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Effect of biochar on anion mobilization in soils polluted with heavy metals

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Abstract

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Soils from three sites located near large metallurgical plants, former Kremikovtsi steel plant, Aurubis – Pirdop copper plant and the Medet open cast copper ore mine in Asarel-Medet were studied. Soils have different physico-chemical characteristics, heavy metal and metalloid contents and land use. The biochar (BC) applied as ameliorant was derived from deciduous vegetation, added in four variants at different rates of 1%, 5%, 10% and 20% w/w. The effect of biochar on the mobilization of anions and dissolved organic carbon (DOC) was evaluated in a climatic chamber. It was found that the behavior and interaction mechanisms of the studied anions (nitrate, chloride, sulfate, phosphate, dissolved organic carbon (DOC) in soil solutions is complex, both due to the specific chemistry of the anions and the soil adsorbent (soil-biochar mixture). There were no clear trends in anionic composition of soil solution between the BC treatments and the control variants at the three sites. However, after a 6-month period there was a decrease in the concentrations of nitrates more pronounced in the neutral to slightly alkaline soils near the Kremikovtsi steel plant. For the acid soils from Aurubis-Pirdop area, DOC exhibited increasing trend in the variants with BC application. The principal component analysis (PCA) for the three types of sites, indicates that BC is mobilised by the biochar itself in the neutral and alkaline soils, while in the acidic soils from Aurubis-Pirdop and Medet sites, DOC is predominantly mobilised by the soil colloids. There were no clearly expressed trends in the contents of the other anions from the BC application among the variants for the different soil types and regions, except for Cl^- ions, which decreased from BC application in the acidic soils and the SO_4^{2-} ions, which increased in the acidic soil of the Medet mine.

The results obtained have implication on metal immobilisation in contaminated soils, both from pH increase, especially in the acidic soils, and the increase of DOC, which may form various complexes with metals in solution and on soil surface.

Keywords: anions; DOC; biochar; heavy metal contaminated solis

Introduction

Soil contamination is a serious challenge of great economic and social importance, that can have irreversible consequences on agro-ecosystems and human health. The major causes of soil pollution are related to industry and urbanization, use of pesticides, chemicals and fertilizers in agriculture, petroleum industry, improper disposal of wastes and extraction and refining of metals and metalloids etc. (Palmeggiani et al., 2021). These serious problems necessitate the search and use of cost-effective amendments. Research on biochar (BC) as soil ameliorant has increased significantly in recent years. The results showed that its application improved cation exchange capacity, nutrient use efficiency and nutrient retention capacity, reduced soil acidity, and could be used for immobilization and removal of pollutants, sequestering carbon, and improving soil properties and fertility (Glaser et al., 2002; Lehmann and Rondon, 2006; Ajayi et al., 2016; Kanthle et al., 2016; Oliveira et al., 2017; He et al., 2021). Despite numerous studies, the mechanisms of biochar interaction with soil complexes and solution are still not well understood. Biochar is a carbon-rich product derived from various organic feedstocks by pyrolysis at different temperatures in the absence of oxygen (Sanford et al., 2019). Its properties to adsorb some or other elements are determined by the raw materials, used and the conditions of its production (Gronwald et al., 2015). For this reason, the mechanisms of interaction with different contaminants are specific and multifaceted. For organic contaminants, functional groups are activated by hydrophobic or electrostatic attraction or repulsion, while inorganic contaminants are removed by ion exchange, surface complexation, precipitation and ionic interactions (Oliveira et al., 2017). A major challenge in using biochar is to increase the anion exchange capacity of the soil. The use of biochar in this aspect to mobilize anions, that are in excess and are likely to wash out of the root zone, or pose a risk of eutrophication (e.g. nitrate, chloride), is considered by Sanford et al. (2019). Zijian et al. (2023) believe that, it is theoretically possible to determine the optimal amount for biochar application based on the adsorption and desorption behavior of biochar at different anion levels in solution.

Dissolved organic carbon (DOC) is an important fraction of organic matter that plays an important role in many biological and chemical processes in soil. When applied to soil, biochar can release soluble organic carbon, which can immediately change soil physicochemical properties, increase soil organic matter content, affect microbial activity, and alter soil organic contaminants and heavy metal mobility (Liu et al., 2019; Feng et al., 2021; Atanassova et al., 2024). The effects of biochar on soluble carbon are controversial. The content and composition of labile forms of carbon in soil are mainly related to the type of feedstock and the pyrolysis temperature of biochar (Cheng et al., 2017; El-Naggar et al., 2018; Li et al., 2022). Biochar derived from woody materials basically includes a larger amount of lignin, which is more thermally stable and rapidly generates fixed carbon rather than soluble organic carbon (Liu et al., 2022). In contrast, biochar derived from herbaceous feedstocks, which contain more cellulose, and is more prone to soluble carbon formation. Lin et al. (2022) found that the concentration of soluble organic matter in biochar decreases as the pyrolysis temperature increases. The structure of soluble carbon at high temperature changes from humic-like substances and neutral to low-molecular substances. The potential of biochar to remove anionic species was found to depend on surface area and charge of biochar, solution pH, and the presence of competitive anions (Chintala et al., 2013).

Biochar, pyrolysed at low temperature, is nutrient rich and contains a large amount of volatile compounds, that can increase labile fractions of organic matter and alter soil microflora and nutrient cycling (Sun et al., 2021). Biochars produced at high temperatures significantly reduce the concentration of soluble organic matter (Feng et al., 2021). Most laboratory and field studies have examined the short-term effects of biochar on soil properties. Biochar addition increases dissolved organic carbon in the short term (Chen et al., 2021). In long-term field studies (over 5 years), the addition of biochar resulted in no changes in soluble organic carbon content (Dong et al., 2018; Lu et al., 2020), however, in other studies of Zhu et al. (2017) and Rombolà et al. (2022), it was shown that biochar addition can adversely affect dissolved organic carbon (DOC) and reduce its release in some soils.

The aim of our study was to determine the effect of biochar on anion mobilization in Technogenic soils from three major metals producing regions in Bulgaria.

Materials and Methods

Soils samples were taken from three sites near the large metallurgical plants of Kremikovtsi, Aurubis – Pirdop smelter and refinery and Asarel-Medet Cu enrichment plant. Soil samples from the former plant Kremikovtsi were taken from the land of the villages of Gorni Bogrov, Yana and Buhovo. Soil samples from site T.1 located near the village of Gorni Bogrov were classified as Fluvisols, deep, sandy-loam, stony with alluvial deposits. Alfalfa (*Medicago sativa* L.) was cultivated in 2023. The soils of Yana site (T.2) were classified as Deluvial soil, moderately deep, medium- sandy and stony with delluvial deposits. During the study period, the land use was with rapeseed (*Brassica napus* L.). The soil from Site 3, Buhovo village, was Deluvial-meadow soil (Fluvisols), shallow, sandy-loam, stony, diluvial deposits, designated as meadow. The vegetation was mixed (black pine, oak, cherry, rose hip etc.). The soil reaction (pH H_2O) varies from moderately acidic in the area of Gornji Bogrov to slightly alkaline in the sites, that are close to the industrial plant on the land of the village of Yana site. The cation exchange capacity (CEC) varied in a narrow range from 23.6 to 29.0 cmol. kg^{-1}. The degree of saturation (V%) was between 95.6 and 100% (Table 1) (Nenova et al., 2023).

Asarel-Medet, near Panagyurishte, is the largest mining company in Bulgaria for open cast mining and enrichment of copper ores. The soils tested (pooled samples from eight sites) were collected from the Great Southern Embankment, which contains materials from the open cast mining of Medet, and was biologically reclaimed between 1998 and 2006, with pine and birch plantations. The soils T1 and T4 were taken from the Great Southern Embankment. Soil T7 was taken from the tailings from the open cast Medet mine, and reclaimed in the period 2001–2007, with pine and birch plantations. Soil samples were collected from 0–20 cm depth in 2023. Soils have a light texture, mostly acid soil reaction, the cation exchange capacity varied from 21.7 to 25.0 cmol. kg^{-1}, base saturation V% was between 63.1–92.3% (Table 1, Atanassova et al., 2023).

