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POTENTIAL ENVIRONMENTAL MANAGEMENT OF WASTE PRODUCTS FROM EXPLORATORY DRILLING ACTIVITIES

MOŻLIWOŚCI ROLNICZEGO ZAGOSPODAROWANIA PRODUKTÓW ODPADOWYCH Z DZIAŁALNOŚCI POSZUKIWAWCZO-WIERTNICZYCH

Abstract: The investigations were undertaken to assess increasing amounts of waste products generated during drilling and supplied to the soil in respect of potential soil and plant contamination with some elements, and determining the effect of salinization degree on plant growth.

The waste used for pot experiments contained, beside considerable amounts of chlorides, also 18 % of $CaCO_3$ which influenced the increase in chemisorption of fertilizer phosphorus. The deposit supplied to the soils almost 14-times increased the quality of exchangeable sodium. Salinization effect was apparent primarily for red fescue emergences, which were irregular and obviously delayed as the waste was added to the pot. The differences in plant appearance diminished during the vegetation. The largest waste supplement caused a decline in red fescue yield cultivated immediately after its addition.

The effect of waste supplement on increase in salinization became visible only when the highest, 40 % supplement was added and led to slight soil degradation due to salinization (over 2 $mS \cdot cm^{-1}$).

Keywords: exploratory drilling wastes, plants, sodium and potassium contents, soil salinization

The concept of environmental management of wastes has the best perspective of development. Usability of various wastes for reclamation depends on their chemical and biological properties.

Environmental management of waste products from exploratory drilling activities deposited in spoil pits and previously cleaned of oil derivative compounds still encounters a problem of the waste pollution with heavy metals and excessive salt contents. Therefore, the investigations aimed to assess increasing amounts of waste products originating from spoil pit of a drilling plant located in Witkowice considering potential soil and plant contamination with some toxic elements and to determine the degree of soil salinization on plant growth. For this purpose, plant experiments were

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conducted with increasing supplement of deposit to the soil to observe its effect on plant growth, increasing their contents of some elements and changes of some soil properties.

Materials and methods

The soil used for the experiments revealed properties similar to the one originating from the area adjoining to the landfill.

The following series of experimental design were used: A – soil without deposit supplement, B – soil with 5 % of deposit, C – soil with 10 % of deposit, D – soil with 25 % of deposit, E – soil with 40 % of deposit.

Phosphorus fertilization in $Ca(H_2PO_4)$ form dosed 0.3 g P_2O_5 per pot was applied once prior to the experiment outset. Nitrogen fertilization was applied in a form of NH_4NO_3 in a dose of 0.75 g N per pot on two dates: 0.5 g N per pot before the experiment outset and the remaining part after grass (*Festuca rubra* L.) harvest but before mustard (*Synapis alba* L.) sowing. Because of the soil high abundance in potassium and high content of water soluble potassium in the deposit, no potassium was included in the fertilizer dose. Chemical composition of plants was assessed by means of dry mineralization at 450 ^oC for 5 hours. Total contents of nutrients and heavy metals in the soils were determined by digesting the soil in a mixture of HNO_3 and $HClO_4$ (3:2) after incinerating organic substance in a furnace at 450 ^oC for 5 hours. The element concentrations in solutions were assessed using ICP method. Because of $CaCO_3$ in the deposit, the soil sorption capacity was determined in NH_4Cl with pH = 8.2 and in the initial, non-carbonate soil with pH = 7.0 following the leaching of water soluble soils with anhydrous ethyl alcohol. The test plant was red fescue grass (*Festuca rubra* L.), Skrzeszowicka c.v., while white mustard (*Synapis alba* L.), Barka c.v., was cultivated as an aftercrop.

Results

A supplement of waste from exploratory-drilling works supplied to the soil affected test plant yielding in the conducted pot experiment. Already 5 % waste addition caused a decline in yield by over 30 % in comparison with the control (Table 1).

Table 1

Plant yielding [g · d.m. per pot]

Fertilizer series	Red fescue			Mustard			Aggregate yield grass + mustard
	AP	R	AP + R	AP	R	AP + R	
A	24.21	4.63	28.84	1.04	0.10	1.14	29.98
B	15.22	3.83	19.05	5.61	0.70	6.31	25.36
C	16.70	3.93	20.63	6.11	0.48	6.59	27.22
D	17.55	3.56	21.11	7.18	0.56	7.74	28.85
E	11.74	2.03	13.77	3.98	0.40	4.38	18.15

Explanation: AP – above-ground parts; R – roots.

