, S. Zagora, 168m)							
A1 0 – 20	2.79	48.6	28.8	19.8	0	100	1.50
A2 20 -39	1.86	46.8	28.4	18.4	0	100	1.50
A3 39 – 65	1.10	46.8	29.4	17.4	0	100	1.70
AC 65 – 89	0.86	44.3	28.1	16.2	0	100	1.7
C1 89 – 106	0.28	40.0	19.1	20.9	0	100	0.9
Profile 14. Calcaric Cambisol - Dialo (1995), (v. Sklave, dis. Blagoevgrad, 183m)							
Akf 0 - 4	0.62	43.55	37.09	0.04	0	100	5.75
Ak 4- 15	0.46	26.8	26.08	0.0	0	100	-
Bwk 15 40	0.16	25.0	0.0	0.04	0	0	-
Ck 40 60	0.11	-	-	-	-	-	-
Profile 15. Calcaric Regosol – Teoharov et al. (2007), (v. Vinogradi, dis. Blagoevgrad, 391m)							
Ak 0 - 17	0.51	39.22	17.65	21.57	0	100	0.82
ACk 17 – 30	0.21	42.86	0	42.86	-	-	
Ck 30 – 50	0.09	33.33	0	33.33	-	-	

Regosols are spread in the valley of rivers and in the downslopes of the mountains in South Bulgaria. They are extensive in eroding lands, in particular in arid and semi-arid areas and in mountain regions. The area of Regosols has increased with time, mainly due to improper use of the land. Erosion of the soil is a common occurrence in southern hilly regions. Regosols are spread mainly over steep slopes, which is the reason for bad soil water regime. As a result of soil erosion the total amount nutrients is reduced and organic carbon content is low. The quantity of organic carbon in the surface horizons is under 0.60 %, and decreases in depth (profile 15). Usually Humic acids are bound 100 % with calcium. Soil organic matter composition shows that Humic and Fulvic acids are almost equal. The ratio Ch/Cf in the surface horizon is 0.82, which indicates the Humic-Fulvic type of humus.

Conclusion

Grouping soil types in five soil temperature and moisture regimes shows that there are similarities in soil carbon content and composition. Soils developed under more cool and moist condition accumulate more organic carbon especially soils with Cryic – Udic regime where carbon stocks is about 255 t.ha^{-1} in the surface horizon. Contrary soils developed under Thermic – Xeric regime have the lowest organic carbon content. The same is with "free" humic acids bound with R_2O_3, which are more in soils with more cool and wet pedoclimate. Soils with dry Mesic – Xeric and Thermic- Xeric regime are 100 % bound with calcium. The type of humus depends mainly from different vegetation over soils. However soils with dry and warm regime have Humic or Fulvic-Humic type of humus (Ch/Cf >1.5 or 1.0 – 1.5). Soils with Cryic – Udic and Mesic – Udic regime usually have Fulvic or Humic - Fulvic type of humus (Ch/Cf<0.5 or 1.0 – 0.5).

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Eurasian Journal of Soil Science

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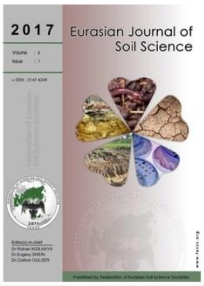

Optimizing land use pattern to reduce soil erosion

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Abstract

Soil erosion hazard is one of the main problems can affect ecological balance in watersheds. This study aimed to determine the optimal use of land to reduce erosion and increase the resident's income of Qushchi watershed in West Azerbaijan province, Iran. Income and expenses for the current land uses were calculated with field studies. Damages resulting from the soil erosion were estimated by soil depth equal to the specified land uses. For three different options including the current status of land uses without and with land management, and the standard status of land uses, multi-objective linear programming model was established by LINGO software. Then the optimization problem of the land use was solved by simplex method. Finally, the best option of land use was determined by comparing erosion rate and its cost in each scenario. Then the circumstances and the recommended conditions were compared. The results indicated that the current surface area of current land uses is not suitable to reduce erosion and increase income of residents and should change in the optimum conditions. At the optimum level, there should change horticulture area of 408 to 507 (ha), irrigated land area of 169 to 136 (ha) and dry farming of 636 to 570 (ha), while conversion of rangeland area not indispensable. In addition, the results showed that in case of the optimization of land use, soil erosion and the profitability of the whole area will decrease 0.75% and increase 3.68%, respectively. In case of land management practices, soil erosion will decrease 42.27% and the profitability increase 21.39% while in the standard conditions, soil erosion will decrease 60.95% and profitability will increase 24.20%. The results of the sensitivity analysis showed that the changes in the horticulture and range land areas have the greatest impact on the increasing profitability and reducing soil erosion of Qushchi watershed. So, it is recommended using Education and Extension to promote the importance of land management to understand how proper use of the land.

Article Info

Received : 14.05.2016
Accepted : 26.08.2016

Keywords: Linear programming, land management, soil erosion sensitivity analysis, profitability

Introduction

Sustainability of the agriculture and natural resources are known as an ecological phenomenon that is in relation to the average income security of the society and relies on the stability of renewable sources (Shively and Coxhead, 2004). The proper management of watersheds to achieve sustainability and most profitable is land use optimization using linear programming and geographic information systems considering conflicting views on the utilization of the earth's limited resources (Riedel, 2003). Although some researchers thought that finalizing dominant economic options should consider ecosystem sustainability and social issues (Pfaff and Sanchez, 2004) some others believe that the economic

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284269

development of many communities is based on proper land use planning with economic respects (Pasour, 1983). The use of different optimization methods have been developed whereby most immersive and reasonable management actions associated with them so that spatial distribution of agricultural land in order to maximize profits modeled (Rounsevell et al., 2003). Both linear and nonlinear programming to optimize and achieve higher profits of land also used (Benli and Kodal, 2003). They resulted that the use of non-linear programming to maximize profits on agricultural land due to water restrictions is more suitable. Increasing of agricultural lands and forests productivity due to proper allocation of land to different uses was approved (Tra and Egashira, 2004). The results of the study by Singh and Singh (1999) showed that the planned cultivation has increased from 60% to 96% and net profit from 23% to 26% with optimizing land use. The appropriate allocation of different land uses was done using geographic information system integrated with optimization models with respect to existing land uses, slope and distance from surface water sources (Wang and Huang, 2004). The results of a research with the multi-linear programming model to optimize land use showed that the use of the resources, consistently improve rural people's income (Liu and Stewart, 2004). The optimal utilization of watersheds resources was determined using plan aimed method showed that the proposed model based on the perspective of economic has relative superiority on the social and environmental attitudes (Mohseny Saravi et al., 2001). Determining the optimal crop rotation using linear programming to obtain high net income and compare it in the current status and the sensitivity analysis showed that net farm income of the four optimal crop rotation and also, limiting inputs, have changes rather flexible (Gholami, 2003). Economical evaluation of the land allocation using linear programming model with respect to the limitations of the land transport, economic and environmental conditions, confirmed the promotion of the local economy with methods and changes in land displacement (Flah-Shamsi, 2004). Multi-purpose linear programming model was used to reduce the environmental and economic effects of soil erosion due to inappropriate management practices of land was used by Nikkami et al. (2002). They also showed that the optimum land use and land management practices can reduce soil erosion and increased income of users. The results show that sediment production decreased 5% and annual profits increased 134%. Linear programming was used to optimize land use that can minimize soil erosion (Jalili, 2004). The results introduced the optimum use of land, reduce erosion and increase the amount of annual profits 7.78% and 118.62%, respectively. Land use and erosion relationship were studied by Yueqin et al. (2011). They showed soil erosion significantly varied among land-use types. Erosion was most serious in dry farmland and the lightest in paddy field and conservation practices should be taken in these areas. Li et al. (2013) resulted that forest and wasteland land conversions induce substantial soil erosion, while transition from wasteland to forest retards soil loss. Analyzing the soil erosion of each land-use it was obtained the following land use erosion vulnerability: Olive orchard>Vineyard>Montado>Alfalfa. The strong erosion variances that were observed in the study area show the importance of locating the 'hot spots' of soil erosion (Ferreira, 2015). Since optimization methods in watershed management leads to conserve resources and provide the optimum solution to achieve sustainable use of land and in compliance with all technical, social, economic and legal restrictions that has not been done in the area. In this study, we have tried to select the best model of land optimization in the Qushchi watershed and its sensitivity to changes so that can designate users to conserve resources and reduce soil erosion.

