The aim of this article is to study the geochemical characteristics of halogenic technosols within oil and gas fields. The composition of both associated waters (AWs) types, from the Ignatovskoe oil and gas-condensate field and the Svyrdivskoe gas-condensate field, was determined in the course of the study. Based on the composition, both AWs types refer to chloro-sodium brines but they differ significantly in salinity and content of particular components. Two types of technosols have been investigated - chernozem ordinary and dark grey. The AWs entry into soils has caused formation of specific technogenic alkali soils with different degree of salinization at both of the sites under study. The increased solution concentrations of ions brought in with the saline waters are responsible for selective accumulation of mobile fractions of separate alkaline and alkaline-earth metals in the soils. It has been found that Na”K” has the highest concentration ratios in the profile of both the soil types concerned. Accumulation has been observed in the 30-60 cm layer. With an increase in the distance to the focus, concentration ratios decrease. Li+ has accumulated primarily in the arable layer of technosoils of dark grey soil. Destruction of the soil carbonates in response to acid waters has caused Rb+ and Cs+ leaching from the soil profile. Based on the ascending geochemical mobility, the triad of alkaline-earth elements in the impact focus is as follows: Sr→Ca→Mg and Mg→Ca→Sr for the periphery.

1. Introduction

Associated waters (AWs) produced when extracting oil and gas comprises the largest byproduct stream in terms of volume. They are one of primary environmental pollutants in oil and gas fields resulting from emergencies, pipeline leakages, repair operations and due to some other reasons [1]. The majority of papers dealing with the environmental impact of AWs focus on the impact on groundwater [2-5] and surface water quality [4, 6, 7]; however, there is much less information available as regards the impact of such liquids on soils [6]. AWs have unique polycomponent continuously changing composition, high geochemical reactivity and toxicity. They include oil products, complex salt mixture, radionuclides and heavy metals. Technogenic halos varying in chemical composition and intensity are formed at the AWs emergency spill sites. The peculiar salt composition of AWs rapidly changes the ion ratio in the original soil solutions and results in an increase in concentration of toxic salts which defines salinization, triggers respective transformations in soil’s absorbing complex and leads to formation of technogenic types of alkaline and sodic soils. The technogenic halogenesis is the most typical soil transformation process occurring within oil and gas fields as a result of emergency AWs spills [1]. AWs contain heavy metals the concentration of which varies depending on geological age [1, 2, 8]. Differences in the composition of AWs result in some additional chemical elements introduced into soils and/or encourage an increase in the content of chemical elements occurring in micro-quantities in natural, non-polluted soils or being completely uncharacteristic of such soils. The most frequently studied chemical elements detected in the AW-affected soils include Ba, Sr, Zn, Cd, Cr, Cu, Pb, Hg, Ni and Ag; however,
the content of Li⁺, Rb⁺ and Cs⁺ has been virtually unstudied [1-10, 12-14].

The issue of soil geochemical composition transformation has become particularly acute in the development zone of chernozem ordinary soils to which a significant fraction of Ukraine’s oil and gas production sites is confined. The losses caused by disusing the soil bodies affected by emergency AWs spills between 1980 and 2017 were quite significant.

The objective - is to study the geochemical characteristics of halogenic technosoils within oil and gas fields.

2. Materials and methods

The soils were studied at two sites being emergency AWs spill locations. The layout of key sites was determined based on visual changes in colour and structure of the soil cover at the emergency spill locations. Control plots were selected in the near-by fields located beyond the impact zone.

Site # 1 is located on a flat plot within the Ignatyske oil and gas-condensate field in Poltava region. The emergency spill gave rise to the formation of a salinization located immediately above the formation water pipeline and taking the form of an elongated circle with a radius of up to 2.5 m. In an attempt to eliminate consequences of the spill, the halo was covered with a layer of control soil, however, due to the action of capillary lift and vertical salt transfer, there were white salt efflorescence spots visually observed on the soil surface in the axial part of the halo at the time of the research (May-June 2016). The soils under study are chernozem ordinary on deluvial loams.

