Trend Analysis of Water-Soluble Salts Vertical Migration in Technogenic Edaphotops of Reclaimed Mine Dumps in Western Donbass (Ukraine)

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Surface evaporation rates that are greater than precipitation rates lead to upward salinization processes and, consequently, man-made contamination of the covering surface layers on coal dumps in Western Donbass, Ukraine. The effectiveness of capping the mine dumps with different layers of black-soil mass, both with and without a shielding layer of loess-like loam, was studied in order to develop the optimal scheme for the reclamation of these dumps. Principal component analyses were carried out in order to reveal the regularities of the upward salt migration to the surfaces of reclaimed coal mine dumps. The parameters of the layer-by-layer variation of the physical and chemical data in soil water extracts (namely, pH, total salinity and concentrations of bicarbonates, chlorides, sulfates, calcium, magnesium, sodium and potassium) which were obtained in 1987, 2003 and 2016 along the reclaimed profiles of various models of technogenic edaphotop, gradually acquire a stable-equilibrium state of mineralization in space and time. The alkaline barrier is the main factor for pH-changes and profile salinization of reclaimed land.

Keywords: mine dump reclamation, water-soluble salts migration, soil profile, principal component analysis.
Introduction

The need for land reclamation in Ukraine’s Western Donbass region is associated with the long-term underground coal development in the Samara River floodplain. The problems associated with environmental restoration after coal mining are relevant even for such developed countries as USA, Germany, UK and others (Chugh and Behum 2014; Bellenfant et al. 2013; Wiessner et al. 2013; Lottermoser 2010; Bian Zhengfu et al. 2010). However, the difference in the ratio of precipitation and evaporation can exclude the automatic application of known reclamation approaches and so requires the development of new technologies for application in Ukraine.

The problem of nature conservation in Western Donbass is very real since almost half of the coal reserves are deposited under Samara River floodplain and its tributaries. Among the negative impacts after coal mining, contamination of surface and groundwater bodies is the most significant. The main sources of such contamination (that is, besides the mine water from beneficiation plant) are the mine-tailing dumps and products resulting from coal dressing. The coal mining also results in the formation of deep fissures and intense subsidence on the floodplain surface (up to 1 m, and sometimes up to 3-7 m). The areas of subsidence are then filled with ground and surface water and turn into a waterlogged reservoirs, leading to subsidence at the surface and, eventually, to the flooding of large areas. The environmental state is aggravated by leaching toxic substances from waste rocks accumulated in slag heaps, which contaminates soils and groundwater (Yevgrashkina et al. 2009).

Reclamation of these floodplain areas has been carried out for almost 50 years using rocks from mine excavation. This may result in the extraction of environmentally hazardous substances at critical concentrations in soils and surface waters (Kostenko and Opanasenko 2005; Kharytonov et al. 2012). In that regard, environmentally harmful substances in mine dumps (such as sulfides and chlorides) vary over time, depending on the physical and chemical conditions (Kharytonov and Yevgrashkina 2009).

At the initial stage of weathering, leaching of water-soluble salts from mine-dump rocks is observed, a process that begins almost immediately after placing the mine rocks at surface level. With the passage of time, the rate of salt removal decreases, and such trends contribute to the improvement of the dumps in terms of their reclamation. The rate of salt removal depends on several factors, such as geomorphological conditions of excavation, the texture and chemical composition of mine rocks, and bioclimatic potential. However, the rate of change in the chemical rock composition can be different, and the main source of harmful chemical influence is sulfides (such as pyrite, pyrrhotite, and marcasite) which, after oxidation, turn into iron sulfate and sulfuric acid (Kharytonov and Yevgrashkina 2009; Hayes et al. 2014; Huff 2014).

