Assessment of chemical composition of soil solution of water repellent soils from Maritza-Iztok coal basin

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Abstract: *The ionic composition and dissolved organic carbon (DOC) in soil solution of four soil profiles, from the area of Obruchishte were analyzed and relationships with soil hydrophobicity were discussed. It was found that the greatest variation and leaching of* NO^{3-}, SO_4^{2-} *and* Ca^{2+} *were from the profile of Obruchishte under ash, while of* Na^+ *from Obruchishte under pine. In Obruchishte profile after cereals the highest content of* Cl^-, *PO43- and* NO_3- *were found in the investigated soil solution. No significant correlation was found between the chemical elements and WDPT, except for Obruchishte, stubble. In this profile a significant correlation was found between the Ca2+ and Mg2+ concentrations and WDPT. Significant relationship (R*=0.63, p<0.05) between DOC and WDPT was established only at the experimental profile Obruchishte under ash. Differences in the distribution of soluble organic carbon in soil profiles in our studies is most likely due to the heterogeneity of the geological materials used as a substrate for reclamation of the studied sites*

Keywords*: CHEMICAL COMPOSITION, DOC, SOIL SOLUTION, TECHNOGENIC SOILS, RECLAMATION, WATER REPELENCY*

1. Introduction

Worldwide mining activities cause serious negative effects on the landscape and relief, hydrosphere, atmosphere, soils, biodiversity, geo-ecological equilibrium, etc. It was found that the overburden dumps at the coal mines in South-Eastern Europe were often characterized by elevated bioavailability of metals, lack of sufficient moisture, increased compaction, relatively low organic matter content and water repellency [1]. According to [2,3,4] water repellency affects infiltration, water flow and the transport of chemical elements in soils. The primary effect of water repellency is poor infiltration and reduction in the rate of water infiltration [5], which also affects the movement of macroelements along the depth of the profile. There are a few studies [1] on the influence of hydrophobicity in Technosols on the behavior and transport of these elements and soil water repellency.

The objective of the present study was to assess the cationic and anionic composition and DOC in the soil solution, obtained from Technosols reclaimed with coal ash by profile depth and investigates their relation with soil hydrophobicity (soil water repellency).

2. Materials and Methods

Four soil profiles of hydrophobic technogenic soils from the area of Maritza-Iztok coal mine region in Bulgaria were studied. The sites were near Obruchishte village, subject to tuft vegetation, pine vegetation, under ash reclamation (investigated in 2017) and stubble (investigated in 2019). The soil properties of the experimental sites and their physico-chemical characteristics are presented in detail in our previous studies [1,6,7,8]. Soil pH/Eh were measured in a soil:water slurry of 1:2.5. Texture was analysed by the method of Kachinski [9]. Soil water-repellency (soil hydrophobicity) was measured by the water drop penetration time (WDPT) method [10]. Soil samples at the field were classified as non-repellent (WDPT < 5 s), strongly (60 s < WDPT< 600 s) and severely > 600s water repellent according to the scale of [5].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 [11]. Anions in the soil solution (Cl^-, NO_3^-, SO_4^{2-}, phosphates and dissolved organic carbon (DOC) were analysed with Spectroquant tests, Merck Millipore (PHARO 100). Cationic composition of soil solution was determined by AAS (Perkin Elmer).

3. Results and Discussion

The data obtained show that in the different profiles the pH values varied from 2.96 (Obruchishte under tuft) to 4.10 (Obruchishte 1-3) and they are classified as strongly acid . The high acidity at the studied profiles is a result of the weathering of black clays, predominantly pyrite present in the overburden layers. The CEC is the highest at Obruchishte under ash (72.0-76.0 $cmol.kg^{-1}$) and is the lowest in Obruchishte pine vegetation (52-58.5 $cmol.kg^{-1}$). The highest levels of the exchangeable Ca (29.1-38.6) was found in the areas of Obruchishte under ash, the lowest Ca (11,9-18,3) and Mg (3.3-3.7) were from Obruchishte under tuft profile. Exchangeable Al was established in Obruchishte profile, under ash 16,0-23,1 $cmol.kg^{-1}$.

It was established that studying the mobility of chemical elements in the liquid phase, as well as their migration through the soil profile, allows a better picture of their behavior than doing other geochemical studies of the terrains. Significant differences in the concentration and distribution of the macroelements in soil solutions from natural and reclaimed soils were observed by [12,13,14]. The results show low pH and high ions concentration (especially of sulfates).