The soils of the Pirdop area sampled near the Aurubis-Pirdop copper smelter, and are Alluvial-delluvial, eroded Cinnamonic forest soils, with a light soil texture, low clay content of 5.7–14.7%, organic carbon (OC) of 0.5–2.9% and pH of 4.7–6.1 (Atanassova et al., 2024). All samples were taken from a depth of 0–20 cm. The soils from sites T1, T4 and T8 were Alluvial-deluvial, soil from site T6 was Cinnamonic forest soil. The vegetation was mixed woody vegetation, shrubs and meadow grasses.

Soil textural composition was analyzed by the method of Kachinski (1958), soil pH/ in a soil: water slurry of 1:2.5, total organic carbon (TOC) was determined by oxidation with K2Cr2O7/H2SO4 by the Kononova method (1966), cation exchange capacity (CEC) and extractable Ca, Mg and AI, by the method of Ganev and Arsova (1980).

An incubation experiment was conducted in a *Climatic Chamber With Phytotron System KK 350 FITDS–POL-EKO, 2022.* Soil samples (300 g) were placed in test vessels with capacity of 500 ml. The following designations were used: Kremikovtsi – T1(Fluvisols), T2 (Deluvial soil) and T3 (Deluvial-meadow soil), Aurubis-Pirdop – T1, T4, T8 (Alluvial-deluvial soils, T6 (Cinnamonic forest soils), and at Medet sites, T1, T4 (soils of the Great South Embankment) and T7 (tailings from the open cast mine). The experimental design included 1 control and 4 variants with different levels of biochar added of 1%, 5%, 10% and 20% in two repetitions. Biochar was obtained from wood (birch, sycamore, ash tree and maple) by temperature pyrolysis 400–420°C (Nikimol, Ltd, Asenovgrad).

A certain amount of distilled water was added to the soil samples to achieve 75% field capacity (FC). Results are presented after the 1st stage (30 days of incubation), 3rd stage (90 days), 4th stage (120 days) and 6th stage (180 days), to examine the interaction processes at the most important stages of the period. Monthly over a 6-months period samples were taken, and pH, electrical conductivity (EC) and Redox Potential (RedOx) were determined, and aqueous extracts were prepared. The water extracts were analysed in soil: water ratio 1:5 and 1 h shaking, centrifuging and filtering through 0.45 µm acetate cellulose filter (Kathoh et al., 2012). Anions in the soil solution, including DOC, were analyzed with Spectroquant tests, Merck Millipore (PHARO 100). Electrical conductivity (EC) was determined in soil:water (1:5) according to (ISO 11265:2002). Soil pH was measured in a soil: water suspension of 1:2.5.

Correlation, Principal component (PCA) and cluster analyses were performed by IBM SPSS Statistics 23 for Windows.

Table 1. Physico-chemical characteristics of experimental soils

Points No	**pH** /H_2**O**	$CEC_{8,2}$	CEC_{SA}	CEC_{WA}	**H**$_{8,2}$	Al	**Ca**	Mg	Base satur.	Clay	TOC
		cmol. kg^{-1}							%		
Kremikovtsi*											
T.1	7.8	26.8	-	-	0.0	0.0	24.0	2.8	100.00	8.7	1.44
T.2	8.0	29.0	-	-	0.0	0.0	26.0	3.0	100.00	9.5	1.22
T.3	6.9	23.0	21.8	1.2	1.0	0.0	19.2	2.5	95.65	8.8	1.16
Aurubis-Pirdop*											
T.1	4.9	23.2	18.1	5.1	7.5	2.5	13.5	2.1	67.7	9.0	1.21
T.4	5.4	25.0	21.9	3.1	4.0	1.0	19.1	2.2	84.0	11.4	2.86
T.6	4.3	21.7	17.0	4.7	8.0	3.1	11.4	2.1	63.1	16.7	0.83
T.8	6.2	24.8	22.8	2.0	1.9	0.0	20.6	2.3	92.34	7.3	1.96
Medet*											
T.1	4.6	17.2	12.2	5.0	7.0	1.8	7.5	2.5	59.3	6.5	1.01
T.4	4.9	19.5	13.0	6.5	8.1	1.5	9.0	2.3	58.46	7.5	1.36
T.7	4.7	19.4	13.4	6.0	7.0	1.2	9.8	2.3	63.92	4.9	0.91

*Kremikovtsi – T1(Fluvisols), T2 (Deluvial soil), T3 (Deluvial-meadow soil), *Pirdop – T1, T4, T8 (Alluvial-deluvial soils, T6 (Cinnamon-forest soils), *Medet – T1, T4 (soils of the Great South Embankment), T7 (tailings from the open cast mine).

Results and Discussion

The capacity of biochar to remove anions in water extracts is different depending on the pyrolysis temperature used (Ortiz-Bobea et al., 2021), such as the mechanism of their removal is mainly through chemisorption. According to the same authors, as well as to (Ao et al., 2020; Tian et al., 2023), due to the negative surface charges of biochar, it is necessary to modify its surface to improve its adsorption capacity. Some types of biochar have significant anion exchange capacity (AEC) that ranges from 0.602 to 27.76 cmol kg^{-1} (Lawrinenko et al., 2015), increases with decreasing pH and pyrolysis temperature, and is attributed to oxonium functional groups, pyridinic groups in the biochar heterocycles, and nonspecific adsorption with protons from the fused aromatic rings of biochar. He et al. (2021) have established, that despite the undeniable benefits of biochar, as a soil improver, its use is varied, which is determined mainly by local soil conditions and the specific management tasks and objectives. It should be taken into account that changes in its physico-chemical properties (aging of biochar) also affects soils. The authors believe that regulations and guidelines are needed for the application of biochar, as well as assessment systems and indicators for the effectiveness of the multilateral impact of applied biochar in the soil. They suggest that such indicators could be the levels of nutrients and the reaction of soil.

Concentrations of anions in soil solutions from the Kremikovtsi site

The concentrations of anions in soil solutions are regulated by complicated mechanisms that determine their mobility. Not all processes are well studied, especially of those, related with organic complexes and major anions, which have specific properties that affect their mobility and adsorption, such as their participation in biological processes or in inorganic chemical reactions (Johnson and Cole, 1980). Nitrogen is the most important biogenic element for the growth and development of crops and for obtaining high yields. The mineral nitrogen in soils is mainly in nitrate and ammonium forms. The soil colloids have a stronger affinity for the NH_4-N of inorganic nitrogen, because they are negatively charged. Soil colloids have a low anion exchange capacity, on the other hand, anion competition (of phosphate and sulfate anions) inhibits the binding of NO_3^-, which can be leached along the soil profile. Accumulation of nitrate nitrogen in soils and soil solution is an indication of a possible risk of groundwater contamination. The biochar, used as soil amendment is aimed at reducing this risk. Studies have shown that despite the large specific surface area of biochar, presence of different functional groups and exchangeable cations, not every biochar type can be useful for nitrate retention. This may be related to the feedstock and pyrolysis temperature, which requires serious research into the capacity of biochar to retain nitrate nitrogen (He et al., 2023). In their study, Sanford et al. (2019) found that the presence of more oxygen functional groups, together with an increased content of positively charged metals Na and Ca, on the surface of biochar suggests that cationic binding might be a mechanism for NO_3 sorption.

Nitrates

The obtained results for the contents of nitrates in solutions from the Kremikovtsi sites (Figure 1), show that in the controls of the studied variants from site T.1, they range from 34 to 56 mg.l^{-1}, in T.2 between 17 and 54 mg.l^{-1}, and in T.3 between 32 and 49 mg.l^{-1}. It was established that the nitrate contents in the solutions of the controls from the 6th sampling (after 180 days of incubation) was the lowest, especially in the variants T.1 and T.2. The average nitrate content in the different variants with added biochar is within the limits of 39.5 mg.l^{-1} (after 30 days of incubation) to 25.7 mg.l^{-1} in the 6th stage of T.1., i.e. the reduction is about 1.5 times. At T.2. on the 1st month with added biochar in the different variants, the average concentration of nitrates was 33.7 mg.l^{-1}, and after 6 months of composting it decreased to 22.0 mg.l^{-1}. A stronger decrease in nitrate concentrations is reported in the variants with 20% added BC. In T.1, the decrease between controls and variant T.1. with 20% BC, at different incubation periods was between 1.3 and 3 times. The trend is similar between the controls and the 20% added BC in T.2. (Figure 1). At site T.3., there was a variation of the concentration in the variants BC 10%, however, at the highest dose of BC 20% there was a notable decrease of NO_3^- concentration. It should be taken into account that the soil samples were taken both from cultivated areas and from mixed forest and meadow vegetation (T.3), which may be the reason for different influence on nitrate content.

