FORMATION AND DISINTEGRATION OF SMALL-SCALE CONCENTRATION GRADIENTS OF TRACE METALS ON AGGREGATE SCALE

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Dedicated to my best teacher,
brilliant mathematician, historian and inventor
Dr. Ashot N. Agadzhanov

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ABSTRACT

Airborne heavy metals are deposited on aggregate surfaces, forming small-scale concentration gradients. Cadmium, Cu, Zn and Pb concentrations were measured in inner and outer aggregate parts in archived soil samples from 1910-1954 and in recently collected soil samples from the same locations. Concentration gradients were higher in recent soil samples, and concentrations of all heavy metals inside aggregates in recent soils were higher than in archived ones. A hypothesis of heavy metal redistribution inside aggregates due to diffusion process has been examined.

Diffusion of Zn, Cd, Ba and Cs cations in repacked soil samples under water-saturated conditions has been studied. Four soil samples from A_l (sample **A**) and B_t (sample **B**) horizons of a luvisol, A_h horizon of a chernozem (sample (**Ch**), and aggregate coatings from B_t horizon of the luvisol (sample **C**) were saturated with distilled water, packed into columns of 1.8 cm in diameter and 1 cm long, and exposed separately to 45 ml of a solution with one of the studied cations ($C(Zn)=10$ mg l^{-1}, $C(Cd)=1$ mg l^{-1}, $C(Ba)=10$ mg l^{-1} and $C(Cs)=40$ mg l^{-1}). The cations were labeled with the corresponding radioactive isotopes ^{65}Zn, ^{109}Cd, ^{133}Ba and ^{137}Cs. After the exposition time (4 to 40 days) the columns were removed from solution and sliced into 0.1 mm slices. Concentrations of the cations in the slices were found by means of γ-spectroscopy, and the diffusion profiles of the cations were obtained. The same repacked and water-saturated soil samples were exposed to 600 ml of $3.5 \cdot 10^{-3}$ M NaCl solution labeled with ^{36}Cl isotope from 18 to 22 hours. The columns were immediately cut into approximately 0.4 mm slices. Linear diffusion equation of non-adsorbing substance was fitted to the diffusion profiles in order to find the tortuousity of the soil. The corresponding parameter - impedance factor (f) was found 0.57 for samples **A** and **B**, 0.54 for sample **Ch**, and 0.52 for sample **C**. The factor values, as well as soil water content and diffusion coefficients of the cations in water were used in mathematical model of adsorption hindered diffusion of cations. The coefficients of linear, Langmuir and Freundlich adsorption isotherms were fit to obtain such reciprocal buffer power, at which the modeled diffusion curves are most close to the experiment. The model based on Freundlich adsorption isotherm described the profiles of Cd, Zn and Cs (except sample **A**) the best. The diffusion profiles of Ba (except sample **C**) were best approximated with the model based on Langmuir adsorption isotherm. Distribution coefficient K_d from linear adsorption isotherm for Cd correlated well with C_{org}, whereas K_d for Zn, Ba and Cs correlated well with soil CEC. The model was found suitable for describing cation diffusion in soils. Disintegration of small-scale gradients of heavy metals on aggregate scale because of diffusion process is unlikely.

ZUSAMMENFASSUNG

Luftbürtige Schwermetalle, die sich auf Aggregatoberflächen ablagern, bilden kleinräumige Konzentrationsgradienten aus. Cadmium, Cu, Zn und Pb-Konzentrationen wurden im äußeren und inneren von Aggregaten aus archivierten (1910-1954) und neu gesammelten Bodenproben bestimmt. Die Schwermetallgehalte im inneren der Aggregate und die Schwermetallanreicherung auf der Aggregatschale waren in den neuen Bodenproben höher als in den archivierten. Geprüft wurde die Umverteilung der Schwermetalle innerhalb der Aggregate durch Diffusion.

Die Diffusion von Zn, Cd, Ba and Cs wurde in gepackten, wassergesättigten Säulen untersucht. Es wurden 4 verschiedene Böden verwendet: (Probe **A**) aus dem A_l Horizont und (Probe **B**) B_t Horizont eines Luvisols, (Probe **Ch**) aus dem A_h Horizont einer Schwarzerde und (Probe **C**) aus Aggregatüberzügen des B_t Horizont des Luvisols. Die vier Bodenproben wurden mit destilliertem Wasser gesättigt und in Säulen mit 1,8 cm Durchmesser und 1 cm Länge gepackt und separat in 45 ml Lösung getaucht ($C_{(Zn)}$=10 mg l^{-1}, $C_{(Cd)}$ =1 mg l^{-1}, $C_{(Ba)}$ =10 mg l^{-1} und $C_{(Cs)}$ =40 mg l^{-1}). Die Kationen der Lösung wurden mit den korrespondierenden radioaktiven Isotopen ^{65}Zn, ^{109}Cd, ^{133}Ba und ^{137}Cs markiert. Nach 4-40 Tagen Exposition wurden die Säulen entnommen und in 0,1 mm Scheiben geschnitten um die Diffusionsprofile mittels γ-Spektroskopie zu bestimmen. Gleichartige Säulen wurden für 18 - 22 Stunden in 600 ml 3,5 $\cdot 10^{-3}$ M NaCl (markiert mit ^{36}Cl) getaucht. Die Säulen wurden nach der Entnahme umgehen in 0.4 mm dicke Scheiben geschnitten. Die lineare Diffusionsgleichung wurde an die Konzentrationsprofile angepasst, um die Tortuosität der Säulen zu bestimmen. Der korrespondierende Impedanzfaktor (f) wurde für die Proben **A** und **B** mit 0.57, für die Probe **Ch** mit 0,54 und für die Probe **C** mit 0,52 ermittelt. Die Impedanzfaktoren als auch die Wassergehalte und die Diffusionskoeffizienten der Schwermetalle in Wasser wurden in ein Modell eingearbeitet. Aus den Koeffizienten der angepassten Adsorptionsisothermen (linear, Freundlich und Langmuir) wurde die reziproke Pufferung abgeleitet, die den experimentell ermittelten Diffusionskurven am besten entspricht.

Dabei ließen sich die Konzentrationsprofile von Ca, Zn und Ba gut durch Freundlich-Isothermen beschreiben (Ausnahme: Probe **A**). Die Diffusionsprofile von Ba wurden am besten durch Langmuir-Isothermen widergegeben (Ausnahme: Probe **C**). Für Cd korrelierte der Verteilungskoeffizient kd der linearen Isotherme gut mit dem C_{org} Gehalt der Proben, während die Koeffizienten für Zn, Ba und Cs mit der KAK korrelierten. Das Modell war gut geeignet, Diffusionsprozesse im Boden zu beschreiben. Der Abbau der kleinräumigen Schwermetallkonzentrationsgradienten auf Aggregatebene durch Diffusionsprozesse ist unwahrscheinlich.

ACKNOWLEDGMENTS

GLOSSARY

CEC – cation exchange capacity

C_{org} – organic carbon

K_d – distribution coefficient

OM – organic matter

1 General introduction

1.1 Influence of heavy metals on the environment and human health

Metals are playing an important role in nature. All living species are dependent on a presence of metal salts in their organisms. Up to now at least 24 different elements are considered as essential for life, and most of them are metals. Although presenting in trace amounts in organisms, metal ions are responsible for numerous enzymatic and metabolic reactions. They usually act as coordination centers for building up or stabilizing structures of enzymes and proteins. Only for zinc 50 enzymes and the corresponding reactions are known (*Mertz*, 1987). A lack of an essential element in an organism leads to an absence of certain enzymes and the corresponding reactions, which may cause intoxication, followed by illness or even death.

Metal-metal interactions have been intensively studied in recent years because of their contribution in human health and probable diseases (*Mills*, 1985). Metals in an organism are transported to cells by means of specific and unspecific mechanisms, which are sometimes identical for different metal ions. An excess of one element can block a transport of another. For example, an excess of zinc produces a deficit of copper and iron, an excess of calcium produces deficit of zinc, manganese – deficit of magnesium, cadmium – deficit of selenium and zinc, etc. Here is the first reason of the metal toxicity for an organism: necessary metal ions of one type can be blocked by surplus of the others.

The second reason of metal toxicity is that these elements are biologically active themselves. Metal ions are interfering biochemical redox processes. It may be formation of active hydroxyl radicals (Fe(II), Cu(I)), oxidation of biologically active groups (for example Cu(II) oxidize thiol-groups in cell membranes to disulfide bridges) and indirect promotion of lipid peroxidation (Pb(II)) (*Halliwell* and *Gutteridge*, 1984; *Christe* and *Costa*, 1984). Ions Cd(II), Zn(II) and Cu(II) lower the oxidant resistance of cells through the formation of very stable complexes with glutathione, which is the major scavenger of active radicals. Active free radicals are destructive not only for enzymes and proteins, but for DNA as well. Heavy metals may also form stable complexes with enzymes, like, for example, Ag(I), Cd(II) and Hg(II) with glutathione peroxidase, thus inhibiting enzymatic reactions (*Fishbein*, 1987).

