

# The effect of pollutants on the content of nutrients in soil

## Wpływ zanieczyszczeń na zawartość składników odżywczych w glebie

Arsen V. Pukish<sup>1</sup>, Olha I. Sydorenko<sup>1</sup>, Oleh M. Mandryk<sup>2</sup>, Yaroslava S. Korobeinykova<sup>2</sup>, Oleh M. Tuts<sup>2</sup>

<sup>1</sup> PJSC “Ukrnafta”

<sup>2</sup> Ivano-Frankivsk National Technical University of Oil and Gas

**ABSTRACT:** Soil degradation occurs as a result of the ingress and accumulation of excessive amount of pollutants in the soil. The article presents the results of theoretical and experimental studies of the complex effect of soil contamination (concentration of petroleum products, toxic salts, dense residue, sodium ions, sulfate ions, magnesium ions, calcium, chloride ions, bicarbonate ions) on the content of nutrients (alkaline hydrolyzed nitrogen, phosphorus, potassium, humus). A detailed analysis of scientific papers has been carried out, based on which the main scientific tasks solved in the article have been formulated. It has been established that soil-salt processes are insufficiently studied and are the object of scientific research in recent years. At the first stage of research, sampling was carried out and the content of nutrients and pollutants in the soil was determined. Determination of element concentrations was performed by collecting soil samples and their subsequent laboratory testing. At the second stage, a correlation-regression analysis of the obtained data was performed and multiple linear regressions were established. The interaction of substances in the soil was determined by analyzing the obtained multiple linear regressions. Two types of soils were studied: with chloride and with sulfate type of salinization. For soils with chloride type of salinity, dependences have been established for the content of humus, alkaline nitrogen and potassium, while in case of phosphorus multiple linear regression does not exist. For soils with sulfate type of salinization, multiple linear regression dependences of concentrations of alkaline nitrogen, phosphorus, potassium have been determined. It is established that the complex influence of the studied elements is decisive. No regression dependence was found for the humus content, which indicates that the concentration of the studied elements has almost no effect on the humus content in the soil. Comparison of the obtained multiple linear regressions with the results of laboratory studies showed a good correlation between these data series. The obtained regularities of pollutant and nutrient interactions in soils are expected in future to enable creation of scientific bases for development of new methods of desalination of soils polluted by formation waters as well as for planning effective reclamation actions.

**Key words:** soil, contamination, salinity, humus, petroleum products, toxic salts, phosphorus, nitrogen, regression.

**STRESZCZENIE:** W wyniku wnikania i gromadzenia się w glebie nadmiernych ilości zanieczyszczeń następuje degradacja gleby. W artykule przedstawiono wyniki badań teoretycznych i eksperymentalnych złożonego wpływu zanieczyszczenia gleby (stężenie produktów naftowych, toksycznych soli, gęstego osadu, siarczanów, jonów sodu, magnezu, wapnia, chlorków, wodorowęglanów), na zawartość składników pokarmowych (hydrolizowanego alkalicznie azotu, fosforu, potasu, humusu). Przeprowadzona została szczegółowa analiza prac naukowych, na podstawie której sformułowano główne zadania badawcze rozwiązane w artykule. Stwierdzono, że procesy glebowo-solne zbadane są w stopniu niedostatecznym i stanowią one przedmiot badań naukowych w ostatnich latach. W pierwszym etapie badań pobrano próbki i wyznaczono zawartość składników pokarmowych i zanieczyszczeń w glebie. Wyznaczenia stężeń pierwiastków dokonano poprzez pobranie próbek gleb i ich późniejsze badania laboratoryjne. W drugim etapie wykonano analizę korelacyjno-regresyjną uzyskanych danych i ustalono wielokrotne regresje liniowe. Oddziaływanie substancji w glebie określono poprzez analizę otrzymanych wielokrotnych regresji liniowych. Badano dwa rodzaje gleb: o zasoleniu chlorkowym i siarczanowym. Dla gleb o zasoleniu chlorkowym ustalono zależności w odniesieniu do zawartości humusu, azotu hydrolizowanego alkalicznie i potasu, natomiast dla fosforu regresja liniowa wielokrotna nie wystąpiła. Dla gleb o zasoleniu siarczanowym wyznaczono zależności wielokrotnej regresji liniowej stężeń azotu alkalicznego, fosforu, potasu. Ustalono, że decydujące znaczenie ma kompleksowe oddziaływanie badanych pierwiastków. Dla zawartości humusu nie stwierdzono zależności regresji, co wskazuje, że stężenie badanych pierwiastków prawie nie wpływa na zawartość humusu w glebie. Porównanie uzyskanych wielokrotnych regresji liniowych z wynikami badań laboratoryjnych wykazało dobrą korelację między tymi seriami danych. Uzyskane prawidłowości oddziaływania zanieczyszczeń i składników pokarmowych w glebach pozwolą w przyszłości stworzyć naukowe podstawy rozwoju nowych metod odsalania gleb zanieczyszczonych wodami złożowymi, jak również planować efektywne prowadzenie prac rekultywacyjnych.

**Słowa kluczowe:** gleba, zanieczyszczenia, zasolenie, humus, produkty naftowe, sole toksyczne, fosfor, azot, regresja.

Corresponding author: O.M. Mandryk, e-mail: [o.mandryk@nung.edu.ua](mailto:o.mandryk@nung.edu.ua)

Article contributed to the Editor: 07.06.2022. Approved for publication: 29.03.2023.

## Introduction

The entry of pollutants into the soil causes deterioration of its physical and chemical characteristics. The soil properties have a significant effect on its fertility. Therefore, the relevant issue is to study the peculiarities of pollutants in the soil and their interaction.

## Literature review

In the study of Nouri et al. (2017), a thorough analysis of the effect of soil salinity on soil properties was performed. According to the authors, the increased concentration of salts has a negative effect on soil quality. In particular, increased concentrations of sodium ion can delimit and expand glial particles, which leads to swelling and dispersion of the soil. The blockage of soil pores and a decrease in its permeability takes place – this complicates the movement of water and air in the soil. Complications of infiltration processes do not provide adequate access of water to plant roots. The structure of the soil is destroyed.

Rhykerd et al. (1995) found that accidental spills during oil production and refining are accompanied by both oil and salt contamination of soils. Increased soil mineralization has a negative effect on the biodegradation of oil. Extraction of salts from oil-contaminated soil helps to accelerate soil regeneration.