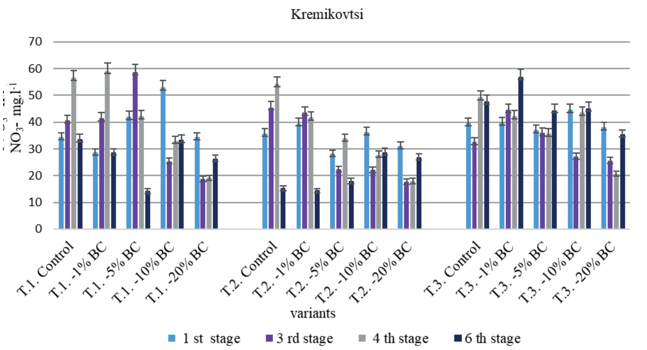

Fig. 1. Content of nitrates (mg.l^{-1}) in water extracts from the soils of the Kremikovtsi site

Chlorides

It was found that the concentrations of chloride anions (Cl^-) (Figure 2) in the solutions during the different stages of the study, did not change significantly at site T2. The concentrations of chlorides in the extracts after 30 days of incubation varied from 7.3 mg.l^{-1} at T.1 to 19.63 mg.l^{-1} at T.2., on average for all the variants 8.78 mg.l^{-1}, during the 1st stage of the incubation. It is established that in the consequtive periods of incubation, chloride average contents in the water extract did not change uniformly, but mainly icreased with stage and did not chage with variant (T2-T3) or were increase at 20% BC at site T1 between 9 and 10.3 mg.l^{-1}. Regarding the variants, no definite trend emerged, except for a slightly higher content at BC 20 % compared to the control, but not at all stages of the study.

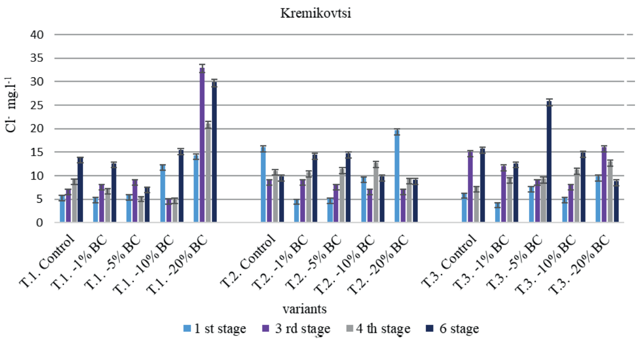

Fig. 2. Content of chlorides (mg.l^{-1}) in water extracts from the soils of the Kremikovtsi site

Sulphates

It was found that the concentrations of SO_4^{2-} (Figure 3) in the solutions from the three sites (T1-T3) vary ununiformly, and there was no clear trend in the sulphate levels with time and BC variants. At T.1, SO_4^{2-}, change both during the different stages of incubation and by BC variants, from 5.0 mg.l^{-1} in the control during the 1st stage to 19.23 mg.l^{-1} at T.1. with 20% BC at the 4th stage. An interesting trend is observed in the extracts from variants T.2 and T.3, where the higher concentrations are at the 1st stage (30 days of incubation), and start to decrease in the following stages. This is more pronounced at T.3, where the decrease between the 1st t and the following stages is about 3 times (Figure 3). The variation in sulfate values is significant, both by variant and by time periods. It was found that the values of sulfates are lower than those of nitrates and do not exceed 20 mg.l^{-1}, which is owing to the higher sorption, including specific sorption of sulphates on soil and biochar colloids. These concentrations are influenced by the pH (7–8), soil surface charge, which is negative (Marsh et al., 1987), and the extent of the positive charge on the biochar in this pH range.

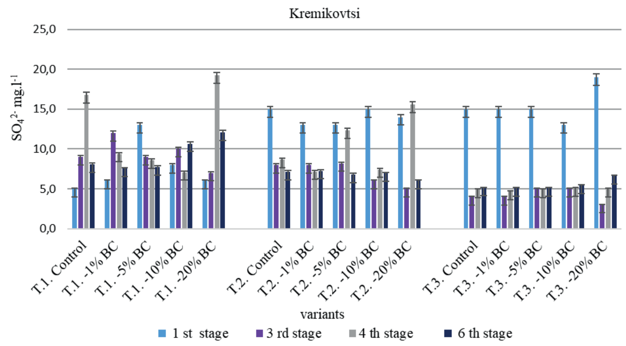

Fig. 3. Content of sulphates (mg.l^{-1}) in water extracts from the soils of the Kremikovtsi site

Phosphates

It was found that the contents of the phosphate anions in the solutions from the Kremikovtsi site varied with stage (time), and were the highest in the control of T.1, 2.40 mg.l^{-1}, and also in the other variants with different amounts of added biochar at the first stage of incubation, between (1.0 and 1.80 mg.l^{-1}). During the following periods in T.1, a decrease in the values of phosphate anions was found, being lower at the 3rd stage (average 1.04 mg.l^{-1}) and at the 6th stage (average 1.17 mg.l^{-1}). It was found that T.2 also had the lowest phosphate content in the 6th incubation period, on average (0.85 mg.l^{-1}) in the different variants with added biochar. Higher values were measured in the solutions from stage 4 of incubation (between 1.1 and 1.45 mg.l^{-1} (Figure 4). It was observed that T.3 had the lowest reported values of phosphates in the solutions at all stages (0.19–0.30 mg.l^{-1}), except for the 4th period (120 days of incubation), reaching between 0.53–1.91 mg.l^{-1}. There is no much information on the effect of biochars on the mobility and availability of phosphates in soils. Generally, phosphorus has a complex chemistry in soils, pH having a decisive influence, and most importantly adsorption by soil sesquioxides at low pH and precipitation as Ca phosphates

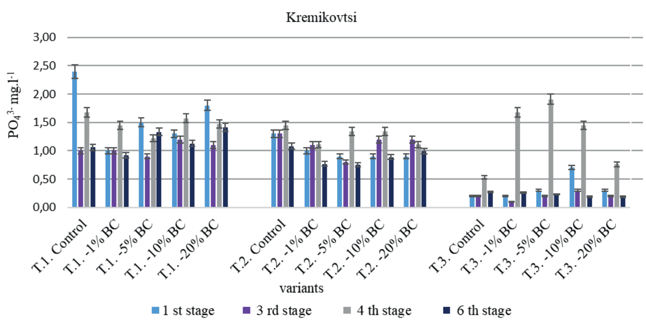

Fig. 4. Content of phosphates (mg.l^{-1}) in water extracts from the soils of the Kremikovtsi site

in non-acidic and alkaline soils, as well as the composition of soil solution, and many other environmental factors (Pierzynski et al., 2005). The established higher values of phosphates in the variants at sites T.1 and T.2 are probably due to the fact that they are cultivated areas, and are subject of fertilizer application and other and chemical products.

Dissolved organic carbon content (DOC)

In the three soils studied after 30 days of incubation (1st stage), the variation of DOC by variants was similar, but the increase at 20% BC at site T1 was most strongly pronounced. The highest values in the variants with 20% biochar were observed in soils T2 and T3, 48 and 42 mg.l^{-1}, respectively. After 120 days of incubation (4th stage), the same trend as in stage 1 of DOC reduction was observed by variant, except for the variant with 20% biochar for all the soils. This may be due to the lower levels of biochar in the 1%, 5% and 10% variants compared to the 20% biochar. Its decrease in theo variants with lower levels (from 1 to 10% of BC) may be related both to adsorption and fixation and to an increase in the activity of microorganisms in the soil at the 20% of biochar applied. These assumptions are confirmed by some concurrant data (unpublished), where different groups of microorganisms increased in the investigated soils from the Kremikovtsi site.