Because of pronounced effects on human and animal health heavy metal concentrations in soil, water and food are strictly regulated by laws. However bioavailability and toxicity of the metals are dependent on a form in which they present in nature.

1.2 Heavy metal deposition and formation of heavy metal concentration gradients in soil aggregates

Human activity leads to increasing amounts of heavy metals venting into the atmosphere. Main sources of the venting are industry (coal power plants, smelteries, waste incinerators, etc.) and automobiles. Heavy metals attached to dust particles may be transferred through air at grate distances before fallen out with rains upon soil. The deposited heavy metals become included in food chain and biological circulation by plants' uptake or groundwater leaching (*Mayer*, 1981).

In structured soils aggregate surfaces are exposed to preferential flow paths. Thus aggregate surfaces provide better conditions for bacterial growth and soil organic matter biodegradation (*Allison*, 1968). Preferential weathering of soil minerals on aggregate surfaces is also faster, compared to the aggregate inner parts (*Horn*, 1987). Differences in chemical properties between aggregate surfaces and aggregate cores may lead to uneven contamination of aggregated soil. *Wilcke* and *Kaupenjohann* (1994, 1997) found higher concentration of heavy metals on aggregate surfaces in contaminated soils. The heavier was the contamination, the higher was the concentration difference between aggregate cores and aggregate surfaces (*Wilcke* and *Kaupenjohann*, 1998).

The second reason of uneven distribution of heavy metals in aggregates is a different availability of dissolved contaminants to aggregate surfaces and cores. A flow rate of water between aggregates is much higher, then inside of them (*Gunzelmann* and *Horn*, 1985). The importance of the fact has been confirmed by *Wilcke* and *Kaupenjohann* (1998), who found statistically significant difference in heavy metal distribution along aggregates in cambisols, whereas no significant difference in chemical properties along the aggregates was found.

Uneven distribution of heavy metals along aggregates is of importance, because this may lead to the underestimation of environmental risks. Plants' roots are growing predominantly on aggregate surfaces, but not inside aggregates (*Whiteley* and *Dexter*, 1983). *Wilcke* and *Kaupenjohann* (1997, 1998) concluded from the results on heavy metal speciation along aggregates that heavy metals on the aggregate surfaces are bounded weaker to weathered minerals and more available for plants and leaching. Thus the availability of heavy metals for plants in aggregated soils is higher, then predicted from a bulk soil analysis (*Hamon* et al., 1998).

1.3   Influence of heavy metal adsorption on the diffusion process

Adsorption plays an important role in the interaction of heavy metals with soil. It is one of the most important factors, controlling mobility and availability of heavy metals in nature. Adsorption of heavy metals on clays may include three different mechanisms: formation of strong inner-sphere complexes, weaker outer-sphere complexes and adsorption on the diffuse layer on a negatively charged surface. Adsorption may also include formation of complexes of heavy metal ions with organic matter (OM). Natural OM is often adsorbed on clay surfaces (*Stumm*, 1992), that is why ternary complexes "mineral surface - OM - metal ion" are common in soil.

The most available and mobile fraction of heavy metals in soils is in dissolved state, whereas adsorbed ions may be considered as immobile. *Street* et al. (1977) found low concentrations of cadmium in soil-water suspension were controlled by adsorption process. The same conclusion has been made by *Welp* and *Brümmer* (1999) for the wide range of Mg, Sr, Co Zn, Ni, Cd, Cu and Pb concentrations in soil solution.

The factors influencing adsorption of heavy metals the most are soil pH (*Welp* and *Brümer*, 1999), especially for higher metal concentrations (*Basta* and *Tabatabai*, 1992), soil organic matter (SOM) (*Catlett* et al., 2002), mineral composition (*Stumm*, 1992) and cation exchange capacity (CEC) (*Abd-Elfattah* and *Wada*, 1981).

Cesium, in contrast to heavy metal ions, does not form strong complexes with OM. Furthermore, an influence of soil organic matter on a sorption of Cs^+ ions was found negative (*Kornilovich* et al., 2000; *Bondar* et al., 2003). Cesium ions may form not only outer-sphere complexes with clays, but also very stable inner-sphere complexes on frayed edges of layer-type silicates vermiculite and montmorillonite (*Bostick* et al., 2002). Organic matter is often adsorbed on clay particles, preventing the access of Cs^+ to the specific sorption sites. On the contrary, Cs complexes with OM are relatively unstable, making Cs available for plants. The most important soil properties for Cs adsorption are CEC and mineral composition (*Bondar* et al., 2003).

Bundt et al. (2000) studied a distribution of ^{137}Cs, ^{210}Pb, ^{239}Pu, ^{240}Pu and ^{241}Am radionuclides along preferential flow paths. All radionuclides were found rapidly immobilized by soil particles and showed slow transport behavior once they are adsorbed. The immobilization is so strong, that even after 15 years of studies no vertical mobility of Cs along the soil profile was found (*Smith* et al., 1997).

These facts allow us confidently suppose that adsorbed ions are not involved into diffusion process on aggregate scale. Although a diffusion of adsorbed heavy metal ions in mineral particles is still possible, it is negligible slow to make any difference on an aggregate-scale distribution of heavy metals. Thus it is necessary to differentiate between adsorbed ions which are not involved into diffusion on aggregate-scale and mobile ions in liquid phase.

1.4   Mathematical model of heavy metal diffusion in a soil

The mathematical model of heavy metal ion diffusion in soil has been developed on the basis of a diffusion equation in porous media with respect to an adsorption process.

One-dimensional diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

when applied to a diffusion of solutes in a soil should include information on porous structure of the soil and its water content.

Nye (1979) proposed to use for non-adsorbing substances an equation

$$D = D_L f$$

where D_L is the diffusion coefficient of a solute in free solution and $f \in [0;1]$ is an impedance factor, the coefficient related to the tortuousity of diffusion paths in porous media.

Nye and *Tinker* (1977) proposed to use an effective diffusion coefficient for adsorbing substances in form:

$$D = D_L f\theta Z \ ,$$

where θ is a volumetric moisture content in soil and Z is a reciprocal buffer power, determined as

$$Z = \frac{\partial C_L}{\partial C}\ ,$$

where C_L is a concentration of substance in liquid phase and C is a substance concentration in both liquid and solid phases. The relationship between C_L and C are usually described in terms of a distribution coefficient or adsorption isotherms.

The simplest model of the adsorption process is so-called linear adsorption. It describes an amount of adsorbed substance as a linear function of the substance concentration:

$$C_{ads} = K_d C_L .$$

The coefficient of proportionality K_d is called "distribution coefficient". Although the model is primitive, it has been used widely in describing adsorption processes because of its simplicity (*Trivedi* and *Axe*, 2000; *Bostick* et al., 2002; *Collins* et al., 2003).

More complicated and more precise adsorption models are non-linear. They are closer to real systems, because soil has a variety of adsorption sites with different adsorption energies. One of the widely used equations has been proposed by Langmuir:

$$C_{ads} = \frac{C_{ads\,max} K C_L}{1 + K C_L}\ ,$$

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where $C_{ads\,max}$ is the maximum amount of a substance which can be adsorbed, K is a coefficient, related to the energy of adsorption. The equation is describing an adsorption of substance from gaseous phase on a solid surface with limited amount of adsorption sites. *Sposito* (1979) derived Langmuir equation for ion-exchange reactions in a soil. Langmuir isotherm was the best in description of Cd adsorption in 30 various soils (*John*, 1972) and in description of Pb and Zn adsorption in different soils (*Diatta* et al., 2003).

The other equation has been proposed by *van Bemmelen* (1888) and widely known as Freundlich adsorption isotherm:

$$C = AC_L^B$$

where A and B are variable coefficients and B is usually between 0 and 1. Although the equation is empirical, it has been successfully applied to adsorption of heavy metals in soil. Freundlich equation can be derived for ion-exchange reactions in soil as well (*Sposito*, 1980). The equation described well an adsorption of trace amounts of Cu, Zn, Pb and Cd onto amorphous iron oxide (*Benjamin* and *Leckie*, 1981) and traces of Cd on soil and clay minerals (*Street* et al., 1977; *Garcia-Miragaya* and *Page*, 1976).

The reciprocal buffer power Z can be unambiguously calculated from an adsorption isotherm and then substituted into the diffusion equation, which can be solved numerically.

1.5 Stability of the gradients of heavy metal concentration in soil aggregates

The relevance of uneven distribution of heavy metals along aggregates depends on a lifetime of heavy metal concentration gradients. The gradients were found decreasing with time, until there were no difference in heavy metal concentration between aggregate cores and surfaces (*Ilg* et al, 2004). There are two possibilities of the process, which are not mutually exclusive:

1) decomposition of old aggregates and formation of new ones;
2) diffusion of heavy metals along the concentration gradient.