The main environmental challenge in developing the optimal scheme for land reclamation in Western Donbass is the prevention of upward salinization and consequent man-made contamination of overlying artificial surfaces which results from the rate of evaporation being greater than the infiltration rate from rainfall precipitation (Kharytonov 2007; Tarika and Zabaluev 2004; Konhke 1950). This imbalance is the most important factor in enhancing the weathering of potentially toxic rocks accumulated in mine dumps. An earlier assessment of the qualitative and quantitative composition of the anions and cations in aqueous extractions from soil and rock samples showed that the main unacceptable consequence is the gradual salinization of the artificial surface layers of reclaimed lands with sodium and magnesium chlorides and sulfates contained in coal dumps (Kharytonov and Kroik 2011; Bender 1983).

Thus, the majority of mine dumps requires measures for protecting the upper layer from the accumulation of toxic salts resulting from their upward migration. For example, high levels of exchangeable aluminum are considered to be the main restriction for plant growth (Shengyin Wang et al. 2016; Silva 2012), and to neutralize this effect it is recommended that chemical ameliorants are applied so as to create geochemical barriers (José Roberto Pinto de Souza et al. 2000). In addition, several methods for land reclamation have been proposed, such as application of various calcium-containing substances (such as lime) (Nkongolo et al. 2016),
fly coal ash (Malik and Thapliyal 2009; Zhenqi Hu et al. 2004), sludge from alumina processing (Kyncl 2008), increased amounts of organic matter (such as sewage sludge and compost) (Baran et al. 2015; Tamanini et al. 2008; Larney and Angers 2012) and mineral fertilizers (Sheoran et al. 2010), plus the imposition of a layer of carbonate rocks (Hoff and Kolff 2012).

Observations of the mine dumps in Western Donbass indicate the need to study the changes in physico-chemical properties of the mine rocks, establish the rate of removal of the weathered rock material, and study the vertical migration of toxic substances along the technogenic edaphopil of the reclaimed land. Thus, experiments suggested a long-term study of the effectiveness of the two- and three-layer reclamation models as geochemical barriers for blocking the upward migration of toxic salts from the mine dumps.

Considering the above-mentioned issues, the goal of the presented study was to identify the regularity, or otherwise, of patterns in the leaching of soluble salts along the profile, and the dynamics of these processes over time, depending on the initial designs of the soil-like bodies at the reclaimed mine dumps.

Materials and methods

The presented study was conducted on the basis of the Pavlograd experimental station for reclamation of disturbed lands in Western Donbass (eastern Ukraine) located near mine "Pavlogradska" (coordinates 48°33′24″ N, 35°58′46″ E). The station was founded in 1976 in the floodplain of the Samara River in order to examine the best restoration measures.

The "Pavlogradska" mine was put into operation in 1968 with the project capacity of 1200 thousands ton per year. The project capacity was reached at 1977. Industrial field of the mine is located in the floodplain of Samara river in Dnipropetrovsk region.

The main reclamation objective included the cultivation of both field and orchard crops. The scheme for reclamation of disturbed land was based on the study of the effectiveness of capping the mine dumps with different layers of black-soil mass (chernozem) both with and without a shielding layer of loess-like loam.

In this study the following models (variants) of technogenic edaphotops were used to look into the peculiarity of upward migration of toxic salts from the mine dumps:

1. Mine rock (MR) + 30 cm of the bulk layer of black soil (30BS);
2. MR + 50BS;
3. MR + 50 cm of the loess-like loam (50LLL) + 30BS;
4. MR + 50LLL + 50BS.

The general scheme of artificial soil profiles creation is presented in Figure 2. It should be noted that in every year (until 1997) all normal variants of plants associated with field crop rotation were grown. Then, due to reformation of the industrial enterprise “Pavlogradska”, the experimental sites were under natural overgrowth (Fig. 1).