Material and Methods

Study area

The study area of Qushchi watershed with the surface area of 5186 ha is located in the of West Azarbaijan province, IRAN, in, 44°51′10″ to ″44°57′52″ E and 37°56′01″ to 38° 00′ 53″. Figure 1 is depicted the location of the study area. The most common Agricultural activities are in form of subsistence and semi-mechanized without any soil and water conservation practices. People are living in difficult conditions and income is scarce. Facilities and infrastructure in the area is not appropriate.

Research Methodology

To determine major land uses including irrigated annual crops, rainfed lands, orchards and rangelands, satellite images (Google-Earth) interpretated by visual method to prepare land use map. Soil erosion was estimated using MPSIAC model. The cost and benefits of existing land uses were calculated with field studies. The amount of erosion damage was estimated by converting amount of soil erosion of a given land surface area and equivalent soil depth. The primary data about climate, geology, hydrology, land use and erosion needed to calculate final results were collected from Forests and Rangelands Organization, field interviews and Iran Statistics Center. Animal husbandry and its effects were considered in rangelands evaluation.

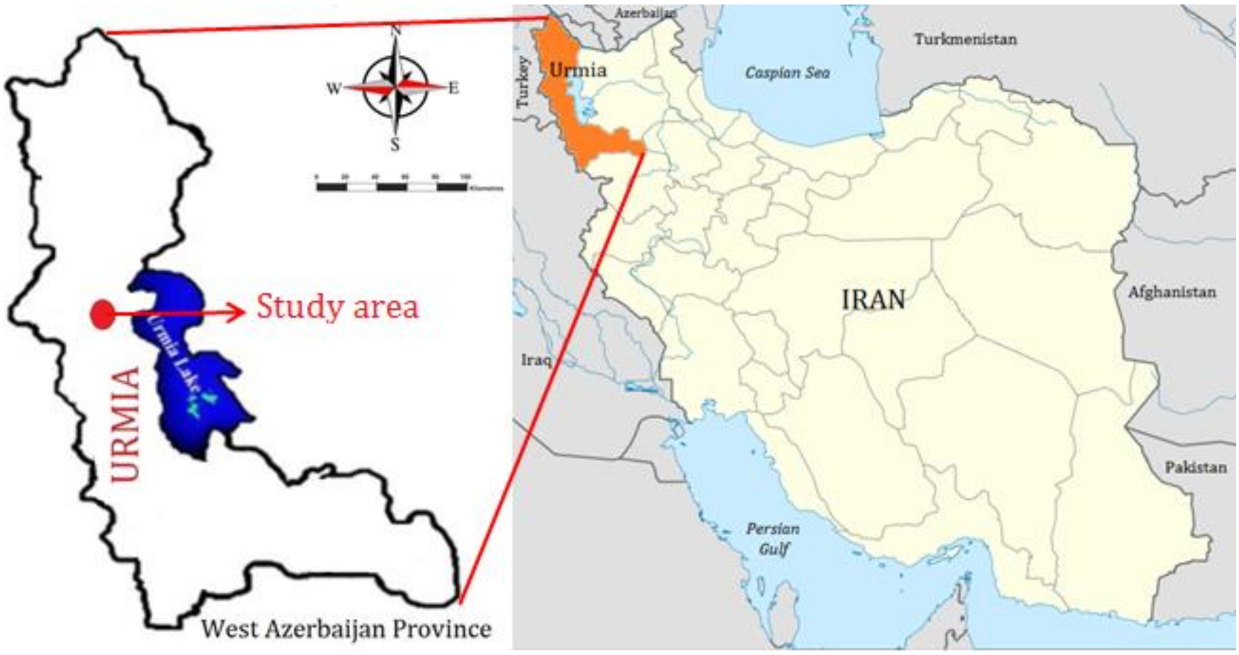

Figure 1. Location of the study area; Qushchi catchment

The land use optimization was carried out as the following three scenarios.

- The current status of land uses
- The current status of land use with land management
- Standard status of land use with soil and water conservation practices, low inputs and high outputs.

Optimizing of the land use pattern problem was solved with the aim of erosion reduction and increase farmers' income using LINGO software and the Simplex method (Equation 1):

$$\sum_{i=1}^{n} X_i = B \qquad X_i \geq 0 \tag{1}$$

Where:
X_i: is the surface area of each land use (ha)
B: total surface area (ha)

Due to the linearity of the objective function, linear programming was selected and since the simplex method does not need to become multi-objective optimization to be a one goal, so it was used to solve the problem.

Multi-objective optimization problem with n decision variables and general constraints and p objective is provided in relations 2 to 8 (Benli & Kodal. 2003 and Singh. 2016). Using these relationships, the general issue for profit maximization function in the watershed is written as Equation 2.

$$\text{Max } (Z_1) = [(A_{i1} - A_{i2} + A_{i3}) X_i] \tag{2}$$

Equation 2 can be simplified as relation 3.

$$\text{Max } (Z_1) = C_{Bi}X_i \tag{3}$$

The general form for function minimization problem of erosion in the Qushchi watershed was written as a simple relationship 4.

$$\text{Min } (Z_2) = C_{Bi}X_i \tag{4}$$

Limited to:

$$X_1 = B \qquad X_1 > 0 \tag{5}$$

In these equations:
Z_1: the annual net income of the watershed (Euro/ year)
Z_2: annual erosion of the watershed (ton/ year)
X_i: The area of each land use (ha)

A_{i1}: annual gross income of each land use unit area Euro/year)
A_{i2}: unit production costs per user (Euro/ year)
A_{i3}: the cost of soil loss per unit area per land use types (Euro/ year)
C_{Bi}: profitability of each land use (Euro/ year)
C_{Bi}: erosion for each land use (ton/ ha/ year)
B: total surface area (ha)

To issue a more detailed description, for four land use of horticulture, rangeland, irrigated and dry farming was written as Equation (6).

$$\text{Max}(Z_1) = [(A_{11} x_1 - (A_{12} x_1 + A_{13} x_1)) + (A_{21} x_2 - (A_{22} x_2 + A_{23} x_2)) + (A_{31} x_3 - (A_{32} x_3 + A_{33} x_3)) + [(A_{41} x_4 - (A_{42} x_4 + A_{43} x_4))] \quad (6)$$

Equation (6) summarized to optimize profits in the form of equation (7).

$$\text{Max}(Z_1) = C_{B1} x_1 + C_{B2} x_2 + C_{B3} x_3 + C_{B4} x_4 \quad (7)$$

Also using equation (8) minimizing soil erosion in the study area was conducted.

$$\text{Min}(Z_2) = C_{E1} x1 + C_{E2} x_2 + C_{E3} x_3 + C_{E4} x_4 \quad (8)$$

$X_1 < B_1$
$X_3 < B_2$
$X_4 < B_3$
$X_1 + X_3 < B_4$
$X_1 + X_2 + X_3 + X_4 = B_5$
Limited to:
$X_1 > B_6$
$X_2 > B_1$ (9)
$X_1 + X_2 + X_3 + X_4 > 0$

