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Assessment of Soil Quality in a Copper Mining Region in Bulgaria

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Abstract. The paper deals with a mining region of Bulgaria in the Sub-Balkan mountain valleys where there is enrichment of the rock material in copper, gold and other valuable metals and minerals. The study area is localized in the South-west of Chelopech mining - close to the watershed of Topolnitsa River. A monitoring network has been set up. The dominated soil types are Cambisols, Luvisols, Fluvisols, and Phaeozems with shallow surface humus horizon. In the mining region, the anthropogenic activities have different negative impacts over soil cover such as contamination, erosion, acidification, waste disposal, inert and other materials spread over soils surface. The assessment of physico-chemical and agrochemical soil parameters is important for its ecological modelling applications. The study found significant fluctuation of these properties in the area. Acidification affects 45% of the studied points, this accompanied by insufficient nitrogen and phosphorus nutrition.

Key words: soil chemical properties, agrochemistry, soil monitoring.

Introduction

The lands around Chelopech mining are parts of the Zlatitsa-Pirdop valley which lies between the Stara planina mountain (The Balkan) and Sredna Gora mountain. The mountains have an influence on the development of soil process, vegetation cover and accumulation of large particles (stony) or fine-grained (clayey) from the surrounding slopes.

The area is characterized by the soils with different stages of development from shallow to deep formed through various geological periods. Contemporary geographic and climatic conditions have a significant effect on their status and agro-ecological characteristics.

The soils, except for meadow varieties (Phaeozems), can generally be defined as low to a medium content of humus and nutritional elements. They are also weak developed, acidic, fragmented, heavy, sandy-loamy and loamy by texture, poor physical and physicochemical properties. These soils are difficult for cultivation and agriculture (Koinov *et al.*, 1974).

The copper enrichment of soils is one of the most significant environmental threats in some parts of Bulgaria. Fluvisols, Cambisols, Phaeozems, Leptosols and Luvisols are the major soil types distributed in the areas around the Cu ore processing plants in Bulgaria such as Elatsite, Chelopech, Assarel-Medet, Aurubis-Pirdop (Benkova *et al.*, 2005; Ilinkin *et al.*, 2014; Nenova *et al.*, 2015; Atanssova *et al.*, 2017).

The lands of the region have been polluted as from the mining industry for copper and gold for centuries (MALINOVA, 1998; DONCHEVA-BONEVA *et al.*, 2011; DINEV *et al.*, 2008). Pollution in the region and intensive agriculture in the last decades have drastically reduced soil productive potential and it needs to be constantly remediated and protected to increase soil fertility (BANOV *et al.*, 2010). Because of low pH and high copper-contamination, the soils have been meliorated with calcium and magnesium-rich amendments. These practices have changed the soil reaction, cation exchange capacity and base saturation. Metal contamination in agricultural soils could affect carbon dynamics. This can significantly affect the capacity of the soil microbial communities to degrade organic matter, thereby leading to a loss of soil fertility and modifications in the balance between CO_2 release and long-term SOC storage. The nitrogen cycle is biologically influenced, but as it was mentioned above, the area is highly polluted in the surface horizons with Cu compounds and many populations able to degrade polymerized or aromatic compounds, such as Sphingomonadaceae and Actinobacteria, have been apparently actively involved in the residue degradation in copper-contaminated soils (BERNARD *et al.*, 2009).

The investigation aims to evaluate the soil quality in the copper mining region of Bulgaria by GIS mapping, spatial distribution and physico and agrochemical parameters.

Materials and Methods

The object of the study is soils is located around the village of Chavdar. They are different soil types- Leptosols, Cambisols, Phaeozems, and Fluvisols. The elevation is about 520 m a.s.l. The vegetation is composed mainly of meadow grasses associations and fields with arable crops such as wheat, sunflower, rape, corn, barley, etc. The study was done by monitoring network with a grid of 0.5 to 0.5 km and sampling to a depth of 0-20 cm (Fig. 1).

The content of soil organic carbon (SOC) was determined using the modified Turin's method (KONONOVA, 1966; FILCHEVA & TSADILAS, 2002; HRISTOVA *et al.*, 2016; FILCHEVA *et al.*, 2018). The content of soil organic matter (SOM) is given as soluble part – humic plus fulvic acids (HA+FA) and an insoluble part called humin. The cation exchange capacity (CEC) and base of saturation (B.S.) were determined by the method of GANEV & ARSOVA (1980). Ammonium and nitrate nitrogen by KEENEY & BREMNER (1966); the mobile forms of phosphorus and potassium by the acetate-lactate method of IVANOV (1984). The pH was determined potentiometrically in compliance with ISO 10390: 2010. MS Excel (Microsoft Co. 2010) is used for statistics.

The applied methodology includes a survey by statistical and graphical processing, classification of the studied physical and agrochemical parameters and their mapping in a geographic information system. For mapping, Kriging Interpolation is used– Isoline maps are created by Surfer ver. 8.02 of Golden Software 2002 and Global Mapper v. 16, for a topographic map. The studied area was assessed by classification for soil pH, CEC and bases of saturation (BS), the content of SOM (PENKOV, 1986) and assessment by sufficient amount of nutrients - nitrogen, phosphorus and potassium (ATANASOV *et al.*, 2006).