3.1. Anions content

Our results show that the nitrate contents in all the studied profiles are low. The values of nitrates are from 10.0 – 14.4 $mg.l^{-1}$, except for Obruchishte under ash where nitrates accumulate in the deeper soil layers, reaching 19.6 $mg.l^{-1}$, while the lack of vegetation, could be the reason for their leaching in the soil profile (Fig. 2). However, in the studied profiles, the maximum permissible concentration level (MPCL) of 50 $mg.l^{-1}$ for the nitrate content of drinking water was not exceeded (Regulation No9/2001) [15]. The concentration of chlorides in all investigated sites for 2017 does not exceed 10 $mg.l^{-1}$. It is found that unlike nitrates the highest content is in the surface and subsurface soil layers of the studied profiles (0-10 and 20-30 cm). Regarding the content of phosphates, highest concentrations and variations are reported in Obruchishte under pine, ranging from 0.1 to 7.7 $mg.l^{-1}$, while in the other profiles phosphates are very low and they almost do not change in depth.

In Obruchishte under pine profile lower content of sulfates are observed, ranging from 580 to 880 $mg.l^{-1}$, with a slight variation along the profile depth (Fig.1), compared to the Obruchishte under ash, where sulfates content is almost double, reaching 1780 $mg.l^{-1}$. At Obruchishte site under tuft, the sulfates are in the range from 1260 to 1500 $mg.l^{-1}$, with a slight variation along the profile depth. The high sulfate contents of the study areas are associated with the materials by which they were reclaimed, predominantly pyrite. Our data correspond with our previous data [1] and those of [16] who also found that soluble compounds, such as SO_4^{2-}were at significant concentrations in the leachates at Technosols.

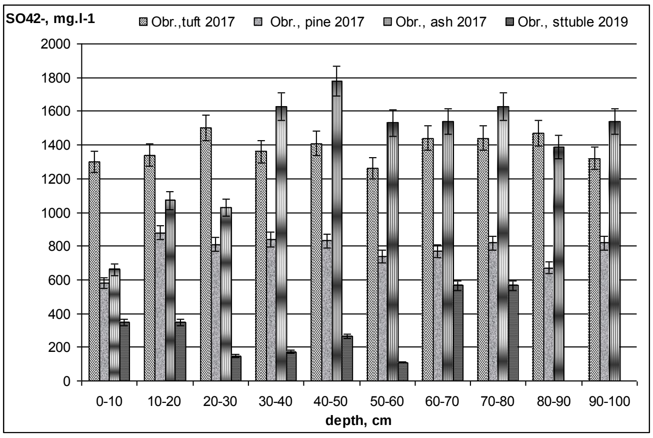

Figure 1. *Content of sulphates (mg.l^{-1}) at soil depth (0-100 cm) at the experimental profiles at Obruchishte sites*

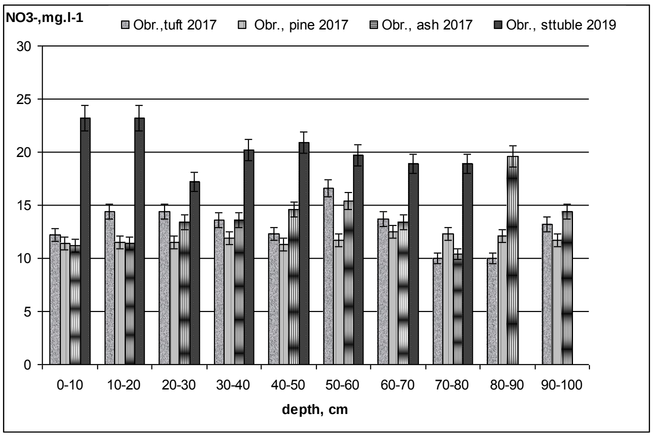

Figure 2. *Content of nitrates (mg.l^{-1}) at soil depth (0-100 cm) at the experimental profiles at Obruchishte sites*

Data show that the concentration of nitrates (17.2 – 23.2 mg.l^{-1}), chlorides (reaching to 27.2 mg.l) and phosphates (0.3-12.6 mg.l^{-1}) in water extracts from Obruchishte, after cereals (stubble), in 2019, are the highest. These concentrations could be explained by the import with fertilizers and herbicides in the cultivation of cereals. Data show that the content of the sulphates anions vary widely from 110 to 567 mg.l^{-1}, such as the highest content is measured in the 65-85 cm layer.

