The Ability of Soils to Protect Groundwater from Heavy Metals Pollution: Approaches, Assessment, and Practical Use of the Experimental Data

Motuzova G., Barsova N. and ***Karpova E.***

Moscow M.V . Lomonosov State University, Faculty of Soil Science 119899,
Vorobiovy Hills, Moscow M.V. Russia
Fax: 7(095)939-09-89, E-mail: motuzova@mail.ru

Abstract: Soils present a natural biogeochemical barrier, which limits the pollution of ground water. The ability of soils to adsorb chemical elements and distribute them among the soil components are the important soil properties, which provide the protection functions of soils. The parameters of these processes were obtained in the field and laboratory experiments. The investigated soils were presented by some noncalcareous soils of Russia: podzol, gray, brown soils. In the field experiment the soils were washed by the solution of Zn salt. Zn adsorption by different soil's horizons and Zn concentrations in percolated water were defined. The adsorption capacity and the strength of Zn fixation by soils were determined in static and dynamic conditions in laboratory. It was estimated the influence of soil texture, the content of organic matter and clay minerals, soil's pH on Zn adsorption. The processes of ion exchange, chemical precipitation, specific adsorption of Zn were established in different soil's horizons. The results of field investigation differ from the laboratory ones because of horizontal migration of soil water through the soil macropores.

Keywords: soil, protection of groundwater, pollution, heavy metals, speciation, adsorption

1 Introduction

Soils as a special natural component carry out the important functions in ecosystem. They represent a powerful natural biogeochemical barrier, which limits migration of chemical elements and pollution of ground water. The metals migration in the landscapes depends on some factors. Two groups of soil properties are important among them: the ability of soils to adsorb chemical elements and to distribute them among the soil components. The theory of adsorption ability of soil and formation of the system of chemical elements compounds are the main sections in soil science and geochemistry.

Widespread is the idea that metals are fixed on to the surface of soil particles as resulted from sorption, ion exchange and sediments formation. However, there is a lack of data about correlation between these processes. Not infrequently, models are elaborated to show that the absorption is increasing with the increasing soil pH, specific surface, cation exchange capacity as well as the content of silt and humus. Special emphasis should be laid on studying how different substances behave in soils and how firmly they are bound to be capable for further migration. There exists a concept of specific and non-specific sorption of chemical elements (1,3). The latter is related to ion exchange. Several equations are offered to demonstrate the ion exchange with a view of characterising selectivity and stability of metal absorption in soil. But the indices of specific sorption have been so far examined insufficiently. The present investigation is aimed to study mechanisms and quantitative indices of metals absorption in noncalcareous soils for the assessment the ability of soils to protect ground water from pollution.

2 Objects and methods

The investigated soils are presented by some noncalcareous soils of Russia: podzol, gray, brown soils. In the field experiment the pollution of soils by heavy metals (Zn, Pb, Cd, As) was imitated. In the spruce forest 6 grounds (0.5m × 0.5m) were daily washed by the solution of Zn salts (50 mg Zn/l) during a month, the total volume of solution accounts for 500 l. The lysimetric plants were placed under the investigated soil profiles, the percolated water were collected. Zn content in the lysimetric solutions and in the polluted soils was determined.

Some series of model laboratory experiments were carried out for the determination of the sorption capacity of above named elements by soils. The method of Zn adsorption by the samples of different soil horizons (L, H, F, A1A2, A2, A2B) in static and dynamic conditions was performed. In the first variant of experiments the series of solutions, containing 0-200 mg/l Zn (pH 3.0 and 4.5) were put into equilibrium with soil samples, the parameters of Zn adsorption capacity were defined. The strength of Zn bounds was studied as steadily replaced by ammonium acetate as well as by 1 n KCl from soils. In the second series the solution with 50 mg/l of Zn was spilled throw the some columns with the samples of each soil horizon, and then Zn concentrations in the solutions and the soil adsorption capacity were defined. The content of ion exchangeable Zn species in polluted soils was determined after their extraction by the solution 0,01 M CaCl2. Experimental data helped drawing isotherms of Zn sorption and desorption, providing flatten lines according to conditions of the experiment. The maximum of Zn adsorption was calculated on the base of the Langmur’s equation of Zn adsorption. Zn content in the solution was determined by AAS method.