Site # 2 is located in trans-accumulative landscape environment of the Svyrydivske field in the north of Poltava region. The salinization formed as a result of air dissemination of emergency water and gas blow-out from the wellhead during a workover. The salinization has a more complex shape due to peculiarities of the relief and stretches out in the form of linear flows downslope the adjacent hollow. The soil is of dark grey leached sandy loam type on glacial deposits.

Mixed soil samples were collected from the 0-30 and 30-60 cm soil layers at each site under study in compliance with DSTU (National Standard of Ukraine) 4287:2004. The soil samples were transported, dried and prepared for physical and chemical tests in compliance with DSTU ISO 11464. The salt composition of the soil water extract was determined in accordance to DSTU 7908, DSTU 7909, DSTU 7943 and DSTU 8346 in the certified laboratory of the National Scientific Centre “Institute for Soil Science and Agrochemistry Research named after O.N. Sokolovsky”. Chemical composition of the soil and AWs samples was determined by the State Scientific Institution “Scientific and Technical Complex “Institutes for Single Crystals” of the National Academy of Science of Ukraine. Emission flame photometry was used to determine the content of Li, Na, K, Cs, Rb and Sr, while atomic absorption was used to determine the content of Mg and Ca. Measurements were taken using spectrometers iCE 3500 and Saturn, and analytical lines Li, Na, K, Cs, Rb, Mg, Ca and Sr – 670.8; 589.0; 766.5; 852.1; 780.0; 285.2; 422.6 and 460.7 nm respectively. The flame gas mixtures used in the process were air-acetylene and propane-butane-dinitrogen oxide. Calcium absorption was measured in the flame of propane-butane-dinitrogen oxide only. Optimal gas and oxidizer rates, as well as photometrically measured flame ranges were selected for each element. Filtrates of water and acid extracts from the soil samples prepared in accordance with DSTU 7944 and DSTU 7945 were used for analysis. The obtained data was processed statistically following the conventional procedures. Based on the chemical composition determination results, concentration ratios (Kc) of chemical elements in technosoils as compared with the control soil [12] and log concentration ratios (log 10 Kc) were calculated.

3. Results

Once salt waters enter soil, a primary salinization halo is formed. Characteristics of this halo (the degree of soil salinization and the area occupied) depend on the scope and rate of AWs emission, water salinity and ion composition, as well as on the landscape features. The shape and size of the primary halo of soils polluted on surface depend to a large extent on the relief of a spill site [10, 11, 13, 14]. The studies have established that technogenic halogenesis in different parts of a salinization halo is characterized by quite a distinctive peculiarity [6, 7, 13, 14]. The following three geochemical zones can be distinguished within a salinization halo: 1) salinization focus, 2) downslope landscapes directly adjacent to the salinization focus
(dispersion area) and 3) transaccumulative and accumulative landscapes in the path of technogenic flows migration. In terms of soil properties and dynamics, each of the above zones is relatively homogenous with rather clear boundaries which, however, may shift at different age stages [13].

The chemical composition of both AWs types, from the Ignativske oil and gas condensate field (geological period Devon-Carboniferous (DC)) and the Svrydivske gas condensate field (geological period Carboniferous (C)), was determined in the course of the study. Based on the composition, both AWs types refer to chloro-sodium brines but they differ significantly in salinity and content of particular components (Table 1). The associated waters of oil accumulations are marked by significantly higher salinity and higher content of microcomponents (Sr²⁺, Li⁺, Cs⁺ and Rb⁺).

Table 1
Chemical composition of associated waters (AWs)

| AWs type                        | pH   | HCO₃⁻ | Cl⁻ | SO₄²⁻ | Ca²⁺ | Mg²⁺ | Na⁺ | K⁺ | Sr²⁺ | Li⁺ | Cs⁺ | Rb⁺ | dry residue |
|---------------------------------|------|-------|-----|-------|------|------|-----|----|------|-----|-----|-----|------------|
| AWs of the oil and gas condensate field (DC) | 5.2  | 0.16  | 95  | 0.002 | 13.0 | 1.66 | 43.0| 0.54| 0.15  | 0.0011| 0.0001| 0.00016| 153.51     |
| AWs of the gas condensate field (C)           | 5.5  | 0.48  | 24.8| 0.02  | 2.3  | 0.95 | 11.5| 0.51| 0.0125| 0.00035| 0.00017| 0.00007| 40.57      |

The study of makeup of the control soil water solution from both sites under study has revealed dominancy of calcium bicarbonate, the soils are non-saline, with the content of toxic salts equaling 0.01% (Table 2).

