

Soil profile as a natural membrane for heavy metals from wastewater

T. Włodarczyk*, B. Witkowska-Walczak, and U. Majewska

Institute of Agrophysics, Polish Academy of Sciences, Doświadczalna 4, 20-290 Lublin, Poland

Received May 31, 2011; accepted August 29, 2011

Abstract. The effect of intensive irrigation with wastewater on the zinc (Zn) and cadmium (Cd) concentration in soil solution was investigated. The experiment was parallel conducted on two soil profiles. The soil microcosms were watered with purified wastewater and purified wastewater with an the addition of zinc and cadmium. The results indicate clearly that neither intensive overhead irrigation of the soil nor its flooding with these wastewater and exceeded sorptive capacity. The application of treated wastewater and wastewater with heavy metals addition did not appear to pose a threat to the natural environment. In all the cases under analysis, zinc and cadmium concentrations in the soil solution were several-fold lower than the permissible levels.

Key words: soil profile, wastewater, zinc, cadmium

INTRODUCTION

Heavy metals commonly occur in soils, due to their release from the parent rocks in the course of soil formation. Their natural concentration, generally do not pose a threat to the ecosystems (Basta *et al.*, 2005). Undesirable concentration of metals can occur in soil as a result of agricultural and anthropogenic activities (Hayian and Stuanos, 2003). The protective role of the soil lasts as long as its biogeochemical balance is not disturbed. Thanks to its sorptive properties, the soil acts as a natural filter and absorbs, among other things, toxic compounds (Malkoc *et al.*, 2010). Soil profile represents a major sink for heavy metals in the terrestrial environment (Foster and Charlesworth, 1996). It is evident that heavy metals introduced with compost or wastewater cause the accumulation of soil organic matter (Hanc *et al.*, 2008) and decrease the turnover rate of organic matter, presumably because of inhibitory effects of heavy metals on microbial biomass. The sorption of heavy metals by organic matter retards metal movement within the soil environment and reduces the potential for toxicity. Usman *et al.* (2005)

found that the addition of clay minerals, especially of Na-bentonite and Ca-bentonite, decreases the extractability of zinc (Zn), cadmium (Cd), copper (Cu) and nickel (Ni) during incubation. Soil reaction (pH) largely determines the mobility and bioavailability of heavy metals with increasing acidification (Kashem and Singh, 2001). Change in soil reaction in alkaline direction reduces the uptake of heavy metals by plants and inhibits their migration to the groundwater (Gondek *et al.*, 2010; Lepp and Madejón, 2007; Li *et al.*, 2010; Singh and Agrawal, 2007). It was found that a woodland dominated by willow (*Salix*) represented a potentially sustainable remediation option for sequestration of zinc and cadmium through the soil and willow downloads (uptake) (Guo and Marschner, 1995).

In some cases industrial wastewater constitutes a serious threat for the water environment, but on the other hand draining liquid wastes to the ground is the oldest form of their disposal (Mehler, 2010). It is the most natural method, as the substances return to the point of their introduction, and also the process of circulation of matter. A study conducted by Stepniewska *et al.* (2009, 2010) did not show any negative effect of metals (Mn, Ni, Pb) from wastewater after the 2nd stage of purification on the growth and yielding of grass communities. The drainage of wastewater to the ground and their agricultural utilization constitute an alternative solution of the problem of protecting the quality of water in reservoirs (Juhler *et al.*, 2001).

In the soil zinc is found as ions bound by soil minerals and organic matter, in plants it regulates the metabolism of carbohydrate and protein compounds and occurs in enzymes. Excessive concentration of zinc inhibits the activity of proteins bonding calcium and affects the copper and iron economy. Zinc is an element of generally limited mobility in soil and

*Corresponding author's e-mail: teresa@ipan.lublin.pl

its content in the arable soils varies between 25 and 300 mg kg⁻¹. Changes in soil reaction (pH) in the alkaline direction, high content of PO₄²⁻, high content of organic matter and low moisture may retard the availability of zinc. Low reaction of soil is the primary factor that is conducive to zinc migration (Andevsson and Nillson, 1974; Sanders *et al.*, 2006).

Cadmium is a heavy metal that is described as highly toxic to some organisms in nature (Alloway, 1990; Mann, 2002). Cadmium belongs to a group of elements that display very rarely physiological function. Lune *et al.* (2005) found that the ocean biota contains a vast reservoir of genomic diversity. They presented the sequence and preliminary characterization of a protein that is a cadmium-containing carbonic anhydrase from the marine diatom *Thalassiosira weissflogii*. The existence of a cadmium enzyme in marine phytoplankton may indicate that there is a unique selection pressure for metalloenzymes in the marine environment.

Its solubility in soil depends on soil reaction; for example, as soil pH increases soluble forms of cadmium decrease (Andevsson and Nillson, 1974). Even relatively low amounts of the metal may have a toxic effect on living organisms (28-day EC50sto soil invertebrates range from 0.01 to >1000 mg kg⁻¹ (Ecotox, 2010). Soil acidity itself tends to increase the solubility and availability of cadmium, and this may increase concentration in some of the tissues of certain plants consumed by animals and humans. Cadmium can be toxic to species occupying trophic levels from primary consumers to upper trophic consumers. Moreover, cadmium, because of its similarity in molecular size and charge, can substitute for essential metals in several biochemical pathways, with resulting toxicity. Among others, Cd also interferes with Ca functioning in cells by blocking or competing for uptake (Stoiber and Shafer, 2010). Intensive irrigation of soils with wastewater constitutes a potential hazard from heavy metal accumulation in amounts that exceed their permissible concentration in soil solutions.

The quantity of municipal and rural wastewater discharged has substantially increased over the last twenty years. Thus efficiently treating wastewater is essential given the potential discharging substantial concentrations of metals. The membrane biological reactors (MBR system consists of a suspended-growth biological reactor combined with a membrane ultrafiltration unit process) seem to be the future for solving wastewater purification problem (Witkowska, 2007). The MBR installation permits the modernization of existing wastewater treatments, decentralization of wastewater purification, as well as the building of near-house treatment systems with possibility of using the purified wastewater, among others, for watering (Wei *et al.*, 2003; Zhou and Smith, 2001). Recent results of investigations have showed that MBR removes nearly of 90% of N compounds and average 46% of P compounds (totalled with precipitating compounds). However, the use of these modern devices does not allow to stop the accumulation of heavy metals (Clara *et al.*, 2005; Fan *et al.*, 2006; Gonzáles *et al.*, 2006; Holakoo, 2007).