Results and Discussion

Descriptive statistic and correlation analysis

The fixed sample points were analyzed for the main physico-chemical properties. The investigated area is best described by using descriptive statistics of main physico-chemical and agrochemical properties (Table 1) and correlation matrix (Table 2). The surface horizons of the survey area show high fluctuations in the soil chemical properties.

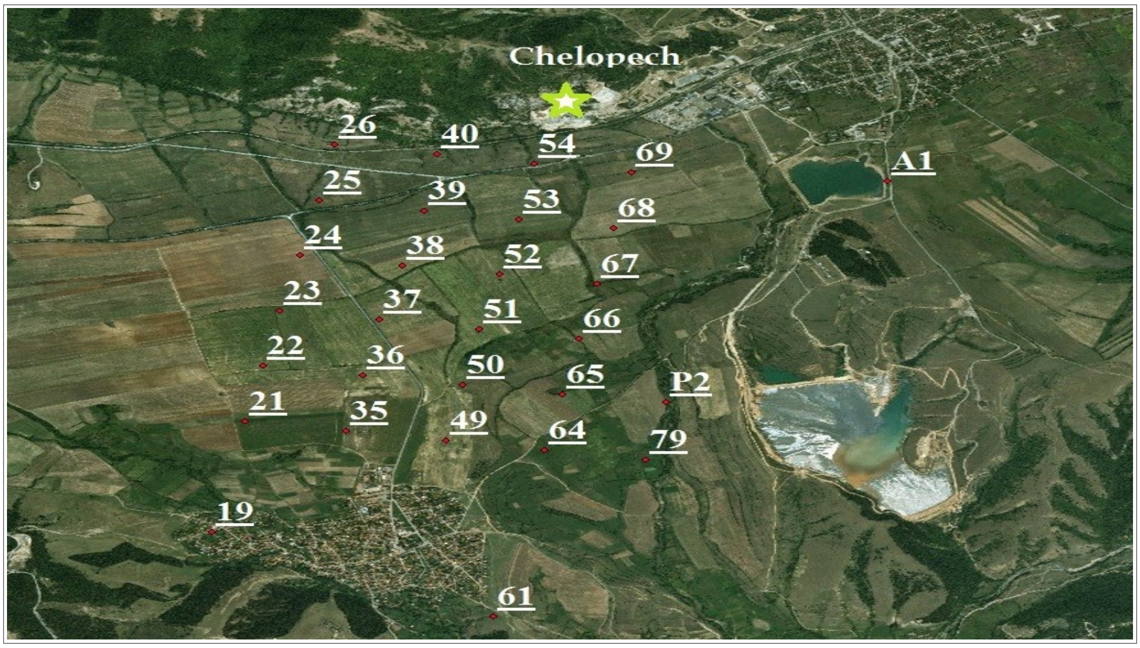

Fig. 1. The satellite, topographic map of the area South Chelopech.

Table 1. Descriptive statistics of main physico-chemical and agrochemical parameters.

	pH	**SOC** %	**HA +FA** %	**CEC** cmol.kg^{-1}	**ex.H^{+}** cmol.kg^{-1}	**ex.Al^{3+}** cmol.kg^{-1}	**ex.Ca^{2+}** cmol.kg^{-1}	**ex.Mg^{2+}** cmol.kg^{-1}	**B.S.** %	**ΣNH$_4$ +NO$_3$** mg.kg^{-1}	**P$_2$O$_5$** mg.100g^{-1}	**K$_2$O** mg.100g^{-1}
Mean	5.94	1.61	0.41	27.25	7.29	0.75	16.90	3.10	72.70	25.64	3.50	22.49
Standard Err.	0.17	0.11	0.03	1.27	0.72	0.16	1.40	0.12	2.89	1.63	0.96	1.59
Median	5.80	1.47	0.38	27.40	7.80	0.40	16.00	3.20	71.40	23.60	1.80	21.70
Mode	5.00	1.54	0.38	24.90	5.50	0.00	16.00	3.20	55.00	23.00	0.20	21.70
Standard Dev.	0.89	0.61	0.15	6.86	3.85	0.84	7.52	0.66	15.58	8.76	5.15	8.59
Sample Var.	0.80	0.37	0.02	47.10	14.84	0.70	56.55	0.44	243	76.78	26.57	73.76
Range	2.40	3.00	0.79	37.40	12.60	2.30	38.70	2.50	49.00	38.10	21.40	27.70
Minimum	5.00	0.73	0.22	18.90	0.00	0.00	9.50	2.00	51.00	8.60	0.20	12.10
Maximum	7.40	3.73	1.01	56.30	12.60	2.30	48.20	4.50	100	46.70	21.60	39.80

Table 2. Correlation matrix between main physicochemical and agrochemical parameters.