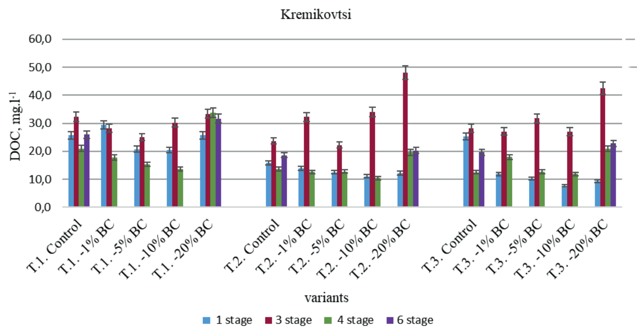

Fig. 5. Dynamics of DOC in water extracts from the soils of the Kremikovtsi site

Concentrations of anions in soil solutions from the area of Aurubis – Pirdop site

Nitrates

From the graphs in Figure 6, no significant trend both in "time" or BC variant is noted both for the four sites studied. It was found that for the variant T.1 at the 1st stage of incubation, the highest values of nitrates were recorded, from 48.5 mg.l^{-1} in the control to 53.8 mg.l^{-1} in variant T.1 with 10% BC, the nitrate content being the lowest in the variant with 20% BC (40.7 mg.l^{-1}). For the other sites T.4, T.6 and T.8 at the 1st stage of incubation with BC, the effect of its interaction with the soil was not, yet observed. In all the variants with added BC, a decrease in nitrate content was found at the 3rd stage of incubation between 11.07 – 21.6 mg.l^{-1} (Figure 6). There is an increase in nitrate concentrations at the 4th stage and a slight decrease at the last, 6th stage. It should be noted that the soil samples were taken from non-cultivated areas (forest, grass vegetation), and that the sampling period was in the late winter or early spring. During this period, the active vegetation has not, yet been developed, and it is possible to concentrate nitrates in the surface soil layers by capillary action, resulting in higher nitrogen content in the initial periods of the incubation. It should also be taken into account that the ongoing processes and changes in nitrogen in these grass and forest areas differ from cultivated areas, where different agricultural techniques are applied, affecting the soil microflora. It is possible that the stabilization of the agroecosystem under these conditions takes place at a later stage of interaction with the biochar. In conclusion, inconsistent trends were observed depending on the BC variant, stage and soil type.

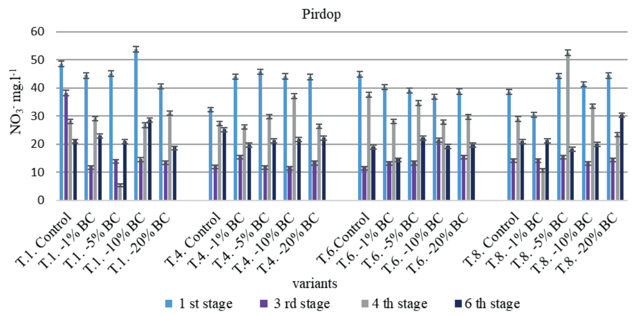

Fig. 6. Content of nitrates (mg.l^{-1}) in water extracts from the soils of the Aurubis-Pirdop site

Chlorides

A decrease in average chlorides values was observed in the variants at sites T.1-T.6 (8.61–11.0 mg.l^{-1}), compared to the site T.8, where the average values were slightly higher (14.23 mg.l^{-1}). It was found that in the water extracts, the chloride content was low during the 1st stage, i.e. between 3 mg.l^{-1} and 15.6 mg.l^{-1}. A decrease was observed in the variants with 20% added biochar, compared to the control in variants (T.1-T.6). During the 3rd stage, after 90 days of incubation, a higher content of chlorides was observed in the control of T.1, reaching 24 mg.l^{-1} and at T.8, with 10% and 20% added biochar, 21-22 mg.l^{-1}, The content of chlorides in all the studied variants and stages is low and does not exceed the maximum permissible concentration (MPC) of 200 mg.l^{-1} (Regulation 12 of 2002). We can discern a decrease in chloride concentration with BC variant and time, esp. in T1 and T6 sites. A similar trend was observed in our previous study (Simeonova et al., 2019), in which biochar (500°C) was applied at lower doses on a Fluvisol (pH 5,8-6,1).

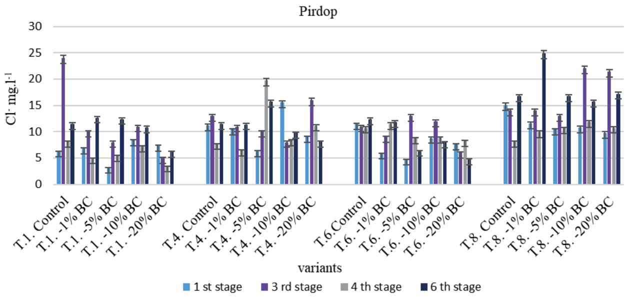

Fig. 7. Content of chlorides (mg.l^{-1}) in water extracts from the soils of the Aurubis-Pirdop site

Sulphates

Low values of sulfates were found in the solutions from the variants at sites T.1 (12–23 mg.l^{-1}), T.4 (5–16 mg.l^{-1}) and T.6, (7–21 mg.l^{-1}), and the differences between controls and variants with biochar are insignificant, except for the controls from site T.1 (reaching 54 mg.l^{-1}) during the 3rd stage of incubation (Figure 8). We observed that adding biochar to these soils did not increase the soil adsorption capacity for sulfate sorption. There were no distinct trends between the individual stages and variants of biochar. There is an exception for site T.8, where the measured concentrations of sulfates are about 3-4 times higher, i.e. from 43 – 78.9 mg.l^{-1} compared to the other variants. However, they do not exceed the maximum permissible concentrations for sulfates content (250 mg.l^{-1}) in the waters (Regulation 12 of 2002). The soil reaction (pH) in this point T.8, is slightly acidic pH 6.20 compared to the other variants (T.1, T.4, T.6), where the pH values are lower (pH 4,3; 5,4, 4,9). These trends are in line with the chemistry of sulphates in acidic soils, which involves specific sorption on Fe and Al sesquioxides, through exchange of OH^- or H_2O groups in the crystal structure of the minerals, while in soils of pH > 6 very little SO_4^{2-}, is sorbed due to pevalence of negative charge on soil colloids (Curtin and Syers, 1990). Other authors (Zhao et al., 2017) conclude that sulfate can be adsorbed on biochar and soil through electrostatic interaction, as well.

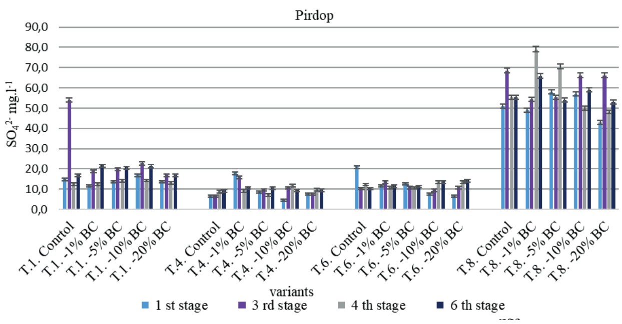

Fig. 8. Content of sulphates (mg.l^{-1}) in water extracts from the soils of the Aurubis-Pirdop site

Phosphates

In the water solutions, the highest values of phosphates were found at the control site T.1, 2.30 mg.l^{-1}, at the 3rd incubation period, while in the variants with biochar they were low, up to 0.70 mg.l^{-1} (Figure 9). In this stage, a significant variation of the phosphate concentrations was also observed. It was found that at the 4th and the 6th stages of incubation with biochar, the concentrations of phosphate anions decreased slightly. The behavior of phosphates is similar in the soil from T.6, where a decrease is observed during the 6th stage, after 180 days of incubation, although not so clearly. For the other sites T.4, T.6, no visible changes were noted either with stage, or the BC variants. In the study of Ghodszad et al. (2022), it was noted that various biochars may exhibit dissimilar effects in P sorption and desorption processes, i.e. those produced at low T (300–450 C) could decrease P sorption and enhance P availability in acidic soils if low in Fe and AI oxides, and if higher labile organic carbon in these types of biochars is present.

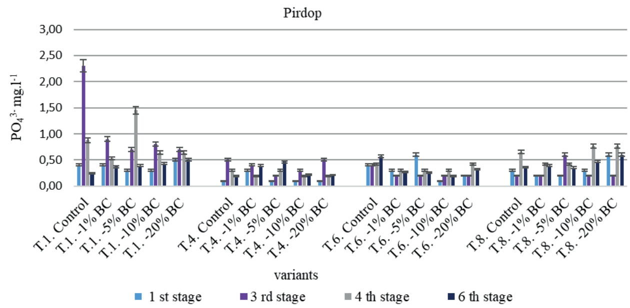

Fig. 9. Content of phosphates (mg.l^{-1}) in water extracts from the soils of the Aurubis-Pirdop site

Dissolved organic carbon content (DOC)

The application of biochar affected the dissolved organic carbon (DOC) content, but the effect was different in the tested soils from Pirdop. For soil T1 the DOC concentration (28–71.3 mg.l^{-1}) was the highest compared to the other soils. At 1st and 6th stages (after 30 and 180 days of incubation), the DOC increased in the biochar variants compared to the control. At the 3rd stage, in all the soils, it is noticeable that the DOC content was 2 times higher compared to the other soils. At this point in soil T1 no differences by variants were observed. At the 4th stage of T1, there is a reduction in DOC by variants compared to the control. For soil T4, the DOC contents at 1st, 4th and 6th stages are within a narrow range (17.1–29.5 mg.l^{-1}), but all four stages show a slight increasing trend in DOC values by variant (except 3rd stage at 5% BC variant) compared to the controls. In soil T6 at 3rd and 4th stages in the variant with 5% BC, there was a sharp increase, then a decrease in the content of DOC. For soil T8, at the 1st and the 3rd stages, there was an increase in DOC values by variants from the control, but after 120 and 180 days of incubation there was no variation by variants (Figure 10).

