EFFECTS OF VEGETATION COVER/LAND USE AND SLOPE ASPECT ON SURFACE SOIL PROPERTIES NEAR THE COPPER SMELTER FACTORY IN MURGUL, TURKEY

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Abstract. The mining activities, one of the most drastic examples of human intervention to nature, have considerably deteriorated the environment. Although being one of the smallest and least populated cities of Turkey, Artvin is notably affected by mining in many ways such as acid rains, water contamination and medical problems. The activities also affect soil properties. The present study aimed to assess the effects of restoration and reclamation of the former smelter factory and determine the changes in some soil properties according to land use/land cover (LULC) and slope aspect. With this purpose, Pearson correlation and two-way ANOVA methods were used. Results showed that while LULC significantly affected ($p < 0.05$) all soil properties except silt content, bulk density, $CaCO_3$ content, C:N ratio, Cd and Zn; slope aspect significantly affected less soil properties such as sand, silt, pH, EC, $CaCO_3$ and Pb. The interaction between factors also significantly affected ($p < 0.05$) soil properties like LULC. According to partial eta squared (η2) values, while the most significantly affected soil properties by LULC, slope aspect and their interaction were found to be Cr (0.93), Clay (0.59) and Cr (0.94), respectively; the ones least affected were found to be total nitrogen (0.12), $CaCO_3$ (0.14) and total nitrogen for 63-day (0.18), respectively. Despite the black alder's and black locust's lack of phytoremediation abilities concerning soil heavy metal content except Pb, *Alnus glutinosa* and *Robinia pseudoacacia* may be suggested for the restoration and reclamation of mining soils in terms of phytoremediation beside their advantages such as improving nitrogen mineralization.

Keywords: *copper mining, two-way ANOVA, black alder, black locust, partial eta squared*

Introduction

The human being has been forced to find new resources for energy and row material and to change land use because of increasing population since ancient times. Pollution, deforestation, erosion, drought-desertification and global climate change are only a few negative results of human activities causing the land use and land cover changes (LUCC) (Deng et al., 2013; Mahmood et al., 2010). The mining, one of the human activities, also has some negative impacts on the environment such as hydrologic, biologic, societal, blasting, subsidence, air quality and land surface effects (Allgaier, 1997).

Artvin has recently come into question with LUCC due to the construction of hydropower plants and mining activities. In this scope, there are 72 mineral deposit reserves determined in Artvin province consisting of 44-Cu-Pb-Zn, 1-Fe, 17-Mn, 5-Cu-Mo and 5-Au (TUİK, 2013). Total copper reserve including Artvin province and Murgul is 329.681 tones (DPT, 2001). Murgul mining entity, dated back to Genoese era, operated in between 1907-1914 by Russians, reactivated in 1951 with the copper smelter by General Directorate of Mineral Research and Exploration (MTA). The

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sulphuric acid factory, operated in between 1963-1975 and 1986-199 was also added to the entity to prevent SO2 emission. The SO2 production, emitted from the factory in between 1951-197 was estimated as 795431 tons (Erdin, 1983; Oruc, 2013). Damages to the ecosystems such as soil loss, lesions and color changes especially on the leaves of fruit trees, lower pH and organic matter content in soil and sulphur accumulation in needles around smelter due to SO2 and other emissions from the factory, were reported by some researchers (Erdin, 1983; Hutchinson and Whitby, 1977; Oruc, 2013). The current physical and chemical properties of soils which influence some vital processes such as carbon storage and nitrogen retention are determined by the duration and the type of land use. On the other hand, heavy metal contamination of soil is another environmental problem, which threatens human health beside the environment by affecting the food chain (Liu et al., 2017; Yesilonis et al., 2016). The area around the factory was planted by Artvin Forest Directorate in 1996 with *Robinia pseudoacacia* and *Alnus glutinosa* sp. to remediate the area. In remediation, beside above mentioned species pine, oak, lime, larch, poplar and birch also have been used in the world. The afforestation of these sites after soil amelioration results in good results (Fischer and Fischer, 2006).

Mining activities cause extreme influences on ecosystem and soil properties and it requires more time to restore soil quality. Therefore, assessing the changes in soil properties is important to see the effects of reclamation of mining areas (Shrestha and Lal, 2011). One of the most important factors affecting restoration and quality of soil is LUCC resulted from human-being, which have an effect on the changes in biological properties. Biomass and forest floor affect many features such as microbial biomass, soil nutrients and soil organic matter (Qi et al., 2018) which have a vital role in carbon balance. The amount of carbon sequestrated in soil in global scale has been estimated 3.3 and 4.5 times more than that in atmosphere and biosphere, respectively (Lal, 2004). The soil properties are expected to change by also slope aspect which is one of the topographic features and closely related to local climate (e.g. precipitation, evaporation and solar incident radiation) (Xu et al., 2008) beside LUCC. Therefore, the slope aspect was taken as the main second factor expected to change selected soil properties.

The aim of the present study was to test our hypothesis that assumes afforestation with black alder and black locust compared to grasslands would improve the soil properties, affecting soil quality after the mining (smelter factory).

Materials and methods

Site description

The study area is located between 41°15’53” - 41°16’21” N latitudes and 41°33’21” - 41°34’04” E longitudes (*Fig. 1*). It is found in Murgul district which is composing of two deep valley surrounded by high mountains with steep slopes (Acatay, 1968). The average elevation of the study site is 600 m above sea level. This region is characterized by mountainous topography with steep slopes. The average slope ranges between 40 and 60%. Soil parent material varies widely from sedimentary marl to igneous dacite, rhyodacite, rhyolite (Anonymous, 2002). The soil texture ranges from clay loam, silty clay loam to sandy loam, loam and loamy clay. Humus form includes both moder and mulls. The soil in the district is generally acidic due to high precipitation causing leaching of base cations (Yener, 2013).