The aim of this study was to examine the possibility to which organic soil can be useful for wastewater purification with their natural charge of zinc and cadmium as well as under increased concentrations.

MATERIALS AND METHODS

The study was conducted on two soil profiles (30 cm in diameter and 100 cm high) in laboratory conditions. The plot was tilled as a grassland and drained. The ground water table was stabilized at 60-70 cm depth. Two soil profiles (monoliths) were taken in their natural state from a drained grassland plot located near wastewater treatment plant (WWTP) Hajdów close to Lublin city (SE Poland), which was experimental plot irrigated with wastewater (3rd stage wastewater purification). After the collection of soil microcosms the initial concentration of heavy metals in soil solutions of the test plot at different profile levels was measured (natural soil – NS). The plot was irrigated with purified wastewater (after 2nd stage – mechanical-biological purification) from the WWTP Hajdów until the soil microcosms collection. The two soil microcosms were transported to the laboratory and secured by wrapping their side surfaces with fabric saturated with an epoxy resin. The soil microcosms prepared in this way were placed in specially prepared containers with water solution corresponding to that of the ground water composition from the area of sampling. Methods for characterization composition and parameters measured are described by Włodarczyk and Kotowska (2005). Six ceramic filters were placed for soil solution sampling with tube derived from outside the microcosm at every 15 cm (starting from 15 cm at soil surface) in each of them. At the end of the tubes were needles to pull the solution through a vacuum produced in bottles (Fig. 1).

The microcosms were built of a muck soil developed from intensively mineralized peat. The surface (0-5 cm) layer of the soil microcosm was turf, the deeper parts were muck (till 40 cm) and peat layers with mineral elements and

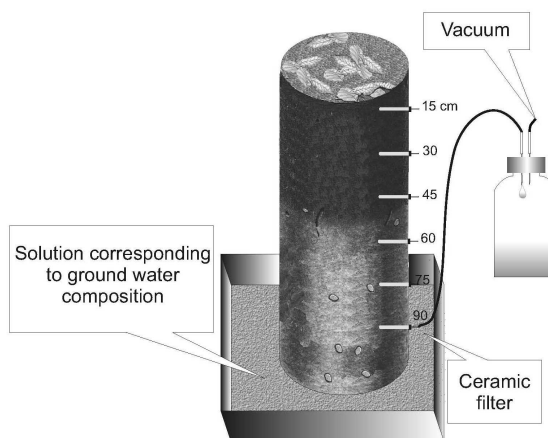


Fig. 1. Scheme of the studied soil microcosm.

ferruginous precipitations. Organic matter content in the soil profile varied from 17.1 to 38.8 g 100 g⁻¹ (its content in the soil profile was as follows: 0-10 cm – 17.1, 10-30 cm – 24.6, 30-50 cm – 38.8, 50-70 cm – 31.0), CaCO₃ from 1 to 7 g 100 g⁻¹, and pH_{KCl} was from 7.14 to 7.18. Bulk soil density was 0.77 (±0.05 as standard error) g cm⁻³. The total and differential porosity were determined using the standard pressure chambers (Soil Moisture Equipment Comp., Santa Barbara, USA). Water conductivity in the saturated zone of the soil was measured by means of a permeameter (Eijkelkamp Comp., Giesbeek, the Netherlands), whereas unsaturated conductivity of the soil – using the Time Domain Reflectometer (TDR-meter – Easy Test Comp., Lublin, Poland) (Walczak *et al.*, 2001; Włodarczyk and Witkowska-Walczak, 2006).

Before the main experiment, two soil microcosms were watered with rainfall water (from pluviometer) by sprinkler during 10 days (three times a day). The total amount watered was 10 mm, the mean day rainfall for this area during the vegetation period. This procedure established uniform conditions during the study.

After 10 days of watered with rainfall water:

- 1st soil microcosm was watered with the wastewater every five days in five irrigation series. Analyses were done after 1st, 2nd, 4th and 5th day after irrigation (the average values of the five irrigation series are shown as data). The wastewater was applied to the microcosm surface once in the amount of 80 mm;
- 2nd soil microcosm was watered in parallel with the wastewater and with heavy metals addition in the following amounts: zinc – 500 µg dm⁻³ and cadmium – 15 µg dm⁻³. Layer of solution in which the microcosms were immersed during the experiment was maintained at a level of several centimeters.

The soil solutions were sampled systematically and Zn and Cd concentrations were measured by the standard methods using an ASA spectrophotometer (Hitachi type Z-8200). In parallel, pH values were measured by an Orion model 231 pH-meter.

RESULTS AND DISCUSSION

The physicochemical properties of wastewater used for irrigation are presented in Table 1. It can be stated that they are near the average values observed during the last 10 years in the municipal wastewater from Lublin. Their variability showed that pH values fell within the range of 6.47-8.41. Zinc and cadmium occurred in amounts not exceeding the permissible (according to Polish standard) concentration for wastewater heavy metals introduced into the soil. The concentrations of heavy metals do not display seasonal changes. Within a 24-hour period the concentration of zinc may vary within a broad range of 20-360 µg dm⁻³, whereas, the mean weekly concentrations of zinc fall within the range of 114-242 µg dm⁻³. Cadmium concentration varies within the range of 0-31 µg dm⁻³, most often averages about 12 µg dm⁻³, and

Table 1. Physicochemical parameters of the used wastewater

Parameters	Units	Wastewater (applied)	Wastewater*
pH	-	7.2	6.47-8.41
N _{tot}	mg dm ⁻³	31.3	22.3-43.6
P _{tot}	mg dm ⁻³	4.3	3.6-6.9
Na ⁺	mg dm ⁻³	50.8	24.3-69.4
K ⁺	mg dm ⁻³	10.7	11.8-27.7
Ca ²⁺	mg dm ⁻³	69.8	58.4-89.2
Mg ²⁺	mg dm ⁻³	14.5	12.5-18.4
Zn	µg dm ⁻³	195.0	20-360
Cd	µg dm ⁻³	14.0	0-31

*Range of max and min values observed in 2001-2010.

often is not observed. It is clear that the concentration of heavy metals in the wastewater depends on whether the technological processes in the treatment plant are running properly, especially the 2nd stage of purification with the biologically active sediment. Heavy metals are absorbed to a considerable extent by the biologically active sediment, provided it is not disturbed by physical or biological conditions. The characteristics of the wastewater used for the irrigations are detailed in Table 1. pH averaged – 7.2, Zn concentration – 195 µg dm⁻³ and Cd – 14 µg dm⁻³. Metal concentrations meet Polish requirements for wastewater introduced in the soil, with respect to heavy metals (Zn < 2 000 µg dm⁻³, Cd < 100 µg dm⁻³) (Kotowski, 1998).

