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CHANGES IN THE CONTENT OF ORGANIC CARBON AND AVAILABLE FORMS OF MACRONUTRIENTS IN SOIL UNDER THE INFLUENCE OF SOIL CONTAMINATION WITH FUEL OIL AND APPLICATION OF DIFFERENT SUBSTANCES*

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Abstract

The aim of the study has been to determine the effect of soil contamination with fuel oil (0-20 g kg^{-1} of soil) on the content of organic carbon and available forms of some macronutrients in soil under the influence of different neutralizing substances and crop cultivation. The content of organic carbon as well as available potassium and magnesium in soil was positively correlated with the increasing rates of fuel oil, whereas the fluctuations in available phosphorus did not show any regularity. Among the analyzed elements, the highest increase in the concentration was found for potassium. The content of available macronutrients in soil was correlated with the plants' yield and uptake of elements. The substances introduced to soil in order to alleviate the effect of fuel oil on soil properties caused the weakest changes in the content of organic carbon but affected most profoundly the content of available potassium and magnesium. Compared to the series without soil amending substances, bentonite caused an increase in the average content of available forms of phosphorus, potassium and magnesium, whereas calcium oxide modified the content of available potassium and magnesium. CaO decreased the content of organic carbon and available phosphorus in soil. The effect of the other tested soil amending substances on the analyzed soil properties was weaker than that produced by bentonite or calcium oxide, and the direction of changes in the levels of the elements depended on the type of a substance.

Key words: fuel oil contamination, nitrogen, compost, bentonite, zeolite, calcium oxide, soil, organic carbon, macroelements.

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ZMIANY ZAWARTOŒCI WÊGLA ORGANICZNEGO I PRZYSWAJALNYCH FORM MAKROPIERWIASTKÓW W GLEBIE POD WP£YWEM ZANIECZYSZCZENIA OLEJEM OPA£OWYM I APLIKACJI RÓ¯NYCH SUBSTANCJI

Abstrakt

Celem badañ by³o okreœlenie wp³ywu zanieczyszczenia gleby olejem opa³owym (0-20 g kg^{-1} gleby) na zawartoœæ wêgla organicznego i przyswajalnych form wybranych makropierwiastków w glebie w warunkach aplikacji ró¿nych substancji i uprawy roœlin. Zawartoœci wêgla organicznego oraz przyswajalnego potasu i magnezu w glebie by³y dodatnio skorelowane ze zwiêkszaj¹cymi siê dawkami oleju opa³owego, zaœ w zawartoœci fosforu przyswajalnego nie wykazano ukierunkowanych zmian.

Najwiêkszy wzrost zawartoœci odnotowano w przypadku potasu. Zawartoœæ przyswajalnych makrosk³adników w glebie by³a skorelowana z plonem i pobraniem pierwiastków przez roœliny. Substancje zastosowane w celu ograniczenia wp³ywu oleju opa³owego na w³aœciwoœci gleby wywo³a³y najmniejsze zmiany w zawartoœci wêgla organicznego, a najwiêksze w zawartoœci przyswajalnego potasu i magnezu w glebie. Bentonit spowodowa³, w porównaniu z seri¹ bez dodatków, zwiêkszenie œredniej zawartoœci przyswajalnych form fosforu, potasu i magnezu, a tlenek wapnia – zawartoœci przyswajalnego potasu i magnezu. Tlenek wapnia wp³yn¹³ tak¿e na zmniejszenie zawartoœci wêgla organicznego i przyswajalnego fosforu w glebie. Wp³yw pozosta³ych substancji na badane w³aœciwoœci gleby by³ mniejszy ni¿ bentonitu i tlenku wapnia, a kierunek zmian w zawartoœci pierwiastków uzale¿niony od rodzaju zastosowanej substancji.

S³owa kluczowe: zanieczyszczenie olejem opa³owym, azot, kompost, bentonit, zeolit, tlenek wapnia, gleba, wêgiel organiczny, makrosk³adniki.