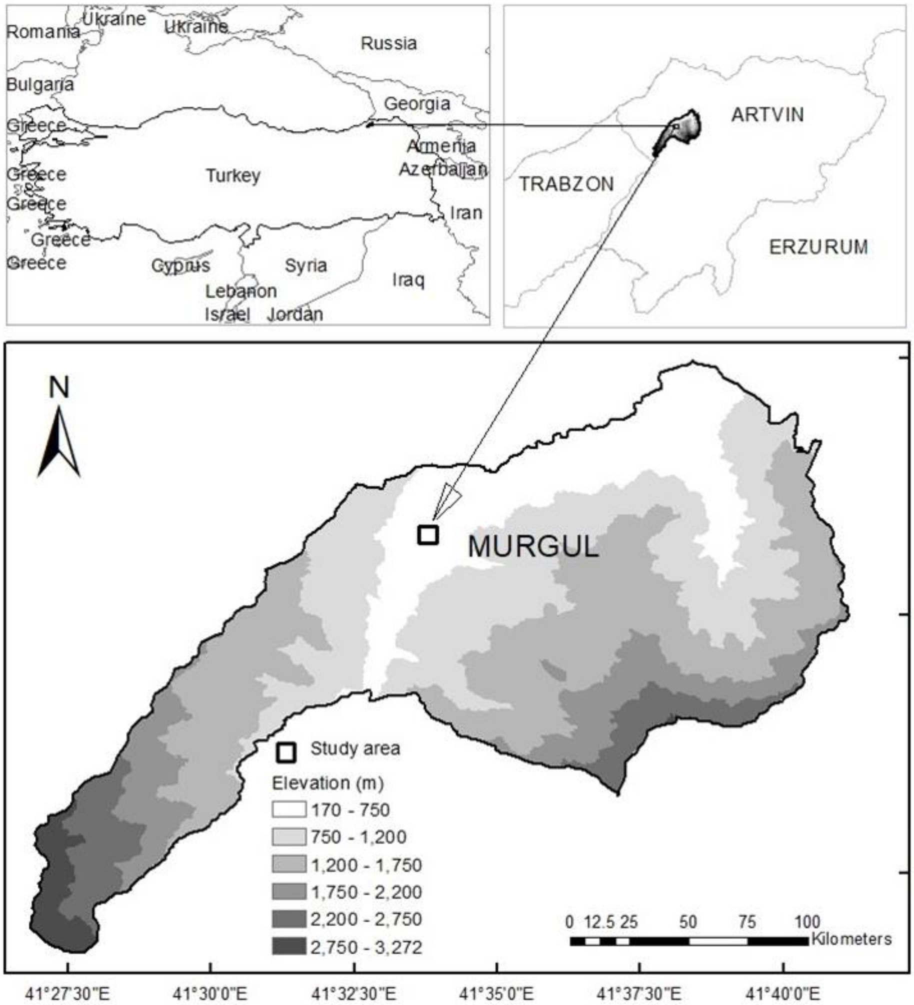

Figure 1. *Location of the study area in Murgul province, northeast Turkey*

The study area shows Eastern Black Sea climate under Black Sea macroclimate type, temperate in winter, warmer in summer and quite rainy in all seasons. According to the extrapolated climate data from the meteorological station closest to the study area, the annual mean temperature and the annual mean precipitation are 11.2 °C and 1213 mm, respectively. Mean annual minimum and maximum temperature are 7.1 °C and 16.6 °C, respectively (DMI, 2005). The growing season in the region is about six months (from May to October). The climate type is AB’1rb’3 (perhumid, mesothermal with no season of water deficiency, close to oceanic climate) according to Thornthwaite (1948).

In the district, along with oriental spruce, beech (*Fagus orientalis*), fir (*Abies nordmanniana)*, Scotch pine (*Pinus sylvestris)* and alder (*Alnus glutinosa)* species are found. Regarding understory vegetation, European mountain ash (*Sorbus aucuparia),* Caucasina laurel *(Prunus officinalis),* black sea holly *(Ilex colchica), common elder (Sambucus nigra),* European blueberry *(Vaccinium myrtillus),* Caucasian honeysuckle *(Lonicera caucasica),* fly honeysuckle *(Lonicera xylosteum),* rock red currant *(Ribes biebersteinii), oriental currant (Ribes orientale),* pontic azalea *(Rhododendron ponticum),* and yellow azalea *(Rhododendron luteum)* species are widely spread on the forest floor (Ansin, 1980).

Soil sampling and analyses

The sampling was done during the summer season of 2017. 54 sample plots were determined and equally distributed in 2-slope aspects such as north facing slopes (NFS) and south facing slopes (SFS), and 3 land use/land cover (LULC) types including 18-black alder, 18-black locust and 18-grassland with 9-replicate (2 slope aspects × 3 LULC × 9-replicate = 54). Top soil is the most common used part in related to LUCC-soil quality studies because of its susceptibility to LUCC (Gol, 2017). Therefore, 54-top soil (disturbed) and 54-soil-core (undisturbed) samples were collected at 0-20 cm soil depth to determine some soil properties. All soil samples were air-dried and sieved through 2-mm mesh before analyses. All measurements were done with two repetitions. Bulk density (BD) was determined by steel core sampler after soil samples were oven-dried at 105 °C (Blake and Hartge, 1986). Soil skeleton (Stoniness) was determined using undisturbed soil core samples. Soil texture analysis was done using Bouyoucos hydrometer method (Bouyoucos, 1962). Soil acidity (pH) and electrical conductivity (EC) were determined in 1:2.5 and 1:5 soil: distilled water ratio, respectively with glass electrode, and organic carbon (SOC) was determined using Walkley & Black wet digestion method and soil organic matter was calculated by multiplying percent of organic carbon with a factor of 1.724 2001 (Kalra and Maynard 1991). Soil lime content ($CaCO_3$) was determined with Schreiber's Calcimeter (Nelson, 1982). Total nitrogen (TN) was determined following Kjelhdal digestion, distillation, and titration method (Pansu and Gautheyrou, 2007). Carbon-nitrogen ratio (C:N) was determined as the ratio of total carbon to total nitrogen. Potentially mineralisable-N (NO_3^--N plus NH_4^+-N) was determined by microdestillation method following Bremner and Keeney (1965) in the beginning and at the 63rd days of incubation, and the net mineral nitrogen was calculated for 63 days (Ammonium for 63 days: Ammon63; Nitrate for 63 days: Nitrate63; Total N for 63 days: T63) using the difference between beginning and 63rd day (Guleryuz et al., 2007). Heavy metals in soil such as Cadmium (Cd), Chromium (Cr), Cupper (Cu), Lead (Pb) and Zinc (Zn) were determined with ICP-OES following EPA (1996) 3051 procedure.

Data analyses

Pearson correlation analysis was performed to determine the significant ($p < 0.005$) relationships among variables. Then, two-way analysis of variance (ANOVA) was used following the general linear model procedure to determine the effects of factors (vegetation cover, slope aspect) and their interaction (vegetation cover*slope aspect) on dependent variables. Tukey HSD test were used to determine differences between vegetation cover groups. To interpret the interaction, six new variables were computed with original cells as a level. Then, one-way ANOVA was run and simple main effects from one-way ANOVA was examined using the contrast results 2005). An anthropogenic index (AI) which indicates antropogenic impacts on selected soil properties with a specific number, using partial eta-squared values from two-way ANOVA, developed by Zhang et al. (2012) was used using the formula below:

$$AI = \frac{1}{n} + \sum_{i=1}^{n} \left(\frac{\eta 2ai}{\eta 2ni + \eta 2ai} \right) \times 100 \qquad \text{(Eq.1)}$$

where $\eta2_{ai}$ and $\eta2_{ni}$ refer to partial eta-squared values of land use and soil series for a certain soil property, respectively, and n is the number of soil properties. In this study, $n = 19$. Anthropogenic index ranges from 0 to 1: the larger the AI value, the higher the anthropogenic impact. All statistical analyses were performed using SPSS v20.0 (IBM.Corp, 2011).

