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MIGRATION OF VARIOUS CHEMICAL COMPOUNDS IN SOIL SOLUTION DURING INDUCTED PHYTOREMEDIATION

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Abstract: The induction of phytoremediation by addition of complex substrates, such as sewage sludge (e.g. from the food industry), allows for better conditions of plant growth, however, it also increases the risk of chemical compounds leaching to the soil solution. Biogenic compounds occurring in sludge such as nitrogen, organic carbon and phosphorus when migrating with soil solution down the soil profile can lead to underground water contamination. The paper assesses the effect of sewage sludge inducted phytoextraction of Zn, Cd and Pb with the use of *Sinapis alba* L. (White mustard), *Medicago sativa* L. (Alfalfa) and *Trifolium resupinatum* L. (Persian clover) as well as the migration of biogenic compounds (nitrogen, organic carbon and phosporus) in soil solution. Research was conducted in controlled conditions of a phytotronic chamber in which the lysimetric experiment was carried out in order to monitor the changes of total nitrogen, ammonia, phosphates, organic carbon and pH every 3 weeks during the 112 days of the entire experiment. Based on the obtained results it was found that there is no risk of underground water contamination by investigated substances present in sewage sludge, because there was no indication of increased ammonia and carbon migration to the deeper parts of the soil profile.The only exception was the migration of nitrogen compounds other than ammonia (possibly nitrates and nitrites). Due to sewage sludge application the highest concentrations of ammonium nitrogen (211 mgN-NH_4 l^{-1}), total nitrogen (299 mg N l^{-1}) and organic carbon (200 mg TOC l^{-1}) were noted at a layer of 30 cm (from top of the column/lysimeter) after 3 weeks of the conducted process. With time a decrease of ammonium nitrogen as well as organic carbon concentration in all columns was noted. There was no indication of phosphates in the soil solution during the entire experiment, which was due to the high cation exchange capacity of the soil matrix.

INTRODUCTION

Nowadays there is a considerable interest in the use of phytoremediation technologies for reclamation of environment contamination and degradation. Numerous studies have examined the ability of plants to take up a variety of elements from divers media [7, 10, 14].

Phytoremediation is an emerging low-cost technology but needs to be inducted to achieve high level of effectiveness. One of the wide range of „phyto-inductors" is sewage sludge from different waste water treatment plants which have unique properties. Their use as fertilizer is increasing because land application is considered a more environmental friendly disposal method and because of its great fertilizer value [3, 5, 6, 13].

Sludge effect upon soil and plants is complex because sludges supply all nutrients indispensable for plants, which become successively available to plants during their growth and also improve physical, chemical and biological soil properties. This is related to high amounts of organic matter, significant quantities of macro- and micronutrient, and also high abundance of microflora (bacteria and fungi). However "sludge-effect" strongly depends on the nature of sludge which varies with the type of sewage and the treatment process. For example, aerobically digested sludges often have higher nitrogen content and sludges from food industry wastewater have low toxic compounds content [8, 10, 11, 20, 21].

However, sludge may contain various contaminants, such as inorganic potentially toxic elements, and persistent organic compounds so it is very important to select sewage sludge correctly to ensure positive "sludge effect" without negative environmental influence. A great controversy still exists concerning the availability of "sludge-born" compounds after the application of this substratum to the soil [1–4, 9, 12].

Therefore, the movement of chemical compounds down the soil profile is of a great importance. It involves the risk of groundwater contamination and deterioration. This can be overcome by selecting the optimum dose of sludge application and plant species, which is very difficult to determine because of restrictions that depend on soil parameters, such as pH, CEC and water content [21].

The composition of sludge may change in time but it is well known that high buffering properties of sludges limit the compouds release to soil solution.

Despite the buffering properties the release of organic matter and macro-, micronutrients to emended soils (as a result of slow decomposition of sewage by microbiological and physico-chemical reactions) may still have significant deleterious effect upon groundwater, crop quality and biological soil fertility [1].

Therefore, the objective of our study was to investigate migration (leachability) of dissolved forms of C, N, P and K down the soil profile where sewage sludge was applied in column experiments in which the fate of chemical compounds in soil profile can be established.