In these equations:
X_1: the surface area of the gardens (ha)
X_2: Area of the rangelands (ha)
X_3: The area of irrigated lands (ha)
X_4: an area of the dry farming (ha)
A_{11}: gross income gardens per hectare (Euro/ ha)
A_{12}: Level of gardens cost of production per unit (Euro// ha)
A_{13}: Unit erosion damage from the gardens (Euro/ ha)
A_{21}: GDP per unit of rangelands (Euro/ ha)
A_{22}: cost of production per unit area of the rangelands (Euro/ ha)
A_{23}: Damage erosion of rangelands (Euro/ ha)
A_{31}: Unit gross income from irrigated lands (Euro/ ha)
A_{32}: cost of production per unit area of the irrigated lands (Euro/ ha)
A_{33}: erosion damage of the surface area of the irrigated lands (Euro/ ha)
A_{41}: GDP unit of the drylands (Euro/ ha)
A_{42}: cost of production per unit area of the drylands (Euro/ ha)
A_{43}: erosion damage unit of the drylands (Euro/ ha)
C_{B1}: annual net profit per hectare gardens (Euro/ ha)
C_{B2}: annual net profit per hectare of the rangelands (Euro/ ha)
C_{B3}: annual net profit per unit of the irrigated lands (Euro/ ha)
C_{B4}: annual net profit of the drylands (Euro/ ha)
C_{E1}: erosion per unit area gardens (ton/ ha/ year)
C_{E2}: erosion per unit area of the rangelands (ton/ ha/ year)
C_{E3}: erosion on irrigated land area (ton/ ha/ year)
C_{E4}: erosion per unit area of the drylands (ton/ ha/ year)
B_1: Max surface area of the gardens (ha)
B_2: surface area irrigated farming lands (ha)
B_3: surface area dryland farming lands (ha)
B_4: surface area of the gardens in addition to irrigated land area (ha)
B_5: the total surface area (ha)
B_6: Min surface area of the gardens (ha)
B_7: Min surface area of the rangelands (ha)

The problem of the optimizing land use pattern in Qushchi watershed, seven restrictions related to the land use, the amount of water, non-negative total area of land allocated for land use and land use optimization model variables were considered for the following two limitations, for example as follows.

The first limitation

This limitation was considered that 408 ha land area in the current status is garden, but this surface area can be increased to 507 ha. The reason for this increase is the possibility of allocating land with a slope and soil depth. This restriction is shown in relation 10.

$$X1 < 507 \qquad (10)$$

The second limitation

The second limitation is related to irrigated land (169 ha) but according to the standard conditions required for irrigation, soil and water availability, only 136 ha have irrigation potential and for this reason the surface area of land will decrease from 169 to 136 ha (relation 11).

$$X3 < 136 \qquad (11)$$

Finally, sensitivity to the changes in the ratio of 10 to 50% of the exchangeable resources, the optimum scenario of the land use and management was determined comparing of the erosion rate and profit of each option.

Results

Of total surface area, 3496 ha includes four types of land uses of gardens, rangeland with the most area, irrigated lands with the minimum surface area and dryland farming (Table 1). The minimum rate of erosion related to the gardens and maximum of it belongs to rangelands (Figure 2). The average slope is 27.4% that 85% of the area is located on the above 12% slope. Elevation ranges 1483 to 2716 meters above see level. Rock units mainly are sandstone and shale. The average rainfall in the area is about 300 mm per year. An area of the rangelands are about 2283 ha including sparse species, forbs, annual grasses and some types like the thymus.

Table 1. Mean value of the coefficients of the problem optimization in the current situation

Soil erosion damage	Net income	Gross income	Cost	Annual erosion (tons/ha/year)	Area (ha)	Land use
	(Euro/ha/year)					
28.80	192.65	340.25	147.60	8	408	Horticulture
5.15	101.17	196.18	95.01	14	2283	Range
69.53	55.05	105.08	50.03	10	169	Irrigated Farm
18.47	61.60	71.02	9.42	12	636	Dry farming

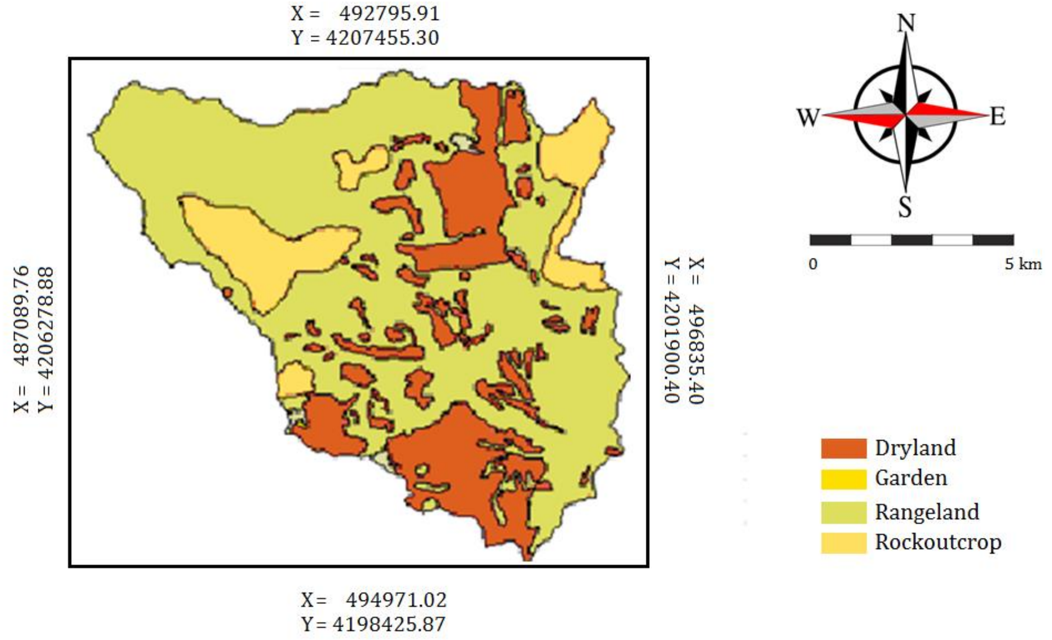

Figure 2. The land use map

Coefficients of the multi-objective optimization problem with n decision variables and constraints, and p goal in three options of: the current situation of land without land management, the current state of land with land management and land use in the standard status were presented in Table 1, 2 and 3.

Table 2. Mean value of the coefficients of the problem optimization of land management practices

Soil erosion damage	Net income	Gross income	Cost	Annual erosion (tons/ha/year)	Area (ha)	Land use
(Euro/ha/year)						
18.82	349.77	57.12	221.40	5	408	Horticulture
5.15	100.89	196.43	95.54	10	2283	Range
43.75	80.30	130.33	50.03	6	169	Irrigated Farm
16.49	57.14	66.00	8.86	9	636	Dry farming

Table 3. Mean value of the coefficients of the problem optimization in the standard setting

Soil erosion damage	Net income	Gross income	Cost	Annual erosion (tons/ha/year)	Area (ha)	Land use
(Euro/ha/year)						
6.32	349.77	571.17	221.40	4	507	Horticulture
2.88	100.14	196.43	95.54	9	2283	Range
25.03	82.83	132.86	50.03	4	136	Irrigated Farm
17.44	76.60	86.02	9.42	8	580	Dry farming

To achieve the most appropriate land use option, tables of simplex method for linear performance for land uses with targeted functions and constraints, was defined as an instance of the tables is provided on the current status of land use in Table 4.

Table 4. Simplex table for problem optimization of Qushchi land use in the current situation

Factors Function	X1 Horticulture	X2 Range	X3 Irrigated Farm	X4 Dry farming	Function Type	Right position of Relationship
Objective Function 1	7706027.84	4046669.70	2202028.22	2464018.26	Max	0
Objective Function 2	-8	-14	-10-	-12	Max	0
Limitation 1	1	0	0	0	<	507
Limitation 2	0	0	1	0	<	136
Limitation 3	0	0	0	0	<	580
Limitation 4	1	0	1	0	<	643
Limitation 5	1	1	1	1	<	3496
Limitation 6	1	0	0	0	>	408
Limitation 7	0	1	0	0	>	2283

Table 4 shows that columns 2 to 5 in the left are decision variables and have the units of money and erosion in rows 2 and 3 respectively. Numbers one and zero in the rest of the rows indicates the presence or absence of the variable in the limits. Rows 2 and 3 in column 6 indicates the type of purpose equation for minimizing or maximizing, while the rest of the rows shows the equality or inequality of the constraint equations to be defined. In the last column, right amount of the constraint equations be seen representing the value of the land surface area. The results showed Lingo software optimization solution for all three options examined included the status quo, the situation with land management and standard conditions, the optimal level of land use that could minimize erosion and maximize revenue will be as Table 5. Using table 5, the calculation of soil erosion and profit before and after land use optimization was done that for example the current situation of land uses is presented in Tables 6 and 7. So, the values obtained for the three land use options of current status options, land management and standard status were compared that the results are showed in Tables 8 and 9. The amounts of increase profitability and reduce erosion resulting after optimizing has been shown in Tables 10 and 11 are provided.