Table 2
Salt composition of the soil water extracts

| Site #                                                       | Depth, cm | pH | Content of anions and cations, mmole/100 g |
|--------------------------------------------------------------|-----------|----|--------------------------------------|
| Technosoils of chernozem ordinary (Site # 1) Impact focus     | 0-30      | 8.7 | HCO₃⁻ 0.63, Cl⁻ 6.47, SO₄²⁻ 0.01, Ca²⁺ 3.01, Mg²⁺ 0.64, Na⁺ 0.10, K⁺ 5.82 |
|                                                             | 30-60     | 8.3 | HCO₃⁻ 0.30, Cl⁻ 30.14, SO₄²⁻ 2.16, Ca²⁺ 3.40, Mg²⁺ 0.86, Na⁺ 27.83 |
| Technosoils of chernozem ordinary (Site # 1) Dispersion area | 30-60     | 9.0 | HCO₃⁻ 0.50, Cl⁻ 6.01, SO₄²⁻ 0.57, Ca²⁺ 1.41, Mg²⁺ 0.41, Na⁺ 6.97, K⁺ 1.15 |
| Chernozem ordinary, (Site # 1) control                       | 30-60     | 8.7 | HCO₃⁻ 0.11, Cl⁻ 8.30, SO₄²⁻ 0.50, Ca²⁺ 0.18, Mg²⁺ 0.18, Na⁺ 0.01, K⁺ 0.05 |
| Technosoils of dark grey soils (Site # 2) Impact focus       | 0-30      | 7.4 | HCO₃⁻ 0.50, Cl⁻ 7.45, SO₄²⁻ 0.05, Ca²⁺ 4.65, Mg²⁺ 1.43, Na⁺ 1.46, K⁺ 1.45 |
|                                                             | 30-60     | 7.95| HCO₃⁻ 0.20, Cl⁻ 3.95, SO₄²⁻ 0.58, Ca²⁺ 7.05, Mg²⁺ 2.14, Na⁺ 0.75, K⁺ 25.22 |
| Technosoils of dark grey soils (Site # 2) Dispersion area    | 30-60     | 9.2 | HCO₃⁻ 0.08, Cl⁻ 9.20, SO₄²⁻ 0.58, Ca²⁺ 9.15, Mg²⁺ 1.53, Na⁺ 0.70, K⁺ 8.48 |
| Dark grey soils, (Site # 2) control                          | 0-30      | 6.5 | HCO₃⁻ 0.08, Cl⁻ 6.50, SO₄²⁻ 0.04, Ca²⁺ 0.08, Mg²⁺ 0.07, Na⁺ 0.07, K⁺ 0.04 |
|                                                             | 30-60     | 6.8 | HCO₃⁻ 0.04, Cl⁻ 6.80, SO₄²⁻ 0.09, Ca²⁺ 0.15, Mg²⁺ 0.05, Na⁺ 0.10, K⁺ 0.02 |

When salt waters enter clean soils, soil solutions are the first to undergo changes. There is an increase in the content of all cations and anions, with a rapid increase in the role of sodium chloride especially in the spill focus. Associated waters with acid pH reaction cause destruction of CaCO₃, as a result of which the content of bicarbonate-ions in soil solution increases and pH rises toward alkali.