Results and discussion

Changes in physical soil properties

Soil texture among the land uses ranged from sandy loam to loamy clay. The texture classes were determined as loamy clay (44%), clayey loam (44%) and the remaining (12%) for black locust; loamy clay (50%), clayey loam (28%) and the remaining (22%) for black alder; and sandy loam (39%), loam (33%) and the remaining (28%) for grasslands. Sand content of soil differed significantly ($p < 0.001$) both for vegetation cover and slope aspect (*Fig. 2b; Table 1*). Sand content of soil on NFS (60.3%) was found significantly ($p < 0.001$) higher than that on SFS (52.1%). Sand content of grassland soils (64.9%) was significantly ($p < 0.001$) higher than that of black alder (52.8%) and black locust (51.4%). Mean sand content did not differ significantly ($p = 0.33$) for their interaction (*Table 1*).

Clay content of soils also differed significantly ($p < 0.01$) with vegetation cover, slope aspect and their interaction (*Fig. 2a; Table 1*). Clay content of NF slope soils (17.3%) was found significantly lower than that of SF slope soils (27.1%). Clay content of grassland soils (14.3%) was significantly ($p < 0.001$) lower than that of black alder (26.1%) and black locust (26.3%). Clay content of NF black alder soils (19.1%) was found significantly ($p < 0.001$) lower than that of SF ones (33.5%) and mean clay content of NF black alder soils (19.1%) was found significantly ($p = 0.015$) higher than that of NF grassland soils (12.0%) (*Table 1*). The lower clay and higher sand contents in grasslands, having little or no protective vegetation cover, may be due to the removal of clay by erosion (Miheretu and Yimer, 2018; Tsehaye and Mohammed, 2013; Bewket and Stroosnijder, 2003). Hung et al. (2017) stated that the higher clay content in tree systems (e.g. forests) compared to other land uses may attribute to the protective cover by tree crowns, roots and litter reducing soil erosion. BD in the present study ranged from 1.38 gr/cm3 to 1.84 gr/cm3 and was not significantly affected by any of the factors according to two-way ANOVA ($p > 0.05$) (*Table 1*). BD in forests was found lower than that in other land uses (e.g. grassland) by some other researchers (Assefa et al., 2017; Gol, 2017; Tesfaye et al., 2016; Toohey et al., 2018; Yesilonis et al., 2016). The lower BD in forests as compared to the other land uses can be attributed to higher clay content and loosening of the surface soil with plant root growth (Qi et al., 2018). Vegetation cover, slope aspect and their interaction significantly affected soil stoniness ($p < 0.001$). The stoniness of soil was not differed significantly between NFS and SFS ($p = 0.91$). The stoniness of grassland soil (46.9%) was higher than that of black alder (38.9%) and black locust (35.6%) soils ($p < 0.005$). The interaction between vegetation cover and slope aspect also significantly affected soil stoniness (*Fig. 2c; Table 1*). Soil stoniness of SF grassland (53.8%) was significantly higher than that of black alder (32.2%) and black locust (32.0%) ($p < 0.001$). The slope aspect significantly affected only grassland soil ($p = 0.005$). The soil stoniness of NF grassland (35.8%) was found lower than that of SF grassland (53.8%).

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Table 1. *Physical properties (mean ± standard error) of surface soils according to LULC and slope aspect*

LULC	SASP	Sand (%)	Clay (%)	Silt (%)	BD (gr/cm^3)	Stoniness (%)
Black locust	NFS	55.9±0.9_a_A	19.1±0.8_a_A	25.0±0.7_a_A	1.6±0.0_a_A	39.2±1.5_a_A
	SFS	46.9±1.9_a_A	33.5±1.1_b_A	19.6±1.4_a_A	1.6±0.0_a_A	32.0±1.6_a_A
Black alder	NFS	58.4±3.2_a_AB	20.7±2.1_a_A	20.9±1.4_a_A	1.7±0.0_a_A	41.9±1.9_a_A
	SFS	47.2±2.5_b_A	31.4±2.0_b_A	21.4±0.9_a_A	1.5±0.0_a_A	35.8±3.8_a_A
Grassland	NFS	66.6±2.4_a_B	12.0±1.3_a_B	21.4±2.6_a_A	1.6±0.0_a_A	39.9±3.4_a_A
	SFS	62.0±1.8_a_B	16.6±1.0_a_B	21.4±1.7_a_A	1.6±0.0_a_A	53.8±2.2_b_B
Two-way ANOVA	LULC	F=20.1	F=43.8	F=0.0	F=0.0	F=10.1
		$p<0.001$	$p<0.001$	$p>0.05$	$p>0.05$	$p<0.001$
	SASP	F=20.3	F=68.5	F=1.7	F=0.0	F=0.0
		$p<0.001$	$p<0.001$	$p>0.05$	$p>0.05$	$p<0.001$
	Interaction	F=1.1	F=5.7	F=2.2	F=3.1	F=10.6
		$p>0.05$	$p<0.01$	$p>0.05$	$p>0.05$	$p<0.001$

LULC: land-use/land cover, SASP: slope aspect, NFS: north facing slopes, SFS: south facing slopes, BD: bulk density. By slope aspect, values of same LULC follow the various lower-case letters indicate significant difference. By LULC, values of same slope aspect follow the various upper-case letters differ significantly