Intensive irrigation of the soil microcosms with simulated rain under laboratory conditions did not cause any notable changes in the soil reaction. The pH values sampled under laboratory conditions varied between 7.3 and 7.7 and they were almost identical to those sampled under natural conditions, with slightly higher values (7.9) observed from time to time. Long-lasting rains usually cause an increase of soil acidification. Because of the short duration of these experiment we did not measure an increase in soil acidification that is usually occurs following natural rainfall.

The hydrophysical characteristics of the soil of which the microcosms were built created good conditions for water retention and movement. The total porosity of nearly 80% vol. indicates that the studied soil is capable of holding amounts of water of all categories. The amount of free water *ie* water subjected to the effect of gravity, was 26% vol. that of capillary water – 54% vol., and within that, water unavailable to plants *ie* very strong bound to soil – 28% vol. Such a characteristic of static hydraulic properties caused the dynamics of soil waters in the experimental object to be favourable. The out flow occurred at the rate of 183 cm day⁻¹ in soil fully saturated with wastewater. When the soil is not

saturated with water *ie* after the wetting front goes down to the ground water table, the hydraulic conductivity coefficient decreases. In extreme conditions for the studied soil microcosms (depth of ground water table equal to 90 cm), its values at the surface are from 3 to 1 cm day⁻¹. Nearly the same conditions for the water retention and movement for organic soils have been reported (Walczak *et al.*, 2001; Włodarczyk and Witkowska-Walczak, 2006).

Irrigation of the soil microcosms with simulated rain (SR) under laboratory conditions did not cause any greater increase in zinc concentration in the soil solutions during the ten-day period of irrigation (Fig. 2a) as compared to the mean concentration of Zn in soil solution under natural conditions (NS), except for the depths of 45–75 cm on the 8th and 10th day of analysis. On the 4th day of analysis Zn concentration in the whole profile was lower than in the control soil. The average concentration of Zn for 10 days of irrigation was lower than or equal to the concentration of Zn in the natural soil (Fig. 2b).

Simulated intensive rainfall caused an increase in cadmium concentrations (Fig. 3a) during the 10-day period of irrigation, in the first 15 cm of soil profile in particular, compared to the mean concentration of Zn in soil solution under natural conditions. It appears that intensive overhead irrigation clearly differentiates Cd concentrations within the microcosm profile, and increases its concentrations in the upper layers (to 45 cm) of the microcosm soil compared to the natural concentration of this element in the soil, especially on the 4th and 6th day of experiment. On the 10th day of the experiment Cd concentration dropped below the natural content in soil. The average concentration of Cd for 10 days

of irrigation was clearly higher in the upper layers (to 45 cm) compared to the concentration of Zn in the natural soil (Fig. 3b). However, simulated intensive rainfall did not cause the liberation and accumulation of Cd in concentrations exceeding the average content of Cd in unpolluted arable soils, but was much lower.

The occurrence of heavy metals selected for the study in the soil solution at the same level of concentration or slightly higher as in the natural conditions may indicate that increased intensity of precipitation should not cause their release for the soil in amounts exceeding the allowable contents of Zn (33 000 µg dm⁻³) and Cd (220 µg dm⁻³) in Polish unpolluted arable soils (Kotowski, 1998).

Irrigation of the soil microcosms with the wastewater at large single dose had no effect on the pH value, but caused notable changes in concentrations of heavy metals. Zinc concentration in the solution increased with time, especially in the top layer of the microcosm during first two days (Fig. 4a). A distinctly greater intensity of Zn release to the solution was observed only in the upper layers (to 45 cm) as compared to the intensive overhead irrigation, especially at 15 cm. Whereas, in the deeper horizon of soil zinc concentration was significantly lower than in the microcosm sprinkled for 10 days. It was found that zinc concentration in the solution from the microcosm irrigated with wastewater reached a value lower than or comparable to Zn concentration attained in the natural soil, except of three measuring samples from upper layer and later days after irrigations. It should be assumed that organic soil irrigation with treated sewage may release additional amounts of zinc to the soil solution compared to mean concentration of zinc in the natural soil.

