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Changes of risky element concentrations under organic and mineral fertilization

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ABSTRACT

The 28-day incubation experiment was carried out to evaluate the impact of the application of digestate (Dig); digestate with straw (DigSt); pig slurry (Slu) and mineral fertilizer (NPK) on Cd, Cu, Mn and Zn availability, on K_2SO_4-extractable carbon content and on the soil pH value in long-term contaminated soil. At days three and seven of the experiment, the 0.01 mol/L $CaCl_2$-extractable fractions of Cd, Zn and Mn significantly decreased under organic treatments (Dig, DigSt and Slu) with the most pronounced effect under Dig treatment. The NPK treatment caused the increase of risky element concentrations since day 21 of incubation which was accompanied with pH decrease. The contents of 0.5 mol/L K_2SO_4-extractable carbon were the highest at day 3 and 7 of incubation in organic treatments. The significant correlations between 0.5 mol/L K_2SO_4-extractable carbon and $CaCl_2$-extractable metal concentrations showed a close relationship between fresh organic matter added in organic fertilizers and risky element availability, suggesting that newly added labile organic matter can form temporary ligands with risky elements and release them later following its decomposition.

Keywords: toxic elements; plant nutrients; residues of anaerobic digestion; heavy metals; mineral and organic fertilizers

The solubility and, in consequence, the availability of risky elements in the environment can change with the change of external conditions, such as application of fertilizers. The fertilizers can contain a considerable amount of risky elements, especially phosphorus fertilizers from North Africa (Uprety et al. 2009). Organic manures can also serve as the source of risky elements as the animal diet contains Cu and Zn, elements important for the right growth or prevention of diarrhoea (Carlson et al. 2008). Herencia et al. (2008) showed that addition of compost has not affected the soil total content of heavy metals, but in comparison with mineral fertilizers increased the content of the extractable micronutrients. The soil organic matter (SOM) plays an important role in forming stable complexes of heavy metals with organic ligands (Clemente and Bernal 2006).

The digestates known as secondary residues of biogas stations could be efficiently used as sources of plant nutrients in daily agricultural practice as base fertilizers, top-dressings, and feed additives (Collet et al. 2011). Still, there is huge uncertainty in defining the benefits of bioenergy utilization and digestate reuse (Meyer-Aurich et al. 2012). While most studies of digestates have focused on its fertility and other active impacts on agricultural production (Lošák et al. 2011, 2016), little attention has been paid to the effects of its application on heavy metal concentrations (Chen et al. 2013).

Recent advances in the treatment of manure byproducts have resulted in reduced bioavailability of metals (Bolan et al. 2014). Pig slurry was used traditionally as a soil amendment in agriculture, but little attention has been devoted to this issue when dealing with reclamation of heavy metal polluted soils (de la Fuente et al. 2010). However, Cu and Zn contamination of cultivated soils following the application of pig slurry was documented (Novak et al. 2004).

Little information is still known about immediate changes of heavy metals and risky elements

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availability following soil treatment with organic and mineral fertilizers and organic manure.

That is the reason why this paper studies early changes in the availability of heavy metals and risky elements and relationships with potentially soluble carbon in a long-term contaminated soil via incubation experiment. In addition, the effects of organic and mineral treatments on soil pH and its relationships with readily and potentially available heavy metals and risky elements in the soil were also studied.

MATERIAL AND METHODS

Area of interest. The experimental soil was sampled in the alluvium of the river Litavka in the village of Trhové Dušníky (60 km south of Prague) near the smelter Příbramské kovohutě, a.s. Příbram, Czech Republic, which is in operation since 1786. The sampling site is situated in mildly warm climate, the mean annual precipitation and temperature is 625 mm and 7.3°C, respectively. The sampling site is contaminated by Cd, Zn and Pb due to waste from smelter setting pits (Borůvka et al. 1996). According to ISSS-ISRIC-FAO (2006), the experimental soil is classified as fluvisol. The content of clay, silt and sand was 13, 57.2 and 44.8%, respectively. Soil organic carbon content was 2%, the cation exchange capacity was 153 $mmol_+$/kg and the soil pH value was 6. The depth of the sampled soil was 0–20 cm. Further soil characteristics are given in Table 1.