INTRODUCTION

Contamination of soil with petroleum derivatives, including fuel oil, is a growing problem. Globally, over 45 million of tons of crude oil and petroleum end products, i.e. 2% of the annual production, contaminate the natural environment. The loss of petroleum during its production and storage on land reaches 5 million tons a year, while another 8 million is lost during its processing and transport – of that amount, 3 million tons pollute soil. Each year, about 27 million tons of petroleum derivatives are lost, of which 9 million permeate soil (VINNIK, OVCHAROV 2004). Once in soil, petroleum derivatives trigger a series of negative changes, for example the morphological and physicochemical soil properties have been observed to undergo very intensive transformations (ZAHAROV, ZHITIN 2008). The content of such macronutrients as carbon, phosphorus, potassium and magnesium in soil depends on a number of factors, including soil contamination with petroleum-based substances. When soil becomes polluted with such substances, the content and availability of the above elements change, which affects their concentrations in plants and the crop weight (WYSZKOWSKI et al. 2004, WYSZKOWSKI, ZIÓ£KOWSKA 2009a,b). The adverse influence of petroleum end products on the quality of crops growing on contaminated land (ZIÓ£KOWSKA, WYSZKOWSKI

2010, WYSZKOWSKA, WYSZKOWSKI 2010) as well as on other live organisms (ZIÓŁKOWSKA, WYSZKOWSKI 2010, WYSZKOWSKA, WYSZKOWSKI 2010) is associated with the fact that such pollutants can be transmitted to subsequent links in trophic chains. Therefore, it is essential to have these contaminants neutralized in the environment in which they occur. There are many methods for the stimulation of degradation of petroleum contaminants, e.g. soil amendment with biogenic substances, aeration, inoculation with active microorganisms or regulation of soil reaction (RUSEK 2006).

The above considerations have encouraged the authors to undertake a study whose aim has been to determine the effect of soil contamination with fuel oil on the content of organic carbon and available forms of some macronutrients in soil treated with different neutralizing substances.

MATERIAL AND METHODS

A pot experiment has been conducted in a greenhouse at the University of Warmia and Mazury in Olsztyn (north-eastern Poland). The tested soil had the following characteristics: pH in 1 mol KCl dm^{-3} 4.52, hydrolytic acidity (Hh) 25.4 mmol(H^+) kg^{-1}, total exchange bases (TEB) 29.1 mmol(+) kg^{-1}, cation exchange capacity (CEC) 54.5 mmol(+) kg^{-1}, base saturation (BS) 53%, C_{org} content 11.28 g kg^{-1}, concentrations of available phosphorus 71.88 mg P kg^{-1}, potassium 118.6 mg K kg^{-1} and magnesium 104.18 mg Mg kg^{-1}. Increasing rates of fuel oil were tested, that is 0, 5, 10, 15 and 20 g kg^{-1} d.m. of soil. In order to reduce the effect of fuel oil on soil, the following neutralizing substances were applied: compost 3% (270 g per pot), bentonite and zeolite 2% (180 g per pot), urea (200 mg N kg^{-1} of soil) and 50% calcium oxide applied in a rate equivalent to one full hydrolytic acidity (10.93 g Ca kg^{-1} of soil). The experiment was run in three replications. Additionally, each pot was supplemented with macro- and micronutrients in the following amounts (in mg kg^{-1} of soil): N – 100 [$CO(NH_2)_2$], P – 30 [KH_2PO_4]; K – 100 [KH_2PO_4 + KCl]; Mg – 50 [$MgSO_4 \cdot 7H_2O$]; Mn – 5 [$MnCl_2 \cdot 4H_2O$]; Mo – 5 [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$]; B – 0.33 [$H_3BO_3$]. To set up the experiment, fuel oil, compost, bentonite and lime as well as the macro- and micronutrients in the form of aqueous solutions were mixed with 9 kg of soil, which was then placed in polyethylene pots. Afterwards, maize (*Zea mays* L.) cv. Reduta was sown. During the experiment, the soil moisture was maintained at the level of 60% of water capillary capacity. Soil samples for analyses were taken while harvesting maize in the intensive stem elongation phase.

The soil samples were dried and passed through a sieve (mesh 1 mm). The following determinations were made: content of organic carbon (C_{org}) with Tiurin method in potassium dichromate with diluted sulphuric acid

(LITYŃSKI et al. 1976), the content of available phosphorus and potassium with Egner-Riehm method (LITYŃSKI et al. 1976), the content of available magnesium with Schachtschabel method (LITYŃSKI et al. 1976). The results were processed statistically by a two-factorial analysis of variance ANOVA using Statistica software package (StatSoft, Inc. 2010).

RESULTS AND DISCUSSION

At present, with the natural environment being exposed to strong man-made pressure, we lack sufficient knowledge about the behaviour of elements, including potassium and magnesium, in soil. Any disturbance in the balance and ratios between particular elements may cause their transfer and modify concentrations in subsequent links of the trophic chain (SAPEK 2007).