3 Results and discussion

The theoretical summarising and experimental investigations show that there are two main groups of metals species in soils: available and firmly tied (Table 1). Metals in structure of primary and secondary minerals and organic matter present the firmly tied species. The mobile (available) species of chemical elements are the most important in view of environment protection. High concentration of these species of heavy metals exerts the ecotoxicological influence. The mobile species are also represented by two following groups, which are found in dynamic equilibrium: compounds of the soil solution, having greater mobility, and compounds of solid phases, considered as potentially mobile ones (2). Processes responsible for the strength of bounds between mobile compounds both in solid phases and in the soil solution provide migration capacity of metals within a landscape, their availability to plant and a higher concentration of substances harmful to the ecosystem, including ground water.

Table 1 The species of metals in soils

Mobile (available) species		Nonmobile firmly tied species
Actually mobile: in the soil solution	potentially mobile: in the soil solid phases	primary minerals, clay minerals, $Fe(OH)_3$, $Al(OH)_3$,weakly soluble salts, organic matter
Me^{2+}, $Me(OH)^+$, $MeSO_4$, $MeAcet^-$ MeOx, $MeFA^-$	exchangeable, sorbed, salts	

FA - fulvic acids, Acet - acetate, Ox – oxalate acids.

The methods of the determination of metals species in soils should allow the assessment of the ability of soil to protect ground water from pollution. The following methods can be recommended for this purpose (Table 2).

**Table 2 The methods of the polluted soils investigation.
Laboratory methods**

The methods of soil Solution receipt	The methods of metal species in soil solution determination	The methods of the mobile forms of metal from the soil solid phases receipt	The methods of the sorption ability of soil determination
– Supplanting by alcohol, – extraction by 0,03-0,05 M $CaCl_2$, $Ca(NO_3)_2$, – vacuum filtration	– ionometric, – division of particles on the ion-exchange resins, – division of particles by the electrodialysis – theoretical calculation on the base of thermodynamic constants	– extraction by 1n. CH_3COONH_4	– static, – dynamic

《In situ》 methods:

ionomethric, lysimetric percolate collection and their analysis, the analysis of the samples from different horizons.

The fulfilled laboratory experiments have showed that the most adsorption ability accordingly to investigated elements is unique for the soil samples with silty composition and high level of pH and humus content. When the metals concentration consists of 2-10 critical levels of these metals for natural water soil samples can adsorb 70%-100% of metals from solution. The absorbed Zn is bound in the soil-adsorbing complex with different selectivity degree. It was estimated, that Zn absorption in noncalcerous soils is manifested though processes of ion exchange, specific sorption in the soil absorbing complex and chemisorption, simultaneously proceeding in the soil. In the composition of Zn compounds conditionally considered as specific ones, there are ions capable to exchange under dynamic conditions. This is true for the other ions too; just by this reason, no similar levels of cation exchange capacity (CEC) have been established for diverse replaced actions. Three fractions of Zn adsorbed can be identified: 1 - firmly tided species of Zn, which are not able to desorption; 2 - species of Zn, which are able to desorption from specific places; 3 - species of Zn, which are able to desorption from non-specific places (Fig.1). The share of metals ions, which are adsorbed nonexchangeably accounts for 50%—70 % from the total amount of adsorbed metals. This dozen depends from metals content in solution and the property of soil horizons. The pH increase is correspondended by the increasing of Zn adsorption in different degree.