Incubation experiment. Soil samples sieved at < 2 mm were placed into the plastic containers (3 dm^3) and were covered with tight-fitting lids seven days before the start of the experiment. The soil was pre-incubated at 40% of water holding capacity (WHC) at 27°C with 25 mL 1 mol/L NaOH (to take up evolved CO_2) and with distilled water at the bottom of the container. At the beginning of the experiment the soil samples were adjusted to 50% WHC, which remained to the end of the experiment.

Five different fertilizer treatments were tested, each in three replications (3 × 500 g of soil on an oven-dry basis). The fertilizer treatments were: unfertilized control (C); mineral fertilizer (NPK); digestate (Dig); digestate with straw (DigSt) and pig slurry (Slu). Nitrogen was applied as calcium ammonium nitrate (CAN, 27 N) (120 mg N/kg), phosphorus was applied as triple superphosphate (25.4 mg P/kg) and potassium as potassium chloride (79.6 mg P/kg). Digestate was applied at the rate of 32 mL/kg and DigSt treatment at the rate of 32 mL/kg of digestate with 3 g of straw/kg. The pig slurry was applied at the rate of 35.5 mL/kg. All doses of applied fertilizers correspond to the doses of 100 kg of N/ha, 48 kg of P/ha and 80 kg K/ha.

Experimental containers were aerated daily to ensure sufficient oxygen supply. Incubation lasted 28 days. The available heavy metals and risky elements, 0.5 mol/L K_2SO_4-extractable carbon content and pH were analysed at the days 3, 7, 14, 21 and 28.

Chemical analysis. Total risky elements concentrations were analysed in air-dried soil samples sieved at < 2 mm at the 20°C temperature. The total concentrations of elements were determined in 1 g subsamples after decomposition in digestion vessels mixed with 6 mL of concentrated HNO_3 and 5 mL of HCl. For digestion MLS-1200 mega microwave system (Milestone s.r.i., Sorisole, Italy) was used. After digestion the samples were transferred to 50 mL vessels, filled up with deionised water and kept at laboratory temperature until the measurement. Mobile fractions of the elements were determined via a slightly modified proce-

Table 1. The total content of P, K and Ca (g/kg) and of Cd, Mn and Zn (mg/kg) in digestate, straw, pig slurry and experimental soil from the Litavka area

	P	K	Ca	Cd	Mn	Zn
Digestate	11.85	33.71	45.46	0.21	314.4	356
Straw	0.55	6.08	3.61	0.05	30.9	8.3
Pig slurry	7.94	16.49	22.53	0.17	228.1	357
Litavka soil	3.34*	225.71*	2740.62*	10.08	5795	3381

*nutrients extracted by Mehlich 3 method

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dure according to Uprety et al. (2009). 10 g of soil samples (on an oven-dry basis) were weighed from incubation containers and then shaken (250 rpm) with 0.01 mol/L $CaCl_2$ aqueous solution (1:1 w/v) for six hours and centrifuged for 10 min (4500 rpm). Supernatants were kept at 6°C before measurement.

The measurement of total and mobile fractions was carried out via the optical emission spectroscopy with inductively coupled plasma (ICP-OES), using an axial plasma configuration (Thermo Jarrel Ash, Nebrasca, USA).

For determination of soil microbial biomass connected organic carbon, the soil samples were extracted with 0.5 mol/L K_2SO_4 for 30 min at the ratio of 1:4 w/v (Vance et al. 1987). For determination of carbon in the extracts digestion in a mixture of H_2SO_4 and $Cr_2K_2O_7$, followed by titration of the excess of dichromate with $(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$, was applied.

