Chemical Composition of Soil Solutions of Technosols from a Coal Mine Region in South-Eastern Europe.

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Abstract

The cationic and anionic composition, i.e. K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, phosphates, SO_4^{2-} and dissolved organic carbon (DOC) in soil solutions of Technogenic soils (Technosols) from the area of Maritsa-Iztok coal mine basin in Bulgaria was analyzed and links with overburden strata were discussed. Two sites are located at the Mednikarovo village with humus and non- humus reclamation under grass vegetation. The other two are situated near the village of Obruchishte (non-vegetated and pine-vegetated). The sites differ in their textural composition, physico-chemical and hydro-physical properties. It was found that major cations and anions in the soil solutions at Mednikarovo site did not exceed the maximum permissible concentration limits (MPCL) for drinking water, while in solutions from the Obruchishte Technosols, composed of black clays intermixed with coal ash maximum permissible concentrations of sulphate (250 $mg.l^{-1}$), phosphate (0.5 $mg.l^{-1}$), calcium (150 $mg.l^{-1}$) and magnesium (80 $mg.l^{-1}$) were exceeded and may pose a threat to contamination of surface and sub-surface water of reclaimed soils.

Key words: chemical composition, soil solution, technogenic soils, reclamation

Introduction

The consumption of solid fuels is progressively increasing, especially at opencast mining due to its economic efficiency (Zhivkova et al., 2003). While in developed countries their part is significantly smaller due to the use of other alternative sources, in developing countries these are the main energy source (Chen et al., 2013). The opencast mining impacts all environmental components. Globally, it is estimated that huge land territories have been destroyed by mining activities, which is the cause of serious negative effects on the landscape and relief, hydrosphere, atmosphere, soils, biodiversity, geo-ecological disasters, etc. (Ghose 2005, Sheoran et al. 2010, Zhivkova et al., 2003., Zheleva 2004, Wong 2003). Therefore, the reclamation of lands affected by mining activities should be an integral part of the whole process through the implementation of effective rehabilitation strategies (Ghose 1989). The deficiency of topsoil is identified as a main problem during rehabilitation because of poor reclamation practices and low content of organic matter in these areas. Sustainable land management will minimize the coal mining impacts on ecosystems and the preservation ecological diversity (Kavamura and Esposito, 2010, Lone et al., 2008, Singh et al., 2002).

The change of environmental factors has a significant effect on all the components in the ecosystem. Technogenic, anthropogenic, etc. impacts on soil have a significant influence on the liquid phase, i.e. the soil solution where all the processes of transformation, synthesis and degradation of organic and mineral substances takes place. Many authors (Christou et al., 2005, Smethurst 2000) point out the role of soil solution in soil formation and plant nutrition. Many researchers have highlighted the needs to study soil solution chemical composition as a very sensitive and dynamic component for assessment and analysis of chemical processes in soil under the influence of various factors (Johnson et al., 2000, Simeonova et al., 2017, Stoicheva et al., 2001, Wolt.,1994).

The aim of this study is to estimate the contents of macroelements (K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, phosphates, SO_4^{2-}) and DOC in soil solutions obtained from Technosols varying in reclamation process from the area of Maritsa Iztok coal mines.

Materials and Methods

The study was carried out at four plots, two of them were near Mednikarovo village, and were subject to humus and non-humus reclamation and the other two at Obruchishte village from the area of Maritsa-Iztok coal mines in Bulgaria (Atanassova et al., 2018). The experimental plots from the area of Obruchishte are located under pine forest (*P. nigra*) and were created more than 30 years ago, and consisted of loam-textured Pliocene overburden sediments from the nearby open-cast mine. Areas of ~200 m^2 non-vegetated plots amongst pine –vegetated areas were found. At the non-vegetated site of Obruchishte, soils were of sandy loam texture mixed with degraded lignitic particles and coal ash, and of sandy clay (0-5 cm) and clay texture at 10-20 cm at the pine vegetated site (Atanassova et al., 2018).