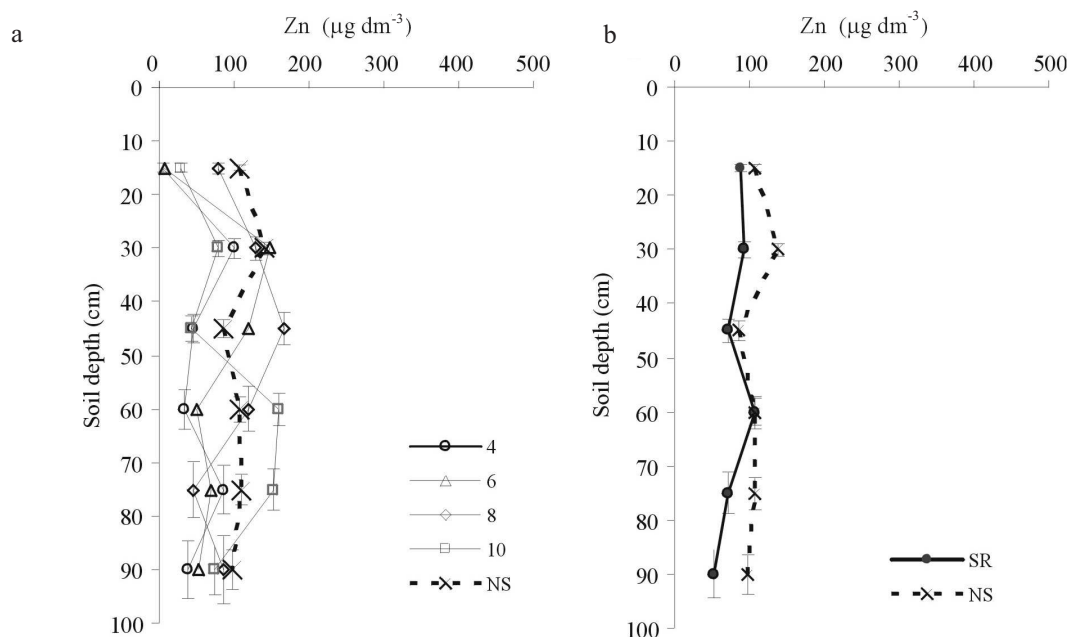


Fig. 2. Concentration (means \pm SE) of Zn in soil microcosms irrigated with simulated rain (a) and an average value (means \pm SE) from 10 days of experiment (SR) (b) compared to concentration in natural soil (NS).

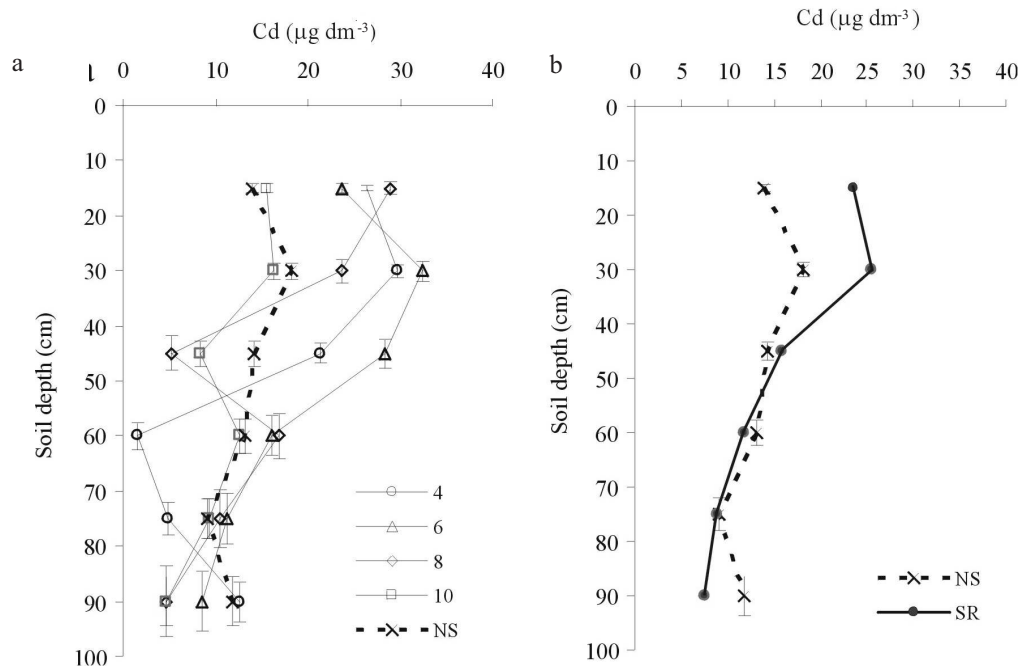


Fig. 3. Concentration (means \pm SE) of Cd in soil microcosms irrigated with simulated rain (a) and an average value (means \pm SE) from 10 days of experiment (SR) (b) compared to concentration in natural soil (NS).

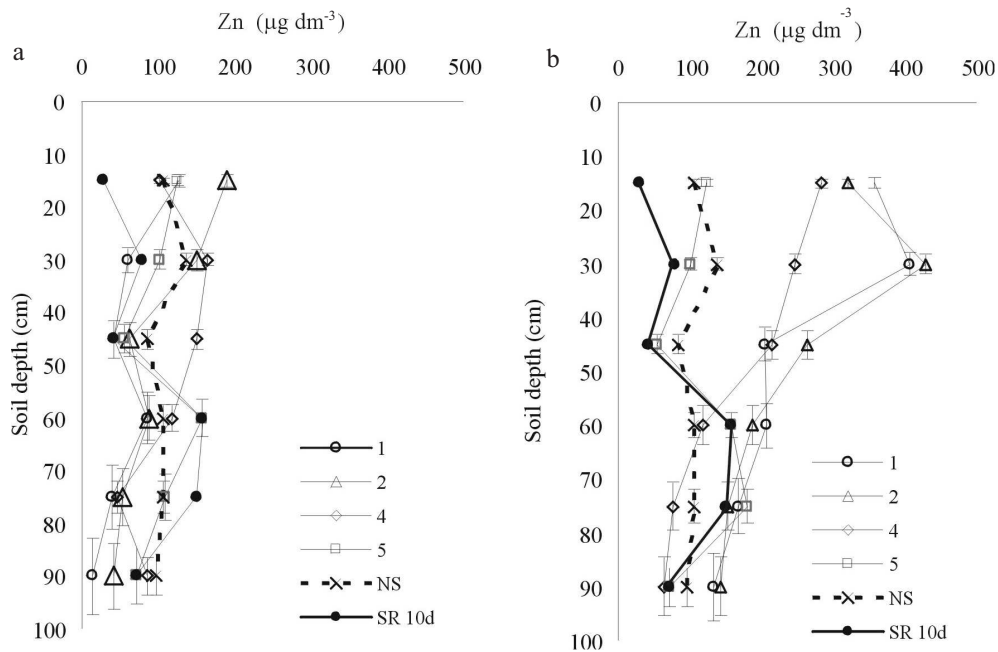


Fig. 4. Concentration (means \pm SE) of Zn in soil microcosms irrigated wastewater (a) and irrigated with wastewater + Zn addition (b) compared to concentration in natural soil (NS) and simulated rain from 10th day of experiment (SR 10d).