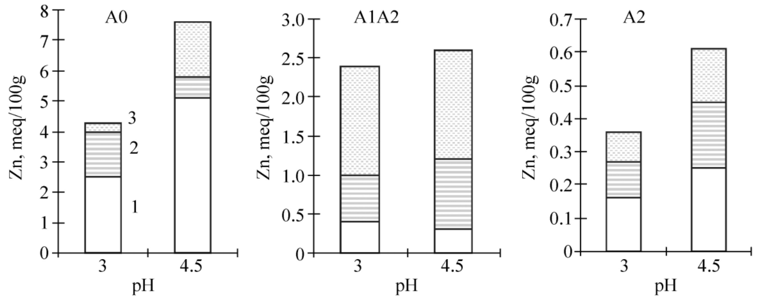

Fig.1 The species of adsorbed Zn in podzolic soil under pH 3.0 and 4.5

Thus, specific sorption is highly depended on properties of absorbed ions inherent in the soil-absorbing complex. The influence of soil texture, the content of organic matter and clay minerals, soil's pH on the adsorption ability of soils in respect of some heavy metals was assigned. In humus horizon the exchange complex is completely saturated by Zn as affected by solution with Zn concentration of 0,3 g/l. Due to a high soil buffering capacity changes in pH of initial solution from 4.5 to 3.0 have no effect upon Zn absorption. In eluvial horizon the amount of absorbed Zn is rather small. At a low level of cation exchange capacity about 50% of Zn have specific and non-specific sorption in the soil absorbing complex, the other 50% yield chemisorption. Due to changes in pH of soil solution (from 4.5 to 3.0) the content of absorbed Zn becomes declined by 1.5 times. The highest Zn absorption is observed in litter (2—3 g/kg), but this process is quite different by nature. Owing to a high level of CEC and the increased content of earth metals of organogenic origin only a small share of Zn appears in exchangeable form (Table 3). Its major part is firmly bound and may be represented by salts of base-rich organic acids, oxalates in particular.

Table 3 The share of adsorbed Zn from cation exchange capacity in podzolic soils

Horizon	CEC, me-equ/100g	Zn adsorbed maximum (Qmax),		Zn capable to desorbtion, % from Zn ads. (Qmax)
		mg-equ/100g	% from CEC	
L	42.0	1 6.0	37.0	50
A1A2	6.1	2.36	38.7	85
A2	2.4	0.25	10.4	70

Apart from Zn absorption in exchangeable form and in the form of heavy-soluble salts, it can be fixed in soils as colloidal particles. Based upon a comprehensive analysis of the soil solution ultrafiltration one can notice, that in mineral horizons of podzolic soils almost a half of total Zn content occurs in the form of colloids, in peat horizons its amount seems to be even much higher. The investigation have shown that each kilogram of soil can adsorb till 100-220 g Zn, or each m2 of the colon of the podzoil's profile can absorb 10-30, till 100 g Zn (Table 4). At the same the significant part of metal can percolate throw the soil and it is not adsorb. This phenomenon connects which the organisation of soil porous space. The migration of the metals along the soil macroporouses disturbs the direct correlation between the concentration of metals in the soil solutions and the soil adsorption ability. The influence both of them showed is taken into consideration when the models of the heavy metals migration throw the soil profile are worked out.

Table 4 The ability of podzolic soils to adsorb Zn (laboratory and field experiment)

Horizon (depth, cm)	Zn sorbed, g/kg of soil			Zn, sorbed by soil horizons, g/m^2*h		
	Laboratory	Experiment	Field	Laboratory	Experiment	field
	Static conditions	Dynamic conditions	Experiment	Static Conditions	Dynamic conditions	experiment
A0 (0-3)	120	94	221	4	3	2
A1A2(3-15)	37	25	15	17	8	2
A2 (15-27)	10	6	4	10	6	2
Total				31	17	6

Different species of heavy metals present in the soil solution: simple ions (free ions) and complex ions with different charge (Table 5). The form of metals in the solution influences on the ecotoxicological effect of metals and the ability of metals to be sorbed by the soil components. The ionomethric methods were used for the determination of the content of free ions in the soil solutions and lysimetric waters. The electrodyalis methods are suited for the separating the particles of the heavy metals according to their charge. The calculated methods have been used for the determination the complex particles of heavy metals in the solutions and lysimetric water. There are numerous examples, which illustrate the proportion of different forms of heavy metals in the soil solutions and lysimetric waters of polluted taiga soils of Russia.