	pH	SOC %	**HA+FA** %	**CEC** cmol.kg^{-1}	**ex. H^{+}** cmol.kg^{-1}	**ex. Al^{3+}** cmol.kg^{-1}	**ex.Ca^{2+}** cmol.kg^{-1}	**ex.Mg^{2+}** cmol.kg^{-1}
SOC	0.20	*						
HA+FA	0.05	**0.85**	*					
CEC	0.18	0.49	**0.58**	*				
ex. H+	**-0.94**	-0.13	0.00	0.00	*			
ex. Al^{3+}	**-0.86**	-0.12	0.06	-0.30	**0.74**	*		
ex. Ca^{2+}	**0.61**	**0.52**	**0.53**	**0.87**	-0.49	**-0.60**	*	
ex.Mg^{2+}	**0.55**	0.08	0.04	0.47	-0.36	**-0.63**	**0.53**	*
B.S.	**0.97**	0.20	0.04	0.19	**-0.96**	**-0.85**	**0.63**	**0.51**
P$_2$O$_5$	**0.50**	0.02	0.11	-0.10	**-0.53**	-0.31	0.16	0.23

The statistics show that the parameters studied vary greatly. The content of SOC and its soluble fraction vary only slightly, while the physical and agrochemical parameters vary greatly (Table 1). The strong positive or negative correlations between the parameters are noted in bold in Table 2. Correlation analysis shows that there are stronger trends related to physicochemical than to agrochemicals parameters.

Classification of the main pysico-chemical and agrochemical parameters

The soil results show that pH varies from 5.0 to 7.0 (Table 1) and the mean value is 5.9, which is consistent with other studies in the area which show that the soil reaction is low acidic values pH approximately 5-6 (DINEV *et al.*, 2008). According to the classification for pH: 59 % of the test points are acidic with pH below 6.0; 38 % have a neutral pH with pH between 6. 0 – 7. 3 and 3% are alkalic with a pH above 7.4.

In the acidic points, harmful effects of exchange hydrogen and aluminium ions were found and they have a positive correlation (r^2 = 0.74). The negative correlation between pH and hydrogen ion content (r^2 = -0.96) is higher than that of aluminium (r^2 = -0.80), but both are indicative of a decrease in pH values associated with their raise.

The reasons for having neutral and alkaline pH points are mainly two. First is that in the area the liming is rare practice - melioration with calcium and magnesium-rich materials which eliminate high acidity and blockade free heavy metals ions mainly copper (NIKOVA, 2008 – pers. comm.). The second is that there are soils in the region which are rich in carbonates, because of calcium-rich parent rock and the river Topolnitsa which brings base cations from the surrounding area (KOINOV *et al.*, 1974). Sorption capacity is from medium to over high values (Fig. 2), CEC is between 18.9 to 56.0 $cmol.kg^{-1}$ (PENKOV, 1986). Over high values of CEC are connected by the content of SOM in a marshy place near river Topolnitsa. The sorption capacity graph shows that the points with high sorption capacity dominate but they are neutralized no more than 70% by positive calcium and magnesium ions. However, we should note that according to the content of base saturation (BS) all point are "*Eutric*", they have BS above 50% by WRBS classification (IUSS Working Group, 2006).The content of SOC has significant variation and it's from 0.73% to 3.73% in the studied survey area (Table 1, Fig. 3). Usually, in the cultivation fields, it is about 1.5% which is something typical for arable lands in Bulgaria (BOGDANOV *et al.*, 2015). The high content of SOC is in the area of marshes close to Topolnitza river, which is situated in the south-east part of the survey filed (point 79 in Fig. 1). The type of humus in the region is predominantly humic-fulvic (Ch/Cf = 1 – 0.5; KOINOV *et al.*, 1974; FILCHEVA *et al.*, 2018). Our research confirms that SOM has high sorption capacity and make complexes with calcium (GANEV *et al.*, 1990). That's why correlations between SOC with a soluble fraction (humic and fulvic acids) and with CEC and exchangeable Ca^{2+} are expected (Table 2). There is no significant correlation between the available forms of nitrogen and the other studied soil parameters. The reason for that could be unequal treatment with different nitrogen fertilizers. The amount of "mineral" nitrogen as the sum of ammonium and nitrate is from low to moderate, ranging between 8.6 to 46.7 $mg.kg^{-1}$, despite the high amount of nitrogen fertilizers that are used in the agricultural lands.The amount of available phosphorus oxide (P_2O_5) in studied soils is low (Table 2, Fig. 4). The values are ranging from 0.2 to 21.00 $mg.100g^{-1}$. Therefore, the amounts of less than 7 $mg.100g^{-1}$ of soil, the plants will suffer a severe shortage of this element (ATANASOV *et al.*, 2006).