In general, the soils from sites T1, T4 and T6, DOC exhibited increasing trend in the variants with biochar application compared to the control soils. These soils are light in soil texture and poor in humus (Atanassova et al., 2023). Jòzefaciuk et al. (1996) found that sandy soils have low capacity to retain organic matter, therefore it can be assumed that biochar application can increase the release of DOC. Three of the soils (T1, T4 and T6) had a pH of 4-5, which increased in the process of biochar treatments, and as the incubation period increased, as well. An increase in pH can induce deprotonation of functional groups on DOC and total organic carbon (TOC) molecules, resulting in more soluble organic carbon. A large number of studies confirm that biochar application to soils directly increases soil organic matter content and soil soluble organic matter stock (Smebye et al., 2016; Zhang et al., 2016).

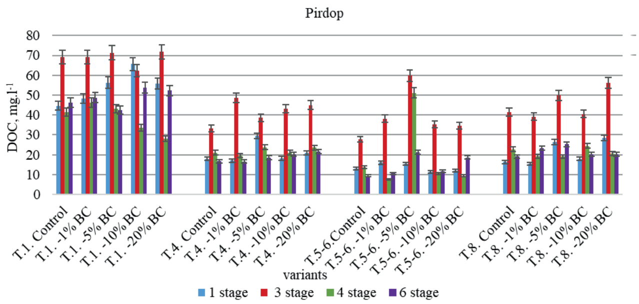

Fig. 10. Dynamics of DOC in water extracts from the soils of the Aurubis-Pirdop site

Concentrations of anions in soil solutions from the area of the Medet site

Nitrates

The reported results show that the highest values of nitrates in the solutions from the Medet region are noted at the 3rd stage, on average of 34.89 mg.l^{-1}, for the other sites there was a decrease in the range of 20–22.0 mg.l^{-1}. Regarding soil reaction (pH), with values of 4.7–5.0, the soil solutions have a similar composition to those of the Pirdop Site, but the samples from Medet, are taken from reclaimed area. In a study by Gronwald et al. (2015), it was found that biochar from wood shavings is particularly effective in the adsorption of nitrates, but the type of reclaimed soil must also be taken into account. An increase was observed, although low on nitrate content in all the variants at the 3rd stage, compared to the 1st stage of incubation and at site T1 and at the 6th stage, compared to the first and somewhat in the 4th stage of incubation. It can be summarised that the nitrate concentrations varied little between different the variants and the incubation stages (Figure 11).

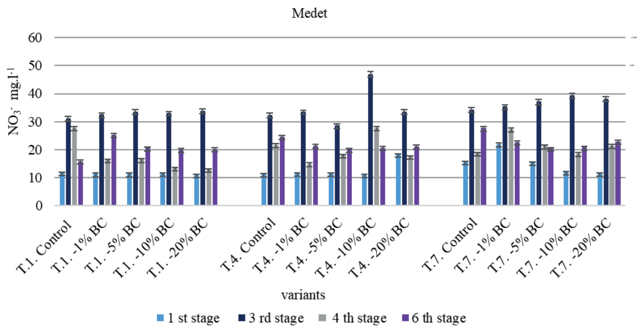

Fig. 11. Content of nitrates (mg.l^{-1}) in water extracts from the reclaimed soils of the Medet area

Chlorides

For these soils, we find that the chlorides content was the lowest during the 1st stage of the study from 2.7 to 6.8 mg.l^{-1}. After 90 and 120 days of incubation, the average chloride content in the solutions was close to 8.10–7.37 mg.l^{-1}. It was observed that during the last incubation stage the content of chlorides slightly increased to 10.56 mg.l^{-1} (Figure 12).

In general, chloride concentrations decreased with BC variant and increased with time at these sites, similarly to Aurubis-Pirdop site and our previos study (Simeonova et al., 2019).

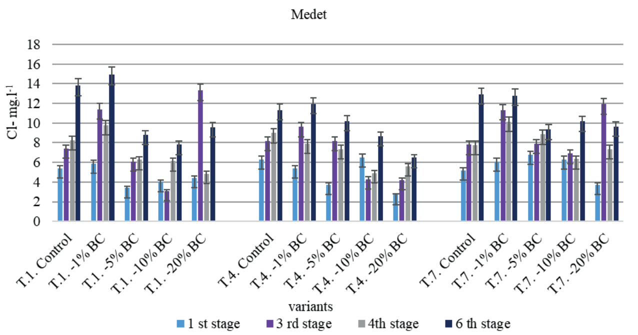

Fig. 12. Content of chloride (mg.l^{-1}) in water extracts from the reclaimed soils of the Medet area

Sulphates

The general trend is, little variation of sulphates, similarly to the Aurubis-Pirdop acidic soils, however an increase was noted at the 6th stage with 20 % BC added at sites T1 and T7, and no variation at site T4. After summarizing the results, it is established that sulfate values are the highest in the variants of T.7 reaching 27 mg.l^{-1}, they are the lowest in T.4 soil, between 0 and 10.32 mg.l^{-1} (Figure 13).

It can be concluded that a slight increase of sulphates is obsereved in T1 and T7 soils from BC application, most probably caused by the increased negative charge on soil and BC colloids, brought about by the alkalization of the soil-biocahar adsorption complex.

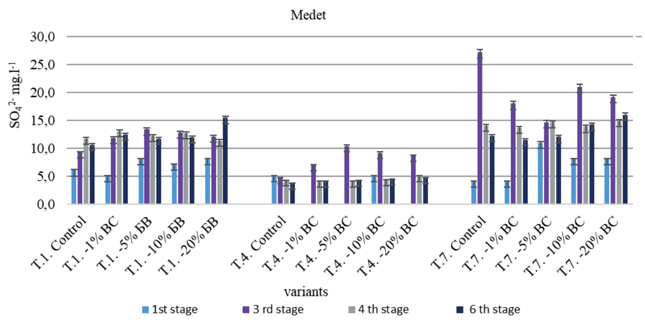

Fig. 13. Content of sulphate (mg.l^{-1}) in water extracts from the reclaimed soils of the Medet area

Phospates

The data show that the highest mobilisation of phosphates was recorded at the 3rd (average 1.49 mg.l^{-1}) and 4th stages of the study (average 1.45 mg.l^{-1}), with consequtive decrease at the 6th stage, probably due to irreversible adsorption of phosphates. No obvious trends were established between the variants with added biochar and the controls from sites T.1, T.4 and T.7. It was found that between the first stage (after 30 days) and the sixth period, (after 180 days of incubation), for sites T4 and T7, there is almost no difference in the content of phosphate anions (Figure 14).

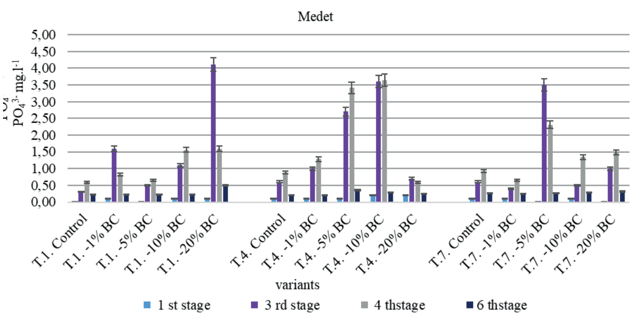

Fig.14. Content of phosphate (mg.l^{-1}) in the water extracts from the reclaimed soils of the Medet area

The results shows that, from the region of Medet, the studied anions did not exceed the maximum permissible concentrations, according to Regulation No. 12/2002. For Kremikovtsi and Pirdop sites, exceeding is reported, albeit slightly, of the MPC for nitrate contents of 50 mg.l^{-1} in drinking waters. In all the investigated sites, the the MPC for sulfate contents of 250 mg.l^{-1} in drinking waters are not exceeded, according to Regulation No. 12/2002.