Up to the moment little is known about the stability of soil aggregates. The process seems to be highly dependent on climate, soil type, microorganism activity, etc. *Wilcke* et al. (2002) found the aggregate turnover in grassland topsoil occur within few weeks. On the other hand, *Bundt* et al. (2000) and *Hagedorn* and *Bundt* (2002) found preferential flow paths in forest subsoil stable at least for several decades. *Ilg* et al. (2004) compared the heavy metal concentrations in aggregate surfaces and cores in recent and archived soil samples, collected in 1910-1950s. The changes in heavy metal concentration in aggregate cores show that the turnover times of aggregates are less then the age of archived samples (50-90 years).

Although diffusion processes in soils has been intensively studied last 50 years, there is not much information on the diffusion of heavy metals in soil aggregates. The only work on studying cation diffusion in natural aggregated soil without sample destruction has been made by *Tokunaga* et al. (2001). The group studied chromium diffusion along soil aggregates and an influence of microorganisms and organic matter on chromium reduction by means of micro X-ray absorption near edge structure spectroscopy (micro-XANES). *Tokunaga* et al. (2001) found organic matter and microorganisms reducing the depth of chromium diffusion. In all cases the diffusion depth was shallow (2-10 mm) after days of exposition. In other words, heavy metal contamination of soil was localized in the outsides of the aggregates. The advantage of the method is that it allows observing the diffusion process in naturally aggregated soil without sample destruction, but micro-XANES technique is rather complicated and hardly available.

1.6 Open questions and hypotheses

It is however not discussed in the work of *Tokunaga* et al. (2001) or elsewhere, whether the diffusion process is slowing down with time and whether the diffusion of heavy metal may cover the distance comparable with an aggregate size. Two hypotheses had been tested:

1) the concentration gradient of heavy metals on aggregate scale may disappear because of the diffusion process;
2) aggregate skins are retarding heavy metal diffusion along soil aggregates.

In order to test the hypotheses, the following experimental setup was developed in close relation to the prospective mathematical model to be used. *Crank* (1979) in his book gives mathematical solutions for different diffusion problems. The simplest systems are those, where the diffusion is one-dimensional, and the concentration of the diffusing substance on the boundary is limited or remains always constant. One-dimensional diffusion is possible if a soil is exposed to the diffusing substance only from one side. This can be easily implemented by packing a soil sample into column.

Barraclough and *Tinker* (1982) and *Moldrup* et al. (1997) found some differences in solute diffusivity between repacked and undisturbed soils, but declared them as insignificant. This finding makes it possible to provide experiments with repacked soils and guarantees the result is close to the real system. The setup of an experiment on diffusion with repacked soil is easier and experimental data become more reproducible.

Pinner and *Nye* (1982) made an experiment on ion diffusion in water-saturated soil samples, which were in permanent contact with a solution of radioactive-labeled ions, and the concentration of the diffusing ion in the reaction chamber maintained constant during the exposition time. When applied to heavy metal diffusion processes, the system produced unsatisfactory results: effective diffusion coefficients of heavy metal ions were found comparable with the diffusion coefficient of chloride ions, what is discordant with findings in stability of the heavy metal concentration gradients in nature.

When an amount of heavy metal applied to a boundary is limited, it is important to find appropriate concentrations to work with. Soil contamination with heavy metals due to atmospheric deposition is normally low. But if the concentration of heavy metal ions applied to the soil was low as well, no diffusion profile was found: all ions were concentrated in the first layer of soil column (0.1 mm). The area of higher heavy metal concentration on the edge of the soil column remained stable for more than 40 days under water-saturated conditions, making the determination of the diffusion coefficient impossible. Such distribution resembles the one observed by *Bundt* et al. (2000) in low soil horizons. On the other hand, an experiment with high concentrations of heavy metal ions makes an experiment less similar to the real systems. I tried to choose possibly lower concentrations of heavy metals for which diffusion profiles were at least 20 experimental points long.

Using radioactive labeled ions in studies of soil-heavy metal interactions is a common practice (*Kennedy* et al., 1997; *Schug* et al., 2000). The radiotracer method allows determination of ultra-low quantities of a substance with extremely high precision. The method is based on the identical chemical properties of radioactive and stable atoms of a certain element. A proportion between radioactive and stable atoms in a close system remains constant. Even if noticeable radioactive decay occurs, it can be taken into consideration. Thus element concentration in a sample can be found from the measured activity.

Considering all written above, the most appropriate experimental setup for our studies would be a soil column with repacked soil under water-saturated conditions subjected to limited amount of radioactive-labeled ions. It is possible to apply a limited amount of heavy metal ions on the surface of water-saturated soil column like it has been made by *Pinner* and *Nye* (1982). But then the interfacial resistance coefficient should be determined. The simpler way is to put the soil column into a solution with dissolved ions. The interfacial resistance in this case is not important, and a concentration gradient in the solution can be neglected, because the diffusion of ions in water is much faster, than in a soil.

The thesis is organized in six chapters: introduction, four papers concerning 1) study of heavy metal concentration gradients in Russian soils, 2) development of method to study diffusion of heavy metals, 3) influence of aggregate coatings on heavy metal diffusion, 4) appropriate mathematical model to describe the diffusion process of heavy metals in soils and conclusions.

2 Heavy metal distribution in soil aggregates: a comparison of recent and archived aggregates from Russia[1]

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2.1 Introduction

Chemical soil properties may vary over distances of millimetres. One of the major reasons for the small-scale heterogeneity is the aggregation of soils (*Horn*, 1987; *Kaupenjohann*, 1989; *Wilcke* and *Kaupenjohann*, 1994). In aggregated soils, water flow occurs at different velocities in and between aggregates (*Gunzelmann* and *Horn*, 1985). Aggregate surfaces are in closer contact to faster moving water containing most of the chemical compounds that enter the soil. One consequence is enhanced weathering of the aggregate exterior because of the preferred buffering of protons (*Kaupenjohann*, 1989). Furthermore, living conditions for microorganisms are more favourable between aggregates than within them because of better aeration and nutrient supply. Therefore, organic matter frequently shows lower concentrations and an advanced degree of degradation in the aggregate exterior compared with the interior (*Allison*, 1968; *Augustin*, 1992; *Amelung* and *Zech*, 1996). As a result of the high resistance of soil aggregates, most plant roots grow on the aggregate surfaces. Therefore, they mainly come into contact with the chemical conditions of the aggregate exterior rather than with the mean properties of the bulk soil (*Whiteley* and *Dexter*, 1983). Thus, a large part of the chemical reactions and biological activity occurs to a larger extent in the aggregate exterior and between the aggregates than in the interior. This implies that for the assessment of effects of pollutants on soil functioning it is crucial to know their small-scale distribution and reactions on the aggregate level.

The work of *Wilcke* and *Kaupenjohann* (1994 and 1997) has shown that heavy metal concentrations and forms are unevenly distributed among aggregate exterior and interior. Stronger weathering and preferential leaching result in the depletion of lithogenic metals in the exterior. In addition, parts of the native metals are transformed from strongly to weakly bound chemical forms. In contrast, heavy metals deposited from the atmosphere accumulate in the aggregate exterior, because of preferential sorption to aggregate surfaces.

Introduced metals are less strongly bound than native metals (*Wilcke*, 1996). With increasing distance from a heavy metal point source the enrichment of heavy metals in the aggregate exterior decreases (*Wilcke* and *Kaupenjohann*, 1998). Thus, anthropogenic metals accumulate preferentially in comparatively weakly bound chemical forms in the biological most active zone of the soil. This zone is also most susceptible to fast leaching of metals.

The ecological relevance of the differences in heavy metal concentrations between aggregate exterior and interior depends on the lifetime of the aggregates that controls the size and persistence of the gradients in heavy metal concentrations across aggregates. Up to now, little is known about the stability of these gradients. While *Wilcke* et al. (2002) have shown that aggregates in grassland topsoils with a high biological activity may be turned over within a few weeks, *Bundt* et al. (2000) and *Hagedorn* and *Bundt* (2002) observed that in acid forest subsoils preferential flow paths and probably also soil aggregation remained stable for several decades. The reason for the prolonged stability of the forest subsoil aggregates is probably the reduced bioturbation because of unfavorable living conditions.

As a result of the relationship between the size of heavy metal concentration gradients across aggregates and the aggregate turnover, the comparison of the former in recent and archived aggregates may be used as indication of the latter. We used the unique opportunity to study aggregates of archived intact soil monoliths from the Moscow region collected between 1910 and 1954. This also provided the opportunity to detect temporal trends in heavy metal concentrations in soils of the Moscow region. We only know of two other studies on this topic. At a semi-rural site in England, *Jones* et al. (1987) found Pb and Cr accumulation since the 1960s because of deposition from the atmosphere and Cu, Pb and Zn accumulation because of the application of farmyard manure by comparing archived and recent samples. *Berghofer* et al. (1997) reported that Cd, Zn, Mn, Ni and Cu concentrations decreased on average and Cr and Pb concentrations increased between 1966-70 and 1994 in a number of Slovak agricultural soils following the same approach.