When zinc was added to the wastewater in the amount of $500 \mu\text{g dm}^{-3}$ it was found that Zn concentration in the upper layers of the soil was $320\text{--}430 \mu\text{g dm}^{-3}$ (Fig. 4b) and exceeded the highest initial level of zinc concentration of $360 \mu\text{g dm}^{-3}$ in the wastewater, but was much lower than the sum of the concentrations Zn added and in wastewater ($195+500 \mu\text{g dm}^{-3}$). This indicates immediate sorption of a part of the zinc

in the soil. Zn concentration decreased with depth and with time from the moment of irrigation of the microcosm. The highest concentration of zinc in the soil solution from the microcosm was observed in the upper layers (to 45 cm) for the initial four days of analysis compared to the concentration of Zn in sprinkled microcosm (Fig. 4b). On the fifth day after irrigation Zn concentration dropped to the amount

of overhead irrigation microcosm throughout the soil profile. Significantly lower concentration of Zn was observed in the lower parts of the profile and it was similar to the amount of Zn in the overhead irrigation microcosm. The presence of heavy metals in soil solution only in the upper horizons of the soil is an excellent opportunity for their uptake by plants and thus their removal from the soil and from the applied liquid sewage.

Comparison of the effect of irrigation with wastewater enriched with heavy metals with Zn concentration in natural conditions showed that the Zn content in the monolit with wastewater was generally higher. On the 5th day from the irrigation, zinc concentration in the soil solution from the microcosm irrigated with wastewater with heavy metals addition, up to the horizon of 45 cm, and from 60 to 90 cm at 4th day, was lower than the concentration of that element in the natural soil. This indicates high sorptive capacity of the soil under study with relation to zinc, especially in lower horizon of soil profile. However, one should take into consideration the time-limited fluctuation in Zn solubility due to dissolved organic carbon. It was found that dissolved organic carbon affected zinc solubility, because water-extractable Zn increased with dissolved organic carbon going up probably due to a flash in the microbial activity (Antoniadis *et al.*, 2007).

Comparing the average zinc concentrations in the microcosms irrigated with wastewater and wastewater with heavy metals (Fig. 5) addition it can be concluded that zinc contained in the wastewater was absorbed by the soil to the concentration of its content in the sprinkled and natural soils. Considering the average concentration of zinc from five days of analysis, zinc addition in an amount of $500 \mu\text{g dm}^{-3}$ caused an increase of Zn concentration in the soil microcosm from $165 \mu\text{g dm}^{-3}$ (at 15 cm) to $6 \mu\text{g dm}^{-3}$ (at 90 cm) compared to natural soil. This means that the entire zinc contents in the wastewater may be absorbed by the soil, while in the case of zinc addition almost all of its quantity was absorbed in the lower parts of microcosms and slightly lower absorption was observed at their upper part.

Wastewater introduction to the microcosm clearly increases cadmium concentration at depths of 15 and 30 cm compared to the sprinkled microcosm and the natural soil (Fig. 6a). Below this level the concentration of Cd was subject to large fluctuations, irrespective of the level within the microcosms and day of analysis, compared to the sprinkled and natural soils. In principle, the concentration of Cd decreased with depth in the microcosm and, in all cases under consideration, did not exceed the concentration of wastewater added. Therefore, the application of treated sewage should not result in the introduction of significant quantities of cadmium to the ground waters as compared to intensive rainfall. Also, no significant increase was observed in Cd concentration compared to the amount released from the natural soil.

When cadmium was added to the treated wastewater at the rate of $15 \mu\text{g dm}^{-3}$, after the first day from the moment of its application, in the upper layers of the soil (15 to 45 cm) average concentration of cadmium was $26.9 \mu\text{g dm}^{-3}$, and in the lower horizons (from 60 to 90 cm) $10.2 \mu\text{g dm}^{-3}$ (Fig. 6b). These concentrations were comparable to the average value for treated sewage water application, as well as in the case of irrigation with simulated rain or somewhat higher than those observed under natural conditions, but only in the upper layer. This may indicate that cadmium was absorbed by the soil studied and that even under conditions of very intensive irrigation its concentration in soil solutions did not increase above Cd concentration in wastewater. Cadmium can also form complexes with organic substances contained in treated sewage and be absorbed by the humus substances of the soil. Previous studies showed that cadmium contained in municipal sewage occurs mainly in complex or chelate organic compounds, which facilitates its uptake by plants (Guo and Marschner, 1995; Hanc, 2008).

Below 30 cm cadmium concentration fluctuated irrespective of the depth and day of analysis compared to sprinkled and natural soils. Those fluctuations mean that Cd was less retained by the soil sorption complex than Zn. The average cadmium concentrations from five days of analysis in the microcosm with the addition of wastewater and wastewater enriched with added Cd are shown in Fig. 7. Based on

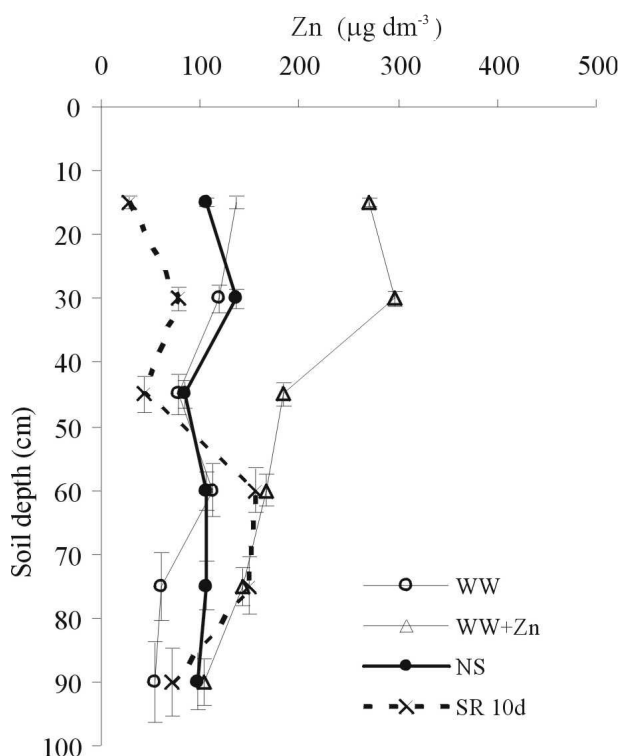


Fig. 5. Average value of Zn in soil microcosms irrigated wastewater and irrigated with wastewater + Zn addition (means \pm SE) from 5 days of experiment compared to concentration in natural soil (NS) and simulated rain from 10th day of experiment (SR 10d).