MATERIALS AND METHODS

Samples of aerobic stored sewage sludge were obtained from the food industry (production of mineral waters) waste water treatment plant. This plant treats wastewater by activated sludge and biological bed processes. The produced sludge was dewatered. A series of initial analyses was carried out for sludge characterization purposes. The physicochemical characteristic of sludge used in experiment is shown in Table 1.

Table 1. Physiochemical characteristics of sewage sludge used in the experiment

Parameter	Unit	Vvalue
Humidity	*%*	**91.3**
pH in H_2O	-	**7.18**
Total nitrogen	*mg kg^{-1} d.m.*	**14 700**
Total phosphorus	*mg P_2O_5 kg^{-1} d.m.*	**4010**
Assimilable phosphorus	*mg P_{og} kg^{-1} d.m.*	**733**
K	*mg kg^{-1} d.m.*	**6 866**
Zn	*mg kg^{-1} d.m.*	**54.5**
Cd	*mg kg^{-1} d.m.*	**0.267**
Pb	*mg kg^{-1} d.m.*	**8.7**

The soil was collected from an industrial area located near a zinc smelter Miasteczko Śląskie. The soil was transferred to one meter high columns in such a way that the natural pattern of soil layers was kept intact. A series of initial analyses was carried out for the purpose of soil characterization. The physicochemical characteristic of soil used in experiment is shown in Table 2.

Table 2. Physiochemical characteristics of soil used in the experiment

Parameter	Unit	Value
Humidity	%	**6.98**
pH in H_2O	-	**4.86**
pH w 1M KCl	-	**4.63**
CEC (cation exchange capacity)	*cmol* kg^{-1} *d.m.*	**273.5**
Humic acids	%	**2.0**
TOC (total organic carbon)	*mg* kg^{-1} *d.m.*	**0.735**
Total nitrogen	*mg* kg^{-1} *d.m.*	**14 760**
C:N	-	**773.5**
Total phosphorus	*mg* P_2O_5 kg^{-1} *d.m.*	**19:1**
Assimilable phosphorus	*mg* P_{og} kg^{-1} *d.m.*	**66.5**
K	*mg* kg^{-1} *d.m.*	**120**
Zn	*mg* kg^{-1} *d.m.*	**406**
Cd	*mg* kg^{-1} *d.m.*	**17**
Pb	*mg* kg^{-1} *d.m.*	**810**

The experiment was performed in 100 cm high, 15-cm diameter plastic columns. In each column on three levels (30 cm, 50 cm and 80 cm) a lysimeter with a membrane filter (Rhizon soil pore water samplers – Eijkelkamp) was present to collect soil filtrate. In all of the columns sludge constituted 30% (w/w) of the upper (30 cm) soil layer. Sewage sludge was added directly to the top of the soil in the column and mixed to the depth of 30 cm. After 2 weeks in nine columns seeds were sown (one genus for three columns). Plants from the following genera: *Sinapis alba* L. subsp. *alba*, *Medicago sativa* L. and *Trifolium resupinatum* L. were used. Other three columns were left without plants (verification column – control).

The experiment lasted for about 4 months. During this time the columns were watered (to 70% of the total water holding capacity) and soil filtrates were collected in 3 weeks intervals. About 2 days were usually required to extract 50 ml of soil solution by lysimeter (by the vacuum). The extracted solutions were clear and ready for analysis (membrane filter average pore size of 2.5 um). Plants were cultivated in a phytotronic chamber at 21 degrees Celsius during day time and 18 at night. Photoperiod was 16 hours day and 8 night.

To determine the initial dissolved C, N, P, K content ISO norms were used [15–18].

RESULTS AND DISCUSSION

Soil has a high binding capacity for a wide range of substances, which is dependent on physical and chemical properties of it. But soil pollution contributes to atrophy of its feature, so there is a need for remediation. It is generally known that sewage sludge supplemented to the soil causes an apparent increase in TOC and TN content (Tabs. 1, 2, 3).