Fig. 1
General view of the experimental site

![General view of the experimental site](image)

Fig. 2
The scheme of the experimental plots with 1-4 variants of reclamation
Samples of the soil substrates were collected at 10 cm depth intervals until the dump material was reached; these samples were then air-dried and sieved through a 2 mm screen for general analytical determinations. The pH, conductivity and dry residue values were determined in accordance with the State Standard 26423-85 “Soils. Methods for determination of specific electric conductivity, pH and solid residue of water extract”. Besides, concentrations of the following cations and anions were determined in accordance with commonly used techniques: bicarbonates, chlorides, sulfates, calcium, magnesium, sodium and potassium (the State Standards 26428-85, 26423-85, 26426-85, 26425-85, 29269-91).

Statistical calculations were carried out using Statistica 7.0. Principal components analyses were applied in order to reveal the regularities of the upward salt migration along the overall surface of reclaimed coal mine dumps. In the presented study the following factors were considered as the predictors:

- the “type” of reclamation factor (factor levels: reclamation variants 1 (MR + 30BS), 2 (MR + 50BS), 3 (MR + 50LLL + 30BS) and 4 (MR + 50LLL + 50BS);
- the “time” factor (factor levels: 1987, 2003 and 2016 years of research);
- the “depth” of sampling factor represented by data from each 10 cm of the soil substrate profile until dump material (factor levels: data of the physical and chemical analysis of the concentrations in soil water extracts, namely pH, total salinity and concentrations of the bicarbonates, chlorides, sulfates, calcium, magnesium, sodium and potassium).

### Results and discussion

The principal component analyses revealed three main components whose eigen values exceeded 1; in aggregate these account for 68.13% of total variance (Table 1).

The principal component 1 (PC1) accounts for 47.01 % of total variance, and this component is characterized by statistically significant correlation coefficients with all features under consideration. The acidity index of soil extract is characterized by a positive coefficient of correlation, in contrast to the other indicators which are characterized by a negative coefficient. Thus, the PC1 reflects the level of total mineralization of the soil solution, indicating that the increase in mineralization is associated with a decrease in pH values.

The general linear model of the effect of the type of technogenic edaphotop, in combination with time and depth of sampling, provides an explanation for 92 % of the PC1 variability (Table 2).

It should be noted that all studied predictors, and their combinations, proved to be statistically reliable predictors of the PC1. The highest value for variation of the PC1 is established for “type” of technogenic edaphotop and “depth” of sampling (Figure 3). Although “time” is a statistically reliable predictor, it plays an insignificant role in the PC1 variation. In general, predictor “time” can be described as one that changes insignificantly during the study period.

The highest general level of mineralization is established in variant 1 (i.e. MR + 30BS), a level a little bit lower is specific for variant 2 (i.e. MR + 50BS), and

### Table 1

<table>
<thead>
<tr>
<th>Variable</th>
<th>Principal components</th>
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<tr>
<td></td>
<td>PC1</td>
</tr>
<tr>
<td>pH</td>
<td>0.86</td>
</tr>
<tr>
<td>Dry residue, %</td>
<td>–0.97</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>–0.73</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>–0.84</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>–0.96</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>–0.95</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>–0.91</td>
</tr>
<tr>
<td>Na⁺ + K⁺</td>
<td>–0.89</td>
</tr>
<tr>
<td>% Total variance</td>
<td>47.01</td>
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Table 2
General linear model of effect of technogenic edaphotop type, in combination with time and depth of sampling on the PC1 value ($R^2 = 0.92$)