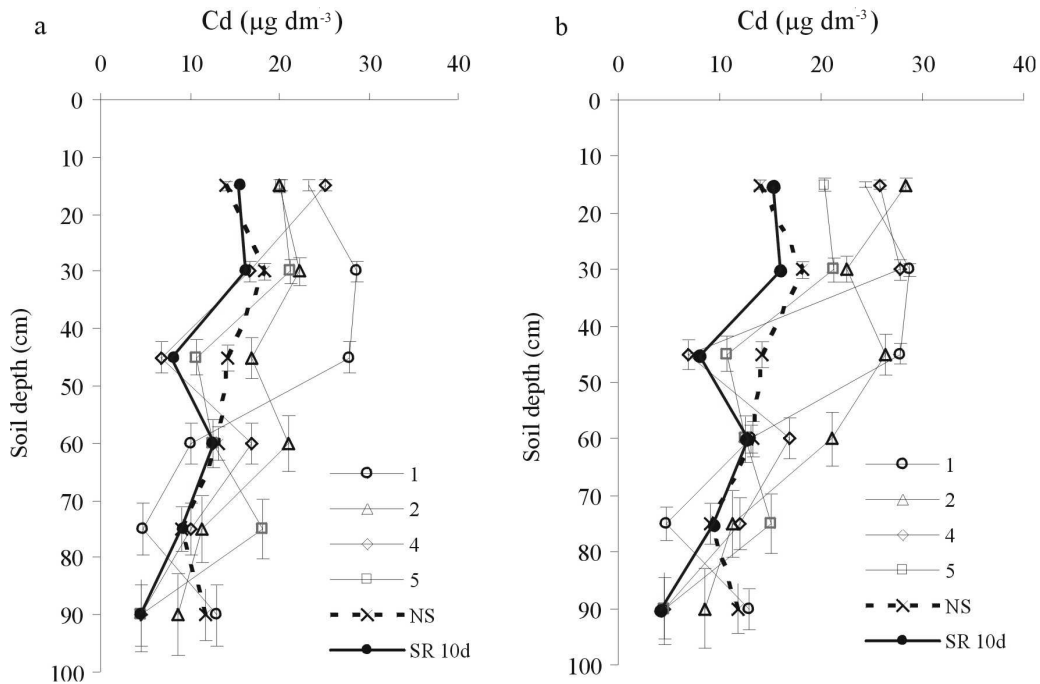


Fig. 6. Concentration (means \pm SE) of Cd in soil microcosms irrigated wastewater (a) and irrigated with wastewater + Cd addition (b) compared to concentration in natural soil (NS) and simulated rain from 10th day of experiment (SR 10d).

a comparison of average Cd concentrations in the two monoliths, it can be concluded that Cd contained in the wastewater was partly absorbed by the soil. It was on average 41 and 17% higher than the Cd content in the sprinkled and natural soils, respectively. The Cd addition ($15 \mu\text{g dm}^{-3}$) caused an increase in the Cd concentration in the soil profile. It was on average 27, 79, and 48% higher than the Cd content in the wastewater enriched microcosm, the sprinkled soil and the natural soils, respectively. This means that only a part of the added cadmium was absorbed by the soil. Taking into account Cd added initially in the form of wastewater and in wastewater with cadmium solution (14 and $29 \mu\text{g dm}^{-3}$) average cadmium concentrations were higher than those in wastewater ($14 \mu\text{g dm}^{-3}$). However, there were three exceptions, all from the deepest soil horizons. Strongly lower absorption was observed at the upper parts of soil profiles compared to the deeper ones. This phenomenon was observed for both elements. Generally, the proportion of Zn and Cd in the soil profile varies depending on various factors. One of the most important factors is the content of substance which forms a rather stable combination (binding) with zinc and cadmium. Organic matter content in the investigated soils increased with depth but the concentration of both elements decreased with depth in the microcosms soil. This means that the ability to absorb the added elements was lower in the upper levels of soil profiles compared to lower ones and closely associated with organic matter content.

The concentration of measured Zn and Cd were similar in the soil solutions from samples from both the natural conditions and the intensively watered with wastewater conditions. This may indicate that significant transport of metals in soils irrigated with metal-polluted wastewater should not occur. It means that the soil retained the Zn and Cd regardless of concentration applied in the experiment. Noteworthy are the almost comparable or slightly higher concentrations of the metals studied within the microcosm profile in the case of overhead irrigation and of wastewater application, in comparable time of experiment. It may suggest that the application of wastewater for irrigation for the purpose of its further purification, even at higher rates, should not result in the release of heavy metals to the soil solution in amounts greater than in the case of intensive rainfall. In the case of zinc there was even a slight decrease in its concentration in relation to the simulated overhead irrigation in deeper horizons, which may be due to complexation of that element by organic matter contained in the wastewater. Thus, the application of treated sewage under the conditions of organic soil does not pose a threat to the natural environment as in all the cases under analysis the concentrations of Zn and Cd in the soil solution were several-fold lower than the average contents of Zn and Cd in Polish unpolluted arable soils (Kotowski, 1998; Stępniewska *et al.*, 2009, 2010).

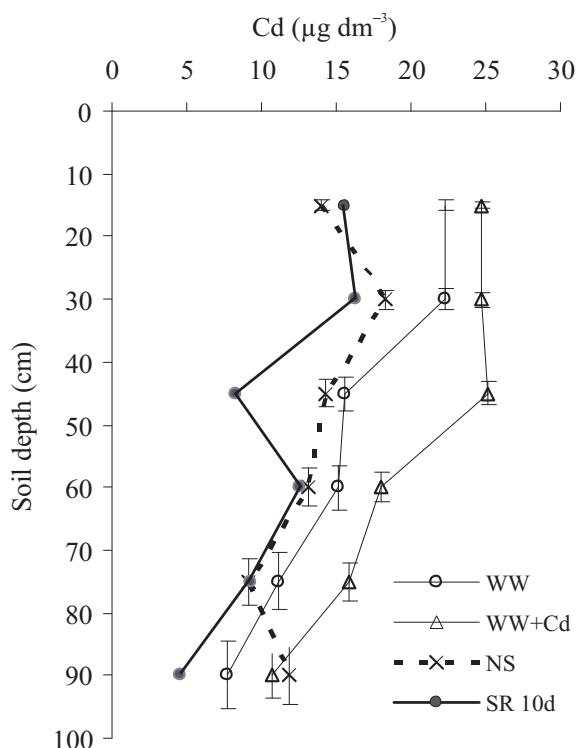


Fig. 7. Average value of Cd in soil microcosms irrigated wastewater and irrigated with wastewater + Cd addition (means \pm SE) from 5 days of experiment compared to concentration in natural soil (NS) and simulated rain from 10th day of experiment (SR 10d).