We used the distribution of heavy metals between the exterior and interior of large aggregates (>1 cm in diameter) in recent samples and in samples archived 50 to 100 years ago from an urban-rural transect in the Moscow region to derive (1) temporal trends in metal concentrations and distribution across aggregates and (2) to assess whether aggregates are stable for 50 and 100 years, respectively.

2.2 Materials and Methods

2.2.1 Sites and samples

We collected soil samples from six sites at distances of ca. 0 (Lesnaja Dacha), 20 (Vidnoe), 30 (Schapovo), 40 (Ramenskoe), 50 (Bronnitsi) and 140 km (Nenashevo) from the city centre of Moscow (Fig. 2-1).
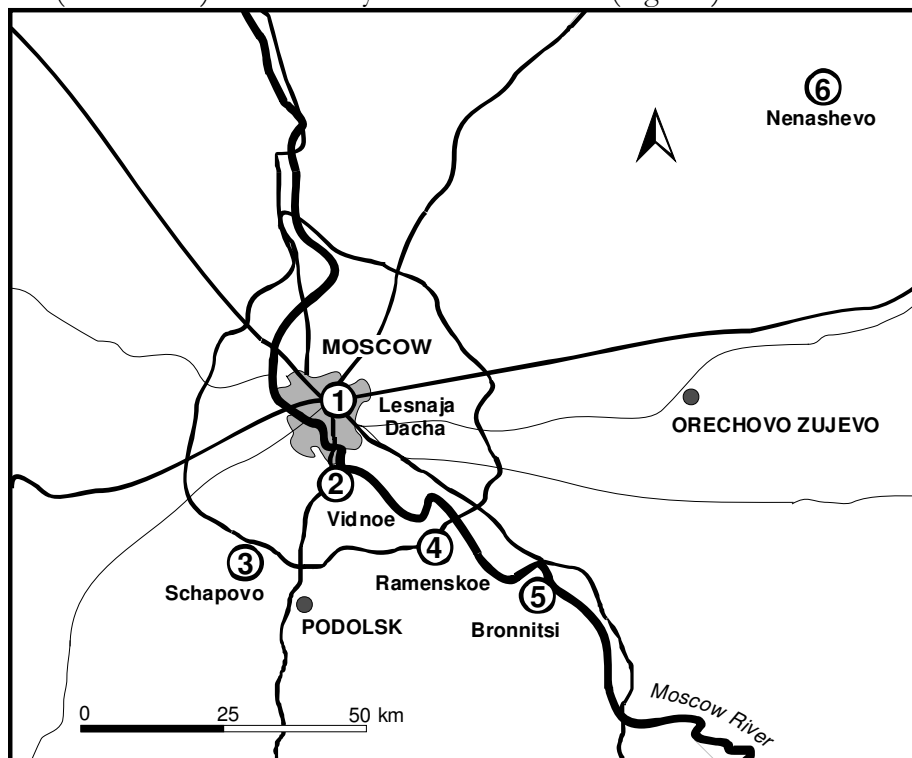
Figure 2-1. Location of the study sites

The site at 140 km distance was considered as unpolluted. All study sites are located in the south Taiga with a mean annual precipitation of 650 mm and a mean annual temperature of 3-3.5°C. The annual amplitude of the temperature is 28°C and the number of days with frost ranges from 120 to 135.

At each location we sampled one forested and one grassland site except at Lesnaja Dacha (two forested sites) and Nenashevo (two grassland sites). The parent material at Lesnaja Dacha is glacial till and at the other sites it is loess-like mantle loam. Soils were mostly Dystric Podzoluvisols, at Nenashevo we found a Histic Gleysol and at Ramenskoe an Eutric Podzoluvisol. Texture was clayey loam with the exception of Lesnaja Dacha, where it was silty loam. The sampling depths ranged between the upper 10 and 20 cm according to the A horizon thickness. At Lesnaja Dacha, we collected additional samples from 20-40 cm depth and at Bronnitsi from 50-60 cm depth for mineralogical analyses to check whether archived and recent samples had similar properties to support

our assumption that archived and recent samples were taken from the same locations. The soil samples were stored air-dried in paper or wooden boxes in a storage room at constant temperature (20°C) and humidity (65-70%). We may not rule out that there was some contact with the surrounding air possibly resulting in sample contamination, which will be considered in the discussion.

Aggregates with a diameter of 10-40 mm were manually peeled with a knife and a brush to separate them into exterior and interior portions. The selected soil aggregates contributed 1.4-34% to the bulk mass. The aggregate exterior comprised ca. 30% of the total aggregate mass. After their separation, the aggregate fractions were crushed with a mortar and sieved to >1 mm.

2.2.2   *Mineralogical and chemical analyses*

We determined clay mineral abundances in the aggregate interior and exterior portions of archived and recent samples from Bronnitsi at 50-60 cm depth, Lesnaja Dacha at 0-20 and 20-40 cm depth and Nenashevo at 0-10 cm depth with X-Ray Diffraction (XRD, Siemens Diffractometer D500). For sample preparation, organic matter was removed chemically with hydrogen peroxide. The clay fraction (<2 μm) was separated from silt and sand by sedimentation in soil-water suspensions. The chemical treatment of the clay mineral suspensions included: 1) clay minerals, saturated with Mg^{2+} ions; 2) a clay minerals-glycerine complex; 3) clay minerals, saturated with K^+ ions and dried at room temperature for 4 days; 4) K^+-saturated minerals, heated to 400°C and 5) K^+-saturated minerals, heated to 600°C. The combination of all spectra allowed a reliable determination of the clay minerals in the samples (*Schlichting* et al., 1995). We also characterized the same soil samples micromorphologically under a microscope in reflected light according to the method of *Cady* et al. (1986).

We determined pH with a glass electrode in 1 M KCl (soil : solution ratio 2:5), organic carbon concentrations with a CN-Analyzer (Leco CN-2000) and carbonate concentration for one sample with pH (H_2O) > 7 by dissolving the carbonates in H_3PO_4 and trapping the developed CO_2 in NaOH (Wösthoff apparatus).

Total concentrations of heavy metals were extracted with concentrated HNO_3 in a microwave oven (mls 1200 mega) for 30 min. Soil : solution ratio was 1:16. The extracts were filtered with paper filters (Schleicher and Schüll, No. 300 114). Reagents were prepared from at least analytical-grade chemicals. Deionized water and acid rinsed polypropylene bottles were used. The concentrations of Cd, Cu, Mg, Pb and Zn in the extracts were measured by atomic absorption spectrometry using graphite tube or flame techniques (Varian SpectrAA 800, Varian SpectrAA 200, Perkin Elmer 3100), those of Ca, K and Na were measured using a flame photometer (Eppendorf ELEX 6361). All analyses were performed in duplicate.

2.2.3 Calculations and statistical evaluation

Heavy metal contents (in g ha^{-1}) were calculated assuming an average soil density of 1.0 g cm^{-3} and considering the weighted mean heavy metal concentrations of the aggregates >1 cm as representative of the bulk soil. Archived and recent samples and interior and exterior of aggregates were compared with the nonparametric Wilcoxon matched pairs test using the software package STATISTICA 6.0 for Windows (Statsoft of Europe, Hamburg, Germany). The level of significance was defined as $p < 0.05$.

2.3 Results and Discussion

2.3.1 Comparability of archived and recent soil samples

All samples contained vermiculite, smectite, illite, kaolinite, quartz and mixed-layer minerals (vermiculite/smectite). There were no significant differences in clay mineral composition between aggregate interior and exterior.

To further confirm the similarity of archived and recent samples, we compared the peak areas of illite and kaolinite in the X-ray diffractograms (XRD) normalized to the highest peak of the same diffractogram (occurring at $2\theta = 6.2°$ typical of minerals with an interlayer distance of 1.40 nm, where θ is the critical angle for X-ray diffraction of a specific mineral) to eliminate differences in the performance of each run of the analysis. The normalized peak areas may be considered as measure of the mineral concentration.