According to Araratyan et al. (2015), a good correlation was found between the nitrogen and carbon content in mountain-meadow and meadow-steppe soils (correlation coefficient of 0.76). The authors explain this peculiarity by similar physical and chemical properties of these elements and their location in the D.I. Mendeleev's periodic table. In addition, the authors note a significant decrease of all nutrients in the soil (nitrogen, potassium, humus (carbon)), except phosphorus, over the past 30 years.

Pitchel et al. (2016) indicate that reservoir water of oil fields contains organic and inorganic components. Such components include dissolved and dispersed oil, salts, heavy metals, dissolved gases, microorganisms and dissolved oxygen. At the same time, scientists have found that the addition of simple components is often successful for solving problems with soil salinity and salinization. Both inorganic additives (e.g.,  $\text{CaSO}_4$ ) and organic materials (animal manure) were effective. The most commonly used dry additives are gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ). Elemental sulfur and aluminum sulfate can be added to lower the pH.

Pathak et al. (2012) prove that reservoir water spills can affect plant growth by changing soil properties. In the case of

salt water entering the soil, the structure of the pores in the soil changes, and their compaction occurs. Therefore, the access of water and air to the root system of plants is restricted. An excess of sodium ions in soils causes dispersion of clays, which limits the availability of nutrients such as iron, manganese, calcium and magnesium for plants. An impermeable film may be formed on the surface of the soil.

In the work of Echchelh et al. (2018), it is stated that formation water contains a mixture of organic and inorganic materials, including dissolved and dispersed petroleum products, dissolved minerals, industrial chemical compounds (introduced upon the formation water processing), solid substances (for example, corrosion products, salt deposits, solid petroleum products). The ingress of such water into the soil environment causes its saturation with pollutants, in particular salts and oil products.

Mandryk et al. (2017) indicate that reservoir waters contain high concentrations of dissolved salts, which under such conditions are pollutants in relation to environmental components, in particular soil. From a technological point of view, the transportation, storage and utilization (burial) of formation water is a complex process, since high pressures are used in the reservoir pressure maintenance (RPM) system, and formation water is an aggressive environment. Based on this, the probability of breaking off reservoir water pipelines, destruction of walls of casing strings and other technological equipment is very high, which may result in a significant amount of pollutants entering the soil environment.

The other authors (Aghalibe et al., 2017) proved the existence of a positive relationship between the rate of decomposition of petroleum hydrocarbons polluting the soil and the presence of organic animal waste and NPP fertilizers in soil microcosms contaminated with crude oil. Thanks to the addition of nutrients, it was possible to remove up to 70% of hydrocarbons from the soil.

In the work of Friedel et al. (2000), the effect of long-term soil irrigation with wastewater of medium or high mineralization with a predominance of sodium ions was studied. Based on the results of research, it was established that salts accumulated in the soil, and denitrification processes also occurred.

The research results obtained by Devatha et al. (2019) show that the physical properties of the soil (moisture content, liquid limit and plasticity) deteriorate due to oil pollution. The hydraulic conductivity of the soil is reduced by 10% because of oil contamination. Soil pollution with crude oil indicates a significant decrease in the hydrogen pH indicator due to an increase in the concentration of crude oil; the soil tends to become acidic. This acidic nature of the soil is explained by the presence of hydrocarbons in crude oil, which can react with salts and minerals in the soil and change alkaline minerals to acidic ones. The total concentration of organic carbon increases

as a result of soil contamination with petroleum products. The content of nitrogen and phosphorus in contaminated soil decreases as the hydrocarbon concentration increases.

All the considered scientific works, in general, give an explanation of the pairwise interaction of the content of certain elements in the soil. At the same time, the complex interaction of the content of nutrients and pollutants in the soil is of interest.

### Research methods

Determination of the components content in the soil was carried out in accordance with the normative methods adopted in Ukraine, namely: determination of the content of bicarbonates conducted by titration with a solution of sulfuric acid in an aqueous extract of carbonate ions; determination of the content of sodium and potassium – by the method of determining the intensity of radiation of the required atoms elements using a flame photometer; determination of the content of chlorides – by precipitation of chloride ions in an aqueous extract with a solution of silver nitrate in the form of slightly soluble silver chloride in a neutral medium; determination of the content of calcium and magnesium – by sequential complexometric titration in one sample of calcium ions at pH 12.5–13.0 and ions magnesium at a pH of about 10 using chromium acid dark blue as a metal indicator; determination of the sulfate content by precipitation of sulfate ions with barium chloride in the form of a suspension of barium sulfate; determination of the hydrogen indicator using a pH meter; determination of the content of oil products – by the method of extraction of organic substances from the weight of the soil with chloroform, evaporation and removal of the solvent, dissolution of the residue in hexane, separation of polar compounds on a column with aluminum oxide, removal of the solvent and gravimetric measurement of the mass of the residue; determination of the humus content carried out by the oxidimetric method, which consists in the oxidation of organic matter soils with a solution of potassium dichromate in sulfuric acid followed by the determination of the organic carbon content through the determination of potassium dichromate after oxidation by the methods of titrimetry or spectrophotometry; determination of the phosphorus content – based on the extraction of mobile compounds of phosphorus and potassium from the soil with a solution of acetic acid with a concentration of 0.5 mol/dm<sup>3</sup> in the ratio of soil to a solution 1:25 and subsequent determination of phosphorus in the form of a blue phosphoromolybdenum complex on a photoelectrocolorimeter; determination of the alkaline hydrolyzed nitrogen content based on the hydrolysis of soil organic compounds with an alkali solution in a thermostat at a temperature of 28°C in a Conway cup with a polished lid. After the end of

hydrolysis, ammonia is quantitatively determined by titration with a solution of sulfuric acid.

We have studied the simultaneous effects of all the identified elements, as the paired relationship may be less significant than the complex one. The complex interaction of substances in the soil was determined by multiple linear regression analysis. Multiple regression, in contrast to the paired one, characterizes the dependence of a certain value on several factors. At the same time, the dependence of the content of some nutrients on other ones was also investigated. The applied type of statistical analysis allows one to determine exactly those elements that will be significant for the studied element, including nutrients. For soils with a chloride type of salinity, 38 soil samples were taken, for soils with a sulfate type 21 soil samples.