The concentration of potassium in the soil solution is an important parameter for assessing the availability of this element

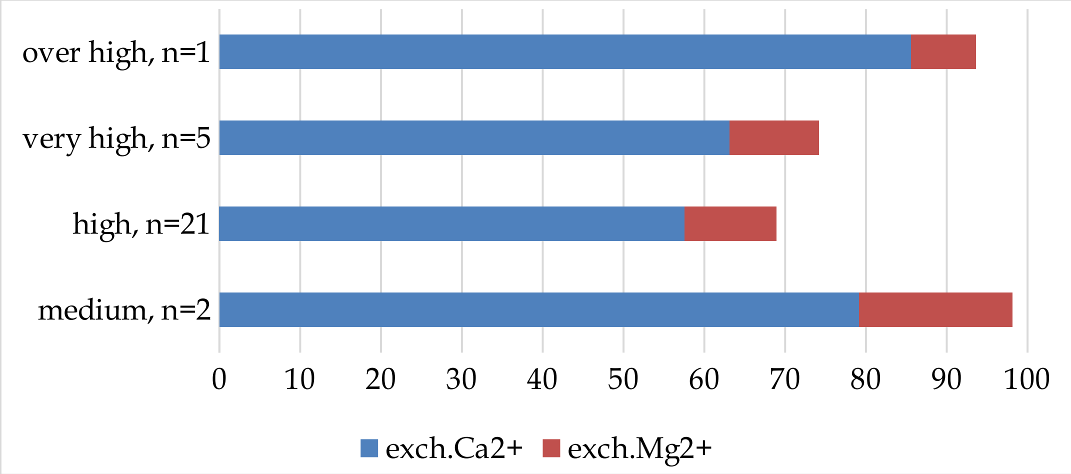

Fig 2. Exchange cations as % of sorption capacity (CEC ($T_{8,2}$)).

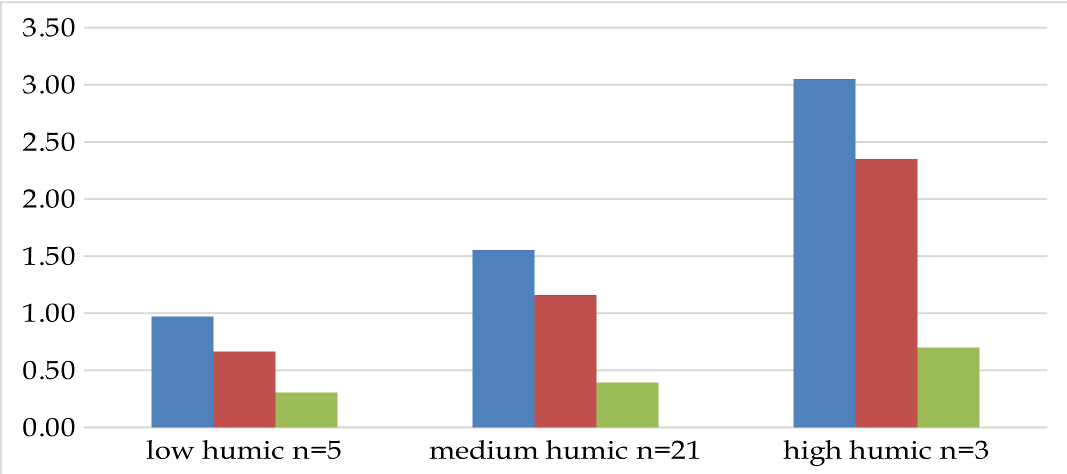

Fig. 3. The average content of SOC, humin and HAs by humic classes (%).

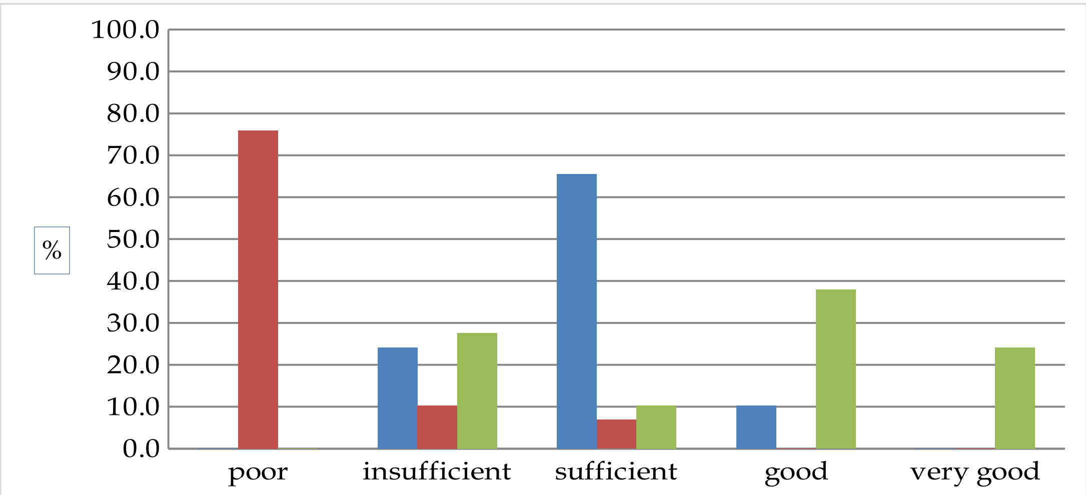

Fig. 4. Soil assessment according to NPK thresholds.

for plant nutrition. The potassium's stock (K_2O), is in a higher content than the mineral nitrogen and phosphorus (Fig. 4).