Dissolved organic carbon (DOC)

The application of different levels of biochar affected the DOC content of the three soils of the Medet area, differently. The data obtained from soil T1 showed that the DOC content increased rapidly after BC application at both sites (after 30 and 90 days of incubation), compared to the controls (from 10 to 17 mg/l and from 7.2 to 20.8 mg.l^{-1}, respectively). For soils T4 and 7 we found that there was a slight variation in organic carbon values at both stages, which decrease for the higher BC variants.

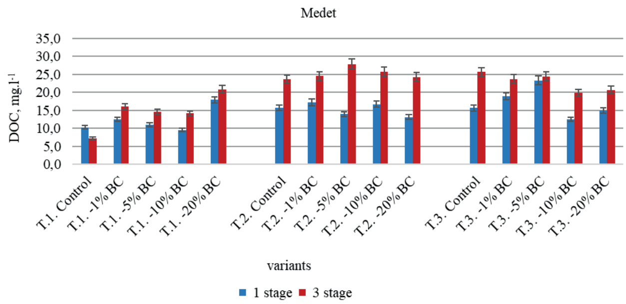

Fig. 15. Dynamics of DOC content in the water extracts from the reclaimed soils of the Medet area

Correlation analysis was performed (at $p \leq 0.05$): between the main physico-chemical soil characteristics (pH, electrical conductivity, exchangeable acidity, Ca and Mg contents, TOC), DOC and anion composition (SO_4^{2-}; NO_3^-; PO_4^{3-}) in the water extracts (Table 2).

A positive significant relationship between phosphate ions and pH, CEC, exch. Ca, exch. Mg and TOC (R= 0.5840, R = 0.4171, R = 0.4662, R = 0.4182 and R= 0.5406) was established in the soils of Kremikovtsi region.

For the soils, the Aurubis-Pirdop area DOC has a positive correlation with phosphates in solution (R = 0.4429). For the sulphates, there was a significant positive correlation with pH, electrical conductivity, exchangeable Ca and Mg and pH and a negative correlation with the clay content (R = -0.5839).

A positive significant correlation between DOC and CEC$^-$ was found in the soils of the Medet region. The sulfates and phosphates anions have a positive correlation with pH,

Table 2. Major significant correlations between anions and the main physico-chemical soil characteristics

Kremikovtsi			Pirdop			Medet		
Parameters	R	p -value	Parameters	R	p -value	Parameters	R	p- value
PO_4^{3-}/pH	0.5840	0.0000	SO_4^{2-}/pH	0.7087	0.0000	DOC/CEC	0.5793	0.0008
PO_4^{3-}/CEC	0.4171	0.0009	SO_4^{2-}/EC	0.9200	0.0000	SO_4^{2-}/Clay	-0.5631	0.0012
PO_4^{3-}/Ca_{exch}	0.4662	0.0002	$SO_4^{2-}Ca_{exch}$	0.5783	0.0000	PO_4^{3-}/pH	0.4432	0.0142
PO_4^{3-}/Mg_{exch}	0.4182	0.0009	SO_4^{2-}/Mg_{exch}	0.7615	0.0000	NO_3^-/pH	0.5464	0.0018
PO_4^{3-}/TOC	0.5406	0.0000	SO_4^{2-}/Clay	-0.5839	0.0000	SO_4^{2-}/pH	0.4542	0.0117
			SO_4^{2-}/pH	0.7087	0.0000	DOC/NO_3^-	0.5930	0.0006
			DOC/PO_4^{3-}	0.4429	0.0000	DOC/PO_4^{3-}	0.5333	0.0024

reflecting a decrease of sorption sites on soil adsorbent with soil alkalization.

Sources of anions in soil solution

In order to reveal sources of anions and establish possible associations and interactions among them, Principal component analysis (PCA) was performed on the soluble concentrations of nitrates, sulphates, chlorides and anionic DOC forms for the studied soils, from the areas of Kremikovtsi steel plant, Aurubis-Pirdop copper smelter and the Medet mine at the 3rd stage of incubation.

Kremikovtsi: Two components with eigenvalues > 1 were extracted, explaining 41.9%, and 27.6% of the total variance 69.5%, respectively. The component matrix (Table 3) reveals two major components. The 1st was loaded by phosphates and sulphates and the 2nd by DOC. Chlorides shows different behaviour and/or sources in the soil. We can suppose that DOC has different source (supposedly biochar) from sulphates and phosphates which are low in concentration and and most probably originate from the soil colloidal complex.

The results of the PCA analysis is confirmed by the cluster analysis indicating groupings of variables (anions) containing clusters of similar characteristics and/or sources. The dendrogram contains two main clusters, the 1st grouping the sulphates and phosphates as a sub-branch of the 1st cluster, and the 2nd, DOC and chlorides, thus indicating different sources.

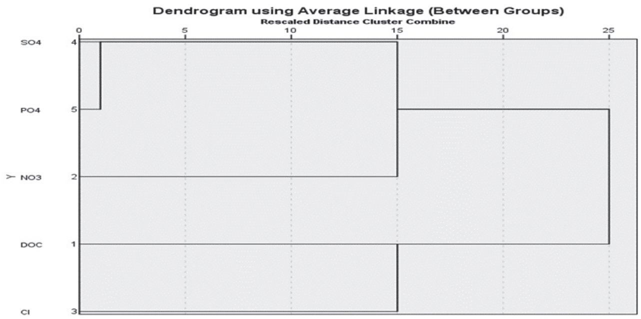

Fig. 16. Cluster analysis with dendrogram of relationships between the anionic species in the soils of the Kremikovtsi site

Table 3. Component matrix of the measured parameters in the soils of the Kremikovtsi site

Rotated Component Matrix[a]		
	Component	
	1	2
DOC	,834	-,037
NO_3	-,852	,023
CI	,396	-,314
SO_4	-,399	,848
PO_4	,168	,943

Aurubis-Pirdop: The data reveal two components with Eigenvalues > 1. The 1st component explains 49 %, and the 2nd 28% of total variance 77.4%. DOC is mobilised simultaneously with the nitrates and the phosphates, thus confirming one source, most probably the soil colloidal complex, due to increased soil alkalisation from BC addition (Table 4). The sulphate and chloride anions are likely to be mobilised from the biochar ameliorant, due to their belonging to a different soil component and the SO_4^{2-} negative correlation with the clay content.

Table 4. Rotated component matrix of the measured parameters in the soils of the Aurubis-Pirdop site

	Component	
	1	2
DOC	,817	-,153
NO_3	,688	,469
CI	,121	,929
SO_4	,036	,860
PO_4	,909	,208

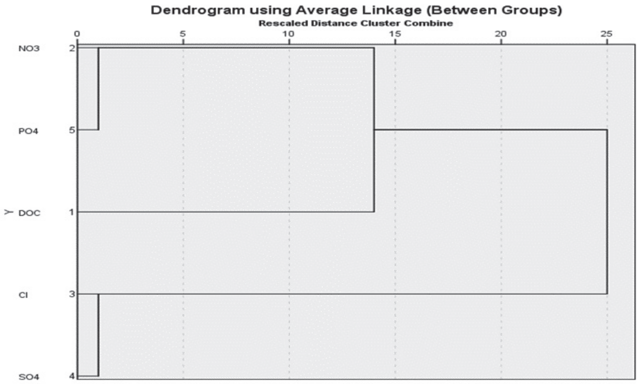

Fig. 17. Cluster analysis with dendrogram of relationships between the anionic species in the soils of the Aurubis-Pirdop site

Medet: The data reveal three components with eigenvalues > 1, 1st reflects 36%, the 2nd 24.7 %, and the 3rd 20.5 % of the total variance of 81.2%.

We discerned the following trends here: DOC is very low in these soils, and is connected in one cluster with the nitrates and the phosphates, and is rather mobilised by the soil colloidal complex, than from the biochar. This finding is confirmed by the significant correlation between DOC and CEC of the soils Sulphates and chlorides have other sources, e.g. biochar, particulate matter, including unmineralized (Table 5).

