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Short communication

Functions of organic matter in polluted soils: The effect of organic amendments on phytoavailability of heavy metals

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ABSTRACT

Soil degradation and/or contamination have significant influence on the quality of food. In such cases immobilization of contaminants in soil may often be applied. In this context, organic matter (especially humic and fulvic acids) presents in soil is favourable component component. It is because of their high sorption capacity with respect to many contaminants, including heavy metals, which may result in their immobilisation and, consequently protection of food and groundwater against contamination. Anthropogenically transformed soils are often poor in organic matter (humic substances), thus their role as a natural barrier is decreased. Therefore, re-generation of humic substances through humification of organic matter from diverse sources added to soils may be the way to re-built the protective function of the soil barrier, and consequently to reduce environmental and/or health risks at the areas under anthropopresion.

The usefulness of organic matter contained in brown coal, brown coal-derived preparations and farmyard manure was studied as a factor decreasing the uptake of heavy metals by plants and/or their migration within groundwater by immobilizing them in soil. A conceptual model was developed for soil as a protective barrier against heavy metals uptake by plants and/or migration towards groundwater. Organic amendments to reduce immobilisation and thus the bioavailability of heavy metals in soils were tested in field stone pots. The phytoavailability of tested heavy metals was the lowest when a brown-coal derived preparation was used as an organic amendment, as indicated by the lowest bio-accumulation index (BI) of: 0.24 for Cd (winter wheat grain), 0.021 for Pb (winter wheat straw), and 0.48 for Zn (spinach).

1. Introduction

Soils are non-renewable resources because their degradation can proceed much faster than formation and remediation processes. Soil acts as a sink for almost all substances released into the environment by human activities. Soil contamination can have lasting environmental and socio-economic consequences and be extremely difficult and costly to remediate (Dai et al., 2004). Highly contaminated sites are usually poor in organic matter content and microbial activity (Baker et al., 2011). Organic matter can work as a factor which causes heavy metals release but it also can immobilize them (Nessner Kavamura and Esposito, 2010). Availability of metal ions in soil and groundwater is influenced among others by the following: the character of organic and mineral combinations of complexes, metal ion saturation degree in a complex, sorption of a complex on mineral matrix and biodegradation of an organic fraction of a complex. Increasing adsorption of heavy metals or decreasing their solubility can reduce the risk of plant uptake, pollutants transport and their redistribution from contaminated sites. Immobilization of metals can be accomplished by the addition of amendments to reduce their solubility and/or bioavailability for plants (Kwiatkowska-Malina, 2015a; De Tendera et al., 2016). The addition of soil amendments, such as organic matter, phosphates, alkalizing agents, and biosolid can decrease solubility of metals in soil thus minimize their leaching to groundwater (Kwiatkowska, 2006; Kwiatkowska-Malina, 2011; Shahid et al., 2014; Sharma1 and Archana, 2016). The protective role of soil organic matter (SOM) for plants lies in its high cation exchange capacity (CEC), and the ability to form simple and chelate compounds with heavy metals ions in soil (Kinniburgh et al., 1999). As an effect of this formation the total concentration of metals in the soil is unchanged during the remediation process, but the bioavailability of them is substantially reduced. In recent years numerous low-cost natural materials were proposed as the potential sources of organic matter in soil, including: leaf mould, moss peat, green algae, coconut waste, rubber, wood, etc. (Gallardo Lara and Nogales 1987; Parr and Hornick 1993; Chaney et. al., 2004; Leszczyńska and Kwiatkowska-Malina 2011). However novel, low-cost and easily available organic amendments are still looked for, because there is a need to solve a global problem of observed rapid depletion of soil organic matter (European

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Environment Agency, 2010, 2010; Yigini and Panagos, 2016). The use of brown coal in agricultural production, protection of soil ecosystems and land reclamation have been described previously (Maciejewska and Kwiatkowska, 1997; Leszczyńska and Kwiatkowska-Malina, 2013).

The aim of this study was to present the usefulness of organic matter contained in brown coal, brown coal-derived preparations and cow manure in decreasing the heavy metals uptake by plants by immobilizing them in soil and, in consequence to reduce heavy metals which may enter the food chain.

2. Materials and methods

The experiment was carried out in Skierniewice located on 20°34′E 51°58′N (Poland). Soil samples originated from Haplic Luvisols, The World Reference Base for Soil Resources (WRB), formed from loamy sand on light clay (7% clay, 6% silt, 87% sand) in stoneware pots of 40 cm diameter and 120 cm height, sank into the ground. The Tertiary earthy soft brown coal from the Konin Basin deposits, a brown coal preparation, the so-called Rekulter containing 85% of brown coal, and cow manure were applied to soil in the amounts of: 140, 180 and 630 g per pot, respectively, which in all cases gives an equivalent to 5 tons of organic carbon per hectare. Not amended soil was used as a control. The contents of organic carbon were of: 6.62 g kg^{-1} soil (a control), 8.48 g kg^{-1} soil (brown coal added), 8.94 g kg^{-1} soil (Rekulter added), and 6.92 g kg^{-1} soil (cow manure added). The contents of total nitrogen were of: 0.6 g kg^{-1} soil, 0.9 g kg^{-1} soil, 0.9 g kg^{-1} soil, and 0.4 g kg^{-1} soil, for the control, brown coal, Rekulter and cow manure amendments, respectively. The soil reactions (pH_{KCl}) were of: 5.05 (a control), 5.20 (brown coal), 5.53 (Rekulter) 5.50 (cow manure). The soil was spiked with heavy metals by mixing up with the liquid form of salts: cadmium as $Cd(NO_3)_2$, lead as $Pb(CH_3COO)_2$ and zinc as $ZnSO_4$, which after blending led to the following concentrations of heavy metals in soil (in mg kg^{-1}): 90.0 (Zn), 60.4 (Pb) and 0.80 (Cd). The bioaccumulation index (BI) was calculated as a ratio of a heavy metal content in a plant to its total content in a soil. The BI was used to evaluate the mobility of cadmium, lead and zinc in the soil, and their availability to plants.