However, aggregate yield of both cultivated crops revealed a decrease only by 15 % in this series. In the series with the 10 and 25 % supplements a decrease in yield was even less visible. Only a 40 % admixture of the deposit caused an over 50 % decline in grass yield and 40 % decrease in the aggregate yield of grass and mustard.

The greatest differences in plant growth occurred during the initial period of red fescue vegetation. This fact is confirmed by a regularity described in literature [1, 2], that young plants, mainly at the seedling stage are most sensitive to unfavourable environmental conditions.

The effect of spoil admixture was also noticeable in the chemical composition of the cultivated plants. It was the most pronounced for sodium (almost 5-fold increase in Na concentration) and potassium, where this element content exceeded 6 % in dry matter (Table 2). $CaCO_3$ present in the deposit, beside the effect on the soil reaction, caused an increase in Ca and also Mg content, but to a lesser degree. For calcium the changes were more visible in mustard (Table 3) cultivated as a consecutive crop, which may be due to the time which elapsed from the moment of application.

Table 2

Macroelement contents in red fescue

Series	K		Ca		Mg		Na		P	
	AP	R	AP	R	AP	R	AP	R	AP	R
	[g · kg^{-1} d.m.]									
A	38.9	9.9	1.0	0.4	1.52	0.80	0.54	0.98	3.49	1.54
B	55.1	15.3	5.2	2.6	3.00	2.65	1.34	4.22	1.66	1.22
C	65.8	17.7	4.7	2.4	2.53	3.36	1.55	4.57	1.76	1.00
D	67.2	23.0	2.9	1.7	3.72	3.13	1.32	5.22	1.72	1.01
E	56.1	25.2	1.7	1.6	3.18	3.48	2.60	5.98	2.38	1.23

Table 3

Macroelement contents in white mustard

Series	K		Ca		Mg		Na		P	
	AP	R	AP	R	AP	R	AP	R	AP	R
	[g · kg^{-1} d.m.]									
A	19.5	6.2	11.6	2.7	3.7	0.6	9.00	1.43	3.64	3.71
B	36.4	23.0	17.8	5.7	1.7	1.2	5.94	2.56	2.50	3.35
C	35.1	27.2	21.4	10.2	1.5	1.5	8.03	3.14	2.39	3.49
D	54.0	30.6	22.4	3.1	1.9	1.3	12.51	3.98	2.72	3.34
E	57.9	30.1	20.4	4.6	2.5	1.5	13.02	2.44	3.14	2.37

Considerable changes were detected also in phosphorus content in plants. Calcium carbonate in the deposit affected higher chemisorption of fertilizer supplied to the soil and its concentration in plants was low.

The tendencies of changes in chemical composition were similar in white mustard, although less pronounced as in case of magnesium or phosphorus.

From the perspective of plants cultivated for animal feed not only the absolute quantity of individual nutrients is important, but also their mutual relationships. Adding increasing quantities of deposit to the soil caused a change in proportions between the studied elements. In very acid soil used for the experiments, equivalent ratio K:(Ca + Mg) was much wider (5.7) than the value (2.2) considered optimal [3]. The smallest supplement of the deposit on the level of 5 % contributed to an improvement of fodder quality, whereas narrowing this ratio to the value of 2.8 and further increase of the admixture to the soil led to its considerable widening (Table 4).

Table 4

Changes of K:(Ca + Mg) and (K + Na):(Ca + Mg) equivalent ratios and K:Na and Ca:P weight ratio in red fescue

Series	K:(Ca + Mg)	(K + Na):(Ca + Mg)	K:Na	Ca:P
A	5.71	5.84	72	0.29
B	2.79	2.90	41	3.13
C	3.81	3.97	42	2.67
D	3.82	3.95	51	1.69
E	4.14	4.47	22	0.71

Weight K:Na ratio in red fescue cultivated on all treatments was too wide, which resulted from excessive potassium content in plants. Although the ratio was narrowing with increasing waste admixture, it still exceeded 10:1 proportion. For fodder reasons Ca:P ratio should be on the level of 2:1. Presented data show that 5 % and 10 % waste supplements led to widening this ratio to values considered as proper, but its further growth led to an excessive narrowing of this ratio.

The waste contained great amounts of colloids (71 % of clay particles including 23 % of colloidal clay) and added to the soil caused an increase in its colloidal clay content (Table 5), therefore worsening water-air relationships. Supplying such great quantities of silt fraction to anyway heavy soils favoured creation of reductive conditions in the soil.