Table 3. Physiochemical characteristics of soil mixed with sewage sludge used in the experiment

Parameter	Unit	Value
Humidity	%	**3.24**
pH in H_2O	-	**6.11**
pH w 1M KCl	-	**5.53**
CEC (cation exchange capacity)	*cmol kg⁻¹ d.m.*	**4.1**
Humic acids	%	**0.863**
TOC (total organic carbon)	mg kg^{-1} d.m.	24 710
Total nitrogen	*mg kg^{-1} d.m.*	**1750**
C:N	-	**14:1**
Total phosphorus	*mg P_2O_5 kg^{-1} d.m.*	**146.7**
Assimilable phosphorus	*mg P_{og} kg^{-1} d.m.*	**630**
K	*mg kg^{-1} d.m.*	**5 787**
Zn	*mg kg^{-1} d.m.*	**302**
Cd	*mg kg^{-1} d.m.*	**12.71**
Pb	*mg kg^{-1} d.m.*	**977**

Though sewage sludge nutrition effect on soil properties may vary, the investigated values have shown that soil sorption increased with increasing pH, TOC and CEC (Fig. 1).

Changes in pH of filtrates from three test layers indicate a lowering tendency during the process. Moreover, the differences observed between the layers where: the highest pH in a layer 30 cm (from 8 to 6.2) and the lowest in a layer of 80 cm (from 5.6 to 4.6). The differences in pH between the levels resulting from natural (layered) character of the tested soil and the changes during experiment are likely to be a result of microbial activity in sewage decomposition.

Soil solution from surface soil amendment with sewage sludge (30 cm layer) increased substantially the concentrations of all the investigated compounds. The maximum concentrations of ammonia reached 160 mg l^{-1} (Fig. 2) in the first 3 weeks in the column with *M. sativa*.

In other columns the same trend was observed but the values were much lower (60 mg l^{-1}). In deeper levels of soil profile (50 and 80 cm layer) an increase of ammonium after the first three weeks of experiment was observed. The maximum concentrations reached from 5 to 20 mg l^{-1} so, if this appreciation indicates leaching, the magnitude of ammonia concentrations was so small that movement from upper to deeper layers is not environmentally dangerous.

Similar tendencies were also observed in changes of TOC and potassium concentrations in soil solution (Fig. 3, 4).

There was no indication of relevant fluctuation in low level potassium concentrations and leaching of dissolved organic carbon into the lower layers in the column.

It is clear that soil amended with s. sludge has a high binding capacity for dissolved ammonia, carbon and K, which is correlated and dependent on physiochemical properties