Mapping with interpolation maps

The distribution of pH, SOC, CEC, available forms of nitrogen, phosphorus, potassium are shown on interpolation maps (Fig. 5, 6, 7, 8, 9 and 10).The acidic points with pH below 6.0 are 59%. It's a big area between points A1, P2, 21, 22, 24, 35, 36, 37, 38, 39, 40, 49, 50, 53, 61, 64, 65, 68 (Fig. 1 and 5).The problem with acid condition is in the same area with pH values below 6.0 and CEC shows insufficient neutralization with calcium, magnesium and harmful amounts of aluminium are present (Fig. 1 and 6).In the studied area there are points of the low humus class and pH below 6.0 but they are only three. Thus a section with degraded soil qualities is drawn by points 21, 37, 68 (Fig. 1 and 8).Insufficient available nitrogen was found at 24.1% of the points, except for p.19 at pH 7.4, all others have a pH below 6.0 (points A1, P2, 22, 37, 40, 61). A major nutrient problem has been identified with phosphorus supply – 75.9% have poor and 10.3% have insufficient phosphorus supply. An exclusion here are the points P2, 19, 25, 52, 79. These points are placed close to one another which confirms the practice that in Bulgaria farmers use very rarely phosphorus fertilizers only in some small spots and only 6.9% of the points have sufficient supply (Fig. 9). The studied soils have a suitable potassium supply. Only 27.6% of sampling points have insufficient available potassium, and at points A1, 35, 40, 50 and 68, it's connected with pH of below 6.0, while points 52 and 79 are not related to acidity. Under the influence of the surrounding mountains in the region and surface waters, potash-containing sediments are weathering and realize good quantities of potassium oxide in low-land fields.

Conclusions

An assessment of the quality of soils in a vulnerable area has been carried out. A monitoring network was used to perform the analysis. The methodology includes an establishment of basic physical and agrochemical indicators. The quantitative evaluation included statistical and correlation analysis. The analysis of complex soil parameters allowed us to point out that the main problem is related to acidity and the lack of nutrient elements. In the studied soils there is a greater need for phosphorus than nitrogen. Mapping indicates zones where there are risks for the environment and human health. In order to overcome the negative effects of the studied degradation processes the meliorative practices such as liming and nutrient fertilization are strongly recommended.

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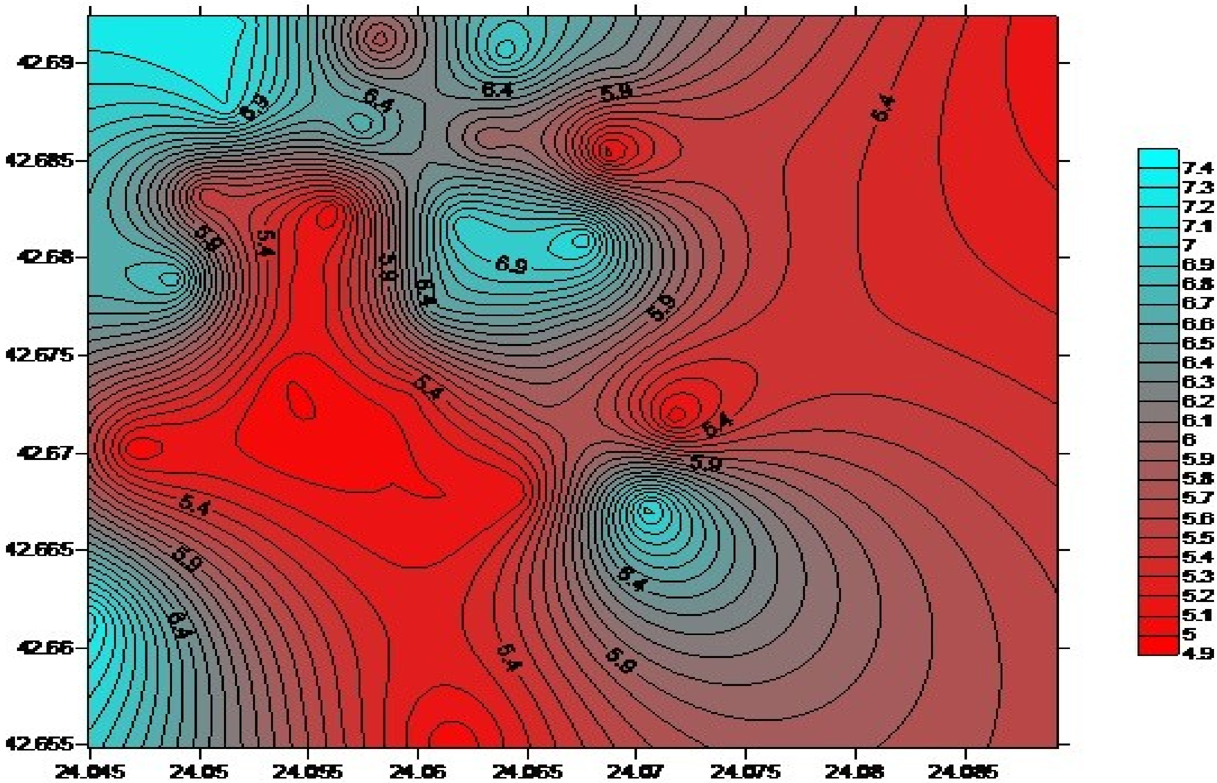

Fig. 5. Isoline map of Soil pH.

