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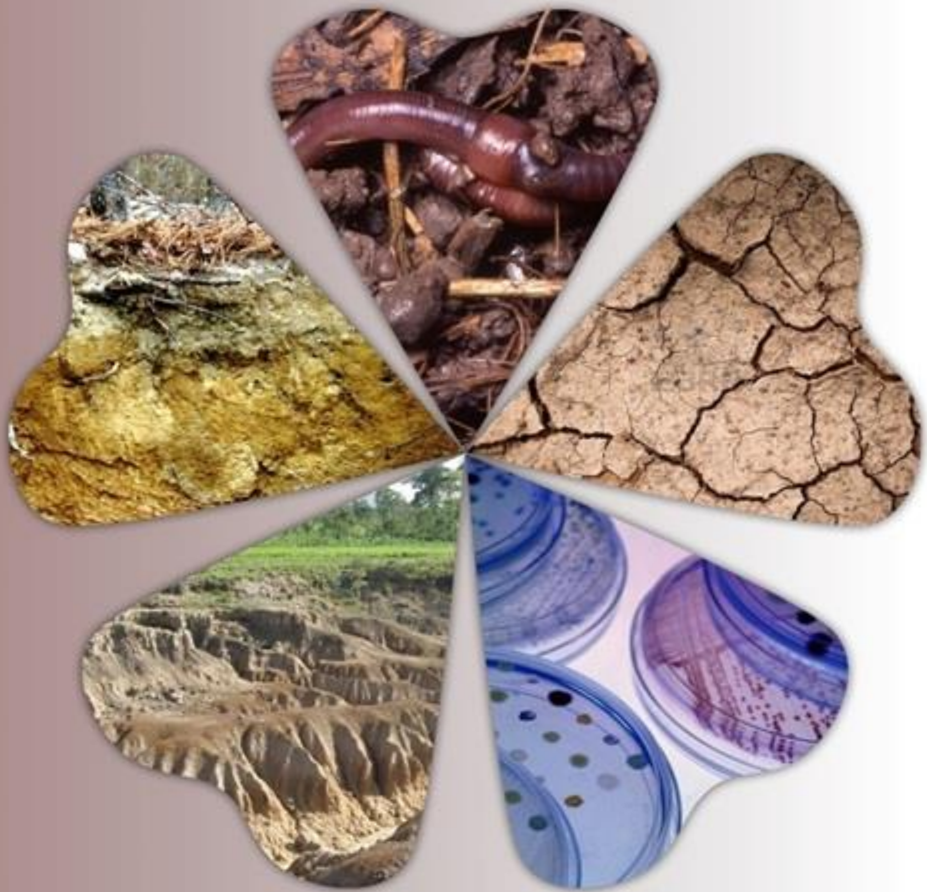

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Isolation, characterization and screening of PGPR capable of providing relief in salinity stress

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Abstract

Environmental stresses such as drought, temperature, salinity, air pollution, heavy metals, pesticides, and soil pH are major limiting factors in crop production because they affect almost all plant functions. Soil salinization is a serious stress condition causing major problem for crop productivity. To combat this salinity stress, Plant growth promoting rhizobacteria (PGPR) is considered as innovative, effective and ecofriendly approach. Plant growth promoting rhizobacteria (PGPR) have various direct and indirect mechanisms which can be correlated with their ability to form biofilms, chemotaxis, and the production of exopolysaccharide, indole-3-acetic acids (IAA) and aminocyclopropane-1- carboxylate (ACC) deaminase Investigations on the interaction of PGPR with other microbes and their effect on the physiological response of crop plants under different soil salinity regimes are still at an incipient stage. An experiment was conducted to investigate the effect of PGPR on lowering down the salt stress. Treatments were control (T_1), Salt tolerant isolate KH-1 (T_2), Salt tolerant isolate KH-2 (T_3), Salt tolerant isolate KH-3 (T_4), PGPR-I (Pseudimonas) (T_5), PGPR-II (Azotobacter) (T_6). Rice was sown under saline conditions at Soil Salinity Research Institute, Pindi Bhattian. With the inoculation of salt tolerant PGPR, plant growth and yield was improved. Result showed significant increase in plant height, biomass and yield over control. Inoculation of salt tolerant isolate KH-2 produced maximum grain yield in rice (4267 kg/ha) followed by PGPR-II and it was statistically significant from all other treatments along with control. It is concluded that with the application of salt tolerant isolate (KH-2), there is significant increase in rice production.

Keywords: PGPR, abiotic stresses, Azotobacter, Pseudomonas, auxin production.

Introduction

Due to salt stress agricultural productivity has been decreased all over the world (Jouyban, 2012). According to an estimate about 20 % of all irrigated and cultivated lands (equivalent to 62 million ha) are negatively affected by salt stress at present time (Khan et al., 2015). In arid and semiarid regions salinity is considered as major hurdle to plant growth and productivity. About 831 mha of land is affected by salt all over the world (FAO, 2008). Agriculture has very special place in Pakistan's economy. Irrigated agriculture in Pakistan is facing the problem of water-logging and salinity therefore productive lands are continuously going out of cultivation (Chaudhary, 2001). The limited rainfall, high evapotranspiration rate and high temperature are the major causes of salinity in arid and semiarid regions (Neto et al., 2006). The occurrence of physiological and molecular disorders due to salinity is under consideration since many years but the actual process is still unknown (Hasegawa et al., 2000). Due to salinity, synthesis of lipids and protein along with photosynthesis are badly affected in plants (Parida and Das, 2005).

Soil salinity is considered as great threat all over the world that affects nearly one billion hectare land and has an adverse effect on crop production of productive lands (Rengasamy, 2006) and considered as a major

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challenge to farmers (Flowers and Flowers, 2005). In irrigated areas this problem is more dominant (Flowers, 1999; Zhu, 2001) that is major cause in loss of food production (Munns and Tester, 2008). There is also problem of salinity in dry land regions (Wang et al., 1993; Rengasamy, 2006). In saline condition more salts are present in soils. NaCl is the most dominant in salt effected soils (Zhang et al., 2010).

Due to salinity uptake and translocation of Na^+ and K^+ is affected which results in poor plant growth and metabolism through reduced uptake, nutritional imbalance and toxic effect of some ions. (Nawaz et al., 2002; Tavakkoli et al., 2010). The increased uptake of K results in decreased uptake of K and Ca (Marschner, 1995; Yildirim et al., 2006). The nitrate reductase activity is inhibited by accumulation and uptake of Cl^- which in return greatly disturb the photosynthetic activity of plant (Tavakkoli et al., 2000). Salts get accumulated in the intercellular spaces when the capacity of cell to store a specific concentration of salt is exceeded and results in cell dehydration which eventually lead to cell death (Sheldon et al., 2004).

Salinity causes a number of biochemical and physiological changes in plant cells that lead to stress symptoms on plants and ultimately reduce growth and development of whole plant (Huang et al., 2012). Plants have different mechanisms to tolerate salinity which includes compartmentation of inorganic ions, adjustment in osmotic balance and reduction in leaf osmotic potential by synthesis of organic solutes etc (Hasegawa et al., 2000).

The use of PGPR is one approach to solve the issue of salinity. Different plant growth promoting rhizobacteria (PGPR) residing near the roots of plants have been reported to provide beneficial effects by different direct and indirect processes. These bacteria have ability to combat salinity stress by different mechanisms which include production of indole-3-acetic acid (IAA), production of ACC-deaminase, solubilization of phosphorus, exopolysaccharide production, production of volatile compounds etc. Auxin (IAA) production by PGPR which stimulates the production of flavonoids by plants, improves nitrogen fixation, nodulation and nutrient uptake which in turn reduced the harmful effects caused by salinity (Dodd and Pérez-Alfocea, 2012). Ethylene act as inhibitor when released during stress by plants and causes reduction in legume's nodulation. In plants the pathway of production of ethylene is Yang cycle in which ACC oxidase enzyme is responsible for the conversion of ACC into ethylene (Tilak et al., 2005). Plant growth promoting rhizobacteria (PGPR) have ability to produce enzyme 1-aminocyclopropane-1-carboxylic acid deaminase (ACC-D), which is actually a precursor of ethylene and reduces the level of ethylene during salt stress (Glick, 2014; Choudhary et al., 2015). The AAC deaminase producing PGPR attached to the root of plants and uptake ACC which is released from plant roots and then hydrolyze it (Glick et al., 1998.) Many scientist have reported in reduction of salinity stress through ACC-D containing PGPR and thus improve plant growth (Glick, 2010; Ahmed and Farag 2011).

Microbial secreted exopolysaccharides (EPS) are responsible for chelation of surplus ions and decreases the availability of these ions (Na^+) to plants. (Choudhary et al., 2015). PGPR are responsible to solubilize the insoluble nutrients like iron, zinc, potassium and phosphorus by secreting organic acids in the rhizosphere which in turn increases the uptake of nutrients by plants. One novel approach of PGPR is the production of VOCs (Volatile Organic Compounds) which are responsible for signalling between plant and microbe. Specific strains of bacteria releases volatile compounds increased the growth of plants by variable processes like osmoprotectant biosynthesis, nutrient uptake, hormone distribution and sodium homeostasis (Singh et al., 2008; Liu and Zhang, 2015). Mitigation of salinity by PGPR inoculants has been shown in rice, wheat, maize, cotton, lettuce, tomato and pepper (da Costa et al., 1998, Bacilio et al., 2004; Parida and Das 2005).

Pakistan is the world's 11th largest producer of rice. Pakistan's exports make up 8% of world's total rice trade. It is an important crop in the agriculture economy of Pakistan. Rice is an important Kharif crop. In the year 2016/17, Pakistan produced 6.7 million tonnes, of which around 4 million were exported, mainly to neighbouring countries, the Middle East and Africa. Rice is grown in fertile lands of Sindh and Punjab region where millions of farmers rely on rice cultivation as their major source of employment. Among the most famous varieties grown in Pakistan include the Basmati, known for its flavour and quality. Pakistan is a major producer of this variety.

The objective of this research is the isolation and characterization of salt tolerant PGPR from salt affected areas. Based on IAA production and their growth promotion abilities, selected bacterial isolates were tested for growth and production of rice under salinity conditions in field experiment.

Material and Methods

Isolation of salt tolerant bacteria

Soil samples were collected from Kheura salt mines situated in Pind Dadan Khan and its nearby areas from rhizosphere of different plants. Samples were shifted to lab and store under cold condition (4 ºC) for further proceedings. Salt tolerant bacteria (STB) were isolated from dilution plate technique on LB medium

(Tryptophane; 10, NaCl; 10, Yeast; 5, Agar; 20g/L). From the preserved soil samples, one gram of soil was weighed and different dilutions were made. Dilutions were spread on petri plates containing LB agar medium and incubated at 28±2 ºC. After growth of bacterial colonies, the isolates having glycery and proliferating growth were frequently streak on LB medium to get purified colonies. Isolated colonies were preserved at -40°C in glycerol solution.

Characterization of selected isolates

Selected bacterial isolates were characterized for IAA production activity (Sarwar et al., 1992). To diagnose the bacterial auxin production the method of Sarwar et al. (1992) was followed. For this 25 mL of General Purpose Media (GPM) media was autoclaved and cooled and inject with bacterial isolates @ 1 mL/flask. The solution was incubated (28 ± 1 ◦ C for 48 hours) and filtered through Whatman No. 2. The filtrate (3ml) was taken and 2 ml Salkowski's reagent (98 mL of 35% $HClO_4$ +2.0 mL of 0.5 M $FeCl_3$) was added. The samples were run on spectrophotometer at 535nm wavelength. An un-inoculated control with GPM broth was also prepared for comparison.

Screening of bacteria for plant growth promotion activities under controlled conditions

An experiment was planned in growth room to check the efficiency of bacteria for growth promotion under normal and controlled condition (Temp 30-35°C). A pot experiment was conducted in the growth room of Soil Bacteriology Section, AARI, Faisalabad, Pakistan. Ten pre isolated salt tolerant isolates were used to check microbial effect on rice growth. Growth parameters were studied after 10 days of seed germination. On the basis of growth parameters (Root and shoot length, and dry biomass), 3 best growth promoting bacterial isolates were selected for further study. Two pre isolated isolates PGPR-I (Pseudomonas) and PGPR-II (Azotobacter) were also used in this experiment. Completely randomized design (CRD) was used for this experiment.

Field Experiment

Field experiment on rice was conducted at the Soil Salinity Research Institute, Pindi Bhattian having EC=06. The main objective of this study was to analyze the effectiveness of salt tolerant bacteria on growth and yield parameters by adaptations against the salt stress conditions on field level**.** Rice variety Super Basmati was used for the experiment. The statistical design was randomized complete block design (RCBD) having three replicates. Treatments were T_1=control, T_2=KH-1, T_3=KH-2, T_4=KH-3, T_5=PGPR I (Pseudomonas) and T_6=PGPR II (Azotobacter).

Statistical Analysis

The analysis of data was done by using analysis of variance technique (ANOVA) with RCBD (Steel et al., 1997). For this purpose, software Statistix 8.1 was used and arithmetic means were compared by using least significant difference (LSD) test.

Results

The present study was conducted to discover the efficiency of salt tolerant bacteria as suppressor of the salt stresses.

Isolation, screening and characterization of salt tolerant bacteria (STB)

The salt tolerant bacteria were isolated from different plant rhizosphere by using dilution plate technique on LB media. Total 20 isolates were isolated from rhizosphere and characterized on the basis of auxin production. Ten isolates were carefully chosen and screened on growth promotion basis through bioassay in lab and three promising isolates wee then selected on the basis of maximum root/shoot elongation. These three isolates along with two pre-isolated PGPR were tested in field conditions having highly saline soils.

Auxin production (μg mL^{-1})

Data expressed the potential of various isolates to produce auxin (as IAA equivalents). The data related to auxin production is presented in Table 1. All isolates produced auxin in broth culture. The maximum auxin production as IAA equivalents was recorded in KH-1 bacterial isolate (13 μg mL^{-1}) followed by KH-2 and KH-3 (11.8 μg mL^{-1}) and it was statistically different from control. The IAA produced by bacterial isolates could be useful with plants especially when interacted with plant exudates that may help the IAA production potential of the bacteria (Harrison et al., 2002; Rani et al., 2012).

Table 1. Auxin level of different isolate

Isolates	Auxin (μg mL^{-1})		Isolates	Auxin (μg mL^{-1})		Isolates	Auxin (μg mL^{-1})	
Control	2.8	j	KH-7	5.8	fghi	KH-14	10.0	bc
KH-1	13.0	a	KH-8	8.6	cde	KH-15	4.1	hij
KH-2	11.8	ab	KH-9	7.8	cdef	KH-16	8.8	cde
KH-3	11.8	ab	KH-10	6.3	fgh	KH-17	9.5	cd
KH-4	5.0	ghij	KH-11	7.5	def	KH-18	9.5	bcd
KH-5	6.7	efg	KH-12	4.9	ghij	KH-19	6.3	fgh
KH-6	3.8	ij	KH-13	6.9	efg	KH-20	7.5	def

Screening of bacteria for plant growth promotion activity through bioassay

Data regarding shoot/root length and biomass are shown in Table 2. The inoculation of bacterial isolates in abiotic stress conditions showed positive response on growth. Maximum shoot length (40.7 cm) was observed in isolate KH-1 and showed significant difference statistically from control. The root length, shoot fresh biomass and root fresh biomass was also showed higher response upon inoculation as compared to control. Among the bacterial isolates KH-10 showed minimum response towards inoculation. The improvement in plant physical parameters may be the result of production of different plant growth regulators and siderophores (Kloepper et al., 1989; Arshad and Frankenberger Jr., 1998).

Table 2. Effect of STB on growth parameters

Isolates	Shoot Length (cm)		Root length (cm)		Shoot fresh biomass (g)		Root fresh biomass (g)	
Control	28.6	d	25.6	e	2.31	de	2.45	de
KH-1	40.7	a	45.9	a	3.98	a	4.49	a
KH-2	38.4	ab	32.4	cd	3.24	bcd	3.98	bc
KH-3	32.4	cd	39.8	bc	3.12	cd	4.24	ab
KH-14	39.6	ab	29.6	de	2.56	cde	3.14	cde
KH-18	35.4	bc	28.4	de	2.35	cde	3.56	bcd
KH-17	36.4	abc	41.5	ab	3.39	ab	3.32	cd
KH-16	34.2	cde	32.5	cd	3.56	bc	3.28	cd
KH-8	39.6	ab	36.7	bcd	3.48	bc	3.92	bc
KH-9	37.6	abc	35.9	bc	2.98	cd	3.52	bcd
KH-11	32.3	cd	33.9	cd	3.48	bc	3.21	cd

Yield parameters

Data of field trial showed that with the inoculation of salt tolerant PGPR plant growth and yield was significantly improved. Result showed that bacterial inoculation significantly enhanced the plant height, biomass, yield and no. of tillers over control.

Plant Height

According to the results (Figure 1) plant height was increased upon inoculation over control and maximum (132.7 cm) was observed in case of KH-2 inoculation.

As compare to control (110.0cm) plant height was increased in all other treatments. In case of PGPR II (Azotobacter) inoculation plant height was more (127.7 cm) as compared to PGPR I (Pseudomonas) inoculation (121.0 cm). Similarly in case of KH-1 plant height was more (124.3 cm) as compared to KH-3 (121.7 cm). But in case of KH-2 plant height was maximum (132.7 cm). So, KH-2 showed the more pronounced response as compare to all other treatments. In case of salt tolerant bacteria KH-2 showed better response and in case of PGPR II (Azotobacter) showed better results.

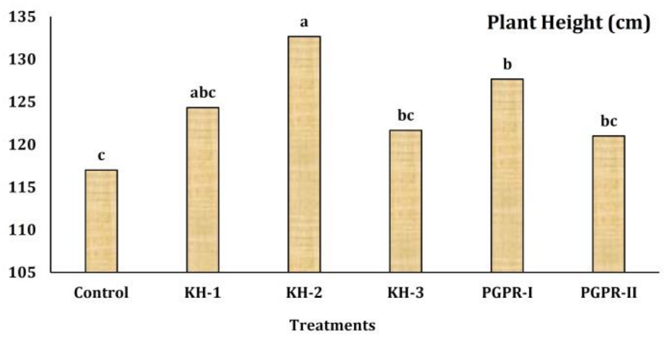

Figure 1. Effect of salt tolerant isolates and rhizobacteria on plant height of rice at SSRI, Pindi Bhattian

No. of Tillers

In case of number of tillers (Figure 2) same trend was found as in plant height. KH-2 showed more pronounced effect as compared to other isolates. As compared to control numbers of tillers (27) were more in all other treatments. In case of PGPR more number of tillers was found in PGPR II (Azotobacter) (41) as compare to PGPR I (Pseudomonas) (36). In case of salt tolerant bacteria maximum number of tillers (46) were found in KH-2 as compare to KH-1 (35) and KH-3 (30). So under salt stress conditions KH-2 shows better response as compare to other isolates.

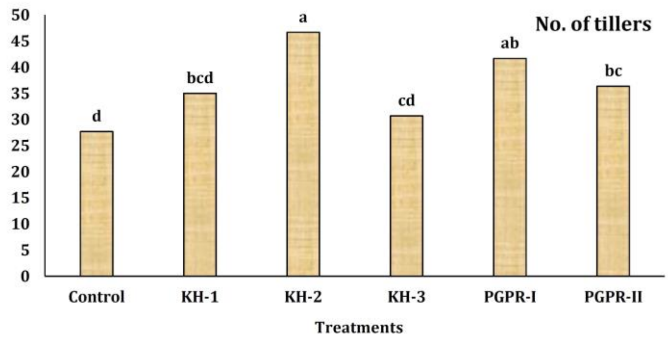

Figure 2. Effect of salt tolerant isolates and rhizobacteria on tillers/m2 in rice at SSRI, Pindi Bhattian

Straw Yield

Straw yield of rice was increased by the inoculation of salt tolerant bacteria and PGPR (Figure 3). In case of salt tolerant bacteria maximum straw yield was found by KH-2 (13.83 t/ha) as compare to KH-1 (12.61 t/ha) and KH-3 (12.25 t/ha). In case of PGPR II (Azotobacter) and PGPR I (Pseudomonas) inoculation trend in straw yield 12.81 and 12.20 t/ha respectively.

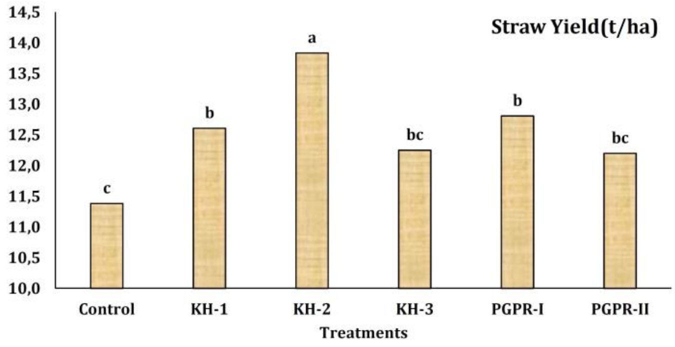

Figure 3. Effect of salt tolerant isolates and rhizobacteria on rice paddy yield at SSRI, Pindi Bhattian

Paddy Yield

Paddy yield of rice was increased with the inoculation of salt tolerant bacteria and PGPR. Inoculation of salt tolerant isolate KH-2 gives maximum paddy yield (4267 kg/ha) as compare to KH-1 and KH-3 3917 and 3557 kg/ha respectively. PGPR II (Azotobacter) inoculation gave more paddy yield (4073 kg/ha) as compare to PGPR I (Pseudomonas) inoculation (3820 kg/ha). So under salt stress conditions isolate KH-2 and PGPR II (Azotobacter) has more pronounced effect on paddy yield of rice crop (Figure 4).

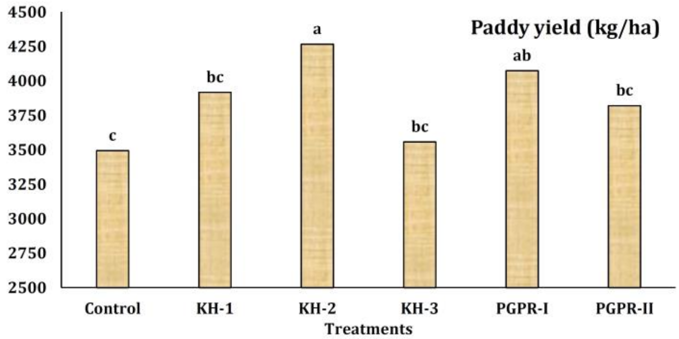

Figure 4. Effect of salt tolerant isolates and rhizobacteria on rice paddy yield at SSRI, Pindi Bhattian

Discussion

Salinity is one of the major problem that badly affects the health of plants and then decreases crop productivity. Plants itself have various defense mechanisms against salt stress but other soil-plant factors also have robust impact on salinity tolerance. One mechanism offered by soil is the presence of soil beneficial bacteria called PGPR possessing different direct and indirect effects to combat salinity. In the present study salt tolerant bacteria were isolated from the rhizospheric soil of different salt prone areas (Kheura mines and their surroundings). Then these bacteria were characterized on the basis of IAA production. Then lab study was conducted to screen out growth promoting abilities of PGPR. After that field trial was conducted at SSRI, Pindi Bhattian on rice. According to the results with the application of salt tolerant bacteria grain yield of rice was improved. They also have positive effect on the physical growth and other parameters of wheat and rice. Our results are related to the work of many other scientists in the literature.

PGPR have different pathways to ameliorate salts from the vicinity of plants. One mechanism is to produce compatible solutes including amino acids, sugars or their derivatives that act as osmolytes and in this way organism can survive the extreme salt conditions (Bacilio et al., 2004; da Costa et al., 1998; Parida and Das, 2005). The other bacterial traits like P-solubilization, auxin production, nutrients availability results in improved growth and yield of crop plants (Glick, 2010). The improvement in plant physical parameters may be the result of production of different plant growth regulators and siderophores (Kloepper et al., 1989; Arshad and Frankenberger Jr. 1998). Additionally, Tilak et al. (2005) suggest that those bacteria which are present in salt prone areas and isolate from those rhizospheres have natural ability to tolerate salinity. The IAA produced by bacterial isolates could be useful with plants especially when interacted with plant exudates that may help the IAA production potential of the bacteria. According to Usha et al., 2012 the most important signal molecule in the regulation of plant development is auxinl. Phosphorus is typically insoluble or poorly soluble in soils under salt stressed conditions and these PGPR helps in the solubilization of insoluble P and thus improve plant growth and development (Harrison et al., 2002; Glick, 2010). In another study carried out by Zhang et al. (2010) reported that through regulation of the potassium transporter HKT1 could reduce the bad effects of salinity which is induced by the inoculation of *Bacillus subtilis* GB03 in *Arabidopsis thaliana* (Hichem et al., 2009; Jeong et al., 2011). Oxidative damage caused by salinity can be reduced through synthesis of polyphenols by plants (Hichem et al., 2009; Nounjan et al., 2012, Amin et al., 2016). Co-inoculation of PGPR with Rhizobium improved plant dry matter significantly upon control (Rahman et al., 2016). Similar findings were reported by Qureshi et al. (2011) who observed a significant increase in concentration of nutrients in grains and other parts of plants by co-inoculation of *Bacillus* and *Rhizobium* in a pot experiment.

Conclusion

All the bacterial isolates showed high resistance to salinity stress. All the bacterial isolates showed significant improvement in plant growth parameters as compared to control. Among the salt tolerant isolates (KH-1, KH-2, KH-3), KH-2 performed better followed by PGPR II (Azotobacter). The grain yield of rice was also significantly increased by these two treatments over other treatments as well as control.

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Spatial variation of soil weathering processes in the tropical high reliefs of Cameroon (Central Africa)

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Abstract

The objective of the present work was to characterize the morphological, geochemical and mineralogical features of soil with regard to weathering processes as a function of topography and spatial variation of climate in tropical high reliefs of Cameroon. Field investigations permit to select three study sites Mbalam, Meleta and Secande respectively in the humid tropical zone, pseudotropical mountainous zone and in the tropical dry climate. Macroscopically, the studied soils are thick in Mbalam, medium thick in Meleta and relatively less thick in Secande. Globally, saprolite, a loose loamy clayey horizon and humiferous horizon were observed from the bottom to the top of the profiles. These profiles differ by their thickness, the differentiation of the saprolite horizons and the presence of humiferous horizons. They are characterized microscopically by in situ replacement of primary minerals by kaolinite/halloysite, gibbsite and iron oxides. Theses minerals are associated to anatase in Mbalam and to montmorilonite and calcite in Secande. Geochemical processes involving in the spatial differentiation of soils are monosiallitisation and allitisation in the humid tropical zone, monosiallitisation and high allitisation in the pseudotropical mountainous zone with Al_2O_3 content reaching 41% in the saprolite, and monosiallitisation associated to bisiallitisation in the tropical dry climate of Cameroon. The development of these geochemical processes is conditioned by topography, elevation, rainfall and temperature, which appear as the main factors responsible of the spatial variation of soil weathering processes in the tropical high reliefs of Cameroon.

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Introduction

The humid inter-tropical zone constitutes an original and extreme morphogenetic milieu. It is where the bioclimatic weathering mechanisms are most developed in the earth surface (Tricart, 1961). In almost all environments, physical and chemical weathering processes operate together, but usually one of these categories dominates. Although water plays a role in both weathering processes, it is essential for all types of chemical weathering. The meteoric water is the most important factor. It dissolves CO_2 from the atmosphere, which is needed to alter minerals and rocks, interacts with them and the vegetation it directly influences, and transports dissolved elements and particles to rivers and oceans (Nahon, 2003). The amount of rainwater that falls on the surface of the continents is decisive on the rates of deterioration and thus on the balance sheets. Therefore, where liquid water is absent, biogeochemical weathering is also virtually absent or negligible and largely dominated by physical weathering (Nahon, 2003; Gabler et al., 2008). Chemical weathering, then, is a dominant process in humid tropical regions, favouring formation of deeply weathered profiles (Voicu and Bardoux, 2002; Nahon, 2003; Gabler et al., 2008). Temperature is another principal climatic variable which influences dominant types and rates of weathering. Most chemical reactions proceed

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faster at higher temperatures. Low-latitude regions with humid climates consequently experience the most intense chemical weathering (Tardy, 1993; Gabler et al., 2008).

In the tropical environments, the study of rock weathering and its products concerns various geo-disciplines including soil science, geology, geochemistry, geomorphology and civil engineering. Each of these disciplines has historically been involved with the description and/or interpretation of weathered materials (Ehlen, 2005; Gracheva, 2011; Bétard, 2012). However, most studies focusing on weathering deal with the description and/or dating of vertical variations of weathered materials at the profile scale (Herrmann et al., 2007; Nguetnkam et al., 2008; Beauvais, 2009). Soils are globally deep and well differentiated, and landforms appear rounded in humid tropical environment (Gabler et al., 2008; Beauvais, 2009). Although chemical weathering is somewhat less extreme in the mid-latitude humid climates, his influence is apparent in the moderate soil depth and rounded forms of most landscapes in those regions (Gabler et al., 2008). Only a few studies bear on spatial variations of soil weathering processes and their controlling factors at the landscape scale (Bourgeon, 2001; Scarciglia et al., 2005; Bétard, 2012), though in Cameroon, climate varies from humid tropical rainforest in the Southern part to tropical dry savannah in the Far North (Suchel, 1987). In addition, spatial studies of rock weathering and its products devoted exclusively to high reliefs in this humid tropical zone are very rare. The present research focuses on soil developed in the high reliefs of Cameroon. The objectives are (i) to characterize the morphological, geochemical and mineralogical variations in soil properties as a function of topography and spatial variation of climate and (ii) to identify the factors that control soil weathering processes in these high reliefs of tropical zone characterized by steep environmental gradients and their variation along the latitude.

Material and Methods

The study sites are located at Mbalam, Meleta and Secande, respectively in the East, West and Far North regions of Cameroon (Figure 1). These three sites were chosen in relation to their bioclimatic contrasts (Table 1).

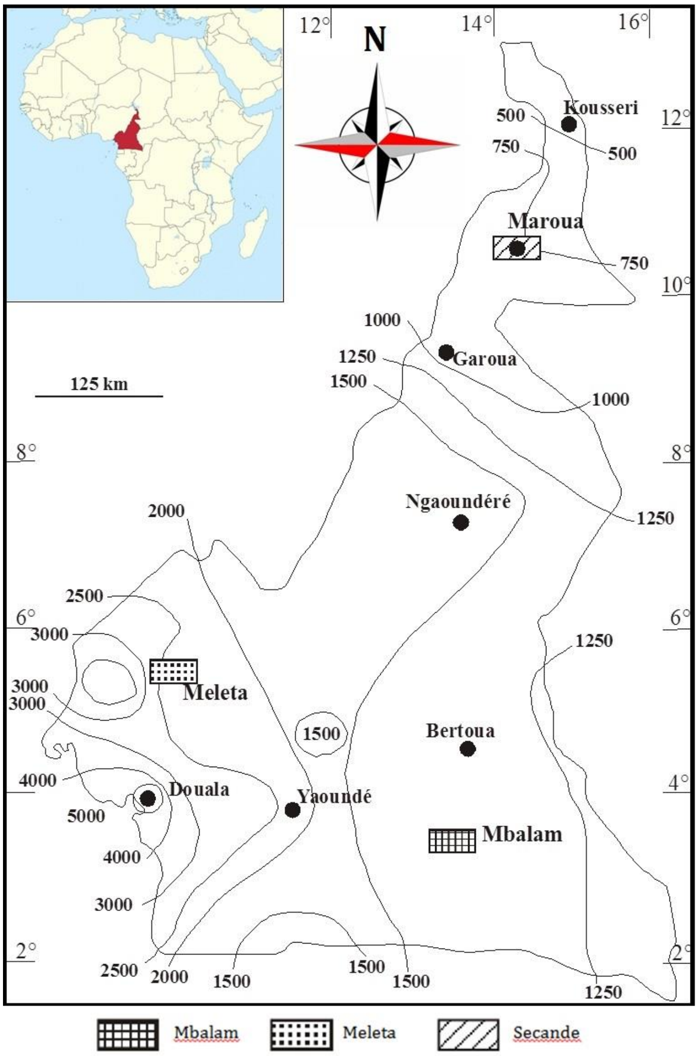

Figure 1. Location of the study area (modified from Nguetnkam et al., 2008).

Table 1. Characteristics of the three bioclimatic zones of Cameroon.

Characteristics	Bioclimatic zones		
	Mbalam	Meleta	Secande
Location	South Cameroon	West Cameroon	North Cameroon
Latitude	3°43'33''N-3°44'45''N	5°36'43''-5°38'31''N	10°35'00''-10°40'30'' N
Longitude	13°23'30''E-13°24'30''E	10°04'16''-10°05'49''E	14°16'04''-14°21'34'' E
Altitude	840m	2740m	640m
Climate	Humid tropical (Suchel, 1987)	Pseudotropical with temperate characteristics due to altitude (Morin, 1988)	Dry tropical (Suchel, 1987)
Mean annual rainfall	1640 mm	2507mm	757.2 mm
Mean annual air temperature	23°C	10-12°C	28.53°C
Vegetation	Evergreen forest (Letouzey, 1985)	lawn (*Sporobolus* prairies) strongly degraded by human activities (Morin, 1988)	Ephemeral grasses, strongly degraded by human activities (Letouzey, 1985)
Relief	Half-orange hills, narrow and outstretched valleys (Olivry, 1986)	Mountainous (Morin, 1988)	Mountainous
Slope gradient	Gentle (6-10%)	Steep	Gentle to steep
Bedrock	Garnet-rich micaschist (Vicat, 1998)	Trachyte (Marzoli et al., 1999; Nono et al., 2004; Gountié et al., 2012).	Microgabbro (Dumort and Peronne, 1966; Lasserre,1975).

Field work consisted firstly of morphological analysis of different topographic profiles in the three study sites. One soil pit was thereafter opened in the high topographic position in each site, described in detail and sampled for laboratory analyses. In the laboratory, soil pH was measured potentiometrically in a 1:2.5 soil: solution ratio (Guitián and Carballas, 1976). Bulk density was determined by clod method (Blake and Hartge, 1986). Optical microscope observations were done on rock and soil thin sections. For soil descriptions, the concepts and terms of Stoops (2003) were used. Soil mineralogy was determined by X-ray diffraction (XRD) on total soil powder. Clay fraction was not separated. X-ray diffraction patterns were recorded at room temperature using a classical powder diffractometer (X'pert Pro/Philips PW3710) instrument equipped with Ni-filtered and Cu anode (quartz monochromator, K-α1 wavelength =1.5405600X) operating at 45 kV and 40 mA. This Philips PW3710 instrument operates in continuous scan mode and in step scan mode range from 2° to 70°, with 2θ step of 0.02° and counting time of 0.50s per step. Minerals were identified using XRD coupled with standard saturation (K), solvation (ethylene glycol), and heat (550 °C) treatments (USDA, 2004). X-ray fluorescence for major element analysis was executed with a Philips spectrometer (PW 1404 WD) on total samples powder. Loss on ignition (LOI) was determined by ignition of samples at 1050°C for two hours. The chemical index of alteration (CIA) corresponds to $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)]\times100$, where CaO* is the amount of CaO incorporated in the silicate fraction of fresh rock while Na_2O, K_2O and Al_2O_3 are their concentrations in the analysed soil samples (Nesbitt and Young, 1982).

Results

Morphological, mineralogical and geochemical features of high reliefs' soils in the humid tropical rainforest of Mbalam

The studied profile is about 10 m thick. It is made up from the bottom to top of coarse saprolite, fine saprolite, nodular horizon and a red clayey horizon (Figure 2).

- Coarse saprolite (10- 8.25 m). It is gray yellow with a well preserved bedrock structure and the presence of numerous pink globular garnet crystals. Under the microscope, there are many gibbsite crystals in the domains with biotite and muscovite (Figure 2). Mineralogically, the horizon consists of muscovite, goethite, quartz, gibbsite, kaolinite, hematite and anatase (Table 2). The loose material is mainly composed of SiO_2 (62.60%), with a small amount of Al_2O_3, Fe_2O_3, K_2O, NaO, CaO and MgO (Table 2). In the "ghost" of garnet, Si contents are low meanwhile Al and Mg contents are high (Table 2).

- Fine saprolite (8.25-6.20 m). It is red (2.5YR4/6), with many isalteritic relicts, ferruginised friable quartz blocks and nodules. The matrix is clayey, with a very weakly developed blocky structure. Microscopically, it is characterized by a locally undifferentiated and stipple speckled b-fabric (Figure 2). Coarse materials are important (30%), with double spaced porphyric c/f related distribution patterns. The mineralogical composition was similar to that of coarse saprolite below (Table 2). SiO_2 contents decrease and 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 2);

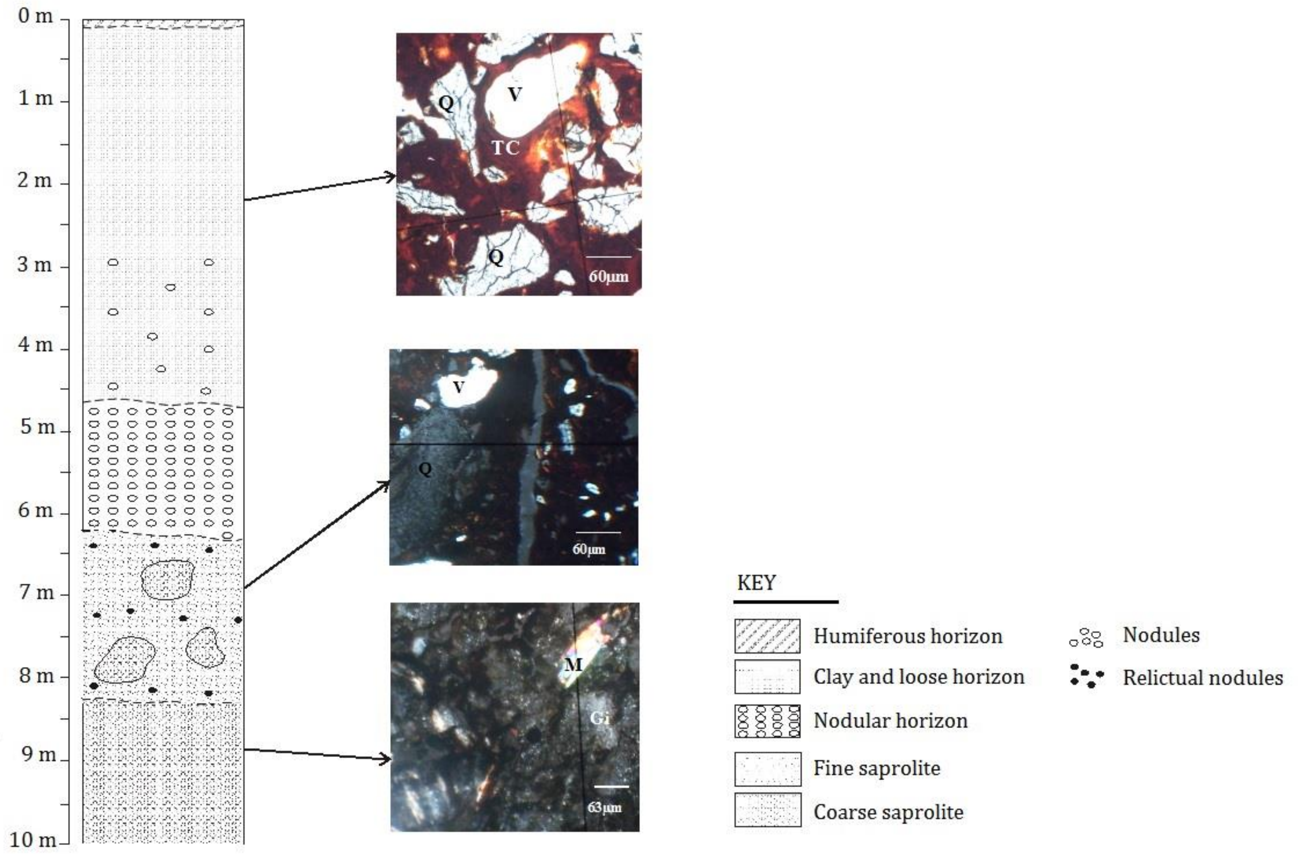

Figure 2. Macroscopic and microscopic organization of soil profile in Mbalam

- Nodular horizon (6.20-4.60 m). It is red (2.5YR4/6), clayey, with fine blocky structure and about 40% of nodules. Under the microscope, nodules are orange-brown (birefringent) or darker, and undifferentiated. The mineralogical composition was similar to that of other horizons below (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). K_2O, MgO, Na_2O and CaO contents remain almost constant but well represented here as in the other horizons (Table 2);

Table 2. Geochemical characteristics of soils developed in the high reliefs in the humid tropical rainforest of Mbalam.

Horizons	Micaschist (Total rock)	Micaschist (Garnet grains)	Coarse saprolite (Fine earth)	Coarse saprolite ("ghost" of garnet)	Fine saprolite (Fine earth)	Fine saprolite (Nodules)	Nodular horizon (Fine earth)	Nodular horizon (Nodules)	Set of clayey and loose horizons
Depth (m)	/	/	9 m	9 m	8 m	8 m	5.5 m	5.5 m	1.25 m
SiO_2	64.01	34.79	62.60	44.23	50.68	42.98	57.38	47.23	52.04
Al_2O_3	14.40	19.34	14.03	19.82	20.34	18.34	15.03	15.83	20.12
Fe_2O_3	6.91	31.16	6.12	5.65	6.02	7.31	5.62	8.12	6.23
CaO	3.01	8.07	2.43	2.20	2.01	2.96	3.13	2.40	1.92
MgO	4.20	0.56	1.98	4.34	3.12	3.01	2.13	2.11	2.70
Na_2O	2.50	0.00	3.11	2.23	2.10	3.36	2.20	3.24	1.32
K_2O	2.08	0.00	3.23	1.38	4.01	2.42	3.12	3.08	4.02
TiO_2	0.71	0.06	0.56	1.21	0.99	1.08	0.79	1.11	0.66
P_2O_5	0.15	0.16	0.31	0.12	0.26	0.31	0.27	0.24	0.09
LOI	2.37	/	6.75	18.53	9.97	17.53	10.36	16.55	10.70
Total	100.34	94.14	101.12	99.70	99.50	99.30	100.03	99.91	99.80
$\frac{Si}{Al}$	/	/	4.00	2.00	2.23	2.10	3.42	2.67	2.32
CIA	65.48	70.56	60.00	62.92	69.04	56.97	64.34	52.38	70.67
pH	/	/	5.2	/	4.4	4.4	4.6	5.2	4.7

Mu: muscovite : 9.96 Å, 9.93 Å, 4.47 Å ; K: kaolinite :7.17 Å, 7.19 Å, 7.21 Å ; Gi: gibbsite : 4.85 Å ; Goe: goethite :4.97 Å, 4.17 Å ; Q: quartz : 4.26 Å, 3.34 Å; He: hematite :2.69 Å, 1.45 Å ; A: anatase : 3.51 Å; F: Feldspar; B: biotite; Ga : garnet.

- Set of red clayey and loose horizons (4.60-0 m). It is constituted of matrix identical to that 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 (Figure 2). Nodules are rare. Coarse materials are important (10 to 20%). It is characterized by double spaced porphyric to open porphyric c/f related distribution patterns. The mineralogical composition was similar to that of other horizons below (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). They are followed by K (4.02% K_2O), Mg (2.70% MgO), Ca (1.92% CaO) and Na (1.32% Na_2O) which remain present here as in the other horizons (Table 2).

Morphological, mineralogical and geochemical features of high reliefs' soils in the humid tropical mountainous of Meleta

The studied profile in the humid mountainous zone of Meleta is about 2 m thick. It constituted of three horizons, which are from bottom to top: a saprolite, a yellowish red horizon and a black humiferous horizon (Figure 3).

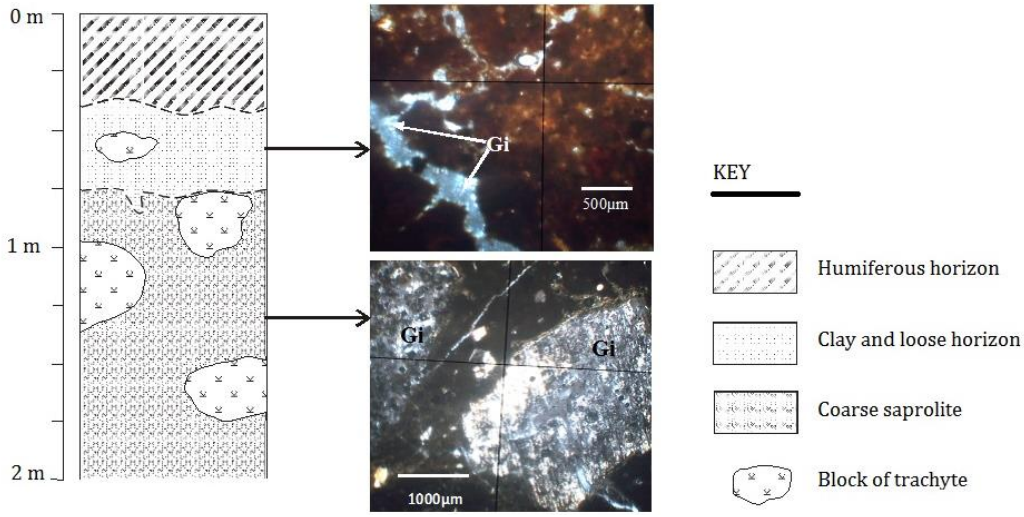

Figure 3. Macroscopic and microscopic organization of soil profile in Meleta.

- Saprolite (2-0.75m). It is composed of yellow brown (10YR6/8) and whitish gray (7.5YR7/0) domains. It is porous, characterized by loamy texture and massive structure, with a well preservation of the structure of the parent rock. Under the microscope, sanidine phenocrysts are partially or totally pseudomorphosed by gibbsite microcrystals (Figure 3). It is constituted of gibbsite, halloysite, quartz, magnetite, goethite and sanidine. On the geochemical point of view, the most important oxides are Al (41.10-39.10% Al_2O_3), Si (23.50-22.70% SiO_2) and Fe (8.94-6.63% Fe_2O_3). Little quantities of Ti (0.44-0.73 % TiO_2) and P (0.25-0.29% P_2O_5) are detected. The alkali and alkaline earth elements quantities are very weak (Table 3).

Table 3. Geochemical characteristics of soils developed in the high reliefs in the humid tropical mountainous of Meleta.

Horizons	Alkaline trachyte	Saprolite		Yellowish red clayey and loose horizon	Black humiferous horizon
Depth (m)	/	1.25-2 m	0.75-1.25 m	0.45-0.75 m	0-0.45 m
SiO_2	58.00	22.70	23.50	23.80	21.50
Al_2O_3	18.40	42.10	39.10	34.00	20.30
Fe_2O_3	5.63	6.63	8.94	8.75	7.05
CaO	2.10	0.01	0.00	0.08	0.23
MgO	0.41	0.09	0.13	0.29	0.30
Na_2O	6.56	0.00	0.00	0.20	0.15
K_2O	5.23	0.08	0.12	0.60	0.48
TiO_2	0.44	0.44	0.73	1.08	0.97
P_2O_5	0.14	0.25	0.29	0.32	0.35
LOI	2.01	26.20	28.00	30.20	48.10
Total	98.92	98.50	100.66	99.30	99.13
$\frac{Si}{Al}$	/	0.49	0.54	0.63	0.95
CIA	56.98	95.08	94.62	92.14	88.15
pH	/	5.4	5.3	5.0	3.9
Mineralogy	Sa Px Op	Sa Ma Ha Gi Q	Ma Ha Gi Goe Q	Ma Ha Gi Goe He Q	Ma Ha Gi Goe He Q

Ma : magnétite : 2.53 Å; Gi : gibbsite : 4.85 Å; Goe : goethite : 4.18 Å ; Q : quartz : 4.29Å, 3.37Å; He : hématite : 2.69 Å ; Ha : halloysite : 10 Å, 7.20 Å ; Sa : sanidine ; Px : pyroxene ; Op : opaque minerals.

- Yellowish red horizon (0.75-0.45m). Beyond the yellowish red colour (5YR4/4), the horizon is clayey, with a fine blocky structure. Under the microscope, the groundmass has moderate separated subangular blocky microstructure, with compound packing voids and undifferentiated b-fabric (Figure 3). Gibbsite crystals are observed in some voids. In addition to the mineralogical composition noted in the saprolite, hematite is present (Table 3). On the geochemical view point, Al (34.00% Al_2O_3), Si (23.80% SiO_2) and Fe (8.75% Fe_2O_3) remain the most important oxides. Ti (1.08% TiO_2), K (0.60% K_2O), P (0.32% P_2O_5), Mg (0.29% MgO) and Na (0.20% Na_2O) are weakly represented and Ca is almost absent (0.08% CaO) (Table 3).

- Humiferous horizon (0.45-0m). It is black (2.5YR2.5/0), characterized by high matrix porosity a loamy texture and a blocky structure. Mineralogically, gibbsite, halloysite, goethite, hematite and quartz still the main minerals (Table 3). On the geochemical view point, Si (21.50% SiO_2), Al (20.30% Al_2O_3) and Fe (7.05% Fe_2O_3) are also the most important elements. The other elements Ti (0.97% TiO_2), K (0.48% K_2O), P (0.35% P_2O_5), Mg (0.30% MgO), Ca (0.23% CaO) and Na (0.15% Na_2O) remain weakly represented (Table 3).

Morphological, mineralogical and geochemical features of high reliefs' soils in the dry tropical zone of Secande

The Secande studied soil profile was ~ 2 m thick. Four main horizons were distinguished from the bedrock to the surface: a coarse saprolite, a fine saprolite, a loose loamy clayey horizon and a humiferous horizon (Figure 4).

