Soil Chemistry

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THE KINETICS OF THE MIGRATION OF LEAD, CADMIUM, COOPER AND ZINC IN THE CONDITIONS OF TURF-PODZOL SANDY LOAM AND CHERNOZEM SOIL

Abstract. In this paper the dynamics of migration of heavy metals (HM), namely Pb, Cd, Cu, Zn, in turf-podzol sandy loam soil and chernozem soil in the presence of impact pollution was investigated. Experimental data were obtained during the period of 1999 to 2006. We applied exponential and Koller models to obtain the ranking of the metals according to their rate of dissipation from a 0–20 cm layer of soil. We also obtain a prediction of the amount of metals present in 20–100 cm layer of soil in mobile form. Our findings are relevant to estimating the metal hazard and controlling the condition of the soil for crop growth.

Investigation of migration processes of heavy metals (HM) in soil in the presence of impact pollution is important because the speed of migration of pollutants in soil profile determines the time and the degree of the disturbance of biogeochemical cycles [6, 7, 11]. Such disturbance causes qualitative and quantitative changes in the agroecosystem which entails reduction in crop growth and quality of the products of agriculture.

Finding patterns of migration of HM in the soil makes it possible to determine not only the length of remediation of the soil (and hence of its effective use in crop growth) but also the time of the appearance of pathological changes resulting from HM pollution [4, 12].

Despite the fact that impact HM pollution constitutes 20–50% of all types of HM pollution, the problem of predicting its consequences often remains unsolved [12]. Such prediction can only be made possible using a mathematical

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model of dynamics and kinetics of migration of HM in the soil. This will allow controlling the quality of the environment more efficiently [12].

HM contamination resulting from impact pollution gradually diminishes due to the uptake of the HM by the plants, HM sorption by the soil, pollutants migration within the soil profile, microbiological activity in the soil etc. The rate of reduction of HM contamination depends on the physical and chemical properties of the metal and the characteristics of the soil (pH, granulometric composition, organic matter, plants canopy, etc.) [3, 5, 9, 13, 14].

The aim of investigation was to construct a model of migration of HM in turf-podzol sandy loam and chernozem soils in the presence of impact pollution by Pb, Cd, Cu and Zn. Turf-podzol sandy loam soil makes up nearly one third of the Ukrainian soil and has a weak buffer capacity [4, 12]. Chernozem soil makes up more than one half of the whole area and is regarded as the most prolific soil in Ukraine.

MATERIAL AND METHOD

The experimental investigation was conducted during the period of 1999 to 2006 at Chernigiv Institute of Agrotechnical of the Ukrainian Academy of Agrarian Science.

The soils under investigation were the turf middle podsol sandy soil (pH_{salt} 5.5; hydrogen acidity 2.7 meq./100g of soil; organic matter according to Turin 0.87%; hydrogen saturation rate 58%.) and the law humus typical chernozem (pH_{salt} 6.2; organic matter according to Turin 2.89%; hydrogen saturation rate 82.3%). The experimental scheme was: 1. – Control; 2. Cu – 50, Zn – 150, Pb – 15, Cd – 1,5 mg/kg; 3. Cu – 100, Zn – 300, Pb – 30, Cd – 3 mg/kg; 4. Cu – 500, Zn – 1500, Pb – 45, Cd – 15 mg/kg. We used the following metals salts: $Pb(NO_3)_2$, $ZnSO_4 \cdot H_2O$, $Cu SO_4 \cdot 7H_2O$, $CdSO_4$. The investigation was conducted in field conditions.

RESULTS AND DISCUSSION

Depending on migrated content Cd, Pb, Cu and Zn, the ranking of the migration paths was obtained. Plant up-taking and vertical migration in soil profile belongs to principal migration paths (makes up more than 10% of the contributed amounts) [3, 5, 9, 12, 13]. Horizontal migration in soil, ruderal species up-taking, and deposition to immobile form in soil belongs to minor migration paths. Evaporation belongs to inessential migration paths and makes up less than 0.001% of the initial quantity [6, 7, 12]. Most of the HM was located in the top layers of soil during the first three years of the experiment (1999–2001). For instance, cadmium amounts in a 0–20 cm turf-podzol sandy loam soil layer were 91.0% (in 1999), 40.1% (2000), 28.2% (2001), 11.2% (2002), 5.6%

(2003), 2.8% (2004), 1.4% (2005), 0.6% (2006) of the initial amount, applied at the start of the experiment. It demonstrates the "principle of active factor refraction within the system" [10]. According to this principle, external action can be weakened by buffer properties of the system. However, in a 20–40 cm soil layer, Cd content declines by 13.1% (1999), 11.4% (2000), 8.5% (2001), 5.1% (2002), 3.8% (2003), 2.0% (2004), 1,1% (2005), 0.8 % (2006).

HM dissipation constant in a 0–20 centimeter layer of soil is described by the exponential model [1, 2]:

$$(k = \frac{2.303}{t} \lg \frac{C_0}{C_t})$$ (1)

where: C_t – final concentration; C_o – initial concentration; k – dissipation constant of heavy metal; t – time or period, days.

Half life period is calculated according to the following equation [4, 1, 2, 8]:

$$T_{50} = \frac{0.693}{k}$$ (2)

Heavy metal mobility in the soil increases with the value of the constant. Cu had the highest speed of dissipation in turf-podzol sandy loam soil in our investigation: the dissipation constant of copper in soil was 1.2 years^{-1} and T_{50} was 0.6 year. The other metal's dissipation constants were 0.91 (Zn), 0.7 (Cd), 0.64 (Pb) years^{-1} and T_{50} were 0.8 (Zn), 1.0 (Cd), 1.1 (Pb) years^{-1} (Table 1). Similar experimental data were obtained for chernozem soil (see Table).