<table>
<thead>
<tr>
<th>Predictors</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean Sum of squares</th>
<th>F-ratio</th>
<th>p-level</th>
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<td>Intercepts</td>
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<td>739.94</td>
<td>1370.08</td>
<td>0.00</td>
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<tr>
<td>Type</td>
<td>396.11</td>
<td>3</td>
<td>132.04</td>
<td>244.48</td>
<td>0.00</td>
</tr>
<tr>
<td>Time</td>
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<td>2</td>
<td>4.40</td>
<td>8.14</td>
<td>0.00</td>
</tr>
<tr>
<td>Depth</td>
<td>908.05</td>
<td>1</td>
<td>908.05</td>
<td>1681.37</td>
<td>0.00</td>
</tr>
<tr>
<td>Type*Time</td>
<td>7.41</td>
<td>6</td>
<td>1.23</td>
<td>2.29</td>
<td>0.04</td>
</tr>
<tr>
<td>Type*Depth</td>
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<td>3</td>
<td>13.59</td>
<td>25.16</td>
<td>0.00</td>
</tr>
<tr>
<td>Time*Depth</td>
<td>15.01</td>
<td>2</td>
<td>7.50</td>
<td>13.90</td>
<td>0.00</td>
</tr>
<tr>
<td>Type<em>Time</em>Depth</td>
<td>12.08</td>
<td>6</td>
<td>2.01</td>
<td>3.73</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>191.18</td>
<td>354</td>
<td>0.54</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 3
Main elements of variations of PCs 1 – 3
the lowest level of mineralization is more representative for variants 3 and 4 (i.e. MR + 50LLL + 30BS and MR + 50LLL + 50BS respectively) (Figure 4).

**Fig. 4**
Variation of PC1 depending on the type of technogenic edaphotop

The profile distribution analysis of the PC1 values indicates the specificity of this feature depending on the type of technogenic edaphotop. Moreover, this index shows a certain invariance over time (Figure 5).

Thus, PC1 reflects the constitutional features of the profile distribution of the technogenic edaphotops properties. The general level of mineralization is sufficiently conservative feature, and its profile distribution is quite stably invariant over time. Similar behavior is observed for the distribution of general patterns of the water-soluble ions and pH.

The principal component 2 (PC2) describes 10.73% of the total variability. It positively correlates with the concentration of the hydrocarbonate ion and negatively with the concentration of the sulfate, magnesium and monovalent ions. It should be noted that the variation of these ions occurs under conditions of stable pH and stable mineralization of the soil solution (Table 3).

**Fig. 5**
Profile distribution of PC1 values depending on the type of technogenic edaphotop in different periods of the study
Table 3
General linear model of effects of technogenic edaphotop type in combination with time and depth of sampling on the PC2 value (R² = 0.99)

<table>
<thead>
<tr>
<th>Predictors</th>
<th>Sum of squares</th>
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<th>Mean Sum of squares</th>
<th>F-ratio</th>
<th>p-level</th>
</tr>
</thead>
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<td>Intercept</td>
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<td>1</td>
<td>3.35</td>
<td>243.93</td>
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<tr>
<td>Type</td>
<td>3.55</td>
<td>3</td>
<td>1.18</td>
<td>86.27</td>
<td>0.00</td>
</tr>
<tr>
<td>Time</td>
<td>148.11</td>
<td>2</td>
<td>74.06</td>
<td>539.96</td>
<td>0.00</td>
</tr>
<tr>
<td>Depth</td>
<td>4.17</td>
<td>1</td>
<td>4.17</td>
<td>304.11</td>
<td>0.00</td>
</tr>
<tr>
<td>Type*Time</td>
<td>0.28</td>
<td>6</td>
<td>0.05</td>
<td>3.38</td>
<td>0.00</td>
</tr>
<tr>
<td>Type*Depth</td>
<td>0.33</td>
<td>3</td>
<td>0.11</td>
<td>7.99</td>
<td>0.00</td>
</tr>
<tr>
<td>Time*Depth</td>
<td>1.30</td>
<td>2</td>
<td>0.65</td>
<td>47.29</td>
<td>0.00</td>
</tr>
<tr>
<td>Type<em>Time</em>Depth</td>
<td>0.25</td>
<td>6</td>
<td>0.04</td>
<td>3.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Error</td>
<td>4.86</td>
<td>354</td>
<td>0.01</td>
<td></td>
<td>–</td>
</tr>
</tbody>
</table>

External factors provide an explanation for 99.14% of the PC2 variation. All investigated predictors are statistically reliable, and the highest PC2 variation value is established for “time” (94.9%). As shown in Figure 6 the PC2 value increases over time. The regression coefficient of depth has a negative sign (–0.10±0.01), which indicates that the influence of the PC2 decreases with depth.