Results of the Table 10 showed that if land use optimized, net profit rate of 3.68% of the land in its current state, 21.39% in the status of land management and 24.20% in standard conditions will increase. Similarly, the results presented in Table 11 shows that with land use optimization, 0.75% erosion in its current state, 42.27% in the status of land management and 60.95% under standard conditions will reduce.

Table 5. Area of land uses in both of optimal and non-optimal state

Allocated area (ha)		Land use type
After Optimization	Before Optimization	
507	408	Horticulture
2283	2283	Range
136	169	Irrigated Farm
570	636	Dry farming

Table 6. Calculation of profit and erosion in the current status of Qushchi watershed

Total net Income (Euro/ year)	Net Income (Euro/ha/ year)	Total erosion (ton/ year)	Annual erosion (ton/ha)	Area (ha)	Land use
78601.50	192.65	3264	8	408	Horticulture
230963.69	101.17	31962	14	2283	Range
9303.58	55.05	1690	10	169	Irrigated Farm
39177.90	61.60	7632	12	636	Dry farming

Table 7. Profit and erosion of the current status of land use optimization model in Qushchi watershed

Total net Income (Euro/ year)	Net Income (Euro/ha/ year)	Total erosion (ton/ year)	Annual erosion (ton/ha)	Area (ha)	Land use
97673.92	192.65	4056	8	507	Horticulture
230963.69	101.17	31962	14	2283	Range
7486.91	55.05	1360	10	136	Irrigated Farm
35112.27	61.60	6840	12	570	Dry farming

Table 8. Comparison of erosion before and after optimization of land use options (tons per year)

Standard setting		Land management practices		Current status		Land use
After Optimization	Before Optimization	After Optimization	Before optimization	After Optimization	Before Optimization	
2028	2028	2535	2040	4056	3264	Horticulture
20547	20547	22830	22830	31960	31962	Range
544	544	816	1014	1360	1690	Irrigated Farm
4560	4640	5130	5724	6840	7632	Dry farming
27679	27759	31311	31608	44218	44548	Total

Table 9. Comparison of annual profits before and after optimization of land use options (Euro per year)

Standard setting		Land management practices		Current status		Land use
After Optimization	Before Optimization	After Optimization	Before optimization	After Optimization	Before Optimization	
233817.44	233817.44	233817.44	233817.44	230963.69	230963.69	Horticulture
14763.26	14763.26	11226.91	13951.08	7486.91	9303.58	Range
47764.02	46940.50	41240.50	46015.71	35112.27	39177.90	Irrigated Farm
443895.11	443895.11	434658.76	413185.73	371236.78	358046.67	Dry farming
233817.44	233817.44	233817.44	233817.44	230963.69	230963.69	Total

Table 10. Changes in total net profit after optimization of the land use in relation to different options

After Optimization						Before optimization
Standard setting		Land management practices		Current status		Current status
Increase (%)	Amount (Euro/ year)	Increase (%)	Amount (Euro/ year)	Increase (%)	Amount (Euro/ year)	
24.20	443895.11	21.39	434658.76	3.68	371236.78	358046.67

Table 11. Erosion rate changes after land use optimizing changes in relation to different options

After Optimization						Before Optimization
Standard setting		Land management practices		Current status		current status
Increase (%)	Amount (Euro/year)	Increase (%)	Amount (Euro/year)	Increase (%)	Amount (Euro/year)	
60.95	0.69	42.27	0.78	0.75	1.11	1.11

Using sensitivity analysis of changes compared to the optimization, critical factors were identified that some of their results in the current situation is shown in the Figures 3, 4 and 5 for example.

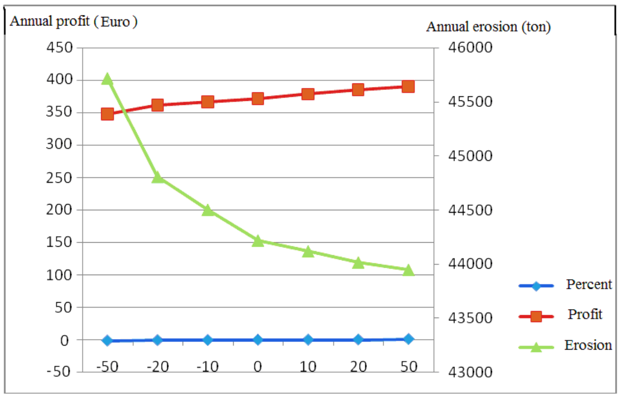

Figure 3. Sensitivity analysis of objective functions in relation to the highest area of horticultural land in current status

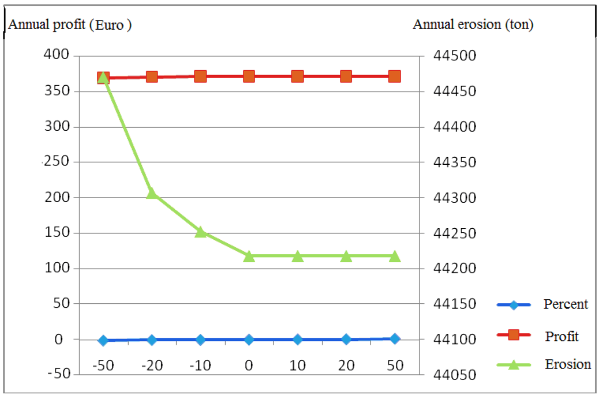

Figure 4. Sensitivity analysis of objective functions in relation to the highest area of irrigated farms in current status

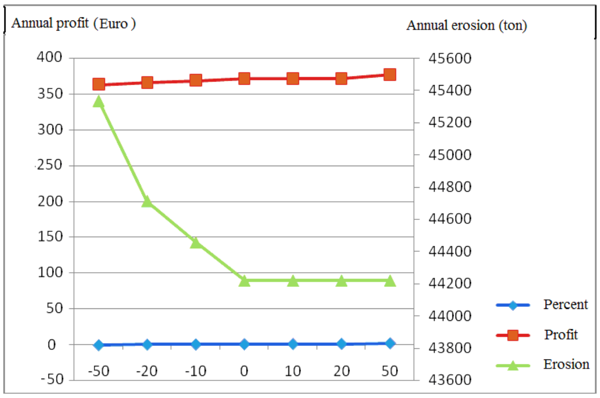

Figure 4. Sensitivity analysis of objective functions ratio to the highest area of irrigated farms and horticulture in current status

Discussion

In this research, we used linear programming to optimize land uses that match with the findings of (Liu and Stewart, 2004) but (Benli and Kodal, 2003) have emphasized on non-linear programming to maximize profits for the agricultural land use. Our results showed that with optimizing land use, erosion rates can be reduced about 61%. Erosion reduce can be due to reduction of the irrigated and rainfed land surface area and increasing the surface area of garden. It also has about 24% the profitability area has been added compared to the before optimizing situation. These results are consistent with the results of previous studies (Jalili, 2004; Nikkami et al., 2002; Singh and Singh, 1999). Results of the sensitivity analysis showed that the change in the surface area of garden and rangeland has the greatest impact on the profitability and erosion rate.

Conclusion

The results of this research showed that the current state of land use in the Qushchi watershed is not suitable to minimize soil erosion because erosion rates only 0.75% reduced after the land use optimization without land management. So it is necessary to optimize land use management practices. It can also reduce soil erosion and increase of the resident income by managing the different land uses. Changes in the garden and range land have the greatest impact on increasing profitability and reducing erosion. Water supply for this change is an important issue that can be provided by watershed management like construction of small water reservior dams and new sprinkler and drip irrigation methods. The animal population dependent on range is six times of the range capacity that led to its destruction and increase erosion. Therefore, it is recommended using Education and Extension to promote the importance of land management and to understand how proper use of the land to the villagers that improper management of land use in a watershed has a disproportionate impact on available resources. Land use optimization is one of the strategies for achieving sustainable development and protection of the soil.