At Mednikarovo site the investigated soils were: humus layer-reclaimed soil of clay loam texture and non-humus reclaimed soil of sandy loam texture. The surface horizon with was translocated humus horizon of natural Vertisol occupying the territory prior to mining. The sub-layers of ~2 m are composed of yellow and green clays comprising the overburden sediments of the stratigraphic profile and possessing suitable physico-chemical characteristics (pH ~7, Atanassova et al., 2018a,b). Cation exchange capacity (CEC) was assessed as sum of titratable acidity (pH 8.2) and extractable Ca, by saturation with K malate at pH 8.2 (Ganev and Arsova 1980).

At the four sites samples were taken from grids Δ2 m, ~ 40 m^2 and sampling was at two depths where water repellency was demonstrated on the field 0-5 (10) cm and at 10-20 cm. The soil solutions were obtained by the following method: in soil water ratio 1:5, shaking for 1 hour, centrifuging and filtering through 0.45 μm acetate cellulose filter (Katoh et al., 2012). Anions in the soil solution (Cl^-, NO_3^-, SO_4^{2-}, phosphates, including dissolved organic carbon (DOC) were analysed with Spectroquant tests, Merck Millipore (PHARO 100). Cationic composition of soil solution was determined by AAS (Perkin Elmer). For the control of chemical indicators of soil solutions, Regulation No 9 of 2001 on the quality of water intended for drinking and domestic purposes has been used.

Results and Discussion

Data in the table show that studied sites are considerably different in physico-chemical properties. For the different sites the pH values varied significantly from strongly acid to neutral (3.0 to 7.20).

The high acidity at the non-vegetated site in Obruchishte is a result of the weathering of black clays present in the overburden layers. The electrical conductivity of the study sites in Obruchishte was significantly higher than in the soils from Mednikarovo (Table 1), due the higher ionic strength of the solution (mostly sulfates, Atanassova et al., 2018a,b). The CEC is the highest at Obruchishte site (non vegetated (60,7-75,0 cmol.kg^{-1}) and is the lowest in Mednikarovo non-humus reclamation (29,4-29,8 cmol.kg^{-1}). The sorption capacity depends on the mechanical composition, the organic matter content and the type of clay minerals which formed the finely dispersed part of the soil.

Table 1. *Physico-chemical properties of the studied sites*

Variants	Depth. cm	pH /H_2O/	EC mS/cm	CEC 8.2	CEC_{CA}	CEC_A	Al	Ca	Mg
				cmol$_c$.kg^{-1}					
		Mednikarovo. humus reclamation							
1/1	0-10	6.80	0.32	56.3	46.5	9.8	0.0	42.0	6.1
1/1	10-20	6.80	0.14	56.5	46.7	9.8	0.0	42.0	6.1
2/2	0-10	6.90	0.04	56.1	46.5	9.6	0.0	42.4	6.0
2/2	10-20	6.90	0.04	56.2	46.4	9.8	0.0	42.5	6.1
1/3	0-10	6.90	0.06	56.4	46.8	9.6	0.0	42.5	6.1
1/3	10-20	6.90	0.04	56.2	46.6	9.6	0.0	42.3	6.1
		Mednikarovo, non humus reclamation							
1/1	0-10	7.20	0.04	29.8	22.7	7.1	0.0	17.5	5.6
1/1	10-20	7.20	0.04	29.7	22.6	7.1	0.0	17.5	5.5
2/2	0-10	7.20	0.04	29.7	22.6	7.1	0.0	17.7	5.8
2/2	10-20	7.10	0.04	29.8	22.6	7.2	0.0	17.6	6.0
1/3	0-10	7.10	0.035	29.4	22.3	7.1	0.0	17.6	5.5
1/3	10-20	7.10	0.035	29.8	22.7	7.1	0.0	17.6	5.6
		Obruchishte, pine vegetation							
1/1	0-5	4.80	0.35	37.1	28.8	8.3	1.6	23.0	4.2
1/1	10-20	5.00	0.73	43.2	35.0	8.2	0.6	32.0	4.0
2/2	0-5	4.30	0.08	44.8	32.0	12.8	2.0	25.0	4.8
2/2	10-20	3.90	0.69	48.6	31.6	17.0	2.3	24.4	4.5
1/3	0-5	4.80	0.15	41.9	29.9	12.0	1.5	22.8	5.6
1/3	10-20	4.50	0.47	42.0	30.2	11.8	2.0	23.0	5.5
		Obruchishte, non vegetated							
1/1	0-10	3.30	1.26	60.8	46.7	14.1	14.6	26.0	6.0
1/1	10-20	3.30	1.12	60.7	44.7	16.0	14.8	25.4	5.8
2/2	0-10	3.20	1.30	70.0	53.8	16.2	14.4	34.0	5.8
2/2	10-20	3.20	1.30	71.0	54.6	16.4	14.5	34.2	5.8
2/3	0-10	3.00	1.80	75.0	58.0	17.0	25.1	31.5	5.4
2/3	10-20	3.10	2.00	75.0	58.2	16.8	20.9	39.6	5.4