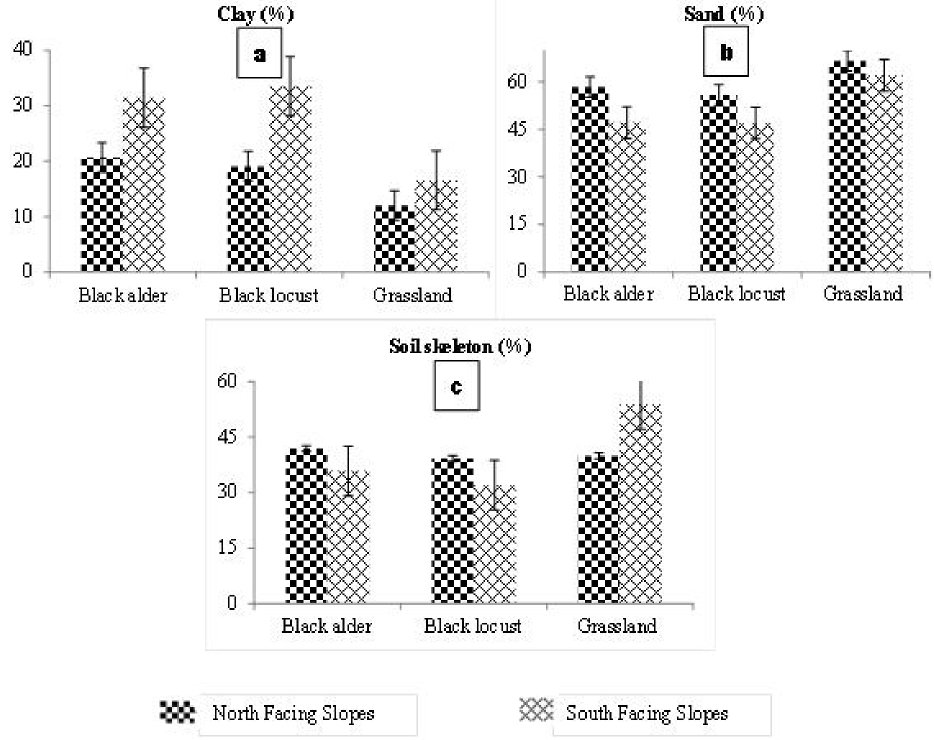

Figure 2. *Physical soil properties significantly affected by LULC and slope aspect*

Changes in chemical soil properties

The pH in the study area ranged from 3.93 (very strongly acidic) to 7.79 (weakly alkaline) according to Hazelton and Murphy (2016). This range is consistent with other studies (Kuo et al., 1983). pH was significantly affected by vegetation cover ($p < 0.001$), slope aspect ($p = 0.005$) and their interaction ($p < 0.001$) (*Fig. 3a; Table 3*). pH of grassland soils (5.29) was found significantly lower than that of black locust (6.03) and black alder (6.72) soils ($p < 0.001$). As the slope aspect changes from north to south for all vegetation covers, soil pH significantly increased from 5.82 to 6.21 (*Table 3*). The interaction also affected soil pH ($p < 0.001$). While, black locust soil pH was significantly found lower than that of other vegetation cover soils in NFS, grassland soil pH was significantly lower than that of other vegetation cover soils in SFS. The change of land use from forests to grasslands resulted in a decrease in soil pH may be attributed to either removal of basic cations by harvesting/grazing or leaching of them because of sparse vegetation cover 2018). Shrestha and Lal (2011) also reported a significant increase in soil pH after reclamation of soil. Some researchers (Kucuk, 2013; Tufekcioglu and Kucuk, 2004) reported the results unlike ours. Kucuk (2013) for example, reported that soil pH in forests (5.35) was lower than that in grasslands (6.87).

Soil EC in the study area changed between 19.5 and 421 µS/cm which is in the class of non-saline soils meaning salinity effects are mostly negligible according to Hazelton and Murphy (2016). All factors including also interaction significantly affected soil EC ($p < 0.001$) (*Fig.3b; Table 3*). EC significantly decreased in the order of black alder > black locust > grasslands. As the aspect changed from north to south, EC increased from 97.5 to 179.1 µS/cm. According to interaction between two-factors, while the lowest soil EC in north and south aspects was determined in black locust and grasslands respectively as 40.1 and 29.9 µS/cm (*Table 3*). This change may be attributed to the leaching of soil bases and subsequent reduction in soil carbonate (Biro et al., 2013). The correlation between EC and $CaCO_3$ in the study area was significant ($r = 0.71$ and $p < 0.01$) (*Table 2*).

Table 2. *Pearson correlation coefficient (r) between selected soil properties*

		(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**	**(8)**	**(9)**	**(10)**	**(11)**	**(12)**	**(13)**	**(14)**	**(15)**	**(16)**	**(17)**	**(18)**	**(19)**
(1)	Sand	1																		
(2)	Clay	$-.87^{**}$	1																	
(3)	Silt	$-.41^{**}$	-.09	1																
(4)	pH	$-.35^{**}$	$.53^{**}$	$-.28^{*}$	1															
(5)	OM	$.48^{**}$	$-.48^{**}$	-.08	$-.38^{**}$	1														
(6)	CaCO3	$-.38^{**}$	$.47^{**}$	-.10	$.53^{**}$	-.20	1													
(7)	EC	$-.50^{**}$	$.69^{**}$	$-.27^{*}$	$.85^{**}$	$-.28^{*}$	$.71^{**}$	1												
(8)	TN	-.03	-.02	.10	-.07	$.35^{**}$	-.13	-.01	1											
(9)	CN	$.33^{*}$	$-.33^{*}$	-.06	-.16	$.27^{*}$	-.12	-.21	$-.49^{**}$	1										
(10)	BD	.01	-.04	.04	.03	-.12	-.10	-.08	.06	-.13	1									
(11)	Stoniness	$.36^{**}$	$-.38^{**}$	-.03	$-.41^{**}$	$.51^{**}$	-.07	$-.34^{*}$	$.36^{**}$	-.04	.12	1								
(12)	Ammon63	$.45^{**}$	$-.51^{**}$	.03	$-.51^{**}$	$.36^{**}$	-.09	$-.41^{**}$	-.12	.13	.12	$.55^{**}$	1							
(13)	Nitrat63	-.04	.17	-.24	$.43^{**}$	-.08	-.05	$.28^{*}$	.24	-.09	.05	-.17	$-.42^{**}$	1						
(14)	T63	.22	-.12	-.24	.16	.13	-.11	.06	.19	-.02	.12	.14	.14	$.84^{**}$	1					
(15)	Cd	.11	-.08	-.07	.02	.07	-.04	.18	.01	-.06	-.17	-.10	.02	.28	.30	1				
(16)	Cr	$-.49^{**}$	$.57^{**}$	-.04	$.69^{**}$	$-.51^{**}$	$.42^{*}$	$.66^{**}$	-.30	-.04	-.14	$-.71^{**}$	$-.49^{**}$	.17	-.12	-.07	1			
(17)	Cu	-.02	-.15	.32	-.26	-.05	-.13	-.16	.05	-.09	$-.35^{*}$	-.18	.00	-.12	-.13	$.38^{*}$	.13	1		
(18)	Pb	.24	-.27	.00	$-.59^{**}$	.28	-.27	$-.37^{*}$	.11	-.03	-.12	$.41^{*}$	$.53^{**}$	-.16	.17	$.45^{**}$	$-.67^{**}$	.27	1	
(19)	Zn	.24	-.26	-.02	-.25	.21	-.22	-.13	.05	.11	-.20	.00	.14	.23	.33	$.81^{**}$	$-.41^{*}$	.29	$.66^{**}$	1

**Correlation is significant at the 0.01 level. *Correlation is significant at the 0.05 level. pH: soil acidity, EC: electrical conductivity, TN: total nitrogen, CN: carbon: nitrogen ratio, BD: bulk density, stoniness: soil skeleton, Ammon6 Nitrat63 and T 63: ammonium, nitrate and total nitrogen mineralization for 63-day, Cd: cadmium, Cr: chromium, Cu: copper, Pb: lead, Zn: zirconium