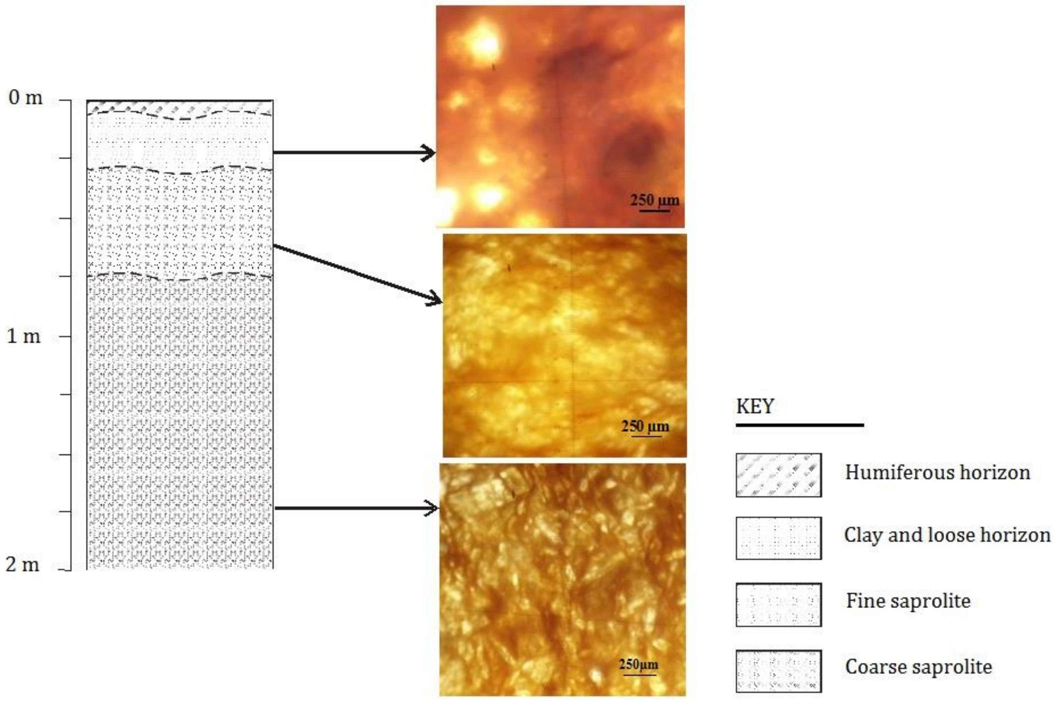

Figure 4. Macroscopic and microscopic organization of soil profile in Secande

- Coarse saprolite (2-0.75 m). The coarse saprolite was yellowish (10YR 7/8), compact, massive, with many fissures surrounding compact undifferentiated blocks. The original structure of the bedrock was preserved. Under the microscope, all the primary minerals had disappeared, and the preservation of the bedrock structure was marked by numerous remnants of altered plagioclases shape (Figure 4). The groundmass was characterized by a double spaced fine, ranging from equal to enaulic c/f-related distribution pattern. It showed a yellowish red birefringent micromass. The secondary minerals were montmorilonite, kaolinite, goethite, quartz, feldspar and calcite (Table 4). From the geochemical point of view, SiO_2 was the most represented oxide (53.90-53.10 %). It was followed by Al_2O_3 (15.00-14.70 %), Fe_2O_3 (10.75-10.90 %), Na_2O (4.11-4.33 %), MgO (1.76-2.06 %) and CaO (1.02-2.06 %) (Table 4).

- Fine saprolite (0.75-0.30 m). The fine saprolite was reddish yellow (7.5YR 6/8), loamy and massive. There were many fissures surrounding small gray compact blocks, globally embedded in loose loamy texture matrix. The structure of the bedrock was preserved only in gray compact blocks. Under the microscope, remnants of altered plagioclases shape had almost disappeared. The groundmass was yellowish, characterized by weakly separated granular microstructure (Figure 4). Secondary minerals were montmorilonite, kaolinite, goethite, quartz, feldspar and calcite (Table 4). From the geochemical point of view, SiO_2 remained the dominant oxide (52.10%), followed by Al_2O_3 (15.55 %), Fe_2O_3 (11.20%), Na_2O (4.76 %) and CaO (3.23 %) (Table 4).

Table 4. Geochemical characteristics of soils developed in the high reliefs in the dry tropical zone of Secande

Horizons	Microgabbro	Coarse saprolite (Bottom)	Coarse saprolite (Top)	Fine saprolite	Loamy clayey horizon	Humiferous horizon
Depth (m)	/	2-0.75		0.75-0.30	0.30-0.07	0.07-0
SiO_2	48.90	53.90	53.10	52.10	51.60	50.80
Al_2O_3	16.95	15.00	14.70	15.55	16.25	15.90
Fe_2O_3	10.55	10.75	10.90	11.20	11.80	11.85
CaO	9.55	1.02	4.22	3.23	3.02	5.12
MgO	6.87	2.06	1.76	1.78	1.68	1.76
Na_2O	2.50	4.11	4.33	4.76	3.55	3.02
K_2O	1.17	0.46	0.27	0.31	0.24	0.30
TiO_2	1.15	1.06	1.14	1.20	1.23	1.20
P_2O_5	0.20	0.22	0.28	0.21	0.08	0.10
LOI	3.38	9.05	8.88	10.10	11.50	10.30
Total	101.39	100.85	99.81	100.68	101.26	100.62
$\frac{Si}{Al}$	2.59	3.22	3.24	3.00	2.85	2.86
CIA	56.18	51.51	50.95	51.54	54.92	55.27
pH	/	7.50	7.60	7.80	6.70	6.50
Mineralogy	A F B Ca	Mo K Goe Q F Ca	Mo K Goe Q F Ca	Mo K Goe Q F Ca	Mo K Goe Q F Ca	Mo K Goe Q F Ca

Mo= montmorillonite: 10Å, 15.48Å, 17.64Å; K= kaolinite: 7.1Å, 3.57Å; Goe= goethite: 4.17Å, 2.45Å; Q= quartz: 4.29Å, 3.37Å, 2.12Å, 1.82Å; F= feldspath: 3.24; Ca= calcite: 3.89Å; B: biotite; A: amphibole.

- Loose loamy clayey horizon (0.30-0.07 m). The horizon was reddish yellow (5YR 6/8), loose and loamy clayey. It was weakly blocky to massive, characterized by a high matrix porosity and the presence of many rootlets. Under the microscope, remnants of altered plagioclases shape were not visible. The groundmass had a vughy microstructure and reddish micromass (Figure 4). It had a speckled and cloudy limpidity (Figure 4). The mineralogical composition was similar to that of saprolite. From geochemical point of view, compared to the coarse and fine saprolite, all the major oxides contents showed a very little variation and remained widely dominated by SiO_2 (Table 4).

- Humiferous horizon (0.07-0 m)**.** The humiferous horizon was yellowish red (5YR 5/8), loamy clayey, characterized by a weakly expressed lumpy structure, a high matrix porosity and the presence of many rootlets. The mineralogical composition was similar to that of the underlying horizons. From geochemical view point, compared to the below horizons, all the major oxides contents showed a very little variation and remained largely dominated by SiO_2. This oxide was followed by Al_2O_3, Fe_2O_3, CaO, Na_2O and MgO as the well represented oxides (Table 4).

Evaluation of weathering trend and intensity

Selected major element–Al_2O_3 variation diagrams plotted on an anhydrous basis are given for each group in Figure 5. 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. Globally, Na_2O, K_2O, CaO and Fe_2O_3 contents exhibit very weak correlations with Al_2O_3 (Figure 5). In detail, these correlations are more expressed on trachyte and microgabbro, except for Fe_2O_3 (Figure 5).

In Mbalam, the $\frac{Si}{Al}$ ratio varies between 2 and 2.67 and CIA ranged from 52.38 to 70.67 (Table 2). In the triangular diagram SiO_2-Al_2O_3-Fe_2O_3, all points appear localized on the SiO_2-Al_2O_3 axis. There is a shift toward the SiO_2 pole, indicating the importance of Al in these soils, whose composition are dominated by Si due to the presence of primary minerals, quartz and muscovite (Figure 6).

In Meleta, the $\frac{Si}{Al}$ ratio varies between 0.49 and 0.95 and CIA ranged from 56.98 to 95.08 (Table 3). A representation in the triangular diagram SiO_2-Al_2O_3-Fe_2O_3 showed that all points appear localized on the SiO_2-Al_2O_3 axis, with a shift toward the Al_2O_3 pole, in line with the high expression of Al in the studied soil in the form of gibbsite (Figure **6**).

In Secande, the $\frac{Si}{Al}$ ratio was high, ranging between 2.85 and 3.24 and CIA ranged from 50.95 to 55.27 % (Table 4). A representation in the triangular diagram SiO_2-Al_2O_3-Fe_2O_3 showed that all samples were also localized on the SiO_2-Al_2O_3 axis, toward SiO_2 pole in line with high $\frac{Si}{Al}$ ratio (Figure 6). This is indicative of an excess of SiO_2 in the studied soils and confirmed the presence of montmorillonite.

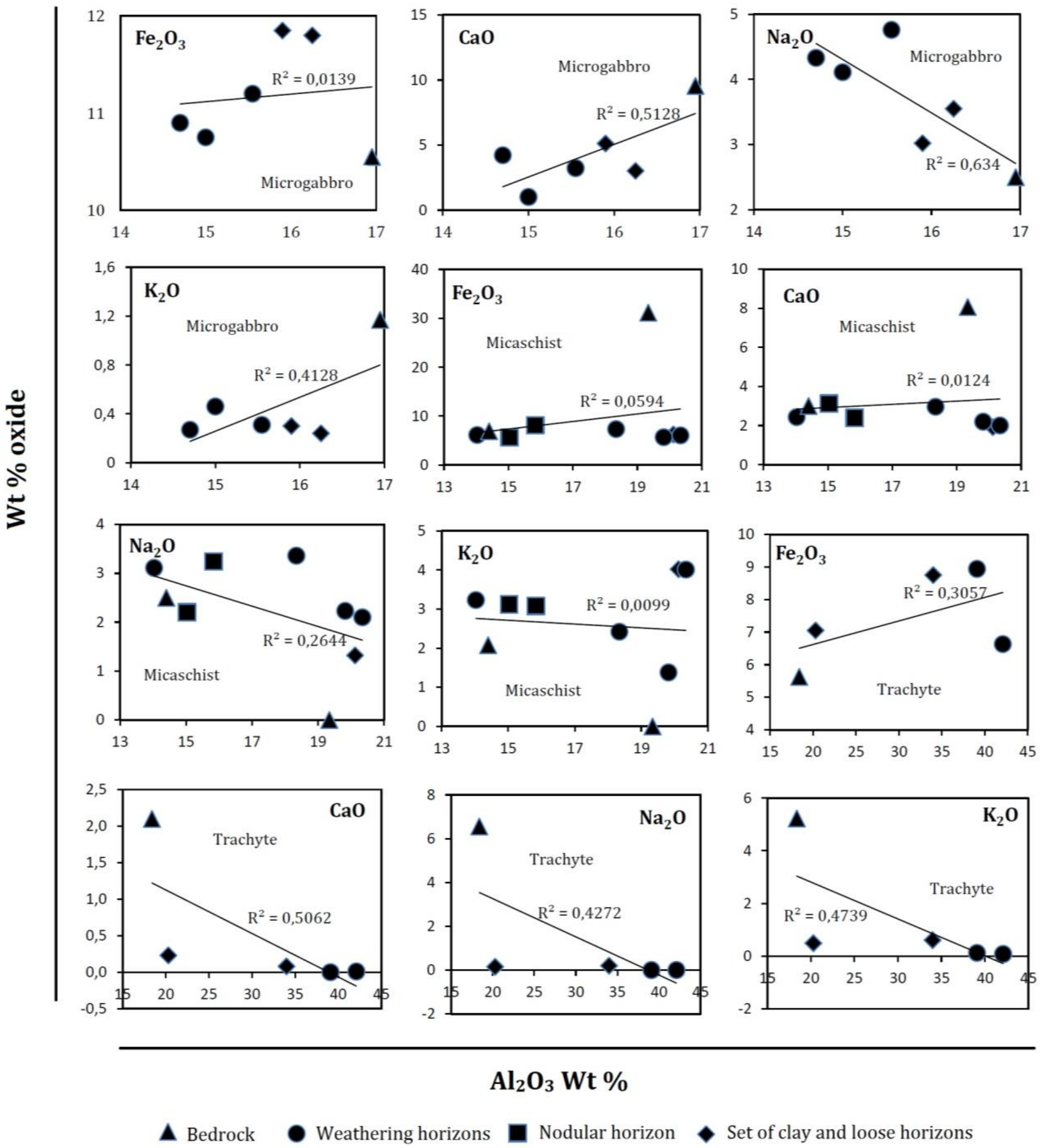

Figure 5. Major element–Al2O3 variation diagrams for samples collected in the studied profiles

Since Al is 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 (Nesbitt and Young, 1982). 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). 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. In the dry tropical ecosystem, weathering is less developed and soil samples are plotted in the interval of CIA corresponding to rock discoloured by weathering to fresh rock although soils are developed on microgabbro (Figure 7). In the humid high reliefs of Meleta at 2740 m a.s.l. on contrary, all material are decomposed and/or disintegrated to soil, favoured by the volcanic nature of the bedrock (Figure 7). In the humid rainforest high reliefs, around 50% of material are decomposed and/or disintegrated to soil, in line with the presence of muscovites in all horizons (Figure 7).

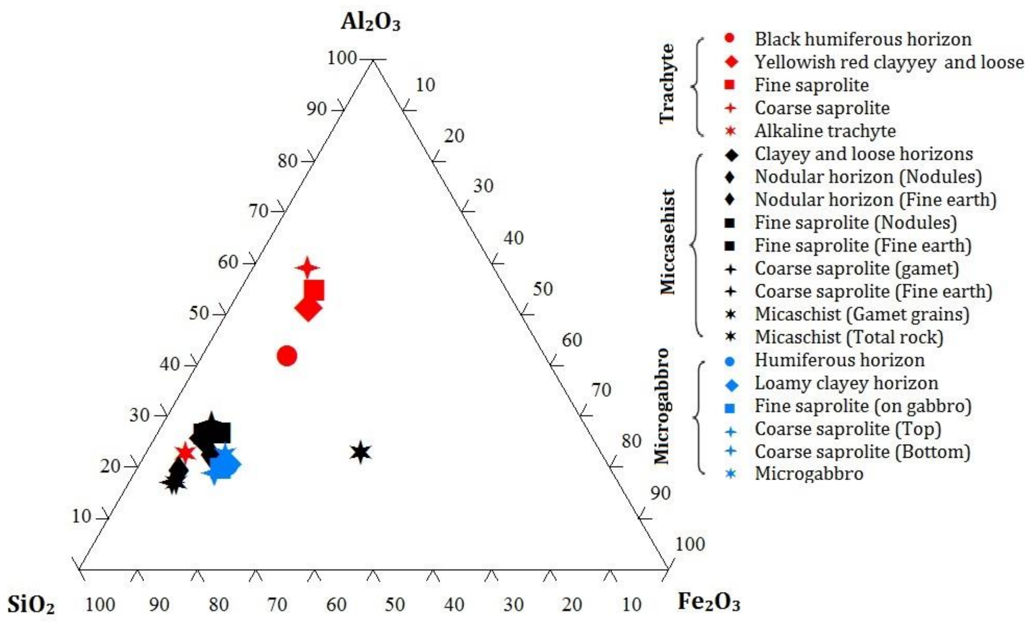

Figure 6. Geochemical composition of the studied soils in SiO_2-Al_2O_3-Fe_2O_3 diagram

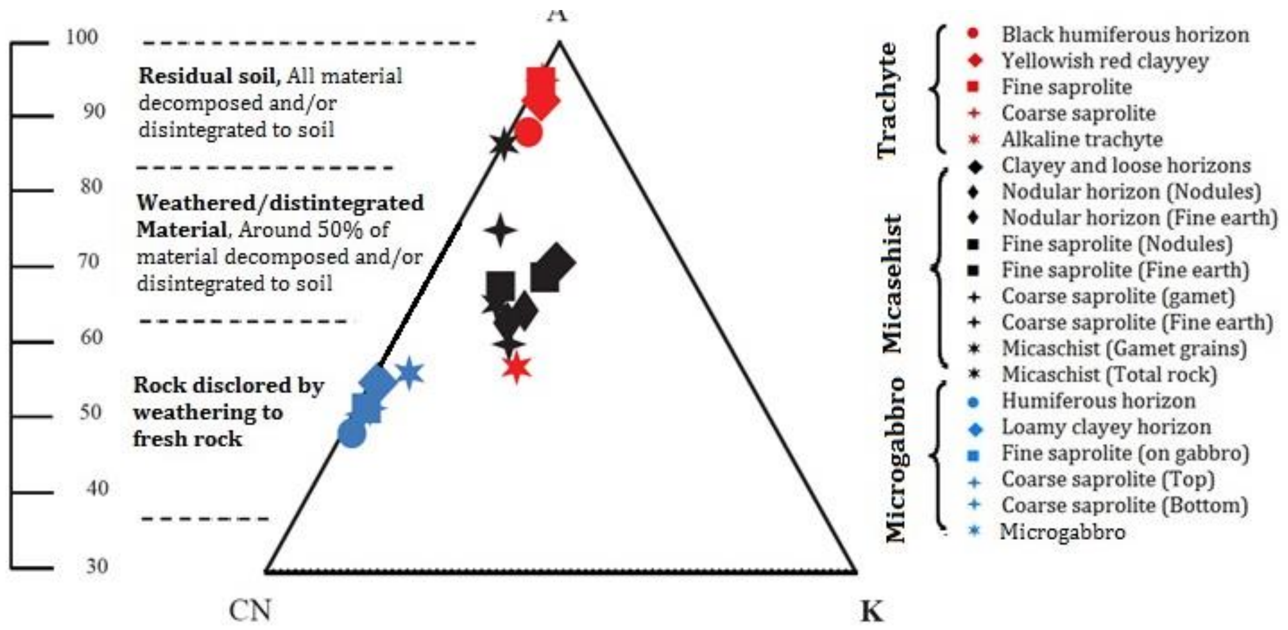

Figure 7. A-CN-K diagram illustrating weathering intensity (CIA values) of all samples collected from the studied profile. The CIA scale is divided into the simplified typical weathering profile described by the Geological Society of London in Lambe (1996)

Discussion

Morphological organization of soils

The studied soils in the high relief of Mbalam are about 10 m thick. This relative high thickness is common to soils developed in the humid tropical rainforest zone which are globally deep and well differenctiated (Beauvais, 1991; Beauvais and Collin, 1993; Irfan, 1996; Voicu and Bardoux, 2002; Nahon, 2003). Their morphology, of ABC type, is characteristic of the humid tropical rainforest zone (Tardy, 1993; Beauvais, 2009; Dzemua et al., 2011). It is however different from observations already made by many authors in this landscape marked by the presence of iron duricrust (Martin, 1966; Novikoff, 1974; Martin et al., 1981; Muller et al., 1981; Muller and Bocquier 1986; Muller, 1987; Colin et al., 1989). It is the result of lateritization processes which homogenize the weathering products through intense leaching of the alkaline, alkaline-earth elements and some silica of the parent rock, and lead to a mineralogical reorganization of silica, alumina and iron oxide (Delvigne, 1965; Nahon, 1991; Beauvais and Roquin, 1996). This process develops in landscape consisting of plateaus ranging globally from 600 to 700 m in elevation and weakly inclined slopes in Central Africa (Beauvais, 1991), well represented in Cameroon as the Southern Cameroon plateau. The study site emerges from this whole Southern Cameroon plateau by its altitude of about 840 m above sea level (a.s.l.). This position enhances soil permeability and drainage (Garner, 1972), leading thus to the development of gibbsite observed under the microscope (Aleva, 1994).

In Meleta, although remaining in the humid tropical zone and on volcanic products susceptible to weather faster, soils are less thick (~2 m), constituted of saprolite, yellowish red horizon and a thick black humiferous horizon and characterized by the presence of gibbsite under the microscope. The less thickness might be related to environmental conditions, characterized by a low temperature which slowdowns microbiological activities, leading to an accumulation of organic matter and the formation of thick humiferous horizon in the soil surface. Temperature increases the agitation of the molecules, promotes their release from the crystalline networks and their dissolution (Delvigne, 1965). It facilitates the exchange between the ions carried by the solutions and the cations trapped in the crystalline structures (Delvigne, 1965). Low temperature might therefore slowdowns the thickening of soil profiles. Direct weathering of feldspars into gibbsite might be an indication of excellent drainage and high soil permeability (Delvigne, 1965; Gardner, 1972), favoured by the mountainous high reliefs.

In Secande, the thickness of soil is also ~ 2 m as in Meleta, but largely dominated by that of the saprolite (~1.70 m) at the base of the profile. This low thickness might be due to the dry Sudano-Sahelian climate, which did not allow intense chemical weathering (Nguetnkam et al., 2008). The humeferous surface horizon observed here is thin and also similar to that described in Mbalam. Globally, in the dry climate, the A horizon would be very thin because there are few plants to become organic matter, and the C horizon would still be present, with nutrients still locked into minerals, because there is not enough water to promote weathering and leaching of minerals, or development of a B horizon (Sindelar, 2015). In addition, in the tropical zone, the humification process is weak and the mineralization is on contrary fast, leading thus to the formation of a thin humeferous surface horizon.

Mineralogical and geochemical characterization of soils

In tropical regions, it is mainly through the quantity of water which percolates into the weathering system that the climatic control exercises its influence on weathering processes (Pédro, 1968; Bourgeon and Pédro, 1992; Bétard, 2012). When hydrolysis is the prominent way of weathering as experiencing in the study area, the development of a particular process (mono- or bi-siallitisation) depends on the rate of removal of silica and basic cations, which itself is influenced by the amount of water flowing into the weathering system (Nguetnkam et al., 2008; Bétard, 2012).

In Mbalam, chemical weathering leads to the decomposition of the entire primary mineral except muscovite and quartz, promoting the development of soils 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 aluminium sesquioxides, goethite and gibbsite (Aristizábal et al., 2005). The neoformation of kaolinite and gibbsite is favoured by the morphoclimatic and hydrological environment of southern Cameroon: the rains are abundant, the hydrographic network, dense and marbled, reflects a good drainage, favoured by the steep slope and good permeability. In this context, the solutions are diluted and renewed regularly, which allows dissolution and almost the total leaching of the bases and partial silica, as evidenced by the results of the chemical analysis (Nguetnkam et al., 2008). The high expression of the bases in the soil profile would be due to the presence of muscovite in all the horizons.

In Meleta, characterized by temperatures ranging between 10 and 12°C, there is low SiO_2 content and high Al_2O_3 content in soils, compared to the parent rock and the site of Mbalam. Also, bases are almost inexistent, and the triangular diagram SiO_2-Al_2O_3-Fe_2O_3 showed that all points were localized on the SiO_2-Al_2O_3 axis, with a shift toward the Al_2O_3 pole. These characteristics lead to the neoformation of 1:1 clay minerals (halloysite) with important amounts of gibbsite, resulting in monosiallitisation process associated to high allitisation in this tropical mountainous environment (Pédro, 1966).

In Secande in the dry tropical zone, weathering leads to the coexistence of monosiallitisation with bisiallitisation, producing a mixture of 2:1 (montmorillonite) and 1:1 (kaolinite) clay minerals. Monosillitisation and bisiallitisation are induced by the morphoclimatic and hydrological conditions prevailing in the study area: rains are scarce and little distributed during the year, high temperature induces a strong evaporation (Ngounou Ngatcha et al., 2005) and high topographic position enhances drainage. The combination of these factors leads to the relative concentration of bases and silica, as shown by the results of the chemical analysis, and creates the favourable conditions for the genesis of montmorillonite and kaolinite (Pédro, 1966; Nahon, 1991; Velde, 1995; Paquet and Clauer, 1997). Similar coexistences of kaolinite and montmorillonite have been reported in the literature by many authors (Amouric and Olives, 1998; Meunier, 2003; Nguetkam et al., 2008). They are carried out via the interstratified clay minerals, beidellite-montmorillonite and beidellite-montmorillonite-kaolinite (Nguetkam et al., 2008).

Spatial variation of soil properties in the tropical high reliefs of Cameroon

The surface geochemical signature in soil is always unique in some respects, due to differences in geological, geomorphological and environmental settings. The mobilization and redistribution of elements during weathering follow thus various pathways, as different elements are affected differently by the various pedogenic processes, including dissolution of primary minerals, formation of secondary minerals, redox processes, transport of material, and ion exchange (Middleburg et al. 1988; Ozaytekin and Uzun, 2012). Soils' genesis and mantles' weathering are not an instantaneous phenomenon and requires long time periods to develop. According to Lageat and Gunnell (2001), tropical soils and weathering mantles may be considered as palimpsests reflecting "average" bioclimatic conditions that prevail at timescales of 1 to 10 Myr. Thus the duration of the Quaternary period appears to be an order of magnitude likely to control soil and saprolite development, given the propagation rates of weathering fronts estimated for tropical regions (1 to 10 $m \cdot Ma^{-1}$: Boeglin and Probst, 1998; Braun et al., 2005; Théveniaut and Freyssinet, 1999; Thomas, 1994). This leads to the soil differentiation in each study site according to the bioclimatic conditions which vary from the equator to the tropical dry climate in Cameroon. In the Meleta site, the rate of percolation is dependent on the ratio rainfall/evapotranspiration. This ratio increases with elevation, since rainfall increases and temperature decreases. Consequently higher shares of gibbsite can be expected (Hermann et al., 2007). The high expression of gibbsite here contrary to Mbalam could be attributed to high elevation and rainfall which induced high drainage. As a general rule, Tardy et al. (1973) state that in very humid climates and under excellent drainage conditions, gibbsite can appear. The absence of gibbsite in Secande might thus be attributed to low rainfall, low topography and high evaporation rate which did not facilitate the total evacuation of bases, leading to the maximum development of 2:1 clay minerals in this area, toward 1:1 clay minerals which remain present. In the tropical high reliefs, topography, elevation, rainfall and temperature appear as the main factors responsible of the soil properties.

Conclusion

The study of spatial variation of soil weathering processes in the tropical high reliefs of Cameroon lead to the following conclusions:

-soils are very thick in humid rainforest tropical high reliefs and this thickness decrease with increasing elevation and latitude;

-geochemical processes involved in the spatial differentiation of soils are monosiallitisation and allitisation in the humid tropical zone, monosiallitisation and high allitisation in the pseudotropical mountainous zone and monosiallitisation associated to bisiallitisation in the tropical dry climate of Cameroon;

-topography, elevation, rainfall and temperature appear as the main factors responsible of the spatial variation of soil weathering processes in the tropical high reliefs.

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Effect of potassium levels on teff (*Eragrostis tef (Zucc.) Trotter*) growth and yield in Central Highland Vertisols of Ethiopia

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Abstract

Nutrient depletion and imbalance are among the major attributes that contribute to declining soil productivity in the highlands of Ethiopia. The blanket fertilizer recommendation, which considered only urea and Di-ammonium phosphate (DAP), was used over the past four decades to improve soil fertility for enhancing crop production. Nevertheless, the average national yields of small cereal including teff were low, despite application of nitrogen and phosphorus (NP) fertilizers. On-farm trials were conducted in the 2015/16 and 2016/17 cropping seasons at 18 locations on Ethiopian highland Vertisols to determine the response of teff to potassium (K) fertilization along with other limiting nutrients. Five K levels (0, 30, 60, 90 and 120 kg ha^{-1}) in the form of murate of potash (KCl) were used in randomized complete block design with three replications. Separate analysis of variance was conducted for each sites and year. Least Significant Difference (LSD) test at P ≤ 0.05 was used to separate means whenever there were significant differences. Analysis of variance revealed a highly significant difference ($P < 0.01$) between treatments in both straw and grain yields and tissue nitrogen (N) and K concentrations of teff over the two-cropping seasons in 67% of the test locations. Additionally, responses to K were obtained on soils with available K test ranging between 166 and 282 mg kg^{-1}. The Ca: K and Mg: K ratios were strongly and negatively correlated with relative yield and the correlations suggest that soil with Ca: K > 50:1 and Mg: K >15:1 are likely to respond to potassium fertilization. The yield advantage accrued due to K application ranged from 30 to 77% in 2015/16 and 8 to 51% in 2016/17 seasons. The economic optimum K fertilizer application rates varied between 60 kg K ha^{-1} in 44% of the sites to 90 kg K ha^{-1} in 23% of the sites. The findings highlighted the need for revisiting fertilizer program to enhance the yield and nutrient uptake of teff in K responsive soils and developing critical levels for K in the study sites.

Keywords: Critical level, murate of potash, grain yield, balanced nutrition, crop response.

Introduction

Teff, *Eragrostis tef* (Zucc.) Trotter is a warm season annual grass native to Ethiopia (Ketema, 1997). It is adapted to environments ranging from drought-stressed to waterlogged soil conditions (Menna et al., 2015). It is a small-grained cereal grass species that has been grown as a food crop in east Africa for thousands of years (D'Andrea, 2008) having the lowest yield per unit area compared with other cereals such as wheat. Some of the factors that cause low productivity are lodging, method of planting and fertilizer application and the combined effect of these factors resulting up to 22% reduction in grain and straw yield (Gebretsadik et al., 2009). Being labeled as one of the latest super foods of the 21st century, teff's international popularity is rapidly growing (Provost and Jobson, 2014; Renton, 2014; Secorun, 2016). Teff grain is gluten free, and is a good flour source for segments of the population suffering from gluten intolerance or Celiac's Disease

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(Miller, 2010). Teff is also an excellent source of fiber and iron, and has many times higher amounts of Ca, K and other essential minerals than in an equal amount of other grains (Piccinin, 2002). Nationally, teff is one of the important cereals that are at the center of the increasingly vibrant agricultural output markets of Ethiopia (Minten et al., 2014). It has the largest share of area (24%, 3.02 million hectares) of the grain crops and second (after maize) in terms of grain production (17.29%, 5.02 million tons) in Ethiopia (CSA, 2017).

Potassium (K) is one of the major plant nutrients and abundant element in soils. It is an essential plant nutrient playing an important role in various physiological and biochemical activities and is required in high amounts. Its uptake frequently exceeds the uptake of nitrogen, to maintain adequate crop growth (Mengel and Kirkby, 2001). Potassium plays a remarkable role in transpiration, stomatal opening and closing and osmoregulation (Cakmak, 2005). The higher K^+ content than the other cations in the plant tissues effectively regulates many physiological and biochemical processes (Bajwa, 1994). While involved in many physiological processes, K's impact on water relations, photosynthesis, assimilate transport and enzyme activation can have direct consequences on crop productivity (Oosterhuis et al., 2014). The production of less photosynthetic assimilates and reduced assimilate transport out of the leaves to the developing fruit greatly contributes to the negative consequences that deficiencies of potassium have on yield and quality production (Pettigrew, 2008).

Vertisols are dark, montmorillonite-rich clay soils with characteristic shrinking and swelling properties (FAO, 2015). They have high montmorillonite clay and when dry show cracks of at least 1 cm wide and 50 cm deep (Eswaran and Cook, 1988). Vertisols are important agricultural soils though primarily poor drainage and difficult workability limit nutrient availability and productivity, and therefore they require proper fertility management practices. In Ethiopian agriculture, Vertisols have an important place since they have diverse chemical properties and are widely distributed (over 12 m ha) covering 11% of the total land mass and the fourth important soil order (Mamo et al., 2002). An estimated 7.6 million ha of Ethiopian Vertisols are located in the central highlands, above 1500 m.a.s.l., and on higher elevations (> 2500 m.a.s.l.) in temperate ecosystems (Debele, 1985; El-Wakeel and Astatke, 1996). Evidence suggests there would be substantial increases in crop yields on Vertisols, if excess surface soil water is drained off and if appropriate cropping practices are used (Wubie, 2015).

Numerous studies reported the yield response of teff to N and P fertilization (Mirutse et al., 2009; Ayalew et al., 2011; Kidanemariam, 2013; Giday et al., 2014; Abebe and Workayehu, 2015). But, there was no detail study on the response of teff to K fertilization in Ethiopia. Unfortunately, application of K did not receive due attention in Ethiopian soils where it is believed to be 'adequate' in native K supply. It is widely recognized that information about crop response to fertilization, as well as nutrient use efficiency, soil nutrient balance and soil test requires updating and re-evaluation (Peck and Soltanpour, 1990). Currently, there is little national and/or regional emphasis on the effect of K fertilization, soil K balance or K critical level in cereals growing areas of the country. This is evident from the highly imbalanced fertilizer consumption ratio with respect to K in Ethiopia, where K fertilizer has not been imported for crop production until 2014. On the other hand, removal of K in proportion to N is very high in cropping systems, particularly in those involving cereal crops (Rana and Rana, 2011). In Ethiopia, application of nutrients other than N and P was started in 2014/15 cropping seasons through series fertilizer demonstrations conducted jointly by Ministry of Agriculture (MoA), Agricultural Transformation Agency (ATA) and partners using compound fertilizers containing other nutrients instead of Di ammonium phosphate (DAP). Application of potassium fertilizer was demonstrated in 2004 and resulted in increases of tons of wheat yields due to application of 50 kg ha^{-1} K_2SO_4 (Astatke et al., 2004). Similarly, other research works conducted in different locations and crops showed that application of potassium resulted in a significant yield increase of wheat (Haile and Mamo 2013; Hailu et al., 2015; Brhane et al., 2017), potato (Haile and Boke 2011; Ayalew and Beyene 2011; Shunka et al., 2016), teff and wheat (Mulugeta et al., 2017). Additionally, it is also common to see farmers in central highlands of Ethiopia applying wood ash on their Vertisols fields because of observing better growing condition due to the ash, which could be taken as an indication for the need of K application.

Both yield and quality, and thus the economic value of teff, could be strongly influenced by potassium fertilizer management. However, information pertaining to the level of K required for optimum yield of teff for different soil test K conditions in Ethiopia is lacking. In this paper, we present the results of field trials on the effect of different levels of K fertilizer on teff in Vertisols of the central highlands of Ethiopia. The objectives of the study were to diagnose teff yield response to K fertilizer at field level and to examine the relationship between soil available potassium and its concentration in the test crop.

Material and Methods

Description of the experimental sites

Field experiments were conducted in soils differing in soil nutrient status during 2015/16 and 2016/17 cropping seasons in the central highland Vertisols of Ethiopia. The locations are in similar agroecology and among the teff growing districts of the country (Figure 1). The experiment was conducted in 18 randomly selected sites: 12 in the first year and repeated in 6 of the sites. The weather data of the sites (Figure 2) were obtained from the National Meteorological Agency of Ethiopia (NMA, 2016).

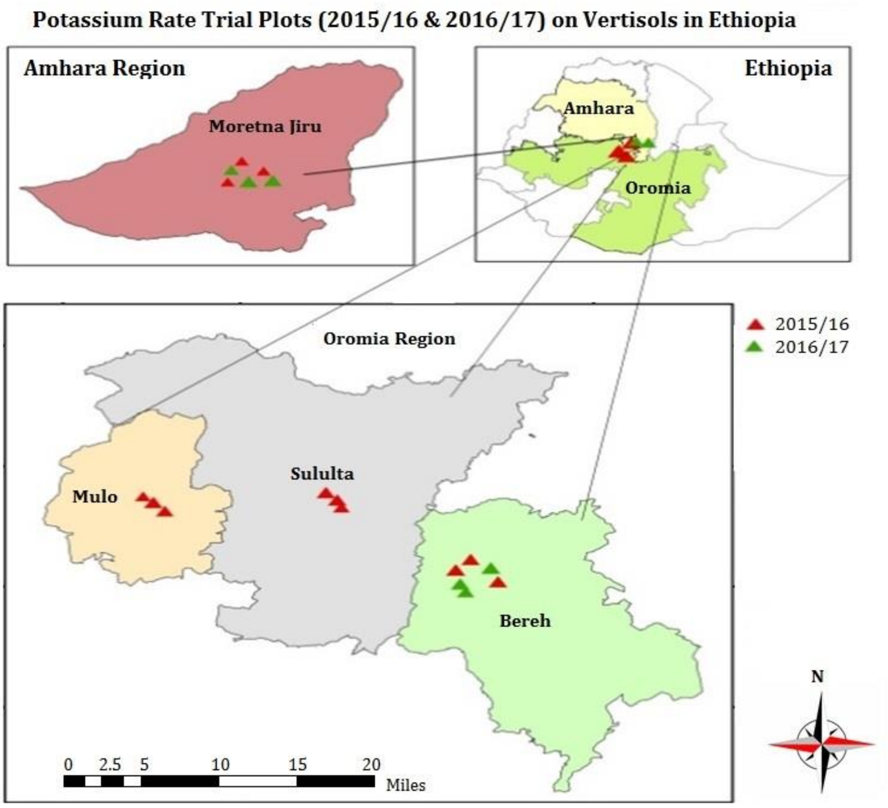

Figure 1. Geographic location of the experimental sites

Ten years (2007-2016) mean monthly minimum and maximum temperatures ranged from 17.9 to 23.9 °C while the mean monthly rainfall ranged from 4.1 to 387 mm with a bimodal pattern (Figure 2). The highest mean monthly rainfall and the lowest mean monthly temperatures were recorded between July and August (Figure 2).

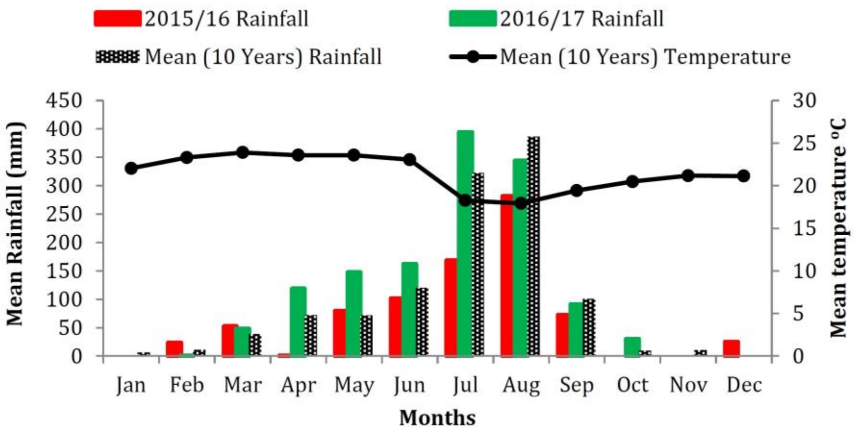

Figure 2. Mean monthly rainfall and temperature of the study sites for the last ten years (2007-2016) and rainfall during 2015/16 and 2016/17 cropping seasons

The mean rainfall of the two cropping seasons showed similar pattern with the mean long-term average of 96 mm per annum (Figure 2) but the amount in 2016/17 was higher than the long-term average. On the other hand, the mean monthly temperature of the two growing seasons was very much similar, both in amount and pattern, to the long-term average (Figure 2).

Experimental design and treatments

Each experiment had five levels of potassium *viz* 0, 30, 60, 90 and 120 kg K ha^{-1} in the form of KCl (murate of potash, 60% K_2O) as basal application. Based on previous national soils survey data that showed deficiency of nitrogen (N), phosphorus (P), sulfur (S), and zinc (Zn) in the experimental sites and considering 30 kg N/ton of grain and the ratio of the different nutrients, optimum rates of N, P, S and Zn at the rates of 120, 60, 15, and 3 kg ha^{-1} respectively were applied using N-P-S-Zn compound fertilizer (12-45-0 + 5 S + 1 Zn). The full amount of P, K, S, Zn, and 1/3 of N were applied during planting. The remaining 2/3 N was applied as top dressing at 30 days after sowing using urea. The treatments were arranged in a randomized complete block design (RCBD) with three replications at each trial site having a net plot size of 4 x 6 m. Improved teff variety, Quncho, seeds were sown between last week of July and first week of August by drilling along the rows spaced at 20 cm intervals at a seed rate of 10 kg ha^{-1}. The experimental fields were managed following the recommended management practices for teff in the areas.

Soil and plant sampling and analysis

Soil samples were obtained by collecting 15 random surface (0-20 cm) augur samples to make one composite for each experimental site prior to sowing the crop during both seasons. The soil samples were well mixed, air dried, ground, and passed through a 2 mm sieve and analyzed for selected physico-chemical properties.

The particle size distribution was determined by the HORIBA-Partica (LA-950V2) laser scattering particle size distribution analyzer (Agrawal et al.,1991) and LA-950 software version 7.01 for Windows (Horiba, 2010), soil pH (glass electrode, soil/water ratio of 1:2.5); CEC was predicted from mid infrared spectra of soil samples. Exchangeable K, Ca, and Mg and available P, Sulfate-S and extractable Zn were extracted following Mehlich-3 procedure (Mehlich, 1984).

At maturity, the above ground biomass was harvested and weighed from 2mx3m area. The teff plant samples were washed with distilled water to remove the dust and soil particles from the samples. The plant samples were kept in paper bags and then dried at 65°C until constant weight. The dried plant samples were powdered in a warring stainless-steel grinder. Dry powdered plant samples were ashed in a muffle furnace at 500 ºC and extracted in 10 ml of 6M HCl and dried on hot plate for 15 minutes at 140 °C. The dried ash was dissolved in 10 ml of 1M HCl and the nutrient contents in the filtrate were analyzed using Inductive Couple Plasma (ICP).

Data collection and analysis

Ten plants were randomly selected from each plot at maturity for recording plant height, panicle length and number of fertile tillers per plant. At harvest, all plants from a 2 m x 3 m plot area were harvested, air dried, and manually threshed to determine straw, grain and total biomass yields per plot, which were later converted to yields per hectare. Grain yields were adjusted to approximately l2% moisture content. The data were analyzed using the general linear model (GLM) procedures of the SAS 9.2 statistical software (SAS Institute Inc, 2008) to evaluate the effect of K levels on yield and yield components of teff. Total nutrient uptakes of the different nutrients were computed by multiplying the concentrations of the nutrients and total yield. Separate analysis was also conducted for each sites and year. Least Significant Difference (LSD) test at $P \leq 0.05$ was used to separate means whenever there were significant differences.

Results and Discussion

Physical and chemical properties of the soils

The experimental soils were clayey in texture, whereby the proportions of sand, silt and clay varied from 3.75 to 27.78, 6.03 to 23.28 and 50.26 to 90.22% respectively, indicating that clay was the most dominant fraction in the soils (Table 1).

The values of soil pH (H_2O) ranged from 5.4 to 7.4 showing that most of the soils were slightly acidic to neutral in reaction. Based on the K critical levels generated for teff (Mulugeta et al., 2019), which categorized the Mehlich-3 K of <210, 210-280, 280-500, and >500 mg kg^{-1} as low, medium, high and very high respectively; the K values of the study soils were in the range from low to very high. On the other hand, according to EthioSIS (2013, 2016) which categorized Mehlich-3 K values of < 90, 90-190, 190-600, 600-900 and >900 mg kg^{-1} as very low, low, optimum, high and very high; the K status of the soils are in the range of low to medium.

Additionally, the available P, S and Zn contents of the experimental soils were also in the low to medium range, whereas available B was medium (Table 1) in accordance with EthioSIS (2013, 2016). The study also showed that the range of Ca and Mg was very high according to (Hazelton and Murphy, 2007) and the concentrations of basic cations were in the order of Ca > Mg > K. From a crop nutrition viewpoint, therefore, the levels of Ca and Mg were adequate to support optimum production of arable crops.

Table 1. Mean values of selected physico - chemical properties of surface soil (0-20 cm) of the experimental sites before planting.

Trial Site	Sand	Silt	Clay	pH	CEC	Av. P	Ex. K	Av. S	Ex. Ca	Ex. Mg
		%		1:2.5	(Cmol (+) kg^{-1})			(mg kg^{-1})		
2015/16										
1	4	6	90	6.1	62	18	170	12	5696	1006
2	10	13	77	5.6	36	6	255	12	7322	1132
3	9	16	75	5.7	55	10	305	13	6801	1324
4	16	18	65	5.4	49	5	282	17	5501	1224
5	19	20	60	5.6	49	20	526	13	5283	1157
6	28	22	50	5.5	45	4	360	19	5408	1178
7	13	19	68	6.3	55	13	343	11	6198	1061
8	14	20	66	6.9	62	15	356	21	7986	1000
9	13	23	64	6.4	54	4	281	18	6546	1004
10	6	8	85	6.2	64	11	225	13	7241	1320
11	9	9	82	6.6	57	3	248	13	9869	1069
12	10	14	76	7.4	73	33	197	15	5809	1171
2016/17										
13	6	11	83	6.3	70	9	264	19	6931	1464
14	9	15	76	5.8	64	9	261	20	8042	1308
15	12	15	73	5.5	62	6	272	19	7649	1462
16	8	19	74	5.6	63	3	331	19	5725	1044
17	8	23	69	6.4	59	7	316	28	5406	1028
18	9	23	68	6.7	58	11	291	29	6239	1274

Av.: available; Ex.: exchangeable;

A soil is regarded "ideal" if the percent base saturations of Ca, Mg and K are in the ranges 65-85, 6-12 and 2-5, respectively (AgKnowledge, 2011). In the present study, the results of the basic cations showed that the percent base saturations of Ca, Mg and K ranged from 70-84, 15-26 and 1-4, respectively indicating that the concentrations of Ca was within the ideal range, whereas that of Mg and K are higher and lower, respectively, than the suggested ideal range. The CEC ranged from 36- 73 Cmol (+) kg^{-1} which was high and very high according to the rating of Hazelton and Murphy (2007). The very high value of CEC is mainly due to high clay content and predominance of 2:1 layer clay minerals. It was in line with Debele (1985) who reported that nearly all the Vertisols have high CEC of 35–70 cmol(+) kg^{-1}.

Effect of K application on teff grain and straw yields

The results showed that grain and straw yields were significantly affected by application of K in 67% of the tested locations, although the responses varied by sites and year (Table 2). Applications of 60 and 90 kg K ha^{-1} were found to be optimum in 23 and 44% of the locations, while the lowest yields were recorded at 0 kg K ha^{-1} across the sites. The result also showed that when the initial K concentration is less than 300 mg kg^{-1}, application of 90/60 kg K ha^{-1} is required. Besides, higher yields in all treatments were observed in the 2016/17 cropping season than the 2015/16 season, although the yield increments due to increasing levels of K were higher in 2015/16 as compared to that of 2016/17 (Table 2). Despite the increment of yields due to K application, the response was not economically feasible in 33% of the test locations and hence the results and discussion in this paper include only the data obtained from 67% of the tested locations.

Grain and straw yields were significantly increased due to application of K (Table 2). The grain yield, which is a function of combined contribution of various yield components, has direct relationship with the growing conditions and management practices of the crop. The increase in grain and straw yields due to the application of K might be due to enhanced accumulation of assimilates, which resulted in heavier grains and straws, and also the involvement of K in physiological and biochemical processes (Wang et al., 2013) resulting in more dry matter production through improvements in plant height and number of tillers per plant.

The lowest grain and straw yields in the control might be attributed to an imbalance uptake of essential elements such as N, P and K, which resulted in poor performance of yield attributes. Low K results in an overall reduction of the amount of photosynthetic assimilates available for growth (Pettigrew, 2008). Our result is in line with the findings of Alam et al. (2010), which showed a significant increase in grain, straw and total biomass yields of wheat when higher dose of K was applied. Positive responses of different crops to K application in terms of growth, yield and potassium accumulation were also reported by different researchers, e.g. sunflower (Chhajro et al., 2014), maize (Nawaz et al., 2006), tomato (Akhtar et al., 2010) and cotton (Zia-Ul-Hassan and Arshad, 2010; Zia-ul-Hassan et al., 2014) .

Table 2. Mean teff grain and straw yields as influenced by increasing K levels at the experimental sites in: 2015/16 and 2016/17

		2015/16												2016/17					
Yield & yield components	Trial sites	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15	Site 16	Site 17	Site 18
	Initial STK (mg kg^{-1})	170	256	305	282	526	360	344	356	281	225	248	197	291	316	331	261	264	272
Grain Yield (kg ha^{-1})	Treatments (kg K ha^{-1})	***	***	***	***	NS	***	***	***	*	***	***	***	***	***	**	***	***	***
	0	1362^{d}	1563^{c}	1642^{c}	1665^{c}	2139	1960^{d}	2088^{c}	2106^{c}	1822^{c}	1747^{c}	1766^{c}	1846^{d}	2140.7^{d}	2315.3^{d}	2989.4^{b}	2164.0^{d}	2143.3^{d}	2461.0^{d}
	30	1555^{c}	1704^{c}	1766^{bc}	1965^{b}	2213	2050^{c}	2538^{b}	2929^{ab}	1939^{bc}	2443^{b}	2537^{b}	2453^{c}	2210.0^{c}	3332.4^{b}	3247.2^{a}	2253.0^{c}	2212.7^{c}	3114.7^{bc}
	60	1838^{b}	1879^{b}	2175^{a}	2161^{a}	2169	2140^{b}	3150^{a}	3091^{ab}	1983^{b}	2886^{a}	2732^{ab}	2761^{b}	2314.7^{b}	3498.5^{a}	3445.7^{a}	2355.7^{b}	2325.7^{b}	3222.9^{b}
	90	2405^{a}	2475^{a}	1890^{b}	2144^{a}	2162	2243^{a}	3050^{a}	3191^{a}	2136^{a}	2881^{a}	2990^{a}	3127^{a}	2456.3^{a}	3053.8^{c}	3322.7^{a}	2432.3^{a}	2437.0^{a}	3391.7^{a}
	120	1884^{b}	1888^{b}	1845^{b}	1876^{b}	2147	2008^{dc}	3000^{a}	2844^{b}	1852^{c}	2800^{a}	2630^{b}	2537^{bc}	2280.0^{b}	3011.9^{c}	2974.4^{b}	2338.7^{b}	2436.3^{a}	3057.3^{c}
	CV	2.63	4.35	4.45	2.53	2.55	1.89	3.28	5.14	3.28	3.97	5.53	5.59	1.28	2.49	3.34	1.28	1.00	2.36
Straw Yield (kg ha^{-1})	Treatments (kg K ha^{-1})	***	***	**	**	*	**	***	***	***	***	*	**	***	***	*	***	***	***
	0	3731^{b}	4420^{c}	5038^{c}	5111^{c}	7707^{b}	6598^{b}	5748^{c}	6129^{c}	5563^{b}	5069^{c}	5624^{c}	5796^{c}	6010.0^{c}	6342.8^{d}	7988.4^{bc}	5734.0^{d}	5963.7^{b}	6794.6^{d}
	30	4087^{b}	4609^{c}	5381^{bc}	5623^{bc}	8321^{a}	5826^{c}	6677^{b}	7538^{b}	5603^{b}	6069^{b}	6464^{bc}	6680^{b}	6385.7^{b}	8799.0^{a}	8385.1^{ab}	6810.0^{a}	6738.8^{a}	8238,6^{b}
	60	3916^{b}	4488^{c}	6251^{a}	6425^{a}	7923^{b}	6718^{ab}	7975^{a}	7889^{ab}	5625^{b}	6985^{b}	7827^{a}	6335^{bc}	6862.7^{a}	8664.3^{a}	8410.6^{ab}	6592.2^{b}	6760.6^{a}	7797.8^{c}
	90	5616^{a}	6408^{a}	5419^{bc}	6400a	7953^{b}	7132^{a}	7843^{a}	8180^{a}	5705^{b}	6972^{b}	7522^{ab}	8113^{a}	6792.0^{a}	7071.2^{c}	8495.5^{a}	6724.0^{a}	6710.4^{a}	8687.6^{a}
	120	5676^{a}	5293^{b}	6009^{ab}	5914^{ab}	7855^{b}	6511^{b}	7692^{a}	7501^{b}	6434^{a}	8055^{a}	6742^{abc}	6568^{bc}	6413.3^{b}	7863.5^{b}	7729.0^{c}	6457.0^{c}	6828.6^{a}	8186.7^{b}
	CV	6.18	6.36	6.38	5.00	2.13	4.13	4.04	4.49	2.16	7.44	9.55	6.58	1.56	2.64	2.97	0.76	1.08	1.44

Significant at * $P \leq 0.05$;** $P \leq 0.01$; *** $P \leq 0.001$ and below; **CV**: Coefficient of variations; Means followed by same letter(s) within a column do not differ at $P \leq 0.05$

Increasing K levels beyond 60 kg ha^{-1} in some locations and 90 kg ha^{-1} in others, however, decreased all the yield and yield components, most probably due to nutrient imbalances caused by excess potassium on other nutrients such as N, and antagonistic effect of K^+ on Ca^{2+} and/or Mg^{2+} (Saifullah et al.,, 2002). The results might also be due to higher affinity of K^+ for membrane carriers compared to other cations. Thus, with the increase of K^+ concentrations in the soil, competition increases at the binding sites of membrane carriers, which might have decreased the uptake of Ca^{2+} (Marschner, 2011). In the nutrient uptake processes; K, Mg, and Ca are strongly antagonistic (Voogt, 2002) resulting in a deficiency of the depressed nutrient. Soils with a low CEC are more likely to develop deficiencies in potassium (K^+), magnesium (Mg^{2+}) and other cations while high CEC soils are less susceptible to leaching of these cations (Cornell University Cooperative Extension, 2007).