Soil pH was determined in the distilled water extract using the ratio 1:2.5 w/v (20 g soil/50 g water). The soil samples were shaken on an overhead shaker for 1 h, then the suspension was shaken again after 20 h for 10 min and then it was immediately measured with a pH metre WTW 315i/SET (Weilheim, Germany).

RESULTS

Cadmium (Cd). The soil's concentration of available Cd was significantly influenced by treatment ($P < 0.01$), time ($P < 0.01$) and by interaction of treatment × time ($P < 0.01$) (Figure 1a). The lowest Cd concentration was recorded in Dig treatment (0.57 mg/kg), while the highest in the NPK treatment (0.81 mg/kg). The mean Cd concentration increased during the time from day 3 (0.46 mg/kg) till day 28 (0.82 mg/kg).

Copper (Cu). Concentrations of available Cu were slightly influenced by treatment ($P < 0.01$) and time ($P < 0.001$) (Figure 1b). The lowest concentration was found in Slu treatment (0.03 mg/kg), the highest in Dig treatment (0.05 mg/kg). Mean concentrations decreased during the time from 0.06 mg/kg (day 3) to 0.03 mg/kg (day 28).

Manganese (Mn). Concentration of Mn was affected by fertilizer treatment ($P < 0.001$), time ($P < 0.001$) and by their interaction ($P < 0.001$) (Figure 1c). The lowest concentration was found in control treatment (0.04 mg/kg), the highest in the NPK treatment (0.16 mg/kg). During the time, the mean concentration of Mn increased from 0.06 mg/kg (day 3) to 0.1 mg/kg (day 28).

Zinc (Zn). The soil available Zn concentration was influenced by fertilizer treatment ($P < 0.01$), time ($P < 0.01$) and by treatment × time interaction ($P < 0.01$) (Figure 1d). The lowest mean concentration was recorded in the Dig treatment (24.03 mg/kg), the highest in the NPK treatment (38.64 mg/kg). The mean concentration of Zn was increasing from day 3 (17.66 mg/kg) till day 28 (38.21 mg/kg).

0.5 mol/L K_2SO_4-extractable C. The 0.5 mol/L K_2SO_4-extractable C content was significantly affected by fertilizer treatment ($P < 0.001$), time ($P < 0.001$) and by treatment × time interaction ($P < 0.001$) (Figure 1e). The lowest 0.5 mol/L K_2SO_4-extractable C content was found in the control treatment (74.84 mg/g), the highest in the DigSt treatment (90.4 mg/g). During the time, the 0.5 mol/L K_2SO_4-extractable C content decreased from the 93.45 mg/g (day 3) to 72.13 mg/g (day 28).

pH. The pH was influenced by fertilizer treatment ($P < 0.001$), time ($P < 0.001$) and by treatment × time interaction ($P < 0.001$) (Figure 1f). The lowest pH value was recorded in the NPK treatment (6.11), the highest in the Dig treatment (6.4). During the time, the mean pH value decreased from 6.58 (day 3) to 6.13 (day 28).

DISCUSSION

The effect of the Dig, DigST and Slu on risky elements availability. The concentration of available Cd and Zn increased systematically from the beginning of our experiment till its end (Figures 1a,d). The soil from the Litavka region is extremely contaminated and during the experiment, possibly due to incubation conditions (moisture and temperature) it slowly released elements from the soil complexes to plant available forms. The addition of the digestate and pig slurry slightly (but significantly) decreased Cd and Zn concentrations and retarded their increase during the first week of incubation. At the end of our experiment no significant differences were recorded between control treatment and Dig, DigSt and Slu treatments for both elements. The depression and retardation could be related to the addition of organic matter in organic fertilizers and manure