### Research results

For research purposes, soil samples were selected in the territory of Romensky and Okhtyrskyi districts of Sumy region, as well as Hadyatskyi district of Poltava region of Ukraine (Figure 1). These are mainly deep black soils with low and medium humus.

The following parameters were determined for soils with chloride type of salinity: critical value of *F*-distribution  $F_{crit} = 1.83$  (significance level – 0.1, number of degrees of freedom of the numerator – 13 – 1 = 12, number of degrees of freedom of denominator – 24), critical value of the Student's *t*-distribution –  $t_{crit} = 2.38$ .

The calculated parameters of the linear regression for humus are presented in Table 1. According to the results, the calculated value is  $f = 2.01$ , and is greater than the value of  $F_{crit}$ , which indicates the presence of regression dependence. Check of the significance of the regression coefficients indicates that only the coefficient a 10 (for which the condition is  $t > t_{crit}$ ), has a significant effect on the resulting parameter which corresponds to the concentration of alkaline hydrolyzed nitrogen (Table 2).

The obtained values of the coefficients allow us to get the following regression equation:

$$K_{humus} = -0.00009187 K_{oil-pr.} + 0.000175 K_{tox.s.} - 0.002356 K_p + 0.025895 K_N - 0.608444 K_d - 0.007511 K_{pi.} + 0.000336 K_{Na} - 0.00122 K_{SO4} - 0.001248 K_{Mg} + 0.000957 K_{Ca} - 0.000364 K_{Cl} - 0.000697 K_{HCO3} - 0.258802 pH + 5.628692 \quad (1)$$

where:

$K_{oil-pr.}$  – content of oil products [mg/kg],

$K_{tox.s.}$  – content of toxic salts [mg/kg],

$K_p$  – phosphorus content [mg/kg],

$K_N$  – alkaline nitrogen content [mg/kg],

$K_d$  – content of dense residue [%],



**Figure 1.** Location diagram of soil sampling sites

**Rysunek 1.** Schemat lokalizacji miejsc pobierania próbek gleby

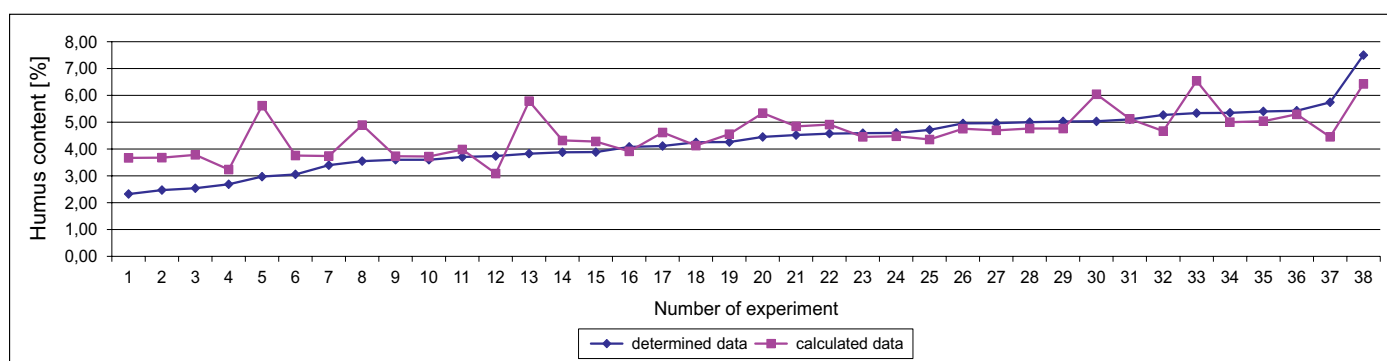
$K_{pi}$  – potassium ion content [mg/kg],  
 $K_{Na}$  – sodium ion content [mg/kg],  
 $K_{SO_4}$  – sulfate ion content [mg/kg],  
 $K_{Mg}$  – magnesium ion content [mg/kg],  
 $K_{Ca}$  – calcium ion content [mg/kg],  
 $K_{Cl}$  – chloride ion content [mg/kg],  
 $K_{HCO_3}$  – bicarbonate ion content [mg/kg],  
 pH – hydrogen index [units pH].

The calculated content of humus correlates well with the values obtained by laboratory analysis, the pairwise correlation coefficient is 0.66. The comparison of calculated and analytical values is shown in Figure 2.

The calculated parameters of linear regression for phosphorus are given in Table 3. According to the results presented in the table, the value of  $f$  is 0.93, which is less than  $F_{crit.} = 1.83$ . This circumstance indicates the lack of regression dependence between phosphorus concentration and the content of other elements in the soil.

When checking the regression coefficients for the phosphorus content as a resulting feature, it was found that none of the obtained coefficients was significant (Table 4).

For the content of alkaline hydrolyzed nitrogen, it was found that the calculated parameter  $f$  is 2.24, which is more than  $F_{crit.} = 1.83$  and indicates the existence of regression dependence (Table 5). Checking the significance of the regression



**Figure 2.** Values of humus content for soils with chloride type of salinity

**Rysunek 2.** Zawartość humusu dla gleb zasolonych chlorkami



**Table 1.** Calculated parameters of linear regression for humus soils with chloride type of salinity  
**Tabela 1.** Obliczone parametry regresji liniowej dla gleb humusowych zasolonych chlorkami

	a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
	-9.10039 E-05	0.000169	-0.002352	0.025837	-0.615726	-0.007459	0.000338	-0.001254	-0.001141	0.000591	-0.000355	-0.000694	-0.25688	5.608638
	5.2572 E-05	0.0005	0.002261	0.007534	0.624878	0.005298	0.000534	0.00159	0.00354	0.000598	0.000534	0.001521	0.285547	2.374681
	0.510653916	0.901161	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
	2.00681439	25	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
	21.18631265	20.30228	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A

**Table 2.** Calculated value of *t* regression coefficient statistics for humus

**Tabela 2.** Obliczona wartość statystyki współczynnika regresji *t* dla próchnicy

<i>a<sub>i</sub></i>	a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
<i>t</i>	-1.64624	0.33512	-1.020732	3.338362	-0.935156	-1.369693	0.615203	-0.704887	-0.305978	0.961149	-0.638915	-0.448697	-0.882088	2.298011

coefficients (Table 6) showed that only the coefficient a11 is significant (humus content –  $t > t_{crit} : 3.34 > 2.38$ ).