The kaolinite concentration was similar in archived and recent samples as revealed by the fact that the normalized peak areas of archived and recent samples plotted near the 1:1 line (Fig. 2-2a) except the subsoil sample from Lesnaja Dacha (20-40 cm depth). This may be attributable to the error of measurement because in this sample the kaolinite concentrations and therefore also XRD peak areas were small. The illite concentration in recent samples was consistently lower than in archived ones (Fig. 2-2b). This may be attributed to the weathering of illite and its transformation to vermiculite and smectite during the last century (*Rampazzo* and *Blum*, 1988). This assumption is supported by the finding that the illite concentration in the archived and recent samples of the Bronnitsi subsoil (50-60 cm) is closer to the 1:1 line than those at Nenashevo (0-10 cm depth), because topsoils are weathered faster than subsoils. In the Lesnaja Dacha subsoil sample (20-40 cm) we found mixed illite-vermiculite layer minerals in the archived sample and mixed illite-smectite layer minerals in the recent sample, which may also be the result of advanced weathering of vermiculite to smectite during the ca. 100 years between the sampling of the archived and recent samples.
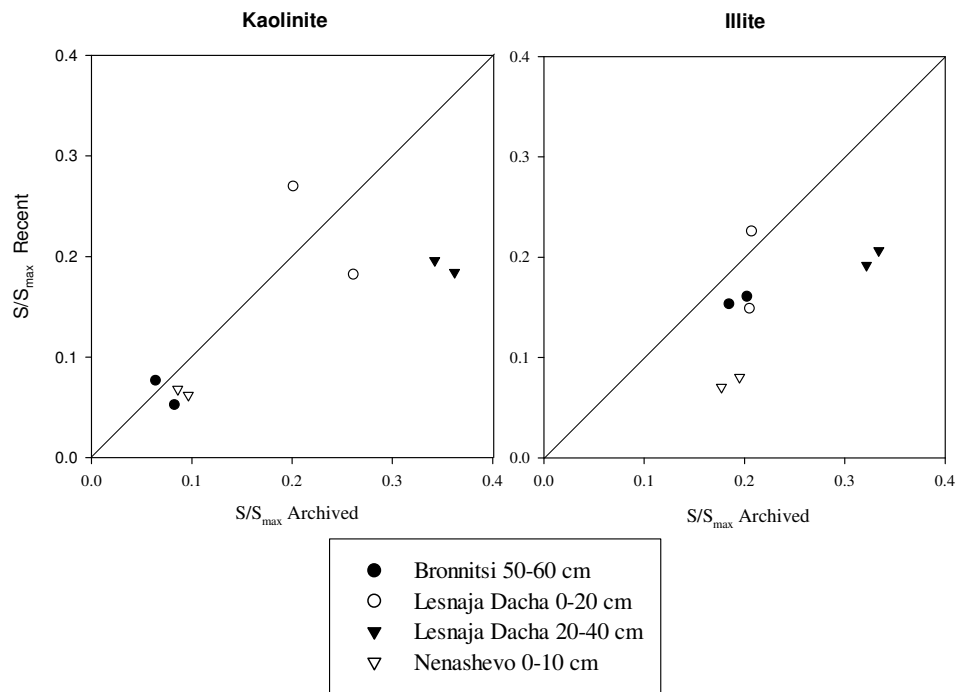
Figure 2-2. Comparison of peak areas of (a) kaolinite and (b) illite normalized to the area of the highest peak in the respective diffractogram in selected archived and recent samples

2.3.2 Heavy metal concentrations

The soils were from slightly to strongly acid. The pH ranged from 3.8 to 6.6. Except for Lesnaja Dacha pH values were similar in archived and recent samples. In some grassland soils recent pH tended to be higher than in archived samples because of liming and in some forest soils pH tended to be lower in recent samples because of the stronger acidification. Carbon concentrations were low (mean 1.6%, s.d. 0.5) except at Nenashevo (5.4%). Therefore, it may be expected that heavy metals are relatively mobile in these soils in spite of the fine texture.

The heavy metal concentrations in the aggregates >1 cm of the soils along the urban-rural transect were similar to those of the uncontaminated background soil at Nenashevo (Table 2-1 and 2-2) and typical of soils at other background locations in Europe (*Kabata-Pendias* and *Pendias*, 2001). The soil at Vidnoe, located near a local heavy metal-emitting industrial plant, had approximately twice the heavy metal concentrations as the background soil at Nenashevo. The heavy metal concentrations in the two Moscow soils were

much lower than in the inner city of Moscow where *Drechsel* and *Wilcke* (1999) found 0.53-7.9 mg Cd, 50-180 mg Cu, 70-160 mg Pb and 160-500 mg Zn kg^{-1}. Even the most contaminated soil of our study at Vidnoe had heavy metal concentrations that were at or below the lower end of these ranges. The heavy metal concentrations in the Moscow soils were also lower than the mean concentrations of Cd (0.7 mg kg^{-1}), Cu (80), Pb (60) and Zn (230) in grassland soils of Moscow (*Obukhov* and *Lepneva*, 1990). The same authors reported that typical heavy metal concentrations in Podzoluvisols of suburban parks in Moscow are by a factor of 4-6 lower than the grassland mean. Thus, our study soils were clearly less contaminated with heavy metals than many urban and peri-urban soils in west and central Europe (*Lux*, 1986; *Thornton*, 1991; *Blume*, 1993). This is in line with the conclusions drawn by *Lepneva* and *Obukhov* (1997) and *Drechsel* and *Wilcke* (1999).

Table 2-1. Mass-weighted mean of the heavy metal concentrations in archived and recent aggregates, annual changes in heavy metal content (archived-recent grassland samples, except the Moscow soils) in aggregates of the topsoils and relative change in concentration (archived-recent grassland, except the Moscow soils), Cd and Cu, standard deviation in brackets (n = 2).

Site	Cd					Cu				
	a[a] mg kg^{-1}	rg[b] mg kg^{-1}	AC[c] g ha^{-1} a^{-1}	SC[d] %	rf[e] mg kg^{-1}	a mg kg^{-1}	rg mg kg^{-1}	AC g ha^{-1} a^{-1}	SC %	rf mg kg^{-1}
Nenashevo	0.33 (0.03)	0.29 (0.05)	-0.48	-12	-	21 (0.91)	24 (5.5)	36	14	-
Bronnitsi	0.31 (0.01)	0.20 (0.01)	-1.4	-35	0.23 (0.03)	14 (0.98)	11 (0.46)	-38	-21	10 (0.37)
Ramenskoe	-	0.09 (0.01)	-	-	0.04 (0.01)	-	10 (0.68)	-	-	6.8 (0.02)
Schapovo	0.26 (0.02)	0.14 (0.01)	-2.6	-46	0.10 (0.00)	12 (0.72)	7.8 (0.74)	-91	-35	17 (1.3)
Vidnoe	-	0.68 (0.03)	-	-	2.1 (0.09)	-	37 (1.5)	-	-	92 (2.6)
Lesnaja Dacha 6th comp.	0.13 (0.01)	-	0.22	15	0.15 (0.01)	9.4 (0.12)	-	51	49	14 (0.58)
Lesnaja Dacha 11th comp.	0.17 (0.01)	-	0.22	12	0.19 (0.01)	10 (0.82)	-	100	90	19 (1.2)

[a] archived, [b] recent grassland, except Lesnaja Dacha where the recent land use is forest, [c] annual content change, [d] content change, [e] recent forest

Table 2-2. Mass-weighted mean of the heavy metal concentrations in archived and recent aggregates, annual changes in heavy metal content (archived-recent grassland samples, except the Moscow soils) in aggregates of the topsoils and relative change in concentration (archived-recent grassland, except the Moscow soils), Pb and Zn, standard deviation in brackets (n = 2).

Site	Pb					Zn				
	a[a] mg kg^{-1}	rg[b] mg kg^{-1}	AC[c] g ha^{-1} a^{-1}	SC[d] %	rf[e] mg kg^{-1}	a mg kg^{-1}	rg mg kg^{-1}	AC g ha^{-1} a^{-1}	SC %	rf mg kg^{-1}
Nenashevo	10 (0.43)	10 (2.8)	0	0	-	54 (8.9)	48 (11)	-72	-11	-
Bronnitsi	31 (2.8)	18 (1.3)	-167	-42	23 (5.3)	43 (2.0)	40 (0.93)	-38	-7.0	35 (0.07)
Ramenskoe	-	10 (1.4)	-	-	9.3 (2.0)	-	24 (2.4)	-	-	28 (0.48)
Schapovo	16 (0.01)	12 (0.26)	-65	-19	13 (0.17)	43 (0.75)	37 (0.3)	-130	-14	37 (0.5)
Vidnoe	-	27 (2.6)	-	-	28 (0.89)	-	111 (5.6)	-	-	228 (3.1)
Lesnaja Dacha 6th comp.	6.7 (0.03)	-	226	303	27 (1.8)	32 (1.9)	-	156	44	46 (0.84)
Lesnaja Dacha 11th comp.	12 (1.0)	-	67	50	18 (0.37)	35 (1.3)	-	122	31	46 (3.2)

[a] archived, [b] recent grassland, except Lesnaja Dacha where the recent land use is forest, [c] annual content change, [d] content change, [e] recent forest

There was no relation between heavy metal concentrations and the distance to Moscow. Thus, Moscow did not seem to be a point source of heavy metals for the study soils. No significant differences between grassland and forest soils occurred, except for Cd, Cu and Zn at Vidnoe where the forest canopy seemed to have scavenged much more heavy metals from the atmosphere than the grassland.