Table 3. *Chemical properties (mean ± standard error) of surface soils according to LULC and slope aspect*

LULC	SASP	pH	OM (%)	CaCO3 (%)	EC (µS/cm)	TN (%)
Black locust	NFS	4.7±0.0_a_A	1.9±0.2_a_A	1.2±0.1_a_A	40.1±2.8_a_A	0.094±0.003_a_AB
	SFS	7.4±0.2_b_A	1.5±0.2_a_A	3.0±0.7_a_A	248.5±30.1_b_A	0.080±0.004_a_A
Black alder	NFS	6.4±0.1_a_B	2.7±0.3_a_A	1.6±0.3_a_A	162.6±26.5_a_B	0.117±0.008_a_A
	SFS	7.0±0.3_a_A	1.5±0.2_b_A	2.8±0.7_a_A	258.8±30.8_b_A	0.085±0.004_b_A
Grassland	NFS	6.3±0.2_a_B	2.0±0.1_a_A	1.2±0.2_a_A	90.0±11.7_a_A	0.078±0.009_a_B
	SFS	4.3±0.1_b_B	3.1±0.4_b_B	1.2±0.1_a_A	29.9±2.9_a_B	0.096±0.007_a_A
Two-way ANOVA	LULC	F=38.5 p<0.001	F=6.5 p<0.01	F=3.2 p>0.05	F=25.3 p<0.001	F=3.3 p<0.01
	SASP	F=8.5 p<0.01	F=0.0 p>0.05	F=7.7 p<0.01	F=22.0 p<0.001	F=3.3 p<0.01
	Interaction	F=103.0 p<0.001	F=10.6 p<0.001	F=1.9 p>0.05	F=20.1 p<0.001	F=7.6 p<0.01
LULC	**SASP**	**CN**	**Ammon63 (kg/ha)**	**Nitrat63 (kg/ha)**	**T63 (kg/ha)**	
Black locust	NFS	11.6±1.1_a_A	28.5±1.3_a_AB	32.0±2.9_a_A	60.5±2.3_a_A	
	SFS	11.1±1.4_a_A	23.8±3.6_a_A	42.5±2.8_a_AB	66.3±4.4_a_A	
Black alder	NFS	13.2±1.2_a_A	22.3±1.9_a_A	66.4±5.9_a_B	88.7±5.8_a_B	
	SFS	10.0±1.4_a_A	21.2±1.9_a_A	51.4±4.7_a_B	72.6±5.4_a_A	
Grassland	NFS	25.7±11.9_a_A	31.2±2.2_a_B	39.7±5.0_a_A	70.9±5.5_a_A	
	SFS	20.0±2.9_a_B	40.6±2.1_a_B	30.5±2.7_a_A	71.2±3.2_a_A	
Two-way ANOVA	LULC	F=3.3 p>0.05	F=20.3 p<0.001	F=19.7 p<0.001	F=19.7 p<0.001	
	SASP	F=0.0 p>0.05	F=0.0 p>0.05	F=1.8 p>0.05	F=1.8 p>0.05	
	Interaction	F=0.0 p>0.05	F=5.2 p<0.01	F=5.1 p<0.01	F=5.1 p<0.01	

LULC: land-use/land cover, SASP: slope aspect, NFS: north facing slopes, SFS: south facing slopes, OM: organic matter, EC: electrical conductivity, TN: total nitrogen, CN: carbon: nitrogen ratio, Ammon6 Nitrat63 and T63: ammonium, nitrate and total nitrogen mineralization for 63-day. By slope aspect, values of same LULC follow the various lower-case letters indicate significant difference. By LULC, values of same slope aspect follow the various upper-case letters differ significantly

Organic matter classes of soils in the study area ranged from weak (1.69%) in black locust to moderate (2.59%) in grasslands according to 2016). Organic matter content of black alder soils (1.70%) were significantly found lower than that of grassland soils (2.59%)($p = 0.002$) (*Fig. 3c; Table 3*). Similar results were found by some other researchers (Pu et al., 2018; Wei et al., 2011; Yesilonis et al., 2016). The slope aspect alone did not affect soil organic matter ($p = 0.46$). In SFS, soil organic matter content of grasslands (3.13%) was higher than that of black locust (1.51%) and black alder (1.49%) (*Fig. 3c; Table 3*). While soil organic matter content of black alder increased from south (1.49%) to north (2.66%) facing slopes ($p = 0.02$), that of grasslands decreased ($p = 0.037$). The positive effect of north aspect on organic matter content by also found by Qin et al. (2017). Increasing organic matter content in north aspect can be attributed to more organic carbon and more total nitrogen accumulation in the soil because of higher soil water content and less evaporation (Johnson et al., 2011).