According to the obtained research results, the regression dependence for the alkaline hydrolyzed nitrogen content will be the following.

$$K_N = 0.001631112 K_{oil-pr.} - 0.006976 K_{tox.s.} + 12.24606 K_{humus} + 0.07798 K_p + 5.372517 K_d + 0.06057 K_K - 0.006962 K_{Na} + 0.027085 K_{SO4} + 0.067932 K_{Mg} - 0.013959 K_{Ca} + 0.015484 K_{Cl} - 0.001208 K_{HCO3} + 6.665785 pH - 62.18329 \quad (2)$$

Figure 3 shows the comparative dependencies between the values of concentrations determined in the laboratory and those calculated according to the obtained regression dependencies. The correlation coefficient between data sets is high and is 0.74.

The results of determining the calculated parameters for the regression dependence of potassium concentration as the resulting feature are shown in Table 7. As can be seen from the table, the calculated parameter  $f = 9.63$  exceeds  $F_{crit} = 1.83$ , which indicates the existence of regression dependence. Check of the significance of the regression coefficients (Table 8) shows that the coefficient a5,  $t = -2.59$  (magnesium content) is significant. Thus, the regression equation for potassium will be the following:

$$K_{pi} = -0.00399 K_{oil-pr.} + 0.014901 K_{tox.s.} - 9.65285 K_p - 0.03874 K_{humus} + 23.59202 K_d + 0.164602 K_N - 0.00587 K_{Na} + 0.000305 K_{SO4} - 0.33478 K_{Mg} + 0.041424 K_{Ca} - 0.02026 K_{Cl} - 0.00655 K_{HCO3} - 13.6091 pH + 184.9476 \quad (3)$$

The correlation coefficient between the determined and calculated values is high and reaches 0.92. In addition, we calculated the potassium concentration in the soil according to the dependence given in the work of Pukish et al. (2018), for the potassium content in soils with toxic salts content of more than 500 mg/kg (Figure 4); the correlation coefficient in this case was 0.83.

Thus, for soils with chloride type of salinity, multiple linear regression dependences have been determined for the content of humus, alkaline nitrogen and potassium; multiple linear regression for phosphorus does not exist. The determination of the significance of regression coefficients showed that the determining factor for the content of nutrients in the soil is the complex effect of all elements that were determined in this study.

The following parameters were set for soils with sulfate type of salinity: critical value of *F*-distribution  $F_{crit} = 2.67$  (significance level – 0.1, number of degrees of freedom of the numerator – 13 – 1 = 12, number of degrees of freedom of denominator – 7), critical value of Student's distribution –  $t_{crit} = 2.75$ .

**Table 3.** Calculated parameters of linear regression of phosphorus content for soils with chloride type of salinity**Tabela 3.** Obliczone parametry regresji liniowej zawartości fosforu dla gleb zasolonych chlorkami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-0.00971	0.01043	-17.6584	1.235795	8.084459	-0.22591	-0.00743	0.196714	-0.10813	-0.01977	-0.01039	-0.17293	-20.54	316.0661
0.004696	0.045164	17.29974	0.772451	57.31934	0.490769	0.047667	0.146011	0.353003	0.054689	0.049725	0.130374	25.46532	225.1538
0.336082	79.61796	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
0.934541	24	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
77012.92	152136.5	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A

**Table 4.** Calculated value of  $t$  regression coefficient statistics for phosphorus**Tabela 4.** Obliczona wartość statystyki współczynnika regresji  $t$  dla fosforu

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-2.06745	0.23093	-1.02073	1.599837	0.141042	-0.46032	-0.15593	1.347251	-0.30632	-0.36151	-0.20901	-1.32642	-0.80659	1.403779

**Table 5.** Calculated parameters of linear regression of alkaline nitrogen content for soils with chloride type of salinity**Tabela 5.** Obliczone parametry regresji liniowej zawartości azotu alkalicznego dla gleb zasolonych chlorkami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
0.001631112	-0.006976	12.24606	0.07798	5.372517	0.06057	-0.006962	0.027085	0.067932	-0.013959	0.015484	-0.001208	6.665785	-62.18329
0.001236245	0.011268	3.668283	0.048743	14.36277	0.123205	0.011895	0.037636	0.087759	0.013477	0.012096	0.033928	6.338613	57.44924
0.547943808	20.00002	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
2.237749612	24	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
11636.32216	9600.02	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A

**Table 6.** Calculated value of  $t$  regression coefficient statistics for alkaline nitrogen**Tabela 6.** Obliczona wartość statystyki współczynnika regresji  $t$  dla azotu alkalicznego

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
1.319408178	-0.619064	3.338362	1.599837	0.374059	0.491617	-0.58526	0.719656	0.774076	-1.035768	1.280087	-0.035614	1.051616	-1.082404

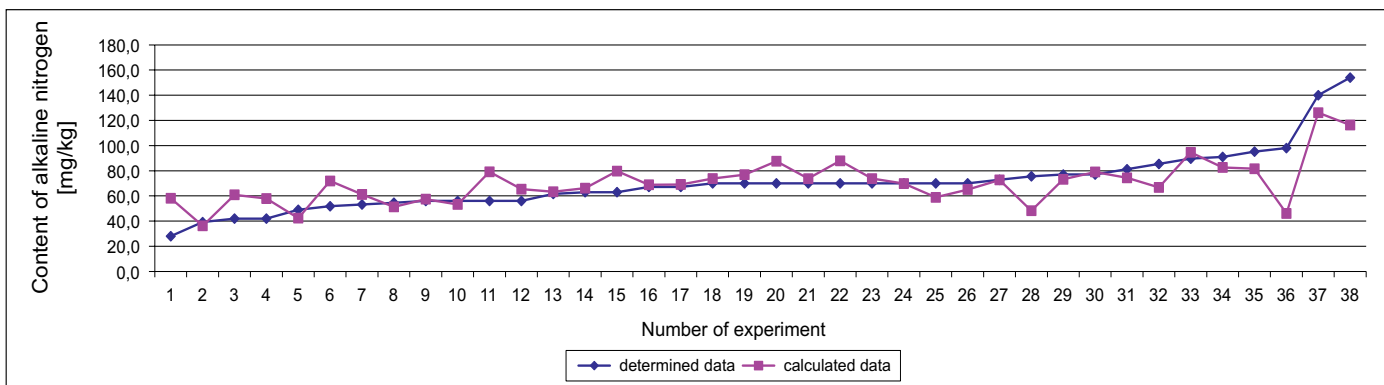


Figure 3. The value of alkaline nitrogen content for soils with chloride type of salinity

Rysunek 3. Zawartość azotu alkalicznego dla gleb zasolonych chlorkami

The calculated regression parameters for the humus content are presented in Table 9. As it can be seen, the calculated value of  $f$  is 0.78 at  $F_{crit} = 2.67$ , which indicates the absence of multiple linear regression. Check of the significance of the regression coefficients showed (Table 10) that none of the coefficients were significant. Thus, the results of research allow to state that the concentration of the studied elements has little effect on the humus content in the soil.