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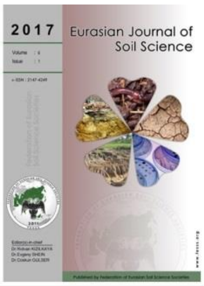
Eurasian Journal of Soil Science

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



The effects of $CaCl_2$ on fruit yield, quality and nutrient contents of tomato under NaCl stress conditions

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Abstract

In this study, the effects of $CaCl_2$ on fruit yield, quality Ca/Na and K/Na ratios and Na content of tomato leaves under NaCl stress conditions were determined. The doses of 0, 6.8 and 16.8 mM $CaCl_2$ were combined with the doses of 0, 44.4, 70.4 mM NaCl in complete nutrient solution. General, NaCl and $CaCl_2$ decreased fruit yield, NaCl decreased stem amount, whereas it increased at 6.8 mM $CaCl_2$. $CaCl_2$ decreased fruit yield without NaCl, but it increased fruit yield significantly at 44.4 mM dose and caused tolerance to NaCl. The 6.8 mM dose of $CaCl_2$ increased stem amount without NaCl. However, $CaCl_2$ did not cause tolerance at high doses of NaCl in terms of growth. $CaCl_2$ decreased brix of fruit, while NaCl increased it. $CaCl_2$ increased brix without NaCl, but decreased it at 44.4 and 70.4 mM NaCl. $CaCl_2$ and NaCl decreased fruit juice pH significantly. Besides, $CaCl_2$ decreased fruit juice pH at 0 and 44.4 mM of NaCl. The number of fruits which were found to have blossom-end rot (NFBER) did not change without NaCl with the influence of $CaCl_2$. However, $CaCl_2$ applied at high doses of NaCl decreased the NFBER and provided tolerance to NaCl. Increasing dose of NaCl increased significantly the Na content in leaves, but the addition $CaCl_2$ decreased significantly the Na content in leaves. Increasing the dose of $CaCl_2$ applications at 0 and 44.4 mM NaCl levels increased the Ca/Na ratio in tomato leaves. But, the effect of $CaCl_2$ on Ca/Na ratio of leaves was statistically insignificant. The addition of NaCl into the solution nutrient decreased the Ca/Na and K/Na ratios in tomato leaves. The effect of $CaCl_2$ on the K/Na ratio of leaves was not found significant.

Article Info

Received : 16.05.2016
Accepted : 26.08.2016

Keywords: Tomato, NaCl stress, tolerance, $CaCl_2$, yield, quality, Ca/Na, K/Na ratios

Introduction

Plants ability to grow and complete their life cycle in settings which contain very high concentrations of various soluble salts is called salt tolerance (Parida and Das, 2005). Salt tolerance is an indicator of resistance to salt stress and varies depending on the plant type, plant environment and the environmental conditions (Gürel and Avcıoğlu, 2001). In order to remove the negative effects of salinity, Tuna et al. (2007) recommended applying Ca and Türkmen et al. (2000) recommended applying K as healer materials in the growth setting.

Ca is an essential element for K/Na and Ca/Na selectivity and helps the prevention of the harmful effects of salinity by regulating ion transport in plants (Renault, 2005). Ca has been reported to be effective in preventing the harmful effects of NaCl in many types of plants (Tuna et al., 2007). Ca has been reported to ease K/Na selectivity and prevent NaCl toxicity by increasing this rate in case of being given to growth environment (Abdel Latef, 2011).

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e-ISSN: 2147-4249
DOI: 10.18393/ejss.284270

According to recent studies, low levels of calcium in the root area of tomato is rarely a factor that limits vegetative growth (Del Amor and Marcelis, 2006). However, calcium nutrition of tomato requires a special attention because this nutrient is closely related to the formation of blossom-end rot, which is a physiological disorder. Blossom-end rot occurs as a result of local lack of calcium on the tip of the tomato plant and calcium deficiency in these areas cause disruption in tissue structure (Adams, 2002). Thus, blossom-end rot decreases the quality and saleability of the fruit (Grattan and Grieve, 1999).

Various factors including variety such as calcium, ammonium, potassium, magnesium, salt and salt stress, oxygen efficacy, relative humidity of air and air temperature can increase or decrease the formation of blossom-end rot (Navarro et al., 2005).

Extreme transpiration and temperature levels increase water intake and thus calcium transportation to leaves through xylem increases (Taylor et al., 2004). Still, under such circumstances the transportation of water to fruits decrease due to its rivaly with leaves. Thus, calcium transportation to fruit is limited at the same time. As a result, there occurs an increase in blossom-end rot (Adams, 2002).

Kaya et al. (2002) showed that Ca addition caused a decrease in the membrane permeability caused by saltiness. It has also been reported that Ca contents of plants showed deficiency in high NaCl levels and this deficiency was made up for by adding Ca. The adverse effects of saltiness on plants were prevented by Ca application, Na formed rivalry with Ca ion on the cell wall and thus high levels of Ca in high settings protected the cell membrane from the adverse effects of saltiness (Busch, 1995).

Jaleel et al. (2007) reported that K^+, Ca^{+2} and Mg^{+2} caused a decrease in the Na^+ of the plant and NO_3^- decreased Cl^- content of the plant. Jaleel et al. (2008) also reported that when NaCl and $CaCl_2$ were applied together, they increased antioxidant enzyme activity and $CaCl_2$ partly fixed the oxidative stress caused by salt.

One of the primary approaches used to decrease the effects of salt on plant growth nutrient addition and especially Ca addition has been reported to play an important role in removing the bad effect of salt on plant growth in glucofits (Yan et al. 1992). Calcium prevents K transportation and K/Na rate from decreasing by stabilizing plants exposed to Na. Significant interaction has been reported between Na and K on plant growth (Rengel, 1992).

In case of sufficient Ca in subtrate setting, K/Na selectivity has been stated to be affected in favor of K by improving K intake (Grattan and Grieve, 1999).

Ca^{+2} ion is another basic element for growth and development. Salt stress affects Ca^{+2} intake negatively, like K^+. Na^+ translocates with Ca^{+2} in the cell membrane and helps the Na^+/Ca^{+2} ion rate in the apoplast part of the membrane to increase. This causes a disruption in the physiological and functional structure of the membrane and Ca^{+2} balance of the cell is affected. High Na^+ concentration frees Ca^{+2} which are bound in the inner membrane structure of the cell and causes internal Ca^{+2} stores to get empty and thus causes an increase in the free Ca^{+2} in the cell (Yokoi et al., 2002).

Grattan and Grieve, (1999) stated that it was necessary to increase the Ca^{+2} levels of plants in order to protect plants from NaCl toxicity. In addition, the authors emphasized the importance of having Ca^{+2} ion concentration at optimum level in order to increase a plant's resistance to salt and stated that Ca^{+2} had a protective effect on plant roots to help the plant to grow well.

In a study which was conducted by making an experiment of pots under climate room conditions to present the effects of salty seedling growing conditions on seedling development, the combinations of 0, 25, 50 and 100 mmol L^{-1} NaCl and 0, 100, 200 and 400 mg kg^{-1} Ca^{+2} doses were applied on seedling growing. In the experiment, the effects of salt and calcium doses on the rate and period of blooming, real leaf apperance period, hypocotyl length, cotyledon length and width, offshoot and root length, offshoot and root weight and offshoot and root dry matter rate were examined. According to the results of the research, increasing doses of salt application had significant but negative effects in measurements and obervations, while increasing doses of calcium had positive but generally insignificant effects (Türkmen et al., 2002).

The purpose of this study is to find out the effects of $CaCl_2$ added to nutrient solutions on the yield, stem+leaf dry matter amount, fruit quality, ratios Ca/Na, K/Na and Na content of leaves tomato under increasing NaCl stress conditions.