The yield increments due to application of K varied significantly (P<0.0001) between the treatments and the cropping seasons (Table 2). Higher values of yield and yield components were recorded in the 2016/17 than 2015/16 season, although the relative yield increments over the control were higher in 2015/16 as compared to that of 2016/17. The high variability of yield and yield components between the two cropping seasons could be due to the variation in rainfall, where the amount and distribution of rainfall was better in the 2016/17 (Figure 2), which in turn might have affected the nutrient availability and the response to applied K. Similar results were reported by Sangakkara et al. (2001) and Catuchi et al. (2012) who showed that K applied as nutrient solution promoted greater growth and development of the plants under drought than unstressed conditions.

The relatively higher yield increments over the control in 2015/16 might be attributed to the influence of K on plant growth during water stress (Marschner, 2012). Catuchi et al. (2012) and Guareschi et al. (2011) indicated that appropriate levels of K in the plant tissues enable better plant development and growth, and increased K availability in the soil enhances plants to exploit a larger soil volume due to better development of their root system, which also improves the support during drought (Sangakkara et al., 2001; Wang et al., 2013; Zörb et al., 2014).

The high variability in response to applied K between experimental sites could probably be related to site differences in initial soil physical and chemical properties such as clay content, moisture content, Ca and Mg contents and the soils' K status (Table 1). Minerals K release to soluble and exchangeable forms and K adsorption by exchange sites depend on the equilibrium between different phases of soil K, which may be affected by such factors as root uptake, applied fertilizer K, soil moisture, soil pH and soil temperature (Niu et al., 2011; Britzke et al., 2012).

Potassium sorption on exchange sites and its fixation depend on the physicochemical properties of the soil, as well as type and content of the clay minerals (Braunschweigh, 1980). More clay contents possessed more K^+ contents whether fixed or exchangeable (Jalali and Zarabi, 2006). The fate of K^+ fertilizers applied to the soil depends upon the clay contents, clay minerals and fractions of K^+ already available in the soil (Wakeel et al., 2013). The amount of water in the soil affects the aeration of the soil, which eventually decreases the K availability possibly due to the negative effects on K-mobility (Afari-Sefa et al., 2004). Soil moisture also affects K availability by affecting both K mobility and root growth (Kuchenbuch et al., 1986).

Effect of K application on nutrient concentrations in teff tissue

In majority of the experimental sites, increasing K rate up to 60/90 kg K ha^{-1} increased nutrient concentrations in the biomass. The influences of site and season on plants nutrient concentrations were also apparent. However, the concentrations of P, Ca and Mg were not significantly influenced by increasing levels of K (Table 3).

Table 3. ANOVA for nutrient concentration across location and year

Source	Nutrient concentration in teff biomass				
	N	P	K	Ca	Mg
	Pr > F				
Year (Yr)	<.0001	0.6994	<.0001	<.0001	0.0278
Location (Loc)	0.0016	<.0001	0.0193	<.0001	0.0002
Yr*Lc	0.2473	<.0001	0.0200	0.0609	0.0050
Block (Yr*Loc)	0.4351	0.7711	0.0466	0.0006	0.0191
Treatment (TT)	0.0016	0.0596	0.0001	0.0122	0.1694
Yr*TT	0.8065	0.8709	0.4076	0.5260	0.4490
Loc*TT	0.0309	0.7666	0.3837	0.3666	0.6873
Yr*Loc*TT	0.9750	0.9998	0.1206	0.6057	0.3659
CV	9.56	19.72	12.83	17.50	42.09

Potash application increased the nitrogen content in teff biomass (Table 4) though significant ($P < 0.01$) increments in nitrogen concentration due to K level were observed only at 3 locations. This could be attributed to imbalance between N and K as also reported by Wahhab and Hussain (1957). Crop response to applied nitrogen fertilizers decreases when the exchangeable potassium content of a soil is below the optimal level and vice versa (Rutkowska et al., 2014; Pradhan et al., 2015). Positive interaction between N and K at balanced supply might be the reason for the increased N concentration in plants. Besides, K also influences nitrogen absorption and reduction, and rapid nitrogen (NO_3) uptake depends on adequate K in the soil solution (IPNI, 1998). This result is consistent with the findings of Ashok et al. (2009).

The differences in N concentrations in the plant tissues at the different sites might be attributed to differences in the physicochemical properties of the experimental soils (Table 1), whereas the differences in N concentration between the two seasons might have been caused by the variations in quantity and distribution of rainfall (Figure 2). Changes in precipitation would alter nitrogen (N) availability and mineralization directly via its impact on soil water availability, erosion and leaching, and indirectly by influencing plant N uptake as well as plant productivity. Increases in precipitation, specifically in large rain events, might lead to large leaching and run-off (Nearing et al., 2005), which could increase N loss and decrease N retention. Crop response to N applications in Vertisols is closely linked to soil moisture variations and, hence, to rainfall pattern (ICRISAT, 1989). Poor drainage, a common characteristic of Vertisols, creates periodic waterlogging (anaerobic) conditions, which favors fertilizer N loss through denitrification (Knowles, 1982). The relative importance of these processes depends on environmental variables such as soil pH, topsoil texture, soil profile characteristics, soil aeration, water supply and temperature, as well as human activities such as type, amount, placement and timing of N fertilizers, available carbon, crop residue management, tillage, soil compaction, drainage, irrigation, land use change and stocking rate on grassland.

Phosphorus concentration in plant biomass was less than 0.2%, which was less than what most crops need for normal growth (0.2 to 0.5%) P in tissue dry matter (Kalra, 1998; Hue et al., 2000;). It was also not significantly influenced by increasing rates of K application but the effect of year and location was significant (Table 3), though slight increments with increasing K levels up to 60/90 kg K ha^{-1} were observed. The increase in P concentration with increasing K levels might be due to the role of K in translocation of nutrients that lead to increased nutrients concentration in plants (Kumar et al., 2015). The relatively low phosphorus concentration in teff biomass might be due to the low level of P in the experimental soils (Table 1) and indicate inadequate supplement of P as fertilizer in the treatments. These results are in line with the findings reported by Roy (1990).

Increasing K application from 0 to 120 kg K ha^{-1} significantly increased its concentration in teff biomass during both growing seasons (Table 4). The highest values of K concentration in teff during both growing seasons were recorded at the application of 120 kg K ha^{-1} in five of the seven sites, whereas the lowest K concentration was obtained from the control treatment, which might be due to the low soluble K in soil solution of the experimental soils (Table 1). Thus, the increase in K concentration in teff with increasing K rates could be due to higher K uptakes by the plants. Kemmler (1983) stated that wheat and other cereal crops require as much K as N and in some cases the need for K exceeds N. Teff, being one of the cereals, is expected to have similar requirements for N and K as wheat. Similar to N, potassium concentration by plants also showed a similar increasing trend with dry matter production. In line with the present study, Kumar et al. (2015) noticed increase in concentration of different nutrients by wheat crop due to increased levels of potassium. The results were also in line with Baque et al. (2006) who reported that concentrations of N, P and K were enhanced by increasing levels of K.

Studies on N:P ratios of teff are lacking but a review by Sadras (2006) indicated that N: P ratios of cereals varied between 1 and 20. A major cause of the variability lies in variations between the supply of nutrients to crops and, in particular, the tendency of crops to absorb far more P than is needed to meet the immediate needs and to store it (Bollons and Barraclough, 1999). However, this cannot explain the variability in the N: P ratio when there is an optimal supply of nutrients (Greenwood et al., 2008). In this study, the N: P: K ratio was 1: 0.2: 0.9, indicating that N and K uptakes by teff are almost the same. MacLeod (1969) also reported that the percentages of N, P, and K in tissue below which final yield of grain decreased by 4.0, 0.7, and 4.0, respectively, for the plants sampled at heading.

The results showed that the 'critical' tissue K concentration, at which about 90% of the maximum yield was obtained, was 0.63% (Figure 3). This can also be taken as the internal K requirement for teff. This value was obtained at a site whose soil test value was 331 mg kg^{-1} with the application of 60 kg K ha^{-1}.

Table 4. Mean N, P K, Ca, and Mg concentrations (% dry matter) in teff above ground biomass as influenced by increasing rates of K at seven selected sites.

Selected Nutrients	Trial sites	Site 6	Site 8	Site 11	Site 13	Site 15	Site 17	Site 18
	Initial STK (mg kg^{-1})	360	356	247	291	331	264	272
	Treatments (kg K ha^{-1})	**	*	*	NS	NS	*	NS
	0	0.91^{c}	0.80^{b}	0.93^{ab}	0.65	0.62	0.65^{bc}	0.68
	30	0.92^{c}	0.83^{ab}	1.03^{a}	0.71	0.70	0.75^{ab}	0.69
N	60	0.99^{ab}	0.88^{a}	1.01^{a}	0.75	0.66	0.79^{a}	0.79
	90	1.04^{a}	0.89^{a}	0.98^{ab}	0.77	0.68	0.68^{bc}	0.69
	120	0.95^{bc}	0.89^{a}	0.82^{b}	0.75	0.69	0.61^{c}	0.64
	CV	3.39	3.43	9.95	14.96	10.84	8.22	13.74
	Treatments (kg K ha^{-1})	NS	NS	NS	NS	NS	NS	NS
	0	0.11	0.13	0.14	0.12	0.08	0.18	0.12
	30	0.13	0.14	0.15	0.13	0.08	0.19	0.13
P	60	0.13	0.14	0.12	0.14	0.09	0.19	0.16
	90	0.12	0.16	0.16	0.13	0.11	0.20	0.17
	120	0.12	0.15	0.15	0.12	0.09	0.18	0.14
	CV	17.30	16.98	20.81	21.18	19.33	13.22	26.90
	Treatments (kg K ha^{-1})	NS	*	**	NS	NS	*	NS
	0	0.53	0.49^{b}	0.46^{b}	0.91	0.88	0.63^{b}	0.78
	30	0.54	0.46^{b}	0.50^{ab}	0.84	0.90	0.74^{ab}	0.82
K	60	0.60	0.49^{b}	0.64^{a}	0.90	0.91	0.77^{ab}	0.79
	90	0.60	0.58^{ab}	0.54^{ab}	0.88	0.92	0.99^{a}	0.90
	120	0.61	0.71^{a}	0.62^{a}	0.94	0.95	0.77^{ab}	0.93
	CV	9.80	16.63	14.14	9.09	11.51	17.54	10.19
	Treatments (kg K ha^{-1})	NS	NS	NS	NS	NS	*	NS
	0	0.17	0.18	0.18	0.21	0.20	0.25^{ab}	0.30
	30	0.15	0.14	0.18	0.21	0.23	0.24^{b}	0.28
Ca	60	0.18	0.17	0.18	0.24	0.22	0.29^{ab}	0.25
	90	0.21	0.18	0.22	0.20	0.20	0.32^{a}	0.31
	120	0.20	0.21	0.20	0.25	0.23	0.26^{ab}	0.32
	CV	19.4	27.59	17.89	13.97	15.38	15.65	14.76
	Treatments (kg K ha^{-1})	*	NS	*	NS	NS	NS	NS
	0	0.09^{b}	0.09	0.11^{ab}	0.09	0.08	0.13	0.14
	30	0.09^{b}	0.09	0.11^{ab}	0.10	0.09	0.14	0.14
Mg	60	0.11^{ab}	0.09	0.10^{a}	0.11	0.09	0.17	0.14
	90	0.13^{a}	0.10	0.13^{a}	0.10	0.10	0.18	0.18
	120	0.11^{ab}	0.11	0.11^{ab}	0.11	0.10	0.31	0.15
	CV	18.24	18.62	11.48	12.05	16.83	67.72	18.39

Significant at * $P \leq 0.05$; ** $P \leq 0.01$; *** $P \leq 0.001$ and below; LSD- least significant difference; CV- Coefficient of variations; Means followed by same letter(s) within a column do not differ at $P \leq 0.05$.

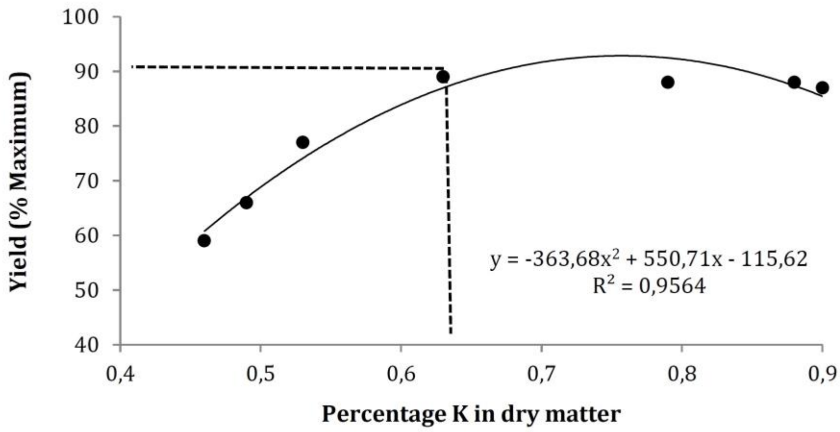

Figure 3. Relationship between K concentration in dry matter and relative yield

There was no statistically significant difference in Ca and Mg concentrations in teff biomass with increasing potassium rates (Table 3). It may be explained by the presence of very high Ca and Mg compared to K in the soil, which was not affected even by the application of K. The uptakes of K, Ca and Mg do not depend only on their concentrations in the soil, but also on their ratios. An excess application of one nutrient may induce deficiency of the others. K, Ca and Mg strongly interfere with each other during the uptake process (Voogt, 2002). High Ca and Mg concentrations in soil inhibit the uptake of K, while high K concentration in nutrient solution also inhibits the uptake of Ca and Mg (Bar-Tal and Pressman, 1996; Nukaya et al., 1997). But this did not happen in the present experiment might probably be as the amount of K was not so high compared to that of Ca and Mg to inhibit their uptakes.

Expressed as simple ratios, the "ideal" soil would have ratios of Ca: Mg about 7:1, Mg: K of 3.3:1 and Ca: K of 23:1 (AgKnowledge, 2011). The results from this study showed that the ratios of Ca: K ranged from 20:1 to 78:1 while that of Ca: Mg was from 3:1 to 6:1 indicating the absence of cation imbalances. On the other hand, the K:Mg ratios were between 0.05:1 and 0.14:1, the average being 0.08:1, showing much lower value than the critical level (0.7:1) suggested by Loide (2004). According to the suggestion by the author, all plots should have been affected by Mg induced K deficiency and responses to application of K fertilizer should have been observed. However, economically significant responses (data not shown) were not observed on soil K tests above 264 mg kg^{-1} (Figure 4). The average proportions of Ca, Mg and K in the experimental soils were 75, 23 and 2% respectively showing normal base saturation ranges of an "ideal" soil. Ologunde and Sorensen (1982) indicated that, when a soil contains adequate absolute quantities of Ca, Mg and K, the ratios of these cations (Ca/ Mg, Ca/K, and K/Mg) do not generally influence plant yield within the ranges commonly found in soils showing that total availability or supply is typically more important than the ratios.

Additionally, the relationships between relative yield (RY) and K concentration as well as RY and the cation ratios (Ca: K, and Mg: K (Figure 4) showed that application of K is required only for soils whose soil test K are below 264 mg kg^{-1}, Ca: K > 50:1 and Mg: K ratio > 15:1 (Figure 5) and responses to the application of K fertilizer was also observed on these soils at the rates of 60/90 kg K ha^{-1}.

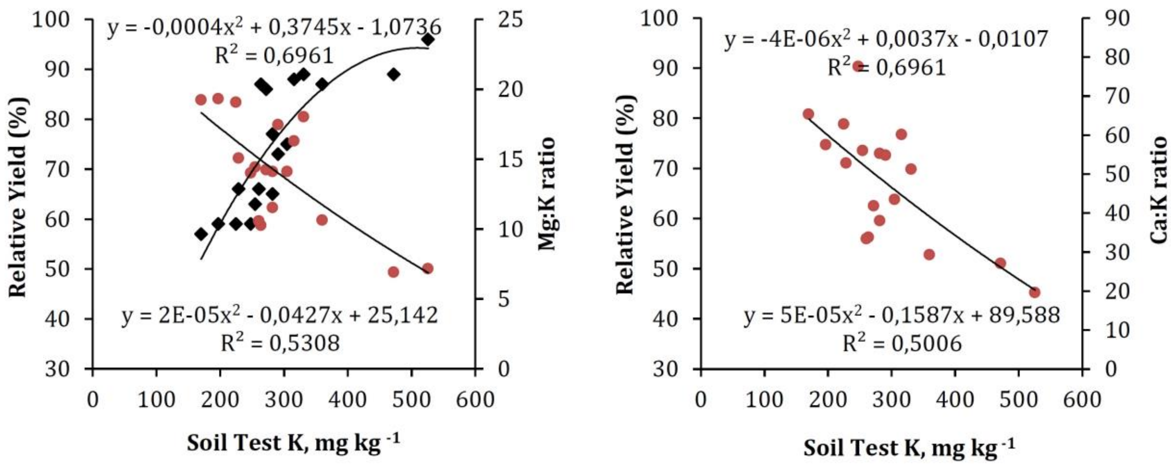

Figure 4. Relationship between soil test K and relative yield; soil test K and cation ratios

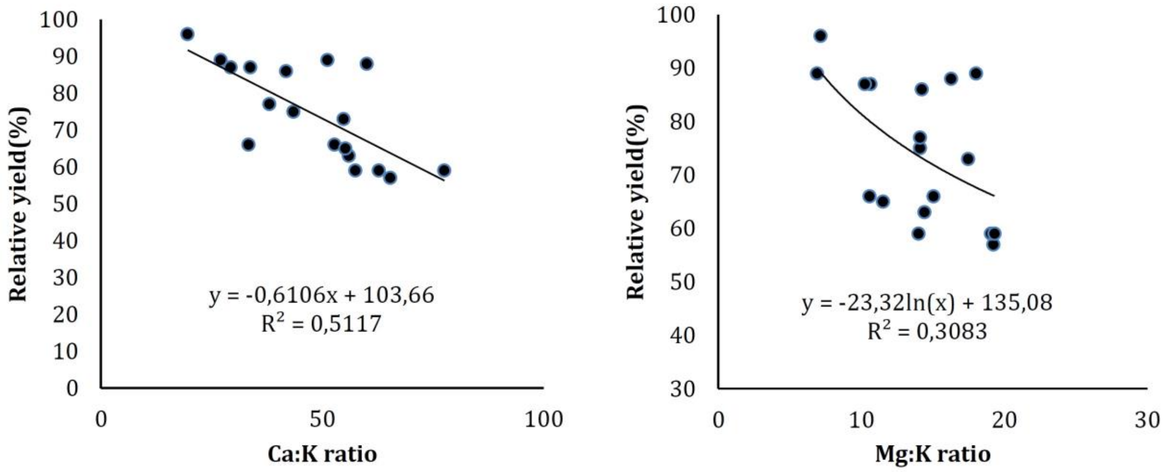

Figure 5. Relationship between cation ratios and relative yield

Conclusion

Potassium is one of the principal plant nutrients determining crop yield and quality. However, K application is not part of the fertilizer program in Ethiopia. Application of K in the study sites could increase yield of teff, reduce the negative potassium balance caused by the absence of K fertilizer and high amounts of K removed through grain and straw harvests.

Our two years on-farm research trials clearly demonstrated significant increase of teff yield with K fertilization for the study sites. Application of K increased grain yield of teff up to 77% over the control (no K). About 44% of the sites showed significant responses to application of 60 kg K ha^{-1} while 90 kg K ha^{-1} resulted in significant yield increases in 23% of the sites. The responsive sites had initial soil test K values ranging from 166 to 282 mg kg^{-1}, which were different from the critical levels developed by EthioSIS program for Ethiopian soils. The concentrations of major nutrients like N and K were also affected by K fertilization in most locations. Different responses of teff to increasing levels of K were obtained from different sites showing the need for developing critical K levels for the different soils. In addition, our result advocates the importance of balanced K nutrition in the study sites and similar areas, particularly where soil potassium level is low and in responsive Vertisols for better crop yields.

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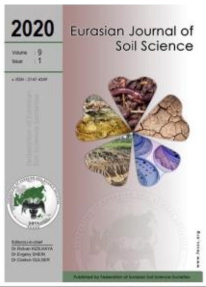

Quantifying the role of chemical weathering rates on soil developed along an altitudinal transect in the mountainous environments, Turkey

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Abstract

Climate and elevations play an important role in controlling rate of weathering and soil formation. The role of chemical weathering rate on soil developed along an altitudinal transect in the mountainous environments in Turkey was investigated to determine the effects of climate on the geochemical characteristics of the soil. The main purposes of this study were: i) To characterize the geochemical characteristics of soils as a function of climate ii) To evaluate the soil formation and decomposition rates in Climosequence depending on the elevation by using geochemical data. For this purpose, four representative profiles were dug at different elevations. The transect of four soils formed in limestone elevations from 1139 to 1809 m. Our results showed that the rate of chemical weathering of CIA, CIW, PIA and MIA indicators decreased with the increase in elevation. In contrast, WIP value increased at higher altitudes and exhibited different weathering directions by deviating from the main trend in the A–CN–K diagram that composition of weathered soils was easily influenced by the quantity of precipitation, degree of gradient and height differences. Therefore, it was concluded that the main factors determining soil development was climate and elevations, and both determine the leaching regime and weathering rates.

Keywords: Climosequence, elevations, geochemical, soil development, weathering index.

Introduction

Soil development is closely associated with specific weathering intensities under special mountainous environmental conditions Baumann et al. (2014). Soil development occurs through numerous physical, biological and chemical weathering processes acting to alter the parent rock on the soil surface. The formation of soils (pedogenesis) is a process by which weathering alters constituents within the parent material through the loss of more mobile (i.e., soluble) elements, concurrent enrichment of less mobile elements Le Blond et al. (2015). It is well established that soil-pedogenesis processes result in losses, gains or redistribution of elements, and that not all elements are affected in the same way. Elements are also recycled by the forest vegetation and such recycling can play a major role in soil development and the redistribution of elements. This is mainly the case with forest ecosystems, which are very efficient at recycling major nutrients. (Barbosa et al., 2015; Rate and Sheikh-Abdullah, 2017). Geochemical-based weathering indices are commonly used to measure and compare the relative extent and intensity of soil pedogenesis based on the chemistry of the surface soils (Osat et al., 2016) and weathering indices are used for evaluating soil fertility and development, demonstrating the impact of climate on soil surface weathering (Price and Velbel, 2003; Baumann et al., 2014). Chemical weathering indices incorporate major element oxides chemistry into a single value for each sample Egli et al. (2006). Studies in the regions of altitudinal gradient characterized by decreasing temperatures and increasing rainfalls, have shown the influence of the climatic contrast on soil formation, studies on sequences

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of soils developed in contrasting climate mountainous environments may be a valuable tool to predict the influence of climate on weathering rates, soil development stage, and soil formation processes (Egli et al. 2003, 2006, 2008, 2009; Lybrand et al., 2011; Moazallahi and Farpoo,r 2012; Barbosa et al., 2015; Zhou et al., 2015; Osat et al., 2016) and provide better understanding of elemental mobility during the weathering. In this study, the soil that has different elevations in Anamas Mountain and develops on locations with different precipitation and leaching regime was examined and the geochemical characteristics of the soil was determined. The geochemical approach in which the concentrations of the major and rare earth elements are used to reveal the weathering of the soils with different climatic characteristics affected by altitude difference be permit study of the effects of various climatic combinations on soil development so that the chemical weathering rates of soils formed on a Climosequence in humid climatic conditions will be comparatively determined. The following research objectives were: i) To characterize the geochemical characteristics of soils as a function of climate and ii) To evaluate the soil formation and decomposition rates in Climosequence depending on the elevation by using geochemical data.

Material and Methods

Study area

Study area Anamaslar, Beysehir, is located within the borders of the Lakes Region. 4 different heights were determined as a result of the studies conducted in the field where the study area is located. For this purpose, 4 profiles were dug between the elevations of 1139-1809 m (Figure 1). The study area is between the coordinates (Table 1). All profiles had limestone primary material and forest vegetation. The profiles were all steep. Profile 4 had the highest slope (> 45) and other profiles had a slope of 30-45 (Table 1). The Anamas Mountains are generally composed of Jurassic-Cretaceous aged limestones in the second time. The Triassic sandstone, claystone and conglomerates and the Triassic limestones and dolomites are observed at the foot of the Anamas Mountains. According to the meteorological station data in the region, the average annual precipitation from 1960 to 2017 was 546.4 mm, the annual evaporation was 1248.1 mm, the average annual temperature was 12.1 ºC, and the average soil temperature in 50 cm was 14.6 ºC. According to the prepared rainfall-evaporation-temperature because of these data, the temperature regime of the region is mesic and the moisture regime is xeric (USDA, 2014) (Figure 2).

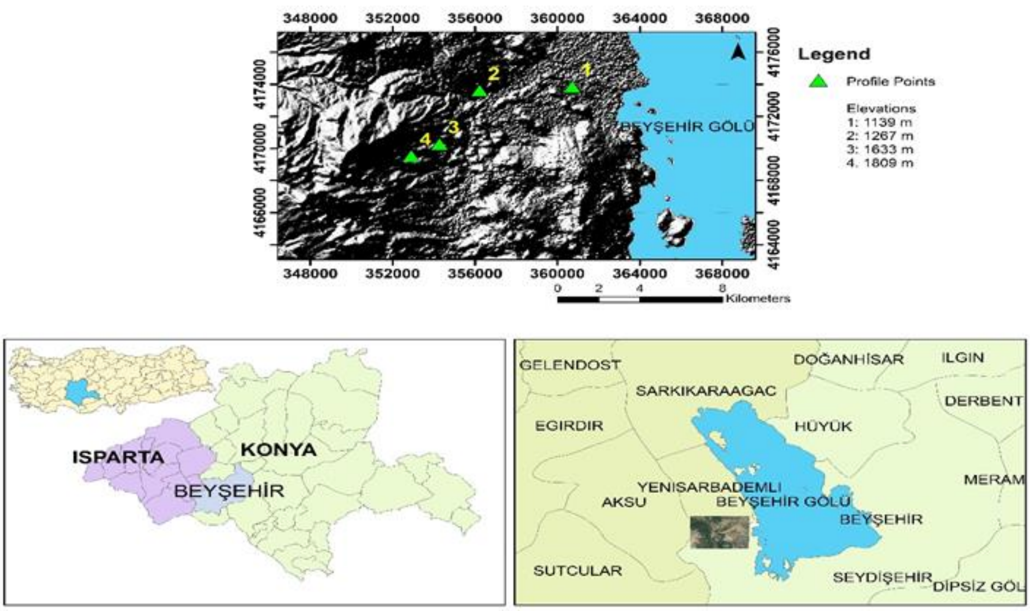

Figure 1. Location map of the study area that shows general transect of the four profiles

Soil sampling and analysis

Elevation is an important factor affecting the climate and could provide insight into the impact of climate on soil processes through affecting the type and rates of geochemical processes. Climatic features in mountainous areas, especially high mountainous regions, vary widely according to their environment. It is known that the amount of precipitation increases with increasing of elevation. Soils have been studied along a transverse section using four representative profiles between the elevations of 1139-1809 m. Soils were described in the field for geochemical properties of these four profiles were identified and samples were collected from each genetic horizon. Sixteen disturbed and undisturbed the samples of soil were taken to the laboratory to search for their geochemical features. Soil samples were air-dried, gently crushed, and passed through a 2-mm sieve to remove coarse fragments. Soil was used for the following analyses: Chemical determination of selected major, trace and rare earth elements was performed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Burt, 2011).

Table 1. Selected site characteristic of the studied profiles

Pedon	Coordinates		Primary material	Elevations (m)	Physiography	Slope (%)	Vegetation
	North	South					
I	4173828	360699	limestone	1139	Steep slope	30-45	forest
II	4173563	335946	limestone	1267	Steep slope	30-45	forest
III	4170197	354065	limestone	1633	Steep slope	30-45	forest
IV	4169545	352906	limestone	1809	Steep slope	>45	forest

Trace elements: A 500-mg <2-mm soil separate that has been air dried and ground to <200 mesh (75 µm) was weighed into a 100-ml Teflon (PFA) sample digestion vessel. To the vessel, 9.0 mL HNO3 and 3.0 mL HCl were added. The vessel was inserted into a protection shield, covered and then placed into a rotor with temperature control. Following microwave digestion, the rotor and samples were cooled and the digestate was quantitatively transferred into a 50-ml glass volumetric of high purity reverse osmosis deionized water. The samples were transferred into appropriate acid-washed polypropylene containers (Burt, 2011). While the samples of study were analyzed at the Advanced technology research & application center Laboratories (Selcuk University in Konya, Turkey).

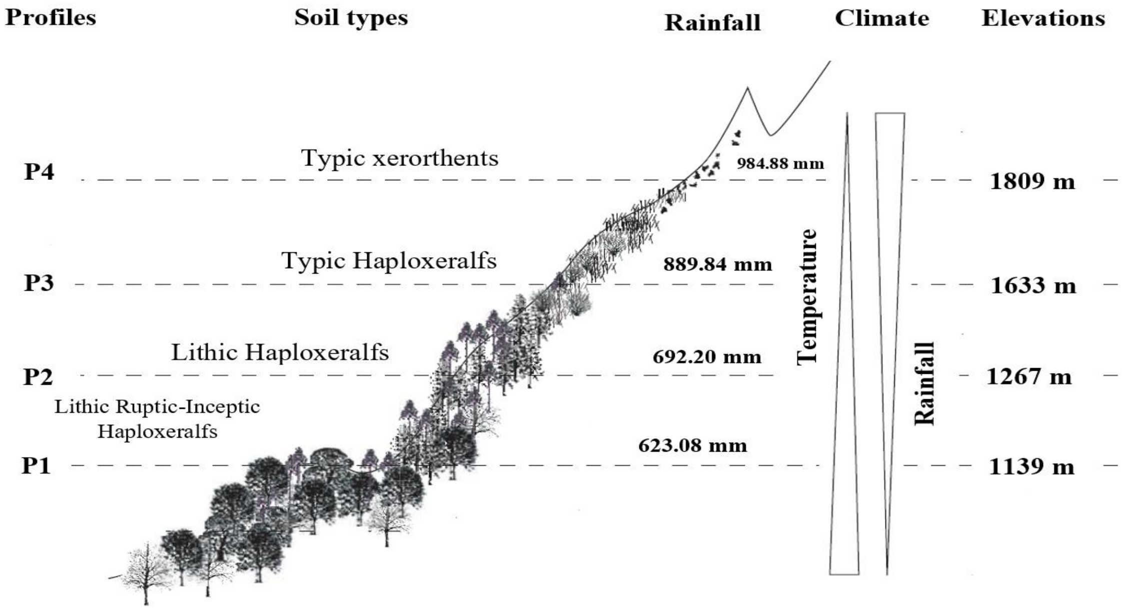

Figure 2. The amount of rainfall and the location of soil profiles during along altitudinal transect in mountain in Anamas

Soil development indicators

Calculation of Chemical Weathering Indices

Several indexes have been defined to characterize chemical weathering in soils, chemical weathering changes the chemical and mineralogical composition of a soil. Some of the mineral elements may be liberated (e.g. Ca, Mg, K, Na), forming secondary minerals, particularly clay minerals. The most commonly used chemical weathering indices are summarized in this study, such as Chemical Index of Alteration (CIA) Nesbitt and Young (1984), Chemical Index of Weathering (CIW) Harnois (1988), Plagioclase Index of Alteration (PIA) Fedo et al. (1995), Weathering Index of Parker (WIP), Parker (1970), and mineralogical index of alteration (MIA), Voicu et al. (1996), of which some of them will be discussed more in detail below.

1. CIA = $(100)[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)]$
2. CIW = $(100)[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O)]$
3. PIA = $(100)[(Al_2O_3 - K_2O)/(Al_2O_3 + CaO^* + Na_2O + K_2O)]$
4. WI P = $(100)\ [(2Na_2O/0.35) + (MgO/0.9) + (2K_2O/0.25) + (CaO^*/0.7)]$
5. MIA = $2 * (CIA-50)$

The mineralogical index of alteration (MIA) evaluates the degree of mineralogical weathering. The MIA value indicates incipient (0-20%), weak (20-40%), moderate (40-60%), and intense to extreme (60-100%)

weathering Voicu and Bardoux (2002). Importantly, all indices are calculated with CaO* and corrected for inputs from carbonate and apatite (McLennan et al., 1993).

A-CN-K diagrams and chemical alteration (CIA)

CIA is the most reliable weathering indices with the highest explanatory power, Therefore suggested the ternary A–CN–K (Al_2O_3 – CaO^*+Na_2O - K_2O) system is useful for evaluating the compositions of fresh plagioclase- and potassium-feldspar- rich rocks and examining their weathering trends, weathering products and clay minerals. (Nesbitt and Young 1984; Nesbitt 1992; Fedo et al. 1995; Nesbitt et al. 1996; Buggle et al. 2011; Shao et al. 2012; Babechuk et al. 2014; Baumann et al. 2014; Regassa et al. 2014).

Conduct of the rare earth elements during weathering

Besides some geochemical ratios and Ce and Eu anomalies were used to the quantification of weathering degree of studied pedons. The REE concentrations are normalized relative to a chondritic reference standard to facilitate the comparison of REE patterns between sites. Europium is the only lanthanide that usually happens in a divalent oxidation state and whose behavior is strongly influenced by plagioclase. This results in the potential for Eu to fractionate from the other lanthanides during weathering, since plagioclase is one of the most susceptible minerals to chemical dissolution (Babechuk et al., 2014). Fractionation of Eu can be tracked using the Eu anomaly of Eu* obtained by interpolation between the normalized values of Sm and Gd, as proposed by Taylor and McLennan (1985). $Eu/Eu^* = Eu_N/\sqrt{(Sm)_N \times (Gd)_N}$. Cerium can track redox-related transformations during pedogenesis in weathering profiles as a result of the potential oxidation of Ce^{3+} to Ce^{4+} (e.g., Middelburg et al., 1988; Braun et al., 1990; Mongell, 1993; Gallet et al., 1996; Murakami et al., 2001; Patino et al., 2003; Dengiz et al., 2013; Babechuk et al., 2014; Vermeire et al., 2016). Cerium anomalies are estimated by comparing the measured concentration of Ce with an expected concentration of Ce* obtained by interpolation between the normalized values of La and Pr. Cerium anomalies can be calculated as follow; $Ce/Ce^* = Ce_N / \sqrt{(La)_N \times (Pr)_N}$.

Results and Discussion

SiO_2 content was lower than 53% in all profiles and ranged from 1.04% to 52.90%. The content of Al_2O_3 ranged from 0.35 to 24.9%. Fe_2O_3 profiles were distributed between 0.07% and 9.56%. MgO values were changed between 0.45% and 7.13%. The enrichment observed in the MgO content was very specific and it is believed that MgO is generally very sensitive to leaching (Arikan et al., 2007; Nordt and Driese, 2010; Regassa et al., 2014). CaO values were found between 0.72 and 58.90%. The K_2O and Na_2O values were found to be 0.04-2.89%, 0.07-0.49%, respectively. Titanium is a mineral that is resistant to decomposition and is an element used in the determination of chemical change. TiO_2 contents were found to be between 0.01-0.19%, MnO 0.02-0.32% and P_2O_5 0.05-0.74% (Table 2).

Table 2. Total elemental analysis in weight percentages, oxides are expressed as weight percentages for the studied soil profiles.

Elevations (m)	Pedon	Horizon	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	LOI (%)	MnO (%)	Sum (%)
1139	P1	Oi	19.8	8.61	3.03	0.84	4.43	0.09	1.03	0.43	0.74	60.1	0.11	99.23
		A	44.8	21.0	8.13	1.38	1.51	0.15	2.65	1.16	0.52	18.2	0.17	99.68
		Bt	46.8	24.9	9.56	1.33	1.24	0.09	2.49	1.17	0.23	11.7	0.15	99.67
		CR	1.04	0.35	0.07	0.45	58.90	0.17	0.04	0.01	0.05	38.7	0.10	99.79
1267	P2	Oi	31.0	13.0	5.26	1.82	2.67	0.19	1.61	0.63	0.24	42.8	0.24	99.48
		A	37.7	16.7	7.10	3.25	4.88	0.21	2.04	0.84	0.22	26.5	0.32	99.77
		Btk	29.7	15.3	5.47	5.05	21.60	0.16	1.66	0.70	0.14	20.0	0.16	99.96
		C	24.0	10.6	3.50	7.13	29.20	0.11	1.04	0.44	0.08	23.5	0.21	99.84
1633	P3	Oi	9.13	4.05	1.19	0.45	2.61	0.07	0.57	0.17	0.12	81.3	0.02	99.70
		A	38.8	17.2	6.04	1.24	2.14	0.20	2.62	0.85	0.17	30.3	0.14	99.71
		Bhw	43.6	20.7	7.57	1.40	5.34	0.21	3.31	0.99	0.20	16.4	0.14	99.87
		Ck	31.4	16.5	5.09	1.13	23.20	0.15	2.60	0.70	0.20	18.8	0.06	99.85
		Cr	48.4	20.5	5.60	1.38	7.49	0.21	3.44	1.00	0.13	11.7	0.04	99.91
1809	P4	A1	39.9	15.7	5.80	1.42	2.90	0.40	2.58	0.87	0.16	30.5	0.13	100.37
		A2	44.1	17.6	6.70	1.47	2.44	0.43	2.89	1.02	0.14	22.9	0.12	99.82
		C1	52.0	21.1	8.25	1.59	0.94	0.49	3.69	1.19	0.15	10.4	0.15	99.96
		Cr	52.9	21.1	8.27	1.53	0.72	0.48	3.68	1.15	0.15	9.78	0.15	99.93

In Figure 3, the depth is plotted against the element content in weight percentages. While the chemical elements show similar tendencies in the 1, 2 and 3 profiles, the trends in the 4 profiles are different. Generally, in the fourth profile: reduced the content of CaO and P_2O_5 and increased SiO_3, Al_2O_3, Fe_2O_3, TiO_2, MgO, Na_2O, MnO and K_2O were shown at decreased depth. Fe, Al, Si the total content increases as the soil depth decreases due to the washing of carbonates. The P_2O_5 line in the first profile also deviates from the general trend to the top.

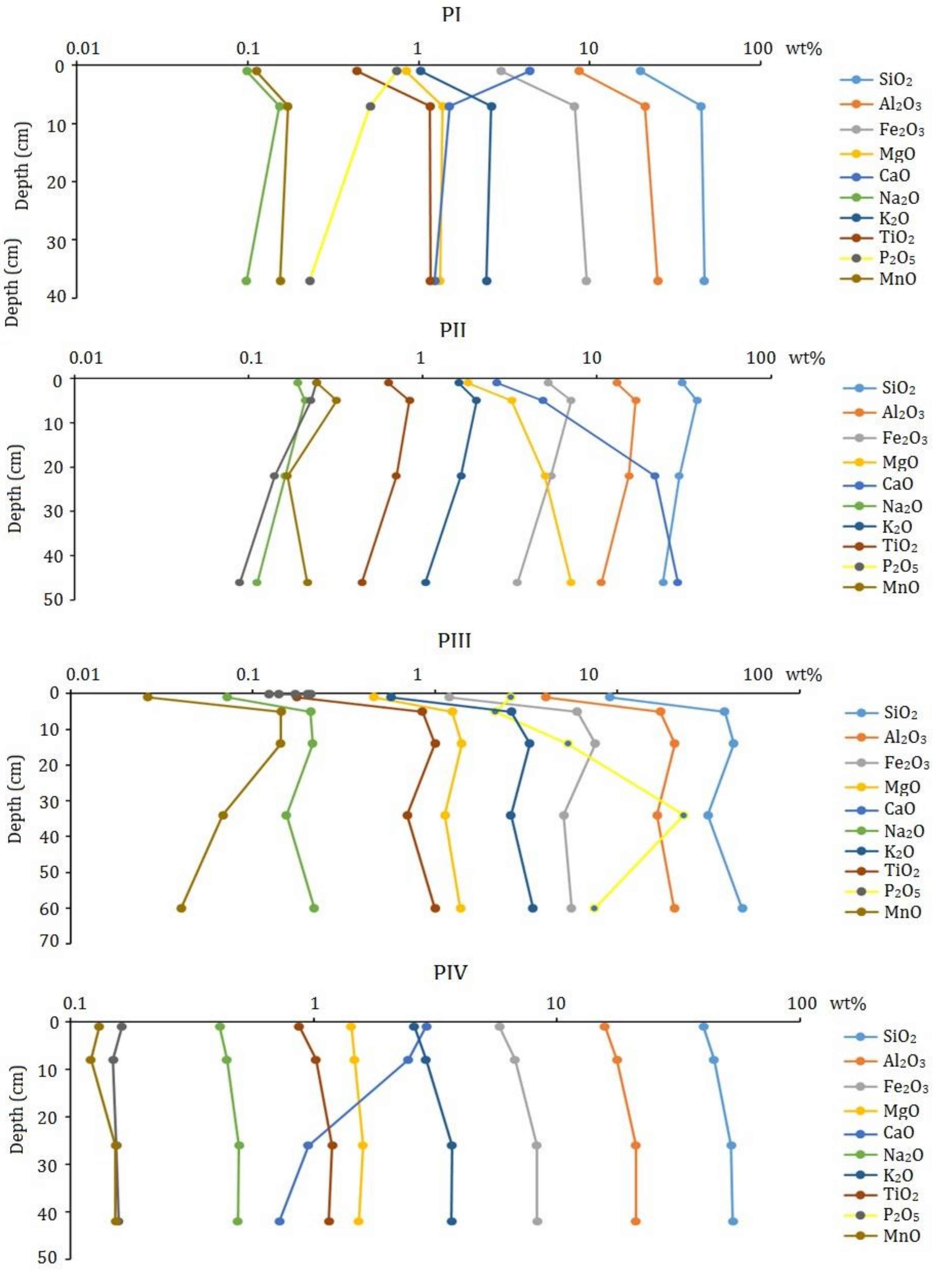

Figure 3. Total elements contents (in wt%) with depths for the studied soil profiles on a logarithmic scale.

The increase in P_2O_5 content may be due to the presence of both micro and macro organisms, causing retention of the element in their tissue. An increase in the amount of free sesquioxides resulting from the weathering of primary minerals also increase the phosphorous fixation capabilities of the weathered material. The effects of geochemical elements and the weathering indices, on the formation of the soils using the total element results, will be explained in the following sections.

Chemical weathering indices

The role of chemical weathering indices is mainly; to determine the amount of yield of the mobile components during weathering, assess soil fertility, to provide better kinetic element mobility in the context of weathering and predict the source of soil nutrients as well as changes in metal nutrients (Harnois 1988; Şenol et al., 2018). The values were gives of chemical weathering indicators for CIA%, CIW%, PIA%, MIA% and WIP. A change is observed for all soil values (89.19-79.00, 98.72-92.11, 79.53-64.04, 78.37-58.00, 41.38-12.21%) respectively. From the figures (4, 5, 6), it was revealed that the depth of the soil profiles (1, 2 and 3) increases with increasing the weathering indexes of the subsurface horizons. In addition, the most soluble elements such as MgO, CaO, Na_2O and K_2O increase the CIA, CIW and PIA due to the fact that they move towards the depth. Due to the low content of Al_2O_3 as a result of clay migration in the soil, the values of the weathering indicators on the surface of the horizons at profiles (1,2 and 3) were lower. It is important to emphasize that the removal of K from potassium feldspar is less than the rates of Na and Ca removal from plagioclase. However, potassium Feldspars is more sensitive to weathering. Accordingly, CIW is equivalent to that of CIA without potassium. If it is not aluminum associated with potassium feldspar, the CIW value will therefore be high and will cause errors in rocks the rich Feldspar. In general, in Figure 7, it was observed that the low WIP value in all soil profiles of surface horizons, and the low WIP value indicate a decrease in the moving cations. At the high altitudes of the fourth soil profiles, the highest WIP was observed and decreased at low altitudes due to the increase in K, Na, Ca, Mg cations. Figure 8 shows the index of mineralogical alteration evaluation to assess the degree of weathering. The amount of MIA increases with increasing depth at profiles (1, 2 and 3) and is considered the most developed soils at medium and low altitudes. The rate of chemical weathering of CIA, CIW, PIA and MIA indicators for all studied soil profiles (as shown in the Figure 9) decreases with the increase in elevation. This is due to the fact that basic cations (K, Na, Ca and Mg) are dissolved in water and descaled by leaching processes, cations accumulate at low altitudes and contribute to the formation of secondary minerals. In contrast, WIP value is increased at higher altitudes due to increased leaching and precipitation at high altitudes causing decrease in movement of cations. Although less developed soils are found at the steepest slopes of the P4 with a height of 1809 m, they contain less mobile elements, due to the leaching of products weathering that cause decomposition conditions and their transfer to low altitudes, which is more pronounced in the soil developed for profile at elevation 1139 m.

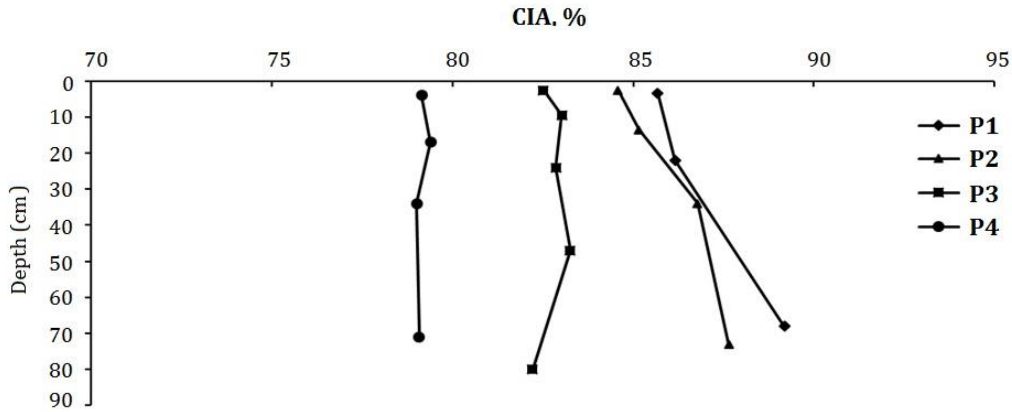

Figure 4. CIA % with depths for the studied soil profiles.

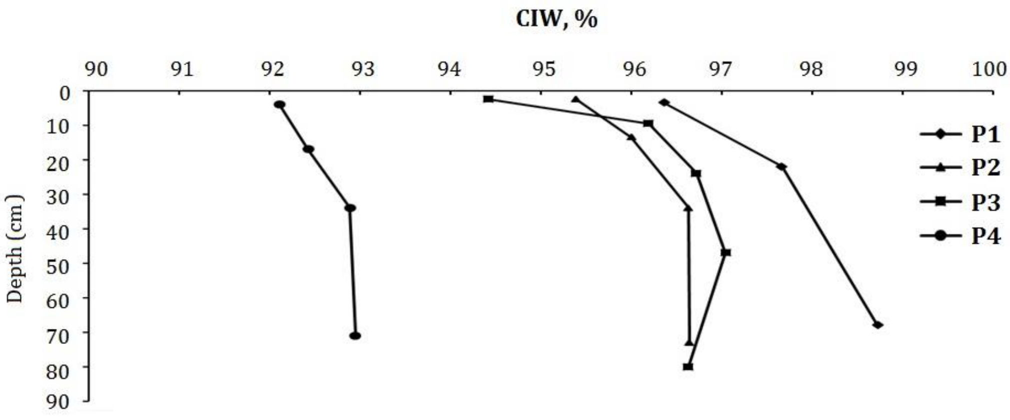

Figure 5. CIW % with depths for the studied soil profiles.

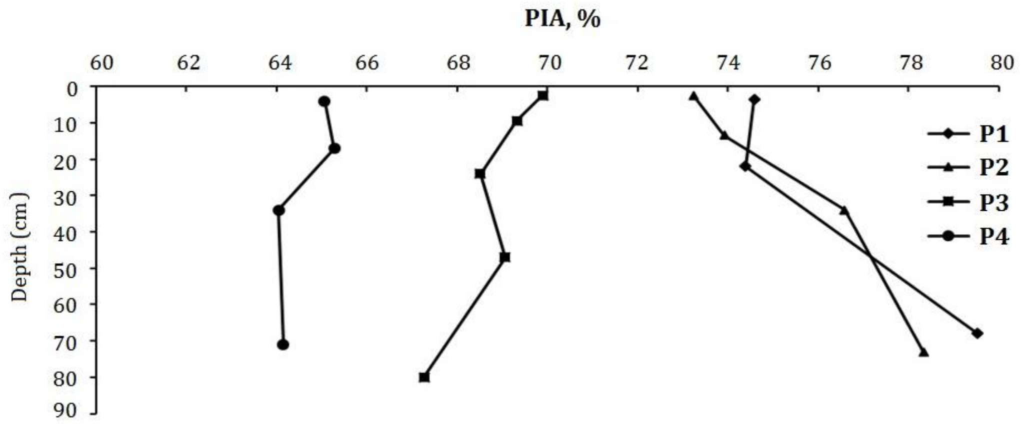

Figure 6. PIA % with depths for the studied soil profiles.

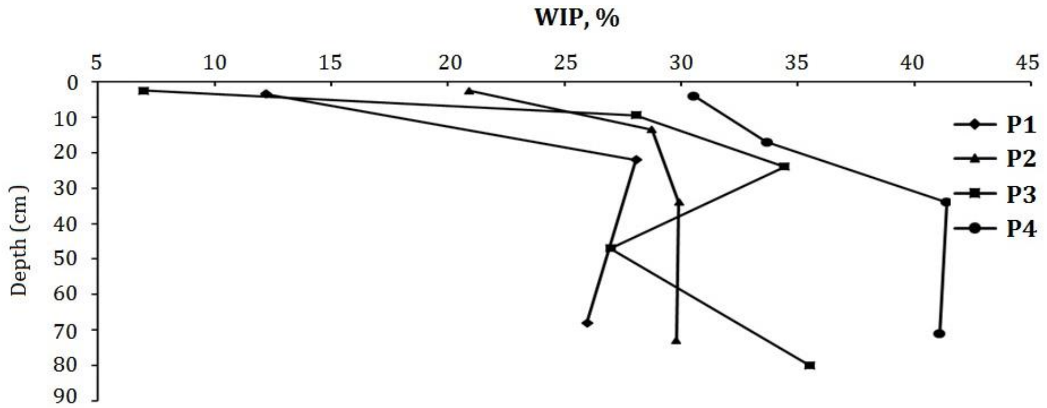

Figure 7. PIA % with depths for the studied soil profiles.