TABLE 1. DISSIPATION CONSTANTS OF HEAVY METALS IN 0–20 CENTIMETERS LAYER OF TURF-PODZOL SANDY LOAM SOIL AND CHERNOZEM SOIL AND T_{50} (YEARS^{-1})

	Pb	Cd	Zn	Cu
Turf-podzol sandy loam soil				
Const.	0.64	0.70	0.91	1.22
T_{50}	1.10	1.00	0.80	0.60
Chernozem soil				
Const.	0.72	0.80	1.07	1.31
T_{50}	0.96	0.80	0.65	0.53

*r^2 0,8–0,9

According to the value of heavy metals dissipation rate in the 0–20 centimeters layer, the heavy metals can be ranked in the following descending order: Cu>Zn>Cd>Pb.

The dynamics of HM content in 20–100 cm profile through each 20 cm layer was approximated by the Koller function (picture). The general form of the equation is:

$$\acute{o} = a_0 \cdot x^{a_1} \cdot \overset{\circ}{a}^{a_2 x} \tag{3}$$

where a_0, a_1, a_2 denote constant indices of each metal migration rate in any examined layer.

1-april 1999; 2-october 1999; 3-april 2000; 4-october 2000; 5-april 2001; 6-october 2001; 7 - april 2002; 8- october 2002; 9 -april 2003; 10-october 2003; 11 -april 2004; 12 -october 2004; 13 -april 2005; 14 - october 2005; 15 - april 2006; 16-october 2006.
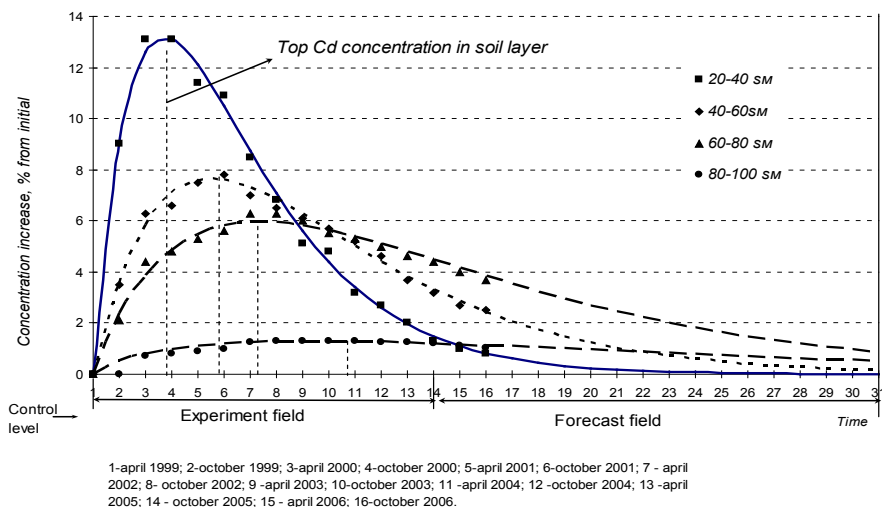
Fig. 1. Dynamics and prediction of Cd concentration in the profile of the turf-podzol soil.

Equation (3) allows to predict the metal concentration in soil (r = 0.87–0.99). For example, 14 years after Cd impact contamination of a 20–40 cm soil layer will present about 1% of the initial amount of Cd.

This simulation model also makes it possible to develop a strategy for safe agriculture on polluted stretches of land.

CONCLUSIONS

1. The migration of Cd, Cu, Zn and Pb in a 20–100 cm layer of soil was described using the Koller model. This model allows predicting the evolution of the amount of metal present in 20–40, 40–60, 60–80 and 80–100 cmlayers of soil after the occurrence of impact pollution.

2. Using the exponential model, we obtained the dissipation constants of Cd, Pb, Cu and Zn in a 0–20 cm layer of turf-podzol sandy loam and chernozem soil. The rate of dissipation of the metal from the 0–20 cm layer of soil increases with the value of the constant. Knowing the value of the constant, one can calculate the length of half-dissipation of the metal in the 0–20 layer of soil.

3. We obtained the following ranking of the metals Cu>Zn>Cd>Pb according the value of their dissipation constant. We conclude that the dissipation constant not only characterizes the migration ability of the metal but also makes it possible to measure the quality of the soil for crop growth.

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KINETYKA MIGRACJI OŁOWIU, KADMU, MIEDZI I CYNKU W GLEBIE DARNIOWO-BIELICOWEJ I CZARNOZIEMIE

W pracy przedstawiono proces migracji metali ciężkich: Pb, Cd, Cu, Zn w lokalnie zanieczyszczonych glebach: darniowo-piaszczystej i czarnoziemie. Dane doświadczalne uzyskano w latach 1999–2006. Stosując model wykładniczy i model Kollera otrzymano szereg metali zgodnie z szybkością ich usuwania z 0–20 cm warstwy gleby. Uzyskane wyniki także pozwalają na prognozowanie wielkości mobilnych form metali ciężkich w warstwie gleby 20–100 cm. Wyniki badań można wykorzystać do oceny zagrożenia metalami ciężkimi i kontroli warunków uprawy roślin w różnych glebach.