3.2. Cations content

Data show that the lowest are the values of potassium and sodium in water extracts received from the Obruchishte under tuft profile (1.13 -3.06 mg.l^{-1} for K^+ and from 1.90 to 8.45 mg.l^{-1} for Na^+, respectively). The highest concentrations are establiched in the Obruchishte under pine reaching to 10.26 mg.l^{-1} for K^+ and to 52.30 mg.l^{-1} for Na^+. An increasing of sodium content in layers 70-100 cm is found at three of the investigeted profiles, but it is most pronounced in Obruchishte under pine vegetation (Fig. 3). In contrast to them at Obruchishte, stubble in 2019 we detected a decrease in the deeper layers. As could be seen that in the solutions obtained from the profile of Obruchishte under ash, that the highest contents of calcium were established reaching 312 mg.l^{-1}, and the lowest in the Obruchishte under pine (47-204 mg.l^{-1}), while the concentrations in Obruchishte under tuft ~ 234 mg.l^{-1} (Fig. 4). The results obtained show that in the water extracts from Obruchishte under stubble in the autumn of 2019, the concentration of calcium varies significantly with values from 17.96 to 302.03 mgl^{-1}, until the magnesium is quite low compared with the other profiles researched to 12.83 mg.l^{1}.

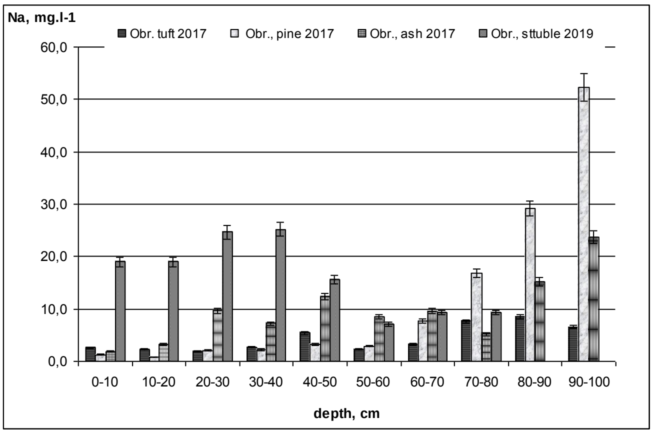

Figure 3. *Content of sodium (mg.l^{-1}) at soil depth (0-100 cm) at the experimental profiles at Obruchishte sites*

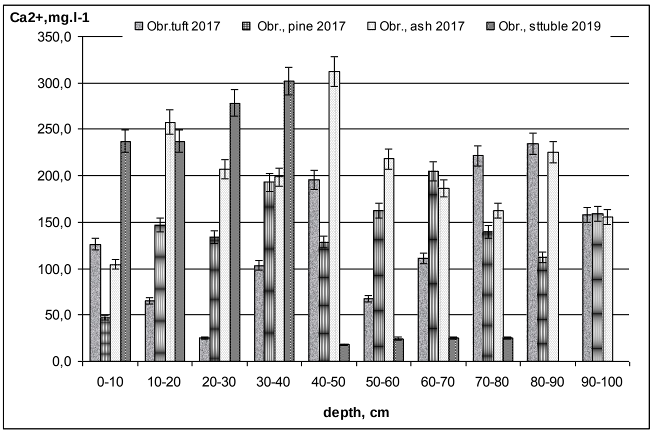

Figure 4. *Content of calcium (mg.l^{-1}) at soil depth (0-100 cm) at the experimental profiles at Obruchishte sites*

Our results showed that the investigated soil profiles are water repellent to a different extent (by small to extreme hydrophobicity, [6,7], but no correlation between the macroelements in the water extracts and water repellency (WDPT, s) was found, with some exceptions, such as in the Obruchishte under stubble where we found a positive correlation with chlorides (R**= 0.917), calcium (R*= 0.518), magnesium (R*= 0.663) and weak with nitrates (R= 0.462).