The calculated parameters of multiple linear regression for phosphorus are presented in Table 11. According to the calculation results, the parameter  $f$  is 10.00, which is significantly higher than  $F_{crit} = 2.67$  and indicates the presence of the regression dependence. The results of the check the significance of the regression coefficients (Table 12) show that none of the coefficients was significant. Multiple linear regression will be the following:

$$K_P = -0.38928 K_{oil-pr.} - 0.92535 K_{tox.s.} - 22.4006 K_{humus} - 3.00105 K_N + 61.25781 K_d + 3.436173 K_{pi} - 0.69179 K_{Na} + 0.795244 K_{SO_4} + 0.481847 K_{Mg} - 3.52747 K_{Ca} + 3.925831 K_{Cl} + 0.512055 K_{HCO_3} + 118.8247 pH - 236.891 \quad (4)$$

A high degree of correlation was found between the calculated and determined values of phosphorus content in soils with sulfate type of salinity (Figure 5). The correlation coefficient is 0.97. The parameters of linear multiple regression for alkaline hydrolyzed nitrogen as a resultant feature in soils with sulfate type of salinity are shown in Table 13. As can be seen based on the calculations results, the calculated parameter  $f$  is 11.372 and significantly exceeds  $F_{crit} = 2.67$ . Check of the significance of the regression coefficients showed that none of the coefficients was significant (Table 14).

The regression dependence of alkaline hydrolyzed nitrogen as a resulting feature will be the following:

$$K_N = -0.01066 K_{oil-pr.} - 0.16195 K_{tox.s.} - 2.85674 K_{humus} - 0.0493 K_P + 21.59208 K_d + 0.342922 K_{pi} - 0.08988 K_{Na} + 0.151203 K_{SO_4} + 0.007241 K_{Mg} - 0.71195 K_{Ca} + 0.340137 K_{Cl} + 0.118577 K_{HCO_3} + 22.63661 pH - 48.1688 \quad (5)$$

The correlation coefficient between the calculated and determined values of alkaline nitrogen content is high and makes 0.98 (Figure 6).

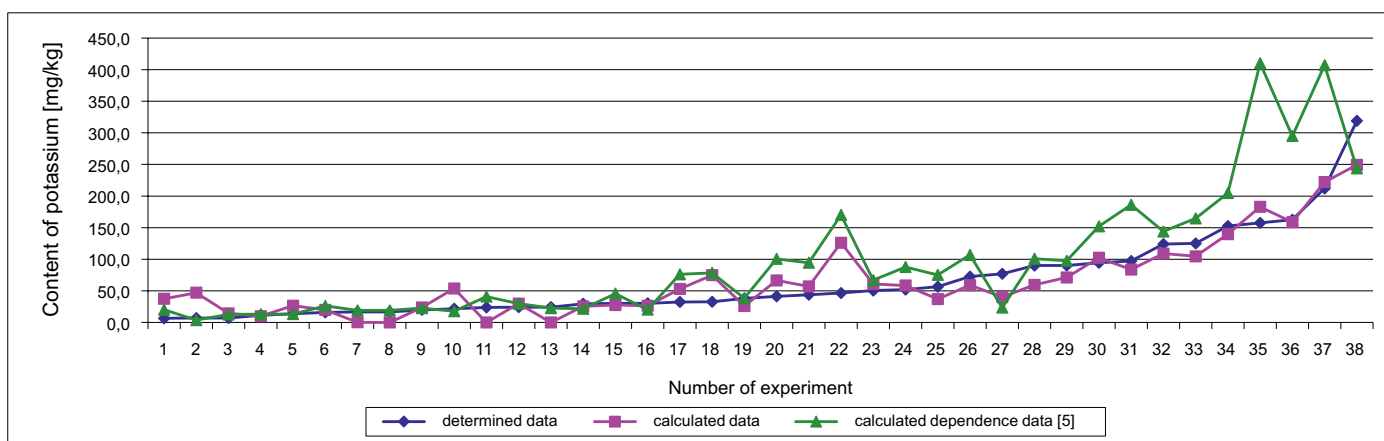


Figure 4. The value of potassium content for soils with chloride type of salinity

Rysunek 4. Wartość zawartości potasu dla gleb zasolonych chlorkiem

**Table 7.** Calculated parameters of linear regression of potassium content for soils with chloride type of salinity**Tabela 7.** Obliczone parametry regresji liniowej zawartości potasu dla gleb zasolonych chlorkami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-0.00399	0.014901	-9.65285	-0.03874	23.59202	0.164602	-0.00587	0.000305	-0.33487	0.041424	-0.02026	-0.00655	-13.6091	184.9476
0.001947	0.018475	7.047457	0.084158	23.25251	0.334817	0.019712	0.062708	0.129536	0.021076	0.020191	0.055916	10.31989	89.34013
0.839172	32.97004	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
9.632913	24	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
136125.6	26088.56	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A

**Table 8.** Calculated value of  $t$  regression coefficient statistics for potassium**Tabela 8.** Obliczona wartość statystyki współczynnika regresji  $t$  dla potasu

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-2.04815	0.806574	-1.36969	-0.46032	1.014601	0.491617	-0.29802	0.004857	-2.58514	1.965474	-1.00342	-0.11716	-1.31873	2.070151

**Table 9.** Calculated parameters of linear regression of humus content for soils with sulfate type of salinity**Tabela 9.** Obliczone parametry regresji liniowej zawartości humusu dla gleb zasolonych siarczanami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-0.00387	-0.01008	-0.00678	-0.0526	-2.54634	0.021578	-0.01469	0.009778	0.0005	-0.04034	0.046992	0.005233	1.807138	-2.57818
0.00387	0.023321	0.006054	0.047278	5.181766	0.032915	0.019577	0.02134	0.023245	0.071301	0.04961	0.020011	2.010954	13.3917
0.593063	1.079682	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
0.784745	7	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
11.89224	8.15999	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A