In the series with no neutralizing substances added to soil, the content of organic carbon in soil rose by 86% (r=0.970) under the influence of increasingly higher rates of fuel oil (Table 1). In all the treatment tested in the present experiment, with or without soil amending substances, the content of organic carbon increased as the rates of fuel oil rose, which can be explained by the structure of petroleum derivatives, which consist of aliphatic (paraffin) hydrocarbons, cycloalkanes (naphthalene oils), arenes and olefins, while light fuel oil in turn contains up to 86% of carbon atoms (SOLECKI 2005). Similar results on the effect of petroleum compounds (diesel oil and petrol) have been reported by WYSZKOWSKI and ZIÓŁKOWSKA (2009c). In their study, the content of organic carbon in soil rose by 82%. Soil contamination with petroleum end products most strongly affects the content of organic carbon (OBIRE, NWAUBETA 2002, CARAVACA, ROLDÁN 2003, RIFFALDI et al. 2006). VINNIK and OVCHAROV (2004) found out a rise in soil pH caused by an increasing concentration of petroleum contaminants, while the content of organic carbon was two- to ten-fold higher. In the authors' own experiment, increased contamination of soil with fuel oil caused a considerable increase in the content of organic carbon in soil. KUCHARSKI and JASTRZĘBSKA (2005) also noticed that soil contamination with fuel oil most profoundly influences the content of organic carbon, which was positively correlated with increasing rates of the contaminant.

The content of available phosphorus in soil, compared to the other analyzed elements, did not show any regular changes in the treatments with increasing rates of fuel oil (Table 1). The content of available potassium in soil rose as the rates of fuel oil added to soil increased. In the series without neutralizing substances, the content of potassium in the treatments with the highest rate of fuel oil (20 g kg^{-1}) was twice as high as in the control soil, without fuel oil (r=0.975) – Table 1. Magnesium behaved similarly to

Table 1

Content of organic-C and available form of phosphorus (P), potassium (K) and magnesium (Mg) in soil after plants harvest

Dose of fuel oil (g kg^{-1} of soil)	Kind of substance neutralizing effect of fuel oil						
	without additions	nitrogen	compost	bentonite	zeolite	CaO	average
Organic (g kg^{-1})							
0	9.2	9.4	9.7	9.8	8.5	8.3	9.1
5	12.4	11.3	12.6	12.6	12.3	12.4	12.2
10	13.1	12.9	14.3	14.5	14.2	11.8	13.5
15	14.2	14.0	15.0	14.2	15.5	12.4	14.2
20	17.1	15.6	18.5	16.0	16.6	14.2	16.3
Average	13.2	12.6	14.0	13.4	13.4	11.8	13.1
r	0.970	0.996	0.978	0.939	0.966	0.861	0.973
LSD	a – 0.8**, b – 0.9**, a· b – 2.1**						
Phosphorus (mg kg^{-1})							
0	100.0	108.7	108.0	135.7	107.4	83.3	107.2
5	96.0	121.4	94.1	135.6	107.5	70.6	104.2
10	97.2	105.0	97.8	136.5	98.9	78.0	102.2
15	105.3	95.4	100.1	129.3	73.1	79.1	97.1
20	99.9	89.9	96.2	117.9	76.3	81.2	93.6
Average	99.7	104.1	99.2	131.0	92.6	78.4	100.8
r	0.401	-0.822	-0.519	-0.841	-0.910	0.141	-0.990
LSD	a – 3.7 **, b – 4.0 **, a· b – 9.0**						
Potassium (mg kg^{-1})							
0	89.3	131.5	128.2	186.6	103.9	131.5	128.5
5	100.7	176.9	129.9	144.5	131.5	147.7	138.5
10	139.6	173.7	147.7	214.2	136.3	157.4	161.5
15	180.2	172.0	178.5	230.4	157.4	199.6	186.4
20	186.6	160.7	183.4	222.3	154.2	186.6	182.3
Average	139.3	163.0	153.5	199.6	136.7	164.6	159.4
r	0.975	0.454	0.959	0.712	0.933	0.914	0.956
LSD	a – 5.3**, b – 5.8**, a· b – 13.0**						
Magnesium (mg kg^{-1})							
0	118.1	119.1	118.3	164.5	145.4	153.8	136.5
5	121.7	116.9	115.7	174.1	157.2	153.8	139.9
10	129.2	118.9	132.6	178.3	159.2	161.3	146.6
15	132.4	116.9	132.6	184.5	158.8	171.5	149.5
20	135.0	126.3	132.6	186.7	173.3	163.5	152.9
Average	127.3	119.6	126.4	177.6	158.8	160.8	145.1
r	0.983	0.587	0.837	0.977	0.916	0.791	0.990
LSD	a – 4.4**, b – 4.8**, a· b – 10.8**						