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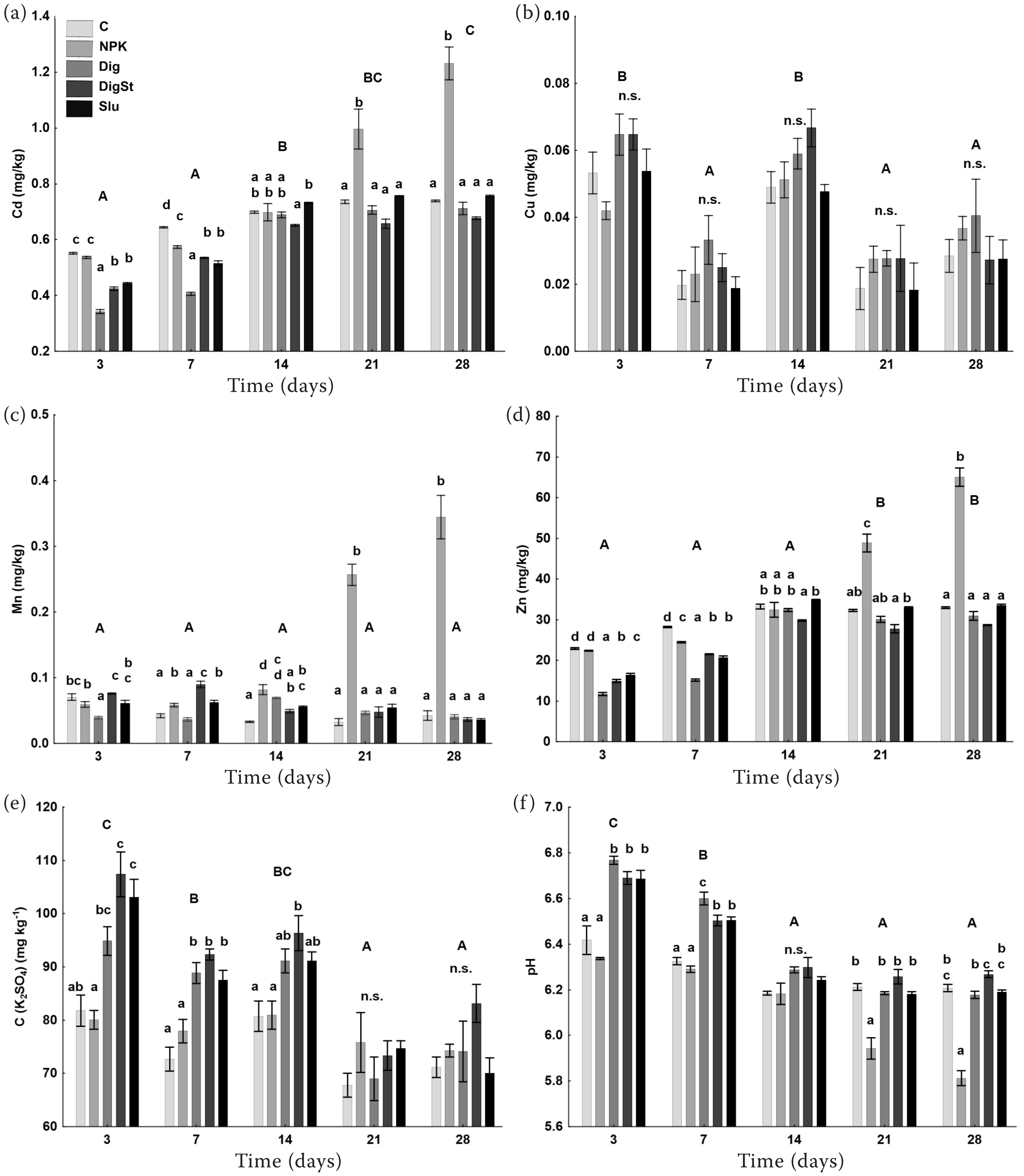