The greatest differences between the studied geological materials are in the %< 0.01 mm particle fraction, which significantly influences on the structure, water regime and the sorption of nutrients (Garbuchev et al., 1975).

The highest levels of the exchangeable Ca (42.0-42.5) and Mg are found in the areas of Mednikarovo with humus reclamation, the lowest (17.5-17.7) are for Mednikarovo with non-humus reclamation. Exchangeable Al was established in Obruchishte, non-vegetated with the highest values (up to 25.1 cmol.kg^{-1}, Table 1).

The authors (Hristov and Banov 1996, Banov and Marinkina 2002) have found that reclaimed soils were of heavy texture which determines unfavorable hydro-physical properties.

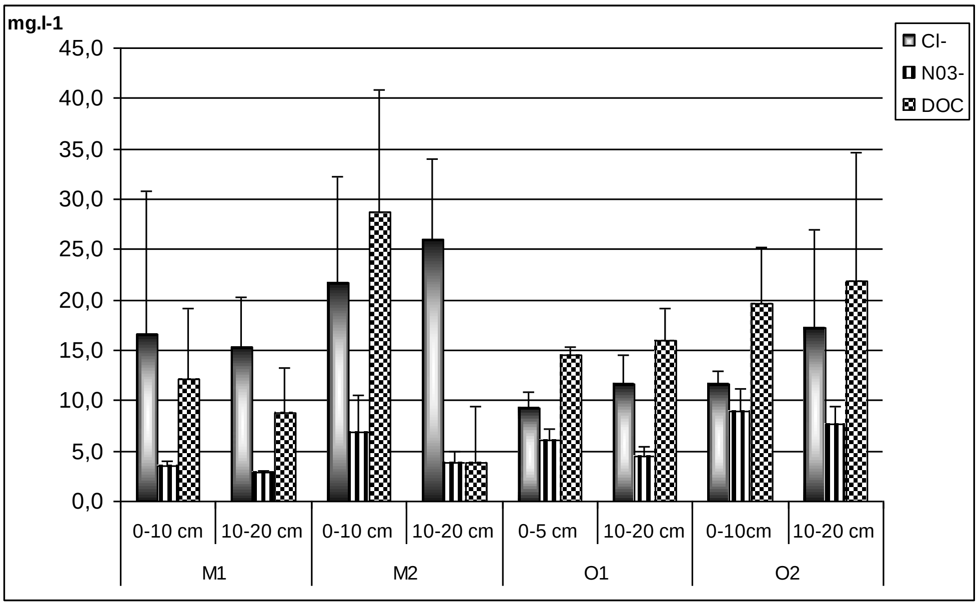

Figure 1. *Average content of Cl-, NO_3^- anions and DOC (mg.l^{-1}) in the studied plots: M1-Mednicarovo humus reclamation, M2-Mednicarovo non-humus reclamation, O1- Obruchishte pine-vegetated, O2- Obruchishte non-vegetated*

The chemical composition of the soil solution depends on soil type, geology, climatic conditions, as well as anthropogenic, technogenic and other impacts. The components of the solution (the cations and anions) are sensitive to these effects and respond in a different way. Significant differences in the concentration and distribution of the macroelements in soil solutions from natural and reclaimed soils were observed (Howell et al., 2017., Schaaf et al., 1999, Wilden et al., 1999). Apart from that, the composition and dynamics of the soil solution depends on the soil reclamation, the type and content of the coal materials, etc. Also low pH and high ion concentrations were observed, especially in the subsurface layers. The additional application of fly ash significantly changes the soil properties (Schaaf et al., 2005).