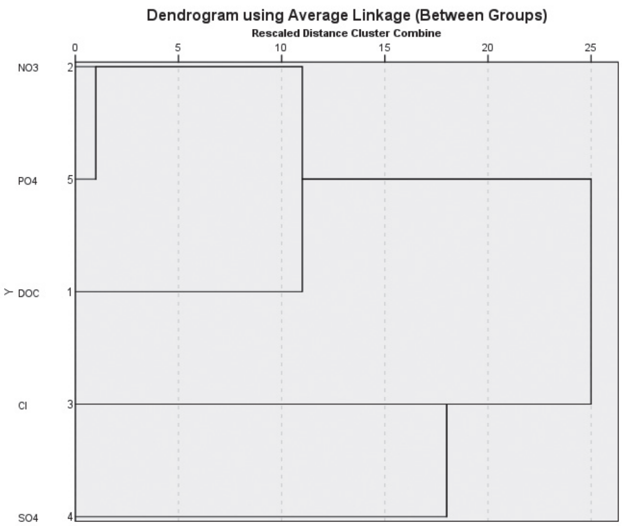

Fig. 18. Cluster analysis with dendrogram of relationships between the anionic species in the soils of the Medet area

Table 5. Rotated component matrix of the measured parameters in the soils of the Medet site

Rotated Component Matrix[a]			
	Component		
	1	2	3
DOC	,693	,058	,355
NO_3	,735	,372	-,398
CI	-,001	,104	,909
SO_4	-,034	,969	,108
PO_4	,867	-,253	-,089

Conclusions

The results of the incubation experiment shows that the measured parameters of the soil solution from the investigated different sites, and soil types show significant dynamics. This is typical of the behavior of elements in solutions, but makes it difficult to interpret. It was established that there are no clearly expressed trends in the content of anions by BC variant for the different soils. Some trends observed are the following: Reductions in nitrates are observed, in the Kremikovtsi soils. The concentrations of sulfates, phosphates, and chlorides in the solutions vary ununiformly, and there was no clear trend in sulphates levels with time and BC variants.

In the Aurubis-Pirdop soils, a general trend was that DOC increased in the variants with biochar application compared to the control soils. For the Medet area, an increase was observed on NO_3^- content in all the variants of the 6th stage, compared to the 1st and somewhat at the 4th stage of incubation. For the sulphates, phosphates and chlorides inconsistent variation with stage, BC variant and soil type was noted.

The observed contents and distribution of anions are due to complex interactions between the solid and the liquid phase, and their copmposition. The changes in DOC content are likely controlled by specific processes, occurring between soluble organic matter and the soil adsorbent (such as pH-dependent adsorption-desorption), soil properties, competition for sorption sites on soil adsorbent and the biochar etc. PCA analysis indicates that in the neutral-to alkaline soils, the source of DOC is the biochar ameliorant, while in the acidic soils from Auribis-Pirdop and Medet, it can be mainly DOC mobilized by soil colloids. There were no clear dependancies of the other anions on the BC doses for the different soil types and regions, except for the Cl^- ions, which decreased from BC application in the acidic soils and the increase of SO_4^{2-} ions in the acidic soil from the Medet mine area.

Acknowledgments

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Referenses

Ajayi, A. E., Holthusen, D. & Horn, R. (2016). Changes in microstructural behaviour and hydraulic functions of biochar amended soils. *Soil and Tillage Research*, *155*, 166 – 175. doi: 10.1016/j.still.2015.08.007.

Ao, H., Cao, W., Hong, Y., Wu, J. & Wei, L. (2020). Adsorption of sulfate ion from water by zirconium oxide-modified biochar derived from pomelo peel. *Science of the Total Environment, 708*, 135092. https://doi.org/10.1016/j.scitotenv.2019.135092.

Atanassova, I., Benkova, M., Nenova, L., Harizanova, M., Ilinkin, V, Kirilov, I., Dimitrov, E. & Simeonova, T. (2023). Geogenic and pedogenic sources of metals inreclaimed Technosols from the area of Asarel-Medet non-ferrous smelter in Bulgaria. *Journal of Environmental Protection and Ecology, 24*(6), 1857 – 1866 (Bg).

Atanassova, I., Nenova, L., Simeonova, T., Benkova, M., Harizanova, M. & Ilinkin, V. (2024). Effect of biochar on heavy metal solubility and speciation in Technogenic soils around Aurubis-Pirdop copper smelter in Bulgaria. *Biology*, 1 – 14. https://doi.org/10.1007/s11756-023-01590-5 (Bg).

Chen, G., Fang, Y., Van Zwieten, L., Xuan, Y., Tavakkoli, E., Wang, X. & Zhang, R. (2021). Priming, stabilization and temperature sensitivity of native SOC is controlled by microbial responses and physicochemical properties of biochar. *Soil Biol. Biochem., 154*, 108139. https://doi.org/10.1016/j.soilbio.2021.108139.

Cheng, H., Hill, P. W., Bastami, M. S. & Jones D. L. (2017). Biochar stimulates the decomposition of simple organic matter and suppresses the decomposition of complex organic matter in a sandy loam soil. *Global Change Biol Bioenergy,* 9, 1110 – 1121. https://doi.org/10.1111/gcbb.12402.

Chintala, R., Mollinedo, J., Schumacher, T. E., Papiernik, S. K., Malo, D. D., Clay, D. E., Kumar, S. & Gulbrandson, D. W. (2013). Nitrate sorption and desorption in biochars from fast pyrolysis. *Microporous and Mesoporous Materials*, *179*, 250 – 257.

Curtin, D. & Syers, J. K. (1990). Mechanism of sulphate adsorption by two tropical Soils. *European Journal of Soil Science, 41*(2), 295 – 304. https://doi.org/10.1111/j.1365-2389.1990.tb00064.x.

Dong, X., Singh, B. P., Li, G., Lin, Q. & Zhao, X. (2018). Biochar application constrained native soil organic carbon accumulation from wheat residue inputs in a long-term wheat-maize cropping system. *Agr. Ecosyst. Environ.,* 252, 200 – 207. https://doi.org/10.1016/j.agee.2017.08.026.

El-Naggar, A., Lee, S. S., Awad, Y. M., Yang, X., Ryu, C., Rizwan, M., Rinklebe, J., Tsang, D. C. W. & Ok, Y. S. (2018). Influence of soil properties and feedstocks on biochar potential for carbon mineralization and improvement of infertile soils. *Geoderma,* 332, 100 – 108. https://doi.org/10.1016/j.geoderma.2018.06.017.

Feng, Z., Fan, Z., Song, H., Li, K., Lu, H., Liu, Y. & Cheng, F. (2021). Biochar induced changes of soil dissolved organic matter: The release and adsorption of dissolved organic matter by biochar and soil. *Science of the Total Environment, 783*, 147091. https://doi.org/10.1016/j.scitotenv.2021.

Ganev, S. & Arsova, A. (1980). Methods for determination of strongly acidic and weakly acidic cation exchange in the soil. *Soil Science and Agrochemistry*, 3, 22 – 33 (Bg).

Ghodszad, L., Reyhanitabar, A., Oustan, S. & Alidokht, L. (2022). Phosphorus sorption and desorption characteristics of soils as affected by biochar. *Soil and Tillage Research*, 216, 105251.

Glaser, B., Lehmann, J. & Zech, W. (2002). Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review. *Biology and Fertility of Soils*, *35*, 219 – 230.

Gronwald, M., Don, A., Tiemeyer, B. & Helfrich, M. (2015). Effects of fresh and aged chars from pyrolysis and hydrothermal carbonization on nutrient sorption in agricultural soils. *SOIL*, 1, 475 – 489. https://doi.org/10.5194/soil-1-475-2015, 2015.

He, M., Xiong, X., Wang, L., Hou, D., Bolan, N. S., Ok, Y. Sik., Rinklebe, J. & Tsang, D. C. W. (2021). A critical review on performance indicators for evaluating soil biota and soil health of biochar-amended soils. *Journal of Hazardous Materials*, 414, 125378. https://doi.org/10.1016/j.jhazmat.2021.125378.

He, Z., Wang, C, Cao, H., Liang, J., Pei, S. & Li., Z. (2023). Nitrate Absorption and Desorption by Biochar. *Agronomy, 13*(9), 2440. https://doi.org/10.3390/agronomy13092440.

ISO 11265:2002. Soil quality. Determination of specific electrical conductivity.

Johnson, Dale.W. & Dale, W. Cole (1980). Anion mobility in soils: Relevance to nutrient transport from forest ecosystems. *Environment International, 3*(1), 79 – 90. https://doi.org/10.1016/0160-4120(80)90040-9.