LSD for: *a* – fuel oil dose, *b* – kind of neutralizing substance;
significant for: ***p*=0.01; *r* – correlation coefficient

organic carbon and potassium in that its concentration in soil increased directly proportionally to the increase in the degree of soil contamination with fuel oil. The maximum increase was 14% (r=0.938) in the pot polluted with 20 g of fuel oil per kg of soil, compared to the control soil. The content of available macroelements in soil was correlated with the yield and uptake of elements by tested plants (WYSZKOWSKI, SIVITSKAYA 2011). The yield and uptake of the analyzed macroelements by plants in uncontaminated pots were higher than in the ones contaminated with fuel oil. A reverse relationship was observed in the content of available macroelements in soil.

WYSZKOWSKI and ZIÓ£KOWSKA (2008) noticed that the content of phosphorus decreased as the rates of diesel oil added to soil rose. A depressed content of phosphorus and an increased content of magnesium in soil exposed to petroleum hydrocarbons have also been reported by OBIRE and NWAUBETA (2002). In the experiments conducted by DIMITROW and MARKOW (2000), or WYSZKOWSKI and ZIÓ£KOWSKA (2009c), a lower content of phosphorus and elevated levels of magnesium and potassium appeared in soil contaminated with diesel oil, which - in terms of its properties – is similar to fuel oil. Such dependences have been confirmed in the present experiment.

Our comparison of the effects produced by all the tested neutralizing substances have demonstrated certain differences (Figures 1-2), which correlated with yields (WYSZKOWSKI, SIVITSKAYA 2011). The strongest effect was produced by bentonite and calcium oxide. In soil polluted with fuel oil (5 to 20 g kg^{-1}), bentonite contributed to a large increase in the average content of available forms of phosphorus, potassium and magnesium, by 30, 34 and 40% respectively, in comparison to the series without soil amending substances. Calcium oxide raised the average content of available potassium by 14% and magnesium by 25%, but lowered the content of organic carbon by an average 11% and that of available phosphorus by 23%. Zeolite favoured the accumulation of magnesium (+25%) in soil contaminated with fuel oil, in contrast to potassium (-5%) and phosphorus (-11%). Compost and nitrogen

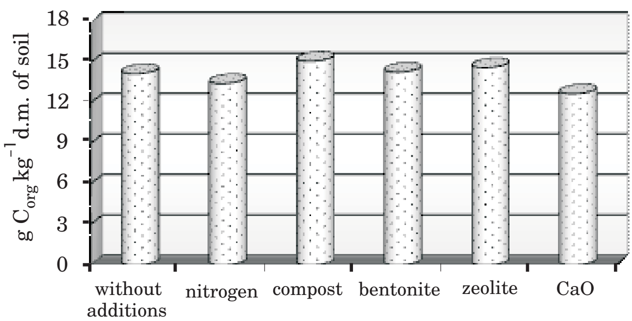

Fig. 1. Content of organic-C in soil after plant harvest
(average from series contaminated with 5-20 g fuel oil per kg of soil)