The content of the chloride anions (Figure 1) in the soil solutions has higher average values in Mednikarovo (non-humus reclamation) at both depths (21.7-26.0 mg.l^{-1}). At the other area at Obruchishte we observed nearly 2 times lower values (Obruchishte, pine vegetated, 9.3-11.7 mg.l^{-1}). Chlorine in the arable soils is the element with the most constant concentration in the soil solution. This could be explained with a transit status of chlorine in the agroecosystems. This element does not take significant part in the plant uptake and its chemical and physico-chemical fixation in soil is poor. According to (Chen et al., 2013) increased concentration of chloride in soil solution is observed in layers of reclaimed soils where fly ash content is higher because the solution equilibrium process is established slowlier. At all the sites the chloride concentrations do not exceed the maximum permissible levels limit for drinking waters (MPCL 250 mg.l^{-1}, Regulation No 9/2001).

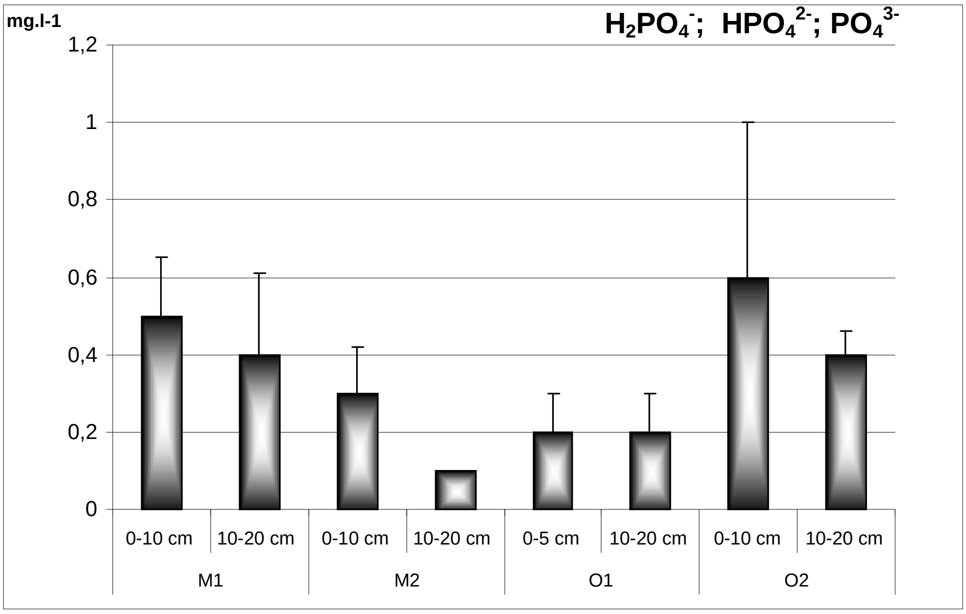

Figure 2. *Average content of the sum of* $H_2PO_4^-$; HPO_4^{2-} ; PO_4^{3-} *(mg.l^{-1}) in the studied plots: M1-Mednicarovo humus reclamation, M2-Mednicarovo non-humus reclamation, O1- Obruchishte pine-vegetated, O2- Obruchishte non-vegetated*