Material and Methods

In the experiment, as a growth media, turf and perlite were mixed with a rate of 1:1 and the prepared mixture was used. 770 g absolute dry growth mixture was put in pots of 3 litres which had a diameter of 1.65 cm and which were 19 cm deep. Holes were made at the bottoms of the pots for a good drainage. The experiment was conducted with a 3x3 factorial experimental design by applying 0-44.4 and 70.4 mM doses of NaCl and 0-6.8 and 16.8 mM doses of $CaCl_2.2H_2O$ in the nutrient solution.

For tomato, the macro element content of the nutrient solution was prepared according to Montesano and Van Iersel (2007) while micro element content was prepared according to the micro element values specified by Hoagland and Arnon (1950) for nutrient solution. Macro and micro nutrient element contents of the nutrient solution are as follows: 11.1 mM NO_3^-; 0.87 mM $H_2PO_4^-$; 6.37 mM K^+; 2.8 mM Ca^{+2}; 1.71 mM Mg^{+2}; 1.71 mM SO_4^{-2}; 2.5 mg L^{-1} Fe; 0.5 mg L^{-1} Mn; 0.5 mg L^{-1} B; 0.02 mg L^{-1} Cu; 0.05 mg L^{-1} Zn; 0.01 mg L^{-1} Mo. $Ca(NO_3)_2.4H_2O$, KH_2PO_4, KNO_3, $MgSO_4.7H_2O$, $MnCl_2.2H_2O$, H_3BO_3, $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, $(NH_4)_6Mo_7O_{27}.4H_2O$, Fe-EDDHA were used to prepare this nutrient solution.

pH and EC values of 9 different nutrient solutions prepared by adding increasing amounts of NaCl and increasing amounts of $CaCl_2$ in the nutrient solution were measured, and the values are given in Table 1.

In the experiment, each nutrient solution was applied with three repetitions. Tybiff Aq tomato seedlings were planted as one plant in each pot on 15.04.2013. After planting, 100 ml nutrient solution was applied to each pot for 35 days until 20.05.2013, and 200 ml nutrient solution was applied until harvest.

In the experiment, the pots were irrigated in a way that a small amount of water would be drained and the setting was continuously kept as a field capacity.

The last fruit harvest of the tomato plant was made on 17.07.2013 and fresh fruit weights were measured. After the harvest, stem samples were taken and dried at 65 °C, dry matter of stem was measured. The contents of Na and K in the leaf samples were determined by flamephotometer and the Ca content was determined by atomic absorption spectrophotometer according to Kacar (2014). Soluble solids in the fruit (brix) were measured in fruit juice using a refractometer and pH was measured with a glass electrode pH meter. The number of fruits with blossom-end rot per plant was found by counting the rotten fruit in each plant. The data obtained from 3x3 factorial experiment was assessed with variance analysis and LSD test (Yurtsever, 1982).

Results and Discussion

The effects of $CaCl_2$ under increasing NaCl doses on the pH, EC and SAR of nutrient solution

The results related to the effect of $CaCl_2$ under increasing NaCl concentrations on the pH, EC and the Na adsorption ratio (SAR) of the nutrient solution are given in Table 1 and 2.

Table 1. The effects of $CaCl_2$ applied in increasing NaCl doses on the pH and EC of the nutrient solution

$CaCl_2$ (mM)	pH				EC(dS/m)			
	NaCl (mM)				NaCl (mM)			
	0	44.4	70.4	Ave.	0	44.4	70.4	Ave.
0	6.09	5.94	5.87	5.96	1.63	4.30	7.10	4.34
6,8	5.65	5.72	5.65	5.67	2.22	3.87	5.43	3.84
16,8	5.59	5.78	5.76	5.71	2.73	4.77	6.13	4.54
Ort.	5.44	5.81	5.76	-	2.19**c***	4.30**b**	6.22**a**	**-**

$LSD_{0,05}$ NaCl:0.66

* There is no difference at the level of 0.05 between averages shown with the same letters

The effects of $CaCl_2$ and NaCl doses on the pH of the nutrient solution were found to be insignificant (Table 1). pH values of 9 different nutrient solutions were found to be between 5.59 and 6.09. The effect of $CaCl_2$ on the EC value of the nutrient solution was found to be insignificant. However, EC of the nutrient solution increased with increasing NaCl dose. EC value of the 9 different nutrient solutions prepared by applying 0, 6.8 and 16.8 mM $CaCl_2$ to the nutrient solution at increasing NaCl doses varied between1.63 and 7.10 dSm^{-1}. SAR of the nutrient solution varied between 0 and 33.2 (Table 2).

Table 2. The effects of $CaCl_2$ applied in increasing NaCl doses on the Na adsorption ratio (SAR) of the nutrient solution

$CaCl_2$ (mM)	Na adsorption ratio (SAR) NaCl (mM)		
	0	44.4	70.4
0.0	0.0	20.9	33.2
6.8	0.0	13.2	21.0
16.8	0.0	9.6	15.2

The effect of $CaCl_2$ under increasing NaCl salt stress on the fruit yield of tomato

The effects of $CaCl_2$ under increasing NaCl stress on the fruit yield are given in Table 3.

Table 3. The effect of $CaCl_2$ under increasing NaCl salt stress on the fruit yield, stem+leaf amount of tomato plant

$CaCl_2$ (mM)	Fruit yield, kg/plant NaCl (mM)				Stem, g/plant NaCl (mM)			
	0	44.4	70.4	Ave.	0	44.4	70.4	Ave.
0.0	1.41**a***	0.86**fgh**	0.81**gh**	1.02**a**	58.11**bc**	41.77**d**	27.81**e**	42.56**b**
6.8	1.31**b**	0.98**de**	0.77**h**	1.02**a**	65.56**a**	41.50**d**	30.69**e**	45.92**a**
16.8	1.03**d**	0.91**ef**	0.62**ı**	0.85**b**	53.43**c**	29.69**e**	29.87**e**	37.66**c**
Ort.	1.25**a**	0.89**b**	0.73**c**		59.03**a**	37.65**b**	29.45**c**	
	$LSD_{0.05}CaCl_2$: 0.052 $LSD_{0.05}$NaCl: 0.052 $LSD_{0.05}CaCl_2$xNaCl: 0.09				$LSD_{0.05}CaCl_2$: 2.85 $LSD_{0.05}$NaCl: 2.85 $LSD_{0.05}CaCl_2$xNaCl: 4.94			

* There is no difference at the level of 0.05 between averages shown with the same letters.

Increasing doses of $CaCl_2$ applied to nutrient solution affected the fruit yield at the 0.01 level (Table 3). While mean fruit yields were 1.02 kg/plant in 0 and 6.8 mM $CaCl_2$ doses, it was 0.85 kg/plant in 16.8 mM $CaCl_2$ dose. Although the effect of 6.8 mM $CaCl_2$ dose on fruit yield was insignificant, 16.8 mM $CaCl_2$ dose decreased the fruit yield significantly. Increasing doses of NaCl applied on nutrient solution significantly decreased the fruit yield at 0.01 level. While fruit yield was (NaCl:0) 1.25 kg/plant in control, it decreased to 0.89 kg/plant in 44.4 mM NaCl dose and to 0.73 kg/plant in 70.4 mM NaCl dose.