The waste used for agricultural management contained over 18 % of $CaCO_3$. Even the smallest (5 %) admixture of the deposit contained over twice more $CaCO_3$ than necessary for the deacidification of the experimental soil. Therefore with increasing deposit addition to the soil growing amounts of $CaCO_3$ remained in free state increasing chemisorption of fertilizer phosphorus. It points to low phosphorus content in plants, despite fertilization with this element.

Significant diversification of soil chemical properties under the influence of liming may affect a decline in yield of crops grown immediately after its application. Gorlach and Gorlach [4] obtained these results while investigating the effect of carbonate forms of calcium and magnesium on yielding of several plant species. A rapid change of exchangeable cation ratios in soil under the influence of applied Ca fertilization

observed in the experiments conducted by Czapla and Nowak [5, 6] caused a decrease in the yield of maize and oat from 10 to 15 %. On the other hand, in the studies of Filipek et al [3] conducted on meadows, no response of meadow sward was noted but only when counted as an average for three years. In the first year after liming even several percent decline in yield was registered. The studies of Gorlach and Curylo [7] on liming of two meadows on soils with various granulometric structure yielded different results. In an experiment conducted on light soil with considerable share of exchangeable aluminum in acidity, liming increased yields of meadow sward, whereas in the experiment on very heavy soil ca 10 % decrease in yield occurred.

A negative result of added deposits was elevated soil salinization (Table 5).

Table 5

Changes of some physical and chemical soil properties after experiment completion

Series	% fraction of mm		pH		$CaCO_3$ [%]	C-org [$g \cdot kg^{-1}$]	Salinization [$mS \cdot cm^{-1}$]
	< 0.02	< 0.002	H_2O	KCl			
Waste	71	23	8.99	8.46	18.09	—	4.75
A	41	15	4.92	4.00	nd	8.40	nd
B	41	18	7.14	6.99	0.22	10.40	0.40
C	46	18	7.46	7.07	0.47	10.00	0.86
D	51	20	7.80	7.33	1.85	9.20	1.27
E	59	22	8.00	7.52	4.87	10.60	2.27

Explanation: nd – not determined.

At waste admixtures of between 5 and 10 % the salinization was still slight. The symptoms of weak soil degradation (Table 5) which might have been the reason of a decrease in yield (Table 1) occurred only at 40 % addition of wastes causing a delay of emergences and weakening of growth at the tillering stage.

The cation exchange capacity was assessed in order to establish the effect of deposit added to the soil on changes of exchangeable cation composition in the sorption complex. Data compiled in Table 5 show that the initial soil with the deposit supplement revealed increasing contents of $CaCO_3$ as the amount of added deposit was growing. Therefore, determining the changes of exchangeable cation composition in the sorption complex was conducted in carbonate soils in NH_4Cl with pH = 8.2 whereas for the initial carbonate-less soil using NH_4Cl with pH = 7.0. Acid cations were assessed in an extract of sodium acetate [8]. Because the soils with waste supplement revealed salinization, they were leached with absolute ethyl alcohol.

In each soil there is a small amount of water soluble cations (so called active forms), yet the contents of this form of cations rarely exceed the value of 1 $mmol \cdot kg^{-1}$ of soil [9].

The quantities of individual cations determined in the anhydrous ethyl alcohol may be considered as water soluble forms. The data given in Table 6 show that not only potassium and sodium were present in the sediment as chlorides. Also a small quantity

of magnesium and considerable part of calcium occurred in water soluble forms. With deposit supplement increasing from 5 % to 40 % the highest, almost fivefold growth was registered for water soluble sodium. It should be expected that calcium and sodium ions would significantly affect the conditions of plant nutrition in the soil with these wastes admixture.

Table 6

Contents of calcium, magnesium, sodium and potassium cations in the extract of anhydrous ethyl alcohol

Series	Ca	Mg	K	Na	Total
	[mmol(+) · kg^{-1}]				
B	15.4	0.56	0.09	3.07	19.12
C	16.6	0.51	0.21	5.60	22.92
D	22.7	0.57	0.14	9.34	32.75
E	26.5	0.69	0.35	14.62	42.16

In the studies by Filipek and Badora [10] conducted on the soil where means for after snow slipperiness control were used, the contents of chloride anions and sodium cations in the 20–40 cm layer was higher by about 0–20 cm, which suggests relatively easy leaching of these ions into deeper soil layers. The soil, on which the pot experiments were conducted belonged to heavy soils, where leaching occurs, though it is weaker.