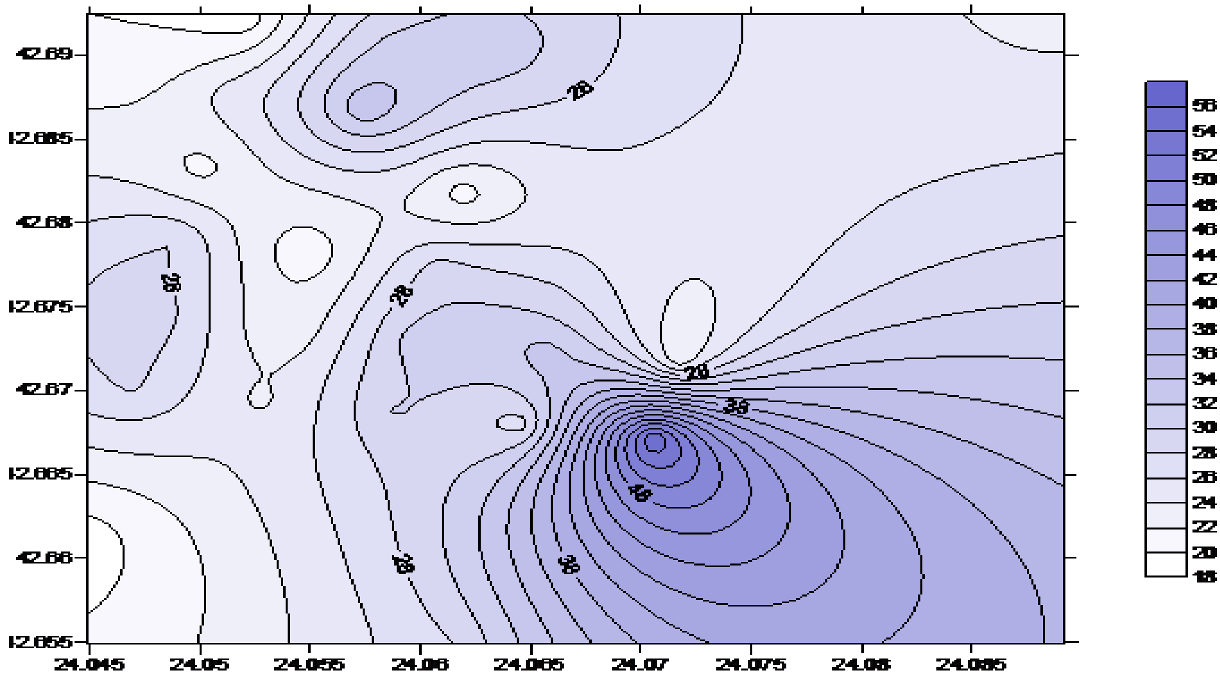

Fig. 6. Isoline map of cation exchange capacity CEC (cmol.kg^{-1}).