**Table 10.** Calculated value of  $t$  regression coefficient statistics for humus in soil with sulfate type of salinity**Tabela 10.** Obliczona wartość statystyki współczynnika regresji  $t$  dla humusu w glebie zasolonej siarczanami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-1.00086	-0.43214	-1.11916	-1.11262	-0.4914	0.655576	-0.75051	0.458195	0.021528	-0.56581	0.947228	0.261516	0.898647	-0.19252



**Table 11.** Calculated parameters of linear regression of phosphorus content for soils with sulfate type of salinity

**Tabela 11.** Obliczone parametry regresji liniowej zawartości fosforu dla gleb zasolonych siarczanami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-0.38928	-0.92534	-22.4006	-3.00105	61.25781	3.436173	-0.69179	0.795244	0.481847	-3.52747	3.925831	0.512055	118.8247	-236.891
0.186969	1.312938	20.01551	2.722157	302.1559	1.454335	1.140499	1.208455	1.324152	3.974801	2.641617	1.139897	113.5569	766.8354
0.948937	62.08059	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
10.00663	7	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
501352	26978	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A

**Table 12.** Calculated value of *t* regression coefficient statistics for phosphorus in soil with sulfate type of salinity

**Tabela 12.** Obliczona wartość statystyki współczynnika regresji *t* dla fosforu w glebie zasolonej siarczanami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-2.08206	-0.70478	-1.11916	-1.10245	0.202736	2.362711	-0.60657	0.658067	0.363891	-0.88746	1.486147	0.449211	1.046389	-0.30892

**Table 13.** Calculated parameters of linear regression of alkaline nitrogen content for soils with sulfate type of salinity

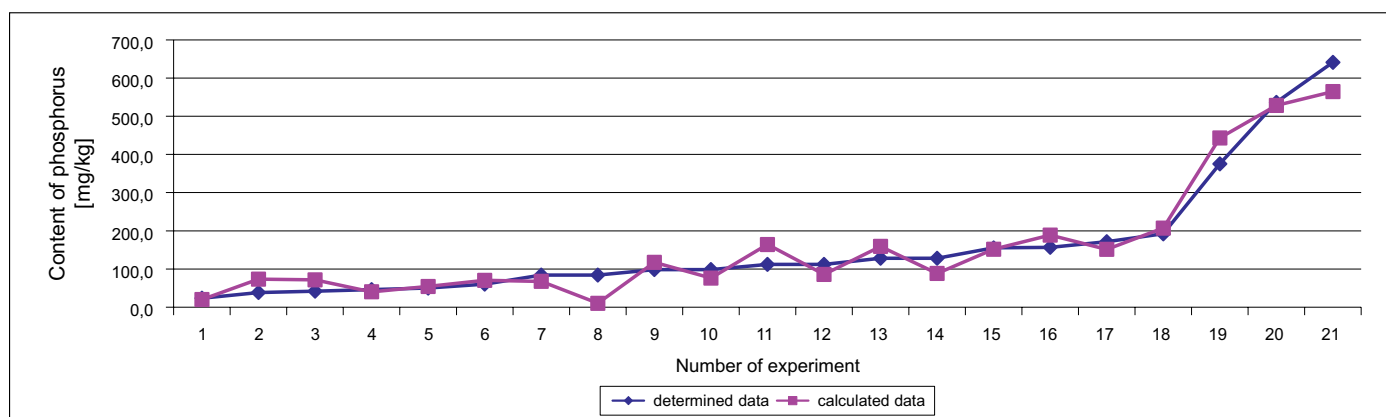
**Tabela 13.** Obliczone parametry regresji liniowej zawartości azotu alkalicznego dla gleb zasolonych siarczanami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-0.01066	-0.16195	-2.85674	-0.0493	21.59208	0.342922	-0.08988	0.151203	0.007241	-0.71195	0.340137	0.118577	22.63661	-48.1688
0.030226	0.163029	2.567579	0.044716	37.97253	0.213662	0.146067	0.149019	0.171287	0.465093	0.366423	0.141247	13.10546	97.26052
0.954791	7.956615	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
11.37214	7	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
9359.273	443.1541	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A

**Table 14.** Calculated value of *t* regression coefficient statistics for alkaline nitrogen in soil with sulfate type of salinity

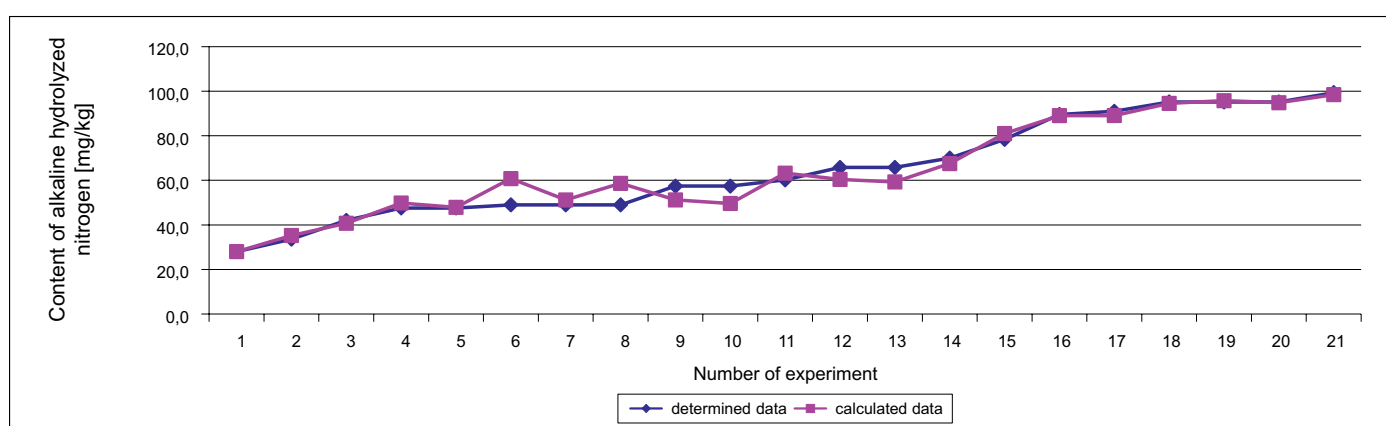
**Tabela 14.** Obliczona wartość statystyki współczynnika regresji *t* dla azotu alkalicznego w glebie zasolonej siarczanami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-0.35263	-0.99339	-1.11262	-1.10245	0.568624	1.604972	-0.1531	1.014656	0.042275	-1.53077	0.928265	0.839502	1.727265	-0.49526