Jòzefaciuk, G., Sokoowska, Z., Hajnos, M. W., Hoffmann, C. & Renger, M. (1996). Large effect of leaching of DOC on water adsorption properties of a sandy soil. *Geoderma, 74*, 125 – 137.

Kachinski, N. A. (1958). Soil Particles and Micro-aggregates Composition, Methods for Analysis. USSR Academy of Sciences. Moscow (Ru).

Kanthle, A. K., Lenka, N. K., Lenka, S. & Tediar, K. (2016). Biochar Impact on Nitrate Leaching as Influenced by Native Soil Organic Carbon in an Inceptisol of Central India. *Soil and Tillage Research, 157*, 65 – 72. https://doi.org/10.1016/j.still.2015.11.009.

Kathoh, M., Satoshi, M. & Sato, T. (2012). Single step extraction to determine soluble lead levels in soil. *International Journal of GEOMATE, 3*(2), 375 – 380.

Kononova, M. M. (1966). Soil Organic Matter. Second Ed. *Pergammon Press, Inc.,* Moscow, 544 (Ru).

Lawrinenko, M. & Laird, D. A. (2015). Anion exchange capacity of biochar. *Green Chemistry*, *17*(9), 4628 – 4636. https://doi.org/10.1039/c5gc00828j.

Lehmann, J. & Rondon, M. (2006). Bio-Char Soil Management on Highly Weathered Soils in the Humid Tropics. *In:* Uphoff, N., Ed., Biological Approaches to Sustainable Soil Systems, *CRC Press,* Boca Raton, 517 – 530. http://dx.doi.

org/10.1201/9781420017113.ch36.

Li, Q., Wang, Y., Li, Y., Li, L., Tang, M., Hu, W., Ch., Li. & Ai, S. (2022). Speciation of heavy metals in soils and their immobilization at micro-scale interfaces among diverse soil components. *Science of the Total Environment*, *825*, 153862. https://doi.org/10.1016/j.scitotenv.2022.153862.

Lin, S., Wang. W., Sardans, J., Lan, X., Fang, Y., Singh, B. P., Xu, X., Wiesmeier, M., Tariq, A., Zeng, F., Alrefaei, A. F. & Peñuelas, J. (2022). Effects of slag and biochar amendments on microorganisms and fractions of soil organic carbon during flooding in a paddy field after two years in southeastern China. *Sci Total Environ*., *824*, 153783. https://doi.org/10.1016/j.scitotenv.2022.153783.

Liu, C. H., Chu, W., Li, H., Boyd, S., Teppen, B., Mao, J., Lehmann, J. & Zhang, W. (2019). Quantification and characterization of dissolved organic carbon from biochars. *Geoderma*, *335*, 161 – 169.

Liu, H., Zhao, B., Zhang, X., Li, L., Zhao, Y., Li, Y. & Duan, K. (2022). Investigating Biochar-Derived Dissolved Organic Carbon (DOC) Components Extracted Using a Sequential Extraction Protocol. *Materials*, *15*, 3865. https://doi.org/10.3390/ma15113865.

Lu, L., Yu, W. T., Wang, Y. F., Zhang, K., Zhu, X. M., Zhang, Y. C., Wu, Y. J., Ullah, H., Xiao, X. & Chen, B. L. (2020). Application of biochar-based materials in environmental remediation: from multi-level structures to specific devices. *Biochar*, 2, 1 – 31.

Marsh, K. B., Tillman, R. W. & Syers, J. K. (1987). Charge relationships of sulfate sorption by soils. *Soil Science Society of America Journal, 51*(2), 318 – 323.

Nenova, L., Atanassova, I., Stoykova, M., Dimitrov, E., Kirilov, I., Benkova, M., Simeonova, T. & Harizanova, M. (2023). Relationships between Heavy Metal and Metalloid Contents and Major Soil Characteristics in Soils around the Former Kremikovtsi Metallurgical Plant Following Its Closure in 2009. *In:* Proceedings of the Bulgarian Academy of Sciences, *76*(11), 1789 – 1798.

Oliveira, F. R., Patel, A. K., Jaisi, D. P., Adhikari, S., Lu, H. & Kumar. S. K. (2017). Environmental application of biochar: Current status and perspectives. *Bioresource Technology,* 246, 110 – 122. https://doi.org/10.1016/j.biortech.2017.08.122.

Ortiz-Bobea, A., Ault, T. R., Carrillo, C. M., Chambers, R .G. & Lobell, D. B. (2021). Anthropogenic climate change has slowed global agricultural productivity growth. *Nat. Clim. Chang*., *11*, 306 – 312.
doi:10.1038/s41558-021-01000-1.

Palmeggiani, G., Lebrun, M., Simiele, M., Bourgerie, S. & Morabito, D. (2021). Effect of Biochar Application Depth on a Former Mine Technosol: Impact on Metal (Loid)s and Alnus Growth. *Environments*, *8*(11), 120. https://doi.org/10.3390/environments8110120.

Pierzynski, G. M., Mcdowell, R. W. & Sims, J. T. (2005). Chemistry, cycling, and potential moment of inorganic phosphorus in soils. *In:* Phosphorus: Agriculture and the Environment (JT Sims, AN Sharpley, eds), American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Inc., Madison, 2005, WI, 53 – 86.

Regulation No. 12 /2002 on the quality of surface water intended for drinking and household purposes. State Gazette No. 63, 28 June 2002 (Bg).

Rombolà, A. G., Torri, C., Vassura, I., Venturini, E., Reggiani, R. & Fabbri, D. (2022). Effect of biochar amendment on organic matter and dissolved organic matter composition of agricultural soils from a two-year field experiment. *The Science of the Total Environment*, *812*, 151422.

Sanford, J. R., Larson, R. A. & Runge, T. (2019). Nitrate sorption to biochar following chemical oxidation. *Sci. Total Environ*., *669*, 938 – 947. https://doi.org/10.1016/j.scitotenv.2019.03.061.

Simeonova, Ts., Benkova, M., Nenova, L. & Atanassova, I. (2019). Physico-chemical, Agrochemical and Eco-chemical Characteristics of Biochar-treated Fluvisol. *Ecologia Balkanica, 11*(2), 203 – 214 (Bg).

Smebye, A., Alling, V., Vogt, R. D., Gadmar, T. C., Mulder, J., Cornelissen, G. & Hale, S. E. (2016). Biochar amendment to soil changes dissolved organic matter content and composition. *Chemosphere, 142*, 100 – 105. https://doi.org/10.1016/j.chemosphere.2015.04.087.

Sun, Y., Xiong, X., He, M., Xu, Z., Hou, D., Zhang, W., Ok, Y. S., Rinklebe, J., Wang, L. & Tsang, D. C. W. (2021). Roles of biochar-derived dissolved organic matter in soil amendment andenvironmental remediation: A critical review. *Chemical Engineering Journal*, 424, 130387. https://doi.org/10.1016/j.cej.2021.130387.

Tian, B., Song, Y., Wang, R., Wang, Y., Wang, T., Chu, J., Qiao, Z., Li, M., Lu, J. & Tong, Y. (2023). Adsorption of sulfate ions from water by $CaCl_2$-modified biochar derived from kelp, *RSC Sustainability*, *4*(**1),** 898 – 913.

Zhang, H., Chen, C., Gray, E. M., Boyd, S. E., Yang, H. & Zhang, D. (2016). Roles of biochar in improving phosphorus availability in soils: A phosphate adsorbent and a source of available phosphorus, *Geoderma,* 276, 1 – 6. https://doi.org/10.1016/j.geoderma.2016.04.020.

Zhao, B., Nan, X., Xu, H., Zhang, T. & Ma, F. (2017). Sulfate sorption on rape (*Brassica campestris* L.) straw biochar, loess soil and a biochar-soil mixture. *Journal of Environmental Management,* 201, 309-314.

Zhu, X., Chen, B., Zhu, L. & Xing, B. (2017). Effects and mechanisms of biochar-microbe interactions in soil improvement and pollution remediation: a review. *Environ Pollut.,* 227, 98 – 115. doi: 10.1016/j.envpol.2017.04.032.

Zijian, He., Wang, Ch., Cao, H., Liang, J., , Pei, Sh. & Li, Z. (2023). Nitrate Absorption and Desorption by Biochar, *Agronomy, 13*(9), 2440. https://doi.org/10.3390/agronomy13092440.

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