2.1. The effect of organic matter on bioavailability of heavy metals in the contaminated soils

Soil presents the most biologically active part of lithosphere and it consists of mineral components, organic matter, water, air and (micro) organisms. Nowadays, soil is a basic place (99%) for food production. At the same time soil serves as a natural barrier preventing plants from an excessive uptake of contaminants as well as leaching to deeper soil layers and groundwater (Fig. 1). Soil organic matter (SOM) is one of the most important indicators of soil quality. It is an essential building block for the soil structure and formation of stable aggregates, it improves the infiltration rates and water storage capacity (Kwiatkowska-Malina, 2015a,b). Moreover, SOM acts as a large carbon sink and plays an important role in the CO_2 balance and carbon sequestration.

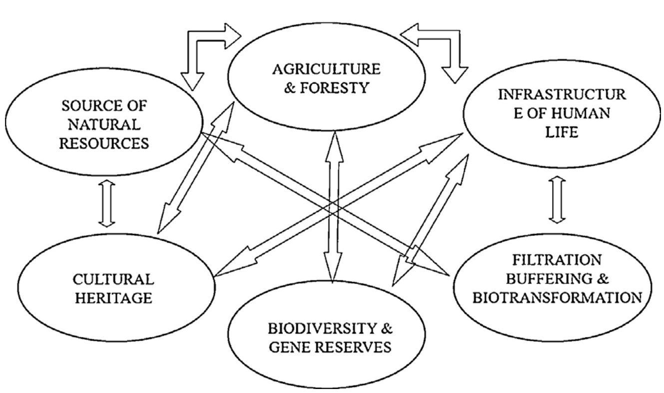

Fig. 1. Main soil functions.

Soil is the first and primary receiver of contaminants, and may or may not serve as a natural barrier to protect groundwater against contamination from the surface. Mobility of metal ions in soil and groundwater is influenced by: soil reaction, character of organic and mineral combinations of complexes, metal ion saturation degree in a complex, sorption of a complex on mineral matrix and biodegradation of an organic fraction of a complex. Therefore, organic amendments containing a high proportion of humified organic matter may be the way to re-built the protective character of soil barrier, and consequently to reduce environmental and/or health risks at areas under anthropopression (Chaney et al., 2004; Hattab et al., 2014; Kwiatkowska-Malina, 2015a).

The conceptual model of soil as a natural barrier is shown in Fig. 2. The low contents of SOM and mineral fractions (FM) with a high sorption capacity (eg. clay fraction) in anthropogenic (degraded) soils (Fig. 2b) in comparison with the unconverted soils (Fig. 2a), may be the reason of loss of sorption capacity (i.e. the possibility of the formation of metalo-organic complexes (MeL), share sorption (S-Me) and precipitation of metal ions (Me-S)), resulting in an increase of free metal ion Me^{+2} concentrations, which can be absorbed by plants or leached into groundwater. Humic substances contain a large number of complexing sites, hence they behave as a natural "multiligand" complexing system (Buffle, 1988). The high selectivity degree of SOM for most trace elements in the cationic form indicates that they form inner-sphere complexes with the functional groups, often forming internal five- or six-member ring structures (Senesi, 1992; Senesi and Loffredo, 1998; Huang and Germida, 2002; Sparks, 2003).

The uptake, accumulation and distribution of heavy metals in biomass are affected by many factors. The most important parameter affecting the uptake is not the total concentration of the element in soil but the fraction that is bioavailable. Amendment with organic matter may change the soil pH and thereby indirectly affect the bioavailability of metals (Xian and Shokohifard, 1989). Sorption of heavy metals in soils is influenced by pH, thus soil ability to retain them will be affected by any changes of pH in soil. The availability of heavy metals for plants in this experiment was the highest in a control (at pH = 5.05) and the lowest in the case when the Rekulter was applied (at pH = 5.53).

Organic amendments are beneficial to soils with respect to their productivity and for reclamation purposes. The calculated BIs (Table 1–3) indicates heavy metals (lead, cadmium, zinc)mobility in soils and their availability to plants.

In the case of roots and above-ground parts of rye and darnel multifloral, the BIs of cadmium where brown coal or the Rekulter were applied, hardly differ (Table 1). The lowest value of BI of cadmium was found in winter wheat grain in the case where the Rekulter was applied. The BIs of cadmium for radish leaves were nearly the same in the case of all organic amendments studied. In the case of chinese cabbage the BIs of cadmium were the same for farmyard manure and without any organic amendment (a control).

The values of BI of lead for rye, winter wheat, mustard, spinach, chinese cabbage and phacelia were higher for plants from soil without organic amendments compare to the BIs where the organic amendments were applied (Table 2). In the case of rye and radish, the BIs of lead where brown coal or the Rekulter were applied were hardly differ. The lowest BI of lead was found for winter wheat straw in the case where the Rekulter was applied. The values of BI of lead for daranel multifloral and radish roots were nearly the same as for plants from soil with organic amendments or without.

The BIs of zinc were the highest for all tested plants from control soil (Table 3). The lowest BI of zinc of spinach was found in the case where brown coal was applied. In the case of rye, darnel multifloral, mustard, spinach and radish, the BIs of zinc where brown coal or the Rekulter were applied hardly differ. The values of BI of zinc for daranel multifloral were nearly the same for plants from soil with farmyard manure