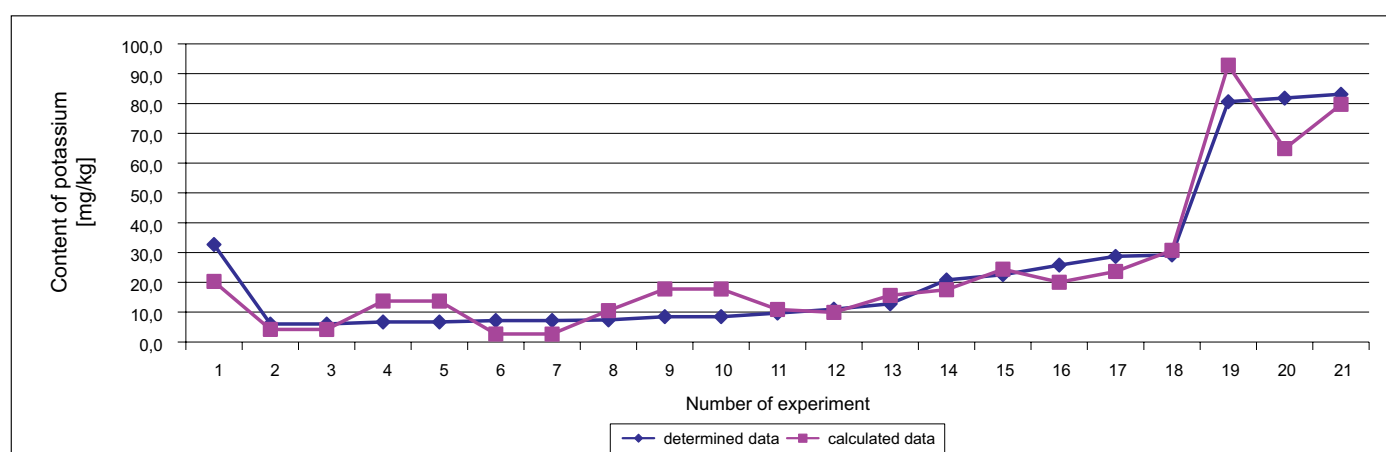
**Figure 5.** Values of phosphorus content for soils with sulfate type of salinity

**Rysunek 5.** Wartości zawartości fosforu dla gleb zasolonych siarczanami



**Figure 6.** Values of alkaline nitrogen content for soils with sulfate type of salinity

**Rysunek 6.** Wartości zawartości azotu alkalicznego dla gleb zasolonych siarczanami



**Figure 7.** Values of potassium content for soils with sulfate type of salinity

**Rysunek 7.** Zawartość potasu dla gleb zasolonych siarczanami

The calculated regression parameters for potassium content in soils with sulfate type of salinity are given in Table 15. According to the table the parameter  $f$  becomes 6.50, which exceeds  $F_{crit} = 2.67$ . According to the results of checking the regression coefficients, no significant coefficients were determined (Table 16).

The regression equation for potassium as a resultant feature will take the following form:

$$\begin{aligned}
 K_{pi} = & -0.00013 K_{oil-pr.} - 0.01507 K_{tox.s.} + 0.129 K_p + \\
 & + 0.784 K_{humus} + 0.235 K_d + 9.993 K_N + 2.681 K_{Na} + \\
 & + 0.008005 K_{SO_4} + 0.113 K_{Mg} + 0.215 K_{Ca} - 0.02 KCl + \\
 & + 0.055 K_{HCO_3} - 28.728 pH + 120.855 \quad (6)
 \end{aligned}$$

**Table 15.** Calculated parameters of linear regression of potassium content for soils with sulfate type of salinity  
**Tabela 15.** Obliczone parametry regresji liniowej zawartości potasu dla gleb zasolonych siarczanami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-0.00013	-0.01507	0.129117	0.784437	9.992885	2.680703	0.235475	0.008005	0.112895	0.21495	-0.02021	0.055376	-28.7283	120.8547
0.046119	0.26332	0.054648	0.488754	58.62146	4.089082	0.208624	0.241371	0.255558	0.808612	0.587267	0.223146	21.03414	142.5152
0.923455	12.03399	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
6.496137	7	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
122297.5	1013.718	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A

**Table 16.** Calculated value of *t* regression coefficient statistics for potassium in soil with sulfate type of salinity

**Tabela 16.** Obliczona wartość statystyki współczynnika regresji *t* dla potasu w glebie zasolonej siarczanami

a13	a12	a11	a10	a9	a8	a7	a6	a5	a4	a3	a2	a1	a0
-0.35263	-0.99339	-1.11262	-1.10245	0.568624	1.604972	-0.61531	1.014656	0.042275	-1.53077	0.928265	0.839502	1.727265	-0.49526

The correlation coefficient between the determined and calculated values is high and is 0.96 (Figure 7).

According to the results of the conducted research, multiple linear regression dependences for concentrations of alkaline nitrogen, phosphorus, potassium in soils with sulfate type of salinity have been determined. The complex influence of the studied elements is decisive. No regression dependence was found for humus content.

### Conclusions

1. For soils with chloride type of salinity, multiple linear regression dependences have been determined for the content of humus, alkaline nitrogen and potassium; for phosphorus there was no multiple linear regression. The determination of the significance of regression coefficients showed that the determining factor for the content of nutrients in the soil is the complex effect of all elements that were determined in this study.
2. For soils with sulfate type of salinization, multiple linear regression dependences for concentrations of alkaline nitrogen, phosphorus, potassium have been determined. The complex influence of the studied elements is decisive. No regression dependence was found for the humus content which indicates that the concentration of the studied elements has practically no effect on the humus content in the soil.

### References

Aghalibe C.U., Igwe J.C., Obike A.I., 2017. Studies on the removal of petroleum hydrocarbons (PHCs) from a crude oil impacted soil amended with cow dung, poultry manure and npk fertilizer. *Chemistry Research Journal*, 2(4): 22–30.

Araratyan L.A., Safrabekyan E.A., Aветisyan M.G., Poghosyan T.E., 2015. Features of the migration of some of the most important nutrients in high – mountain ecosystems. *Newsletter of NAS RA. Sciences about the country*, 68(1): 82–90.