Obtained results showed that even wastewater amended with heavy metals did not cause any additional liberation and accumulation of Zn and Cd in the studied peat-muck soil in amounts exceeding permissible concentration in Polish arable land. Furthermore results indicate that the average concentration of zinc in the whole soil profile was at the level of purity by first-class Polish standards for groundwater ($500 \mu\text{g dm}^{-3}$), while the concentration of cadmium in the profile from 15 to 75cm meets the requirements for fifth class of purity ($> 10 \mu\text{g dm}^{-3}$) and in the lowest part of soil profile (75-90 cm) corresponds to the requirements of class fourth ($10 \mu\text{g dm}^{-3}$) (PKN, 2004). Moreover, the range of Zn concentration do not appear to adversely affect microbiological processes (Gondek *et al.*, 2010; Mann *et al.*, 2002; Sanders *et al.*, 2006; Singh and Agrawal, 2007). According to previous studies (Gondek *et al.*, 2010; Guo and Marschner, 1995; Mann *et al.*, 2002; Usman *et al.*, 2005), $10^6 \mu\text{g dm}^{-3}$ of Zn content influences negatively most microbiological activity. Even nitrification could occur because only $10^5 \mu\text{g dm}^{-3}$ of Zn can limit this process. It means that the studied peat-muck soil can be used for the heavy metals utilization in conditions similar to studies. The results indicate, given the conditions studied that neither intensive overhead irrigation of the soil nor its irrigation with wastewater amended with

heavy metals not exceeded the sorptive capacity of the studied soil with respect to Cd and Zn. The effect of the soil studied should be considered in two aspects:

- the effect of overhead irrigation on the release of heavy metals,
- the effect of wastewater amended with heavy metals on the sorptive capacity.

The duration of overhead irrigation adopted in the experiment did not cause acidification of the soil, typical for intensive and long-lasting rainfalls, which indicates good buffering capacity of the studied soil. But may be the duration (10 days) was not long enough to observe whether acidification would have occurred. Alkaline reaction of the studied soil solutions and their content of organic matter counteracted the release of heavy metals to the soil solution during the overhead irrigation. A similar phenomenon was observed in the case of application of wastewater and wastewater amended with heavy metals. The alkaline reaction of the soil, in conjunction with its organic matter content, constituted a sufficient barrier for maintaining heavy metals in their insoluble forms. In general, it can be stated that both intensive rainfalls and irrigation of the soil with wastewater with increased content of heavy metals, in doses comparable to those used in the experiment, do not pose a hazard of heavy metals contamination of ground water of peat-muck soils, because in all analyzed cases the concentrations of heavy metals were much lower than the permissible concentration of Zn and Cd in the wastewater introduced in the soil. Surdyk *et al.* (2010) demonstrates that low quality water, in their case channel water containing domestic wastewater, can be used for irrigation without major accumulation of inorganic trace compounds in soil and crops even after three years of cropping at field scale under normal farm practices. The principal conclusion of the study is therefore that, when appropriately treated, even input wastewaters with higher heavy metal contents (simulated by the heavy metal spiking of channel water) can be used over three years without visible degradation of soil and products.

CONCLUSIONS

1. The investigated organic soil can be useful for wastewater purification with their natural charge of Zn and Cd as well as under increased concentrations.
2. The use of wastewater for peat-muck soils in doses and frequencies used in the experiment does not pose a threat to the groundwater.
3. Zinc contained in the wastewater was absorbed by the soil to its concentration in the sprinkled and natural soils.
4. Zinc addition ($500 \mu\text{g dm}^{-3}$) caused an increase in the concentration of Zn in the soil microcosm from $165 \mu\text{g dm}^{-3}$ (at 15 cm) to $6 \mu\text{g dm}^{-3}$ (at 90 cm) comparing to the values for natural soil at the same depth.

5. Cadmium contained in the wastewater was partly absorbed by the soil in quantities about 41 and 17% higher than the cadmium content in the sprinkled and natural soils, respectively.

6. Cadmium addition ($15 \mu\text{g dm}^{-3}$) caused an increase of Cd concentration in the soil profile. It was about 27, 79, and 48% higher than the cadmium content in the wastewater enriched microcosm and the sprinkled and natural soils, respectively.