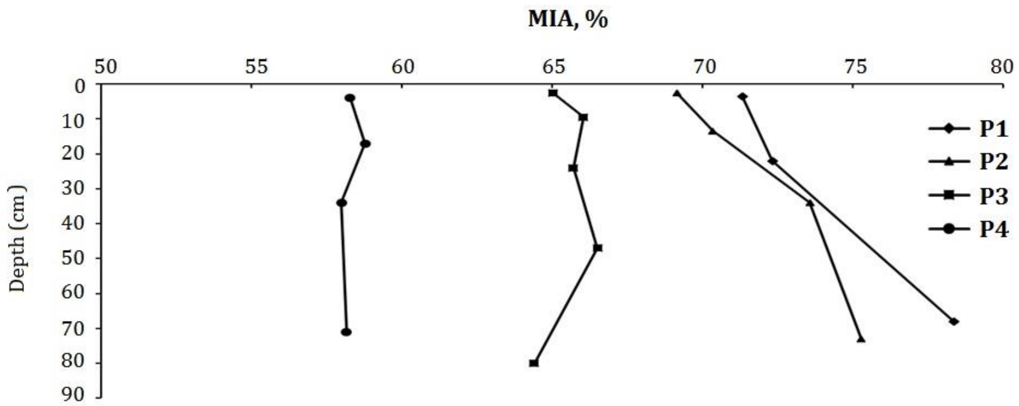

Figure 8. MIA % with depths for the studied soil profiles.

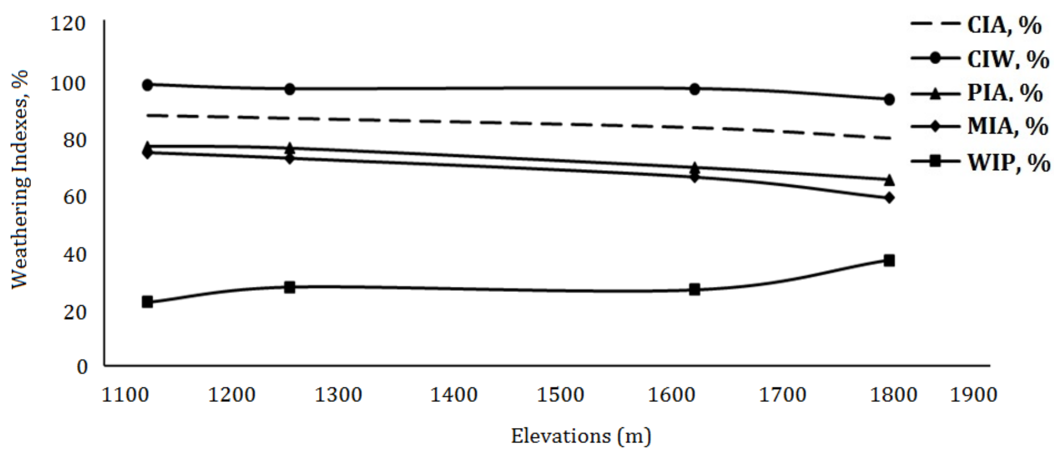

Figure 9. Weathering Indexes % with elevations for the studied soil profiles.

A-CN-K diagrams and chemical alteration (CIA)

Generally, the CIA is considered as a measure of the extent of the conversion of feldspar to clay (Nesbitt and Young, 1982; Nesbitt and Young, 1989; Fedo et al., 1995; Nesbitt et al., 1996; Yang et al., 2004; Buggle et al., 2011; Che et al., 2012; Shao et al., 2012; Babechuk et al., 2014; Baumann et al., 2014; Regassa et al., 2014).

Degradation of feldspar and concomitant formation of clay minerals are the dominant processes during chemical weathering of the soil. The A–CN–K (Al_2O_3–Ca^*O+Na_2O–K_2O) diagram was proposed to intuitively reflect the trends and the degree of silicate weathering and to evaluate the clay minerals (Nesbitt and Young, 1989; Fedo et al., 1995; Nesbitt et al., 1996; Von Eynatten et al., 2003; Yang et al., 2004; Li and Yang, 2010; Buggle et al., 2011). On the A–CN–K diagram, the main trend of silicate weathering in leaching of CaO and Na_2O and then K_2O, and relative enrichment of Al_2O_3. Note that most of the investigated soils indicate weathering trends in parallel with the A–K line. Most likely reflecting strong removal of K-bearing minerals from the parent rocks. The most weathered soils plot at the top of the triangle located the A apex reflecting high concentrations of Al-bearing minerals (Figure 10). The CIA values are directly represented on the A-CN edge of the A-CN-K triangle Figure 10 as the elements involving this edge are the same as needed for the calculation of CIA. High CIA values reflected 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).

In contrast, the soils at elevation 1139 m are parallel to the A–K line and approach the A apex more than the other soil elevations, most likely reflecting strong removal of K-bearing minerals from the parent rocks (Figure 10). This was due to the degree of weathering that they are higher than other heights, so the soil is considered the most developed. Despite the different weathering intensities registered in studied soil profiles, most of the investigated studied soils seem to be weathered from similar parent rocks. However, exhibited different weathering directions by deviating from the main trend in the A-CN-K diagram Figure 10, suggesting that composition of weathered soils more easily influenced by quantity of precipitation and the climate differences by the difference in altitudes.

Conduct of the rare earth elements during weathering:

It is known that the soil's REE concentration is influenced by sequential soil processes during pedogenesis (REE), REE is affected by a series of processes leading to internal degradation, such as solubility, oxidation, reduction, precipitation Babechuk et al. (2014). Table 3 gives the values in the distribution of rare elements except for the fourth profile, there is no regular trend between the horizons, and the content of the elements increased with decreased depth, because of the increase in the amount of precipitation and thus increasing the leaching process in the fourth profile.

Table 3. The rare earth elements analysis (REE) are expressed as $\mu g.kg^{-1}$ for the studied soil profiles.

Elevations (m)	Pedon	Horizon	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1139	P1	Oi	36	73	7.7	28	5.0	1.14	5.0	0.63	3.5	0.66	2.0	0.27	1.8	0.26
		A	75	142	15.9	58	10.7	2.4	10.5	1.36	7.5	1.42	4.2	0.57	3.8	0.56
		Bt	82	144	16.9	61	10.7	2.5	10.5	1.31	7.2	1.36	4.0	0.55	3.6	0.53
		CR	0.36	0.67	0.15	0.56	0.1	0.0	0.0	0.0	0.07	0.01	0.0	0.0	0.02	0.00
1267	P2	Oi	31	64	7.4	29	5.7	1.2	5.8	0.81	4.5	0.86	2.5	0.34	2.2	0.33
		A	35	72	8.4	32	6.5	1.39	6.7	0.92	5.2	0.98	2.9	0.4	2.7	0.38
		Btk	23	48	5.4	21	3.9	0.82	3.9	0.55	3.2	2.65	1.9	0.28	1.8	0.26
		C	15.2	34	3.7	13.8	2.7	0.54	2.7	0.39	2.3	0.45	1.4	0.19	1.3	0.20
1633	P3	Oi	13.8	28	3.3	11.9	2.3	0.52	2.3	0.32	1.8	0.35	0.98	0.16	0.98	0.16
		A	39	81	9.2	35	6.8	1.43	6.8	0.92	5.06	0.97	2.9	0.42	2.66	0.41
		Bhw	40	79	9.4	35	6.8	1.44	6.7	0.91	5.2	1.0	3.0	0.4	2.8	0.42
		Ck	26	51	5.9	21	3.9	0.79	3.7	0.5	2.9	0.56	1.8	0.25	1.74	0.26
		Cr	33	68	7.9	30	5.5	1.09	5.0	0.68	3.8	0.71	2.3	0.32	2.2	0.34
1809	P4	A1	35	70	8.3	32	6.2	1.32	6.2	0.83	4.8	0.9	2.6	0.37	2.5	0.37
		A2	38	78	9.2	35	6.9	1.44	6.8	0.95	5.3	1.02	2.9	0.42	2.8	0.41
		C1	41	84	9.9	38	7.4	1.5	7.3	1.03	5.7	1.09	3.2	0.45	3.0	0.44
		Cr	40	81	9.7	37	7.2	1.5	7.0	0.97	5.6	1.11	3.3	0.47	3.0	0.47

Table 4 gives the values in the indicators were calculated according to their geochemical percentages to determine weathering and soil enrichment rates. According to this; Yb (N), La (N) and Lu (N) values representing the LREE / HREE values in the soil were examined, La /Lu and La/Yb were found to be positive and strong, all of them were subjected to leaching as a result of all soil values. The low rate of 1809 m of La/Lu in P4 indicates a relatively low weathering condition and a low amount of clay found in the soil. On the other hand, the distribution of the Sm (N) and La (N) ratios is very close to the MREE, the middle rare enrichment element. The low negative Sm/Nd ratio for the values of all the soil profiles studied was found to be related to the intensity of the increased weathering in relation to the LREE enrichment. The ratios obtained using REE trace elements in (Table 4) showed that the clay movement in P1 was denser and thus the weathering was more developed than the other studied soil profiles. In addition, for La /Sm, La/Lu and La/Yb ratios for P1, it is due to the increased elevation of 1139m without any other soil profiles studied.

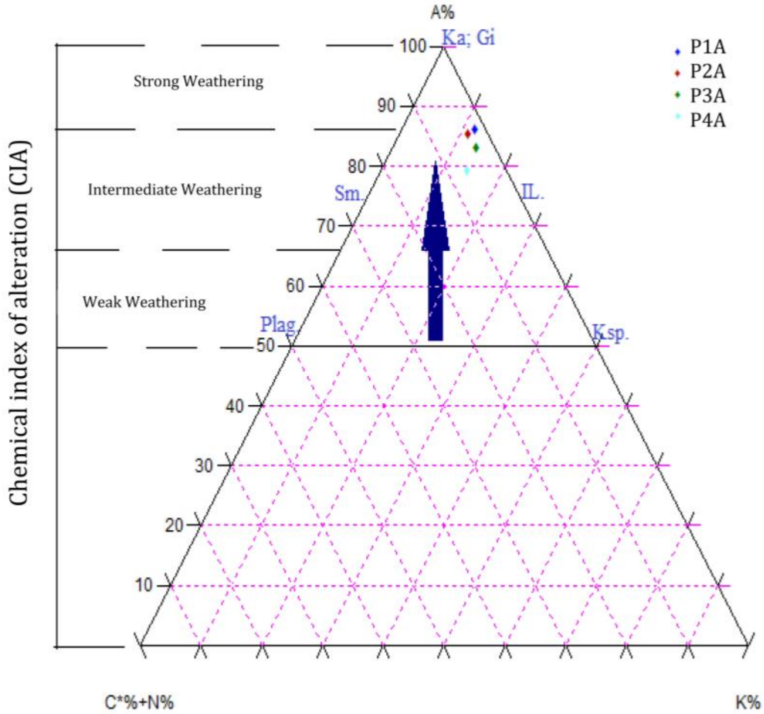

Figure 10. A-CN-K diagrams (Nesbitt and Young, 1989) with indication of the weathering index CIA for studied soil profiles only for horizon A. Arrow indicates the general weathering trend and the minerals plagioclase (Plag.), K-feldspar (Ksp.), Illite (IL.), Smectite (Sm.), Kaolinite (Ka.), and gibbsite (Gi.) is give for orientation.

Ho is a leachable element with weathering. Therefore, Er/Ho ratios tend to decrease by increasing weathering. In Table 4, P4 means that the highest Er/Ho ratio for height 1809m, was the lowest density of weathering at this height. However, the lowest value of Er/Ho ratio at the elevation of 1139m indicates that the density of weathering has increased.

It is clear that all values in the samples of the soil profiles examined have Eu negative. Eu/Eu* values are between 0.61 – 0.72% as shown in Table 4. More importantly, the difference in the Eu/Eu* value is inversely proportional to the increased weathering. Similar reports of a decrease in the negative values of Eu/Eu* as a function of intensity of weathering are presented (Condi et al., 1995; Huang and Gong, 2001; Ma et al., 2011; Babechuk et al., 2014).

Cerium can monitor cases of oxidation due to the potential oxidation bond between Ce^{+3} and Ce^{+4} during pedogenesis processes in populations of soil profiles studied. Cerium (cerium) was estimated by using the formulas of Ce, La and Pr. In Table 4, Ce/Ce* values are weak positive and negative. These oxidation values show that in the weathering of all studied soil profiles, Ce will decompose on a smaller scale.

Conclusion

The aim of this research was characterizing the geochemical characteristics of soils as a function of climate to evaluate the soil formation and weathering rates in Climosequence depending on the elevation by using geochemical data. The rate of chemical weathering of CIA, CIW, PIA and MIA indicators decreased with the increase in elevation. This was because basic cations (K, Na, Ca and Mg) were dissolved in water and descaled by leaching processes, and cations accumulated at low altitudes and contributed to the formation of secondary minerals. In contrast, WIP value was increased at higher altitudes due to increased leaching and precipitation at high altitudes causing decrease in movement of cations. Although less developed soils were found at the steepest slopes of the P4 with a height of 1809 m, they contained less mobile elements, due to the leaching of products weathering that cause decomposition conditions and their transfer to low altitudes, which is more pronounced in the soil developed for the first profile at elevation 1139 m.

Despite the different weathering intensities and anomalies registered in studied soil profiles, most of the investigated studied soils seemed to be weathered from similar parent rocks. However, it exhibited different weathering directions by deviating from the main trend in the A-CN-K diagram suggesting that the formation of weathered soils more easily influenced by quantity of precipitation, degree of gradient and difference elevations. Therefore, it was concluded that the main factors determining soil formation are climate and elevations, both of which determine the leaching regime and weathering rates.

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Use of sewage sludge in agricultural soils: Useful or harmful

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Abstract

Sewage sludge is an important type of organic wastes among the various categories of solid waste. Organic matter resources in soils are relatively low and frequently require replenishment. Therefore, the use of sewage sludge in agricultural soils is a desirable method of their utilisation. The addition of sewage sludge to soils may be an inexpensive and effective alternative to the methods applied currently (mineral fertilisation, manure etc.). In spite of the undisputable advantages resulting from the application of sewage sludge in agriculture, it also involves some serious threats. Among those we should mention the presence of pathogens, heavy metals, and organic pollutants. In the current scenario of increasing global population, the generation of solid wastes like biosolids is bound to increase remarkably. Improper and unscientific disposal of biosolids results in several environmental issues such as surface and groundwater contamination, degradation of land, and food chain contamination. According to the principles of waste management hierarchy, agricultural recycling of biosolids will be a more environmentally preferred option over the traditional disposal methods. Utilizing the potential of biosolids to recycle valuable plant nutrients and as an effective soil amendment will not only help in sustainable management of this waste but also in minimizing the negatives associated with its traditional disposal. Every country must obey their regulations and legislations for managing their sewage sludge as a basic solution for use of sewage sludge in agricultural soil.

Keywords: Sewage sludge, biosolids, organic matter, waste management.

Introduction

Sewage sludge is an important type of organic wastes among the various categories of solid waste (Singh et al., 2014). In the present day, because of population growth, world of diminishing natural resources and energy crisis, the importance and need of developing a sustainable approach towards environmentally sound solid waste management cannot be ignored (Pappu et al., 2007). The improper disposal of solid wastes like biosolids and other biowastes pose a serious threat to the environmental quality leading to problems like groundwater contamination, degradation of soil quality, etc. Over the time, different approaches of safe biosolids disposal such as incineration, soil application, land filling (Kominko et al., 2017) and sea dumping have been explored (Sanchez Monedero et al., 2004). Disposal methods like land filling and ocean dumping have their own demerits due to scarcity of land, pollution problem and also don't lead to reuse of the beneficial constituents of biosolids (Wong, 1995; Singh and Agrawal, 2008). As a result, the United States and several European countries have banned the ocean dumping of biosolids since 1991 and 1998 (USEPA, 1999a,b; Zhidong and Wenjing, 2009).

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Efficient municipal waste water treatment produces vast amounts of sludge. For example, in the countries located wholly or partly on the Baltic Sea watershed the amount of sewage sludge generated is about 3.5 million tonnes of dry solids annually. This is expected to increase to almost four million tonnes by 2020. Sludge management is an integral part of any modern municipal waste water treatment plant: it is important not to lose nutrients in the sludge, to make use of its material and energy, and to dispose of it efficiently and sustainably. During recent years, much effort has been put to efficient nutrient removal from the municipal waste waters in the Baltic Sea region. The aim is to reduce the eutrophication burden to the fragile Baltic Sea by fulfilling the relevant requirements: the newer EU member states on the eastern and southern shores of the Baltic Sea have started to implement the Urban Waste Water Directive (see chapter 12 for legislation) and also to strive for the stricter HELCOM recommendations for nutrient removal (www.purebalticsea.eu). Also, in the non-EU countries of the region, actions have been taken and are still on-going to improve the level of waste water treatment. The two main sludge fractions are primary and excess secondary sludge. If phosphorus is removed from the sewage by chemical precipitation, the amount of the sludge increases by the amount of chemicals used for the precipitation. The nutrients removed from waste water are contained in the sludge, which must be handled so that the nutrients are not released back to the watercourses, while the material and energy content of the sludge can be utilised. The large amounts of sewage sludge generated in waste water treatment plants provide numerous opportunities for beneficial use; for example, in power generation, soil improvement and even nutrient recycling. The possibilities of use are dependent on the quality and amount of the sludge in question, the processes used in a particular treatment plant, and the national legislation and policies. The sludge handling strategy of an individual waste water treatment plant is shaped, for example, according to: its location, transportation costs; the quality of incoming waters; nutrient removal technology used; legal restrictions concerning sludge disposal; the availability and price of conditioning agents; and the possibilities to outsource the treated sludge products. An accurate and unbiased assessment of the risks connected to the use of sewage sludge is needed. The question is how to deal with various chemical substances present in municipal sewage sludge originating from households and how to recycle the nutrients. The issue of hazardous chemicals of the sludge is currently under debate and regulatory issues are also open with the EU Sewage Sludge Directive currently being revised (www.purebalticsea.eu). There are international political dimensions to the sludge handling issue, not only in differing legislation, energy strategies and sludge handling costs, but also because the world's mineral resources of phosphorus are depleting. The question on nutrient recycling is emerging: according to some estimates, phosphorus resources may only be sufficient for the next 50 years. These resources are located mostly in northern Africa, China and the USA. Even though there have been some optimistic estimations on the global reserves, the dependency on a single country, Morocco, is expected to grow over the century. Thus, EU food security has to rely on imported phosphorus (Schröder et al., 2011). Municipal sewage sludge contains large amounts of precious phosphorus; however, the possibilities for recycling should be taken into account already when planning sludge management alternatives. Moreover, some sewage treatment methods do not allow the phosphorus to exist in an easily usable form in the sludge (www.purebalticsea.eu).

Land application of sewage sludge has a great incentive in view of its fertilizer and soil conditioning properties, unless it contains toxic substances. The heterogeneous nature of sewage sludge produced at different treatment plants and the variations between seasons necessitates knowledge of the chemical composition of sewage sludge prior to the land application. Characteristics of sewage sludge depend on the waste water treatment processes and sludge treatment. Generally sewage sludge is composed of organic compounds, macronutrients, a wide range of micronutrients, non-essential trace metals, organic micro pollutants and microorganisms (Kulling et al., 2001).

The practical and technical challenges of sludge handling are the following:

a) stabilising sludge is not inert and can have an unpleasant odour; b) reducing the water content and sludge volume to the minimum; c) utilising the energy potential when economically possible; d) reducing the amount of harmful micro-organisms if people, animals or plants are in contact with the sludge; e) recovering phosphorus for agriculture (www.purebalticsea.eu).

The macronutrients in sewage sludge serve as a good source of plant nutrients and the organic constituents provide beneficial soil conditioning properties (Logan and Harrison, 1995).

Chemical characterization of sewage sludge collected for over 2 years from eight cities of Indiana, USA, showed that sewage sludge contained approximately 50% organic matter and 1–4% inorganic carbon. Organic N and inorganic P constituted the majority of total N and P, respectively, of sludge. Organic and inorganic C, organic N and inorganic P, Ca and Mg were present in relatively constant concentrations in a given sludge throughout the sampling period. Inorganic N, organic P, K and all other metals were quite variable during the entire period of study The largest deviations were found for trace elements/heavy metals such as Cd, Zn, Cu,Ni and Pb (Sommers et al., 1976).

Bradford et al. (1975) studied trace element concentrations of sludges from certain metropolitan areas of southern California to evaluate their interactions with soils to determine their effects on plant growth. The total concentrations of trace elements in sludges were highly variable depending on the sources, which were related to different industries discharging effluents in the sewerage system. Concentrations of Cu, Zn, Ni, Co and Cd were consistently greater in saturation extracts obtained from sludges than those obtained from soils of any sampling sites. The maximum total concentrations of B, Cd, Ni, Cu, Pb and Zn showed positive correlations with concentrations of these elements found in soil solution.

Effects of the sewage sludge application on soil properties

Physico-chemical properties

Land application of the sewage sludge is becoming more popular due to the possibility of recycling valuable components such as organic matter, N, P and other plant nutrients (Martinez et al., 2002). Sewage sludge application to soil enables the recycling of nutrients and may eliminate the need for commercial fertilizers in cropland (Sommers, 1977). The fertility of soil increased over a long period of time, as sludges are organic fertilizers (Archie and Smith, 1981).

Unwise sludge amendment may, however, disturb the soil properties especially when it bears high concentrations of metals and toxic constituents. The soil physical conditions have been improved by sewage sludge application (Epstein, 1975, Table 2). An increase in soil pH has been reported in soils applied with municipal sewage sludge (Tsadilas et al., 1995). Lowering of soil pH is also reported (Epstein et al., 1976). The changes in soil pH have been correlated with the calcium carbonate content of sludge and acid production during sludge decomposition (Sommers, 1977). Soil pH consideration is especially important in view of trace metal abundance in sewage sludge. Maiti et al. (1992) characterized the sewage sludges of Calcutta, India, to assess their fertilization value. Sewage sludge pH was found to be neutral to slightly alkaline and to have a higher salt content in winter than in the monsoon season. The cation exchange capacity (CEC) was higher during monsoon. Exchangeable Ca^{2+} was the dominant cation followed by Mg^{2+}, Na^{+}, and K^{+}. The sludges were rich in organic carbon and available N.

A comparison of the data on physico-chemical characterization of selected sewage sludge from different countries collected during 1998–2002 clearly showed that pH may vary from an acidic to an alkaline range (Parkpain et al.,1998; Martinez et al., 2002; Nandakumar et al., 1998).

Organic matter added to the soil as sewage sludge composts improved the soil properties, such as bulk density, porosity and water holding capacity (Ramulu, 2002; Table 1).

Table 1. Effect of sewage sludge amendments on selected soil physical, chemical, and biological properties (Singh and Agrawal, 2008)

Properties	Effect	References
Physical		
pH	Decrease	Epstein (1975), Nielson et al. (1998)
	Increase	Tsadilas et al. (1995), Nielson et al. (1998)
Soil aggregate stability	Increase	Ojeda et al. (2003)
Bulk density	Decrease	Ramulu (2002), Ojeda et al. (2003)
Water holding capacity	Increase	Epstein (1975), Ramulu (2002)
Porosity	Increase	Ramulu (2002)
Erosion	Decrease	Ojeda et al. (2003)
Humus content	Increase	Kulling et al. (2001)
Chemical		
Toxic elements	Increase	Kulling et al. (2001), Lopez-Mosquera et al. (2000)
Soil organic carbon	Increase	Kladivko and Nelson (1979)
Electrical conductance	Increase	Martinez et al. (2002), Ramulu (2002)
N and P	Increase	Martinez et al. (2002), Sommers (1977), Walter et al. (2000)
Cation exchange capacity	Increase	Ramulu (2002), Soon (1981)
Biological		
Yeast population	Increase	Kulling et al. (2001)
Pathogenic organisms	Increase	Kulling et al. (2001), Ramulu (2002)
Aerobic bacteria	Increase	Kulling et al. (2001), Ramulu (2002)

A study conducted to determine the effect of 0.5% sewage sludge application to soil on water retention, hydraulic conductivity and aggregate stability showed that raw, as well as digested sludge, increased the total soil water retention capacity with the greatest increase in the raw sludge amended soil (Epstein,1975). Sludge addition in soil caused a significant increase in soil hydraulic conductivity after 27 days of incubation. Effect of sewage sludge amendments on selected soil physical, chemical, and biological properties was given on Table 1 (Singh and Agrawal, 2008).

The metal concentrations in the sewage sludge depend on several factors such as: i) sewage origin, ii) sewage treatment processes, and iii) sludge treatment processes (Hue and Ranjith, 1994). The bioavailability of the sludge borne metals to soil is further influenced by soil properties such as pH, redox potential (Eh), sesquioxide content and organic matter, as well as sludge application rate (Hue and Ranjith, 1994; Delibacak and Ongun, 2018).

Assuming that Zn, Cu and Ni behave similarly as pH varies, maintenance of a pH above 6.0 for grassland and 6.5 for arable soil to which the sewage sludge is applied, was recommended (Department of The Environment, 1981).

A study to evaluate the effect of pH on release of Zn, Cu and Ni from the sewage sludges showed that metal concentration released to the supernatant liquid increased as pH decreased below the threshold value, which was 5.8 for Zn, 6.3 for Ni and 4.5 for Cu loaded sludge (Adams and Sanders, 1984).

Hernandez et al. (1991) conducted a study to analyze the influence of sewage sludge application to a Calciorthid soil on the soil availability of macronutrients (N, P, and K) and

heavy metals (Fe, Cu, Zn, Mn, Ni, Cr, Cd, and Pb). Total N and extractable N and P contents increased in the sludge-amended soil, whereas the extractable K remained unaltered. Extractability of Fe, Cu, Mn, Zn and Pb increased due to sludge application as compared to the control. Relatively high rates of sludge application increased the cation exchange capacity, which helped to retain essential plant nutrients within the rooting zone due to additional cation binding sites (Soon, 1981).

Such responses, however, depend upon the sewage:soil ratio. The higher organic matter proportion in sludges decreased bulk density and increased the aggregate stability (Ojeda et al., 2003; Table 2). These improvements in soil physical properties increased water-holding capacity by promoting higher water retention in sludge-amended soils (Ojeda et al., 2003; Table 1).

Korboulewsky et al. (2002) studied the effects of the sewage sludge composts applied at the rates of 10, 30, and 90 t/ha fresh wt. on a vineyard in southeastern France to quantify in situ N mineralization and soil organic matter, and to evaluate environmental risks such as N and P leaching and accumulation of heavy metals in soil. It was found that soil organic matter increased at all of the treatment doses, but neither total nor available heavy metal concentrations increased. As the sewage sludge contained very low levels of heavy metals, mainly in nonextractable and nonexchangeable forms (Breslin, 1999), composting reduced the

heavy metals availability in the raw material due to adsorption or complexing by humic substances. Mineral N increased in the first and in the second summers in the topsoil of amended plots. The risk of N leaching was very low, but P appeared to be the limiting factor at the recommended sludge amendment rate. Increase in P was significant in the top and in the subsoil of all of the treatment plots, with maximum increase at the highest rate of sludge application. At lower rates, no significant differences were observed. In soil, trace elements are distributed in various forms such as solid phases, free ions in soil solution, soluble organic mineral complexes, or adsorbed on colloidal particles. Sewage sludge addition to soils therefore could affect potential availability of heavy metals (Wang et al., 1997).

The solubility and consequently the mobility of metals added with sewage sludge are at least in part controlled by organic matter decomposition and the resultant soluble organic carriers of metals (Chaney and Ryan, 1993). Trace metal bioavailability is also dependent on the form of organic matter, i.e., soluble (fulvic acid) or insoluble (humic acid) (McBride, 1995). Insoluble organic matter inhibits the uptake of metals, which are tightly bound to organic matter and reducing the bioavailablity. Soluble organic matters, however, increase the availability by forming soluble metal organic complexes (McBride, 1995).

The high organic matter content of acid soil led to the formation of complexes with Cu and thus impaired its uptake by plants. A contrasting trend was found with respect to metal concentrations in acid and alkaline soils. The concentrations of Zn, Cu, Pb and Ni in plants decreased with increase in sludge doses for acid soil, The study further suggested that soil type has a larger effect on the metal bioavailability than sludge doses (Morera et al., 2002).

Microbial properties and soil enzymes

Land application of biosolids often results in significant changes in the structure, diversity, or richness of plant and animal communities at a given site, due directly, and indirectly, to resulting soil improvements and changing environmental conditions (USEPA, 1994). Few studies, however, have examined the soil microbial community in ecologically based studies, particularly in semi-arid grasslands (Dennis and Fresquez 1989; Pascual et al. 1999; Barbarick et al. 2004; García-Gil et al. 2004). Such research is crucial, considering that among other functions, microbial populations control decomposition and nutrient cycling in soils (Coleman and Crossley 1996), which in turn, control aboveground dynamics (Reynolds, 2018). Furthermore, a greater understanding of biosolids long-term effects on above- and belowground dynamics will lead to a greater understanding of ecosystem-level effects. Dennis and Fresquez (1989) found that cultivable fractions of the soil microbial community from a semi-arid grassland increased linearly with the biosolids application rate (22.5, 45, and 90 Mg ha^{-1}), and they noted that improvements in soil fertility and site restoration were reflected in diversity and composition of the soil microbial community. García-Gil et al. (2004) reported increased microbial biomass, basal respiration, metabolic quotient, and enzymatic activities in another semi-arid soil, amended 9 or 36 months previously, with biosolids at approximately 36 Mg ha^{-1}. Barbarick et al. (2004) examined microbial responses to biosolids in both semi-arid grassland (0 and 30 Mg ha^{-1}) and shrubland (0 and 40 Mg ha^{-1}) sites 6 years after biosolids surface application. At both sites, CO_2 evolution and actively metabolizing microbial biomass were greater in plots 6 years following biosolids application than in control (nonamended) plots. Pascual et al. (1999) examined microbiological and biochemical parameters of semi-arid soils 8 years after biosolids amendment (65 and 260 Mg ha^{-1}). Compared to control plots, the amended plots exhibited greater total organic C, microbial biomass, basal respiration rate, and enzymatic activity even 8 years after biosolids incorporation. Enzymatic activities have often been estimated to establish the indices of soil fertility. Microorganisms as well as plants synthesize enzymes, which act as a biocatalyst of important reactions to produce essential compounds for both soil microorganisms and the plants. Soil enzymatic activities can be indirectly affected by heavy metals present in the sewage sludge (Kandeler et al., 2000). The effect of sewage sludge on biological activity may be used as indicator of soil pollution (Fließbach et al., 1994). According to some researches sewage sludge amendment increased the soil microbial activity, soil respiration and soil enzymes activities (Banerjee et al., 1997; Kayikcioglu and Delibacak, 2018). However, reduction in soil enzyme activities has also been reported at longer incubation period with high heavy metal availability (Fließbach et al., 1994). Effects of adding different doses (0, 100, 200 and 300 t/ha dry wt.) and C/N ratios (3:1, 6:1 and 9:1) of the sewage sludge on activities of b-glucosidase, alkaline phosphatase, arylsulphatase and urease in a clay loam soil at 25ºC and 60% water holding capacity were studied by Kizilkaya and Bayrakli (2005). Nitrogen was added in the form of $(NH_4)_2SO_4$ solution to the sludge to obtain different C/N ratios. Rapid and significant increase in the soil enzymatic activity has been noted at different doses and C/N ratios of the sewage sludge amendments as compared to unamended ones. Enzyme activities varied with differences in incubation period. Soils with the highest C/N ratio and sludge dose had the highest b-glucosidase activity. Alkaline phosphatase and aryl sulphatase showed an increment in their activity during the first 30 days of incubation followed by a pronounced decrease compared to unamended soil. Urease activity, however, showed an increase within 15 days, and thereafter activity declined. The highest activities of urease, alkaline phosphatase and arylsulphatase were observed in soil amended with a low C/N ratio and the highest dose of sludge (Kizilkaya and Bayrakli, 2005).

Harmfull effects

Application of sewage sludge in agriculture or for soil reclamation is an interesting solution. It is more and more frequently used in practice due to the advantageous effect of sewage sludge on the properties of soils fertilised/reclaimed with its application. Apart from soil enrichment in nutrients (Fytili and Zabaniotou, 2008), an addition of sewage sludge causes an increase in organic matter content in soil (Epstein, 2003). Organic matter resources in soils are relatively low and frequently require replenishment. Therefore, the use of sewage sludge in agriculture is a desirable method of their utilisation. The addition of sewage sludge to soils may thus be an inexpensive and effective alternative to the methods applied currently (mineral fertilisation, manure etc.). In spite of the undisputable advantages resulting from the application of sewage sludge in agriculture, it also involves some serious threats. Among those we should mention the presence of pathogens, heavy metals, and organic pollutants (Harrison et al., 2006; Oleszczuk, 2006a; Smith, 2009). Standards for maximum concentrations of pathogens in sewage sludge were given on Table 2.

Table 2. Standards for maximum concentrations of pathogens in sewage sludge (European Commission, 2009).

Country	Salmonella	Other pathogens
Poland	No occurrence	Faecal streptococci: < 100/g
France	8 MPN/10g DM	Enterovirus: 3 MPCN/10g of DM Helminths eggs: 3/10g of DM
Finland	Not detected in 25 g	Escherichia coli < 1000 cfu
Italy	1000 MPN/g DM	-
Luxembourg	-	Enterobacteria: 100/g no eggs of worm likely to be contagious
Hungary	-	Faecal coli and faecal streptococci decrease below 10% of original number
Poland	Sludge cannot be used in agriculture if contains salmonella	-

Proposed limit values on potentially toxic elements (PTE) in sewage sludge and in soil were presented in Table 3.

Table 3. Proposed limit values on potentially toxic elements (PTE) in sewage sludge and in soil (mg kg^{-1} dw) (European Commission, 2009).

Metal	Sludge	Soil		
		5<pH<6	6<pH<7	pH>7
Cd	10	0.5	1	1.5
Cr	1000	50	75	100
Cu	1000	30	50	100
Hg	10	0.1	0.5	1
Ni	300	30	50	70
Pb	750	70	70	100
Zn	2500	100	150	200

The treatment of sewage sludge for agricultural purposes in Russia is regulated by two main documents, which allow to exclude to a certain extent the negative impact on the environment and human health. These are State All-Union Regulations R 17.4.3.07-2001 "Requirements for the composition and properties of sewage sludge when used as fertilizers" (Table 4), focusing on agrochemical and soil indicators, and Sanitary and epidemiological rules 2.1.7.573-96 "Hygienic requirements for the use of wastewater and its precipitation for irrigation and fertilizer" (Table 5), which determines the requirements for the quality of precipitation from a hygienic point of view.

Table 4. Permissible total content of heavy metals and arsenic in sewage sludge

Metals	Concentration, mg kg^{-1} dry matter	
	1	2
Pb	250	500
Cd	15	30
Ni	200	400
Cr	500	1000
Zn	1750	3500
Cu	750	1500
Hg	7,5	15
As	10	20

Table 5. Sanitary-bacteriological and sanitary-parasitological indicators of sewage sludge

Indicator	Standard	
	1*	2**
E.coli group bacteria, cells g^{-1} actual moisture	100	1000
Pathogenic microorganisms, including Salmonella, cells g^{-1}	-	-
Geohelminth eggs and cysts of intestinal pathogenic protozoa, sample kg^{-1}	-	-

1,2 - groups of sewage sludge

*Sewage sludge of group 1 is used for all kinds of crops, except vegetables, mushrooms, green and strawberries.

**Sewage sludge of group 2 is used for leguminous, cereals and industrial crops.

Sewage sludge of both groups is used in industrial floriculture, green building, forest and ornamental nurseries, for biological reclamation of disturbed lands and landfills.

Very rarely do urban sewerage systems transport only domestic sewage to the treatment plants. Industrial effluents and storm-water run off from roads and other paved areas are frequently discharged into the sewerage system. Thus sewage sludge may also contain many toxics in addition to organic material. Sewage sludge may also contain other harmful toxics such as detergents, various salts and pesticides due to effluents from municipal, industrial premises, toxic organics and harmone disruptors (Sommers et al., 1976). Organic pollutants are particularly important, due to its diversity. That diversity is related both with the method of toxic effect, and with diversified effects on living organisms (mutagenic effect, carcinogenic effect, endocrine disrupting effect) (Singh and Agrawal, 2008). With the development of analytical techniques, more and more often new potentially toxic organic compounds are identified in sewage sludge (Müller et al., 2006; Clarke and Smith, 2011; Davis et al., 2012).

Due to the multitude of those substances, and to the fact that their identification requires professional equipments, such contaminants are usually not the subject of routine chemical analyses. The lack of accurate information in this respect increases the risk involved in the application of sewage sludge. In this situation, biological tests may be helpful in the identification of potential threats. Biological tests permit not only measurable determination of a threat (toxic effect) but also take into account the possible interactions among the particular contaminants (antagonism/synergy effect). Moreover, the use of biological tests permits estimation of threats related with the presence of so far unidentified contaminants with potentially toxic effect. In this aspect, the estimation of phytotoxicity of sewage sludge is of particular importance due to its frequent utilisation for natural purposes. Moreover, plants are essential primary producers in the terrestrial ecosystem, whereas crop yield and quality are important success criteria in agriculture.

The application of phytotoxicity tests, therefore, permits not only to evaluate the applicability of sewage sludge for agricultural or soil reclamation purposes, but also to identify potential threats for the environment and for human health. Most of the studies concerned with the estimation of phytotoxicity of sewage sludge have been focused on the estimation of toxicity of the sewage sludge as such (Ramírez et al., 2008a;b; Hu and Yuan, 2012). Those studies, however, do not take into account other significant parameters, important in the assessment of the natural utilisation of sewage sludge. The toxicity of sewage sludge can also be significantly affected by the type of soil in which it is introduced (Domene et al., 2010), as well as by the kind of matrix under estimation (water extract or solid phase) (Domene et al., 2008). On the basis of studies conducted so far (Suchkova et al., 2010), it is also to be supposed that the species of plants grown can have a significant effect of the phytotoxicity of soil amended with sewage sludge, especially in the long-term approach. In spite of the importance of those problems, however, the literature lacks a comprehensive approach to those issues.

Oleszczuk et al. (2012) stated that their study aim was the estimation of changes in the phytotoxicity of soils amended with sewage sludge with relation to Lepidium sativum, Sinapis alba and Sorghum saccharatum. The study was realised in the system of a plot experiment for a period of 29 months. Samples for analyses were taken at the beginning of the experiment, and then after 5, 17 and 29 months. Two kinds of sewage sludge, with varying properties, were added to a sandy soil or a loamy soil at the dose of 90 t/ha. The addition of sewage sludge to the soils at the start of the experiment caused a significant reduction of both seed germination capacity and root length of the test plants, the toxic effect being distinctly related to the test plant species. With the passage of time the negative effect of sewage sludge weakened, the extent of its reduction depending both of the kind of sewage sludge applied and on the type of soil. Phytotoxicity of the soils amended with the sewage sludges was significantly lower at the end of the experiment than at the beginning. The species of the plants grown on the soils also had a significant effect on their phytotoxicity. The greatest reduction of toxicity was observed in the soil on which no plants were grown (sandy soil) and in the soil under a culture of willow (loamy soil). Solid phase of sewage sludge-amended soils was characterised by higher toxicity than their extracts. Most likely the reason of phytotoxicity was high doses of sewage sludge application.

A number of studies concerning the fate of organic and inorganic pollutants in soils amended with sewage sludge indicate that those compounds undergo a variety of processes (e.g. adsorption, desorption, bioformation, volatilisation, photodegradation, bioaccumulation, leaching and incorporation into humic substances structures -sequestration or bound residue formation-) (Hesselsøe et al., 2001; La Guardia et al., 2001; De Jonge et al., 2002). Those processes significantly determine the bioavailability of the pollutants (Alexander, 2000) and, indirectly, also their toxicity. In a study, after 29 months, in almost all treatments a significant decrease of phytotoxicity was observed in soils amended with sewage sludge in relation to the beginning of the experiment. Most probably that was a result of combination of all of the processes mentioned above. Moreover decreasing of the toxicity of the sewage sludge amended soil could be related with quickly degraded labile compounds which very often occurs in sewage sludges and act as phytotoxins. The increase of phytotoxicity observed after 5 months in most of the experimental treatments was most probably related with remobilisation of pollutants, fairly frequently observed in soils amended with sewage sludge or composts (Oleszczuk, 2006b). Terry et al. (1979) and Rowell et al. (2001) stated that 26-42 % of the organic matter introduced together with the sludge underwent mineralisation very quickly. As a result of that process, formerly unavailable pollutants related with organic matter undergo remobilisation. An increase in the phytotoxicity after 5 months wasmost probably related to the fact that the organic contaminants, initially adsorbed to the sewage sludges/soil mixture, were temporarily less available. As a result of organic matter mineralization, the strength of these bonds could weaken, and hence, there was an increase in the bioavailability of pollutants which had not been bioavailable earlier (Oleszczuk, 2006b).

It is commonly accepted that toxicity largely depends on the water solubility of pollutants. However, studies on the sewage sludge phytotoxicity concentrate mainly on the analysis of water extracts (Wong et al., 2001; Fuentes et al., 2006; Mantis et al., 2005). The application of water extracts provides important information; however, they do not give a fully comprehensive description of the toxicity of sewage sludges. The results obtained in a study showed clearly that the analysis of extracts is not sufficient for the full characterisation of risks related with sewage sludge. This is also supported by earlier studies conducted with relation of other organisms and environmental matrices (Chial and Persoone, 2003; Ramírez et al., 2008a).

Organic pollutants

Sewage sludges can contain significant concentrations of toxic heavy metals and organic pollutants (Guo et al., 2009). The sources of these pollutants in the waste waters are discharges from domestic and industrial facilities and atmospheric deposition as well as urban runoff (Blanchard et al., 2001; Harrison et al., 2006; Guo et al., 2009). Hence, these kinds of pollutants are concentrated in the sewage sludge during waste water treatment. This issue is of great risk to human health because transfer pathways of these pollutants into the human food-chain might be food crops or grazing livestock which eat contaminated feed grown on sludge-amended soil (McLachlan et al., 1996). Among these organic pollutants, polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants that originate from different emission sources, like the incomplete combustion of fossil fuels, industrial processes or the use of motor vehicles (Ozcan et al., 2013).

According to the data of Russian studies of the urban sewage sludge of Moscow, there are more than 200 polluting organic substances of anthropogenic nature, belonging to different groups of chemical compounds: acyclic saturated hydrocarbon, unsaturated hydrocarbons, aromatic cyclic hydrocarbons, polycyclic aromatic hydrocarbons, oxygen-containing compounds. Among them, 1.16% by weight belonged to toxic aromatic hydrocarbons, of which toluene was found in concentrations on average up to 10 times higher than MPC (maximum permitted concentrations) for soil. Also found naphthalene, methylnaphthalene, fluorene, phenanthrene, anthracene, pyrene and fluoranthene, belonging to the highly toxic group of polycyclic aromatic hydrocarbons (Kasatikov et al., 2017).

Concerning organics, the following are considered of primary importance for EU as limits are to be set in the revision of Sewage Sludge Directive: AOX (sum of halogenated organic compounds) linear alkylbenzene sulphonates (LAS) di(2-ethylhexyl)phthalate (DEHP) NPE (nonylphenole and nonylphenole ethoxylates with 1 or 2 ethoxy groups) polycyclic aromatic hydrocarbons (PAHs) polychlorinated biphenyls (PCBs) polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs). Limit values for concentrations of organic compounds in sludge of different countries and as suggested in the 3rd draft of the Working paper on sludge for EU (Langenkamp et al., 2001) were presented on Table 4.

Table 4. Limit values for concentrations (mg kg^{-1} dw) of organic compounds in sludge of different countries and as suggested in the 3rd draft of the "Working paper on sludge" for EU (Langenkamp et al., 2001).

	AOX	DEHP	LAS	NP/NPE	PAH	PCB	PCDD/F, ng TEq/kg dm
EU	500	100	2600	50	6[1]	0.8[2]	100
Denmark	-	50	1300	10	3[1]	-	-
Sweden	-	-	-	50	3[3]	0.4[4]	-
Lower Austria	500	-	-	-	-	0.2[5]	100
Germany	500	-	-	-	-	0.2[5]	100

[1] Sum of acenapthene, phenanthrene, fluorine, fluoranthene, pyrene, benzo(b+j+k) fluoranthne, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-c,d)pyrene

[2] Sum of 6 congeners PCB 28, 52, 101, 138, 153, 180

[3] Sum of 6 compounds

[4] Sum of 7 congeners

[5] Each of the six congeners PCB 28, 52, 101, 138, 153, 180.

Polycyclic aromatic hydrocarbons (PAHs) contents and sources

Polycyclic aromatic hydrocarbons are one of the most important groups of ecotoxicants due to their high toxicity, considerable stability in the environment, a cumulative effect. They are chemically inert and are hardly affected by the action of acids and oxidizing agents. Certain members of the PAH class have been listed as priority pollutants by Environmental Protection Agencies of the United States, Europe and China. The PAHs often detected in sewage sludge are mainly naphthalene, phenanthrene, anthracene, fluorene, acenaphthene, acenaphthylene, 1,2benzanthracene, benzo(a)pyrene, benzo(b) fluoranthene, benzo(g,h,i)perylene, benzo(k) fluoranthene, fluoranthene, indeno(1,2,3-cd)pyrene and pyrene (Zhai et al., 2011).

The origin of PAHs in sewage can be from combustion of petroleum, kerosene, grass, coal, and wood. Concentration ratios of some PAHs are often used to estimate the sources of PAHs, i.e., combustion and petroleum sources (Soclo et al., 2000). Using molecular mass of 178 as an indicator, anthracene to(anthraceneşphenanthrene) ratio with <0.10 usually represents the petroleum sources PAHs, while the ratio with >0.10 is often considered as an indication of combustion sources (Budzinski, 1997). Yunker et al. (2002) reported that the ratio of (benz[a]anthracene)/(benz[a]anthraceneschrysene) lower than 0.20 implies a petroleum source; the ratio from 0.20 to 0.35 means either petroleum or combustion sources; and the ratio higher than 0.35 indicates combustion sources.

The study of samples collected at a waste-water treatment plant in Shanghai (China) indicates that PAHs release regularly according to temperature changes in the process of sewage sludge incineration treatment (Zhang et al., 2016). Over 90% of total PAHs in sewage sludge are released at the temperature of 300–750°C. The transformation of naphthalene to indeno (1, 2, 3cd) pyrene may be related to the temperature of the treatment system. It has been shown that the output rate of transformation reactions for indeno (1, 2, 3-cd) pyrene is 94% at 300°C.

The source of wastewater, wastewater treatment methods and different treatment process affect the PAH concentrations in sludge. The PAHs concentrations varied strongly between the sludges from primary and secondary treatment processes: the sum of PAHs in the primary sludge were 1.5973 and 0.3402 mg/kg, in the secondary sludge they were 8.7884 and 2.0185mg/kg respectively (Zhai et al., 2011). An enrichment of PAHs over time can be explained by the longer retention time of secondary sludge in comparison with primary sludge.

Previous studies reported a large range in the total concentration of PAHs in sewage sludge from Asian, African, and European countries, varying from below detection to 33,000 ng/g dry weight (Cai et al. 2007; Man et al. 2016; Poluszyńska et al. 2017).

According to Turkish regulation, concentration of total PAHs (naphthalene, acenaphthylene, acenapthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene Indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, benzo[j]fluoranthene) should be <6 mg kg^{-1} dry matter. According to EU regulation, concentration of total PAHs (acenapthene, phenanthrene, fluorene, plouranthene, pyrene, benzo[b;j;k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene) should be <6 mg kg^{-1} dry matter. If the ratio is >0.50, the combustion of kerosene, grass, coal, and wood results in the PAH contamination. If fluoranthene/(fluoranthenespyrene) ratio for sludge was <0.50, which means the origin of PAHs was petroleum combustion. While this ratio for sludge was >0.50, indicating possible source of PAHs was combustion of kerosene, grass, coal, and wood (Ozcan et al., 2013).

Russian legislation in the field of health and environmental protection provides the standards only for the content of benzo (a) pyrene -0,02 mg kg^{-1} (SanPiN GN 2.1.7.2041-06).

Polychlorinated biphenyls (PCBs) contents

Although sewage sludge improves soil properties, numerous studies have demonstrated that they also contain toxic organic compounds, such as polychlorinated biphenyls (PCBs) (McLachlan et al. 1996; Urbaniak et al. 2014; Wyrwicka et al. 2014), PCBs are found in the natural environment because of human activities (Borja et al., 2011). Approximately 30% (i.e., 10 million tonnes) of the total worldwide production of PCBs has entered the environment (Benabdallah El-Hadj et al., 2007). The presence of these compounds in sewage sludge significantly decreases the potential for the sludge to be used in agriculture. According to proposed changes to EU Directive 1986/278/EEC, the polychlorinated biphenyl (PCB) concentration (expressed as the sum of the concentrations of the indicator congeners, PCBs 28, 52, 101, 118, 138, 153, and 180) should not exceed 0.8 mg/kg dry matter (DM) in sewage sludge used as a crop fertilizer. Many researches confirm the presence of PCBs in sewage sludge and organic waste, which should be utilized (Blanchard et al., 2004). Two biological methods are generally used: composting and the anaerobic digestion. Rosinska and Dabrowska obtained decrease of PCB content over 50% during anaerobic digestion of sludge (Rosińska and Dabrowska, 2014). Despite the fact that PCBs show a strong affinity to organic matter which predispose them to be stored in the sediments (Gdaniec-Pietryka et al., 2013) and surface layer of the soil, it has been also shown that they can be transferred deeper into the soil profile (Bi et al., 2002; Kobasić et al., 2008; Zhang et al., 2011). Hence, the continued use of such contaminated sludge for agricultural purposes can present problems associated with the risk of soil, subsurface and groundwater contamination (Bi et al., 2002). This also concerns nutrients, which despite being valuable from the perspective of agriculture, their combined application with sewage sludge may lead to health and environmental risks associated with subsurface and groundwater pollution (Kang et al., 2011).

The Turkish and EU regulations describes that levels of PCBs (sum of PCB 28, 52, 101, 118, 138, 153, and 180) in sewage sludges should be <0.8 mg kg^{-1} (dry weight) in order to be used in agriculture (Ozcan et al., 2013). Ozcan et al. (2013) indicated that the PCB concentrations of all investigated sewage sludges in their study were less than the limit value, it was found that use of them for agricultural purposes was suitable.

Conclusions

Sewage sludge to be utilised in agriculture must be subjected to comprehensive evaluation comprising not only the determination of the basic physicochemical properties, content of pollutants or pathogenic bacteria, but also of the ecotoxicological properties. i) phytotoxicity of sewage sludge and its changes overtime are significantly determined by the soil type. In this case, the soil type is one of the most important factors regulating the phytotoxicity of sewage sludge, especially in the long-term aspect; ii) with the passage of time the phytotoxicity of soils amended with sewage sludge undergoes a change, not always in a direction causing a lowering of their toxicity. The extent of particular changes depends both on the properties of the soils and on the kind of sewage sludge, and for various kinds of sludge, it can have different direction in a single soil; iii) the extent of changes in the toxic effect on the test plants is related to the species of the plant under cultivation; iv) in spite of similar initial toxicity displayed by various kinds of sewage sludge in relation to particular plants, further changes of phytotoxicity may vary with relation to the sewage sludge and the type of soil; v) the intensity of toxicity towards various plants depends not only on the kind of sewage sludge but also on the soil type; vi) proper selection of the conditions of management sludge-amended soil can be conducive to a reduction of phytotoxicity; and vii) estimation of extracts is not sufficient for the full characterisation of the risk involved in the utilisation of sewage sludge in agriculture.