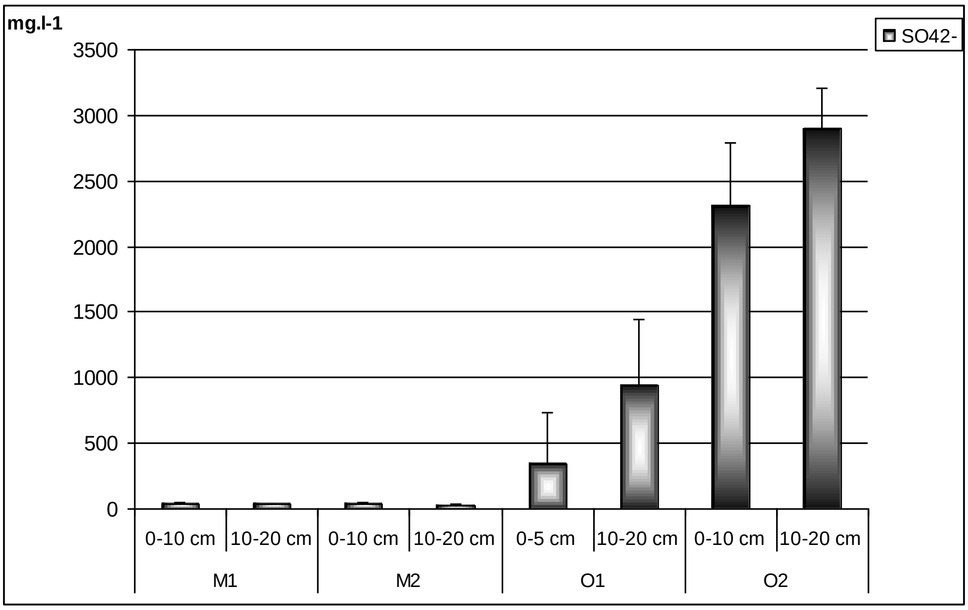

Figure 3. *Average content of* SO_4^{2-} *(mg.l^{-1}) in the studied plots: M1-Mednicarovo humus reclamation, M2-Mednicarovo non-humus reclamation, O1- Obruchishte pine-vegetated, O2- Obruchishte non-vegetated*

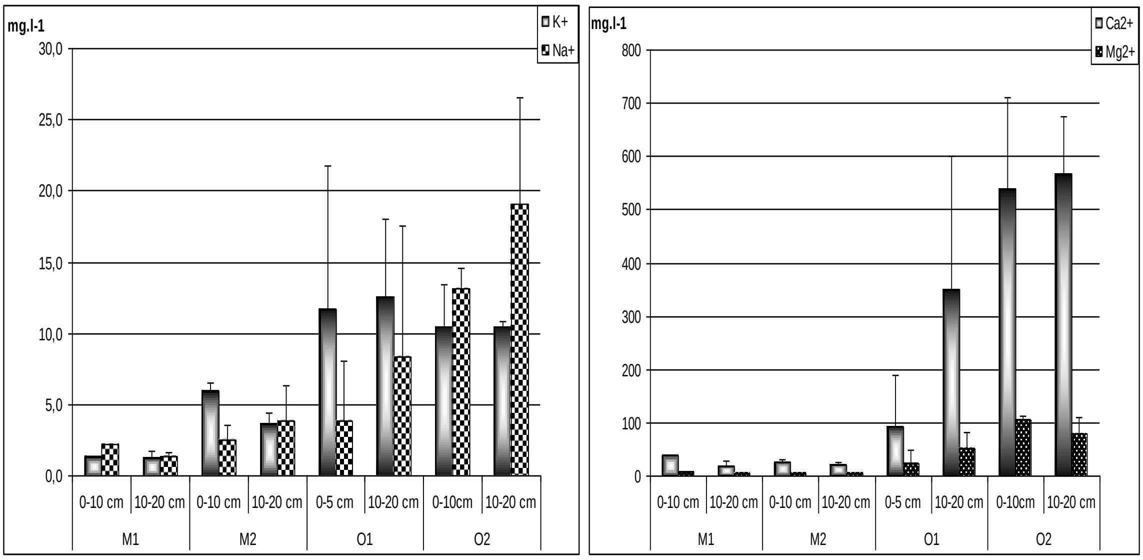

Figure 4. *Average content of K^+, Na^+, Ca^{2+} and Mg^{2+} ($mg.l^{-1}$) in the studied plots: M1-Mednicarovo humus reclamation, M2-Mednicarovo non-humus reclamation, O1- Obruchishte pine-vegetated, O2- Obruchishte non-vegetated*

It is found that a significant limiting factor in the reclaimed soils for growth of plants is the deficit of available nitrogen and phosphorus (Davies 1995). It was found that the average values of nitrate anions in all studied areas are low (from 2.8 to 8.9 $mg.l^{-1}$). A slightly higher nitrate concentration was recorded at Oruchishte, (non-vegetated site, 0-10 cm depth) but did not exceed the maximum permissible concentration limit for nitrate in drinking waters of MPCL 50 $mg.l^{-1}$ (Regulation No 9/2001). Results show that in arable soils, nitrates and hydrocarbonates are usually the predominant anions balancing the ionic changes in solution caused by various sources (Stoicheva et al., 2003).