Table 1. *Correlation coefficients between anions and cations and water repellency (WDPT, s) at Obruchishte sites*

WDPT, s / ions, mg.l	Obr.,tuft 2017	Obr., pine, 2017	Obr., ash, 2017	Obr., stubble,2019
NO_3^-	R= 0,30	R= -0,38	R= 0,14	R= 0,46
Cl-	R= -0,77	R= 0,49	R= - 0,39	R= 0,91
PO_4^{3-}	R= 0,02	R= -0,50	R= -0,20	R= -0,07
SO_4^{2}	R= 0,15	R= 0,39	R= 0,24	R= 0,07
K^+	R= -0,07	R = -0,70	R= -0,29	R= -0,48
Na^+	R= -0,32	R= -0,55	R= -0,05	R=0,36
Ca^{2+}	R= -0,26	R= 0,28	R= 0,01	R= 0,51
Mg^{2+}	R= -0,43	R= -0,66	R= -0,17	R= 0,66

3.3. DOC content

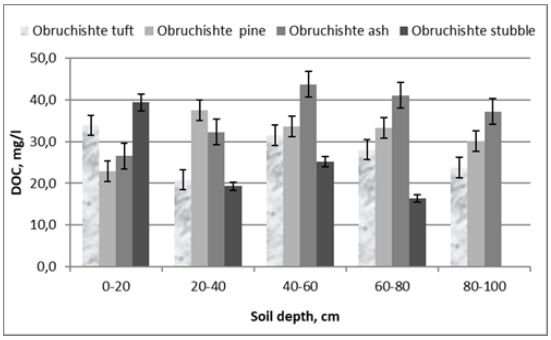

***Figure 5**. Variation in DOC (mg.l^{-1}) at soil depth (0-100 cm) at the experimental profiles at Obruchishte sites*

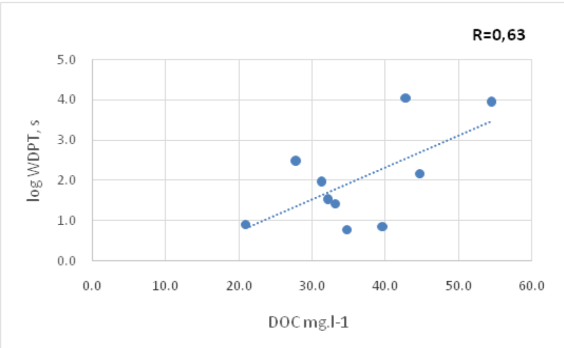

***Figure 6**. Correlation between DOC and WDPT*

The higher concentrations of DOC in the surface layers (0-20 cm) in the profiles of Obruchishte under tuft (34 mg.l^{-1}) and Obruchishte (for stubble - cereals) (39 mg.l^{-1}) were observed (Fig 5). The reason for it is probably the vegetation that develops on them and the decomposition of plant residues, which directly affect the concentration of the soluble matters in surface soil layers. Changes in the DOC usually concern the surface layers, and in the deeper soil layers changes in the concentration of soluble forms of organic carbon are much lower or not found [17,18].

In the Obruchishte profile under the pine forest vegetation, the concentration of DOC showed an increase in the depth of the soil layers. The ability of DOC to vary the depth of the soil within even a single site is usually related to the different intensity of formation, transformation and sorption of soluble compounds along the depth of the soil profile [19].

Significant relationship ($R^*=0.63$, $p<0.05$) between DOC and WDPT was established only at the experimental profile Obruchishte under ash (fig. 6). A positive weak correlation was found ($R = 0.40$, $p <0.05$), between DOC and WDPT in the profile Obruchishte (for stubble - cereals).

4.Conclusion

The data obtained show that in 2017, the greatest variation and leaching of nitrates and sulfates was found for the profile from Obruchishte under ash (without vegetation), followed by Obruchishte under tuft, and the lowest values and movement of these anions were found under pine vegetation. Higher content and variation of chlorides and phosphates were found in Obruchishte under pine, unlike the other two profiles. In 2019, the highest content of chlorides, phosphates and nitrates was found in the investigated water extracts from Obruchishte under stubble compared with the other profiles. Obviously, the cultivation of cereals has influenced to different extent the content and behavior of chemical elements in the soil profiles studied. Our data show that the nutrients in the profiles of reclaimed soils are very different from those in the natural soils and the levels of nitrates, available phosphorus and potassium are significantly lower, while of sulfates are much higher than those in natural soils. No positive correlation was found between WDPT and chemical elements (anions and cations) except for Obruchishte under stubble after cereals. Differences in the distribution of soluble organic carbon in soil profiles in our studies is most likely due to the heterogeneity of the geological materials of yellow-green, gray-green and black clays, used as a substrate for reclamation of the studied sites, which form the mineral layers of these hydrophobic soils.

Acknowledgements

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5. References

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