On the other hand, biosolids is a good source organic matter as well as plant macro and micro-nutrients and in future can be substituted for expensive inorganic fertilization. Addition of treated biosolids to soil has been found to be beneficial to soil health, enriching soil with essential nutrient elements as also increasing the pH of the soil. Further, soil amendments with biosolids has been reportedly effective in increasing a number of agro morphological attributes as well as yield in different crop species. However, use of biosolids for commercial agriculture has to be done cautiously. It is common knowledge that biosolids often contains toxic metal residues (heavy metals), as well as toxic organic residues, indiscriminate use of it can be detrimental to the productivity of the soil as well as cause harm to the food chain. Moreover the character of the biosolids changes over time and hence stringent and periodic monitoring of biosolids for agricultural use should be done. In general, a potential waste management depends on several tiers like disposal, recovery, recycle, reuse and prevention. This hierarchy is also suitable for managing biosolids. It is evident that implication of biosolids induce agricultural productivity to a certain level; but the application of this waste in major food generation and supply chain is still needs more study.

International as well as national guidelines on the carrying capacity of toxicants in biosolids composts should be set and stringent monitoring of such guidelines should be enforced in agricultural use of biosolids. Attempts for commercial production of biosolids based fertilizer and soil health amendments can be setup and can be used to boost agricultural production, and minimizing the dependency on inorganic fertilization. This will further reduce the carbon footprint, as most inorganic fertilizers are manufactured at high energy costs. Biosolids can be used for regaining soil fertility in agricultural lands deemed infertile by prolonged and indiscriminate use of synthetic inorganic fertilizers. In such conditions, depletion of soil nutrients as well as decreased soil pH can be rejuvenated with the rational use of biosolids. Owing to high nutrient efficiency and its importance in agriculture and soil fertility, stringent and persistent monitoring of biosolids and its products should be done before introduction in agricultural systems.

In the current scenario of increasing global population, the generation of solid wastes like biosolids is bound to increase remarkably. Improper and unscientific disposal of biosolids results in several environmental issues such as surface and groundwater contamination, degradation of land, and food chain contamination.

Hence, according to the principles of waste management hierarchy, agricultural recycling of biosolids will be a more environmentally preferred option over the traditional disposal methods. Utilizing the potential of biosolids to recycle valuable plant nutrients and as an effective soil amendment will not only help in sustainable management of this waste but also in minimizing the negatives associated with its traditional disposal. Every country must obey their regulations and legislations for managing their sewage sludge.

Researchers around the world are looking for the most optimal set of substances for priority analysis. The knowledge of which will be used to find the best path to deal with the problem of rational and, necessarily, environmentally-safe way of disposal of sewage sludge. Perhaps more fundamental research using new modern chemical methods for the analysis of hazardous organic compounds can tighten the control on the qualitative composition of sewage sludge used in agriculture.

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Quantifying the role of chemical weathering rates on soil developed along an altitudinal transect in the mountainous environments, Turkey

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Abstract

Climate and elevations play an important role in controlling rate of weathering and soil formation. The role of chemical weathering rate on soil developed along an altitudinal transect in the mountainous environments in Turkey was investigated to determine the effects of climate on the geochemical characteristics of the soil. The main purposes of this study were: i) To characterize the geochemical characteristics of soils as a function of climate ii) To evaluate the soil formation and decomposition rates in Climosequence depending on the elevation by using geochemical data. For this purpose, four representative profiles were dug at different elevations. The transect of four soils formed in limestone elevations from 1139 to 1809 m. Our results showed that the rate of chemical weathering of CIA, CIW, PIA and MIA indicators decreased with the increase in elevation. In contrast, WIP value increased at higher altitudes and exhibited different weathering directions by deviating from the main trend in the A–CN–K diagram that composition of weathered soils was easily influenced by the quantity of precipitation, degree of gradient and height differences. Therefore, it was concluded that the main factors determining soil development was climate and elevations, and both determine the leaching regime and weathering rates.

Keywords: Climosequence, elevations, geochemical, soil development, weathering index.

Introduction

Soil development is closely associated with specific weathering intensities under special mountainous environmental conditions Baumann et al. (2014). Soil development occurs through numerous physical, biological and chemical weathering processes acting to alter the parent rock on the soil surface. The formation of soils (pedogenesis) is a process by which weathering alters constituents within the parent material through the loss of more mobile (i.e., soluble) elements, concurrent enrichment of less mobile elements Le Blond et al. (2015). It is well established that soil-pedogenesis processes result in losses, gains or redistribution of elements, and that not all elements are affected in the same way. Elements are also recycled by the forest vegetation and such recycling can play a major role in soil development and the redistribution of elements. This is mainly the case with forest ecosystems, which are very efficient at recycling major nutrients. (Barbosa et al., 2015; Rate and Sheikh-Abdullah, 2017). Geochemical-based weathering indices are commonly used to measure and compare the relative extent and intensity of soil pedogenesis based on the chemistry of the surface soils (Osat et al., 2016) and weathering indices are used for evaluating soil fertility and development, demonstrating the impact of climate on soil surface weathering (Price and Velbel, 2003; Baumann et al., 2014). Chemical weathering indices incorporate major element oxides chemistry into a single value for each sample Egli et al. (2006). Studies in the regions of altitudinal gradient characterized by decreasing temperatures and increasing rainfalls, have shown the influence of the

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climatic contrast on soil formation, studies on sequences of soils developed in contrasting climate mountainous environments may be a valuable tool to predict the influence of climate on weathering rates, soil development stage, and soil formation processes (Egli et al. 2003, 2006, 2008, 2009; Lybrand et al., 2011; Moazallahi and Farpoo,r 2012; Barbosa et al., 2015; Zhou et al., 2015; Osat et al., 2016) and provide better understanding of elemental mobility during the weathering. In this study, the soil that has different elevations in Anamas Mountain and develops on locations with different precipitation and leaching regime was examined and the geochemical characteristics of the soil was determined. The geochemical approach in which the concentrations of the major and rare earth elements are used to reveal the weathering of the soils with different climatic characteristics affected by altitude difference be permit study of the effects of various climatic combinations on soil development so that the chemical weathering rates of soils formed on a Climosequence in humid climatic conditions will be comparatively determined. The following research objectives were: i) To characterize the geochemical characteristics of soils as a function of climate and ii) To evaluate the soil formation and decomposition rates in Climosequence depending on the elevation by using geochemical data.

Material and Methods

Study area

Study area Anamaslar, Beysehir, is located within the borders of the Lakes Region. 4 different heights were determined as a result of the studies conducted in the field where the study area is located. For this purpose, 4 profiles were dug between the elevations of 1139-1809 m (Figure 1). The study area is between the coordinates (Table 1). All profiles had limestone primary material and forest vegetation. The profiles were all steep. Profile 4 had the highest slope (> 45) and other profiles had a slope of 30-45 (Table 1). The Anamas Mountains are generally composed of Jurassic-Cretaceous aged limestones in the second time. The Triassic sandstone, claystone and conglomerates and the Triassic limestones and dolomites are observed at the foot of the Anamas Mountains. According to the meteorological station data in the region, the average annual precipitation from 1960 to 2017 was 546.4 mm, the annual evaporation was 1248.1 mm, the average annual temperature was 12.1 ºC, and the average soil temperature in 50 cm was 14.6 ºC. According to the prepared rainfall-evaporation-temperature because of these data, the temperature regime of the region is mesic and the moisture regime is xeric (USDA, 2014) (Figure 2).

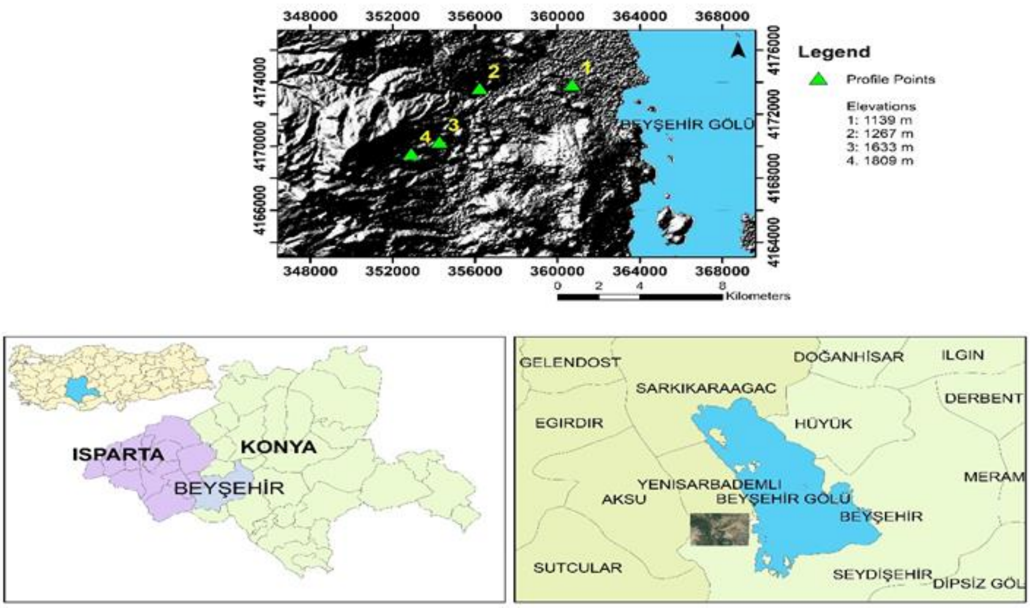

Figure 1. Location map of the study area that shows general transect of the four profiles

Soil sampling and analysis

Elevation is an important factor affecting the climate and could provide insight into the impact of climate on soil processes through affecting the type and rates of geochemical processes. Climatic features in mountainous areas, especially high mountainous regions, vary widely according to their environment. It is known that the amount of precipitation increases with increasing of elevation. Soils have been studied along a transverse section using four representative profiles between the elevations of 1139-1809 m. Soils were described in the field for geochemical properties of these four profiles were identified and samples were collected from each genetic horizon. Sixteen disturbed and undisturbed the samples of soil were taken to the laboratory to search for their geochemical features. Soil samples were air-dried, gently crushed, and passed through a 2-mm sieve to remove coarse fragments. Soil was used for the following analyses: Chemical determination of selected major, trace and rare earth elements was performed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Burt, 2011).

Table 1. Selected site characteristic of the studied profiles

Pedon	Coordinates		Primary material	Elevations (m)	Physiography	Slope (%)	Vegetation
	North	South					
I	4173828	360699	limestone	1139	Steep slope	30-45	forest
II	4173563	335946	limestone	1267	Steep slope	30-45	forest
III	4170197	354065	limestone	1633	Steep slope	30-45	forest
IV	4169545	352906	limestone	1809	Steep slope	>45	forest

Trace elements: A 500-mg <2-mm soil separate that has been air dried and ground to <200 mesh (75 µm) was weighed into a 100-ml Teflon (PFA) sample digestion vessel. To the vessel, 9.0 mL HNO3 and 3.0 mL HCl were added. The vessel was inserted into a protection shield, covered and then placed into a rotor with temperature control. Following microwave digestion, the rotor and samples were cooled and the digestate was quantitatively transferred into a 50-ml glass volumetric of high purity reverse osmosis deionized water. The samples were transferred into appropriate acid-washed polypropylene containers (Burt, 2011). While the samples of study were analyzed at the Advanced technology research & application center Laboratories (Selcuk University in Konya, Turkey).

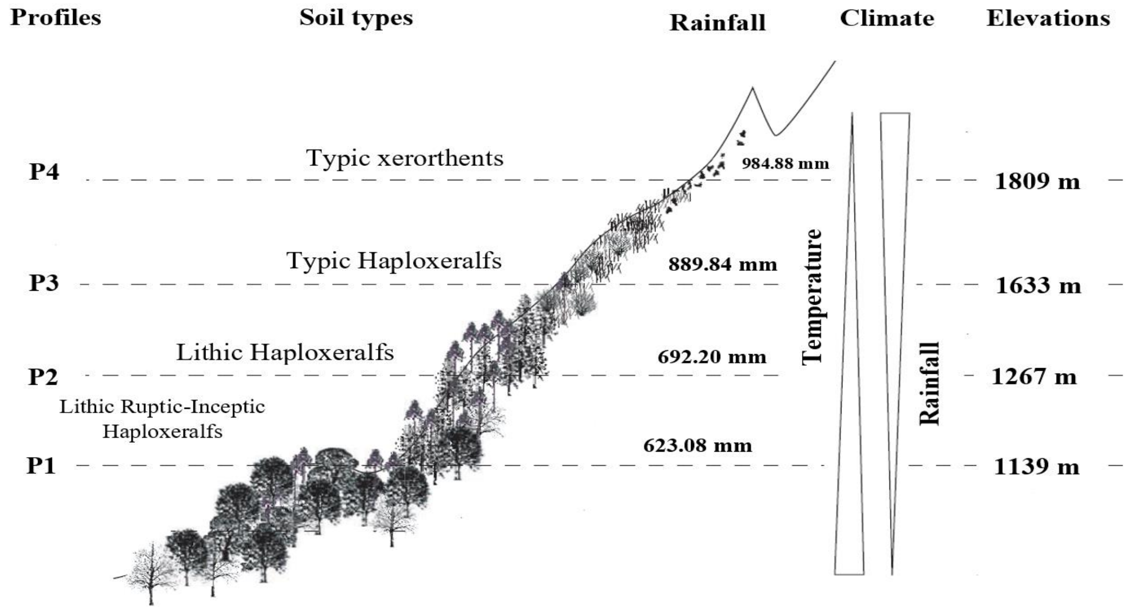

Figure 2. The amount of rainfall and the location of soil profiles during along altitudinal transect in mountain in Anamas

Soil development indicators

Calculation of Chemical Weathering Indices

Several indexes have been defined to characterize chemical weathering in soils, chemical weathering changes the chemical and mineralogical composition of a soil. Some of the mineral elements may be liberated (e.g. Ca, Mg, K, Na), forming secondary minerals, particularly clay minerals. The most commonly used chemical weathering indices are summarized in this study, such as Chemical Index of Alteration (CIA) Nesbitt and Young (1984), Chemical Index of Weathering (CIW) Harnois (1988), Plagioclase Index of Alteration (PIA) Fedo et al. (1995), Weathering Index of Parker (WIP), Parker (1970), and mineralogical index of alteration (MIA), Voicu et al. (1996), of which some of them will be discussed more in detail below.

1. CIA = $(100)[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)]$
2. CIW = $(100)[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O)]$
3. PIA = $(100)[(Al_2O_3 - K_2O)/(Al_2O_3 + CaO^* + Na_2O + K_2O)]$
4. WI P = $(100)[(2Na_2O/0.35) + (MgO/0.9) + (2K_2O/0.25) + (CaO^*/0.7)]$
5. MIA = $2 * (CIA-50)$

The mineralogical index of alteration (MIA) evaluates the degree of mineralogical weathering. The MIA value indicates incipient (0-20%), weak (20-40%), moderate (40-60%), and intense to extreme (60-100%)

weathering Voicu and Bardoux (2002). Importantly, all indices are calculated with CaO* and corrected for inputs from carbonate and apatite (McLennan et al., 1993).

A-CN-K diagrams and chemical alteration (CIA)

CIA is the most reliable weathering indices with the highest explanatory power, Therefore suggested the ternary A–CN–K (Al_2O_3 – CaO^*+Na_2O - K_2O) system is useful for evaluating the compositions of fresh plagioclase- and potassium-feldspar- rich rocks and examining their weathering trends, weathering products and clay minerals. (Nesbitt and Young 1984; Nesbitt 1992; Fedo et al. 1995; Nesbitt et al. 1996; Buggle et al. 2011; Shao et al. 2012; Babechuk et al. 2014; Baumann et al. 2014; Regassa et al. 2014).

Conduct of the rare earth elements during weathering

Besides some geochemical ratios and Ce and Eu anomalies were used to the quantification of weathering degree of studied pedons. The REE concentrations are normalized relative to a chondritic reference standard to facilitate the comparison of REE patterns between sites. Europium is the only lanthanide that usually happens in a divalent oxidation state and whose behavior is strongly influenced by plagioclase. This results in the potential for Eu to fractionate from the other lanthanides during weathering, since plagioclase is one of the most susceptible minerals to chemical dissolution (Babechuk et al., 2014). Fractionation of Eu can be tracked using the Eu anomaly of Eu* obtained by interpolation between the normalized values of Sm and Gd, as proposed by Taylor and McLennan (1985). $Eu/Eu^* = EuN/\sqrt{(Sm)N \times (Gd)N}$. Cerium can track redox-related transformations during pedogenesis in weathering profiles as a result of the potential oxidation of Ce^{3+} to Ce^{4+} (e.g., Middelburg et al., 1988; Braun et al., 1990; Mongell, 1993; Gallet et al., 1996; Murakami et al., 2001; Patino et al., 2003; Dengiz et al., 2013; Babechuk et al., 2014; Vermeire et al., 2016). Cerium anomalies are estimated by comparing the measured concentration of Ce with an expected concentration of Ce* obtained by interpolation between the normalized values of La and Pr. Cerium anomalies can be calculated as follow; $Ce/Ce^* = CeN / \sqrt{(La)N \times (Pr)N}$.

Results and Discussion

SiO_2 content was lower than 53% in all profiles and ranged from 1.04% to 52.90%. The content of Al_2O_3 ranged from 0.35 to 24.9%. Fe_2O_3 profiles were distributed between 0.07% and 9.56%. MgO values were changed between 0.45% and 7.13%. The enrichment observed in the MgO content was very specific and it is believed that MgO is generally very sensitive to leaching (Arikan et al., 2007; Nordt and Driese, 2010; Regassa et al., 2014). CaO values were found between 0.72 and 58.90%. The K_2O and Na_2O values were found to be 0.04-2.89%, 0.07-0.49%, respectively. Titanium is a mineral that is resistant to decomposition and is an element used in the determination of chemical change. TiO_2 contents were found to be between 0.01-0.19%, MnO 0.02-0.32% and P_2O_5 0.05-0.74% (Table 2).

Table 2. Total elemental analysis in weight percentages, oxides are expressed as weight percentages for the studied soil profiles.

Elevations (m)	Pedon	Horizon	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	LOI (%)	MnO (%)	Sum (%)
1139	P1	Oi	19.8	8.61	3.03	0.84	4.43	0.09	1.03	0.43	0.74	60.1	0.11	99.23
		A	44.8	21.0	8.13	1.38	1.51	0.15	2.65	1.16	0.52	18.2	0.17	99.68
		Bt	46.8	24.9	9.56	1.33	1.24	0.09	2.49	1.17	0.23	11.7	0.15	99.67
		CR	1.04	0.35	0.07	0.45	58.90	0.17	0.04	0.01	0.05	38.7	0.10	99.79
1267	P2	Oi	31.0	13.0	5.26	1.82	2.67	0.19	1.61	0.63	0.24	42.8	0.24	99.48
		A	37.7	16.7	7.10	3.25	4.88	0.21	2.04	0.84	0.22	26.5	0.32	99.77
		Btk	29.7	15.3	5.47	5.05	21.60	0.16	1.66	0.70	0.14	20.0	0.16	99.96
		C	24.0	10.6	3.50	7.13	29.20	0.11	1.04	0.44	0.08	23.5	0.21	99.84
1633	P3	Oi	9.13	4.05	1.19	0.45	2.61	0.07	0.57	0.17	0.12	81.3	0.02	99.70
		A	38.8	17.2	6.04	1.24	2.14	0.20	2.62	0.85	0.17	30.3	0.14	99.71
		Bhw	43.6	20.7	7.57	1.40	5.34	0.21	3.31	0.99	0.20	16.4	0.14	99.87
		Ck	31.4	16.5	5.09	1.13	23.20	0.15	2.60	0.70	0.20	18.8	0.06	99.85
		Cr	48.4	20.5	5.60	1.38	7.49	0.21	3.44	1.00	0.13	11.7	0.04	99.91
1809	P4	A1	39.9	15.7	5.80	1.42	2.90	0.40	2.58	0.87	0.16	30.5	0.13	100.37
		A2	44.1	17.6	6.70	1.47	2.44	0.43	2.89	1.02	0.14	22.9	0.12	99.82
		C1	52.0	21.1	8.25	1.59	0.94	0.49	3.69	1.19	0.15	10.4	0.15	99.96
		Cr	52.9	21.1	8.27	1.53	0.72	0.48	3.68	1.15	0.15	9.78	0.15	99.93

In Figure 3, the depth is plotted against the element content in weight percentages. While the chemical elements show similar tendencies in the 1, 2 and 3 profiles, the trends in the 4 profiles are different. Generally, in the fourth profile: reduced the content of CaO and P_2O_5 and increased SiO_3, Al_2O_3, Fe_2O_3, TiO_2, MgO, Na_2O, MnO and K_2O were shown at decreased depth. Fe, Al, Si the total content increases as the soil depth decreases due to the washing of carbonates. The P_2O_5 line in the first profile also deviates from the general trend to the top.

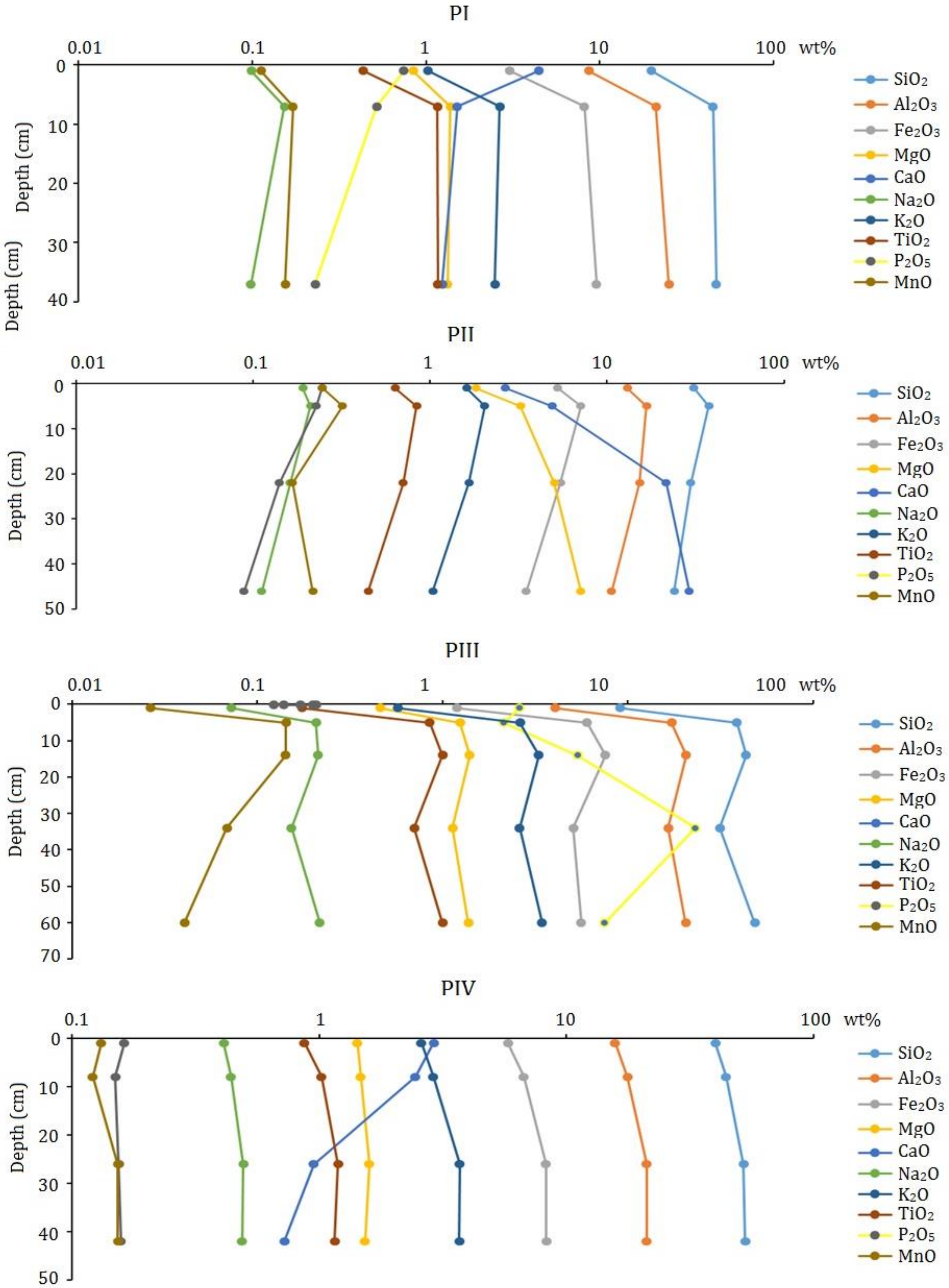

Figure 3. Total elements contents (in wt%) with depths for the studied soil profiles on a logarithmic scale.

The increase in P_2O_5 content may be due to the presence of both micro and macro organisms, causing retention of the element in their tissue. An increase in the amount of free sesquioxides resulting from the weathering of primary minerals also increase the phosphorous fixation capabilities of the weathered material. The effects of geochemical elements and the weathering indices, on the formation of the soils using the total element results, will be explained in the following sections.

Chemical weathering indices

The role of chemical weathering indices is mainly; to determine the amount of yield of the mobile components during weathering, assess soil fertility, to provide better kinetic element mobility in the context of weathering and predict the source of soil nutrients as well as changes in metal nutrients (Harnois 1988; Şenol et al., 2018). The values were gives of chemical weathering indicators for CIA%, CIW%, PIA%, MIA% and WIP. A change is observed for all soil values (89.19-79.00, 98.72-92.11, 79.53-64.04, 78.37-58.00, 41.38-12.21%) respectively. From the figures (4, 5, 6), it was revealed that the depth of the soil profiles (1, 2 and 3) increases with increasing the weathering indexes of the subsurface horizons. In addition, the most soluble elements such as MgO, CaO, Na_2O and K_2O increase the CIA, CIW and PIA due to the fact that they move towards the depth. Due to the low content of Al_2O_3 as a result of clay migration in the soil, the values of the weathering indicators on the surface of the horizons at profiles (1,2 and 3) were lower. It is important to emphasize that the removal of K from potassium feldspar is less than the rates of Na and Ca removal from plagioclase. However, potassium Feldspars is more sensitive to weathering. Accordingly, CIW is equivalent to that of CIA without potassium. If it is not aluminum associated with potassium feldspar, the CIW value will therefore be high and will cause errors in rocks the rich Feldspar. In general, in Figure 7, it was observed that the low WIP value in all soil profiles of surface horizons, and the low WIP value indicate a decrease in the moving cations. At the high altitudes of the fourth soil profiles, the highest WIP was observed and decreased at low altitudes due to the increase in K, Na, Ca, Mg cations. Figure 8 shows the index of mineralogical alteration evaluation to assess the degree of weathering. The amount of MIA increases with increasing depth at profiles (1, 2 and 3) and is considered the most developed soils at medium and low altitudes. The rate of chemical weathering of CIA, CIW, PIA and MIA indicators for all studied soil profiles (as shown in the Figure 9) decreases with the increase in elevation. This is due to the fact that basic cations (K, Na, Ca and Mg) are dissolved in water and descaled by leaching processes, cations accumulate at low altitudes and contribute to the formation of secondary minerals. In contrast, WIP value is increased at higher altitudes due to increased leaching and precipitation at high altitudes causing decrease in movement of cations. Although less developed soils are found at the steepest slopes of the P4 with a height of 1809 m, they contain less mobile elements, due to the leaching of products weathering that cause decomposition conditions and their transfer to low altitudes, which is more pronounced in the soil developed for profile at elevation 1139 m.

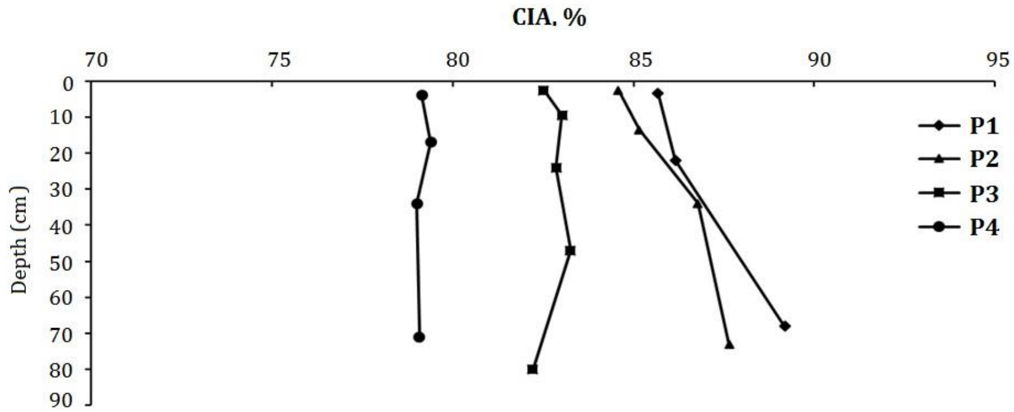

Figure 4. CIA % with depths for the studied soil profiles.

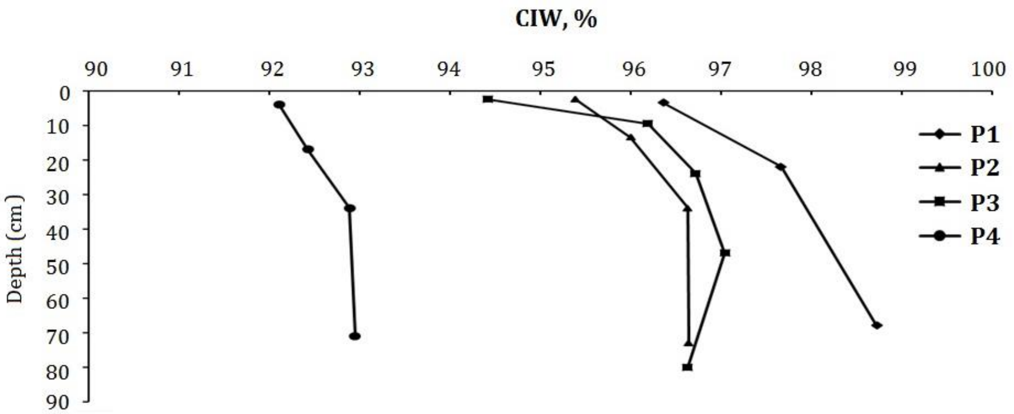

Figure 5. CIW % with depths for the studied soil profiles.

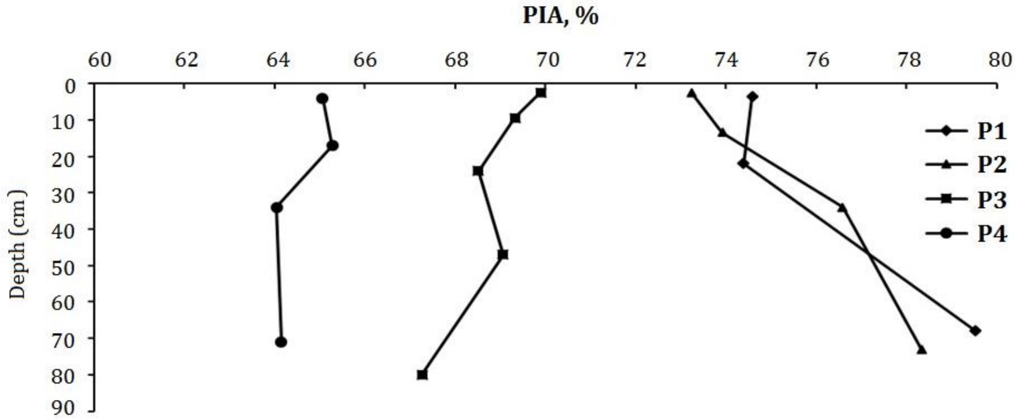

Figure 6. PIA % with depths for the studied soil profiles.

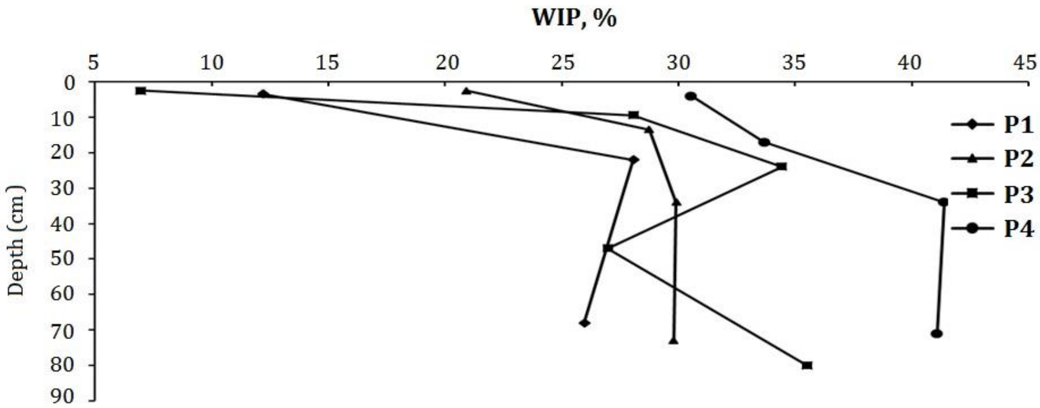

Figure 7. PIA % with depths for the studied soil profiles.

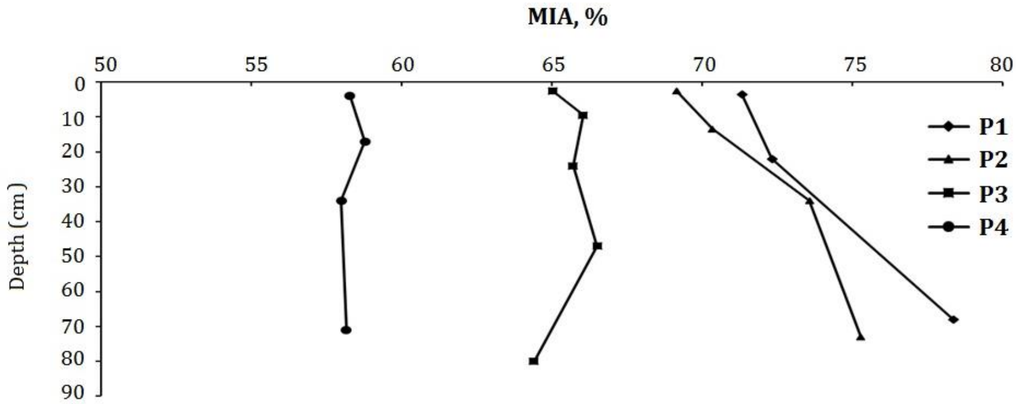

Figure 8. MIA % with depths for the studied soil profiles.

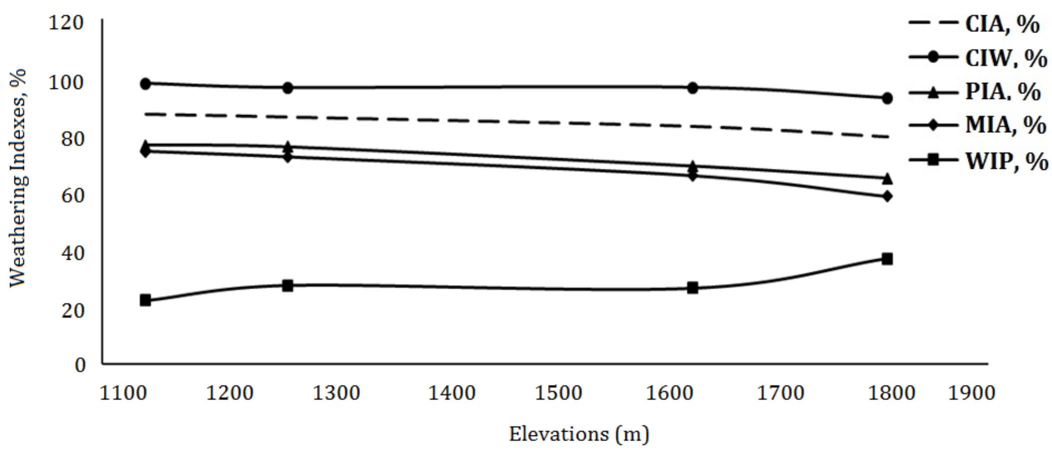

Figure 9. Weathering Indexes % with elevations for the studied soil profiles.

A-CN-K diagrams and chemical alteration (CIA)

Generally, the CIA is considered as a measure of the extent of the conversion of feldspar to clay (Nesbitt and Young, 1982; Nesbitt and Young, 1989; Fedo et al., 1995; Nesbitt et al., 1996; Yang et al., 2004; Buggle et al., 2011; Che et al., 2012; Shao et al., 2012; Babechuk et al., 2014; Baumann et al., 2014; Regassa et al., 2014).

Degradation of feldspar and concomitant formation of clay minerals are the dominant processes during chemical weathering of the soil. The A–CN–K (Al_2O_3–CaO+Na_2O–K_2O) diagram was proposed to intuitively reflect the trends and the degree of silicate weathering and to evaluate the clay minerals (Nesbitt and Young, 1989; Fedo et al., 1995; Nesbitt et al., 1996; Von Eynatten et al., 2003; Yang et al., 2004; Li and Yang, 2010; Buggle et al., 2011). On the A–CN–K diagram, the main trend of silicate weathering in leaching of CaO and Na_2O and then K_2O, and relative enrichment of Al_2O_3. Note that most of the investigated soils indicate weathering trends in parallel with the A–K line. Most likely reflecting strong removal of K-bearing minerals from the parent rocks. The most weathered soils plot at the top of the triangle located the A apex reflecting high concentrations of Al-bearing minerals (Figure 10). The CIA values are directly represented on the A-CN edge of the A-CN-K triangle Figure 10 as the elements involving this edge are the same as needed for the calculation of CIA. High CIA values reflected 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).

In contrast, the soils at elevation 1139 m are parallel to the A–K line and approach the A apex more than the other soil elevations, most likely reflecting strong removal of K-bearing minerals from the parent rocks (Figure 10). This was due to the degree of weathering that they are higher than other heights, so the soil is considered the most developed. Despite the different weathering intensities registered in studied soil profiles, most of the investigated studied soils seem to be weathered from similar parent rocks. However, exhibited different weathering directions by deviating from the main trend in the A-CN-K diagram Figure 10, suggesting that composition of weathered soils more easily influenced by quantity of precipitation and the climate differences by the difference in altitudes.

Conduct of the rare earth elements during weathering:

It is known that the soil's REE concentration is influenced by sequential soil processes during pedogenesis (REE), REE is affected by a series of processes leading to internal degradation, such as solubility, oxidation, reduction, precipitation Babechuk et al. (2014). Table 3 gives the values in the distribution of rare elements except for the fourth profile, there is no regular trend between the horizons, and the content of the elements increased with decreased depth, because of the increase in the amount of precipitation and thus increasing the leaching process in the fourth profile.

Table 3. The rare earth elements analysis (REE) are expressed as $\mu g.kg^{-1}$ for the studied soil profiles.

Elevations (m)	Pedon	Horizon	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1139	P1	Oi	36	73	7.7	28	5.0	1.14	5.0	0.63	3.5	0.66	2.0	0.27	1.8	0.26
		A	75	142	15.9	58	10.7	2.4	10.5	1.36	7.5	1.42	4.2	0.57	3.8	0.56
		Bt	82	144	16.9	61	10.7	2.5	10.5	1.31	7.2	1.36	4.0	0.55	3.6	0.53
		CR	0.36	0.67	0.15	0.56	0.1	0.0	0.0	0.0	0.07	0.01	0.0	0.0	0.02	0.00
1267	P2	Oi	31	64	7.4	29	5.7	1.2	5.8	0.81	4.5	0.86	2.5	0.34	2.2	0.33
		A	35	72	8.4	32	6.5	1.39	6.7	0.92	5.2	0.98	2.9	0.4	2.7	0.38
		Btk	23	48	5.4	21	3.9	0.82	3.9	0.55	3.2	2.65	1.9	0.28	1.8	0.26
		C	15.2	34	3.7	13.8	2.7	0.54	2.7	0.39	2.3	0.45	1.4	0.19	1.3	0.20
1633	P3	Oi	13.8	28	3.3	11.9	2.3	0.52	2.3	0.32	1.8	0.35	0.98	0.16	0.98	0.16
		A	39	81	9.2	35	6.8	1.43	6.8	0.92	5.06	0.97	2.9	0.42	2.66	0.41
		Bhw	40	79	9.4	35	6.8	1.44	6.7	0.91	5.2	1.0	3.0	0.4	2.8	0.42
		Ck	26	51	5.9	21	3.9	0.79	3.7	0.5	2.9	0.56	1.8	0.25	1.74	0.26
		Cr	33	68	7.9	30	5.5	1.09	5.0	0.68	3.8	0.71	2.3	0.32	2.2	0.34
1809	P4	A1	35	70	8.3	32	6.2	1.32	6.2	0.83	4.8	0.9	2.6	0.37	2.5	0.37
		A2	38	78	9.2	35	6.9	1.44	6.8	0.95	5.3	1.02	2.9	0.42	2.8	0.41
		C1	41	84	9.9	38	7.4	1.5	7.3	1.03	5.7	1.09	3.2	0.45	3.0	0.44
		Cr	40	81	9.7	37	7.2	1.5	7.0	0.97	5.6	1.11	3.3	0.47	3.0	0.47

Table 4 gives the values in the indicators were calculated according to their geochemical percentages to determine weathering and soil enrichment rates. According to this; Yb (N), La (N) and Lu (N) values representing the LREE / HREE values in the soil were examined, La /Lu and La/Yb were found to be positive and strong, all of them were subjected to leaching as a result of all soil values. The low rate of 1809 m of La/Lu in P4 indicates a relatively low weathering condition and a low amount of clay found in the soil. On the other hand, the distribution of the Sm (N) and La (N) ratios is very close to the MREE, the middle rare enrichment element. The low negative Sm/Nd ratio for the values of all the soil profiles studied was found to be related to the intensity of the increased weathering in relation to the LREE enrichment. The ratios obtained using REE trace elements in (Table 4) showed that the clay movement in P1 was denser and thus the weathering was more developed than the other studied soil profiles. In addition, for La /Sm, La/Lu and La/Yb ratios for P1, it is due to the increased elevation of 1139m without any other soil profiles studied.

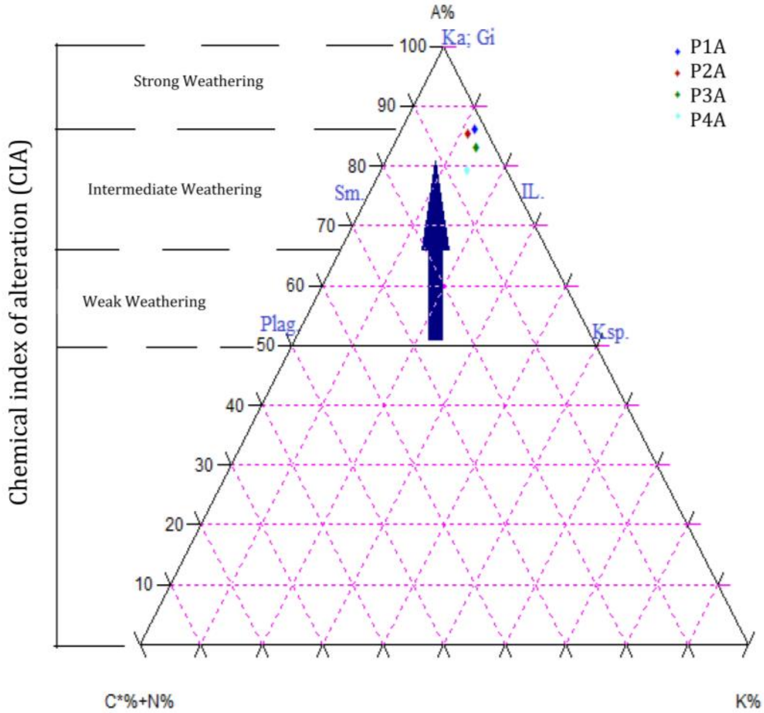

Figure 10. A-CN-K diagrams (Nesbitt and Young, 1989) with indication of the weathering index CIA for studied soil profiles only for horizon A. Arrow indicates the general weathering trend and the minerals plagioclase (Plag.), K-feldspar (Ksp.), Illite (IL.), Smectite (Sm.), Kaolinite (Ka.), and gibbsite (Gi.) is give for orientation.

Ho is a leachable element with weathering. Therefore, Er/Ho ratios tend to decrease by increasing weathering. In Table 4, P4 means that the highest Er/Ho ratio for height 1809m, was the lowest density of weathering at this height. However, the lowest value of Er/Ho ratio at the elevation of 1139m indicates that the density of weathering has increased.

It is clear that all values in the samples of the soil profiles examined have Eu negative. Eu/Eu* values are between 0.61 – 0.72% as shown in Table 4. More importantly, the difference in the Eu/Eu* value is inversely proportional to the increased weathering. Similar reports of a decrease in the negative values of Eu/Eu* as a function of intensity of weathering are presented (Condi et al., 1995; Huang and Gong, 2001; Ma et al., 2011; Babechuk et al., 2014).

Cerium can monitor cases of oxidation due to the potential oxidation bond between Ce^{+3} and Ce^{+4} during pedogenesis processes in populations of soil profiles studied. Cerium (cerium) was estimated by using the formulas of Ce, La and Pr. In Table 4, Ce/Ce* values are weak positive and negative. These oxidation values show that in the weathering of all studied soil profiles, Ce will decompose on a smaller scale.

Conclusion

The aim of this research was characterizing the geochemical characteristics of soils as a function of climate to evaluate the soil formation and weathering rates in Climosequence depending on the elevation by using geochemical data. The rate of chemical weathering of CIA, CIW, PIA and MIA indicators decreased with the increase in elevation. This was because basic cations (K, Na, Ca and Mg) were dissolved in water and descaled by leaching processes, and cations accumulated at low altitudes and contributed to the formation of secondary minerals. In contrast, WIP value was increased at higher altitudes due to increased leaching and precipitation at high altitudes causing decrease in movement of cations. Although less developed soils were found at the steepest slopes of the P4 with a height of 1809 m, they contained less mobile elements, due to the leaching of products weathering that cause decomposition conditions and their transfer to low altitudes, which is more pronounced in the soil developed for the first profile at elevation 1139 m.

Despite the different weathering intensities and anomalies registered in studied soil profiles, most of the investigated studied soils seemed to be weathered from similar parent rocks. However, it exhibited different weathering directions by deviating from the main trend in the A-CN-K diagram suggesting that the formation of weathered soils more easily influenced by quantity of precipitation, degree of gradient and difference elevations. Therefore, it was concluded that the main factors determining soil formation are climate and elevations, both of which determine the leaching regime and weathering rates.

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The evaluation of basal respiration and some chemical properties of soils under cover crop treatments in a cherry orchard

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Abstract

Effects of different cover crops (CCs), mechanical cultivation and herbicide treatments on some soil chemical properties [pH, EC, total N, available P, exchangeable cations (Ca, Mg, K, Na) and the DTPA-extractable micronutrients (Fe, Mn, Zn, Cu)] and basal soil respiration (BSR) were investigated in a cherry orchard from 2013 to 2014. The present study was conducted in a cherry orchard located at the Experiment Station of Black Sea Agricultural Research Institute in Samsun province on the Northern side of Turkey. CC treatments, included *Trifolium repens* L. (TR), *Festuca rubra subsp. Rubra* (FRR), *Festuca arundinacea* (FA), *T. repens* (40%)+*F. rubra rubra* (30%)+*F. arundinacea* (30%) mixture (TFF), *Vicia villosa* (VV) and *Trifolium meneghinianum* (TM). Control treatments included mechanical cultivated (weed-free), herbicide treated (weed-free) and control plots, i.e., bare ground plots (with no cover crop) were allowed to become weedy. The experiment was conducted in a randomized complete block design with four replicates. The CCs were mowed in the flowering stages of the plants. After 90 days following seed harvest, soil samples were collected from two depths (0-20 and 20-40 cm) in each plot. All cropping species showed positive effects on soil chemical properties and BSR. The CC treatments decreased soil pH and exchangeable Na and increased EC, total N, available P, exchangeable cations (Ca, Mg, K) and the DTPA-extractable micronutrients (Fe, Mn, Zn). Effects of mechanical cultivation and herbicide treatments on soil chemical properties and BSR values were not found significant for both soil depths as compared to control ($p<0.01$). Results of the study showed that CCs, especially TR and VV treatments as legume plants improved soil chemical properties and BSR values in short term period. However, longer term studies are needed to evaluate the long-term effects of these sustainable management practices which have the potential to improve soil quality variables are encouraged.

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Introduction

Turkey is a unique country in the world where several types of fruit can be cultivated under good conditions and with superior quality owing to vast, fertile agricultural fields suitable for production and with the help of the ecological diversity in various regions (Erogul, 2018). Turkey has a considerable share in fruit production, which is like apple, orange, banana, carob, loquat and cherry are the most prominent fruits regarding their share in Turkey's production. Cherry is an significant agriculture product which is generally produced and exported. For regional rural development one of the most significant sectors is agricultural production in Turkey. Recently in agriculture sector another activity is orchard production which increasing areas and economic importance (Doğanay, 1998). Among major countries producing cherry in the world, in our country ranks the first both in the northern hemisphere and in the world with 599.650 tons of

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production in 2017, corresponding to 20.3% of world cherry production (FAOSTAT, 2017). Cherry fruit cultivation is carried out in an area of 847.461 da in Turkey (TURKSTAT, 2018). The U.S. with 288.480 tons of production and 13.8% share and Iran with 220.393 tons of production and 11.8% follow it. Turkey is leader country in terms of volume of cherry production in the World (FAOSTAT, 2017). Cherry production is an significant production activity for the Turkish Economy (Bal and Cercinli, 2013).

Cover crops (CCs) is defined as crops that provides soil protection, seedling protection, and soil improvement between vines in vineyards and trees in orchards between periods of normal crop production, or between periods of normal crop production (SSSA, 2001). Cover crop management systems affect soil quality variables (Demir and Gülser, 2015; Çerçioğlu et al., 2019) and health and thereby orchards growth and productivity. CCs also are precisely grown to prevent loss of nutrients in deep layers through surface runoff and leaching (Kaye and Quemada, 2017). The CCs can be used as legume or non-legume. Leguminous crops are used to fix atmospheric nitrogen (N) which is used by succeeding crop (Blanco-Canqui et al., 2011). N fixation by leguminous helps to decrease the use of N fertilizers for next crop (Ladha et al., 2004). Genelrally, the legumes and non-legume crops are the plants that are grown to provide soil cover and help to enhance chemical, biological and physical characteristics of the soil (Reddy, 2016). A bicultural of leguminous and non-leguminous may be used with the purpose to provide both benefits together (Ranells and Wagger, 1996). The CCs provide some benefits to soils used for agriculture production. CCs primarily effect soil nutrient dynamics and balance by scavenging nutrients, fixing atmospheric N_2, decreasing nutrient erosion and decreasing nutrient leaching. Including CCs in intensively managed agroecosystems could thus effect nutrient recovery, accumulation, cycling and storage. In addition, the CCs can be utilized to manage N in agricultural soils by altering N cycling and availability. The CCs grown during fallow periods in cropping systems change the annual patterns of N uptake and mineralization. The CCs also impact soil N availability by increasing total N through prevention of N losses or additions of fixed N. The CCs that are grown during fallow periods in cropping systems to take up nutrients, especially N, that would be lost if plants are not present. Ultimately, successful management of N using the CCs requires that N availability be synchronized. Various aspects of the relationship between the CCs and total N have been discussed in a number of previous studies (Thorup-Kristensen et al., 2003; Demir et al., 2019a; Demir and Işık, 2019a).