Ion-exchanging sorption plays an important role is soils in storing and mobilization of nutrients. Determining sorption capacity in soil containing carbonates encounters analytical problems, irrespectively if conducted using indirect method (the sum of individually assessed alkaline cations, eg in ammonium chloride with pH = 8.2), or using a direct method through exchange of sorption complex cations using barium chloride.

As may be seen from the data presented in Table 6, a considerable part of not only sodium but also calcium may occur as water soluble compounds not adsorbed by sorption complex, which will be counted to exchangeable cations.

The waste added to the soil caused deacidification of the very acid, initial soil. After the experiment completion sorption capacity increased over twice, mainly owing to the almost 3-fold growth of the exchangeable calcium and magnesium quantity and over 14-fold increase in the amount of exchangeable sodium. Changes in the quantity of exchangeable potassium were observed only at the 25 % and 40 % waste admixtures. In the presented experiment even at the highest deposit supplement the sum of exchangeable cations K+Na does not exceed 7 %, ie much less than in the salinized soils. Therefore a decrease in yield observed in the conducted experiment already on the treatments with 5 % addition of the waste product should be associated rather with high content of $CaCO_3$ than with the soil salinization, which on these treatments was 0.40 mS · cm^{-1}.

Table 7

Contents of calcium, magnesium, sodium and potassium cations in an extract of neutral ammonium chloride (series A) and ammonium chloride with pH = 8.2 (series B, C, D and E)

Series	Ca	Mg	K	Na	Total	H	T	V
	[mmol(+) · kg^{-1}]							[%]
A	125.0	7.87	2.10	1.01	135.98	81.0	216.98	63
B	441.2	17.88	2.14	14.42	475.64	—	475.60	100
C	441.8	18.16	2.77	21.56	484.29	—	484.30	100
D	472.4	25.91	4.14	29.96	532.40	—	532.40	100
E	547.8	40.12	5.48	35.25	628.60	—	628.60	100

The category of degradation which may reveal itself as a decline in yield, particularly of plants sensitive to salinization, is apparent only on the soil with 40 % admixture of waste.

Conclusions

1. Waste product from exploratory drilling activities added to the soil decreased yielding of the test plants cultivated immediately after its introduction to the soil, mainly in the initial period of development.

2. Changes in the plant chemical composition concerned mainly sodium causing almost 5-fold increase in its contents in plants.

3. $CaCO_3$ present in the waste increased chemisorption of fertilizer phosphorus, which limited its bioavailability and decreased its uptake by plants.

4. Increase in the soil salinization became apparent only at the greatest admixture of waste (40 %) causing its slight degradation but the increase in exchangeable sodium did not exceed the values characteristic for salinized soils.

5. A significant amount of mineral colloids present in the waste introduced to heavy soils may lead to worsening of air and water relationships and occurrence of reductive conditions in soil.

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MOŻLIWOŚCI ROLNICZEGO ZAGOSPODAROWANIA PRODUKTÓW ODPADOWYCH Z DZIAŁALNOŚCI POSZUKIWAWCZO-WIERTNICZYCH

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Abstrakt: Celem podjętych badań była ocena wzrastających dodatków do gleby produktów odpadowych powstających w trakcie prowadzenia prac wiertniczych w aspekcie możliwości skażenia gleby i roślin niektórymi pierwiastkami oraz określenie wpływu stopnia zasolenia gleby na wzrost roślin.

Użyty do doświadczeń wazonowych odpad oprócz znacznych ilości chlorków zawierał 18 % $CaCO_3$, który wywoływał wzrost chemisorpcji fosforu nawozowego. Dostarczony do gleby osad zwiększał prawie 14-krotnie ilość wymiennego sodu. Wpływ zasolenia uwidaczniał się przede wszystkim we wschodach kostrzewy czerwonej, które były bardzo nierównomierne i wyraźnie opóźnione w miarę dodatku odpadu do wazonu. W trakcie trwania wegetacji różnice w wyglądzie roślin zmniejszały się. Największy dodatek odpadu powodował spadek plonu kostrzewy czerwonej uprawianej bezpośrednio po jego dodaniu.

Wzrost zasolenia gleby pod wpływem dodatku odpadu uwidocznił się dopiero przy największej jego dawce wynoszącym 40 %, powodując słabą degradację gleby na skutek zasolenia (ponad 2 $mS \cdot cm^{-1}$).

Słowa kluczowe: odpady poszukiwawczo-wiertnicze, rośliny, zawartość sodu i potasu, zasolenie gleby