2.3.3   *Temporal trends in heavy metal concentrations and contents.*

At the Moscow sites, the concentrations of all studied heavy metals in the aggregates >1 cm increased whereas outside Moscow they decreased during the last 50-100 years except for Cu and Pb at Nenashevo. However, differences are not significant, which may be attributable to the small data set (Table 2-1 and 2-2). The fact that heavy metal concentrations were low in all archived samples and that accumulation rates varied considerably among the different study sites reduces the likeliness that our results have been caused by post-sampling contamination in the storing room. Nevertheless, there is still a risk that there were small heavy metal inputs into the archived samples during storage because samples were stored in wooden or paper boxes that might not have completely prevented very fine particles from entering the sample. This would have shifted the calculated depletion and accumulation rates systematically. However, the possible contamination did change the relative differences in heavy metal concentrations among the different soils along the urban-rural transect and the classification of all samples as relatively uncontaminated.

To assess the change in heavy metal contents during the last ca. 50-90 years and derive mean annual accumulation or depletion rates, we assumed that the weighted mean of the heavy metal concentrations in the aggregates <1 cm represented the heavy metal concentration of the bulk soil. Decreasing heavy metal contents in most studied Russian soils outside Moscow are in contrast to findings of *Wilcke* and *Döhler* (1995) that the contents of all heavy metals increased at the time of their study in agricultural soils of Germany based on budget calculations. A similar mean increase of heavy metal contents in agricultural soils was reported by *Nicholson* et al. (2003) for England and Wales. Increasing heavy metal contents in topsoils during the second half of the 20th century were also reported for Pb and Cr in English and in Slovak soils (*Jones* et al. 1987; *Berghofer* et al., 1997). The mean annual decrease in heavy metal contents in the soils outside Moscow during the last ca. 50-90 years was similar to that in mainly rural Slovak soils between 1966-70 and 1994 for Cd (Slovak depletion rate: -2.1 g ha^{-1} yr^{-1}), much higher for Cu at Bronnitsi and Schapovo (-0.13 g ha^{-1} yr^{-1}) and lower for Zn (-385 g ha^{-1} yr^{-1}, *Berghofer* et al., 1997).

The increase in Pb contents of the two Moscow soils reflects the greater proximity of these soils to Pb sources in the city. The increase rate of the Pb content at Lesnaja Dacha was similar to that in Slovak soils of 138 g ha^{-1} yr^{-1} (*Berghofer* et al., 1997). The mean increase rates of Cd, Pb and Zn in the Moscow soils are at the lower end of the range of German heavy metal deposition rates in the 1970s and 1980s of 2-33 g Cd, 50-640 g Pb and 90-4900 g Zn ha^{-1} yr^{-1} (*Brechtel*, 1989), probably representing the

highest rates of the 20th century. They are also at the lower end of rural deposition rates in England and Wales in the 1990s of 0.7-6.1 g Cd, 19-139 g Pb and 126-356 g Zn ha^{-1} yr^{-1} (*Nicholson* et al., 2003) The mean increase rate of the Cu content in the Russian soils is well within the range of German deposition rates of 20-88 g ha^{-1} yr^{-1} (*Brechtel*, 1989) but in the lower half of the range of rural deposition rates in England and Wales of 32-347 g ha^{-1} yr^{-1} (*Nicholson* et al., 2003). Thus, the mean annual accumulation rates, which are the result of deposition from the atmosphere and (small) leaching and plant uptake during the last 90 years at the two Moscow sites were lower for Cd, Pb and Zn and similar for Cu than in central and west Europe. This coincides with the generally low level of soil contamination in the study soils.

2.3.4   *Small-scale distribution of heavy metals in large aggregates*

Differences between aggregate exterior and interior were small. Most ratios of the heavy metal concentrations between aggregate exterior and interior ($R_{ex/in}$) were ≥1, but mean differences in individual metal concentrations between exterior and interior are not significant because of the large scattering among the different study sites (Table 2). This indicates that there were recent inputs (presumably mainly from the atmosphere) at most study sites for most elements that accumulated preferentially on aggregate surfaces (*Wilcke* and *Kaupenjohann*, 1998).

Table 2-3. Ratio of the heavy metal concentrations in the exterior to that in the interior ($R_{ex/in}$)

Site	Cd			Cu			Pb			Zn		
	a[a]	rg[b]	rf[c]	a	rg	rf	a	rg	rf	a	rg	rf
Nenashevo	1.03	0.90	-	0.86	1.52	-	1.15	0.90	-	0.93	1.15	-
Bronnitsi	1.24	1.05	1.09	1.07	1.37	0.80	0.82	1.67	0.48	0.95	1.03	1.00
Ramenskoe	-	1.11	1.00	-	1.00	0.87	-	1.44	1.22	-	1.08	0.86
Schapovo	1.00	1.07	1.44	1.01	0.94	1.06	0.82	1.00	1.00	0.95	1.03	1.00
Vidnoe	-	1.25	1.11	-	0.95	1.00	-	0.83	0.93	-	1.09	1.04
Lesnaja Dacha 6th comp.	1.17	-	1.54	1.01	-	1.50	1.06	-	1.38	1.00	-	1.44
Lesnaja Dacha 11th comp.	0.94	-	1.22	1.01	-	1.00	0.92	-	1.18	0.94	-	1.02

[a] - archived,
[b] - recent grassland,
[c] - recent forest.

There was no relation between distance to Moscow and $R_{ex/in}$ both in archived and recent samples. This finding further confirmed the above conclusion that the studied urban-rural transect did not represent a deposition gradient caused by the city of Moscow as a point source and fits well into the general classification of our study sites as comparatively little affected by environmental pollution with heavy metals. The observed accumulation of heavy metals on aggregate surfaces at many of the study sites must therefore be attributed to varying local sources.

Except for the mean $R_{ex/in}$ of Cd outside Moscow, all mean $R_{ex/in}$ were higher in recent than in archived soils (Table 2-2, Fig. 2-3). This indicates that the heavy metal inputs preferentially sorbed to the aggregate exterior (minus the small leaching and plant uptake) during the lifetime of the aggregates were higher for the recent samples than for those from the beginning (or the middle) of the 20th century. The clearly larger mean $R_{ex/in}$ in the recent samples from the Moscow sites than in the recent samples outside Moscow reflect the higher deposition of heavy metals in Moscow than outside the city, which coincides with the positive mean annual accumulation rates of heavy metals at the Moscow sites and the negative ones outside Moscow.
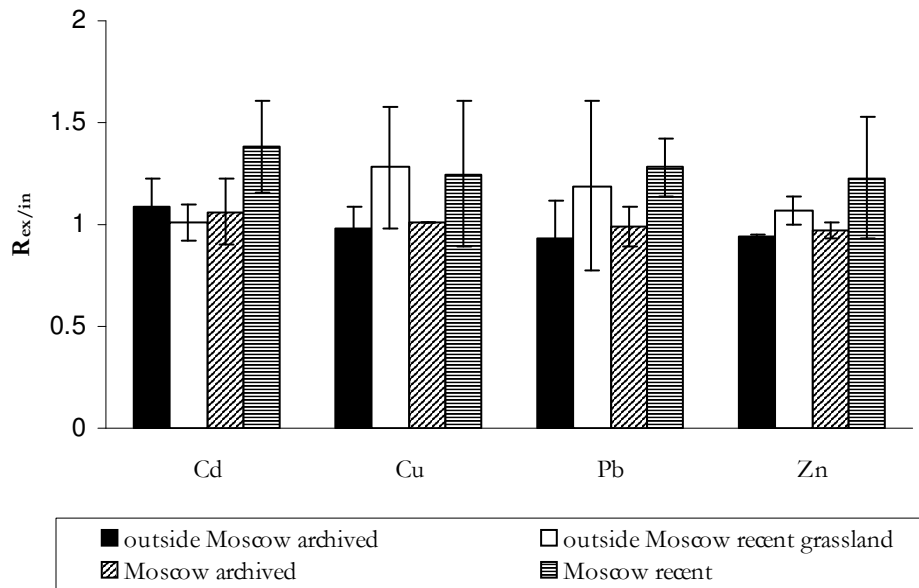
Figure 2-3. Mean $R_{ex/in}$ in archived and recent samples in Moscow soils and in soil outside Moscow. Error bars represent standard deviation.

2.3.5 Aggregate turnover

If the aggregates >1 cm of the studied soils had been stable during the last century, the differences in concentrations of heavy metals between aggregate exterior and interior should have grown, because of the low mobility of heavy metals in soils and because metal convection and diffusion along the concentration gradient between exterior and interior is negligibly small as a consequence of the strong metal binding to the soil matrix. However, the gradients would also be larger if the aggregates were turned over at a faster rate than ca. 50-90 years and the heavy metal deposition rates during the lifetime of the recent aggregates were higher than those during the lifetime of the archived aggregates. In the first case, there should be no change in the heavy metal concentrations of the aggregate interior. In the second case, the heavy metal concentrations of the aggregate interior should reflect the change in heavy metal concentrations of the bulk soil (as approximated by the weighted aggregate mean) during the last ca. 50-90 years.