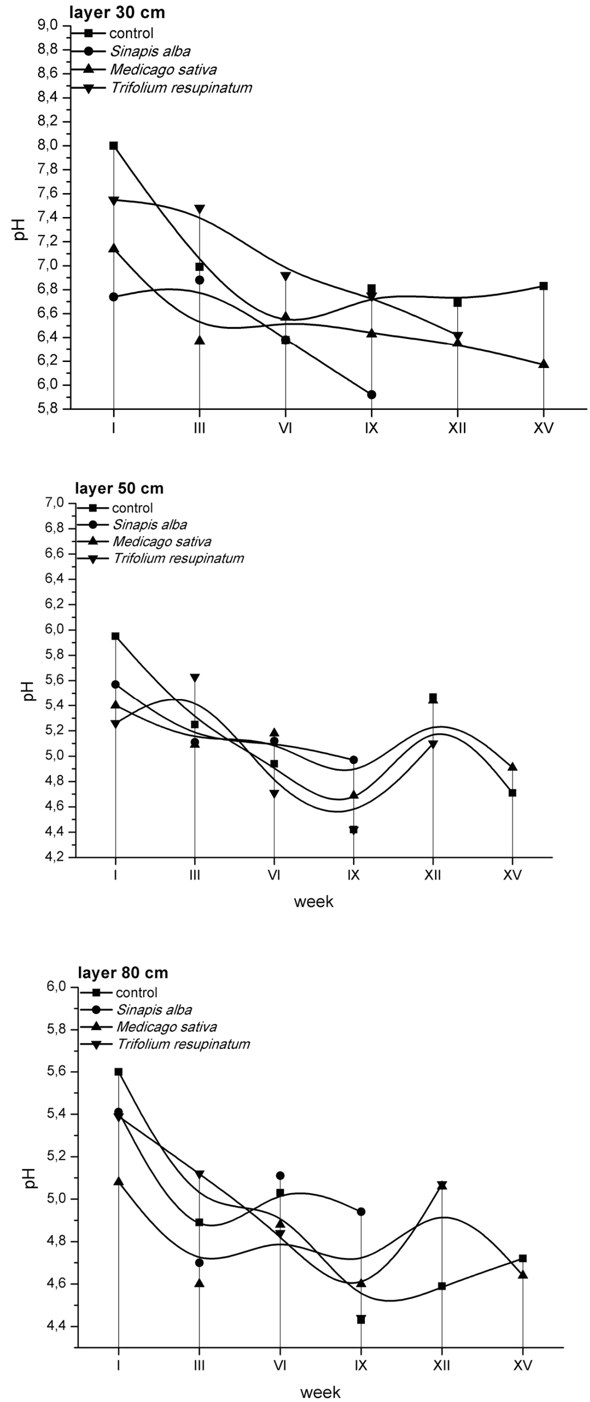

Figure 1. Changes of pH in soil solution from different layers

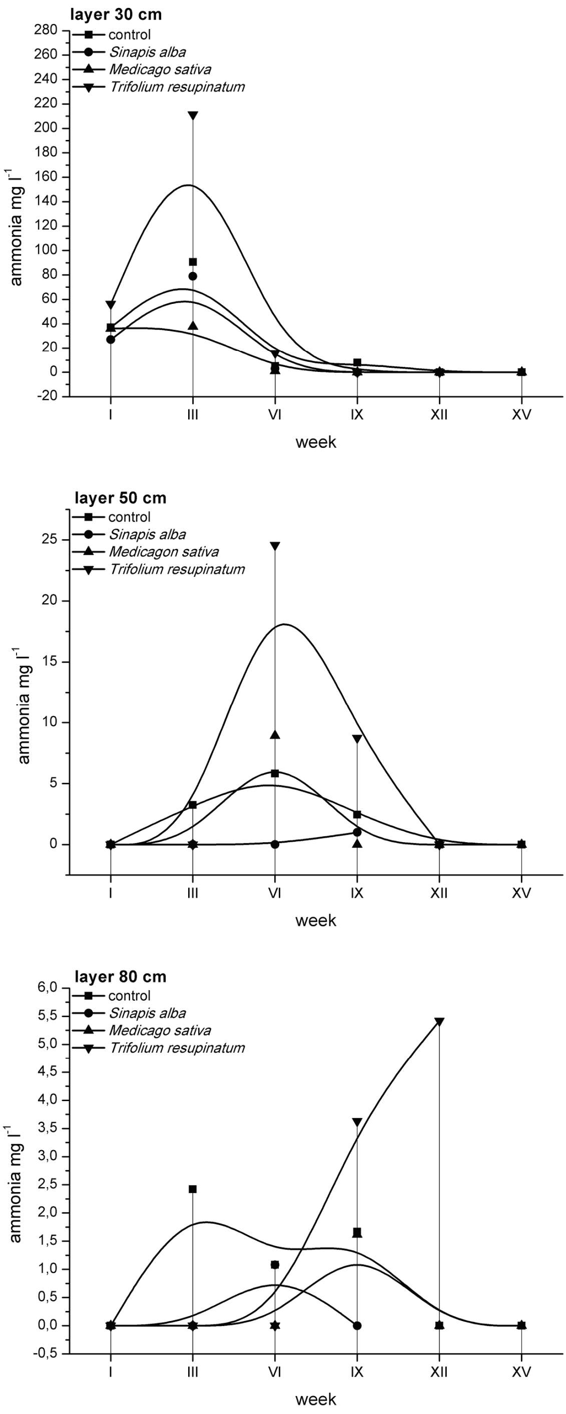

Figure 2. Changes of ammonium in soil solution from different layers