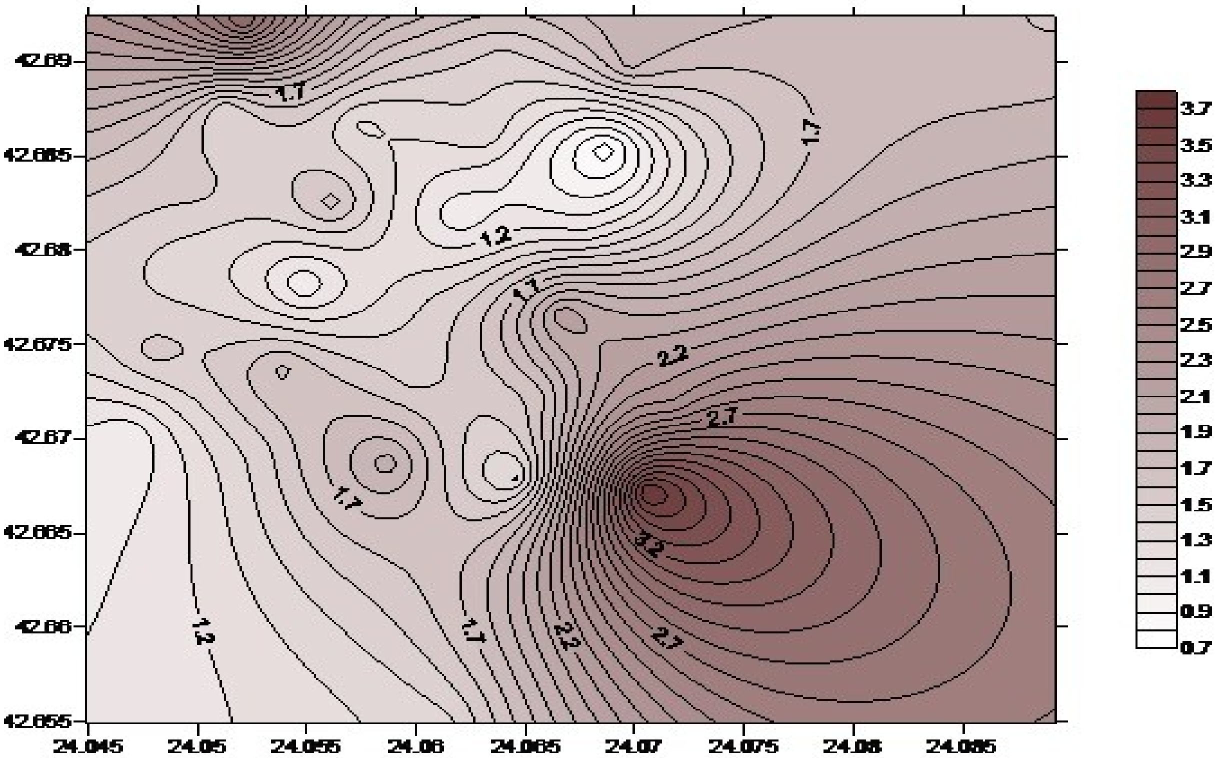

Fig. 7. Isoline map of SOC, % .

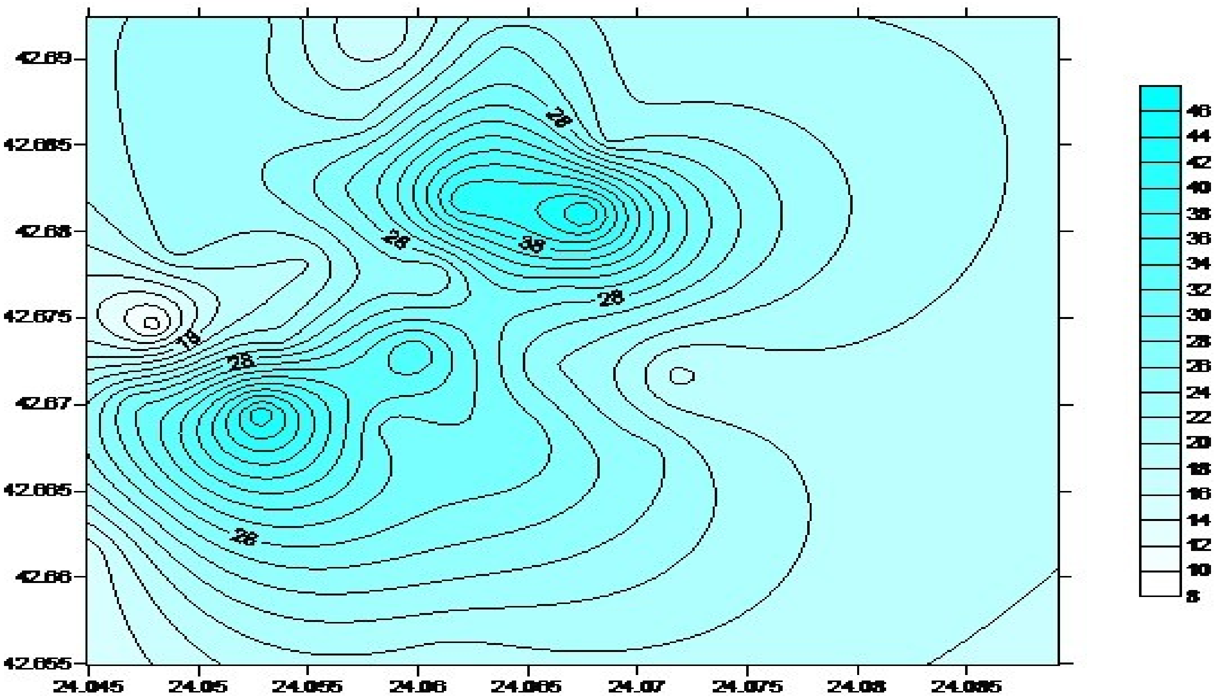

Fig. 8. Isoline map of available nitrogen $\sum NH_4 + NO_3$, $mg.kg^{-1}$.