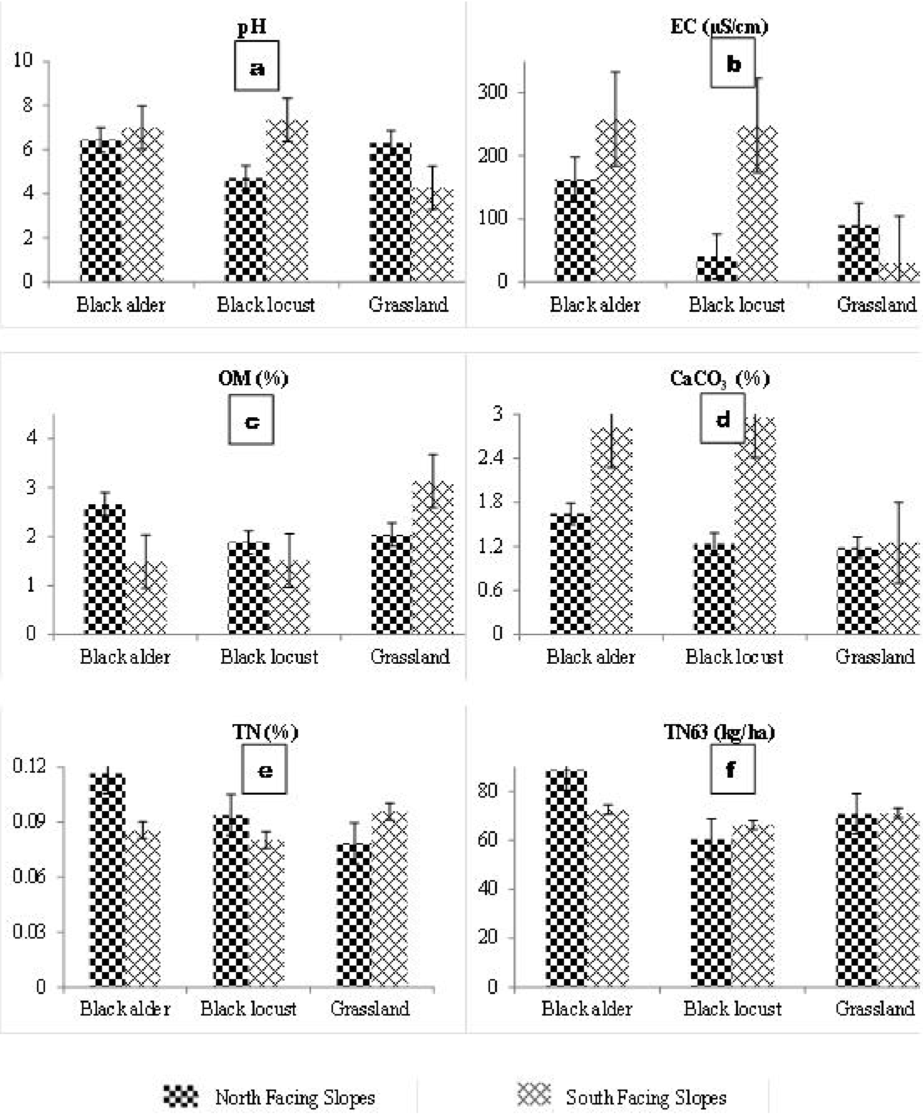

Figure 3. *Chemical soil properties significantly affected by LULC and slope aspect*

On the one hand, $CaCO_3$ content of soils was not significantly affected by vegetation cover ($p = 0.05$) and vegetation cover*slope aspect interaction ($p = 0.164$), on the other hand, the content decreased from south (2.34%) to north (1.35%) without considering vegetation cover effect ($p = 0.008$) (*Fig. 3d; Table 3*).

When not considered the effects of vegetation cover, soil EC in SFS (179.1 µS/cm) was also significantly greater than that in NFS (97.5 µS/cm)($p < 0.001$). Soil EC in grasslands (59.9 µS/cm) was found significantly lower than that in black locust (144.3 µS/cm, $p = 0.01$) and black alder (210.7 µS/cm, $p < 0.001$) without considering slope aspect effect. In SFS, soil EC of grassland (29.9 µS/cm) was found significantly less than that of other vegetation covers ($p < 0.001$). Soil EC of vegetation covers except grasslands increased from NFS to SFS (*Table 3*).

TN of soils was not affected by vegetation covers ($p = 0.05$) and slope aspect ($p = 0.07$) but significantly affected by their interaction. It significantly increased from south (0.085%) to north (0.117%) for only black alder ($p = 0.012$) (*Fig. 3e; Table 3*). That increase may be attributed to improving ecological condition depending on more

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moisture in north. Similar results were found by some other researchers (Bangroo et al., 2017; Gol, 2017; Rezaei et al., 2006). Soil TN of north –facing black alder (0.117%) was found significantly greater than that of NF grasslands (0.078%) ($p = 0.001$). This can be attributed to removal of organic matter with grazing and higher level of N-fixation in black alder (Ripley et al., 2010; Wilson et al., 2011). Similar results were reported by some other researchers (Beheshti et al., 2012; Miheretu and Yimer, 2018; Tesfaye et al., 2016; Wilson et al., 2011). Soil C:N ratio was not significantly affected by vegetation cover ($p = 0.05$), slope aspect ($p = 0.46$) and their interaction ($p = 0.87$) (*Table 3*). While Miheretu and Yimer (2018) and Chacon et al. (2009) also found similar results like in the present study. Significant effects of land use on soil C:N ratio also found in some other studies (Assefa et al., 2017; Kucuk, 2013).

Looked at variables regarding 63-day nitrogen mineralization (ammonium, nitrate and total); slope aspect alone had no significant effect on 63-day nitrogen mineralization. Vegetation cover alone had significant effect on 63-day ammonium, nitrate and total nitrogen mineralization. 63-day ammonium mineralization of grassland soils (35.9 kg/ha) was found significantly higher than that of black locust (26.1 kg/ha) and black alder (21.8 kg/ha) ($p < 0.001$). Higher ammonium mineralization in grassland soils can be attributed to lower pH (Xue et al., 2013). The correlation between NH4-N and pH was negative ($p < 0.0$ $r = -0.59$) (*Table 2*). Similar results were found by Wei et al. (2011) in loess plateau of China who reported higher nitrogen mineralization in grassland soils compared to others due to lower bulk density. Nitrate and total nitrogen mineralization in 63-day period of black alder soils (58.8 kg/ha and 80.6 kg/ha) were found significantly higher than that of the other vegetation covers (*Fig. 3f; Table 3*). Higher nitrate mineralization in forest (alder) soils compared to the other land uses can be attributed to that on the one hand, black alder, being one of the N-fixing trees provides resources both easily accessible and abundant for soil microbes and facilitates N mineralization, on the other hand, it contributes to the supply of organic substrates which are easily decomposed and decrease C:N ratio (Cui et al., 2018). The higher nitrate mineralization can also be attributed to positive correlation with pH ($r = 0.4$ $p < 0.01$) (*Table 2*). Similar results were found also by some other researchers (Hart et al., 1997; Tecimen et al., 2013; Uri et al., 2008). Uri et al. (2008), for example, reported higher annual net nitrogen mineralization (99 kg/ha) in the birch stand than that (51 kg/ha) of in grasslands in Estonia. Tecimen et al. (2013) explained the difference with the effect of increasing organic carbon. The 63-day ammonium mineralization of SF grassland soils (40.6 kg/ha) was found significantly higher than that of SF black locust (23.7 kg/ha) and black alder (21.2 kg/ha) soils ($p < 0.001$). Both in NFS and SFS, 63-day nitrate mineralization of black alder soils (66.4 kg/ha and 51.4 kg/ha respectively) was significantly higher than that of grassland soils (39.7 kg/ha and 30.5 kg/ha respectively). 63-day total nitrogen mineralization of NF black locust soils (60.5 kg/ha) was lower than that of black alder soils in the same aspect (88.7 kg/ha).

Changes in heavy metal concentrations

Average Cd and Zn contents of soils in the study area were 0.7 ppm (0 to 6.3 ppm) and 148.5 ppm (72 to 312 ppm), respectively. These values are slightly higher than the average concentrations (0.5 ppm for Cd and 64 ppm for Zn) reported by Kabata-Pendias and Mukherjee (2007). This can be due to the copper mine near the study area. Cd and Zn concentrations among heavy metals did not significantly differed according to vegetation cover, slope aspect and their interaction ($p > 0.05$) (*Table 4*).