Fig. 6
Variation in PC2 over time

The peculiarities of the profile distribution variation of the PC2 values reflect the biogenic nature of this component, the value of which accumulates in time and attenuates with the depth of the soil layer (Figure 7). Thus, the PC2 reflects the trend of an increasing content of hydrocarbonates and a reduction of sulfates, magnesium, potassium and sodium in the aqueous solution of soil extractions. This trend can be linked to the effects of the biogenic factor. Probably, the increase in the content of hydrocarbonates may occur due to the metabolic activity of the microbiota, which leads to a certain desalinization of the soil profile. Reclamation process usually requires huge amounts of water to provide desalinization from soil profile. It is imperative to know that leaching is not required until soil salinity exceeds the salt tolerance threshold of the crop (Gharaibeh et al. 2012). Musslewhite et al (2006) concluded that all weathered minesoils are expected to have little or no reduction in permeability based on established threshold EC and SAR relationship. Cover-soil (e.g., topsoil) enhances remediation through physical and chemical buffering between sodic root-zone material and the reconstructed soil surface.

The principal component 3 (PC3) accounts for 10.39% of the total variability. It correlates positively with the calcium content, and negatively with the pH value, as well as the content of hydrocarbonates, chlorines and monovalent ions. The general linear model of influence of the type of technogenic edaphotop, time, depth of sampling and their combination, explains 98% of the PC3 variability (Table 4).
Fig. 7
Profile distribution of PC2 values depending on the type of technogenic edaphotop in different periods of the study

Thus, the PC2 reflects the trend of an increasing content of hydrocarbonates and a reduction of sulfates, magnesium, potassium and sodium in the aqueous solution of soil extractions. This trend can be linked to the effects of the biogenic factor. Probably, the increase in the content of hydrocarbonates may occur due to the metabolic activity of the microbiota, which leads to a certain desalinization of the soil profile. Reclamation process usually requires huge amounts of water to provide desalinization from soil profile. It is imperative to know that leaching is not required until soil salinity exceeds the salt tolerance threshold of the crop (Gharaibeh et al. 2012). Musslewhite et al (2006) concluded that all weathered minesoils are expected to have little or no reduction in permeability based on established threshold EC and SAR relationship. Coversoil (e.g., topsoil) enhances remediation through physical and chemical buffering between sodic root-zone material and the reconstructed soil surface.

Table 4
General linear model of effect of technogenic edaphotop type in combination with time and depth of sampling on the PC3 value ($R^2 = 0.98$)

<table>
<thead>
<tr>
<th>Predictors</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean Sum of squares</th>
<th>F-ratio</th>
<th>p-level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>1.42</td>
<td>1</td>
<td>1.42</td>
<td>38.95</td>
<td>0.00</td>
</tr>
<tr>
<td>Type</td>
<td>74.60</td>
<td>3</td>
<td>24.87</td>
<td>683.24</td>
<td>0.00</td>
</tr>
<tr>
<td>Time</td>
<td>6.80</td>
<td>2</td>
<td>3.40</td>
<td>93.40</td>
<td>0.00</td>
</tr>
<tr>
<td>Depth</td>
<td>0.49</td>
<td>1</td>
<td>0.49</td>
<td>13.47</td>
<td>0.00</td>
</tr>
<tr>
<td>Type*Time</td>
<td>1.09</td>
<td>6</td>
<td>0.18</td>
<td>5.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Type*Depth</td>
<td>8.07</td>
<td>3</td>
<td>2.69</td>
<td>73.87</td>
<td>0.00</td>
</tr>
<tr>
<td>Time*Depth</td>
<td>2.51</td>
<td>2</td>
<td>1.26</td>
<td>34.55</td>
<td>0.00</td>
</tr>
<tr>
<td>Type<em>Time</em>Depth</td>
<td>1.67</td>
<td>6</td>
<td>0.28</td>
<td>7.65</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>12.88</td>
<td>354</td>
<td>0.04</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
The most important factor in the PC3 variation is the type of technogenic edaphotop (i.e. 88.1% of the PC3 variation depends on this predictor). The PC3 indicates a relatively high content of hydrocarbonates in the technogenic edaphotop with a layer of black soil 50 cm (variant 2), while in other types the higher content of hydrocarbonates, chlorines and monovalent ions is observed at a higher pH. In time, the PC3 values increase harmonically for the technogenic edaphotop with a layer of black soil 50 cm. However, for other types the variation with respect to time is not harmonic (Figure 8).