Additionally, the CCs are helpful in sustaining and increasing microbial biodiversity in soils. The CCs that biologically fix atmospheric N can provide a source of orchard tree nutrition. Many crops are excellent nutrient scavengers and can aid in the recycling of orchard nutrients and prevention of runoff and groundwater losses, particularly of N (Delgado et al., 2007). In recent times, the CCs are also used for increasing exchangeable nutrients such as K^+ and Mg^{2+}. Lal et al. (1991) found that following factors effect soil fertility when the CCs are grown in the rotation cycle: cover crop species, quantity of biomass produced by cover crop, length and time of cover crop growth, and soil and weather conditions. Aside from the various benefits or effects of the CCs on soil discussed above, very little is known about the affect of the CCs on soil micronutrients and exchangeable cations. The amount of exchangeable cations (Ca, Mg, K and Na) are important attributes of soils and sediments for different processes.

Herbicide treatment and mechanical cultivation are significant among the current weed control practices in orchards. Using CCs for weed control in orchards is one of the broadly applied alternative methods to the mechanically cultivation and herbicide treatment (Mennan et al., 2009; Işık et al., 2009). Herbicide and mechanical cultivation are expected to provide weed-free orchards. However, coverless (bare) fields can bring about increased run-off and erosion, damage the soil chemical and physical properties (Keesstra et al., 2016). In this study, effects of different cover crops, mechanically cultivation and herbicide treatments on some chemical properties and basal respiration of soil were investigated in a cherry orchard (Latitude, 41°22′93′′ N; Longitude, 36°50′19′′ E) in Samsun province on the Northern side of Turkey between 2013 and 2014.

Material and Methods

Experimental site and treatments

The study was conducted in a cherry orchard at the Experiment Station of Black Sea Agricultural Research Institute in Samsun province (Latitude, 41° 22′ 93′′ N; Longitude, 36° 50′ 19′′ E) on the Northern side of Turkey from 2013 to 2014. The location of the orchard was in the Middle Black Sea region. Annual average precipitation was 685.5 mm and annual average temperature was 14.5 °C. There was 1 m spacing between the plots and 3 m between the blocks. Each plot had a size of 35 m^2 (5 × 7 m). Experiments were conducted in randomized complete blocks design with four replications.

The cover crop (CC) treatments consisted of *Trifolium repens* L. (TR), *Festuca rubra rubra* L. (FRR), *Festuca arundinacea* (FA), *Trifolium repens* (40%) + *Festuca rubra rubra* (30%) + *Festuca arundinacea* (30%) mixture (TFF), *Vicia villosa* (VV) and *Trifolium meneghinianum* (TM). *Vicia villosa* and *Trifolium meneghinianum* were used annual legume plants and *Trifolium repens* L. were used perennial legume plants. *Festuca rubra rubra* L. and *Festuca arundinacea* are perennial grass cover plants. Control treatments included mechanical cultivated (weed-free), herbicide treated (weed-free) and control plots, i.e., bare ground plots (with no cover crop) were allowed to become weedy. *Trifolium meneghinianum* seeds were supplied from Black Sea Agricultural Research Institute and the others were purchased from private seed companies. During the experiment, the CCs were continued to be applied in the same plots and no fertilizers were applied. Consecutive plots were separated with a buffer zone without any cover crops. Before the plantation of the CCs, existing weeds were manually or mechanically removed. Irrigation was performed twice (one in July and the other in August). CCs were planted through broadcast seeding at 50, 80 and 70 kg·ha^{-1} for *T. repens, Festuca* spp. and mixture of perennials respectively in April 2012. *V. villosa* (100 kg ha^{-1}) and *T. meneghinianum* (40 kg ha^{-1}) were sown in October 2012 and November 2013. Following the sowing, seeds were incorporated into the soil by shallow cultivation. Primary tillage was performed through chisel plow and disk harrow. The CCs were mowed at the flowering stages of the plants. Mowing was performed carried out with a motorized back-scythe. Following mowing, incorporation of the CCs into the soil was done by disking. While mowing of the CCs was performed on 23 June 2013 during the flowering stage in the first year, it was performed on 26 June 2014. A rotary hoeing machine was used for mechanical weed control. In the herbicide control plots, the glyphosate isopropylamine salt (360 g a.i L^{-1}) was implemented at a dose of 2880 ml ha^{-1} (1.39 kg a.i ha^{-1}). Glyphosate was implemented at 3 atm pressure (303.97 kPa) and 250 L ha^{-1} spraying volume with a portable hand sprayer (Honda WJR 2225).

Soil sampling and analyses

Soil samples were collected from 0–20 and 20-40 cm depths in each plot using a corkscrew-shaped soil drill 90 days after harvest period. Samples were sieved through 2 mm sieve and prepared for soil analyses. Initial soil properties were given in Table 1.

Table 1. Soil physico-chemical characteristics of the experiment

Parameters	Soil depth (cm)	
	0-20	20-40
Texture class	C	C
Clay, %	61.28	54.04
Silt, %	21.37	30.86
Sand, %	17.35	15.10
Organic carbon (OC), %	1.05	0.74
pH (1:1)	7.11	7.28
EC25°C, mmhos cm^{-1}	0.81	0.67
Ca, me 100g^{-1}	29.1	25.2
Mg, me 100g^{-1}	10.32	8.41
K, me 100g^{-1}	1.09	0.85
Na, me 100 g^{-1}	0.17	0.15

Particle size distribution was identified by using Bouyoucos hydrometer method (Bouyoucos, 1962). Soil reaction (pH) was measured by using a pH meter with glass electrode in a 1:1 (w:v) ratio soil-water suspension (Jackson, 1958). Electrical conductivity ($EC_{25ºC}$) was measured with an EC meter in a 1:1 (w:v) ratio soil-water suspension (Richards, 1954). Basal soil respiration (BSR) at field capacity (CO_2 production at 22°C without addition of glucose) was measured, as reported by Aşkın and Kızılkaya (2009); by alkali ($Ba(OH)_2.8H_2O$ + $BaCl_2$) absorption of the CO_2 produced during the 24h incubation period, followed by titration of the residual OH^- with standardized hydrochloric acid, after adding three drops of phenolphthalein as an indicator. Data are expressed as µg CO_2 g^{-1} dry soil. Exchangeable cations (Ca, Mg, K, Na) were identified with the 1N ammonium acetate (NH_4OAc) extraction (Rowell, 1996). Soil organic carbon was identified by the modified Walkley-Black method (Black, 1965). Available P contents were determined through extraction with 0.5 M $NaHCO_3$ at pH 8.5 by Olsen's method (Olsen et al., 1954). Total N was identified by the LECO model (with a Tru-Spec CHN elemental analyzer). Micronutrients were identified by the extraction with DTPA extraction solution according to Kacar (1994).

Statistical analysis

Analysis of variance (ANOVA) was performed to evaluate experimental data using SPSS statistical package. Statistical disfferences were evaluated using Duncan's multiple range test at 0.01 and 0.05 alpha probability levels. Correlation analyses were performed to express the relationships between experimental parameters (Yurtsever, 2011).

Results and Discussion

Soil reaction (pH) and electrical conductivity ($EC_{25°C}$)

The pH of the soil is a determining factor of soil fertility greatly influenced by the crop residues incorporated in the soil. The simplest and most important factor in all growing systems is to maintain optimal soil pH levels. The pH level of soil influences microbial activity, nutrient solubility and root growth. Soil pH values were significantly affected by CC management in both years of the experiment ($p<0.01$). The CC treatments significantly reduced pH from 7.48 in control plot to 6.92 for VV treatment at the 0-20 cm soil depth in 2013 (Table 2). Soil pH significantly decreased from 7.46 in the control plot to 6.90 in TR treatment at 0-20 cm soil depth in 2014. Gülser (2004) found that values of soil pH importantly reduced with the cropping applications and percent decreases in pH compared the control soil were between 5.96% for crownvetch and 0.31% for bromegrass treatment. Similarly, cover cropping significantly reduced soil pH (Demir and Işık 2019b; Demir and Işık 2019c; Demir et al., 2019b), due to the acidic root exudates, and this may alter nutrient availability at the root surface (Rengel and Marschner, 2005). Such decreases were mainly because of CO_2 release into the soil ambient, decomposition of organic amendments and conversion of these organic amendments into carbonic acid (H_2CO_3) through reactions with water. Besides, when the organic matter is mineralized there is a production of organic acids that could raise the soil acidity (Garcia and Rosolem, 2010). In present study, when compared to the control plot, percent decreases in soil pH values between -3.3% in FRR treatment and -7.5% in VV treatment in 2013 and between -4.8% in TM treatment and -7.6% in TR treatments in 2014. The differences in soil pH values were not found to be statistically significant for the 20-40 cm soil depth in both years of the experiment (Table 3). The mean pH values for 20-40 cm soil depth were 7.46 in 2013 and 7.51 in 2014.

The CC treatments increased soil $EC_{25°C}$ values at 0-20 cm soil depth as compared to the soil of an untreated control plot (Table 2). The highest $EC_{25°C}$ values were obtained from TR treatment 1.185 ds m^{-1} in 2013 and 1.186 ds m^{-1} in 2014. $EC_{25°C}$ values significantly increased from 0.689 ds m^{-1} in the control to 1.186 ds m^{-1} in TR treatment at 0-20 cm soil depth at the end of the experiment. $EC_{25°C}$ has been used successfully as an indirect indicator of significant soil quality variables, such as soil salinity hazard (Demir and Gülser, 2015), soil water content (Khakural et al., 1998), topsoil thickness (Kitchen et al., 1999), clay pan thickness (Doolittle et al., 1994), nutrient levels (Heiniger et al., 2003) and depth of sand deposition (Kitchen et al., 1996). The soil EC is also a significant indicator of dissolved nutrients and can be used to monitor mineralization (Candemir and Gülser, 2010). The findings of this research suggest that soil EC may serve as a useful indicator of available N in soil as suggested by Gajda et al. (2000). Three potential pathways of EC exist in soil: through the liquid phase (via salts contained in soil water), through the solid phase (soil particles in direct and continuous contact with one another), and through the liquid-solid phase (primarily via the exchangeable cations associated with clay minerals) (Corwin and Lesch, 2003). Therefore, many soil attributes affect EC in soil (Sudduth et al., 2003). In this study, EC values significantly increased with the cropping treatments and percent increases in $EC_{25°C}$ over the control soil were between 37.7% in FRR and 69.9% in TR treatments in 2013 and between 41.0% in FA and 72.1% in TR treatments in 2014. Gülser (2004) reported that highest percent change in $EC_{25°C}$ values over the control plots was determined as 124.6% for alfalfa treatment while lowest percent increase in $EC_{25°C}$ values was 15.97% for bromegrass treatment. Eigenberg et al. (2002) determined that EC was effective in determining the dynamic changes in plant available soil N throughout the growing season of crops, i.e. over a range of soil water conditions. Zhang and Wienhold (2002) reported very strong correlation between EC and soil N in the upper 15 cm. In this study, increasing total N content in the soil due to crop applications caused increased in soil EC. However, legume cover crops (*Trifolium repens* L., *Vicia villosa* and *Trifolium meneghinianum*) were found more effective non-legume (*Festuca rubra rubra* L. and *Festuca arundinacea*). The differences in $EC_{25°C}$ values were not found to be statistically significant for the 20-40 cm soil depth in both years of experiments (Table 4). $EC_{25°C}$ values ranged from 0.624 ds m^{-1} in control treatment to 0.711 ds m^{-1} in TR treatment for the 20-40 cm soil depth in 2013. $EC_{25°C}$ values ranged from 0.611 ds m^{-1} in HC treatment to 0.733 ds m^{-1} in VV treatment for the 20-40 cm soil depth in 2014 (Table 3).

Total N

The CC treatments increased total N at 0-20 cm soil depth as compared to the soil of an untreated control plot in both years of the experiments (Table 2). The highest total N values (0.206%) were seen at 0-20 cm in 2013 in the VV treatment while the lowest total N value (0.120%) was seen in HC treatment. Total N significantly increased from 0.121% in the control to 0.210% in VV treatment at 0-20 cm soil depth in 2014.

Table 2. Effects of the treatments on soil properties at 0-20 cm soil depth in a cherry orchard

Treatments	pH, (1:1)	EC, ds m-1	Total N, %	NH_4OAc extractable, me 100 g-1				P, mg kg-1	BSR, mg CO_2 100 g-1	DTPA-extractable micronutrients, mg kg-1			
				Ca	Mg	K	Na			Fe	Mn	Zn	Cu
2013													
TR	7.02 b	1.185 a	0.205 a	33.36 ab	6.25 a	0.36	0.13 b	19.5 a	19.4 a	23.32 a	12.41 a	1.86 a	9.81
FRR	7.23 ab	0.960 c	0.177 c	32.74 ab	5.88 ab	0.30	0.16 ab	16.4 c	14.2 c	21.86 b	9.58 b	1.52 bc	9.80
FA	7.04 b	0.962 c	0.174 c	32.34 b	5.88 ab	0.30	0.18 ab	16.2 c	14.9 c	21.62 b	10.18 b	1.56 bc	8.81
TFF	7.09 b	1.031 bc	0.191 b	33.09 ab	6.02 a	0.33	0.16 ab	17.5 b	16.2 b	21.88 b	9.96 b	1.58 b	8.94
VV	6.92 b	1.153 ab	0.206 a	34.24 a	6.31 a	0.39	0.11 b	19.3 a	19.9 a	23.13 a	12.23 a	1.80 a	8.79
TM	7.20 ab	1.005 bc	0.190 b	32.43 b	6.01 a	0.30	0.18 ab	17.8 b	16.9 b	21.84 b	9.67 b	1.61 b	9.22
HC	7.52 a	0.735 d	0.120 d	29.65 c	4.87 c	0.27	0.24 a	13.9 d	9.1 d	19.89 c	8.17 c	1.44 c	9.19
MC	7.50 a	0.742 d	0.126 d	30.46 c	5.05 bc	0.29	0.22 a	14.6 d	10.2 d	20.24 c	8.62 c	1.46 c	9.12
C	7.48 a	0.698 d	0.123 d	30.67 c	4.99 bc	0.29	0.24 a	14.5 d	9.8 d	19.89 c	8.55 c	1.44 c	9.05
2014													
TR	6.90 b	1.186 a	0.207 a	35.79 a	6.50 a	0.40 a	0.12 b	20.6 a	20.1 a	23.60 a	12.53 a	1.89 a	9.59
FRR	7.04 b	0.978 b	0.182 c	34.03 ab	5.95 c	0.32 cd	0.15 b	16.9 c	14.9 c	22.04 b	9.36 c	1.57 bc	9.12
FA	7.04 b	0.972 b	0.178 c	33.05 ab	6.11 bc	0.34 bc	0.16 b	16.9 c	16.6 c	21.87 b	9.56 bc	1.57 c	9.27
TFF	6.98 b	1.046 b	0.192 b	32.48 ab	6.44 ab	0.37 ab	0.16 b	18.0 b	17.1 b	22.11 b	10.15 b	1.61 bc	9.55
VV	6.94 b	1.154 a	0.210 a	36.03 a	6.66 a	0.42 a	0.12 b	20.5 a	20.5 a	23.50 a	12.19 a	1.86 a	9.11
TM	7.10 b	1.031 b	0.194 b	33.67 ab	6.39 ab	0.31 cd	0.16 b	18.8 b	17.2 b	22.14 b	10.09 b	1.67 b	8.93
HC	7.50 a	0.722 c	0.123 d	30.93 b	5.03 d	0.27 d	0.25 a	13.9 d	8.9 d	19.56 c	8.34 d	1.41 d	9.17
MC	7.53 a	0.756 c	0.130 d	31.48 b	5.10 d	0.29 d	0.24 a	14.7 d	10.9 d	20.28 c	8.43 d	1.39 d	9.08
C	7.46 a	0.689 c	0.121 d	31.23 b	5.13 d	0.28 d	0.24 a	14.4 d	9.1 d	19.65 c	8.20 d	1.39 d	8.99

TR: *Trifolium repens* L., FRR: *Festuca rubra* subsp. *rubra*, FA: *Festuca arundinacea*, TFF: *T. repens* (40%) + *F. rubra rubra* (30%) + *F. arundinacea* (30%) mixture, VV: *Vicia villosa*, TM: *Trifolium meneghinianum*, MC: Mechanically cultivated, HC: Herbicide treatment, C: Control. pH: Soil reaction, EC: Electrical conductivity, Total N: Total Nitrogen, Ca: Exchangeable calcium, Mg: Exchangeable magnesium, K: Exchangeable potassium, Na: Exchangeable sodium, P: Available phosphorus, BSR: Basal soil respiration. Fe: Iron, Mn: Manganese, Zn: Zinc, Cu: Cupper.

Table 3. Effects of the treatments on soil properties at 20-40 cm soil depth in a cherry orchard

Treatments	pH, (1:1)	EC, ds m^{-1}	Total N, %	NH_4OAc extractable, me 100 g^{-1}				P, mg kg^{-1}	BSR, mg CO_2 100 g^{-1}	DTPA-extractable micronutrients, mg kg^{-1}			
				Ca	Mg	K	Na			Fe	Mn	Zn	Cu
2013													
TR	7.48	0.711	0.113	30.2	5.05	0.23	0.21	13.50	6.34	18.64	8.17	1.07	6.99
FRR	7.43	0.641	0.110	30.5	4.73	0.21	0.22	12.44	5.25	18.35	8.38	1.13	6.34
FA	7.55	0.668	0.108	31.7	4.96	0.26	0.21	13.07	6.33	17.87	9.33	1.01	6.12
TFF	7.55	0.703	0.112	29.4	5.85	0.25	0.23	13.75	5.25	17.64	8.35	1.17	5.88
VV	7.43	0.695	0.108	31.6	5.04	0.25	0.21	13.48	6.57	18.31	6.69	1.10	6.59
TM	7.42	0.668	0.105	31.4	5.52	0.22	0.23	12.84	5.53	18.36	6.74	1.07	6.14
HC	7.43	0.633	0.106	30.4	4.33	0.27	0.22	13.11	5.48	19.00	8.15	1.12	7.07
MC	7.48	0.691	0.113	30.9	4.37	0.26	0.20	13.14	5.43	18.60	7.55	1.09	6.15
C	7.41	0.624	0.107	29.4	4.39	0.27	0.19	12.78	5.65	17.49	7.65	0.91	6.26
2014													
TR	7.58	0.689	0.112	29.6	4.14	0.21	0.20	13.92	6.69	18.69	7.88	1.11	6.47
FRR	7.41	0.687	0.106	30.7	4.59	0.28	0.22	12.79	5.89	17.76	7.26	1.09	7.14
FA	7.49	0.723	0.109	28.7	5.00	0.22	0.20	12.97	5.94	17.59	8.00	1.08	6.58
TFF	7.57	0.620	0.107	31.0	4.07	0.29	0.21	13.21	5.96	18.99	6.74	1.08	6.21
VV	7.45	0.733	0.114	30.4	5.48	0.20	0.23	13.95	6.45	18.64	8.41	1.12	7.52
TM	7.53	0.698	0.108	29.2	5.00	0.28	0.23	12.42	6.11	17.99	8.14	1.17	7.89
HC	7.52	0.611	0.109	30.2	5.02	0.26	0.20	12.23	5.97	18.13	6.56	1.09	5.97
MC	7.54	0.722	0.105	30.1	5.25	0.20	0.22	13.20	6.10	19.00	8.12	1.06	6.50
C	7.47	0.631	0.105	29.4	4.81	0.25	0.21	13.65	5.82	17.99	7.58	1.15	6.57

TR: *Trifolium repens* L., FRR: *Festuca rubra* subsp. *rubra*, FA: *Festuca arundinacea*, TFF: *T. repens* (40%) + *F. rubra rubra* (30%) + *F. arundinacea* (30%) mixture, VV: *Vicia villosa*, TM: *Trifolium meneghinianum*, MC: Mechanically cultivated, HC: Herbicide treatment, C: Control. pH: Soil reaction, EC: Electrical conductivity, Total N: Total Nitrogen, Ca: Exchangeable calcium, Mg: Exchangeable magnesium, K: Exchangeable potassium, Na: Exchangeable sodium, P: Available phosphorus, BSR: Basal soil respiration. Fe: Iron, Mn: Manganese, Zn: Zinc, Cu: Cupper.

The results of this study showed that the CCs can be used to manage N in agricultural soils by altering N cycling and availability. The affects of CCs on soil nutrients, especially N, have been previously investigated (Dabney et al., 2010; Kaspar and Singer, 2011; Blanco-Canqui et al., 2011). Dabney et al. (2010) investigated this subject for four regions in the United States. The researchers found that significant total N can be derived from cover crops. Blanco-Canqui et al. (2011) reported that, after four rotation cycles, total N increased by 279 kg ha^{-1} under sunn hemp and by 258 kg ha^{-1} under late-maturing soybean compared with non-CCs plots when both leguminous CCs were planted after each winter wheat harvest in a winter wheat-grain sorghum rotation in eastern Kansas. Others also reported high total N contributions from legume CCs (Mansoer et al., 1997). Ramos et al. (2011) reported in a previous study that two cover crop (oat-vetch-*Vicia sativa* L. and oat-*Avena sativa* L.) treatments increased total N (32.5%) according to control. Similarly, greater N accumulation by hairy vetch compared to non-legume CCs like cereal rye, austrian winter pea (*Lathryrus hirsutus* L.), annual ryegrass (*Lolium multiflorum* Lam. cv. *Billion*), canola (*Brassica napus* L. cv. *Santana*), and no CC treatments was also reported by Kuo et al. (1997). Previous studies have found that legume crops have greater total N content due to their higher N concentration (Shipley et al., 1992). In this study, the CC treatments increased total N supply through improving the availability of residual N and through N_2 fixation with legume crops. The legume crops can have great effects on soil N. Gülser (2004) found that present increases in the total N over the control were between 8.85% for the crownvetch and 36.46% for the alfalfa application. Harris et al. (1994) determined that CCs impacted soil N availability by increasing total N through additions of fixed N or prevention of N losses. Reeves (1994) found that growing CC treatments contributed 36 to 226 kg N ha^{-1} by legumes and 25 to 50 kg N ha^{-1} by small grains. Similar results were found at by Kuo et al. (1997), who determined that leguminous CC treatments provide important quantities of total N. In this study, percent increases in the total N over the control soil varied between 41.4-66.9% in 2013 and 47.1-72.8% in 2014. Hoagland et al (2008) reported that a cover of mixed leguminous established in an cherry orchard raised the total N, potentially available N and soil biological activity for trees over a two-year period. Ingels et al. (1994) found that winter legumes can add 112-224 kg N ha^{-1} and cowpea and other summer legumes can contribute 112-145 kg N ha^{-1} to the soil nitrogen pool. Ladha and Peoples (1994) reported inputs of N from N fixation between 124-185 kg ha^{-1} for crimson clover, and 9-201 kg ha^{-1} for cowpea. Wagger (1989) reported crimson clover N fixation of 100-150 kg ha^{-1}, and Odhiambo and Bomke (2000) concluded that crimson clover could provide the rapid release of enough N to sustain the growth of crops. Present findings of total N well comply with the findings of those earlier studies. However, the differences in total N values were not found to be statistically significant for the 20-40 cm soil depth in both years of experiments (Table 3). Mean total N values at 20-40 cm soil depth varied between 0.105-0.129% with a mean value of 0.109%.

Basal soil respiration (BSR)

In both years of the experiment, the basal soil respiration (BSR) importantly increased with the CC treatments ($p<0.01$). In 2013, BSR values was the lowest (9.10 mg CO_2 100 g^{-1}) in the herbicide treatment followed by HC < C < MC < FRR < FA < TFF < TM < TR < VV treatments. The highest BSR values (26.48 mg CO_2 100 g^{-1}) were seen at 0-20 cm in 2014 in the VV treatment while the lowest BSR value (8.89 mg CO_2 100 g^{-1}) was seen in HC treatment (Table 2). CCs increase the potential for macro- and microfaunal activity in soils because they increase the total inputs of organic material to soils (Kaspar and Singer, 2011; Demir, 2019). CCs also are broadly growing strategy to improve soil microbial growth in agricultural systems. The soil microbial activity reflects the soil's ability to store and cycle nutrients. Crop residues are also known to enhance N fixation in soil by asymbiotic bacteria. Conventional tillage (Canadian Environmental Protection Act, 1993) and no-tillage system with a ryegrass cover crop in cotton (*Gossipium hirsutum* L.) was investigated for the microbial count in soil. Ryegrass cover crop in conventional tillage and no-tillage system maintained a higher microbial population in the upper layer compare to no-cover plots (Sharma et al., 2018a). Demir et al (2019a) found that highest basal soil respiration values (41.5 mg CO_2 100 g^{-1}) was obtained in the *Vicia villosa* Roth treatment while the lowest BSR values (12.5 mg CO_2 100 g^{-1}) was in the control in the apricot orchard with a clay textured. Reddy et al. (2003) found that after 3 yr with crimson clover or cereal rye CCs soil had greater microfaunal activity than the soil without a cover crop. In their research, the crimson clover cover crop had a greater stimulatory affect on soil biology than cereal rye. The researchers speculated that the leguminous CCs had more readily available amino acids and carbohydrates than the grass CCs due to a lower C to N ratio. In this study, the greatest increase in BSR values was obtained in VV treatment (164.9%) and the least increase was observed in MC treatment (4.0%) in 2013. As compared to control, percent increases in BSR values between 19.4% in MC treatment and 190.3% in VV treatment in 2014. Lundquist et al. (1999) found on the short-term (42-d) effects of cereal rye incorporation in contrasting vegetable management systems. Their findings illustrated that following rye incorporation, counts of active bacteria increased 24 to 52% in the first 7 d and populations of bacterial-feeding nematodes increased 400 to 600% between 7 and 14 d. Active fungal hyphal lengths and fungal-feeding nematodes were less responsive to rye incorporation during the 42-d period. In this study, legume cover crops (*Trifolium repens* L., *Vicia villosa* and *Trifolium meneghinianum*) treatments were found mostly more effective non-legume (*Festuca rubra rubra* L. and *Festuca arundinacea*) treatments. CC treatments enhance nutrient utilization when the species have root systems that are able to extract and mobilize nutrients from deeper layers and the leguminous may add nutrients to the soil by biological fixation (USDA, 1996). Therefore, in this study, the improvements in soil properties were more pronounced with legume and grass cover crops mixture (*T. repens* (40%) + *F. rubra rubra* (30%) + *F. arundinacea* (30%)) than with grass cover (*Festuca rubra* subsp. *rubra* and *Festuca arundinacea*) treatments. Availability of nutrients like N and P is especially dependent upon soil microbial activity and microbial biomass, which in turn depend on the supply of organic substrates in soil. The population of soil flora and fauna is positively correlated with the phyto-biomass present in soil. Beri et al. (1992) and Sindu et al. (1995) obtained that soil applicated with crop residues held 5-10 times more aerobic bacteria and 1.5-11 times more fungi than soil were either burn or removed. The study of Verhulst et al. (2011) reveled that, soil microbial activity increased with increasing amount of crop residues retained on the soil surface in the zero till treatments. Present findings of basal soil respiration well comply with the findings of those earlier studies. However, the differences in the BSR values were not found to be statistically significant for the 20-40 cm soil depth in both years of experiments (Table 3). The mean BSR values for 20-40 cm soil depth were 5.76 mg CO_2 100 g^{-1} in 2013 and 6.10 mg CO_2 100 g^{-1} in 2014.

Available P

The CC treatments significantly increased available P at 0-20 cm soil depth as compared to the soil of an untreated control plot in both years of experiments ($p<0.01$). In 2013, available P value was the lowest (13.9 mg kg^{-1}) in the herbicide treatment followed by HC< C< MC <FA < FRR < TFF < TM < VV < TR treatments (Table 2). Available P significantly increased from 14.4 mg kg^{-1} in the control to 20.6 mg kg^{-1} in TR treatment at 0-20 cm soil depth in 2014. In a study conducted on loamy sand soil by Beri et al. (1995), it has been seen that the incorporation of cover crops as increased the available P and K content. Gupta et al. (2007) reported from the 3 year study that P consantrations in soil increased with the incorporation of cover crops. Some research has been conducted using cover crops within orchard tree rows for potential nutrient contribution (Atucha et al., 2011; Mays et al., 2014). The potential benefits of cover crops use in annual cropping systems have been supported by many studies (Parr et al., 2011). Labarta et al. (2002) reported that available P values was higher for legume cover crops than for grass cover crops, probably due to higher P requirements for legumes due to the mechanisms involved in nitrogen fixation. In this study, available P values significantly increased with the cropping applications and percent increases in available P over the control soil were between 11.9% in FA and 35.2% in TR treatments in 2013 and between 17.5% in FRR and 43.2% in TR treatments in 2014. However, the differences in available P were not found to be statistically significant for the 20-40 cm soil depth in both years of experiments (Table 3). Available P values at 20-40 cm soil depth varied between 12.44-13.75 ppm with a mean value of 13.12 ppm in 2013 and between 12.23-13.95 ppm with a mean value of 13.15 ppm in 2014.

Exchangeable cations (Ca, Mg, K, Na)

In this study, it was found that whereas the CC treatments significantly increased the Ca, Mg and K, it reduced the Na in the soil (Table 2). The CC treatments significantly increased extractable K at 0-20 cm soil depth as compared to the soil of an untreated control plot ($p<0.01$). In addition, significantly higher exchangeable K was obtained in 2014 than in 2013. While the exchangeable K contents varied between 0.27 me 100 g^{-1} in HC treatment and 0.42 me 100 g^{-1} in VV treatment. Percent increases in the extractable K over the control soil varied between 3.4–34.5% in 2013 and 9.5–49.4% in 2014. Aside from the diverse benefits or effects of cover crops on soil, very little is known about the effect of CCs on exchangeable cations and micronutrients of soils (Sharma et al., 2018a). The amount of exchangeable Ca, Mg, K and Na are vital attribute of soils. They relate information on soils' abilities to sustain plant growth, retain nutrients, sequester toxic heavy metals, or buffer acid deposition. Sharma et al. (2018b) obtained accumulation of K at the surface due to deposition of crop residue and lack of incorporation. Eckert (1991) found that the accumulation of exchangeable K at the surface soil was improved by inclusion of rye cover crop. Sharma et al. (2018a) determined that incorporating cover crops in no-tillage seed soybean or maize cropping systems might help in maintaining the exchangeable Mg content better than no cover crop application.

Table 4. Correlation matrix among the soil properties in the 0-20 cm soil depth at the end of the experiment

	EC	Total N	BSR	P	Ca	Mg	K	Na	Ext. Fe	Ext. Mn	Ext. Zn	Ext. Cu
pH	-0.840**	-0.777**	-0.760**	-0.725**	-0.585**	-0.747**	-0.694**	0.964**	-0.653**	-0.675**	-0.681**	0.353*
EC		0.933**	0.941**	0.922**	0.811**	0.905**	0.836**	-0.855**	0.877**	0.883**	0.896**	-0.031
Total N			0.978**	0.948**	0.917**	0.980**	0.789**	-0.775**	0.939**	0.864**	0.906**	0.085
BSR				0.972**	0.919**	0.970**	0.848**	-0.781**	0.956**	0.922**	0.841**	0.073
P					0.895**	0.955**	0.841**	-0.763**	0.959**	0.965**	0.882**	0.054
Ca						0.924**	0.801**	-0.591**	0.929**	0.835**	0.865**	0.137
Mg							0.810**	-0.737**	0.947**	0.871**	0.911**	0.067
K								-0.686**	0.829**	0.876**	0.847**	0.015
Na									-0.674**	-0.725**	-0.727**	0.371*
Ext. Fe										0.923**	0.953**	0.171
Ext. Mn											0.988**	0.094
Ext. Zn												0.100

**correlation is significant at 0.01 level, *correlation is significant at 0.05 level.
pH: Soil reaction, EC: Electrical conductivity, Total N: Total Nitrogen, Ca: Exchangeable calcium, Mg: Exchangeable magnesium, K: Exchangeable potassium, Na: Exchangeable sodium, P: Available phosphorus, BSR: Basal soil respiration. Fe: Iron, Mn: Manganese, Zn: Zinc, Cu: Cupper.

Table 5. Correlation matrix among the soil properties in the 20-40 cm soil depth at the end of the experiment

	EC	Total N	BSR	P	Ca	Mg	K	Na	Ext. Fe	Ext. Mn	Ext. Zn	Ext. Cu
pH	-0.249	-0.065	-0.129	-0.092	-0.076	-0.156	-0.125	0.288*	-0.189	0.091	-0.275	0.145
EC		0.216*	0.379**	0.309*	-0.235*	0.254*	0.256	-0.264*	0.124	0.215	0.069	0.044
Total N			0.347**	0.125	-0.312	-0.024	0.189	0.109	0.301*	0.157	0.004	-0.118
BSR				-0.009	0.290	0.256*	0.274	-0.324*	0.289*	-0.104	0.165	0.086
P					0.280*	0.237*	-0.008	0.051	0.012	0.100	0.127	0.081
Ca						0.102	-0.241*	-0.195	-0.202	-0.230	0.222	0.136
Mg							0.014	0.133	0.259	0.208	0.340*	0.076
K								0.114	0.165	0.136	0.223	0.032
Na									0.190	0.081	0.317	0.306
Ext. Fe										0.198	0.103	-0.036
Ext. Mn											0.294*	0.127
Ext. Zn												0.073

**correlation is significant at 0.01 level, *correlation is significant at 0.05 level.
pH: Soil reaction, EC: Electrical conductivity, Total N: Total Nitrogen, Ca: Exchangeable calcium, Mg: Exchangeable magnesium, K: Exchangeable potassium, Na: Exchangeable sodium, P: Available phosphorus, BSR: Basal soil respiration. Fe: Iron, Mn: Manganese, Zn: Zinc, Cu: Cupper.

This would depend on the cover crop species used, as the crop rooting depths and nutrient uptake effect the distribution and magnitude of the nutrients and micronutrients in the soil profile. The CC treatments significantly reduced exchangeable Na from 0.248 me 100 g^{-1} in control to 0.116 me 100 g^{-1} in *Trifolium repens* (TR) treatment in 2014. As compared to control, percent decreases in exchangeable Na value at the 0-20 cm soil depth in 2014 varied between 30.6% in TFF treatment and 50.4% in TR and VV treatments. Demir et al (2019a) cover crop treatments in an apricot orchard with clay soil significantly reduced exchangeable Na and pH from 0.35 me 100 g^{-1} and 7.47 for the bare control treatment to 0.20 me 100 g^{-1} for the *Vicia pannonica* Crantz treatment and to 7.02 for the *Vicia villosa* Roth and *Vicia pannonica* Crantz treatments, respectively. The differences in the exchangeable cations (Ca, Mg, K, Na) were not found to be statistically significant for the 20-40 cm soil depth in both years of experiments (Table 3). The exchangeable Ca concentrations varied between 28.7-31.7 me 100 g^{-1}, the exchangeable Mg concentrations between 4.07-5.85 me 100 g^{-1}, the exchangeable K concentrations between 0.20-0.29 me 100 g^{-1}, the exchangeable Na concentrations between 0.19-0.23 me 100 g^{-1}.

The DTPA-extractable micronutrients (Fe, Mn, Zn, Cu)

Ext. Fe concentration of the soils generally increased with the CC treatments according to the control in the cherry orchard (Table 2). Ext. Fe contents (mg kg^{-1}) in the cherry orchard in 2013 was ordered as; HC (19.87) < C (19.89) < MC (20.24) < FA (21.62) < TM (21.84) < FRR (21.86) < TFF (21.88) < VV (23.13) < TR (23.32). As compared to control, percent increases at 0-20 cm soil depth in ext. Fe content varied between 8.7% in FA and 17.3% in TR treatments. The highest ext. Fe content (23.60 mg kg^{-1}) in 2014 was obtained in the TR application while the lowest ext. Fe content (19.56 mg kg^{-1}) was in the HC treatment at 0-20 cm soil depth. As compared to control, percent increases in ext. Fe content at 0-20 cm soil depth varied between 11.3% in FA and 20.1% in TR treatments in the cherry orchard. In addition to exchangeable cations, soil micronutrients also play an significant role in plant yield and growth. Shortage of micronutrients may limit the plant growth and could even cause plant death. The importance of micronutrients to a plant's health has gotten more attention recently with increasing trends of per area basis crop yields. This trend removes very high amounts of micronutrients from the fields, and soils can not be able to compensate this loss naturally. However, cover crops may have a big effect on soil micronutrients and help in their replenishment (Sharma et al., 2018a). The differences in ext. Fe content were not found to be significant for the 20-40 cm soil depth in both years of experiments (Table 3). Ext. Fe contents ranged from 17.49 mg kg^{-1} in control plots to 19.00 mg kg^{-1} in HC treatment for the 20-40 cm soil depth in 2013. Ext. Fe contents ranged from 17.59 mg kg^{-1} in FA treatment to 19.00 mg kg^{-1} in MC treatment for the 20-40 cm soil depth in 2014.

Ext. Mn contents of the soils generally increased with the CC treatments according to the control in the cherry orchard (Table 2). The highest ext. Mn content (12.41 mg kg^{-1}) in 2013 was observed in the TR application while the lowest ext. Mn content (8.17 mg kg^{-1}) was in the HC treatment at 0-20 cm soil depth. As compared to control, percent increases in ext. Mn content at 0-20 cm soil depth in 2013 varied between 12% in FRR and 45% in TR treatments in the cherry orchard. Ext. Mn contents (mg kg^{-1}) in the cherry orchard in 2014 was ordered as; C (8.20) < HC (8.34) < MC (8.43) < FRR (9.36) < FA (9.56) < TM (10.09) < TFF (10.15) < VV (12.19) < TR (12.53) treatments. As compared to control, percent increases in ext. Mn content in 2014 varied between 14.2% in FRR and 52.8% in TR treatments in the cherry orchard. The increase might be due to decline in soil reaction and improved dissolution of Mn compounds. Similar conclusions were also determined by Sidhu and Sharma (2010) and Yadav (2011). In this study, the CC treatments caused notable changes of ext. Mn. Wei et al. (2006) studied the influence of cropping practices on soil micronutrients in China. They suggested an important correlation between cropping practices and plant available micronutrients. Their conclusions indicate that available Fe and Mn consantrations in the surface layer were higher in cropped applications compared to the control treatment. Sharma et al. (2018a) found that CCs have the potential in maintaining the optimum levels of Fe, Mn and Zn in the topsoil as compared to the control. The differences in ext. Mn content were not found to be significant for the 20-40 cm soil depth in both years of experiments (Table 3). Ext. Mn contents ranged from 6.69 mg kg^{-1} in VV treatment to 9.33 mg kg^{-1} in FA treatment for the 20-40 cm soil depth in 2013. Ext. Mn contents ranged from 6.56 mg kg^{-1} in HC treatment to 8.41 mg kg^{-1} in VV treatment for the 20-40 cm soil depth in 2014.

Ext. Zn consantrations of the soils generally increased with the CC treatments according to the control in the cherry orchard (Table 2). Ext. Zn contents (mg kg^{-1}) at 0-20 cm soil depth in 2013 was ordered as; HC (1.43) < C (1.44) < MC (1.46) < FRR (1.52) < FA (1.56) < TFF (1.58) < TM (1.61) < VV (1.80) < TR (1.86). The highest ext. Zn concentrations (1.89 mg kg^{-1}) in 2014 was observed in the TR application while the lowest Zn concentration (1.39 mg kg^{-1}) was in the control at 0-20 cm soil depth. As compared to control, percent increases in ext. Zn over the control soil were between 6.1% in FRR treatment and 29.3% in TR treatment in

2013 and between 13.6% in FRR treatment and 36.7% in TR treatment in 2014. Franzluebbers and Hons (1996) also determined increases in ext. Zn consantration in soil under CC treatments. The differences in ext. Zn content were not found to be significant for the 20-40 cm soil depth in both years of experiments (Table 3). Ext. Zn contents ranged from 0.91 mg kg^{-1} in control plots to 1.17 mg kg^{-1} in TFF treatment for the 20-40 cm soil depth in 2013. Ext. Zn contents ranged from 1.06 mg kg^{-1} in MC treatment to 1.17 mg kg^{-1} in TM treatment for the 20-40 cm soil depth in 2014.

The differences in the ext. Cu concentrations of soils in the cherry orchard were not found to be statistically significant for 0-20 cm soil depths in both years of experiments (Table 2). Ext. Cu content in 2013 varied between 8.81 mg kg^{-1} in HC treatment and 9.81 mg kg^{-1} in TR treatment. Ext. Cu content at 0-20 cm soil depth in 2014 varied between 8.99 mg kg^{-1} in control and 9.59 mg kg^{-1} in TR treatment. Mengel et al. (2001) determined that Cu is taken up by the plants in very little amounts because the Cu requirement of crop plants is relatively low. The differences in the DTPA-extractable Cu of soils in the orchard were not found to be statistically significant for 20-40 cm soil depth in both years of experiments (Table 3). The ext. Cu contents between 5.88-7.89 me 100 g^{-1}.

Relationships among the selected soil properties

Significant positive correlations were observed between total N and EC (0.933**), BSR and EC (0.941**), total N and BSR (0.978**), total N and P (0.948**), EC and P (0.922**), BSR and P (0.972**), total N and ext. Fe (0.939**), P and ext. Fe (0.959**), total N and Mg (0.980**) at the 0-20 cm soil depth in a cherry orchard (Table 4). The positive association between total N, exchangeable Mg, K, Na, and soil micronutrients (Fe, Mn and Zn) indicate an increase in exchangeable Ca, Mg, K and ext. Fe, Mn and Zn consantrations with increasing total N contents. The pH had important negative correlations with EC (-0.840**), total N (-0.777**), BSR (-0.760**), ext. Fe (-0.653**), P (-0.725**), K (-0.694**) and important negative correlations with BD (-0.954**), RS (-0.821**) and PR (-0.869**) at the 0-20 cm soil depth in a cherry orchard (Table 3). Exchangeable Na consantration had important negative correlations with EC (-0.855**), total N (-0.775**), BSR (-0.781**), P (-0.763**), Mg (-0.737**), Ca (-0.591**) and K (-0.686**) at the 0-20 cm soil depth in a cherry orchard. Ext. Cu concentrations gave the lower correlations with all properties. The soil pH and exchangeable Na concentrations decreased with increase in total N, BSR, EC, available P, exchangeable cations (Ca, Mg and K) and the DTPA-extractable micronutrients (Fe, Mn and Zn). These results indicated that other than total N, EC, available P, exchangeable cations (Ca, Mg, K and Na) and the DTPA-extractable micronutrients (Fe, Mn, Zn and Cu) were useful indicators to define soil chemical properties and BSR under different cropping treatments. Correlation matrix among the soil properties in the 20-40 cm soil depth at the end of the experiment was given in Table 5. Significant correlations were observed between EC and BSR (0.379^{**}), between the total N and BSR (0.347^{**}), between the BSR and Na (-0.324^{*}), between EC and total N (0.216^{*}).

Conclusion

The findings of this study indicated that the cover crop managements in a cherry orchard with clay textured soil have ability to contribute to sustainable agriculture production. However, benefits of using cover crops depend on the selection of species (leguminous, non-leguminous and grasses). The cover crop treatments improved the chemical properties and basal respiration of soils at 0-20 cm depth compared to the control. These treatments decreased soil pH and exchangeable Na and increased total N, EC, available P, exchangeable cations (Ca, K, Mg) and the DTPA-extractable micronutrients (Fe, Zn, Mn). Effects of mechanical cultivation and herbicide treatments on chemical properties and basal respiration of soils were not found statistically significant for the 0-20 and 20-40 cm soil depths as compared to control ($p<0.01$). The improvements in soil quality variables were more pronounced with legume and grass cover crops mixture (*T. repens* (40%) + *F. rubra rubra* (30%) + *F. arundinacea* (30%)) than with grass cover (*Festuca rubra subsp. rubra* and *Festuca arundinacea*) treatments. It is clearly known that leguminous and grass crops have positive effects on soil quality variables, but these impacts vary depending on plant species. Therefore, it is very important to select the right cover crop species to enhance the soil quality variables. Researchers needed to demonstrate with farmers for long-term integrated studies that enhancing or maintaining soil productivity with cover crop provides long-term financial benefits. As a conclusion, cover crops especially *Vicia villosa* (VV) and *Trifolium repens* (VV) could be incorporated into cropping systems to improve soil chemical properties, basal respiration and to provide sustainable soil management.

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Accumulating capacity of herbaceous plants of the Asteraceae and Poaceae families under technogenic soil pollution with zinc and cadmium

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Abstract

In this study, the environmental monitoring of the long-term technogenic pollution zone of Novocherkassk, a region containing numerous heavy metal contaminations, was carried out. In the plants growing in the 5 km zone around Novocherkasskaya power station, contamination with the studied elements was revealed. The dependence of the content of Zn and Cd in herbaceous plants of the families *Asteraceae* and *Poaceae* on the distance to the source of the anthropogenic load was established. The selectivity of accumulation of metals by studied species of herbaceous plants at different levels of technogenic pollution is revealed. *Achillea nobilis* has the least pollutants resistant from the soil. *Poa pratensis* has the highest resistance to Zn and Cd pollution in terms of the set of assessment indicators. The granulometric composition of the soil has a significant impact on the availability of metals to plants.

Keywords: Heavy metals, technogenic pollution, soil-plant system.

Introduction

Environmental pollution is one of the most serious problems nowadays. These pollutants are found to be common wherever industrial enterprises or urban infrastructure presented. Emissions from chemical and energy industries are the most significant sources of pollutant release into the environment. Among the chemical elements, heavy metals (HM) are the most toxic; many of them exhibit high toxicity even in trace amount levels (Seregin and Ivanov, 2001; Zhuikova and Zinnatova, 2014). The concentration of HM in the natural environment tends to increase over time due to their persistence and non-biodegradability. For this reason, territories subject to long-term industrial pollution are important cases for research aiming at evaluating the distribution of trace elements in plant communities (Plyaskina, Ladonin, 2005; Chaplygin et al., 2018; Minkina et al., 2018). The risk associated with metals is attributed to an accumulation and toxicity characteristic which makes them remain in the soil for a long time.

Technogenic pollution mainly targets and affects the soil as the basis of any terrestrial ecosystem. The HM contamination of soils can impose major threats to agricultural sectors for a long period of time. Soil-to-crop transfer mechanism of HM is considered as the direct transformation pathway to humans. Food crops grown on the metal contaminated soil can easily uptake and accumulate metals in high quantities which in turn affect food quality and safety. To this end, special attention should be given to herbaceous plants as they represent the majority of agricultural crops and the convenient indicator for studying technogenic stress.

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Moreover, wild herbaceous plants as recourses of livestock feed and raw medicinal can be of a possible threat case to humans and animals.

Zn and Cd are some of the most common HM in industrial emissions related to the first hazard class. Cd and Zn are the most toxic elements that have multiple toxic effects on plants (Andresen and Kupper, 2013; Zhao et al., 2014; Shtangeeva et al., 2019). In addition, these elements demonstrate similar geochemical behavior and have additive properties, replacing each other in the physiological processes in plants. The results of studying the Zn-Cd interaction are controversial since there is evidence of both antagonism and synergism between these elements during absorption and transfer (Andresen and Kupper, 2013; Zhao et al., 2014). For example, there is evidence that Cd is able to replace Zn in many vital enzymatic reactions, leading to their rupture or inhibition. It is assumed that Cd-Zn interaction mechanisms are controlled by the ratio of their concentrations in the plant habitat, the physico-chemical properties of the soil, and the biological characteristics of the absorbing plants (Kabata-Pendias and Pendias, 2001; Maksimov et al., 2018). Interdependent physico-chemical and biological factors affect the release of metal ions into soil solution and, therefore, the capacity of plants to absorb them from the soil would increase.

The aim of the work is to study the accumulation of Cd and Zn in various species of wild herbaceous plants of the *Asteraceae* and *Poaceae* families under long-term technogenic pollution.

Material and Methods

The object of the present work is soil of monitoring plots laid at a distance of 1-20 km from Novocherkassk Power Station (NPS). It is the largest enterprise in the south of Russia. This enterprise emits 1% of all pollutants into the atmosphere in the Russian Federation, over 50% in Rostov Region, and about 90% in Novocherkassk (Environmental Bulletin, 2018).

Monitoring plots were laid at a distance of 1-20 km from NPS. The choice of the plots was done in accordance with the air sampling plot conducted within the project in order to organize and set a sanitary protection zone of the northern industrial hub in Novocherkassk. Besides, all herbaceous plant species under investigation were grown on the chosen monitoring plots. Plant samples were collected in accordance with the prevailing north-west direction of the winds at monitoring plots No. 4, No. 8, No. 9, No. 10, and plot No. 5, located close to this direction. Points No. 1, No. 2, No. 3, No. 7, No. 11, No. 12, No. 16, and No. 17 were laid at a distance of 1-3 km from NPS in various directions to determine the pollution level of the territories located to the side away from the prevailing wind direction. Plot No. 10 was located 400 meters from the highway. Over the decades of vehicle emissions, a significant amount of HM has entered the soil of plot No. 10, which currently continues to move from soil to plants as an additional source of anthropogenic load. Plot No. 9 was selected as the background due to its great remote location (15 km) from the NPS and the absence of additional sources of pollution.

The soils at the monitoring plots were represented by Haplic Chernozem, Meadow-Chernozemic, and alluvial soil. Haplic Chernozem (plots No. 1, No. 4, No. 5, No. 7, No. 9, No. 10, No. 16, and No. 17) has 3.6 – 4.2% humus content, 50.6 – 56.3% physical clay, 40.4 – 44.6% silt, 0.5–1.1% $CaCO_3$, 7.4–7.7 pH, 31–36 cmol (+)/kg CEC. Meadow-chernozemic soils was monitored at plots No. 3, No. 6, No. 8, No. 11 with 4.2–5.1% humus content, 65.3–67% physical clay, 44.0–49.3% silt, 0.2–0.7% $CaCO_3$, 7.3–7.7 pH, 31–45 cmol (+)/kg CEC. Alluvial soil of the Tuzlov river floodplain (plots No. 2, No. 12) was characterized to have 1.3–3.1% humus content, 7.5–7.9 pH, 5.9–6.9% physical clay, 0.9–2.9% silt, 0.4–0.5% $CaCO_3$,12–21 cmol (+)/kg CEC.

Study objects were grass plants of the *Asteraceae* family and *Poaceae* family. Plants of these families were found to be predominant at the monitoring plots including ragweed (*Ambrosia artemisiifolia* L.), Austrian wormwood (*Artemisia austriaca* Pall. Ex. Wild.), Noble yarrow (*Achillea nobilis* L.), and common tansy (*Tanacetum vulgare* L.), as well as bluegrass (*Poa pratensis* L.) and creeping wheatgrass (*Elytrigia repens* (L.) Nevski). Plant samples were collected in triplicate in the second half of June during the mass flowering stage. The sampling period was chosen due to the fact that the maximum entry of elements into the plants takes place at this stage (Ilyin and Syso, 2012).