The AWs entry into soils has caused formation of specific technogenic alkali soils with different degree of salinization at both of the sites under study. The salinization degree rises based on both total salt and toxic salt amount.
The technosols of chernozem ordinary in the focus of spill of AW with the salinity of 153.5 g/dm$^3$ (Site #1), even after the spill halo was covered with a layer of non-saline control soil, due to the vertical salt transfer under action of capillary lift, have demonstrated a 40-fold increase in the content of toxic salts in the 0-30 cm layer and a 200-fold increase in the 30-60 cm soil layer as compared with the control soils. The content of toxic salts decreases 3 to 3.5 times in the dispersion area and equals 0.08 and 0.12 % respectively (Fig. 1). In technosols of dark grey soils (Site #2) the ingress of AWs, with the salinity of 40.5 mg/dm$^3$, has resulted in a 100 times increase in the total toxic salts in the 0-30 cm soil layer and a 180 times increase in the 30-60 cm one as compared with the control soils. There is also a 3 to 3.5 times decrease in the content of toxic salts in the technosols profile farther from the spill focus (Fig. 2).

In both cases under study, it has been noted that there is a prevalence of sodium chlorides in the cation-and-anion composition of the technosols water extract (Table 2). Based on the salt concentration distribution over the profile, there is a clear differentiation with salts tending to primarily accumulate in the 30-60 cm soil layer. Based on the salt amount, the soils under study are highly salinized. The chemical composition changes in the AW-affected soils. The chemical elements under study belong to Groups 1 and 2 of the Periodic Table. Their natural occurrence varies widely and there are quite different compound forms. The elements commonly occurring in soils in the greatest amounts are Na$^+$, Mg$^{2+}$, K$^+$ and Ca$^{2+}$. The content of other elements under study varies in micro-quantities [15]. The soils under study are not an exception with the content of chemical elements being in line with the general trend. The chernozem ordinary are richer in chemical elements (Table 3).

**Table 3**

| Soil type            | Depth, cm | Na$^+$ | K$^+$ | Li$^+$ | Rb$^+$ | Cs$^+$ | Ca$^{2+}$ | Mg$^{2+}$ | Sr$^{2+}$ |
|----------------------|-----------|--------|-------|--------|--------|--------|-----------|-----------|----------|
|                      |           |        |       |        |        |        |           |           |          |
| Chernozem ordinary   | 0-30      | 36.0   | 13.0  | 0.020  | 0.05   | 0.17   | 125.0     | 15.0      | 0.85     |
|                      | 30-60     | 20.0   | 3.0   | 0.025  | 0.40   | 0.19   | 100.0     | 15.0      | 0.50     |
| Dark grey soil       | 0-30      | 17.0   | 7.0   | 0.015  | 0.10   | 0.50   | 75.0      | 12.0      | 0.23     |
|                      | 30-60     | 15.0   | 7.0   | 0.015  | 0.11   | 0.15   | 125.0     | 19.0      | 0.55     |
The increased solution concentrations of ions brought in with the saline waters are responsible for selective accumulation of mobile fractions of separate alkaline and alkaline-earth metals in the soils. Most of the elements under study at both sites accumulate in the 30-60 cm soil layer; however, there are some differences in their distribution.

It has been found that Na$^+$ has the highest concentration ratios in the profile of both the soil types concerned. Sodium is an active migrant in any geochemical environment; it forms readily soluble salts and can accumulate in soils in significant amounts [12]. Sodium accumulation has been observed in the 30-60 cm layer. Within the spill focus, the Na$^+$ concentration ratio rose with depth from 45 to 400, by more than 6 times, in the profile of technosols of chernozem ordinary at Site # 1, and it rose from 6.3 to 23.5, a 3.5 times increase, in the dispersion area (Fig. 3A). The technosol profile of dark grey soils at Site # 2 demonstrated similar patterns but the concentration ratios were somewhat lower due to a lower salinity of AWs (Fig. 3B). With an increase in the distance to the focus, sodium concentration ratios decrease by 5 times in the arable soil layer and by 7 times in the subsurface layer.

There is an intensive accumulation of K$^+$ primarily in subsurface layer of technosols of chernozem ordinary in the spill focus at Site # 1. The K$^+$ concentration ratio in the spill focus area increased by more than 6 times (from 7.7 to 300) when measured at a deeper point, and it increased 1.5 times in the dispersion area (from 7.7 to 11.7) (Fig. 3A). In contrast, the dark grey soils at Site # 2 showed that K$^+$ accumulates primarily in the arable soil layer in the spill focus. However, there was minor variance between the concentration ratios measured in the arable layers of soil types both from the spill focus and dispersion area.