Leonardi et al. (2004) examined the quality of tomato based on the NaCl content in nutrient solution and found that the EC of the nutrient solution was increased as 2.7-4.5-6.0-7.5-8.6 dSm^{-1} and NaCl caused a decrease in yield but an increase in the soluble solid and dry matter content of the fruit. The researchers emphasized that salt stress affected yield level of tomato negatively, but had positive effects on blossoming. In addition, it was stated that salty water did not affect the nutrient properties such as carotenoid and antioxidant activity negatively. The effect of NaClx$CaCl_2$ interaction on fruit yield was found to be significant at 0.01 level. In other words, the effect of $CaCl_2$ on fruit yield was found to be dependent on NaCl doses. As the dose of $CaCl_2$ applied to nutrient solution without NaCl (NaCl:0) increased, fruit yield decreased. These decreases were statistically significant and they were found to be higher in high doses of $CaCl_2$. Increasing $CaCl_2$ doses applied to nutrient solution with 44.4 mM NaCl increased the fruit yield significantly and this increase was also found significant at 6.8 mM $CaCl_2$ dose. The fruit yield which was 0.86 kg/plant in control ($CaCl_2$:0) at 44.4 mM NaCl level increased 13.95% at 6.8 mM $CaCl_2$ dose and went up to 0.98 kg/plant and when $CaCl_2$ was applied at this dose, it increased the plant's tolerance to 44.4 mM NaCl.

Tabatabaeian (2014) reported that salinity in tomato decreased stem dry matter amount, the lowest yield was found at the level of 90 mmol/L NaCl and 10 mmol L^{-1} $CaCl_2$ prevented salt damage in tomato. Kaya et al. (2002) stated that $CaCl_2$ application removed the negative effect of salinity on the growth and yield of the strawberry plant and reported that plant water use efficiency increased with Ca and decreased as NaCl increased. $CaCl_2$ applied to nutrient solution at 70.4 mM NaCl decreased the fruit yield. These decreases were found insignificant at 6.8 mM $CaCl_2$ dose, while they were found significant at 16.8 Mm $CaCl_2$ dose. $CaCl_2$ applied to nutrient solution when 70.4 mM NaCl was added did not provide tolerance to NaCl.

The effect of $CaCl_2$ under increasing NaCl stress on the stem amount of tomato

The results of the effect of $CaCl_2$ under increasing NaCl stress on the stem dry matter amount of tomato plant are given in Table 3. $CaCl_2$ of increasing doses applied to nutrient solution increased stem amount significantly at the level of 0.01 (Table 3). While stem amount was 42.56 g/plant in control ($CaCl_2$:0), it increased to 45.92 g/plant in 6.8 mM $CaCl_2$ dose significantly. On the contrary, 16.8 mM $CaCl_2$ decreased yield to 37.66 g/plant. The effect of NaCl on stem amount was found to be significant at 0.01 level and as NaCl dose increased, stem amount decreased significantly. The effect of NaClxCaCl$_2$ interaction on stem+leaf amount was found to be significant at 0.01 level. In other words, the effect of CaCl$_2$ on stem amount was found to be dependent on NaCl doses.

Increasing doses of CaCl$_2$ applied to nutrient solution without NaCl (NaCl:0) increased the stem dry matter amount significantly at the dose of 6.8 mM but decreased at the dose of 16.8 mM; however, this decrease was found to be insignificant. CaCl$_2$ applied to nutrient solution with 44.4 mM NaCl did not affect the stem dry matter amount at the dose of 6.8 mM, but significantly decreased at the dose of 16.8 mM. CaCl$_2$ applied to nutrient solution with 70.4 mM NaCl increased the stem dry matter amount; however, this increase was found to be insignificant.

The effect of CaCl$_2$ under increasing NaCl stress on the soluble solid (%) content of fruit (brix)

The results of the effect of CaCl$_2$ under increasing NaCl stress on the brix (%) content in tomato are given in Table 4.

Table 4. The effect of CaCl$_2$ under increasing NaCl salt stress on brix in the fruit of tomato and the content Na in leaves

CaCl$_2$ (mM)	Brix in the fruit,% NaCl (mM)				Na content in leaves,% NaCl (mM)			
	0	44.4	70.4	Ave.	0	44.4	70.4	Ave.
0.0	4.3e*	7.8a	6.3b	6.1a	0.21	1.01	1.05	0.76a
6.8	5.1d	5.9bc	5.0d	5.3b	0.14	0.59	0.80	0.51b
16.8	5.7bc	5.6cd	5.4cd	5.6b	0.08	0.45	0.70	0.41b
Ort.	5.0c	6.4a	5.6b		0.14c	0.68b	0.85a	
	LSD$_{0.05}$CaCl$_2$: 0.36 LSD$_{0.05}$NaCl: 0.36 LSD$_{0.05}$CaCl$_2$xNaCl: 0.62				LSD$_{0.05}$CaCl$_2$: 0.12 LSD$_{0.05}$NaCl: 0.12			

* There is no difference at the level of 0.05 between averages shown with the same letters

The effect of CaCl$_2$ added in nutrient solution on the soluble solid content of the plant was found to be significant at the level of 0.01. As a result of CaCl$_2$ addition to nutrient solution, a decrease was observed in soluble solid content and no difference was found between CaCl$_2$ doses in terms of their effects on soluble solid content. The effect of NaCl on the soluble solid content of the fruit was found to be significant at 0.01 level and NaCl addition was found to increase the soluble solid content of the fruit significantly. This increase was found to be higher at 44.4 mM NaCl dose. Thybo et al. (2006) reported that soluble solid (brix) values of greenhouse tomato were between 4.3-5.0 while Peet et al. (2004) reported that they were between 3.8 and 4.7. Soluble solid (brix) concentration and antioxidant content of the fruit was reported to increase as the level of salt increased.

The effect of NaClxCaCl$_2$ interaction on soluble solid rate was found to be significant at the level of 0.01. In other words, the effect of CaCl$_2$ on soluble solid rate was found to be dependent on NaCl doses. CaCl$_2$ of increasing doses applied to nutrient solution without NaCl (NaCl:0) increased the soluble solid rate significantly, the soluble solid rate which was 4.3% at control (CaCl$_2$:0) increased to 5.1% at 6.8 mM CaCl$_2$ dose and to 5.7% at 16.8 mM CaCl$_2$ dose. As the CaCl$_2$ dose added at levels of 44.4 and 70.4 mM NaCl increased, the soluble solid rate decreased significantly. No difference was found between CaCl$_2$ doses at levels of 44.4 and 70.4 mM NaCl in terms of their effects on the soluble solid rates. However, in tomato grown by applying CaCl$_2$ of 70.4 mM NaCl, the soluble solid rate was found to be lower.

The effect of CaCl$_2$ under increasing NaCl stress on the fruit juice pH of tomato

The results of the effect of CaCl$_2$ under increasing NaCl salt stress on the fruit juice pH of tomato plant are given in Table 5.

The effect of CaCl$_2$ added in the nutrient solution on the fruit juice pH of tomato plant was found significant at the level of 0.01. As CaCl$_2$ dose increased, fruit pH decreased significantly; however, no difference was found between CaCl$_2$ doses in terms of their effect on fruit pH. The effect of NaCl added in the nutrient solution on fruit pH was found significant at the level of 0.01 and fruit pH was found to decrease significantly as NaCl dose increased.

Table 5. The effect of CaCl$_2$ under increasing NaCl salt stress on fruit juice pH and the number of fruits with blossom-end rot (BER)

CaCl$_2$ (mM)	Fruit juice pH NaCl (mM)				Fruit number with BER/plant NaCl (mM)			
	0	44.4	70.4	Ave.	0	44.4	70.4	Ave .
0.0	4.29a	4.05b	3.92ef	4.08a*	7.0b	13.6a	5.0b	8.5a
6.8	4.04bc	3.94def	3.85f	3.94b	5.7b	2.3c	2.7c	3.6b
16.8	3.93ef	3.95cde	4.0bcde	3.96b	6.0b	2.0c	0.7c	2.9b
Ort.	4.09a	3.98b	3.92c		6.2a	6.0a	2.8b	
	LSD$_{0.05}$CaCl$_2$: 0.057 LSD$_{0.05}$NaCl: 0.057 LSD$_{0.05}$CaCl$_2$xNaCl: 0.099				LSD$_{0.05}$CaCl$_2$: 1.35 LSD$_{0.05}$NaCl: 1.35 LSD$_{0.05}$CaCl$_2$xNaCl: 2.33			

* There is no difference at the level of 0.05 between averages shown with the same letters

The effect of NaClxCaCl$_2$ interaction on fruit pH was found to be significant at the level of 0.01. In other words, the effect of CaCl$_2$ on fruit pH was found to be dependent on NaCl doses. Increasing doses of CaCl$_2$ without NaCl addition (NaCl:0) decreased fruit juice pH significantly. Similarly, increasing doses of CaCl$_2$ at the level of 44.4 mM NaCl decreased fruit juice pH significantly; however, the difference in the effect of CaCl$_2$ doses at this NaCl level on the fruit juice pH was not found to be significant. 6.8 mM CaCl$_2$ addition at the level of 70.4 mM NaCl decreased fruit juice pH; however, it was not found to be significant. On the other hand, 16.8 mM CaCl$_2$ at the level of 70.4 mM NaCl increased fruit juice pH and this increase was found to be insignificant when compared with the control.