The Cd and Zn are the metals of the first hazard class found remarkably in the emissions of NPS (Environmental Bulletin, 2018). The content of these metals was determined in the samples of plants and soils. Mineralization of plant samples was carried out by the dry ashing method according to GOST 26929-94. Afterward, HM were extracted from ash by dissolving in a 20% HCl solution with further determination using atomic absorption spectrophotometry (AAS) (Guidelines for the determination..., 1992). The HM pollution in plants was assessed by comparing the concentration of elements in plants with the maximum permissible level (MPL) of metal content in farm animals feed (Provisional maximum permissible levels..., 1987).

The total content of Cd and Zn in soil samples was determined by the X-ray fluorescence method. The loosely bound HM compounds in soil, the most available for plants, include exchangeable, complex, and specifically adsorbed forms. The loosely bound HM compounds determined by parallel extraction using the reagents by the method of Minkina (2018): 1 M ammonium acetate buffer (NH_4Ac) at pH 4.8 (soil:solution ratio = 1:5, extraction time of 18 hours) capable of extracting exchangeable metal forms; a 1% solution of EDTA in NH_4Ac at pH 4.8 (soil: solution ratio = 1:5, extraction time of 18 hours) which along with the exchangeable forms of metals supposedly extract their relatively fragile complex compounds into the solution; and acid-soluble metal compounds extracted with a solution of 1 M HCl (soil: solution ratio = 1: 10, extraction time of 1 h). Based on the difference between the metal content in HCl and NH_4Ac extracts, the content of specifically adsorbed metal compounds was calculated. The content of metals in firmly bound compounds was determined as the difference between the total amount of metals in soils and their loosely bound HM compounds. The metal content in extracts from soils was determined by AAS.

The reaction of plants to the content of elements in the medium depends on the barrier and/or non-barrier type of their uptake by the plant. The non-barrier uptake of chemical elements and their compounds to a certain concentration is a widespread phenomenon (Zhuikova and Zinnatova, 2014). Plants have barriers to the absorption of most elements due to specific physiological and biochemical mechanisms (Ghazaryan et al., 2019). Roots, as a rule, are characterized by non-barrier uptake, while the aerial part follows the barrier one.

To characterize the accumulating capacity of plants, the accumulation coefficient (AC) was used, which is presented as the ratio of the metal content in plant roots to the content of its mobile forms in the soil. This indicator reflects the root intake of metal ions from the soil into the underground organs. Loosely bound compounds of elements in the soil are taken into account for this indicator as these are the ones that are available to plants (Minkina et al., 2008). The choice of these compounds was due to the close correlation of their content in the soil with content in plants was established, while for the total content it was characterized as medium and low (Nkongolo et al., 2013). In the case of a high root barrier, the AC is <1. When the entry of metal ions into plant organs is not hindered, the AC is ≥ 1.

The distribution of metals in plant organs was assessed by the value of the distribution coefficient (DC) as it calculated by the ratio of HM content in the root system to the aerial part of the plant (Kabata-Pendias, Pendias, 2001).

Results and Discussion

The studies of soils at monitoring plots revealed the presence of long-term HM pollution. Plots located at a distance of 5 km to the north-west of the NPS and those adjacent to them are characterized by a content of total Zn exceeds approximate permissible concentrations in 1.1-1.4 times (GN 2.1.7.2511-09, 2009) (Figure 1). It was found that the content of Cd exchangeable forms exceeded the maximum permissible concentrations in 1.2–7.0 times (GN 2.1.7.2042-06, 2006), while no pollution was observed in terms of total content, which was probably due to the high mobility of the element in the soil. Loosely bound compounds were accounted for 12-57% of total Zn content and 22.5-59.5% total Cd content (Figure 2). Monitoring plots No. 4, No. 5, No. 6 and No. 7, which were closest to the source of emissions in the north-west, north-north-west and north directions, demonstrated the maximum content of loosely bound compounds of HM. This indicated an increase in the mobility of elements in soils under technogenic load. A general tendency toward an increase in the portion of more mobile forms (exchangeable and complex forms) with the rise in the total HM content is observed. The HM concentration at the plots farthest from the emission source corresponded to their background level. A larger part of the HM (95–98%) is firmly fixed by the soil components. Loosely bound Cd compounds were mainly represented by specifically metal adsorbed form.

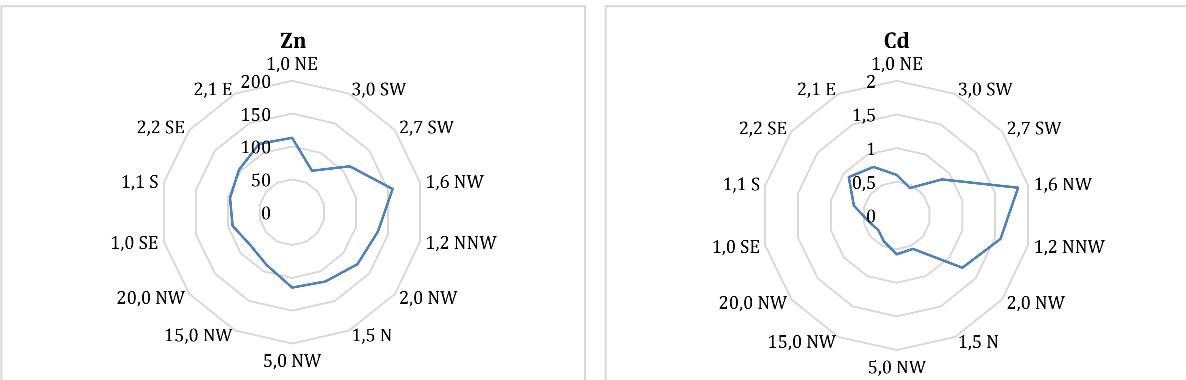

Figure 1. Total content of Zn and Cd in 0-20 cm soil layer of the different monitoring plots, mg kg^{-1}

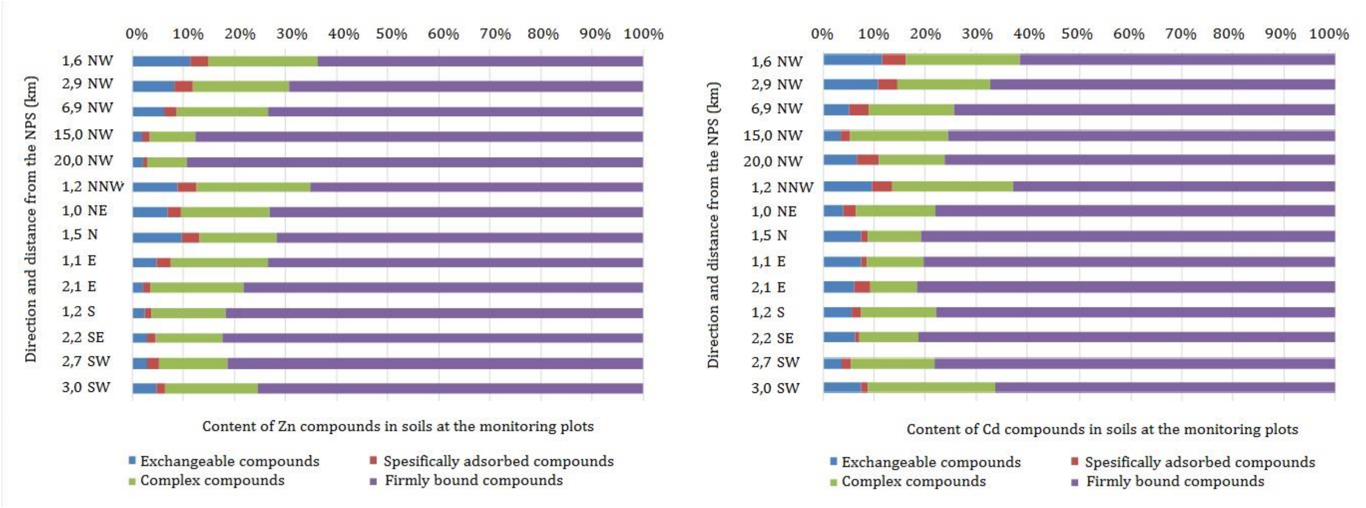

Figure 2. The content of Zn and Cd compounds in soils at the monitoring plots, %

The dependence of the metal content in soils on the particle size distribution was determined. The content of elements in alluvial sandy soils at plots No. 2 and No. 12 was lower than at neighboring monitoring plots located approximately at the same distance from the NPS and represented by chernozem and meadow-chernozemic soils of heavy loam and light clay size distribution (Figure 1).

The dependence between HM content in plants and the level of the anthropogenic load was also established. With the distance from the NPS the content of elements in plants decreases to their average content in grassy plants of Rostov Region (Environmental Bulletin, 2018). Due to the selectivity of the element accumulation, different types of plants accumulated various amounts of HM in their organs (Minkina et al., 2018), therefore, representatives of several herbaceous plant species were studied (Figure 3, 4).

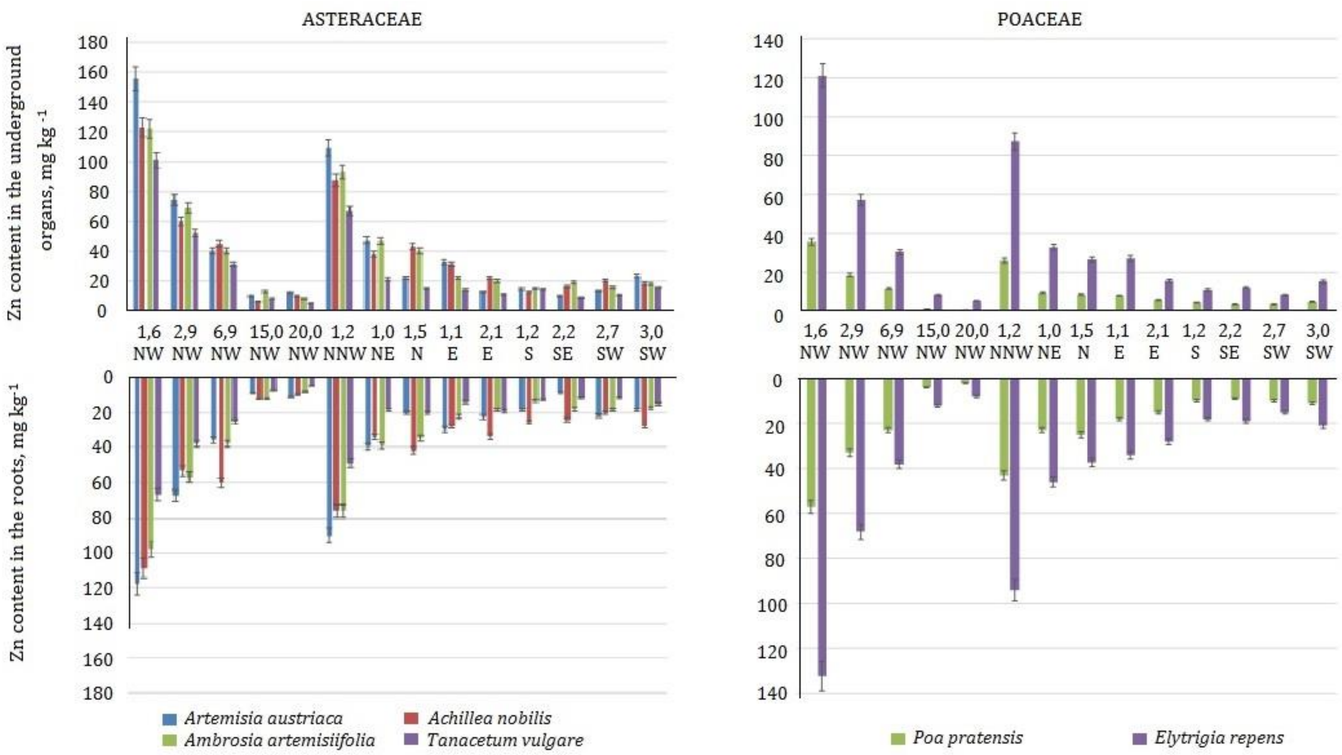

Figure 3. The Zn content in various species of wild herbaceous plants at the different monitoring plots, mg kg $^{-1}$

At monitoring plots No. 4, No. 5, and No. 6, where the greatest technogenic load experienced, Zn pollution (from 1.2 to 3.1 MPL) was established for all plant species studied, except for bluegrass. It is important to note that the MPL excess for this element was recorded only under maximum technogenic load, while at the other monitoring plots, Zn content corresponded or did not exceed the background content (Figure 3). Plants of the *Asteraceae* family demonstrated a higher Zn content, compared with the *Poaceae* family. Zn accumulated mainly in the aerial parts of *Asteraceae* family plants, while plants in the *Poaceae* family were characterized by Zn accumulation predominantly in the root system. The highest metal content was characteristic for wormwood; the minimum Zn content was found in bluegrass. The content of Zn in plants was two times higher than that of Cd. This could be associated with the high demand of Zn in plants for performing a number of biological functions (Figure 3, 4).

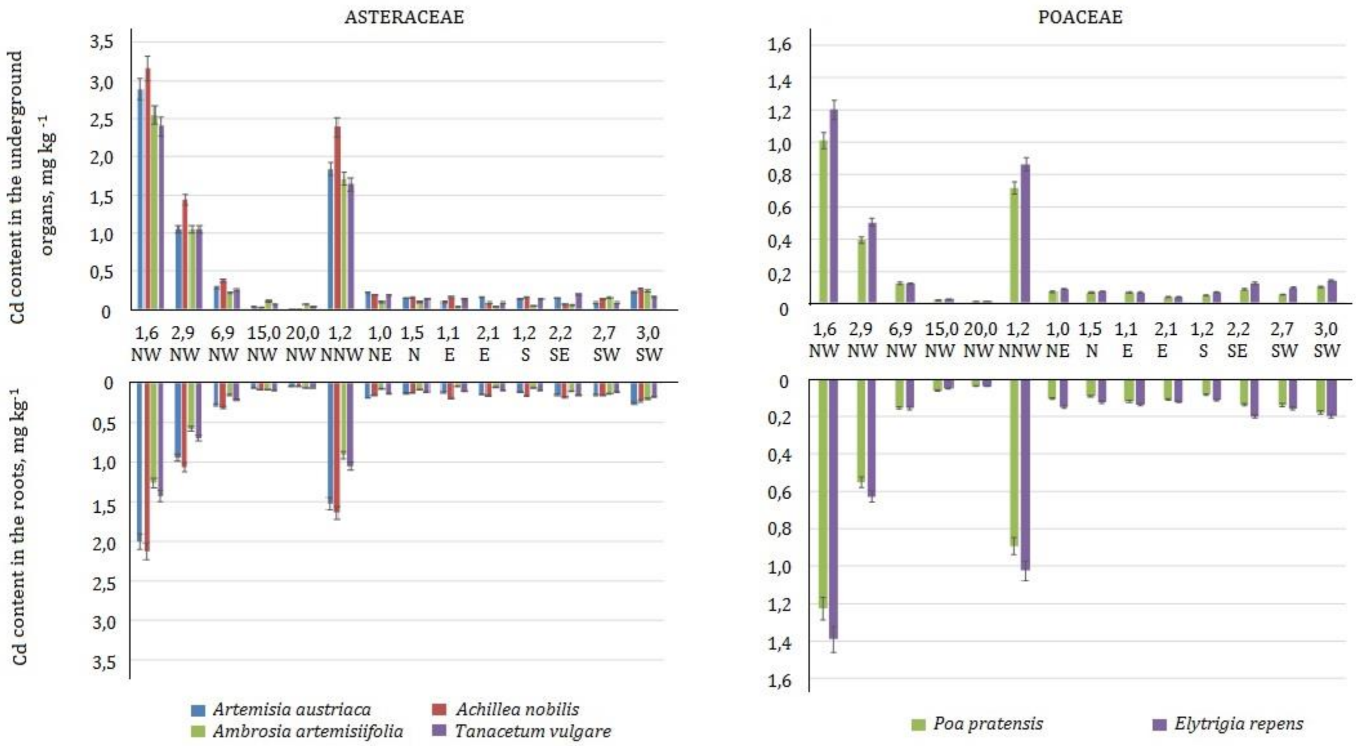

Figure 4. The content of Cd in various species of wild herbaceous plants at the different monitoring plots, mg kg^{-1}

The excess of MPL for Cd was detected in all studied plant species. It was found to be 3.5–9.6 times for wormwood, 1.3–10.5 times for yarrow, 3.5–8.5 times for ragweed, 3.5–8.0 times for tansy, 2.7-4.0 times for wheatgrass and 1.3-3.4 times for bluegrass. Under Cd pollution, a clear localization of contaminated plants was also observed at monitoring plots that were severely affected by technogenic pollution. Wormwood and yarrow demonstrated either slight excesses of MPL for Cd or relatively close to the threshold within the entire 5 km zone. Cd, similar to Zn, was predominantly accumulated in the aerial parts of plants of the *Asteraceae* family and in the root system of the *Poaceae* family. The maximum concentration of Cd was detected in yarrow, while the minimum was observed in bluegrass.

The selectivity of accumulating HM by plants depending on the level of anthropogenic load and plant species along with their associated biological barriers (Kabata-Pendias and Pendias, 2001). They are created by plants to regulate the number of nutrients entering the body in order to avoid accumulating phytotoxic concentrations of HMs. They identify the resistance of plants to anthropogenic pollution. The first of these barriers is located at the soil–root system boundary. The effect of this barrier determines the amount of HM in which the plants can uptake since the soil is the main source of elements entering them. For this reason, the entry of Zn and Cd into plants from the soil was studied.

The most objective of the indicators that makes it possible to evaluate the effectiveness of "soil-root system" barrier is AC. Based on the AC data obtained, the maximum translocation of HM from the soil to the plants was observed at the plots located in accordance with the prevailing wind direction and within 5 km from the NPS (Figure 5). For Zn, AC>1 was observed in all plants, except tansy and bluegrass. The highest coefficient values were obtained for creeping wheatgrass, while bluegrass was characterized by minimum Zn accumulation. This indicates that the selectivity of the element accumulation by plants is manifested not only at the family level but also at the species level. A possible reason for the feature established for tansy may be the atmospheric influx of HM into the plant, which is not taken into account by the value of AC.

Values of AC>1 for Cd were calculated for all plants under the investigation, which indicates the active uptake of HM from the soil. The noble yarrow was characterized by the highest values of AC for Cd and had AC> 1 at most monitoring plots. The lowest coefficient values were determined for bluegrass, as in the case of AC for Zn. Wormwood and yarrow had significantly higher AC values, compared with the rest of the plants under the study. Tansy and ragweed had approximately the same level of AC values equivalent to those of bluegrass and wheatgrass. This observation confirms the fact that the level of anthropogenic load and the plant species, as well as the properties of the element itself, impact the entry of HM into plants.

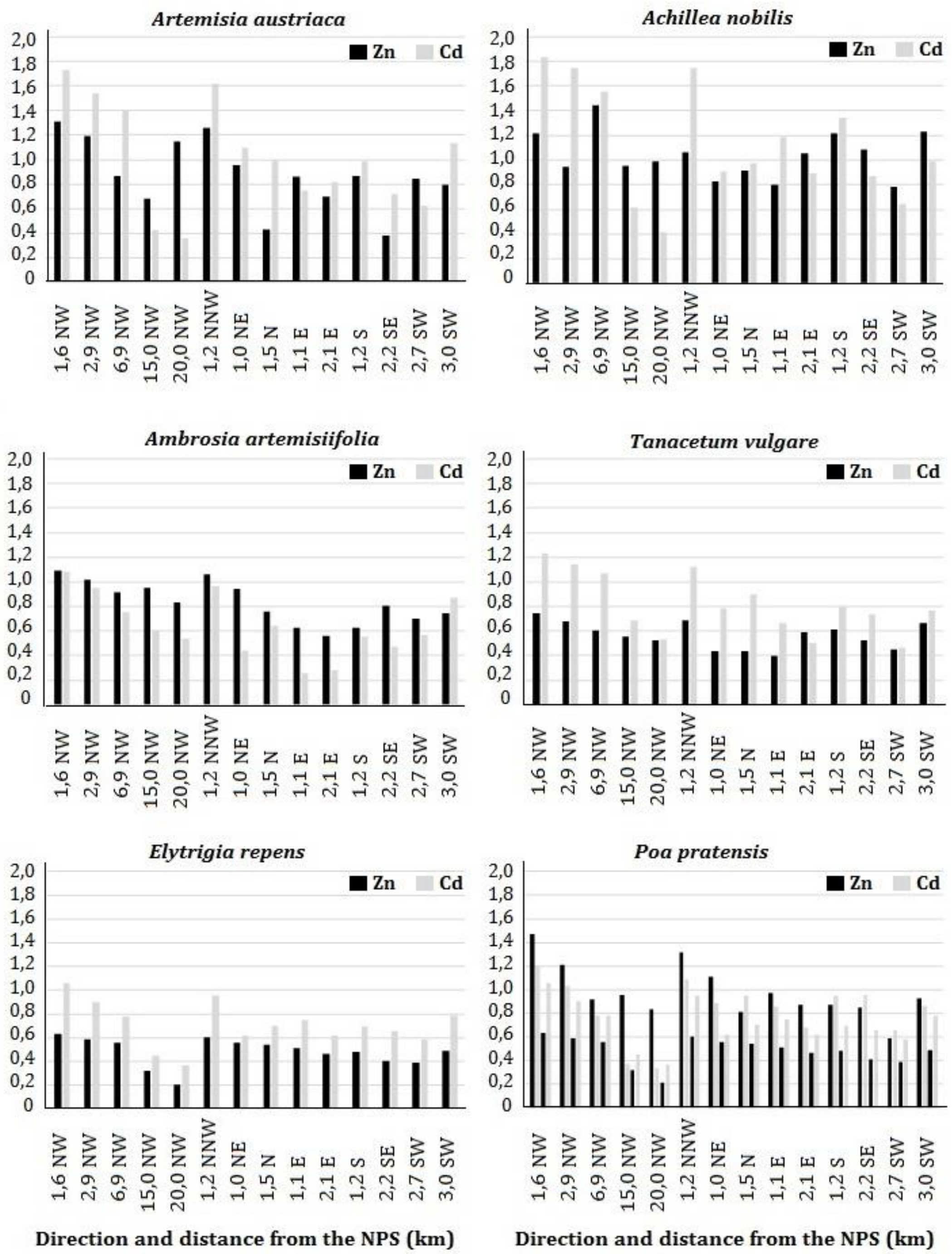

Figure 5. The accumulation coefficient (AC) of Zn and Cd in various species of wild herbaceous plants at the different monitoring plots

Another important factor affecting the accumulation of HM by a plant is the particle size distribution of the soil (Burachevskaya et al., 2019). At plots No. 2 and No. 12, represented by alluvial soil, a higher accumulation of Zn and Cd in plants was observed compared to neighboring plots. This dependence was more pronounced in plants of the *Poaceae* family. Among the *Asteraceae* family, yarrow and tansy demonstrated this dependency most clearly. Apparently, this was due to the fact that soils of light particle size distribution did not retain the fixing HM well, leaving them in forms available to plants.

The second barrier to HM entry into plants is located at the root system - aboveground part border. It determines the nature of element distribution in the organs of the plant and indicates the internal stability of the plant. The calculated DC values make possible to assess the degree of translocation of elements from the root system to the aerial part of the plants under the study (Table 1). It was established that although Zn translocation from plant roots to the aboveground organs varied depending on the level of anthropogenic load, its general tendencies remained the same for all plant species under study. At monitoring plots experiencing the greatest technogenic stress (No. 4, No. 5 and No. 6), tansy, wormwood, and ragweed were characterized by maximum DC values. The bluegrass was observed at minimum values. At plot No. 9, considered as the background, maximum and minimum DC values were distributed in a similar way. In general, ragweed, tansy, and wormwood demonstrated the most intense Zn translocation from the roots, whereas bluegrass and wheatgrass possessed the least intense Zn translocation. It should be noted that although tansy, along with wormwood and ragweed, had a high Zn content in the aerial parts and one of the highest DC indices, the AC for this plant was significantly lower than that of other representatives of the *Asteraceae* family. This pattern indicates a lower resistance of the tansy to technogenic pollution with Zn.

Table 1. The distribution coefficient (DC) of Zn in various types of wild herbaceous plants at the different monitoring plot

Plot no., direction and distance from the NPS (km)		*Artemisia austriaca*	*Achillea nobilis*	*Poa pratensis*	*Ambrosia artemisiifolia*	*Tanacetum vulgare*	*Elytrigia repens*
				Zn			
1.	1.0 NE	1.19	1.11	0.40	1.21	1.17	0.71
2.	3.0 SW	1.30	0.65	0.41	1.06	1.02	0.71
3.	2.7 SW	0.62	1.02	0.34	0.89	0.91	0.53
4.	1.6 NW	1.32	1.13	0.63	1.24	1.51	0.92
5.	1.2 NNW	1.21	1.15	0.60	1.22	1.37	0.93
6.	2.9 NW	1.11	1.13	0.55	1.21	1.37	0.84
7.	1.5 N	1.10	1.02	0.34	1.14	0.75	0.71
8.	6.9 NW	1.12	0.75	0.50	1.05	1.24	0.80
9.	15.0 NW	1.16	0.50	0.25	1.08	1.14	0.67
10.	20.0 NW	1.09	1.05	0.15	1.00	1.00	0.63
11.	1.2 S	0.81	0.50	0.41	1.15	1.14	0.60
12.	1.1 E	1.09	1.11	0.43	1.00	1.00	0.79
13.	2.2 SE	1.19	0.68	0.38	1.06	0.76	0.63
14.	2.1 E	0.57	0.65	0.37	1.11	0.58	0.55
				Cd			
1.	1.0 NE	1.13	1.21	0.69	1.39	1.35	0.60
2.	3.0 SW	0.88	1.19	0.57	1.22	0.92	0.71
3.	2.7 SW	0.58	0.87	0.39	1.09	0.83	0.61
4.	1.6 NW	1.44	1.49	0.82	2.02	1.68	0.86
5.	1.2 NNW	1.21	1.46	0.80	1.88	1.56	0.84
6.	2.9 NW	1.12	1.36	0.71	1.81	1.51	0.80
7.	1.5 N	1.07	1.19	0.73	1.16	1.13	0.61
8.	6.9 NW	1.04	1.24	0.81	1.47	1.19	0.79
9.	15.0 NW	0.72	0.44	0.37	1.30	0.84	0.55
10.	20.0 NW	0.36	0.33	0.31	1.41	0.79	0.34
11.	1.2 S	1.10	0.98	0.62	0.94	1.39	0.62
12.	1.1 E	0.83	0.84	0.57	1.16	1.19	0.49
13.	2.2 SE	0.97	0.45	0.62	0.69	1.27	0.62
14.	2.1 E	1.03	0.55	0.38	0.88	1.03	0.33

Under technogenic pollution, the highest Cd translocation was observed in ragweed, yarrow, and tansy, and the lowest level was established for bluegrass (Table 1). At plot No. 9, ragweed, tansy, and wormwood had the maximum DC values while bluegrass was characterized by the least intense Cd translocation from the roots to the aerial part as in case of the increased anthropogenic load. In general, the highest and lowest Cd translocation among the studied species was established for ragweed and bluegrass, respectively. Thus, for the plants of the *Asteraceae* family, there was a significantly higher accumulation of Zn and Cd, as well as translocation of these HM from roots to aboveground organs, compared to the *Poaceae* family. Bluegrass (*Poa pratensis* L.) according to this indicator was the most resistant plant to HM pollution.

Conclusion

High levels of soil pollution lead to excessive accumulation of heavy metals in the plants. Long-term technogenic pollution is established at NPS. The negative effects of emissions from NPS affect wild herbaceous plants growing within a 5 km zone, primarily in the north-west direction. The Zn and Cd were found to be the priority soil contaminants of the territories under study. Plant species specificity with respect to the studied pollutants was revealed. Plants of the *Asteraceae* family were found to accumulate larger amounts of HM than that of the *Poaceae* family. The *Asteraceae* family demonstrated the predominant accumulation of Zn and Cd in the aerial part, while the *Poaceae* family accumulates them in the root system. Ragweed, wormwood, and tansy were found to be characterized by the greatest translocation of elements from the roots to the aboveground parts, as a consequence, demonstrating low resistance to HM pollution. The least resistance to HM entry from the soil is established for yarrow noble. Bluegrass demonstrates the highest resistance to Zn and Cd pollution in terms of the aggregate DC and AC indicators. The light granulometric composition of soil contributed to greater HM availability to plants. Along with general patterns, specific features of Zn and Cd accumulation by plants were revealed. The Cd exhibited a noticeably greater mobility in soils than Zn, which led to a higher level of plant contamination and higher AC values. A successful integrated approach suggested in for studying Zn and Cd accumulation along with consideration of plant barrier functions pave the way to successfully predict the negative effects of technogenic environmental pollution in the future.

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Changes in selected soil properties across a chronosequence of exclosures in the central dry lowlands of Ethiopia

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Abstract

In Ethiopia, rehabilitation of the natural resource-base in degraded lands through area exclosures has become a necessary intervention, albeit empirical studies on the impact of these exclosures are limited. This study was conducted to investigate changes in selected soil properties along exclosures' age and slope positions in Kewet district, central dry lowlands of Ethiopia. Soil samples were collected from three slope positions of three purposively selected exclosures of 5, 15 and 20 years old and one adjacent open grazing land from 0-10 cm soil depth for analysis of pertinent soil properties. The effect of exclosure age on bulk density, contents of sand, clay, organic carbon, total nitrogen, available phosphorus, CEC, and exchangeable Mg+ and K+ was significant ($P<0.05$). All exclosures had low bulk density (1.14-1.16 g cm^{-3}) as compared to the grazing land. Higher available water content (173 mm m^{-1}) was recorded in the old exclosure. Soil organic carbon ranged from 2.58% (young exclosure) to 3.37% (middle age exclosure). Soil total nitrogen increased from 0.24-0.34%, while available phosphorus increased from 27-34%, from young to the old exclosure respectively. However, the influence of exclosures' age on other soil properties was not significant. The young exclosure had the highest CEC (57 $cmol_c$ kg^{-1}), whereas the grazing land had the highest total nitrogen and exchangeable Ca^{2+}. From this result, it can be concluded that area exclosures, if managed properly, can improve some of the dynamic soil properties of open degraded grazing lands in the dry lowlands of Ethiopia.

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Introduction

Land degradation is widely recognized as a global problem occurring in most terrestrial biomes and agro-ecologies (Nkonya et al., 2015). Land degradation refers to processes that diminish the capacity of the land to perform essential functions and services of ecosystems (Hurni et al., 2010). In Ethiopia, land degradation has been identified as the most serious environmental and economic problem (Gebrehiwot and van der Veen, 2013). Deforestation, unsustainable land-use practices on deforested lands (Haile et al., 2006), traditional practice of free grazing and population pressure (Taddese, 2001), limited agricultural inputs per unit area combined with rapid population growth (Nyssen et al., 2009) have been cited as the major contributing factors for land degradation in the Ethiopian highlands.

The disturbance of natural ecosystems in Ethiopia causes widespread soil degradation (soil erosion, nutrient depletion, and salinization) (Girmay et al., 2008), and ecosystem services (Mekuria et al., 2018). Particularly, soil loss, nutrient depletion, and a decline in soil quality are some of the manifestations of land degradation (Haile et al., 2006). Soil fertility depletion is one of the most important consequences of land degradation (Girmay et al., 2008). Land degradation resulted in erosion induced soil carbon depletion at a rate of up to 970 kg ha^{-1} (Shiferaw et al., 2013). As a result of land degradation due to deforestation, the country loses 30

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kg of nitrogen and 15 - 20 kg of phosphorous ha^{-1} yr^{-1} (Haile et al., 2006). The effects of land degradation also include sedimentation of reservoirs and the sediments are prone to gully erosion (Hurni et al., 2010). The average annual rate of deforestation in Ethiopia is estimated to be around 1.25% (FAO, 2015). Therefore, environmental rehabilitation becomes a necessary intervention to combat the fast deterioration of the natural resource base in the country.

Since the 1980s, restoration of degraded lands of steep slopes through interventions that involve area exclosures have been a common practice in many parts of Ethiopia (Descheemaeker et al., 2006b). Area exclosure refers to a practice of land management whereby humans and livestock are excluded from openly accessing severely degraded lands to promote natural regeneration of vegetation cover and foster natural ecological succession (Aerts et al., 2009; Mekuria et al., 2018). Excluding degraded lands from livestock and human interference is commonly performed in two forms; 1) without additional management activities and 2) involving the planting of seedlings, aerial seeding, and construction of soil water and conservation structures (Lemenih and Kassa, 2014). The second form of exclosure speeds up succession through modification of microclimate and soil conditions.

Exclosures are believed to play a significant role in restoring soil fertility, limiting nutrient loss, and reducing soil erosion (Damene et al., 2013; Mekuria et al., 2018). The response of selected soil properties to exclusion of degraded lands from interference depends largely upon plant community composition and climate, and most likely initial soil conditions (Raiesi and Riahi, 2014). Studies have suggested that soil organic carbon (SOC) and total nitrogen (TN) (Damene et al., 2013) and available phosphorus (AP) (Mekuria et al., 2007), were influenced positively by excluding degraded lands from human and livestock interference. The improvement of soil nutrient content is attributed to the high sediment trapping capacity (i.e., relatively fertile) of exclosures (Nyssen et al., 2008).

Rehabilitation efforts of open degraded grazing lands in the Kewet district were initiated in the early 1990s (Bizuayehu and Tefera, 2013). Despite the potential role of exclosures in the recovery of vegetation and improvement of soil nutrients, some studies have indicated that the impact of exclosure on soil properties is not consistent. For example, (Aynekulu et al. 2017) did not find any difference in SOC and TN between exclosure and the adjacent open grazing land. Mekuria et al. (2007) and Raiesi and Riahi (2014) have also reported a lack of difference in soil properties among exclosures and open grazing lands. Slope position is one of the factors that affect soil properties. Mostly, area exclosures are situated at the moderately to very steep slope landscapes (Descheemaeker et al., 2006b) from shoulder to foot slope positions. Studying the change of soil properties along a chronosequence of exclosures and slope position may elucidate the role of exclosures in restoring soil fertility on degraded landscapes. This may create more opportunities to evaluate the effectiveness of area exclosures on the rehabilitation of degraded lands and to improve their management for better ecosystem services in the dry low land areas. Such baseline information is useful to assist policymakers to recognize and consider the value of exclosures as necessary parts of packages of activities in natural resource planning and management (Appanah et al., 2015). Therefore, this study was conducted to investigate the change in some selected soil physical and chemical properties along area exclosures' ages and slope positions in the central dry lowlands of Ethiopia.

Material and Methods

Site description

Kewet district is located at 213 km northeast of Addis Ababa at the foot of the western escarpment of the Ethiopian highlands within the coordinates of 9°49' and 10°11' latitude North and 39°45' to 40°6' longitude East in the Amhara National Regional State (Figure 1). Elevation of the district ranges from 1062 to 3148 m a.s.l. The area is characterized by a dry lowlands climate with an average annual rainfall of 916 mm and annual mean minimum and maximum temperature of 16 and 31^{0}C, respectively (Figure 2). The district covers an area of about 74600 ha of land.

Kewet district is situated at Robit marginal graben (small rifts), which is widely covered by transitional and sub-alkaline basalt with minor rhyolite and trachyte eruptive developed from early Tertiary age basalt rock (Tefera et al., 1996). All alluvial and colluvial deposits that occur in the valley are derived from these rocks. Eutric Cambisols and Pellic Vertisols are the dominant soil groups at the alluvial fan area of the district, while the lower Piedmont areas are dominantly covered by Calaric Gleysols and Calcic Cambisols (Paris, 1986). Over 41 and 26% of the district's land is covered by cultivated land, and forest and shrubland, respectively.

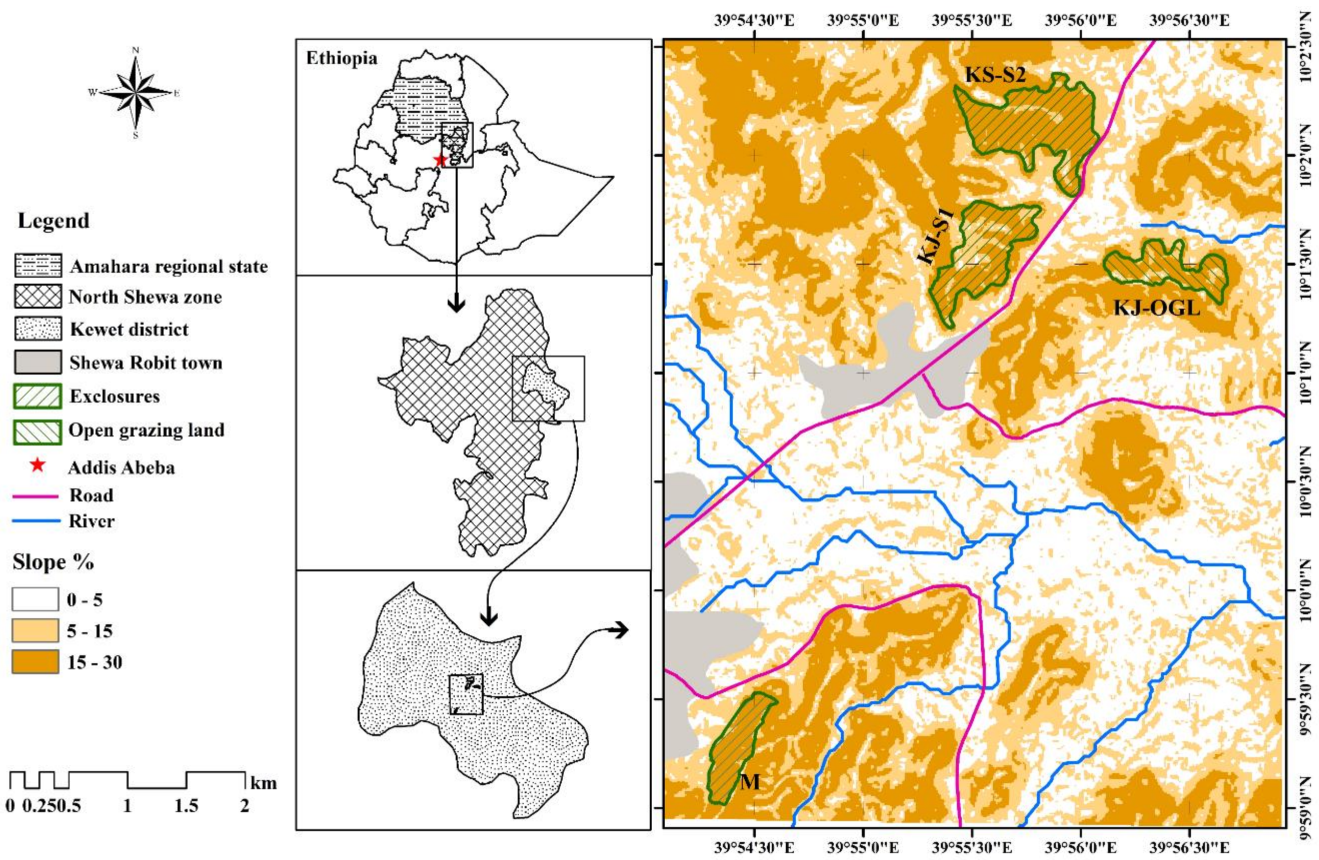

Figure 1. Location map of the study area: M = Merye old exclosure, KJ-S1 = Karajejeba middle age exclosure, KJ-S2 = Karajejeba young exclosure and KJ-OGL = Karajejeba open grazing land.

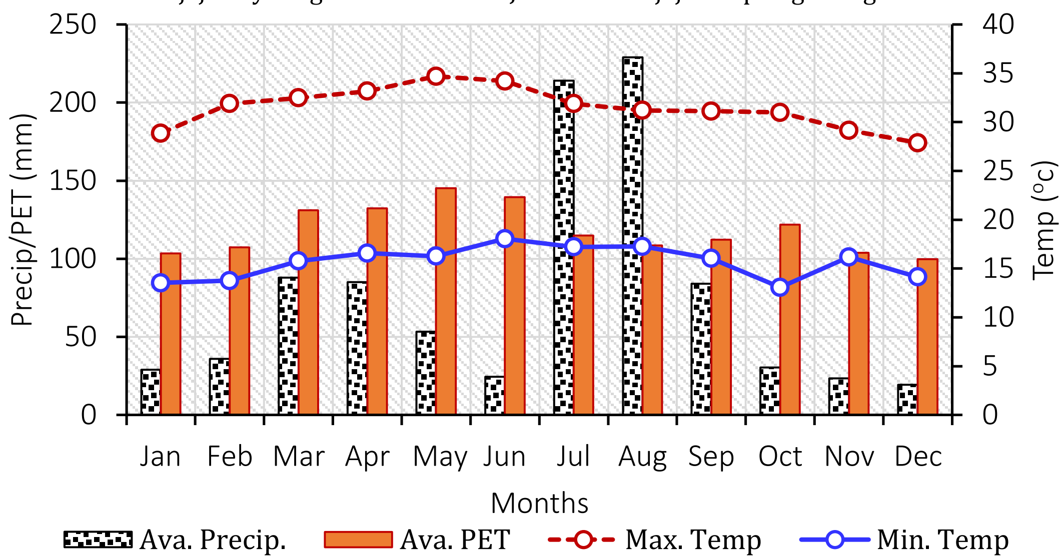

Figure 2. Monthly average rainfall (mm) and monthly maximum, minimum and average temperature (°C) at Kewet district (2006-2017). *Source*: Ethiopian National Meteorology Agency.

Experimental design

For the purpose of this study, three exclosure sites of different age class which are about five years old (Karajejeba site 2), 15 years old (Karajejeba site 1), and 20 years old (Merye) were selected from Kewet district. Concurrently, as a baseline, one open grazing land adjacent to the respective exclosures was also selected. A detailed description of each exclosure is presented in Table 1. All exclosures and open grazing land exist on a moderately steep slope (15-30%) gradient (Figure 1). The exclosures are dominated by woody species such as *Acacia senegal, Acacia nilotica, Acacia brevispica, Acacia tortilis, Acacia etbaica, Ehretia cymosa* and *Dichrostachys cinerea* (Ibrahim et al., 2018, unpublished). These exclosures were open degraded grazing land-use systems before they were excluded from free access to domestic animals and humans.

Table 1. Description of exclosures used for studying a change in soil properties in Kewet district, central dry lowlands of Ethiopia

Exclosure	Site Name	Location	Year Est.	Area (ha)
Open grazing land	Karajejeba	10° 01' 29"N and 39° 56' 23"E	-	-
Young exclosure	Karajejeba	10° 02' 08"N and 39° 55' 49"E	2011	~ 60
Middle exclosure	Karajejeba	10° 01' 28"N and 39° 55' 32"E	2009	~ 44
Old exclosure	Merye	09° 59' 11"N and 39° 54' 22"E	1996	~ 20

To locate the sampling points in each exclosure and the adjacent open grazing land, three parallel line transects perpendicular to contour lines were laid systematically. At regular distances along each transect lines, three sampling points representing three slope positions i.e., upper (shoulder), middle (backslope), and lower (foot slope) were located. Approximately 0.5 kg of composite sample was obtained from each sampling points from 0–10 cm soil depth. These composite soil samples were air-dried at room temperature (25^{0}C) and passed through different mesh sizes based on the requirements for chemical analysis. Additional undisturbed core samples collected using a cylindrical soil core were taken from 0 - 10 cm depth for determination of bulk density and soil water retention at field capacity.

Soil analysis

Particle size distribution was determined by the Bouyoucos hydrometer method (Bouyoucos, 1962). Textural class names were determined using the USDA soil texture triangle. Soil bulk density was determined by the core method (Blake and Hartge, 1986) and Total soil porosity was calculated as shown below (Landon, 2014):

$$\text{Total porosity}(\%) = \left[1 - \left(\frac{\text{bulk density}}{\text{Particle density}}\right)\right] \times 100$$

Soil water retention at -1/3 (field capacity (FC)), -1, -3, -5 and -15 (permanent wilting point (PWP)) bar was determined using pressure-membrane extraction following the procedure mentioned in van Reeuwijk (2002). Available water content (AWC) was calculated using the following formula (Lal and Shukla, 2004):

$$\text{AWC}(\text{mm}/\text{m}) = 1000 \times \left[\frac{(\theta_{FC} - \theta_{PWP})}{100} \times \frac{\rho_b}{\rho_w}\right]$$

where ρb (g cm^{-3}) is the overall bulk density of soil, ρw (g cm^{-3}) is the density of water, θ FC (% on mass basis) is field capacity, θ PWP (% on mass basis) is the permanent wilting point, and D (cm) is the depth of soil. 1000 is a conversion factor to mm m^{-1}.

Soil pH was measured in water suspension of 1:2.5 (soil:liquid ratio) using a pH meter (glass–calomel combination electrode) as described in Thomas (1996). Soil electrical conductivity (EC) was determined from the saturated paste extract using conductivity meter (Rhoades, 1996). Calcium carbonate ($CaCO_3$) was measured by the rapid titration method (Allison and Moodie, 1965). Soil organic carbon (SOC) was determined according to the Walkley and Black method (Nelson and Sommers, 1982). Determination of total nitrogen (TN) was done following the Kjeldahl digestion method (Bremner and Mulvaney, 1996). The Olsen and Dean (1965) bicarbonate extraction was used to analyze available phosphorus (AP) using a spectrophotometer. Cation exchangeable capacity (CEC) was estimated titrimetrically by distillation of ammonia that is displaced by sodium (Chapman, 1965). Exchangeable calcium (Ca), magnesium (Mg) and potassium (K) were determined from the extraction of 1 M ammonium acetate (NH_4OAc) solution buffered at pH 7.0. Exchangeable Ca and Mg were read using atomic absorption spectrometry, while K was read using the flame photometry (Thomas, 1982).

Statistical analysis

The various data on soil chemical and physical parameters were subjected to two-way analysis of variance (ANOVA) following the general linear model (GLM) procedure. Post Hoc Test of Tukey's Honest Significant Difference (HSD) test was used for mean separation if the analysis of variance showed statistically significant differences (P<0.05). Pearson correlation analysis was performed for some selected soil properties to evaluate whether the soil parameters associate with each other. All statistical analyses were performed using SAS 9.2 statistical software.

Results and Discussion

Soil physical properties

Except for PWP, interaction effect between land uses and slope position was statistically non-significant (P>0.05) for all the measured soil physical parameters. Furthermore, there was no significant (*P*>0.05) difference in sand, clay, bulk density, FC, PWP and AWC between slope positions.

Soil particle size distribution, bulk density, and total porosity

Statistical analysis of particle size distribution revealed that both sand and clay content differed significantly (*P*<0.05) among the different ages of exclosures and grazing land (Table 2). Significantly (P<0.05) higher sand content (60%) and lower clay content (18.33%) was recorded in the old exclosure. The remarkably higher sand content could be due to the dense vegetation cover in the oldest exclosure which is good at trapping sediments. The sediment is mainly dominated by coarse materials. Vegetation cover is the key factor controlling overland flow generation (Cerdà, 1998). A study in North Ethiopia indicated that 20 years old exclosure on steep slopes (35–50%) trapped about ~55 tonne of sediment ha^{-1} yr^{-1} because of the restored vegetation. The sediment deposits on these exclosures are characterized by 15 - 40% rock fragments contents (Descheemaeker et al., 2006b). Another study showed that exclosures can trap up to 50% of sediment resulting from sheet and rill erosion (Nyssen et al., 2008).

Table 2. Mean ±S.E values of particle size distribution (%), textural class, ρb (g cm^{-3}) and total porosity (%) of exclosures and grazing land at Kewet district, central dry lowlands of Ethiopia

Factors	Attribute of factors	Particle size distribution			Textural class	ρ_b	Total porosity
		Sand	Silt	Clay			
LU	GL	43.19±2.60^b	27.22±1.84	29.58±2.04^a	CL	1.19±0.03	55.01±1.10
	YO-Ex	45.42±2.64^b	26.39±2.57	28.19±1.85^a	SCL	1.16±0.03	56.10±1.10
	MI-Ex	44.31±3.95^b	25.28±2.55	30.42±2.86^a	CL	1.14±0.02	56.81±0.87
	OL-Ex	60.00±2.76^a	21.67±1.44	18.33±1.53^b	SL	1.16±0.02	56.31±0.86
	P-value	0.004	0.229	0.001		0.584	0.58
SP	US	48.86±3.58	25.31±2.48	25.83±2.35	SCL	1.16±0.02	56.32±0.89
	MS	47.29±3.65	24.79±1.36	27.92±2.54	SCL	1.18±0.03	55.41±0.98
	LS	48.54±2.58	24.38±1.31	27.08±1.93	SCL	1.15±0.02	56.44±0.67
	P-value	0.917	0.918	0.722		0.619	0.62
LU*SP		61.44^{ns}	64.92^{ns}	36.46^{ns}		0.01^{ns}	14.40^{ns}
CV %		20.17	22.50	23.45		6.38	5.00
Error		94.66	31.21	39.93		0.006	7.86

Means ±S.E. with different letters within a column are significantly different (*P*<0.05) (Tukey's test HSD). ρ_b = bulk density, LU = land use, SP = slope position, GL= Grazing land, YO-Ex = Young age exclosure, MI-Ex = Middle age exclosure, OL-Ex = Old age exclosure, US = upper slope, MS = middle slope, FS = foot slope. LU*SP mean square ^{ns} is non-significant.

Although soil texture is not directly affected by land-use system, this study indicated that the dense vegetation in the exclosure influenced the proportion of sand content. The middle-age exclosure and grazing land have a clay loam soil texture, whereas the soil texture in the young and old age exclosures was sandy clay loam and sandy clay, respectively. In contrast terms of the overall slope position, soil texture class exhibited variability along slope position in each exclosure and the grazing land (Table 2). Overall, all the exclosure and the adjacent grazing land has moderately fine-textured soil. The sediment deposition on exclosure can accelerate fertile soil buildup (Descheemaeker et al., 2006b).

According to Landon (2014) soil bulk density in all the exclosures and grazing land was in the range of not compacted for surface mineral soils (Table 2). The total porosity the soils under the exclosure and the grazing land was in the range of relatively high porosity (Landon, 2014). This could be due to the relatively low bulk density and high SOM in all sites.

Available water content and water retention curve

The difference in water retained at FC and PWP was statistically significant (P<0.05) among the age of exclosures and grazing land. Lower water content at both FC (21.35%) and PWP (9.94%) was recorded in the young and old exclosures than the middle age exclosure and grazing land. This might be attributed to the higher sand content of the young (45%) and old (60%) exclosures (Table 2). The highest (39.17%) content of water at FC in the middle age exclosure and grazing land and higher PWP in the exclosures and grazing land is probably associated with the high soil organic matter (SOM) content. Qasim et al. (2017) obtained significant higher soil moisture content in soils of protected as compared to the grazed site in Chiltan Mountain rangeland, Northwest of Pakistan. Interaction effect among land-use type (different age of exclosures and grazing land) and slope position were significant (*P*<0.05) for PWP (Table 3). This indicates that the difference in PWP is not only due to change in the age of exclosure but also due to a variation of soil texture (Table 2) and other related soil properties along slope position in the exclosures and the grazing land.