The PC3 indicates the specific features of the profile salts distribution in the variant 2 which were formed at the moment of laying the technogenic edaphotops and the processes of salts redistribution in this variant during the study period (Figure 9).

Variant 2 is characterized by a higher content of calcium ions and lower values of pH and HCO$_3^-$, Cl$^-$ and Na$^+$ K$^+$ concentrations. During the overall time of observation, the aligned distribution of the appointed indices tends...
towards those indicators, which are typical for other types of technogenic edaphotops mainly in the topsoil. The observed tendency of acquired characteristics is similar to other types of reclamation; this is in contrast to processes in the deeper layers where their dynamics slow down in the top soil of the profile in variant 2. However, the appointed features retain their stability over time.

Conclusions

It is established that the parameters of the layer-by-layer reactions variations, and the ion composition of the aqueous extract along the reclaimed profiles of various models of technogenic edaphotop, gradually acquire a stable-equilibrium state of mineralization, both spatially and over time. This tendency reflects the characteristics of the zonal soils. It should be noted that the alkaline barrier is the main factor in both pH changes and in the surface salinization of reclaimed lands. The absence of a protective shielding layer of loess-like loam, for example, leads to rapid acidification of the soil solution due to the processes of chemical weathering of rocks at layers in contact with the mine dump.

References


Shengyin Wang, Xiaoyan Ren, Bingru Huang, Ge Wang, Peng Zhou and Yuan An (2016). Aluminium-induced Reduction of Plant Growth in Alfalfa (Medicago sativa) is Mediated by Interrupting Auxin Transport and Accumulation in Roots. Scientific Reports, 6: 30079. https://doi.org/10.1038/srep30079


State Standard 26423-85 “Soils. Methods for determination of specific electric conductivity, pH and solid residue of water extract”


Vandenyje tirpių druskų vertikalios migracijos tendencijos analizė iš sąvartynų Ukrainoje

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Siekiant išvystyti optimalią sąvartynų utilizavimo schemą, buvo ištirtas sąvartynų su skirtingais juo-do dirvožemio masės sluoksniais, tiek su ir be lakštinio priemolio apsauginio sluoksnio. Pagrindinės komponentų analizės buvo atliktos, siekiant atskleisti dugninės aukštumos migracijos į atsinaujinančių anglies paviršių dėsningumus. Fizinių ir cheminių duomenų sluoksnio pokyčiai dirvožemio vandens ekstraktuose (būtent, pH, bendras druskingumas ir bikarbonatų, chloridų, sulfatų, kalcio, magnio, natrio ir kalio koncentracijos), gautų 1987 m. 2003 ir 2016 m. kartu su įvairiais technogeninio edaphoto modelio regeneruotais profiliais, palaipsniui įgyja stabilios pusiausvyros mineralizacijos būklė. Šarminis barjeras yra pagrindinis veiksny, lemiantis pH pokyčius ir regeneruotos žemės profilių šalinimą.

Raktiniai žodžiai: sąvartynai, vandenyje tirpių druskų migracija, dirvožemis.