Figure 1. The average soil concentrations of (a) Cd; (b) Cu; (c) Mn; (d) Zn; (e) 0.5 mol/L K_2SO_4-extractable C (mg/kg) and (f) pH as affected by fertilizer treatment (C – control; NPK; Dig – digestate; DigSt – digestate with straw; Slu – pig slurry) and by time of incubation (3, 7, 14, 21 and 28 days from the beginning of incubation). Days of incubation marked by the same big letter (A) are not significantly different. The average concentrations (within the same day of incubation) marked by the same small letter (a) are not significantly different

as the relationship between Cd concentrations and 0.5 mol/L K_2SO_4-extractable C was weakly negative (r = −0.24) and moderately negative between Zn concentrations and 0.5 mol/L K_2SO_4-extractable C (r = −0.34) during the first week and strongly negative (Cd: r = −0.63; Zn: r = −0.58) over the

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whole time of the experiment (calculated over the Dig, DigSt and Slu treatments).

The behaviour of Mn was not as clear during the first week of the experiment as in the case of previous elements (the concentrations changed rapidly from the beginning till the day 14), but in the end, again, no significant differences were recorded between the control and organic treatments (Figure 1c). The concentrations of Cu, similarly to Zornoza et al. (2013), were not affected by fertilizer treatment at all (Figure 1b).

The influence of the addition of organic matter and substances on heavy metal availability and distribution in the soil was reported i.e. by Bolan et al. (2014) and it is possibly achieved due to complexation of the risky elements with the organic matter (forming of more or less soluble metal-organic ligands). The SOM plays an integral part in sustaining soil cation exchange capacity and soil aggregation (Kimetu et al. 2009). Therefore, the distribution of heavy metals between the soil solution and sorbed phase could be described as a function of organic carbon content (Cappuyns et al. 2006). Heavy metals, such as Cd and Zn, can form stable complexes with the SOM (Yang et al. 2013). Therefore, the addition of organic amendments and following interaction of heavy metals with fresh organic matter could explain the depression and retardation of Cd and Zn available concentrations in the Dig, DigSt and Slu treatments during the first week of our experiment. As the amount of added organic carbon depleted and degraded over the time, the concentrations of Cd and Zn increased again and reached the same level as in the control treatment.

The straw can play a significant role in mechanisms of heavy metal exchange in the soil environment. The straw is cheap and due to its molecular structure it can figure as ion-exchange mechanism between risky elements and main nutrients (Gorgievski et al. 2013). However, the synergic mechanisms of straw, added into digestates, on the availability of elements need to be studied further. Our experiment showed that element availability in DigSt decreased in comparison with Dig treatment in a lesser extent and was similar to the Slu treatment.

The effect of mineral fertilizer on risky elements availability. The soil's pH is one of the most important aspects influencing soil heavy metal availability. Application of NPK can decrease soil's pH significantly via dissociation of phosphoric acid into P and hydrogen ions (Bolan et al. 2003) and via principal N components, such as urea. According to Kim et al. (2009) there is a negative relationship between the pH value and Cd concentration. In our experiment a rapid decrease in the pH value (Figure 1f) was recorded and, simultaneously, a significant increase in Cd, Mn and Zn concentrations at the 21th day from incubation and further. The increase of the Cd in the soil treated with NPK was also reported by Carbonell et al. (2011). Concentration of Cu was not affected by fertilizer treatment at all. Similar results were reported by Singh and Agrawal (2013), who found the highest heavy metal availability under NPK treatment and the lowest under organic manure treatment.

The effect of fertilizer treatment on 0.5 mol/L K_2SO_4-extractable C content. Application of organic fertilizers can positively influence the soil organic carbon content (Gonet and Debska 2006). In our experiment, the organic treatments significantly increased the 0.5 mol/L K_2SO_4-extractable C content at the beginning of experiment (Figure 1e), influencing soil metal concentrations. A decrease of the 0.5 mol/L K_2SO_4-extractable C content occurred after two weeks of the experiment. The decomposition and subsequent stabilization of fresh organic matter in time, the microbial interactions and mineralization of soil organic matter (Gude et al. 2012) and changes of contents of organic carbon are probable reasons for the subsequent decrease of easily available carbon fractions and increase of available metals in our experiment.

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