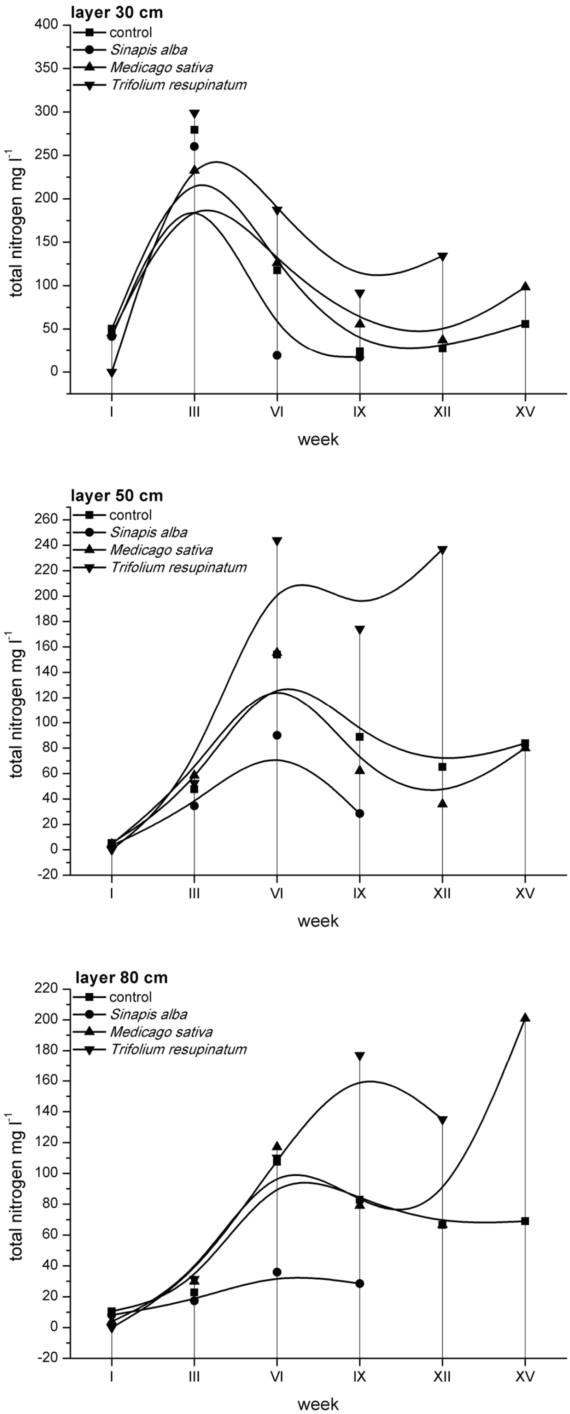

Figure 3. Changes of total nitrogen in soil solution from different layers

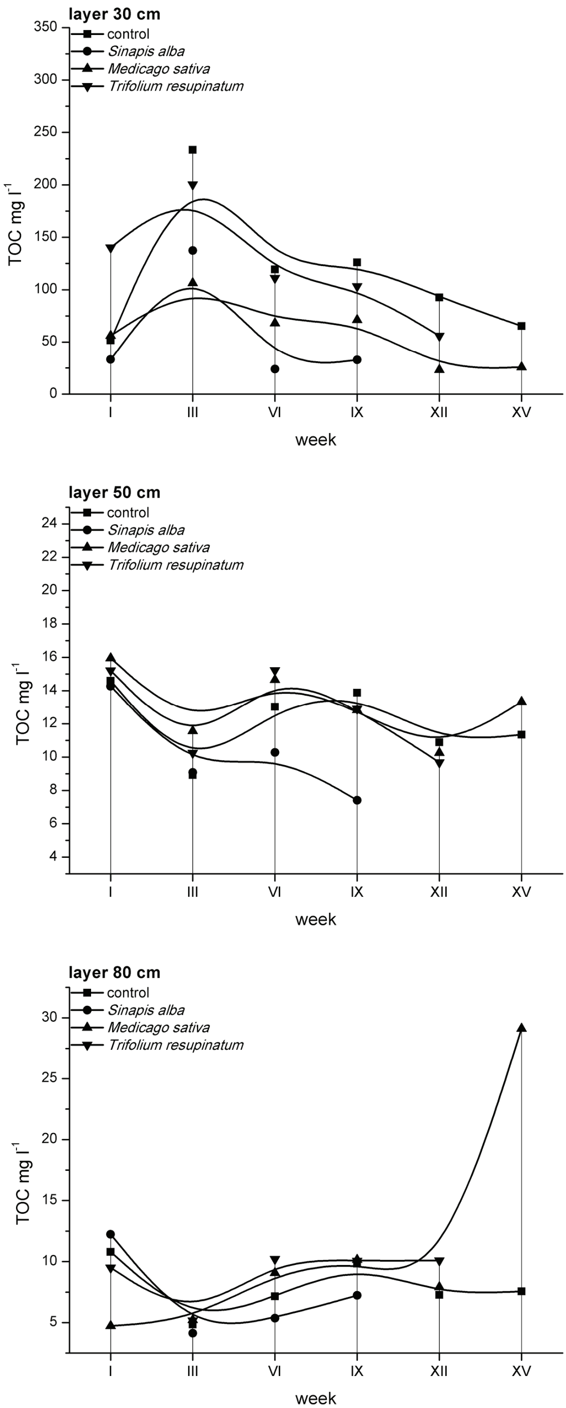

Figure 4. Changes of TOC in soil solution from different layers