The content of Li$^+$ Rb$^+$ Cs$^+$ in soils has been underexplored and thus, is of a particular interest. Li$^+$ is marked by weak mobility in any environment and accumulates primarily on an evaporation geochemical barrier [12]. This explains why it has accumulated primarily in the arable layer of technosols of dark grey soil at Site # 2, both in the focus and area of dispersion of chemical elements after drying of the soil. It is likely that a similar trend was recorded for the chernozem ordinary (Site # 1) prior to covering the AWs spill area with a layer of control soil. However, under the action of capillary lifting, the content of Li$^+$, just as of the other chemical elements under study, has gradually increased in the 0-30 cm layer of technosolsof chernozem ordinary.

A common characteristic of Rb$^+$ and Cs$^+$ is their ability to migrate in acid environment and accumulate on sorption geochemical barrier. The AWs under study did not have high content of the given chemical elements as compared with the lithosphere clarke. However, destruction of the soil carbonates in response to acid waters has caused Rb$^+$ and Cs$^+$ leaching from the soil profile. The technosols under study contain Rb$^+$ mostly in the arable layer of the dispersion area.
A minor accumulation of Cs⁺ is noted only in the AWs impact focus in both soil types under study. Ca²⁺, Mg²⁺ and Sr²⁺ of Group 2, being similar in geochemical behaviour, differ in mobility. Strontium is the most active migrant leaving behind both calcium and magnesium in terms of geochemical mobility. As a result, under the conditions of steppe landscapes strontium can reach abnormal concentration in salinization halo focus soils only. With an increase in distance from the halo focus to periphery, the content of this element decreases drastically [12]. The researches have established that the Sr²⁺ concentration ratio equaled 24 for technosoils of chernozem ordinary in the arable soil layer in the spill focus and 5 for technosoils of dark grey soil, and it decreased by 5-10 times with an increase in distance to the focus. Strontium was noted to accumulate in the 30-60 cm layer (Fig. 4). With an increase in depth the Sr²⁺ concentration ratio increased by 17 times (from 5.1 to 90) in the profile of common black technosol at Site # 1 in the spill focus and it increased by 7 times (from 24 to 160) in that of technosoils of dark grey soil at Site # 2.

Under the conditions of technogenic halogenesis, calcium appears to be similar to strontium and it has also accumulated rather intensively in the soil water solutions from the spill focus [12, 13]. Magnesium is characterised by slightly lower mobility but it also shows a trend to higher accumulation in the spill focus. The supergene migration of magnesium is caused by good solubility of its sulfates and chlorides to a large extent; however, as part of such compounds Mg²⁺ can form temporary concentrations on an evaporation geochemical barrier in the soil humus horizon [12]. Based on the ascending geochemical mobility, the triad of alkaline-earth elements in the impact focus is as follows: Sr→Ca→Mg. The triad is Mg – Ca – Sr for the periphery of the Site # 1 halo and it is Sr–Mg – Ca for that of Site # 2. The Ca/Sr ratio equals 0.2-0.4 in the spill focus and 0.9 in the periphery.

4. Conclusions

The study completed has established that the entry of AWs into soils caused formation of specific technogenic alkaline soils with varying salinization degrees at both sites under study, and the salt accumulation is observed mainly in the 30-60 cm soil layer. There is a differentiation in the accumulation and enleaching of alkaline-earth and alkaline metals depending on the AWs properties, ways of the AWs entry into soil and distribution by technogenic zone. The results obtained may be used to assess the impact of emergency spills of associated waters on soils, with the chernozem ordinary and dark grey soil being of frequent occurrence in Ukraine.
Геохімічні особливості галогенних техноземів територій нафто-газових родовищ

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Мета роботи – дослідити геохімічні особливості галогенних техноземів територій нафтогазових родовищ.

Визначено хімічний склад двох видів супутніх пластових вод (СПВ) Ігнатівського нафтогазоконденсатного родовища нафто-газових родовищ. За складом обидва типи СПВ є хлоридно–натрійові.

Ключові слова: галогенни техноземи; фононі ґрунту; супутні пластові води; СПВ; геохімічний склад; концентрації.