Table 3. Mean ±S.E values of soil water content at FC (% mass/mass), PWP (% mass/mass) and AWC (mm m^{-1}) in exclosures of different ages and grazing land at Kewet district, central dry lowlands of Ethiopia

Factors	Attribute of factors	FC	PWP	AWC
LU Type	Grazing land	30.69±2.44^{ab}	16.48±1.97^{b}	169.84±22.78
	Young age exclosure	21.35±2.74^{b}	9.94±1.28^{c}	133.73±18.44
	Middle age exclosure	39.17±0.78^{a}	24.76±1.18^{a}	164.44±4.44
	Old age exclosure	28.65±3.28^{b}	13.75±1.28^{bc}	173.20±18.44
	P-value	0.000	<.0001	0.396
SP	Upper slope	31.65±2.09	16.51±2.00	175.08±9.84
	Middle slope	28.43±3.14	16.34±2.25	143.97±16.44
	Lower slope	29.82±3.13	15.93±2.35	161.86±17.81
	P-value	0.570	0.951	0.374
LU*SP		70.59^{ns}	60.37*	2244.99^{ns}
CV		24.56	28.01	33.31
Error		54.17	4.55	2851.65

Means ±S.E. with different letters within a column are significantly different ($P<0.05$) (Tukey's test HSD). FC = filed capacity, PWP = permanent wilting point and AWC = available water content, LU = land use, SP = slope position. LU*SP mean square is significant at p<0.05 level and ^{ns} is non-significant.

Available water content was not significantly different ($P>0.05$) between the age of exclosure and grazing land. According to Landon (2014), the mean value of AWC in the exclosures and grazing land is rated as medium (133-173 mm m^{-1}) (Table 3). This could be associated with the high SOM in the sites. A study conducted by Descheemaeker et al. (2006a) in Tigray, North Ethiopia found higher water retention in exclosures with relatively high SOM. Analysis of Pearson's correlation illustrated AWC was significantly and positively correlated with SOC ($r^2=0.57$, $P<0.01$) (Table 7). The mean value of AWC showed a slightly increasing trend (from 133 mm m^{-1} in the young exclosure to 173 mm m^{-1} in the old exclosure) with age of exclosure.

As illustrated in Figure 3, in addition to the soil texture, SOM might have affected the shape of the water retention curve (WRC). For instance, the old exclosure has high sand content (Table 2) and sandy loam soil texture, which is characterized by low water retention capacity. However, the WRC of the old exclosure showed more or less close water content with the other exclosure and the grazing land which have relatively high clay content. The very high SOM content in the old exclosure might explain this. Even if the middle age exclosure and the grazing land have clay loam soil texture, difference in WRC was observed (Table 2) following their variation is SOM content. SOM affects the shape of WRC directly due to its ability to adsorb water and indirectly due to its effect on soil structure (Lal, 2004).

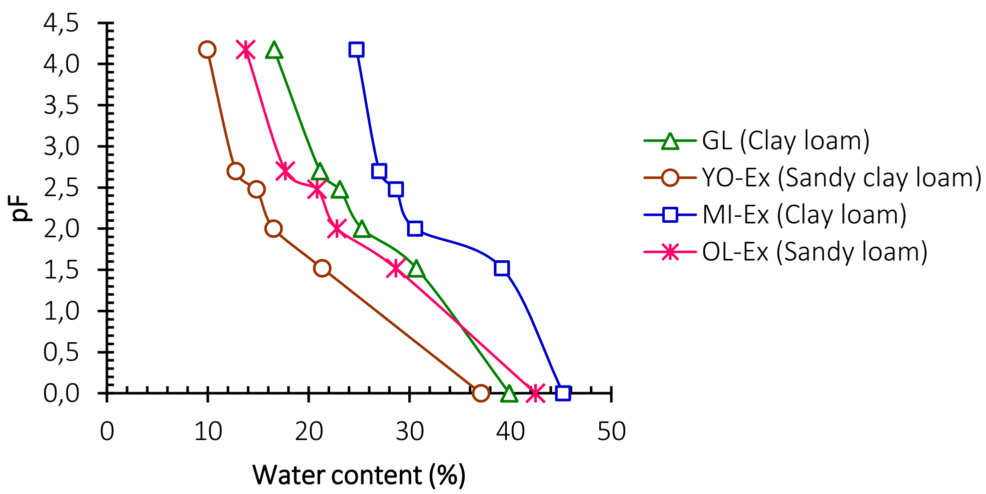

Figure 3. Soil water characteristic curve of exclosures and grazing land as affected by soil texture at Kewet district, central dry lowlands of Ethiopia: YO-Ex = Young age exclosure, MI-Ex = Middle age exclosure and OL-Ex = Old age exclosure.

Soil chemical properties

Soil pH, electrical conductivity (EC) and $CaCO_3$

Significant difference in soil pH was detected between the age of exclosures and grazing land (P<0.05). Accordingly, the highest pH values were recorded under the middle age (6.81) and grazing land (6.78), while the lowest were recorded under the young (6.58) and old age (6.60) exclosures (Table 4). The high SOM content in the grazing land and exclosures might have contributed to the medium soil pH. In line with this, soil pH showed a positive correlation with soil OC content (r^2=0.33, P>0.05) (Table 7). This result is in agreement with the findings of Feyisa et al. (2017) who reported a high soil pH in the middle age and the adjacent open grazing lands. Soil pH in all the exclosures and grazing land was rated as neutral (Tadesse. 1991), which indicates optimum soil conditions for plant growth.

Table 4. Mean ±S.E values of pH-H_2O, EC (dS m^{-1}) and $CaCO_3$ (%) of exclosures and grazing land at Kewet district, central dry lowlands of Ethiopia

Factors	Attribute of factors	pH (H_2O)	EC	$CaCO_3$
LU Type	Grazing Land	6.78±0.03^{a}	0.12±0.01	1.31±0.03^{ab}
	Young age exclosure	6.58±0.19^{b}	0.13±0.02	1.12±0.05^{b}
	Middle age exclosure	6.81±0.15^{a}	0.13±0.01	1.34±0.07^{a}
	Old age exclosure	6.60±0.11^{b}	0.13±0.01	1.23±0.02^{ab}
	P-value	0.001	0.832	0.019
SP	Upper slope	6.62±0.03	0.14±0.10	1.23±0.05
	Middle slope	6.74±0.14	0.12±0.01	1.24±0.05
	Lower slope	6.71±0.11	0.12±0.01	1.28±0.04
	P-value	0.06	0.072	0.690
LU*SP		0.02^{ns}	0.00^{ns}	0.02^{ns}
CV		1.91	24.01	11.63
Error		0.02	0	0.02

Means ±S.E. with different letters within a column are significantly different (P<0.05) (Tukey's test HSD). LU = land use, SP = slope position. LU*SP mean square ^{ns} is non-significant.

Unlike soil pH, statistically significant difference in soil EC was not exhibited between the age of exclosure and grazing land (Table 4). Calcium Carbonate ($CaCO_3$) showed a significant (P<0.05) variation between the age of exclosures and grazing land. The lowest (1.12%) (P<0.05) and the highest $CaCO_3$ (1.34%) was recorded in the young and middle age exclosures, respectively. The generally low $CaCO_3$ concentration in all the exclosures and grazing land might be attributed to the parent materials from which the soils are derived (Paris, 1986). The soils are derived from transitional and sub-alkaline basalt rock parent material (Tefera et al., 1996). Soil pH, EC, and $CaCO_3$ were not influenced (P>0.05) by slope position.

Soil organic carbon, total nitrogen, C:N ratio, and available phosphorus

Soil organic carbon, TN, and AP were significantly (P<0.05) different among the age of exclosures and grazing land (Table 5). The lowest SOC (2.58%) content was recorded in the young exclosure as compared to the grazing land and the other exclosure ages. This may be because of the influence of several factors. Harvesting grass for domestic animal feed in late October and November during the first five years is a common practice in most exclosures in Ethiopia (Yayneshet et al., 2009). Similarly, in the study area grass is harvested annually in the young and middle age exclosures. Furthermore, since domestic animals are excluded, there will be no more input of animal dung into the exclosures. Thus, the complete reduction of the considerable input of organic matter through grass harvest and absence of animal dung might have contributed much to the low content of SOC in the young age exclosure. Exclosures in the study area are also not supported by soil and water conservation (Figure 4). Until the area is covered with perennial vegetation that enables minimization of soil erosion, a considerable amount of top SOC will leave the site through soil erosion with the fine particles.

Furthermore, the significantly lower SOC content in the young age exclosure indicates excluding grazing land from intervention up to 5 years may not favor the improvement of SOC. Due to the favorable condition (input of biomass) for microorganisms, an increase in the microorganism population is expected in the 1st five years of exclusion. This exposes the SOM for further decomposition and liberation of CO_2 (Khalil et al., 2005). The accumulation of microbial residues is ultimately associated with long-term SOM accumulation (Liu et al., 2019) and to a steady-state level (Mohammadi et al., 2011).

Table 5. Mean ±S.E. values of soil OC (%), TN (%), C:N and AP (mg kg^{-1}) in exclosures of different ages and grazing land at Kewet district, central dry lowlands of Ethiopia

Factors	Attribute of factors	OC	Total N	C:N	AP
LU Type	Grazing Land	3.17±0.14^{a}	0.36±0.03^{a}	9.37±0.32	21.75±1.99^{b}
	Young age exclosure	2.58±0.21^{b}	0.24±0.01^{b}	9.44±0.33	27.64±3.42^{ab}
	Middle age exclosure	3.37±0.09^{a}	0.34±0.02^{a}	9.76± 0.49	29.24±2.99^{ab}
	Old age exclosure	3.15±0.09^{a}	0.34±0.01^{a}	9.24±0.20	33.79±3.81^{a}
	P-value	0.003	0.000	0.073	0.039
SP	Upper slope	3.20±0.14	0.34±0.03	8.74±0.21	30.65±2.28
	Middle slope	2.91±0.15	0.30±0.02	9.74±0.30	28.08±3.64
	Lower slope	3.09±0.15	0.32±0.02	9.88±0.28	25.58±2.60
	P-value	0.211	0.330	0.720	0.342
LU*SP		0.23^{ns}	0.01^{ns}	8.51^{ns}	169.61^{ns}
CV		13.25	17.00	18.70	29.47
Error		0.17	0	3.49	68.58

Means ±S.E. with different letters within a column are significantly different (P<0.05) (Tukey's test HSD). LU = land use, SP = slope position. LU*SP mean square ^{ns} is non-significant.

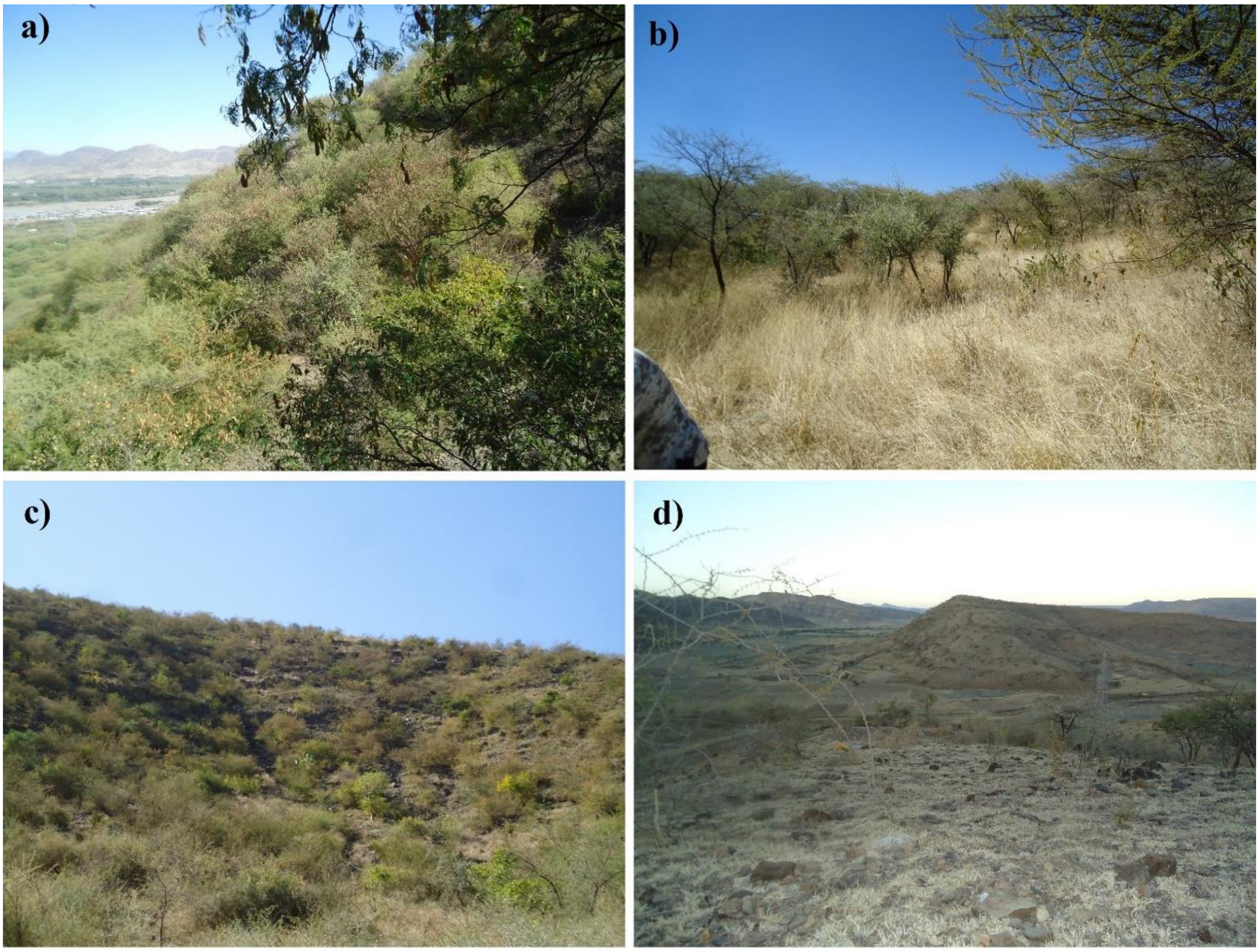

Figure 4. Partial view of the exclosures and grazing land at Kewet district, central lowland of Ethiopia: a) Merye site old exclosure, b) Karajejeba middle age exclosure, c) Karajejeba young exclosure and d) Karajejeba open grazing land.

Soil organic carbon did not exhibit a significant difference between middle and old age exclosures and grazing land. Similar studies by Mekuria et al. (2017) in Gondar, northwest Ethiopia, and Aynekulu et al. (2017) in Borana rangelands, Southern Ethiopia did not detect any significant differences in SOC between exclosure and the adjacent communal grazing land. The SOC content of the middle and old age exclosure and grazing land was rated as high, whereas as the SOC in the young exclosure was rated as medium (Tadesse et al., 1991). A study conducted in the highlands of Tigray, Northern Ethiopia reported higher SOC content in old age than young age exclosures (Birhane et al., 2017). Abebe et al. (2014) in Siltie area, south Ethiopia and Mekuria et al. (2017) in Northwestern Ethiopia also reported higher SOC in middle age of (8 and 7 years old, respectively) exclosures. This study provides evidence that in the process of vegetation restoration through exclosure (Figure 4), SOC content was changed with the change of vegetation cover and age of exclosure. This implies the SOC level is ultimately the result of the balance between addition and loss of organic carbon.

Soil TN was significantly (P<0.05) affected by age of exclosures and grazing land. It followed a similar trend with SOC in that the lowest TN was recorded in the soils under the young exclosure age. The high TN content in the grazing land could be due to the urine and dung inputs by livestock which provides large amounts of plant-available nitrogen (Aynekulu et al., 2017). The high TN content in the middle and old exclosure might be attributed to a subsequent increase in organic matter input derived from herbaceous species biomass and from reduced soil erosion through effective ground cover (Abebe et al., 2014). Total nitrogen showed a positive correlation (r^2= 0.33, P>0.05) (Table 7) with SOC. Except in the young exclosure, the TN content was in the range of medium (Landon, 2014). This finding is in agreement with the previous study by Mekuria et al. (2017) who reported significantly higher TN content in grazing land than in the three and four years old (young) exclosures. On the other hand, the litterfall input, exudates from plant roots and residue of microorganisms on the old exclosures might favor the accumulation of relatively high soil TN.

Regardless of its non-significant difference, the C:N ration from both exclosures and grazing land indicated that there is a decomposition of SOM. The C:N ration in all the exclosures and grazing land is in the range for soil with high temperature and microbial activity and it is rated as slightly lower (Landon, 2014). The C:N ration value range is also in line with the finding of Damene et al. (2013) who reported 9:1 and 10:1 C:N ration for 27 and 10, respectively, years old exclosures in Wello, Northern highlands of Ethiopia. This process will mineralize the nitrogen in the SOM and this could result in loss of nitrogen. Therefore, in addition to the low input of biomass, the decomposition of SOM might have also contributed to the low content of TN in the young exclosures.

The statistical analysis (Table 5) showed that exclosure exerts significant (P<0.05) influence on the available phosphorus. The significantly high AP concentration in exclosures could be the result of restoration of natural vegetation, which increased the organic inputs to the soil through litterfall and silt trap. Because of reduced disturbance, exclosures have the ability to restore the soil microbial population. A study conducted by Birhane et al. (2017), in north Ethiopia, has shown that exclosures have a high population of soil microorganism such as arbuscular mycorrhiza fungi (AMF) than adjacent rangeland. The considerably higher restored soil microorganisms are capable of extensively decomposing organic insoluble phosphorus compounds (Zhu et al., 2018). Thus, the relatively higher AP in the exclosures than the grazing land could be due to an increase of phosphorus in the soil from phosphatase and organic acids produced by plant roots and microorganisms. The solubility of various phosphorus compounds is also largely affected by a series of pH-dependent abiotic reactions that influence the availability of phosphorus in the soil (Zhu et al., 2018). The soil pH range in all exclosure favors optimum availability of phosphorus in the soil solution. The optimum and high SOM may also favor the high concentration of AP in the middle age exclosures. Available phosphorus showed a significant positive correlation with soil pH (r^2=0.35, P<0.05) and soil OC (r^2=0.47, P<0.01) (Table 7). Importantly, similar results were obtained by Mekuria et al. (2007), in Tigray, Northern Ethiopia, and Abebe et al. (2014) in Siltie Southern Ethiopia. However, Damene et al. (2013) did not find any significant variation in AP between open grazing land and exclosures in Wello, Northern highlands of Ethiopia. According to Landon (2014) the available phosphorus in all the exclosures and grazing land was rated as high. Generally, unlike SOM and TN, AP showed an increasing trend with increasing age of exclosure. Contrary to the age of exclosure and grazing land, the effect of slope position on SOC, C:N and AP was not statistically significant (P>0.05).

Cation exchange capacity (CEC) and exchangeable Ca, Mg and K

Difference in CEC between the age of exclosure and grazing land was statistically significant (P<0.05) (Table 6). The lowest (37.57 cmolc kg^{-1}) and the highest (56.78 cmolc kg^{-1}) CEC was recorded in the middle age and young age exclosures, respectively. The higher CEC in the young exclosure could result from the cumulated properties of the clay and the relatively high SOM (Table 4) in the exclosures and grazing land (Saidi, 2012). The contribution of SOM to CEC varies between 25% and 90% (Trivedi et al., 2018). Cation exchange capacity primarily varies according to the type of clay (Nešić et al., 2015). Since all the exclosures have low clay content (Table 2), it is more likely that the high CEC in the exclosures is due to high SOM of the site. Even if the young exclosure has a low SOC in comparison with other exclosure and grazing land, according to Tadesse et al. (1991) it is rated as high. The cumulated contribution from the SOM and clay might explain the high CEC in the young exclosure (Parfitt et al., 1995).

Table 6. Mean ±S.E. values of soil CEC ($cmol_c$ kg^{-1}), Ex. Ca ($cmol_c$ kg^{-1}), Ex. Mg ($cmol_c$ kg^{-1}) and Ex. K ($cmol_c$ kg^{-1}) in exclosures of different ages and grazing land at Kewet district, central dry lowlands of Ethiopia

Factors	Attribute of factors	CEC	Ex. Ca	Ex. Mg	Ex. K
LU Type	Grazing Land	41.07±4.70[b]	8.09±0.36[a]	2.30±0.33[ab]	0.18±0.04[b]
	Young age exclosure	56.78±2.43[a]	6.27±0.24[b]	2.82±0.43[a]	0.20±0.02[ab]
	Middle age exclosure	37.53±1.89[b]	6.52±0.39[b]	1.27±0.13[b]	0.32±0.04[a]
	Old age exclosure	44.07±2.12[b]	6.19±0.55[b]	1.89±0.17[ab]	0.12±0.02[b]
	P-value	0.000	0.001	0.010	0.002
SP	Upper slope	45.45±2.78	7.67±0.33[a]	1.93±0.25	0.21±0.03
	Middle slope	44.28±3.08	6.31±0.32[b]	2.26±0.31	0.22±0.03
	Lower slope	44.85±4.09	6.33±0.44[b]	2.03±0.32	0.18±0.04
	P-value	0.505	0.002	0.654	0.472
LU*SP		37.60[ns]	1.99[ns]	0.67[ns]	0.01[ns]
CV		16.14	13.62	43.49	45.80
Error		53.49	0.85	0.81	0.01

Means ±S.E. with different letters within a column are significantly different ($P<0.05$) (Tukey's test HSD). LU = land use, SP = slope position. LU*SP mean square [ns] is non-significant.

Normally, CEC of clay minerals ranges from less than 5 $cmol_c\ kg^{-1}$ for kaolinite to over 100 $cmol_c\ kg^{-1}$ for vermiculite and smectite (Parfitt et al. 1995; Landon, 2014). Therefore, the significantly higher CEC in the young exclosure could be associated with the variation in clay type between the sites. Because of the type of clay mineralogy, soils with substantially lower clay content may have higher CEC (Landon, 2014). A Pearson's correlation coefficient analysis also indicates that there is a positive correlation of CEC with soil pH (r^2=0.23, $P<0.05$) and clay content (r^2=0.34, $P<0.05$) (Table 7). Overall, the CEC in young and old exclosures and grazing land is rated as very high, whereas in the middle age exclosure it is rated as high (Landon, 2014). The result of this study is in line with the findings of Abebe et al. (2014) in Siltie area from South Ethiopia who reported significantly greater CEC in eight years old (young) exclosures. Higher CEC was also reported in a four-year old exclosure than adjacent grazing land in Gojam, Northwestern Ethiopia (Mekuria et al., 2018).

Table 7. Pearson's correlation coefficient matrix of selected soil properties in exclosures of different ages and grazing land at Kewet district, central dry lowlands of Ethiopia

	pH	SOC	TN	AP	CEC	Clay	AWC
pH	1						
SOC	0.325	1					
TN	0.034	0.610**	1				
AP	0.350*	0.468**	0.114	1			
CEC	0.207	-0.130	-0.198	0.329	1		
Clay	0.592**	0.197	-0.050	0.080	0.343*	1	
AWC	0.089	0.571**	0.555**	0.303	0.068	-0.065	1

*. Correlation is significant at the 0.05 level (2-tailed) and **. Correlation is significant at the 0.01 level (2-tailed). Values are correlation coefficients

Exchangeable Ca, Mg, and K varied significantly ($P<0.05$) between exclosures and the grazing land (Table 6). In the grazing land and all exclosures, exchangeable Ca dominated the exchange complex, followed by Mg and K. In comparison with the grazing land, the exchangeable Ca concentration was lower (6.19 cmolc kg^{-1}) in all age of exclosures. The mean value of exchangeable Ca and Mg in all exclosures and the grazing land was rated as medium (Landon, 2014). A similar study by Mekuria et al. (2007) in Tigray, Northern Ethiopia revealed a higher Ca in grazing lands than exclosures. The moderate exchangeable Ca and Mg content in all sites could be due to the high SOM content due to litterfall in the exclosures and grass in the grazing land. The sub-alkaline basalt rock from which the young soils of the study area are forming could also be one of the reasons for the high exchangeable Ca and Mg.

Exchangeable K in the exclosures and grazing land is rated as low (Landon, 2014). Similarly, Mekuria et al. (2017) reported a lower exchangeable K in grazing land and seven years old exclosure in Godar, Northwestern Ethiopia. Often, K availability is more dependent on its concentration relative to Ca and Mg than on the total quantity of K present in the soil solution. The levels of K in solution, as well as the release of K, are dependent on the concentrations of Ca and Mg in soil solution (Akbas et al., 2017). Except exchangeable Ca, there was no significant ($P>0.05$) difference in CEC, exchangeable Mg and K between slope positions. Upper slope position had significantly ($P<0.05$) higher Ca as compared to middle and lower slope positions. The higher Ca in the upper slope position might be explained by the high CEC on the upper slope position. This result is in line with the study of Moges and Holden (2008) in Southern Ethiopia which revealed higher Ca on upper slope position. In Gerado catchment, Northeastern Ethiopia, slope gradient was found to be the major factor that affects the variation of exchangeable Ca (Asmamaw and Mohammed, 2013).

Conclusion

This study generated clear evidence on the importance of exclosure in improving soil properties on degraded landscapes in the central dry lowlands of Ethiopia. Most soil parameters showed a change along chronosequence of exclosures. Nevertheless, almost all the measured soil properties were not affected by slope position. It seemed that the impact of slope position is masked by vegetation coverage in the exclosures. It can be concluded that soil properties such as SOC, TN and AP can be influenced positively by excluding open degraded grazing land from unmanaged human and domestic animal intervention for a longer period of time to ensure remarkable rehabilitation. It should be noted that the current study only focused on the effect of exclosure age and slope positions on some selected soil properties. To deeply understand exclosure's influence on soil fertility and understand its carbon sequestration potential, further analysis of other aspects of soil characteristics such as soil aggregate size distribution, water-stable aggregates, soil carbon stock, and soil microbial biomass is recommended.

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Efficiency of using the rangeland hydrology and erosion model for assessing the degradation of pastures and forage lands in Aydarly, Kazakhstan

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Abstract

This study examined the use of a novel web-tool for Rangeland Hydrology and Erosion Model (RHEM) as a prediction runoff and erosion as a function of vegetation structure and behavior of different plant community phases and the amount of coverage for the different states in the Aydarly village of Jambul district of Almaty province. US Department of Agriculture experts and Kazakhstani scientists jointly conducted this study, where, based on the results, they received recommendations on improving rangeland. Results suggested that the model could be further improved with additional measured experimental data on infiltration, runoff, and soil erosion within key ecological sites in order to better quantify model parameters to reflect ecosystem changes and risk of crossing interdependent biotic and abiotic thresholds. These additions were further improved and implemented in other regions of Kazakhstan on other projects.

Keywords: RHEM, Kazakhstan, Rangeland, Aydarly, soil erosion, pastureland erosion.

Introduction

At all times, the main value of any nation was their land. Land degradation is a significant phenomenon on the world particularly arid, semi-arid and semi-humid terrestrial ecosystem environments due to variety of factors such as through unsustainable land management, and through physical and climatic characteristics. One of the main indicators and commonly used in the land degradation and desertification is the soil quality level (Demirağ Turan et al., 2019). Therefore, the quantity and quality of soil is an important indicator of the sustainable development of each country, which feeds and provides livelihoods for the people (Bekturova and Romanova, 2007).

For the population of Kazakhstan, due to arid climatic conditions and scarcity of water resources, land use problems have always been quite acute. The people used the best land use methods to obtain maximum efficiency and at the same time preserve the fertility of the land, which is important for the country (Strategic Measures, 2015; Bekturova and Romanova, 2007; Final report, 2018). The main areas of land use were farming and animal husbandry (FAO, 2010). For those who are interested in working in cooperation with feedlots and meat processing plants in the development of farms in beef cattle and sheep farming is an opportunity to increase export potential for the long term. In Kazakhstan, the State Agro-Industrial Complex Development Program for 2017-2021 was adopted by the Ministry of Agriculture to implement long-term sectoral programs for the development of livestock industries, which currently encourages pasture owners and stakeholders to promote and manage pastures (FAOLEX, 2017). The aridity of the climate, the nature of soils and the existing biodiversity of pasture vegetation in Kazakhstan historically determined a peculiar

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form of nature management and livelihoods of the population as nomadic cattle breeding on seasonal pastures. Pasture feed in the south-east of Kazakhstan makes up 70-75% of the annual ration of grazed animals. Therefore, the welfare of the rural population with livestock directly depends on the condition of grazing sites (PF, 2007). The most convenient for changing pastures were natural pasture complexes. One of these classic complexes is Alatau-Pribalkhashsky, combining mountain summer pastures, winter sand pastures and flat spring-autumn pastures between them, using the example of the Aydarly rural district.

The complex interactions of climate, topography, soil, vegetation, and human economic activity depend on the nature and intensity of erosion processes in the pasture soil, which contribute to a general decrease in the intensity of water erosion processes and increased deflation in unprotected areas of the territory. Pasture degradation, namely a decrease in vegetation cover, changes in vegetation composition and associated loss of ecosystem productivity, are likely consequences of cyclical climatic events (UNCCD, 1994). Land degradation in Kazakhstan has a serious socio-economic impact on living standards and public health, especially on socially vulnerable groups. One of the main reasons for the impact on degradation is a decrease in efficiency and a high risk for cattle breeding as a result of pasture degradation and lack of feed. In many lands, there is a tendency toward a deterioration of the state of pastures in places of constant concentration of livestock (PF, 2007; Shimyrbaeva, 2013). This is primarily due to the areas of pastures used and the number of livestock grazed on them, the productivity and nutritional value of pasture, irrigation of pastures, etc. Using new technologies for forecasting erosion, it is possible to simulate complex interactions between the characteristics of the vegetation cover, soil properties, hydrological and erosion processes on pastures (Nearing, 2011a,b). The purpose of this article is to describe the results of the study using a web-based tool for modeling hydrology and pasture erosion by presenting in detail the structure of the mathematical model and reporting on the results of applying the model (Hernandez, 2017). The pasture hydrology and erosion assessment tool is designed to provide reliable, scientifically sound technologies for modeling and predicting runoff and erosion rates on rangelands, as well as to help assess the impact of pasture conservation practices (Herrick, 2009, 2017).

The approach used in this study has some aims: (i) to assess forage resources of a rangeland using a tool, measuring and driving research data on 13 indicators on a small semi-arid plain spring-autumn pasture of Aydarly rural district, (ii) to identify resource requirements local livestock farms through research interviews; (iii) to study the improvement of tool performance; and (4) to provide guidance for interested farmers to participate in more detailed land conservation and management plans.

Material and Methods

Study area

The current investigation involved sampling and analyzing from Aydarly village (44°11'58.39"N, 75°50'31.57"E), lying on the edge (Kazakh: jeek) between the desert-steppe to the south, and the Sarytaukum ("yellow mountain of sand") desert to the north. Aydarly lies in the northern part of Jambul district of Almaty province, in the south east of the country (Figure 1).

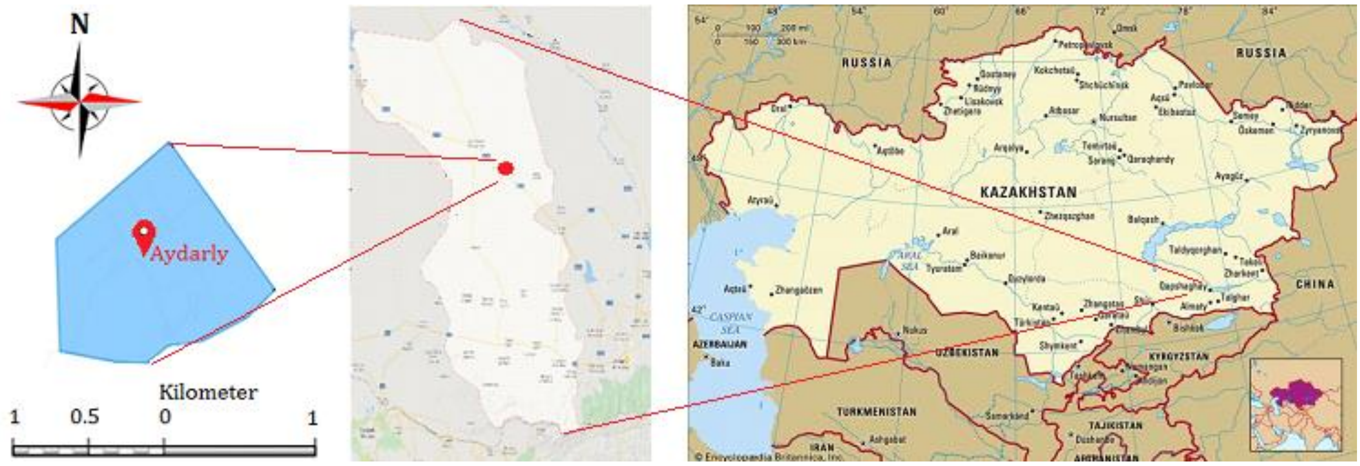

Figure 1. Location of the study site in Kazakhstan

The total pasture area of the rural district as of September 2017 is 110,062 ha. General features and location of the studied area are shown in Figure 1. The average annual precipitation is 230 mm, while temperatures range from a minimum −35°C in January to a maximum of 45°C in July. Vegetation in the northern sand dune area of the Sarytaukum is mainly composed of shrubs, *Haloxylon persicum*, *Artemisia species*, small shrubs of *Salsola* and *Kochia*, and in spring, ephemeral grasses of which *Carex physodes* is the most important. Some 20 km south of the village lie some low hills with springs, dominated by Artemisia species and ephemeral spring grasses (Kerven, 2008).

Method

This current study consists of 3 phases, which was divided the 9 planning stages used by scientists when working with farmers in the research area (Figure 2).

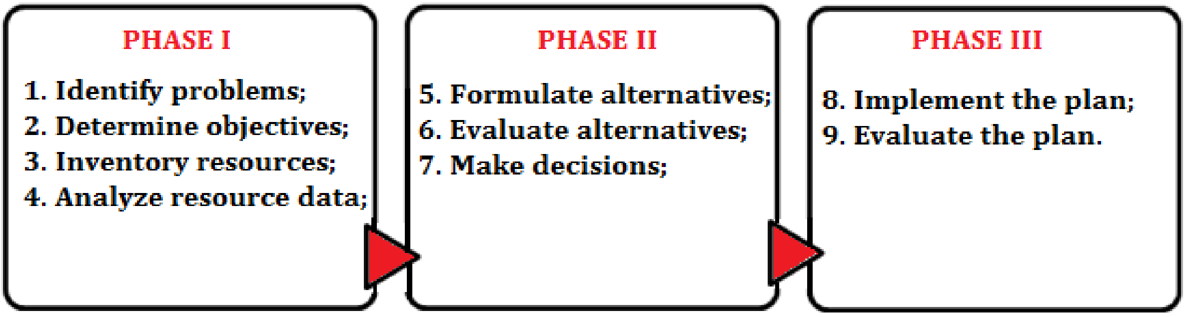

Figure 2. Farm Visit Objectives

For the main assessment, the RHEM model was used, which is a comprehensive assessment tool, rangeland degradation estimates runoff, soil loss, speed and volume of soil transported from wastewater and the timeline of a single precipitation event. For the model, we entered data on 13 parameters presented in Table 1, which as a result provides information for assessing erosion of rangelands. The group of soil parameters in Table 1 is calculated using the equations of pedoprotection (parameter estimates) obtained from Nearing et al. (2011a,b). An important aspect of the model regarding the use of pasture by managers is that RHEM is parameterized on the basis of four groups of classification of plant life forms (bunchgrass, shrub, sodgrass, and annual grass /forbs).

Table 1. Standard Indicators included in the Rangeland Health protocol and attribute (soil and site stability, hydrologic function, and/or biotic integrity) to which each indicator applies. The "X" indicates that the indicator is applied to the attribute.

Rangeland Health Indicator		Rangeland Health Attribute		
		Soil and Site Stability	Hydrologic Function	Biotic Integrity
1.	Rills	X	X	
2.	Water flow patterns	X	X	
3.	Pedestals and/or Terracettes	X	X	
4.	Bare ground	X	X	
5.	Gullies	X	X	
6.	Wind scoured, blowouts, and/or deposition areas	X		
7.	Litter movement	X		
8.	Soil surface resistance to erosion	X	X	X
9.	Soil surface loss or degradation	X	X	X
10.	Plant community composition and distribution relative to infiltration and runoff		X	
11.	Compaction layer	X	X	X
12.	Functional/structural groups			X
13.	Plant mortality/decadence			X
14.	Litter amount		X	X
15.	Annual aboveground production			X
16.	Invasive plants			X
17.	Reproductive capability of perennial plants			X

Results and Discussion

As a result of research on methodological recommendations, a calculation was made of the rate of harvesting feed in livestock. Since the plot has rangeland with different vegetation conditions, higher and lower productivity levels, the feed calculation for the selected plot was not carried out for the whole farm. The calculations give an example of the significance of how the team planned a series of tasks to determine farm production and throughput of all livestock.

The initial assessment of the stock level for this site was carried out by various types of livestock: These are initial calculations that require adjustment in accordance with annual climatic data, monitoring the performance of animals and the grazing regime in the pasture. Using half of the production (1.982 kg.ha^{-1}) additionally provides an opportunity for about 15-25% of the yield of livestock waste with food.

In Table 2, we can estimate the calculation of the annual feed requirements for animal feed and livestock feed. The calculation is carried out in such a way that half of the production is 1.982 kg.ha^{-1} x 50% utilization rate = 991 kg.ha^{-1} x 15% lack of use efficiency, which leaves about 842.4 kg ha^{-1} aft on an annual basis. According to the calculation results, an adult cow (454 kg) with a calf up to 6 months eats 4980 kg of dry matter per year. Thus, to provide nutrition for several years, about 6 ha per year is needed for one mature cow and calf. A mature horse (500 kg) eats 5,388 kg of feed per year. Therefore, 6.4 ha of feed per horse is needed annually. For a 68 kg sheep with a lamb (up to 2 months), it is estimated that about 69.4 kg of feed (dry weight) per month is required. If the plot has 842.4 kg.ha^{-1} of feed, then: 842.4 kg.ha^{-1} of products / 69.4 kg (sheep consumption per month) would mean that 1 ha would support 12 sheep and lambs (in the first 2 months of life) for one month or 1 hectare per sheep and lamb for 12 months (1 year) (Figure 3).

Table 2. Forage Needs for Livestock

	Air-dry weight of forage consumed		
	Day, kg	month, kg	Year, kg
Cow, dry (1000 lbs.) (454 kg cow)*	11.6	347.0	4164.0
Cow (1000 lbs.) (454 kg cow), with calf to 6 months	13.6	415.0	4980.4
Cow (1100 lbs.) (498 kg), with calf to 4 months	15.0	449.1	5388.7
Cow (1200 lbs.) (544 kg), with calf to 4 months	16.3	489.9	5878.6
Cow (1300 lbs.) (589 kg) with calf to 4 months	17.7	530.7	6368.4
Calf, 4 months to weaning	4.1	122.5	1469.6
Yearling cattle, 7-12 months	8.8	265.4	3184.2
Yearling cattle, 12-17 months	10.2	306.2	3674.1
Heifers, 18-24 months	11.8	353.8	4245.6
Bulls, 12-24 months	16.3	489.9	5878.6
Bulls, mature (1850 lb. 839 kg. average)	20.4	612.3	7348.2
Horse, yearling	10.2	306.2	3674.1
Horse, 2 year old	13.6	415.0	4980.4
Horse, mature (1100 lbs. 500 kg)	15.0	449.1	5388.7
Sheep, mature lactating ewe (150 lbs. 68 kg), with lamb, less than 2 months	2.3	69.4	832.8
Sheep, mature non-lactating ewe	2.0	61.2	734.8
Lamb, 2 months to weaning	0.8	24.5	293.9
Lamb, weaned to yearling	1.6	49.0	587.9
Lamb, yearling	2.0	61.2	734.8
Ram (200 lbs. 91 kg)	2.3	69.4	832.8
Goat, mature	2.0	61.2	734.8

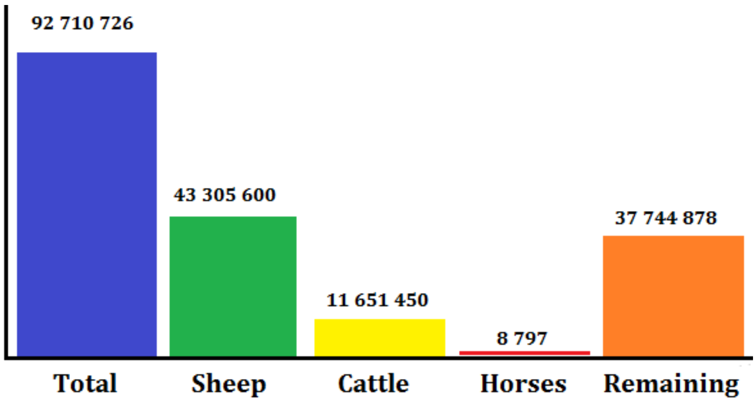

Figure 3. Graph of Estimated total forage and use by current sheep, cow/calf, and horses in Aidarly

In the Aydarly rural district, sheep herds number approximately 52,000 animals, which require uninterrupted supply of full-fledged feeds up to their mature age of about 52,000 ha during the year. Depending on the conservation and sale of the lambs locally, additional land should be set aside to meet their feed requirements. For one separated lamb from 2 months to a year (10 months in assortment), 490 kg of dry matter feed is required. This will require 0.58 ha per lamb for 2 months (estimated weaning age) to 1 year. Since the possibility of preserving the lamb and the proportion of paired lambs is unknown, it is impossible to calculate the territory needed for the lambs after weaning. However, the above calculations can be used to determine this based on the management of the lambs. For a herd of 2162 cows, approximately 13,832 ha is required, provided that the pastures have the same annual feed production to maintain herd productivity and maintain the productivity of the selected site. Approximately 8,800 ha of land are needed to meet both animal characteristics and environmental sustainability requirements for a herd of horses, 1,375 animals. All these initial calculations of the harvest depend on the estimated mass of the animal, breed, feed quality, access to water, climate and topographic aspects of the pasture. In general, it is not recommended to use land with an inclination of more than 30% in calculations of harvesting speed, but it is possible to use grazing by animals. Areas with slopes of more than 30% are very susceptible to accelerated soil erosion and loss of productivity if they are severely degraded or simply “knocked down”. Rangeland health assessment was assessed using 18 parameters, which are presented in Table 3:

- **Soil and site stability** is the capacity of a site to limit redistribution of loss of soil resources (including nutrients and organic matter) by wind and water.
- **Hydrologic function** characterizes the capacity of the site to capture, store, and safely release water from rainfall, run-on and snowmelt (where relevant), to resist a reduction in this capacity and to recover this capacity following degradation.
- **Biotic integrity** is defined as the capacity of a site to support characteristic functional and structural communities in the context of normal variability, to resist loss of this function and structure caused by disturbance, and to recover following such a disturbance.

Table 3. Rangeland Health Assessment Worksheet

Indicator	NS	SM	M	ME	EX
1. Rills (SSS,HF)	✓				
2. Water Flow Patterns (SSS,HF)		✓			
3. Plant Pedestals (SSS,HF)		✓			
4. Bare Ground		✓			
5. Gullies (SSS,HF)	✓				
6. Wind Scoured Areas, Blowouts (SSS)		✓			
7. Litter Movement (wind or water) (SSS)			✓		
8. Soil Surface Resistance to Erosion (SSS,HF,BI)			✓		
9. Soil Surface Loss (SSS,HF,BI)			✓		
10. Plant Community composition and distribution relative to infiltration and runoff (HF)			✓	✓	
11. Compaction Layer (SSS,HF,BI)	✓				
12. Plant Functional Group Changes (BI)				✓	
13. Plant Mortality/Decadence (BI)		✓			
14. Litter Amount on Soil Surface (HF,BI)		✓			
15. Annual Plant Production (BI)			✓		
16. Invasive Plants (BI)					✓
17. Reproductive Capability of Plants (BI)		✓			
18. Native Plant Composition and Diversity (BI)					✓
Soil and Site Stability (Evidence)			✓		
Hydrologic Function (Evidence)			✓		
Biotic Integrity (Evidence)				✓	

NS= None-to-slight change from reference plant community. The reference plant community represents native rangeland with healthy stands of native plants that may include grasses, forbs (non-woody herbaceous plant), and shrub that have not been impacted by severe disturbances such as livestock, machinery, climate extremes.
SM= Slight to Moderate Departure from Reference Conditions
M= Moderate Departure from Reference Conditions
ME= Moderate to Extreme from Reference Conditions
EX= Extreme Departure from Reference Conditions

The studies on the state of pastures in Aydarly indicate a complex of negative processes occurring on rangeland s over the past decade. The content of humus (the main indicator of soil fertility) is reduced by 37%; the level of pasture productivity drops to 2.6 times; land is exposed at 63-90%; instead of *Kóchia*, *Artemísia*, wheatgrass and other valuable fodder plants, *Peganum harmala*, *Pseudosophora alopecuroides*, *Melilótus officinális*, *Ceratocarpus arenarius* and other less eaten species appear (Figure 4, 5, 6).

Figure 4. Invasive annaul for forb Sálsola (Russian Thistle)

Figure 5. Invasive annual forb Ceratocarpus arenarius

Figure 6. Wild Rue Peganum harmala

The overall superiority of evidence of soil and site stability and hydrological function is the approach to a moderate approach to a moderate yield. The general evidence of biotic integrity is moderately extreme. Corrective action is needed at the research facility before conditions worsen. According to the results of the model shown in Table 4, the projective cover of vegetative vegetation is low. Average annual indicators for Aydarly per year, if precipitation is 163.33 mm, then the washout of the surface horizon is 1.016 mm per year. In planning a 100-year scenario, degradation is possible at 10.573 mm.

Table 4. Rangeland Hydrology and Erosion Model Web Tool

Parameters					**AYDARLY**	
Version					2.3	
State ID					WY	
Climate Station					Basin	
Soil Texture					Sandy Loam	
Soil Water Saturation %					25	
Slope Length (meters)					50	
Slope Shape					Uniform	
Slope Steepness %					2	
Bunch Grass Foliar Cover %					0	
Forbs and/or Annual Grasses Foliar Cover %					0	
Shrubs Foliar Cover %					49	
Sod Grass Foliar Cover %					0	
Total Foliar Cover %					49	
Basal Cover %					0	
Rock Cover %					0	
Litter Cover %					46	
Biological Crusts Cover %					0	
Total Ground Cover %					46	
Annual averages (AYDARLY)						
Avg. Precipitation (mm/year)					163.330	
Avg. Runoff (mm/year)					1.016	
Avg. Sediment Yield (tonne/ha/year)					0.016	
Avg. Soil Loss (tonne/ha/year)					0.016	
Return frequency results for yearly values						
Variable	2 yr	5 yr	10 yr	25 yr	50 yr	100 yr
Rain (mm)	18.100	25.200	30.000	36.000	39.100	46.700
Runoff (mm)	0.011	1.305	3.323	5.494	8.924	10.573
Soil Loss (tonne/ha)	0.000	0.016	0.056	0.104	0.141	0.226
Sediment Yield (tonne/ha)	0.000	0.015	0.055	0.103	0.141	0.224

Initial estimates of pasture resources indicate that the area has undergone degradation and requires conservation. A plan is needed for planting crested wheat grass or a hybrid of wheat grass in an existing stand (Figure 7) and a grazing management system for managing restored pasture. Once crested wheat is established, grass will compete with invasive weeds (*Sílybum mariánum* and *Ceratocarpus*), and these invasive species will become less numerous and the quantity and quality of the desired feed will be increased.

Reclamation of the contaminated area along with the elimination of disturbing factors, such as overgrazing, is the best way to restore land contaminated with this weed.

A few kilometers from the highway, the research team observed a very successful sowing of wheat seeds in good condition, although previously there was haymaking on this field. As local economies and resources allow, local shepherds need to develop a sowing program for the most affected pasture areas and continue the sowing program in subsequent years along with the development of a grazing system for proper crop management.

In the spring, cattle and sheep mainly feed on Sálsola until they become flowers and become prickly. Among the vegetation, there is *Sálsola*, which can accumulate toxic levels of nitrates, which can cause acute respiratory failure and sudden death of cattle and sheep. Dangerous *Sálsola* milk with a nitrate content of more than 1.0%; animals can die if they consumed only 0.075 percent of their weight in nitrate. Environmental factors often affect nitrate. For example, nitrate poisoning is more likely if the plant grows in soils with a high nitrogen content, for example, in adhesive tape or in fertilized areas. Excessive shade, lack of water, and stress or physical damage can also increase nitrate levels. *Sálsola* also contains oxalates, which can lead to kidney failure in cattle and sheep if swallowed.

Figure 7. Crested Wheatgrass drilled into sagebrush rangeland to increase forage.

In Aydarly, there is a real opportunity to systematize the use of rangeland by driving away the non-milked part of the livestock to summer mountain pastures and winter sand pastures. It is extremely important to get rid of individual grazing, which is carried out in a radius of no more than 3 km from the village. The most real and acceptable areas of problems with the use of land resources here may be, first of all:

- Restoration of traditional methods of livestock husbandry when a rotational sparing mode of grazing is used. As is known, large livestock owners with up to 500 heads of small cattle, and especially medium and small livestock breeders in the village of Aydarly, do not take livestock to seasonal pastures due to the lack of watering and conditions for herders. Therefore, it seems necessary to improve the living conditions of shepherds, as well as the reconstruction of previously existing wells on the distillation;
- Since some small and medium-sized cattle owners often do not have the ability to take livestock to the districts, because of the need to leave part of the livestock in the village, it is necessary to strengthen the feed base to prevent overgrazing around the village. This affects the location of the village and all its land in a desert natural zone with an arid climate, where high-quality hay harvesting is limited to the growing season and droughts (Figure 6). Many livestock owners buy livestock feed in neighboring villages. The solution to this issue is complicated by the lack of irrigated land, as the channel through which water came to the irrigated lands of Aydarly village in past periods has not been cleared for several years and is very silty, overgrown with shrubs. The most real way to solve the problem of overgrazing in the village is to switch to the livestock livestock type, traditionally used in these places and being a resource-saving technology in the use of land. In this case, it is necessary to solve the issues of water supply to distant pastures through the restoration of wells.

Conclusion

In summary, we have presented a new technique new web-tool for Rangeland Hydrology and Erosion Model (RHEM) by a detailed presentation of the structure of the mathematical model and a report on the results of the application of the model. RHEM can predict runoff and erosion as a function of vegetation structure and behavior of different plant community phases and the amount of coverage for the different states. A web-tool for Kazakhstan is a novelty, Aydarly became a pilot study that showed a good result on the assessment of rangeland by territory. Based on the results, we received recommendations for improving Aydarly rangeland. But the implementation of the recommendation requires the active work of members of the local government and the community, thanks to which it is possible to strengthen the food supply, improve the socio-economic situation of farmers. To our knowledge, similar tools have not yet been developed in Kazakhstan, but for the perfection to determine an estimate of farm stocks, for future research, drone and satellite imagery will be planned to complement field sampling and identify different types of grassland plant communities. Then, these images are processed on a map of the geographic information system (GIS) of the farm to determine the actual availability of feed by the plant community and pastures. We expect this web-tool to open up an entirely new range of materials and numerous novel rangeland hydrology and erosion estimate device applications.

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