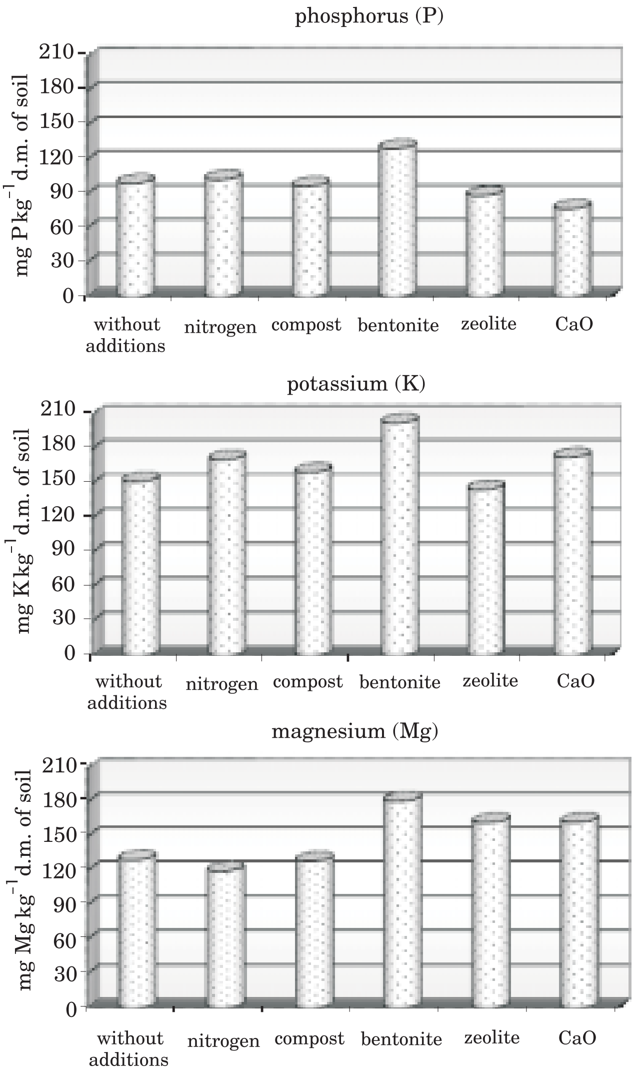

Fig. 2. Content of available forms of phosphorus, potassium and magnesium in soil after plant harvest (average from series contaminated with 5-20 g fuel oil per kg of soil)

produced much weaker effects. In the compost amended soil, a slight increase in the mean content of organic carbon and available potassium was noticed when compared to the series without any neutralizing substances. In turn, nitrogen caused a small decrease in the content of organic carbon and available magnesium but an increase in the content of potassium in soil.

The results obtained in the present experiment have been confirmed by studies reported by other authors (Kwiatkowska, Maciejewska 2008, Wyszkowski, Zió£kowska 2008, 2009c). Organic substance present in soil plays a very important role as it determines the quality of soil environment. The content of organic substance in soil can be raised by application of various substances, e.g. composts (Riffaldi et al. 2006, Quintern et al. 2006). In another experiment run by Wyszkowski and Zió£kowska (2008, 2009c), the biggest changes in soil properties were caused by bentonite and compost, while in the present study such modifications were attributed to bentonite and calcium oxide. In the study by Wyszkowski and Zió£kowska (2009c), application of compost to soil had a positive effect on the content of organic carbon and available potassium in soil, causing a two-fold and 24% increase in their concentrations, respectively. In another trial conducted by the same authors (Wyszkowski, Zió£kowska 2008), application of compost to soil did not have any significant effect on the content of magnesium but raised the content of phosphorus in soil contaminated with diesel oil. Kwiatkowska and Maciejewska (2008) also demonstrated that enrichment of soil with organic substance caused an increase in the content of macronutrients in soil, and lignite was a better source of organic substance in soil than peat or manure.

Wyszkowski and Zió£kowska (2008, 2009c) did not find evidence suggesting that bentonite had any significant effect on the content of organic carbon but proved that it significantly raised the content of potassium and magnesium, analogously to the results provided by the present experiment. Depending on a tested plant, bentonite either had no effect on the content of phosphorus (Wyszkowski, Zió£kowska 2009c) or caused an increase in the content of this element in soil (Wyszkowski, Zió£kowska 2008).

Soil liming improves soil porosity, stability and other physicochemical properties; it also creates a more suitable environment for soil microorganisms (Kucharski, Jastrzêbska 2006), which may have a favourable influence on the content of available elements in soil. In the study conducted by Gruba (2009), increased solubility of organic matter was found out in soils of pH less than 4-4.5, and two elements, i.e. aluminium and iron, which are capable of saturating function groups (mainly COOH), played the most important role in dissolving and precipitating organic matter. In the experiment conducted by Wyszkowski and Zió£kowska (2008, 2009c), calcium oxide had a favourable effect on the content of phosphorus, potassium (Wyszkowski, Zió£kowska 2008) and magnesium in soil (Wyszkowski, Zió£kowska 2009c).

Mercik et al. (1995) observed that an increase in the content of organic carbon in soil was the smallest when mineral nitrogen had been applied, bigger after application of farmyard manure and the biggest – when both fertilizers had been introduced to soil simultaneously and leguminous plants had been sown.

CONCLUSIONS

1. The content of organic carbon and available potassium and magnesium in soil was positively correlated with the increasing rates of fuel oil, whereas changes in the content of available phosphorus did not show any regularity. The highest increase in the concentration of the analyzed soil components was found for potassium.

2. The substances introduced to soil in order to neutralize the effect of fuel oil on soil properties caused the weakest changes in the content of organic carbon but affected most profoundly the content of available potassium and magnesium.

3. Compared to the series without soil amending substances, bentonite caused an increase in the average content of available forms of phorphorus, potassium and magnesium, whereas calcium oxide modified the content of available potassium and magnesium. CaO decreased the content of organic carbon and available phosphorus in soil.

4. The effect of the other tested soil amending substances on the analyzed soil properties was weaker than that produced by bentonite or calcium oxide, and the direction of changes in the levels of the elements depended on the type of a substance.

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