The heavy metal concentrations in the aggregate interior have changed, reflecting the mean change rates in heavy metal contents of the individual soils. In the soils outside Moscow the heavy metal concentrations of the aggregate interior, except for Cd, decreased to a larger extent than those of the exterior. This may be derived from the finding that outside Moscow the mean $R_{ex/in}$ was higher although the heavy metal concentrations consistently decreased during the last ca. 50-90 years (Fig. 2-3). In the Moscow soils, the mean concentrations of all studied heavy metals increased both in the aggregate interior (by 62±s.d.

86%) and exterior (by 104±110%). From these findings we conclude that the mean turnover time of the aggregates in the studied surface soil horizons is shorter than the observed period of ca. 50-90 years. This conclusion is supported by the fact that there was no differential weathering of aggregate interior and exterior which should have resulted in different illite concentrations of the aggregate interior and exterior those were not observed (Fig. 2-2). Thus, aggregate turnover time in the studied soils seems to be closer to that in nearly neutral grassland topsoils in England (*Wilcke* et al., 2002) than to that in strongly acid forest subsoils in Switzerland (*Bundt* et al., 2000; *Hagedorn* and *Bundt*, 2002). The fact that we detected gradients in heavy metal concentrations that probably need more time to be built up than a few weeks, given the low heavy metal inputs, points at a longer aggregate lifetime than a few weeks as in the English grassland soil of *Wilcke* et al. (2002). We speculate that bioturbation might be the key process controlling aggregate turnover, because there is an earthworm activity in the soils. However, additional research work is needed to support this hypothesis.

2.4   Conclusions

The contamination of the studied soils in the Moscow region with heavy metals is lower than at some similarly exposed locations in west and central Europe. Only at our Moscow sites in an interurban forest, there was a small accumulation of heavy metals in the last 90 years when compared with accumulation rates reported from other locations in Europe whereas outside Moscow the heavy metal contents even decreased in most cases. As there was no relation between distance to Moscow and heavy metal concentrations in soils, we conclude that Moscow was no point source of heavy metals for the study soils. This was further confirmed by the lack of correlation between the size of the differences in heavy metal concentrations between aggregate exterior and interior and distance to Moscow.

The commonly existing gradient in heavy metal concentrations between aggregate exterior and interior was larger in recent than in archived aggregates. However, this was related with changes in heavy metal concentrations in the aggregate interior that reflected the changes in metal content of the soils during the last ca. 50-90 years. As changes in heavy metal concentrations of the aggregate interior may only be explained by the destruction and reformation of aggregates because of very limited diffusional and convectional exchange of metals between exterior and interior, we conclude that aggregate turnover times were smaller than ca. 50-90 years at all study sites.

3 Cation diffusion in repacked soils studied by isotopic labeling. I. Development of the method

3.1 Abstract

Diffusion of heavy metals in soils from an aggregate surface into an aggregate core may affect heavy metal leaching and plant uptake. The aim of our study was to develop a simple and reliable method to study cation diffusion in soil samples. Samples from A_l and B_t horizons of a luvisol and A_h horizons of a chernozem were sieved, packed into columns and exposed from 4 to 40 days to solutions of differently labeled metal chlorides (Cs, Cd, Zn and Ba) under water-saturated conditions. After the exposition, the columns were dried, sliced (0.1 mm thick), and the concentrations of cations in each soil slice were determined. The technique was found to be precise and accurate (total error of sampling and measurements was $\pm 2\%$). Penetration depth of ions was less than 4 mm in each case. I conclude that diffusion of cations within soil aggregates is controlled by adsorption to the soil matrix.

3.2 Introduction

Airborne heavy metals enter soil through interaggregate pore network with precipitation. Accordingly, *Wilcke* and *Kaupenjohann* (1997) found heavy metals unevenly distributed in structured soils, with higher concentrations on aggregate surfaces. In agreement with this *Ilg* et al. (2004) observed higher heavy metal concentrations in external parts of the aggregates sampled from Russian soils. *Ilg* et al. (2004) found also higher concentration of heavy metals in aggregate interiors of recent soil samples, then that of archived samples with lower heavy metal pollution. This indicates heavy metal redistribution within the aggregates. Such redistribution may affect plant uptake of heavy metals, as the roots of plants are mostly growing between aggregates, but not into them (*Whiteley* and *Dexter*, 1983).

There are two possible explanations for the redistribution of heavy metals: (i) decomposition of aggregates and formation of new ones, and (ii) diffusion of heavy metals from the external part into an aggregate due to the gradient of concentrations.

There is not much information on aggregate stability, and the estimations of aggregate lifetime are very different. *Wilcke* et. al. (2002) found an aggregate turn over in British grassland topsoils of one month. In contrast, *Bundt* et al. (2000) and *Hagedorn* and *Bundt* (2002) reported preferential flow paths in forest subsoils and, probably, soil aggregation, to remain stable over decades.

Another explanation of heavy metal redistribution between outer and inner parts of aggregates is diffusion due to a concentration gradient. Diffusion of heavy metals in soils was described mostly as self-diffusion (*Graham-Bryce*, 1963; *Phillips* and *Brown*, 1965, 1966; *Mott* and *Nye*, 1968). However, this concept is not

applicable to bulk diffusion in a real soil system (*Nye*, 1966). The exchange-resin paper method of *Vaidyanathan* and *Nye* (1966) allows getting diffusion coefficients of ions in soils for different water-saturation conditions. In the work of *Warnke* and *Barber* (1972) effective diffusion coefficient for Zn under water-saturated conditions was 10^{-8} cm^2 s^{-1}. The Einstein equation (*Einstein*, 1905) can predict the mean square diffusion run of a single particle

$$D = \frac{\overline{X^2}}{2t} \tag{3.1}$$

where D is the diffusion coefficient, (cm^2 s^{-1}), t is the time, (s) and $\overline{X^2}$ - the mean of the square of the diffusion distance, (cm^2).

If $D = 10^{-8}$ cm^2 s^{-1} and $t = 3$ days, according to equation (3.1), $X = 0.072$ cm. In contrast the experiments of *Tokunaga* et al. (2001) showed that diffusion profiles of Cr under water-saturated conditions may be as long as 1.5 cm in 51 hours. These significant differences have to be explained.

Although the method of *Tokunaga* et al. (2001) allows obtaining diffusion profiles of metal ions in soil aggregates, it requires complicated tools to perform X-ray absorption near edge structure microscopy (micro-XANES). I developed a simpler method to study diffusion of heavy metals within soils using isotopic labeling. The development, characteristics and results of that new method will be introduced in this paper. The second paper will represent the influence of organic matter on the diffusion process.

3.3   Materials and methods

The experiments were performed with labeled Zn, Cd, Ba and Cs cations. The diffusion experiments were made in soil columns under water-saturated conditions. Experiment duration ranged from 4 to 40 days.

3.3.1   Soil samples

Two different soil types from grassland were sampled for our experiment. Samples were taken from A$_l$- (sample **A**) and B$_t$- (sample **B**) horizons of a luvisol 10 km from the city of Aleksandrov (120 km north-east from Moscow, Russia) and from the A$_h$ horizon (sample **Ch**) of a chernozem near Voronezh city, Russia.

Sampling did not disturb the soil structure. The aggregates were dried in the laboratory at room temperature, 10-40 mm aggregates were manually removed from the soil structure, gently ground so that clay minerals were not damaged, and then plant residues and stones were removed from the soil material on a 1mm sieve. Cation exchange capacity (CEC), C$_{org}$, N and pH of soil samples are given in Table 3-1.

*Table 3-1. Organic carbon (C_{org}) and nitrogen (N) concentration, pH and cation exchange capacity (CEC) of luvisol A_l (sample **A**) and B_t horizons (sample **B**) and chernozem A_h horizon (sample **Ch**).*

Soil sample	C_{org}, g kg^{-1}	N, g kg^{-1}	pH	CEC, mmol$_c$ kg^{-1}
A	19.9	1.9	6.19	63
B	4.4	0.9	6.02	142
Ch	44.5	2.6	6.54	404

3.3.2   Column preparation

Because of expected low penetration of cations into soil column, techniques of thin soil sectioning and determination of low concentrations were both necessary. The radiotracer method is known for its sensitivity; it is a common method for determining the rate of ion transport in soils (*Phillips* and *Brown*, 1966; *Pinner* and *Nye*, 1982). I used ^{65}Zn, ^{109}Cd, ^{133}Ba and ^{137}Cs labels for corresponding heavy metal ions. All diffusion experiments were conducted separately, so there were no effects from one type of ion to the other.