As regards the average content of DOC in the soil solutions (Figure1) from Mednikarovo (humus reclamation) and Obruchishte (pine-vegetated site), values are of low variation (in the range of 8.7 to 12.2 $mg.l^{-1}$ and 14.4-15.9 $mg.l^{-1}$ as compared to Mednikarovo (non-humus reclamation). At this site and at Obruchishte (non – vegetated site) the DOC content has the highest values (28.7 $mg.l^{-1}$ and 21.9 $mg.l^{-1}$) .

Average concentrations of phosphates in solution at all sites ranged from 0.1 to 0.6 $mg.l^{-1}$ (Figure 2). Higher values are established at Mednikarovo (humus reclamation) at both depths, and at Obruchishte (non-vegetated), which are near the limit or slightly exceeded the maximum concentration level of phosphates in drinking water (0.5 $mg.l^{-1}$). At the other sites the average content of phosphates is lower and varies less (Table 1).

Significant differences are found in the sulphates content in soil solutions for all sites (Figure 3). The average values are from 29.3 to 42.7 $mg.l^{-1}$ at Mednikarovo and are in the range from 345.3 to 943.7 $mg.l^{-1}$ at Obruchishte under pine forest. The highest concentrations (2313 - 2897 $mg.l^{-1}$) were observed at the non-vegetated site of Obruchishte as in depth of the profile sulphates were increased at all sites. Exceeded were the MPCL for sulphates of 250 $mg.l^{-1}$ for drinking waters over 5 to 10 times.

The high sulphate salinity was caused by the high amount of sulphates in overburden materials associated with high contents of calcium and magnesium ions (Zheleva et al., 2004). The studies of (Garbuchev et al., 1975) have shown that yellow and green clays could be a suitable substrates for development of vegetation, however the high acidity of the black “greasy”clays may cause serious environmental consequences.

Some authors (Schaaf et al., 1999) have reported that mine soils containing a considerable amount of lignite and pyrite materials under pine vegetation had very low pH values and high concentrations of Fe^{n+} and SO_4^{2-}. These extremely acidic conditions are the precondition for the weathering of aluminum silicates and movement of acid products in depth of the profile. It often takes hundreds of years to improve soil structure and fertility. Our data correspond with those of Howell et al. (2017) who also found that nutrients in the profiles of reclaimed soils are very different from those in the natural soils and the levels of available phosphorus and potassium are significantly lower, while of S, Ca and Mg are much higher than those in natural soils.

Regarding the average K^+ and Na^+ concentrations in the solutions, the highest concentrations for sodium were recorded at the non-vegetated Obruchishte site (up to 19.1 $mg.l^{-1}$), and for potassium at Obruchishte under pine forest 12.53 $mg.l^{-1}$ for the 10-20 cm layer (Figure 4). As could be seen from the data in figure 4, in the solutions from the area of Obruchishte the highest contents of calcium and magnesium were found. A source of calcium can be the fly ash added as an amendment to the acidic Obruchishte spoils in 1970s with alkaline pH (Zheleva et al., 2004). At this site the variation in the average calcium content was very high reaching 567 $mg.l^{-1}$ which exceeds about four times the maximum permissible concentration limits MPCL 150 $mg.l^{-1}$ for drinking waters. In natural soil solutions calcium cations predominate, as well, and serve as ions-compensators of the negative charge of anions and dissociated acids in the soil solution.

Conclusion

The results from this study show that the measured soil solution parameters from the studied reclaimed sites from the area of Maritsa-Iztok coal mines show significant dynamics. A considerable variation in pH values was found at all tested sites, varying from neutral to extremely low pH at the area of Obruchishte. It was established that the content of the studied elements in the soil solutions does not exceed the MPCL for drinking water at Mednikarovo. Very high ionic concentrations were established at Obruchishte, (non-vegetated), especially sulphates, phosphates, calcium and magnesium ions, which significantly exceeded the maximum concentration limits for drinking water. The geological materials represented by yellow-green and gray-green clays used as a substrate for reclamation of the investigated sites do not considerably increase the ionic strength of the soil solution, but the presence of black “greasy” clays and fly ash which are mixed with the these substrates may cause a significant increase in ionic concentrations of major ions, thus posing a threat to contamination of the liquid phase of reclaimed soil.

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