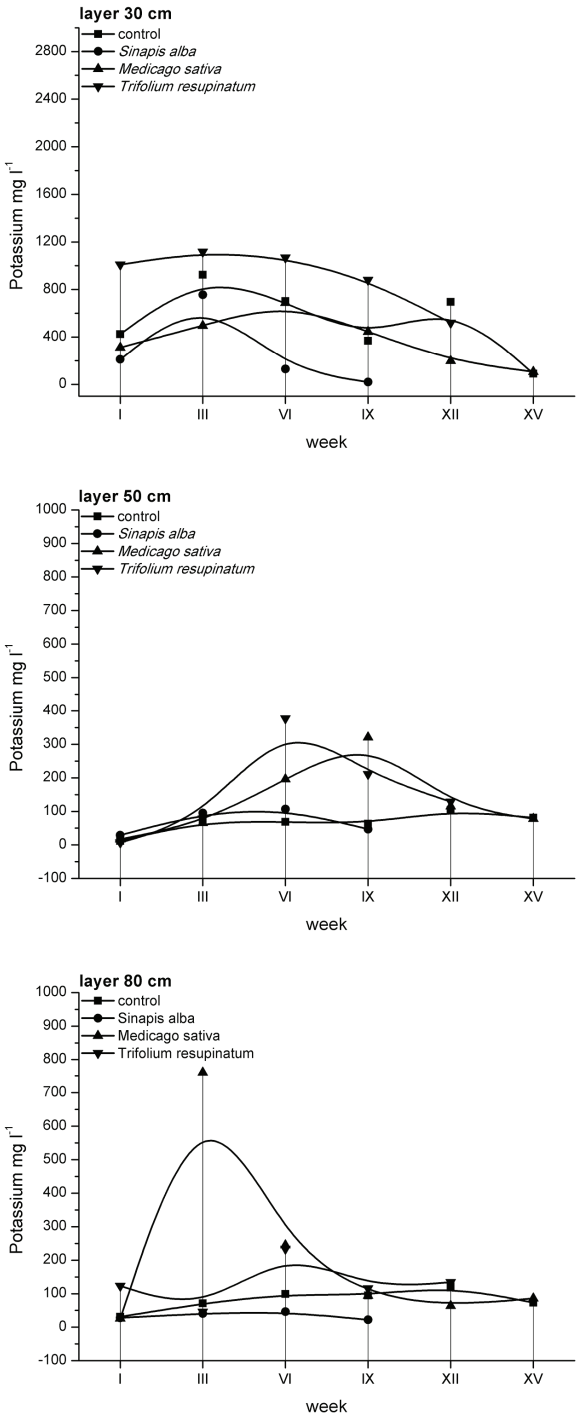

Figure 5. Changes of K in soil solution from different layers

of s. sludge in the soil and soil itself. Similar tendencies were observed by Samaras *et al.* [19].