The effect of CaCl$_2$ under increasing NaCl salt stress on the number of fruits with blossom-end rot (NFBER)

The results of the effect of CaCl$_2$ under increasing NaCl salt stress on the number of fruits with blossom-end rot in tomato plant are given in Table 5. The effects of CaCl$_2$ added in the nutrient solution on the number of fruits with blossom-end rot were found to be significant at the level of 0.01. As CaCl$_2$ dose increased, the number of fruits with blossom-end rot was found to decrease significantly. The difference between CaCl$_2$ doses was not found to be significant in terms of their effects on the number of fruits with blossom-end rot. Similarly, the effects of NaCl on the number of fruits with blossom-end rot were found to be significant at the level of 0.01. The number of fruits with blossom-end rot was found to be lower at 70.4 mM NaCl dose, however, the number of fruits with blossom-end rot were found to be the same with the control at 44.4 mM NaCl dose. It was also reported that salt decreased yield in tomato and caused blossom-end rot and acidity was reported to increase with saltiness in tomato (Cuartero and Fernández-Muñoz, 1999).

The effect of NaClxCaCl$_2$ interaction on the number of fruits with blossom-end rot was found to be significant at the level of 0.01. The effect of CaCl$_2$ on the number of fruits with blossom-end rot was found to be dependent on NaCl doses. The effect of CaCl$_2$ added in the nutrient solution without NaCl addition (NaCl:0) on blossom-end rot was found to be insignificant. However, as the dose of CaCl$_2$ added at the levels of 44.4 and 70.4 mM NaCl increased, the number of fruits with blossom-end rot decreased.

The effect of CaCl$_2$ doses at these NaCl levels on the number of flowers with blossom-end rot was found to be similar or the same. Kacar and Katkat (2010) reported that Ca in the form of pectate had a primary duty on the strengthening of cell walls and plant tissues and Caldwell and Haug (1981) Ca made cell walls stronger by forming a bridge between the carboxyl and phosphate groups of phospolipids.

The effect of CaCl$_2$ under increasing NaCl salt stress on the Na content and the Ca/Na, K/Na ratios of leaves

The results of the effect of CaCl$_2$ under increasing NaCl salt stress on the content of Na and the ratios of Ca/Na and K/Na of tomato leaves are given in Table 4 and Table 6, respectively. The effect of CaCl$_2$ and NaCl applied to the nutrient solution on the Na content was found statistically significant at 0.01 level. The addition of NaCl to the nutrient solution increased the Na content of leaves. The symptom toxicity in leaves was observed due to higher sodium content (Na content > 0.40%). The addition of CaCl$_2$ to the nutrient solution decreased the Na content of leaves. But this decrease in the Na content of leaves did not prevent the Na toxicity. The effect of NaClxCaCl$_2$ interaction on the Na content of leaves was found insignificant statistically. The CaCl$_2$ addition at the doses of 44.4 and 70.4 mM NaCl decreased the Na content of leaves, but this decrease was found insignificant statistically.

Table 6. The effect of $CaCl_2$ under increasing NaCl salt stress on the ratios Ca/Na and K/Na of tomato leaves

$CaCl_2$ (mM)	Leaf Ca/Na ratio NaCl (mM)				Leaf K/Na ratio NaCl (mM)			
	0	44.4	70.4	Ave.	0	44.4	70.4	Ave .
0.0	28.29c	3.21f	2.33f	11.28c	4.37	0.37	0.64	1.76
6.8	44.63b	8.78ef	6.70ef	20.04b	4.95	0.78	0.88	2.20
16.8	91.98a	15.25de	7.27ef	38.17a	5.72	1.17	1.16	2.68
Ort.	54.97a	9.08b	5.43b		5.01a	0.77b	0.86b	
	$LSD_{0.05}CaCl_2$: 6.60 $LSD_{0.05}$NaCl: 6.60 $LSD_{0.05}CaCl_2$xNaCl: 11.43				$LSD_{0.05}$NaCl: 0.98			

* There is no difference at the level of 0.05 between averages shown with the same letters

The effect of NaCl, $CaCl_2$ and NaClx$CaCl_2$ interaction on the Ca/Na and K/Na ratios of leaves were found significant statistically at 0.01 level. Increasing dose of NaCl decreased significantly the Ca/Na ratio of leaves. Increasing dose of $CaCl_2$ increased significantly the Ca/Na ratio of leaves. The effect of $CaCl_2$ on the Ca/Na ratio varied depend on the NaCl dose. Increasing dose of $CaCl_2$ at the levels of 0 and 44.4 mM NaCl increased the Ca/Na ratio significantly. But the effect of $CaCl_2$ on the Ca/Na ratio of leaves at the dose of 70.4 mM NaCl was not found significant. The effect of NaCl on the K/Na ratio of leaves was found significant statistically at 0.01 level. As the dose of NaCl increased, the K/Na ratio of leaves decreased significantly. The effect of $CaCl_2$ and NaClx$CaCl_2$ interaction on K/Na ratio of leaves was found insignificant. In order to decrease the uptake of sodium by plant at the growing media with higher salt, the elevation of calcium in growing media is important method for providing the tolerance of plant against salt. In general, it is determinated that the ratios of Ca/Na and K/Na of the plant which has tolerance to salt stress is higher. Especially, it is suggested that the ratios of Ca/Na, K/Na and sodium concentration of leaves and tissue is determinated for assess the degree of plant's tolerance against salt (Marschner, 1995; Daşgan et al., 2002). Yetişir and Uygur (2009) reported that the ratios of Ca/Na and K/Na in watermelon and zucchini genotype decreased with the application of salt. The researchers reported that the plants which have higher both dry matter and Ca/Na, K/Na ratios are resistant to the salt.

Conclusion

In general, NaCl and $CaCl_2$ decreased fruit yield, NaCl decreased stem amount whereas $CaCl_2$ increased it at 6.8 mM. $CaCl_2$ decreased fruit yield without NaCl, but it increased fruit yield significantly at 44.4 mM dose and caused tolerance to NaCl. However, $CaCl_2$ did not cause tolerance at high doses of NaCl in terms of growth. Calcium chloride used together with sodium chloride reduces more than without sodium chloride the fruit yield and stem dry matter. $CaCl_2$ decreased brix of fruit, while NaCl increased it. $CaCl_2$ increased brix without NaCl, but decreased it at 44.4 and 70.4 mM NaCl. $CaCl_2$ and NaCl decreased fruit juice pH significantly. $CaCl_2$ applied at high doses of NaCl decreased the NFBER and provided tolerance to NaCl. Increasing dose of $CaCl_2$ increased significantly the Ca/Na ratio of leaves. The effect of $CaCl_2$ on the Ca/Na raito varied depend on the dose of NaCl. Increasing dose of $CaCl_2$ at the levels 0 and 44.4 mM NaCl increased the ratio Ca/Na significantly. But the effect of $CaCl_2$ on the ratio Ca/Na of leaves at the dose of 70.4 mM NaCl was not found significant. As the dose of NaCl increased, the K/Na ratio of leaves decreased significantly. The effect of $CaCl_2$ and NaClx$CaCl_2$ interaction on K/Na ratio of leaves was found insignificant.

Acknowledgement

We thank to Agricultural Faculty Deanery of Ondokuz Mayis University for all support and contributions. This study is a partition of MSc thesis prepared by Arife Karagöl.

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