Devatha C.P., Vishnu Vishal A., Purna Chandra Rao J., 2019. Investigation of physical and chemical characteristics on soil due to crude oil contamination and its remediation. *Applied Water Science*, 9: 1–10. DOI: 10.1007/s13201-019-0970-4.

Echchel A., Hess T., Sakrabani R., 2018. Reusing oil and gas produced water for irrigation of food crops in drylands. *Agricultural Water Management*, 206: 124–134. DOI: 10.1016/j.agwat.2018.05.006.

Friedel J.K., Langer T., Siebe C., Stahr K., 2000. Effects of long-term waste water irrigation on soil organic matter, soil microbial biomass and its activities in central Mexico. *Biology and Fertility of Soils*, 31: 414–421. DOI: 10.1007/s003749900188.

Mandryk O., Zelmanovych A., Pukish A., 2017. Formation peculiarities of physical and chemical composition of highly mineralized edge water. *Mining of Mineral Deposits*, 11(1): 72–79. DOI: 10.15407/mining11.01.072.

Nouri H., Borujeni S.Ch., Nirola R., Hassanli A., Beecham S., Alaghmand S., Sain Ch., Mulcahy D., 2017. Application of green

- remediation on soil salinity treatment: A review on halophytoremediation. *Process safety and environmental protection*, 107: 94–107. DOI:10.1016/j.psep.2017.01.021.
- Pathak C., Mandalia H.C., 2012. Petroleum industries: environmental pollution effects, management and treatment methods. *International Journal of Separation for Environmental Sciences*, 1(1): 55.
- Pichtel J., 2016. Oil and gas production wastewater: Soil contamination and pollution prevention. *Applied and Environmental Soil Science*, 2016: 24. DOI: 10.1155/2016/2707989.
- Pukish A., Adamenko Ya., Coman M., 2018. Pedological processes in technosoils. *Scientific Bulletin Series D: Mining, Mineral Processing, Non-Ferrous Metallurgy, Geology and Environmental Engineering*, 32(1): 73–79.
- Rhykerd R.L., Weaver R.W., McInnes K.J., 1995. Influence of salinity on bioremediation of oil in soil. *Environmental Pollution*, 90(1): 127–130. DOI:10.1016/0269-7491(94)00087-T.



Oleh Mykolayovych MANDRYK, Ph.D.  
Deputy Rector  
Ivano-Frankivsk National Technical University  
of Oil and Gas  
15 Karpatska St., 76019, Ivano-Frankivsk, Ukraine  
E-mail: o.mandryk@nung.edu.ua



Yaroslava Stepanivna KOROBEINYKOVA, Ph.D.  
Candidate, Lecturer  
Ivano-Frankivsk National Technical University  
of Oil and Gas  
15 Karpatska St., 76019, Ivano-Frankivsk, Ukraine  
E-mail: yaroslava.korob@gmail.com



Oleh Mykhaylovych TUTS, M.Sc.  
Postgraduate  
Ivano-Frankivsk National Technical University  
of Oil and Gas  
15 Karpatska St., 76019, Ivano-Frankivsk, Ukraine  
E-mail: olehtuts@ukr.net



Arsen Volodymyrovych PUKISH, Ph.D.  
Head of the Service for Environmental Protection  
and Monitoring Research PJSC “Ukrnafta”  
2 Pivnichnyi Blvd, 76019, Ivano-Frankivsk, Ukraine  
E-mail: arsenpukish@ukr.net



Olha Ihorivna SYDORENKO, M.Sc.  
Specialist of service  
Service for Environmental Protection and Monitoring  
Research PJSC “Ukrnafta”  
2 Pivnichnyi Blvd, 76019, Ivano-Frankivsk, Ukraine  
E-mail: sydorolya1@gmail.com

## OFERTA BADAWCZA ZAKŁADU OCHRONY ŚRODOWISKA

- analiza zagrożeń środowiska naturalnego, związanych z działalnością przemysłu naftowego i gazowniczego,
- inwentaryzacja wielkości emisji metanu z sektora poszukiwania, wydobycia, magazynowania oraz przesyłu i dystrybucji gazu wraz oceną możliwości jej redukcji,
- inwentaryzacja wielkości emisji gazów cieplarnianych,
- weryfikacja i ocena wpływu technologii na środowisko w przemyśle naftowym i gazowniczym, zgodnie z najnowszymi trendami,
- wyznaczenie śladu węglowego (Carbon Footprint) w przemyśle naftowym i gazowniczym,
- monitoring i badania laboratoryjne elementów środowiska (powietrza, wód i gleby) na terenach poszukiwania i eksploatacji złóż węglowodorów i innych terenach przemysłowych,
- badania laboratoryjne ścieków i odpadów (w tym odpadów wiertniczych, odpadów po zabiegu hydraulicznego szczelinowania, odpadowych wód złożowych i cieczy technologicznych) oraz ocena ich potencjalnej szkodliwości dla środowiska,
- klasyfikacja odpadów wydobywczych wraz ze sporządzaniem charakterystyki odpadu, zgodnie z obowiązującymi regulacjami,
- oznaczanie wybranych nanocząstek metali i tlenków metali w próbkach środowiskowych,
- analiza zawartości rtęci w próbkach środowiskowych (stałych i ciekłych), mieszaninach gazowych i materiałach przemysłowych,
- ocena jakości paliw węglowodorowych, w tym gazu ziemnego i jego mieszanin z wodorem, a także gazów wytwarzanych w przemyśle (np. koksowniczego),
- kompleksowa analiza biogazu, w tym analiza związków krzemu, chloru i fluoru oraz amoniaku,
- monitoring jakości gazu ziemnego w systemie gazowniczym,
- sporządzanie oraz aktualizacja kart charakterystyki substancji i mieszanin niebezpiecznych, zgodnie z obowiązującym prawodawstwem,
- akredytowany pobór próbek odpadów oraz gazu ziemnego, biogazu i innego typu mieszanin gazowych.



Kierownik: mgr Jadwiga Holewa-Rataj      Adres: ul. Bagrowa 1, 30-733 Kraków  
Telefon: 12 617 74 36, 797 727 103      Faks: 12 653 16 65      E-mail: holewa-rataj@inig.pl



INSTYTUT NAFTY I GAZU  
– Państwowy Instytut Badawczy