Cr concentration in soil ranged from 5.2 to 29.5 ppm with the average value of 20.2 ppm. This value is consistent with the range of world mean (54 ppm) reported by Kabata-Pendias and Mukherjee (2007). Soil Cr concentration of grasslands (13.8 ppm) was found significantly lower than that of black alder (23.3 ppm) and black locust (24.4 ppm)($p < 0.001$). The soil Cr content of black alder and black locust significantly increased from NFS to SFS unlike grasslands ($p < 0.05$). The soil Cr content of SF grassland (6.7 ppm) was significantly lower than that of black alder (28 ppm) and black locust (26.8 ppm) in the same aspect (*Fig. 4a; Table 4*). Higher Cr contents of forest soil may be related to higher pH ($r = 0.6$ $p < 0.01$) (*Table 2*) (Kabata-Pendias and Mukherjee, 2007).

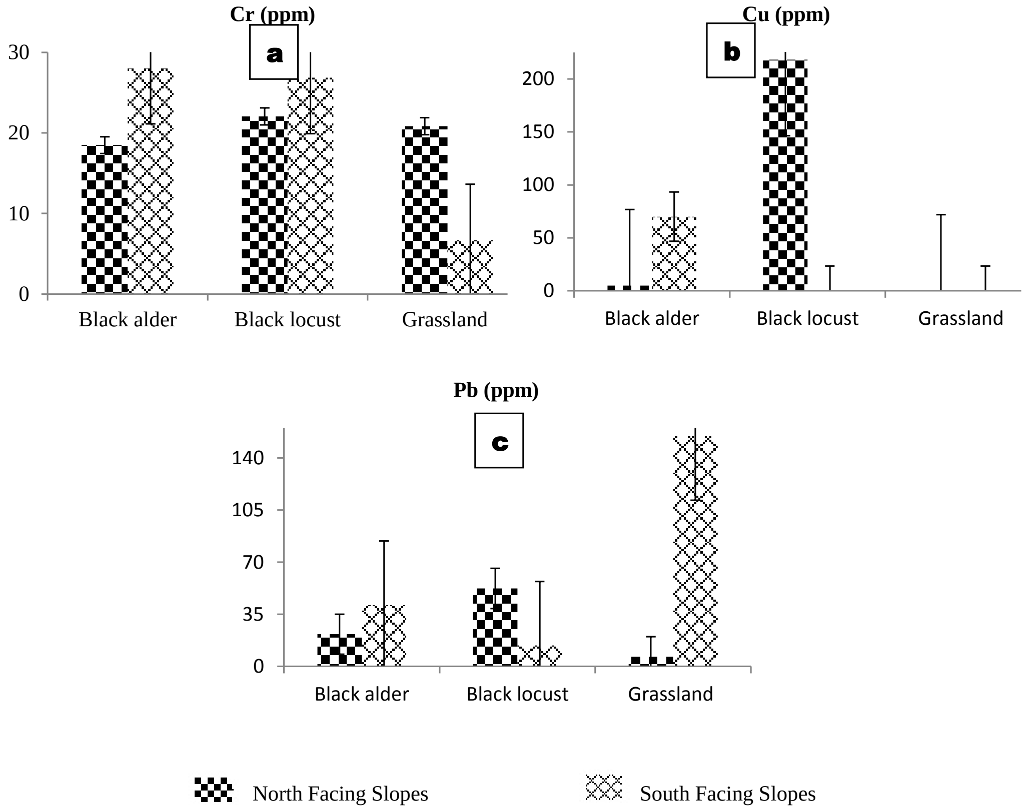

Figure 4. *Heavy metal contents of soils significantly affected by LULC and slope aspect*

Cu content of soils in the study area ranged from 0 to 380 ppm with the average value of 49 ppm. This range is consistent with the range in the world (2 to 250 ppm) reported by Kabata-Pendias and Mukherjee (2007). Soil Cu concentration of black locust (109.1 ppm) was significantly higher than that of grassland (0.001 ppm) ($p = 0.007$). While in north aspects, the lowest and the highest soil Cu concentrations belonged to grasslands (0.001 ppm) and black locust (218.3 ppm), respectively, in south aspects, the lowest and highest soil Cu concentrations belonged to grassland (0.001 ppm) and black alder respectively (70.0 ppm) (*Fig. 4b; Table 4*). Higher Cu contents in forest soils might be related to higher clay contents than that in grassland soils ($r = 0.7$ $p < 0.001$) (*Table 2*). Zheng et al. (2016) also reported positive correlation between Cu and clay contents of soil for coastal soils in China.

Pb content of soils in the study area ranged from 0 to 254.2 ppm with the average value of 48 ppm. This value is higher than that in the world (up to 90 ppm) Kabata-Pendias and Mukherjee (2007). Pb concentration was found significantly highest in grassland soils (80.5 ppm) compared to black locust (33.2 ppm) and black alder (31.3 ppm) soils. The Pb concentration significantly increased from north (26.8 ppm) to south (69.9 ppm) ($p = 0.002$). In SFS, grassland soils had significantly higher Pb concentration than others ($p < 0.001$). Grassland soil Pb concentration increased from north (6.5 ppm) to SFS (154.5 ppm) (*Fig. 4c; Table 4*). The lower Pb content in forest soils may be related to higher pH ($r = -0.5$ $p < 0.01$) and higher clay content ($r = 0.7$ $p < 0.001$) (*Table 2*). The lower Pb content in black alder and black locust may be related to phytoremediation (Escobar and Dussan, 2016; Babu et al., 2013; Escobar and Dussan, 2016; Lee et al., 2009). *Alnus acuminata* subsp. acuminata for example, took Pb and Cr up as 135 mg/kg and 71 mg/kg, respectively (Escobar and Dussan, 2016).

Many studies have been performed to determine the effects of copper smelter on heavy metal concentration (Adamo et al., 2002; Dudka et al., 1996; Hutchinson and Whitby, 1977; Kuo et al., 1983). For example, Adamo et al. (2002) found the related heavy metal concentrations of soil near the smelter in Ontario, Canada as 43 3 5 2.7 and 63 ppm for Cu, Pb, Zn, Cd and Cr, respectively. Hutchinson and Whitby (1977) reported heavy metal concentrations in soils for Cu, Pb and Zn near the Sudbury smelting region of Canada as 134 51 and 62 ppm, respectively. Cai et al. (2015) reported the average heavy metal concentrations in soil near Tonglushan copper mine in Hubei, China for Cu, Pb and Cd as 38 120 and 2.59 ppm, respectively. While Cu, Pb, Cd and Cr concentrations in soils determined in the present study was consistent with those in the other studies (Adamo et al., 2002; Dudka et al., 1996; Hutchinson and Whitby, 1977; Kuo et al., 1983), Zn was found higher than the others.

Comparison of main factors' effects with partial eta squared (η2)

The anthropogenic index was computed using *Equation 1*. This index indicates which main factor was more effective on selected soil properties, natural (slope aspect) or anthropogenic (land use/land cover). This index was computed as 0.75 closer to indicates adverse human impact on soil properties.