The investigated polluted soils take place near the metallurgical plants in the north regions of Russia. These plants throw the aerosol waste, which are enriched in Cu and Ni, and pollute the surrounding soils during more than 60 years. The available forms of heavy metals exceed the permissible limit in soils 20-30 times. The content of metals in soil water increased in the same degree. The part of the simple Cu^{2+} ions in the soil solutions and lysimetric waters accounts for 10% - 20%. The most part of the metals presents in the soil solution as the organic complexes with the negative charge. The organic complexes of metals with negative charge have the most migration ability in the polluted landscapes. Nevertheless the adsorption ability in the soils of this region is enough to protect ground water from pollution: they are not enriched by Cu and Ni in comparison with background conditions.

Table 5 The content of Cu and Ni and their species (% from total content) in the lysimetric waters from A0 horizons of the polluted podzolic soils around the Cu-Ni plant

Element	Total content, mg/l	Amount of species of metals (% from the total content)			
		anions	Neutral	Cations	
			Particles	simple ions	complexes
Cu	0,0085	55	22	12	11
Ni	0,0101	57	20	7	16

4 Conclusion

It is impossible to receive the parameters of adsorption ability of soil indirectly, i.e. on the base of chemical and physical properties of soils. Direct analytical measuring of the sorption parameters of the soils are necessary in the field and (or) laboratory experiments. We must determine the sorption capacity and the strength of the metals fixation of soils, to study the mechanisms of metal fixation by soils for prognosis the ability of soils to protect ground waters from contamination. It is insufficiently to use only the soil sorption characteristics, which are obtained, in the laboratory to predict the metals migration in the landscapes. The type of soil organisation, the structure and size of soil pores, cracks, holes of plants roots and soil animals, the conditions of experiment influence the migration of metals too and must be taken into account when the models of the metals migration in soils are worked out.

Experiments with podzols have shown that mechanisms responsible for Zn absorption in these soils proved to be different. In litter salt sediments with anions of organic acids are dominant. In humus horizons specific and non-specific Zn sorption takes place. The amount of absorbed Zn is found to be proportional to CEC and can be replaced by water to be capable for migration. In mineral horizons the Zn sorption is lower by one order, but 50%—90% of Zn have a high strength of bounds and not capable for further migration. Under the load 80—120 Zn g/m^2 80%—90% of added Zn can be fixed by the profile of podzolic soil, but the last is able to leave the soil profile because of "full" through macroporoses

It was estimated that practically all the theoretical approaches which deals with soil adsorption ability under the ecological modelling do not correspondent to the experimental data in the full degree. The metals ions in the solutions of the natural and technogenic soils are not free; they are predominantly connected with the organic and nonorganic ligands in the form of anions. The share of adsorbed metals decreases to 3—5 times when the metals concentration in water exceeds the limited level for the natural water in 2—5 orders. In these conditions the CEC of soil can be filled no more than 20%—50%. Metals ions, which soils retain during adsorption and ion exchange processes, are fixed with different strength. In humus horizons the most part of them is retained in easily exchangeable form. The material of the litters and mineral horizons adsorb heavy metals predominantly in nonexangeable form and retain them firmly. Kinetic factor is not taken into account as a rule. The experimental parameters of ability of soils to adsorb metals very often characterise their potential ability. The parameters that have been received in the field conditions do not coincide fully to those ones, which were obtained in the laboratory conditions. It depends on the structure of soil porous space and horizontal migration of soil water. Incomplete correspondence realistic ability of soils to adsorb metals to potential ones can lead to the revaluation of the soil ability to protect ground water from pollution.

References

[1] Hodgson J.F. , 1960. Cobalt Reactions with Montmorillonit. Soil Sci. Soc. of Amer. Proceed., 24, 3: 165- 168;

[2] Sposito G. , 1984. The thermodynamics of soil solutions. Gidrometeoizdat, Leningrad, 240;

[3] Sposito G., 1984. The Surface Chemistry of Soils. Oxford Univ., Pr. N.Y., 310.