7. Both zinc and cadmium were less absorbed in the upper part of soil profiles than in the deeper one.

REFERENCES

- Alloway B.J., 1990.** Heavy Metals in Soils. Wiley Press, London, UK.
- Andevsson A. and Nilsson K.O., 1974.** Influence of time and soil pH on Cd availability to plants. *Ambio*, 3, 189-198.
- Antoniadis V., Tsadilas C.D., and Stamatiadis S., 2007.** Effect of dissolved organic carbon on zinc solubility in incubated biosolids-amended soils. *J. Environ. Qual.*, 36, 379-385.
- Basta N.T., Ryan J.A., and Chaney R.L., 2005.** Trace element chemistry in residual-treated soil: key concept and metal bioavailability. *J. Environ. Qual.*, 34, 49-63.
- Bo Li, Yibing Ma, McLaughlin M.J., Kirby J.K., Cozens J., and Jifang Liu, 2010.** Influence of soil properties and leaching on copper toxicity to barley root elongation. *Environ. Toxicol. Chem.*, 29, 835-834.
- Brzezińska M., 2006.** Impact of treated wastewater on biological activity and accompanying process in organic soils (in Polish). *Acta Agrophysica*, 131, 5-164.
- Clara M., Strenn B., Gans O., Martinez E., Kreuzinger N., and Kroiss H., 2005.** Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Res.*, 39, 4797-4807.
- Ecotox, 2010.** <http://cfpub.epa.gov/ecotox/>.
- Fan F., Zhou H., and Husain H., 2006.** Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor processes. *Water Res.*, 40, 205-212.
- Foster I.D. and Charlesworth S.M., 1996.** Heavy metals in the hydrological cycle: trends and explanations. *Hydrol. Proc.*, 10, 227-261.
- Gondek K., Filippek-Mazur B., and Koncewicz-Baran M., 2010.** Content of heavy metals in maize cultivated in soil amended with sewage sludge and its mixtures with peat. *Int. Agrophys.*, 24, 35-42.
- González S., Müller J., Petrovic M., Barceló D., and Knepper T.P., 2006.** Biodegradation studies of selected priority acidic pesticides and diclofenac in different bioreactors. *Environ. Poll.*, 144, 926-932.
- Guo Y. and Marschner H., 1995.** Uptake, distribution, and binding of cadmium and nickel in different plant species. *J. Plant Nutr.*, 18, 2691-2706.
- Hanc A., Tlustos P., Szakova J., Habart J., and Gondek K., 2008.** Direct and subsequent effect of compost and poultry manure on the bioavailability of cadmium and copper and their uptake by oat biomass. *Plant Soil Environ.*, 54, 271-278.
- Hayian W. and Stuanes A.O., 2003.** Heavy metal pollution in air-water-soil-plant system of Zhuzhou, China. *Water Air Soil Poll.*, 147, 79-107.
- Holakoo L., Nakhla G., Bassi A.S., and Yanful E.K., 2007.** Long term performance of MBR for biological nitrogen removal from synthetic municipal wastewater. *Chemosphere*, 66, 849-857.
- Juhler R.K., Sorensen S.R., and Larsen L., 2001.** Analyzing transformation products of herbicide residues in environmental samples. *Water Res.*, 35, 105-111.
- Kashem M.A. and Singh B.R., 2001.** Metal availability in contaminated soils. I. Effects of flooding and organic matter on changes in Eh, pH, and solubility of Cd, Ni and Zn. *Nutr. Cycl. Agrosys.*, 61, 247-255.
- Kotowski M., 1998.** Study of integrated system of municipal wastewater treatment combined with irrigation of industrial crop (in Polish). Report PBZ-31-03. Ministry of Science, Warsaw, Poland.
- Lane T.W., Saito M.A., George G.N., Pickering I.J., Roger C., Prince R.C., and Morel F.M.M., 2005.** Biochemistry: A cadmium enzyme from marine diatom. *Nature*, 435, 42. doi: 10.1038/435042a
- Lepp N.W. and Madejón P., 2007.** Cadmium and zinc in vegetation and litter of a voluntary woodland that has developed on contaminated sediment-derived. *Soil J. Environ. Qual.*, 36, 1123-1131.
- Malkoc S., Yazıcı B., and Kopalal A.S., 2010.** Assessment of the levels of heavy metal pollution in roadside soils of Eskisehir, Turkey. *Environ. Toxicol. Chem.*, 2720-2725.
- Mann S.S., Rate A.W., and Gilkes R.J., 2002.** Cadmium accumulation in agricultural soils in western Australia. *Water Air Soil Poll.*, 141, 281-297.
- Mehler W.T., Maul J.D., You J., and Lydy M.J., 2010.** Identifying the causes of sediment-associated contamination in the Illinois river (USA) using a whole-sediment toxicity identification evaluation. *Environ. Toxicol. Chem.*, 29, 158-167.
- PKN, 2004.** Classification the present status of surface water and groundwater - admissible concentrations of heavy metals in particular classes (I-V) of ground water quality. Regulation of the Directive of Polish Ministry of Environment, February 11.
- Sanders J.R., McGrath S.P., and Adams T.M., 2006.** Zinc, copper and nickel concentrations in ryegrass grown on sewage sludge-contaminated soils with different pH. *J. Sci. Food Agric.*, 37, 961-968.
- Singh R.P. and Agrawal M., 2007.** Effect of sewage sludge amendment on heavy metal accumulation and consequent responses of *Beta vulgaris* plants. *Chemosphere*, 67, 2229-2240.
- Stępniewska Z., Sochaczewska A., Wolińska A., Szafranek-Nakonieczna A., and Paszczyk M., 2010.** Manganese release from peat soils. *Int. Agrophys.*, 24, 369-374.
- Stępniewska Z., Wolińska A., and Klin R., 2009.** Heavy metals release from eroded loess soil. *Int. Agrophysics*, 23, 377-382.
- Stoiber T.L., Shafer M.M., and Armstrong D.E., 2010.** Differential effects of copper and cadmium exposure on toxicity endpoints and gene expression in *Chlamydomonas reinhardtii*. *Environ. Toxicol. Chem.*, 29(1), 191-200.
- Surdyk N., Cary L., Blagojevic S., Jovanovic Z., Stikic R., Vucelic-Radovic B., Zarkovic B., Sandei L., Pettenati M., and Kloppmann W., 2010.** Impact of irrigation with treated low quality water on the heavy metal contents of a soil-crop system in Serbia. *Agric. Water Manag.*, 98(3), 451-457.

- Usman A., Kuzyakov Y., and Stahr K., 2005.** Effect of clay minerals on immobilization of heavy metals and microbial activity in a sewage sludge-contaminated soil. *Soil Sci. Sedim.*, 5, 245-252.
- Walczak R., Sławiński C., and Witkowska-Walczak B., 2001.** Water retention and conductivity in moorsh soils in Poland (in Polish). *Acta Agrophysica*, 53, 201-209.
- Wei Y.S., Van Houten R.T., Borger A.R., Eikelboom D.H., and Fan Y.B., 2003.** Minimization of excess sludge production for biological wastewater treatment. *Water Res.*, 37, 4453-4467.
- Witkowska E., 2007.** Wastewater treatment in single-tank membrane biological reaction (in Polish). Univ. Technol. Press, Warsaw, Poland.
- Włodarczyk T. and Kotowska U., 2005.** Nitrogen transformations and redox potential changes in irrigated organic soils. Eds T. Włodarczyk *et al.*, Institute of Agrophysics, PAS, Lublin, Poland.
- Włodarczyk T. and Witkowska-Walczak B., 2006.** Water-air characteristics of mucky-like soils. *Polish J. Soil Sci.*, 39, 1-9.
- Zhou H. and Smith D.W., 2001.** Advanced treatment technologies in water and wastewater treatment. *Can. J. Civil Eng.*, 28, 49-66.