The partial eta-squared values (η2) were also used to compare the effect size (explained proportion of variance by any factor) of main factors and their interaction on selected soil properties. The related values (η2) were presented in *Tables 4* and *Figure 5*. Regarding soil texture, clay was the most affected texture component by land use, slope aspect and their interaction with η2 values of 0.6 0.59 and 0.1 respectively (*Fig. 5*). pH, EC and OM were the most significantly affected soil chemical properties after Cr by land use, slope aspect and their interaction respectively, were pH with values of 0.6 0.1 0.81; EC with values of 0.5 0.3 0.46 and OM with values of 0.2 0.0 0.31 (*Fig. 5*).

The most significantly affected soil properties by land use and interaction was found Cr with values of 0.93 and 0.94 (*Fig. 5*). The significant interaction effect on soil properties such as pH, OM, TN, Stoniness and heavy metals except Cd was found higher than that of main factors. That means the interaction between main factors strengthen the effect. For example, while effect size of land use and slope aspect on Pb content were 0.29 and 0.27 respectively, the interaction effect was found 0.54 which was about two times higher than that of the other factors (*Table 4*).

Table 4. *Heavy metal contents (mean ± standard error) of surface soils according to LULC and slope aspect*

LULC	SASP	Cd (ppm)	Cr (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Black locust	NFS	0.3±0.2_a_A	22.0±0.6_a_A	218.3±66.0_a_A	52.3±17.6_a_A	140.6±8.0_a_AB
	SFS	0.0±0.0_a_A	26.8±0.9_b_A	0.0±0.0_b_A	14.0±5.2_a_A	113.3±12.9_a_A
Black alder	NFS	0.7±0.3_a_A	18.5±0.5_a_B	4.9±3.1_a_B	21.6±5.6_a_AB	164.5±15.1_a_B
	SFS	2.1±1.3_a_A	28.1±0.5_b_A	70.0±45.9_a_A	41.1±22.7_a_A	167.2±40.5_a_A
Grassland	NFS	0.0±0.0_a_A	20.8±0.4_a_A	0.0±0.0_a_B	6.5±1.7_a_B	119.5±11.8_a_A
	SFS	1.0±0.3_a_A	6.7±0.5_b_B	0.0±0.0_a__A	154.5±25.1_b_B	186.0±12.1_a_A
Two-way ANOVA	LULC	F=2.4 p>0.05	F=196.1 p<0.001	F=5.7 p<0.01	F=6.1 p<0.01	F=2.0 p>0.05
	SASP	F=2.2 p>0.05	F=0.0 p>0.05	F=3.6 p>0.05	F=11.0 p<0.01	F=0.0 p>0.05
	Interaction	F=1.2 p>0.05	F=221.3 p<0.001	F=10.2 p<0.001	F=18.0 p<0.001	F=2.9 p>0.05

LULC: land-use/land cover, SASP: slope aspect. NFS: north facing slopes, SFS: south facing slopes. By slope aspect, values of same LULC follow the various lower-case letters indicate significant difference. By LULC, values of same slope aspect follow the various upper-case letters differ significantly

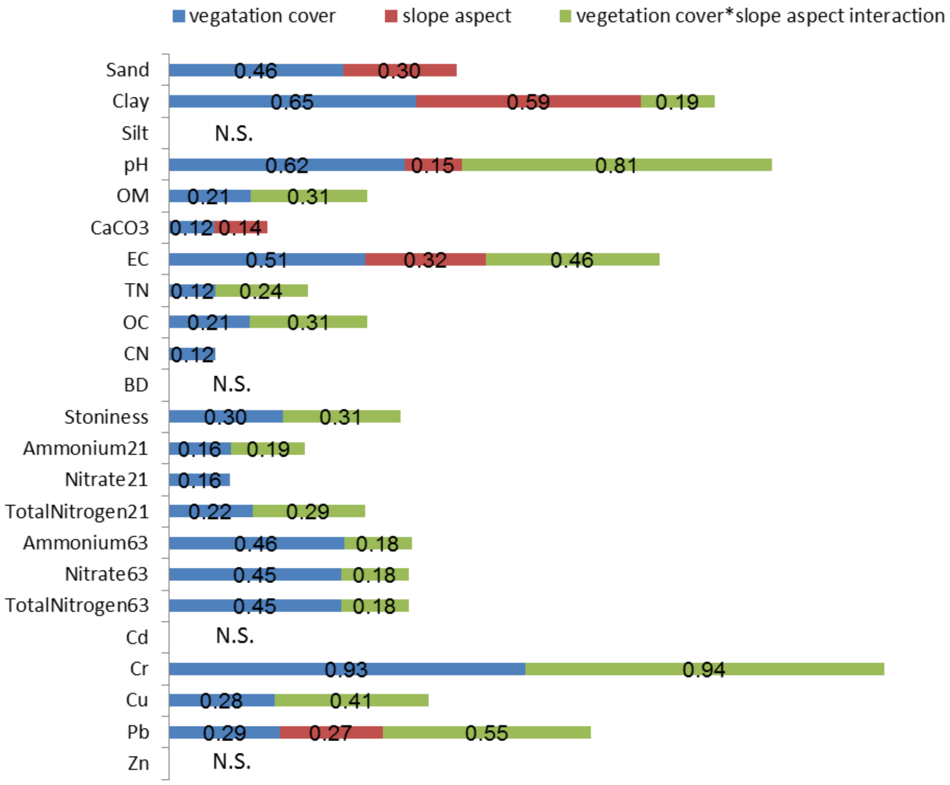

Figure 5. *Effect size (η2) of independent variables on selected soil properties*

Conclusion

The results from the present study showed significant interaction effect beside LULC and slope aspect on selected soil properties. In general, main factors and their interaction improved selected soil properties affecting soil quality. The most affected soil properties by LULC and slope aspect were Cr content and clay content, respectively. The improving effects of afforestation compared to grasslands was revealed on only clay contents and soil skeleton among physical properties; pH, nitrate and total nitrogen mineralization for 63-day among chemical properties. Our study showed that changes in LULC from grasslands to forest (especially to black alder) promoted soil quality in terms of total nitrogen and NO_3-N, playing a fundamental role in ecological restoration, beside other soil properties. Although decreasing effect (phytoremediation) of black alder and black locust on heavy metals except Pb in soil was not found In the present study, *Alnus glutinosa* and *Robinia pseudoacacia* may be suggested for the restoration/reclamation of mining soils in terms of phytoremediation beside their advantages such as improving nitrogen mineralization. However, further periodical studies are needed to determine the improving effects of afforestation on soil properties after mining. Results from the present study may be generalized to larger areas which are similar to the study area in terms of land-use and vegetation cover

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