However, changes in total nitrogen concentration in whole soil profile indicates the possibility of leaching. The maximum TN values reached approx. 220 mg l^{-1} in all layers and increasing tendency in lower layers (50 and 80 cm) was related with decreasing one in upper layers. This indicates the repositioning of nitrogen compounds (except ammonium) deep in soil profile.

In the presented experiment it was found that the concentrations of "sludge-born" substances are generally greatest immediately following sludge addition to the soil due to soluble/readily degradable organic matter and unstable organic compounds. Some researchers call this phenomena "initial peak" measured in soil solution followed by the reduction in availability. In addition, very important is the magnitude of the initial flush, and how long it takes.

CONCLUSIONS

The column experiment may be useful to study the movement of "sludge-born" substances in soil profile, which is necessary to determine potential groundwater contamination.

In the conducted experiment a decline in pH (during process) of soil solution at all tested levels in the column was found.

There were no significant changes between the columns in the content of TOC, ammonia, and measuring levels of potassium, and therefore also there was no risk of leaching of these compounds into the soil profile.

There has been observed a washout of nitrogen compounds (other than ammonia) to the deeper layers of soil in the column at concentrations similar to all tested levels (about 250 mg l^{-1}), which indicates the possibility of groundwater contamination.

Surface soil amendment with sewage sludge posed a risk of groundwater contamination with nitrates other than ammonium. A balance should be achieved between plant nutrients to optimize crop vegetation and control of nitrogen leaching to protect the environment and human food chain. This matter is of a great importance due to the fact that the degradation of the more easily degradable forms of sewage sludge organic matter by soil microflora is rapid and it is followed by a period of slower degradation.

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MIGRACJA WYBRANYCH ZWIĄZKÓW CHEMICZNYCH W ROZTWORZE GLEBOWYM PODCZAS INDUKOWANEJ FITOREMEDIACJI GLEB

Wspomaganie procesu fitoekstrakcji wprowadzeniem do gleb substratów złożonych takich jak osady ściekowe (z przetwórstwa spożywczego), niesie ze sobą nie tylko stworzenie warunków do poprawy wzrostu roślin, lecz także ryzyko zwiększenia wymywania związków chemicznych do roztworu glebowego. Związki biogenne pochodzące z osadów, tj. azot, węgiel i fosfor, przemieszczając się z roztworem glebowym w głąb profilu, mogą przyczynić się do zanieczyszczenia wód podziemnych. W pracy oceniono wpływ indukcji osadami ściekowymi procesu fitoekstrakcji Zn, Cd i Pb w uprawach gorczycy, lucerny i koniczyny na zmiany pH oraz migrację związków biogennych (azotu, węgla i fosforu) w roztworze glebowym. Badania prowadzono w kontrolowanych warunkach komory fitotronowej, w której założono doświadczenie lizymetryczyne, monitorując zmiany azotu całkowitego, amoniaku, fosforanów, węgla organicznego i pH co 3 tygodnie w ciągu 112 dni trwania całego procesu. Na podstawie przeprowadzonych badań stwierdzono, iż w przypadku większości badanych związków pochodzących z osadów ściekowych nie istnieje ryzyko zanieczyszczenia wód podziemnych, ponieważ nie zaobserwowano wzmożonej migracji amoniaku i węgla do głębszych warstw profilu glebowego. Odstępstwem od tej zależności jest migracja związków azotu innych niż amoniak (przypuszczalnie azotany i azotyny). Aplikacja osadów ściekowych spowodowała, iż po 3 tygodniach prowadzenia procesu odnotowano najwyższe stężenie azotu amonowego (211 mg $N\text{-}NH_4$ l^{-1}), azotu całkowitego (299 mg N l^{-1}) oraz węgla organicznego (200 mg TOC l^{-1}) na poziomie pomiarowym 30 cm (od początku kolumny). W miarę upływu czasu we wszystkich kombinacjach obniżyła się zawartość zarówno azotu amonowego, jak i węgla organicznego. Natomiast w przypadku fosforanów nie stwierdzono ich obecności w roztworze glebowym w ciągu całego procesu w związku z silną sorpcją zachodzącą w glebie.