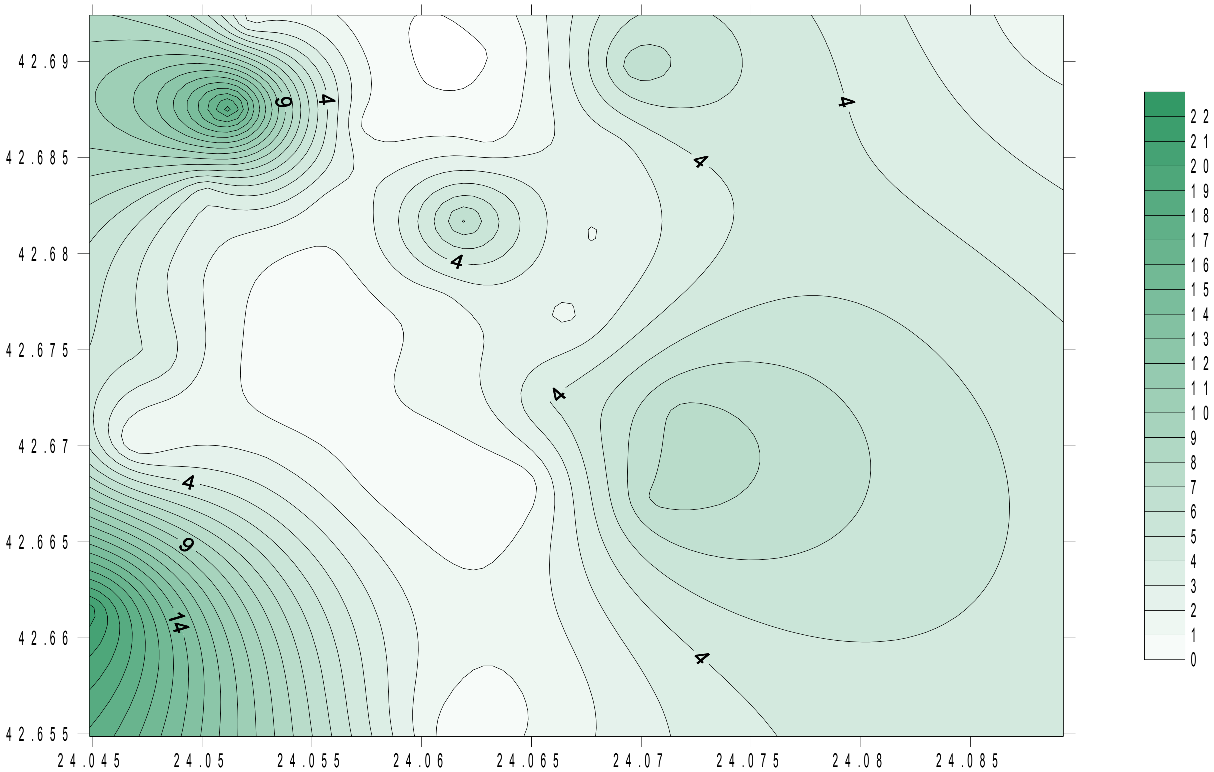

Fig. 9. Isoline map of available phosphorus oxide - P_2O_5, mg.100g^{-1}.

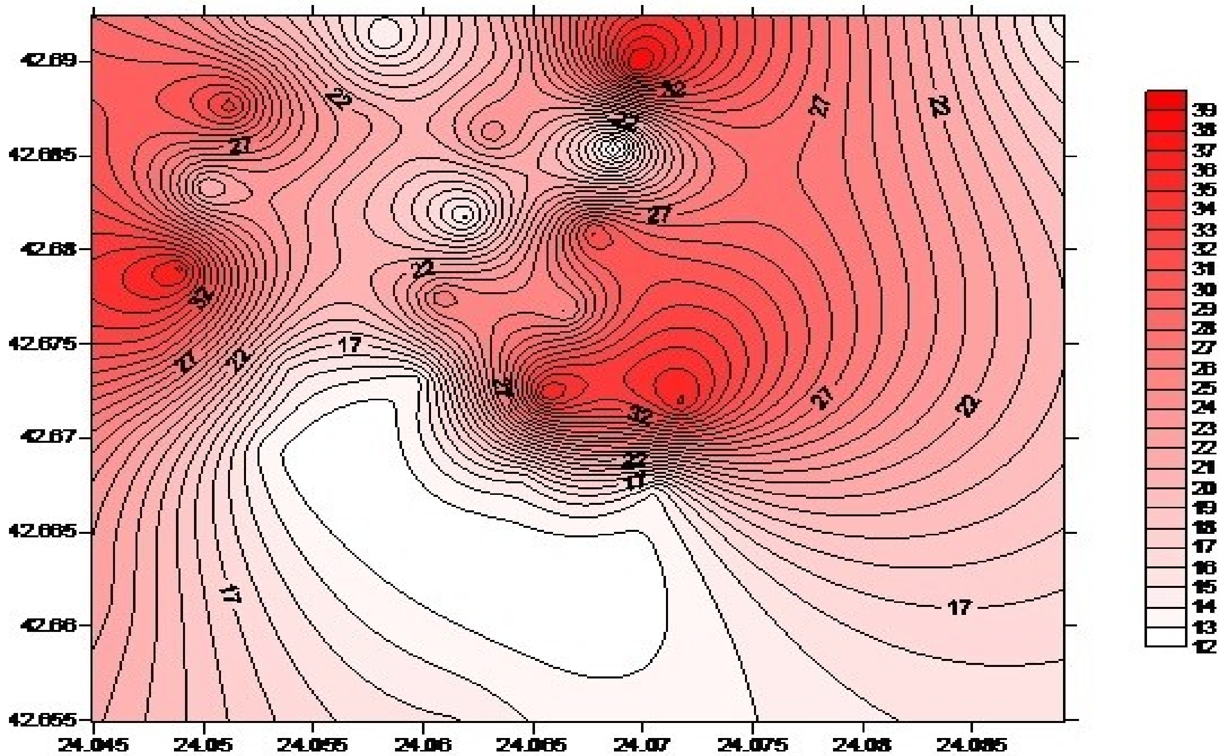

Fig. 10. Isoline map of mobile potassium oxide - K_2O, mg.100g^{-1}.

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