Sieved and ground soil was mixed with an amount of water necessary to get water-saturated samples. The mixture was manually packed into columns. Columns were made of plastic and had cylindrical shape with 18 mm in diameter and 10 mm height, with an open top side.

The bulk density of the water saturated soil in columns was similar to the density of individual water saturated undisturbed aggregates. Repacked and water saturated samples in vessels were dried at 60°C for 24 hours, then the weight of dry soil samples was measured, and the bulk density was calculated. The difference between real aggregate and repacked soil was lower than 2% for all cases, this is in the range of measurement error. The water content (% of total weight) of the soils was 40% for sample **A**, 37% for sample **B** and 43% for sample **Ch** in each experiment.

After soil columns were prepared, they were dipped into distilled water for 24 hours until complete saturation to prevent solute mass transfer with water flux. Afterwards it was immediately put into a vessel containing 45 ml labeled chloride salt solution of heavy metal. The concentration of Cs was 40 mg l^{-1}, the concentration of Ba and Zn was 10 mg l^{-1} and Cd concentration was 1 mg l^{-1}. The vessel was closed tightly; nothing was added to the system during the experiment.

3.3.3 Column processing

After exposure (96-100 hours for Cs and Ba; 7 days for Zn, 40 days for Cd) the columns were carefully removed from solutions and dried at 60°C for 24 h. The drying of the columns did not affect the heavy metal distribution, since the heavy metals are strongly adsorbed to the soil matrix. Due to shrinkage of the soil samples in the column during drying, it was possible to easily remove them without disturbing.

The dry soil columns were transferred to a microtome, fixed in it with paraffin and sliced manually into approximately 0.1 mm layers in the direction parallel to the opened side of the column (normal to the direction of diffusion). Slices were put into plastic test-tubes, and the activity of label in each section was measured using a "LKB Wallac Compugamma 1282" gamma-spectrometer.

Detailed curves of heavy metal distribution along the column require a thin slicing technique. The problem of this manual sample processing is a significant difference in the weight of different slices. According to measurements it was 0.037 ± 0.002 g (P=0.95, n=60). To minimize the error I normalized the activity to the dry weight of each slice, which was determined as follows: soil slices, of which the activity was already measured, were transferred into crucibles of known weight and were heated for 2 hours at 450°C. This removes paraffin which has been used to fix the soil columns in the microtome. Each crucible was weighed again afterwards. The difference gave an exact weight of a soil slice.

3.3.4 Validation of the method

To prove whether the transport of ions is even in different column parts, two of the columns were exposed to labeled ion solutions, dried and then cut along the direction of diffusion. The profiles were tightly attached to X-ray sensitive film, which was afterwards developed and analyzed. On the autoradiograph one can see distinctive black line on the top of the column, which is equally wide in the center part and in the edges. This suggests that the ion movement is equal in all column parts.

3.4 Results and discussion

3.4.1 Precision and accuracy of the method

Figure 3-1 represents the diffusion profiles of two columns, each filled with soil from sample B and exposed to CsCl solution with ^{137}Cs as radioactive tracer for 96 hours.

In this study I performed piecewise continuous spline-interpolation of the curves from Fig. 3-1 to evaluate the precision of our method. The values of the interpolated functions in 20 even-distributed points along the X-axis within the range of experimental points were compared. The standard deviation was

σ=0.155 mmol kg^{-1}. The reproducibility may be further increased by introducing higher amount of the labeled ions for improved sensitivity and by an automated slicing.
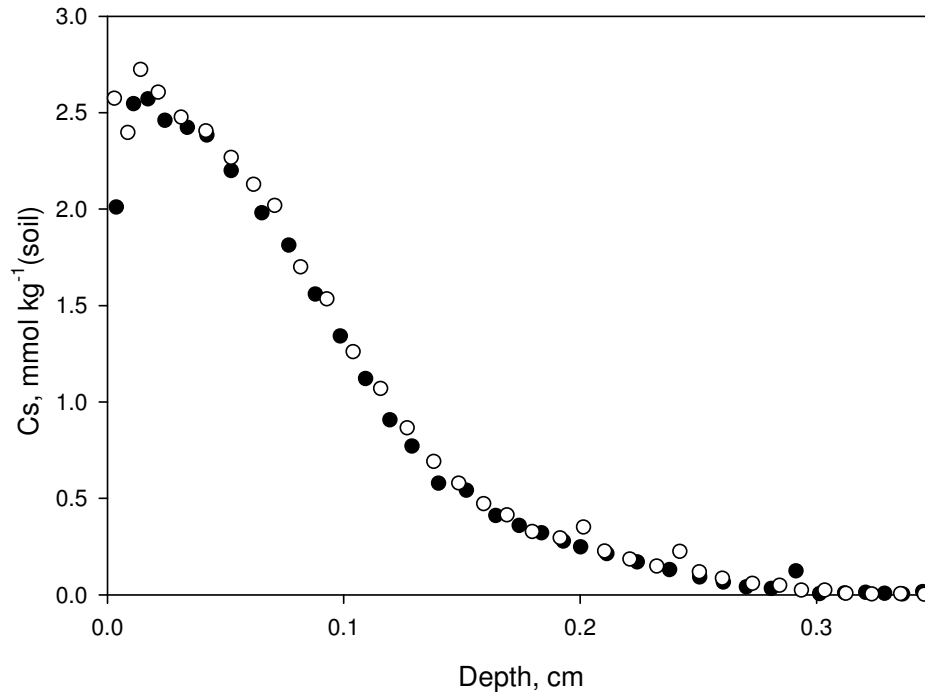
*Figure 3-1. Reproducibility of the experiment. Diffusion profiles of Cs in column with repacked water-saturated luvisol soil of B$_t$ horizon (sample **B**). Two replicates, 4 days of exposition, C(Cs)= 40 mg l^{-1}.*

Another way to evaluate the precision is to parameterize the diffusion profiles and to compare the parameters of the replicates. Parameterization was done by solving partial differential equations, numerically. Parameters obtained are very similar for the replicates, further proving the precision of the method (*Safronov* and *Kaupenjohann*, in prep.).

The accuracy of the method has been examined. I measured the decrease of radioactivity in the solution and compared it to the total activity found within all slices of the sample. The differences between the amount of diffused and measured heavy metal for 2 replicates were +2.01 and –1.86%. The numbers represent the total error of the method: errors of activity measurements and losses during sampling and paraffin burning.

3.4.2 Comparison of heavy metal distributions in different soils

The total concentration of studied heavy metals in the soil columns is highest in **Ch** samples, showing also the lowest penetration depth (Fig. 3-2, 3-3 and 3-4). This point out the higher retention capacity of sample **Ch** compared to the other samples.
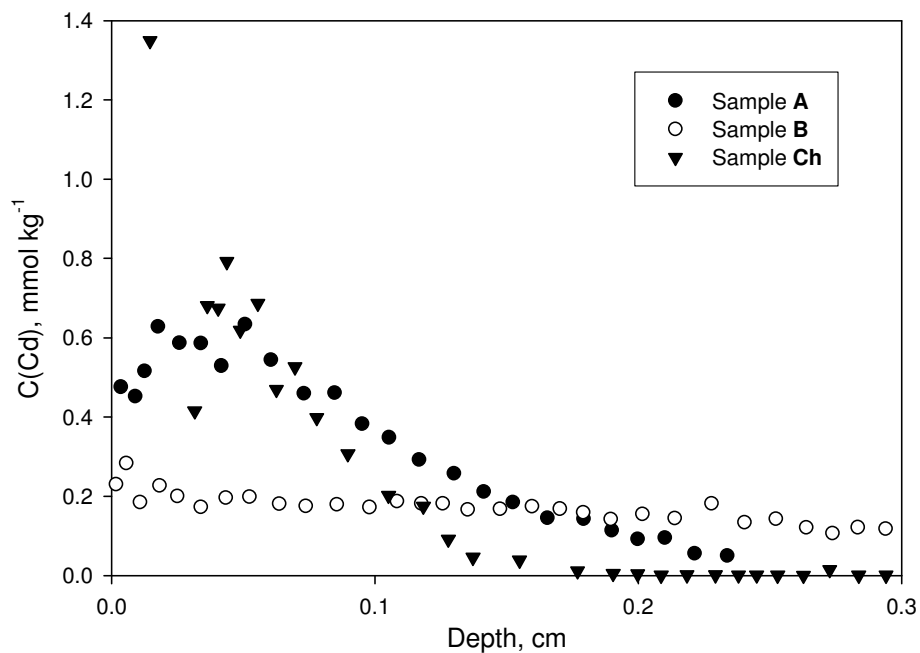
*Figure 3-2. Cadmium diffusion profiles in soil columns of luvisol A_l horizon (**A**), B_t horizon (**B**) and A_h horizon of chernozem (**Ch**) soil columns. Zn concentration in solutions was 10 mg l^{-1}, the solution volume was 45 ml and exposition time was 7 days.*
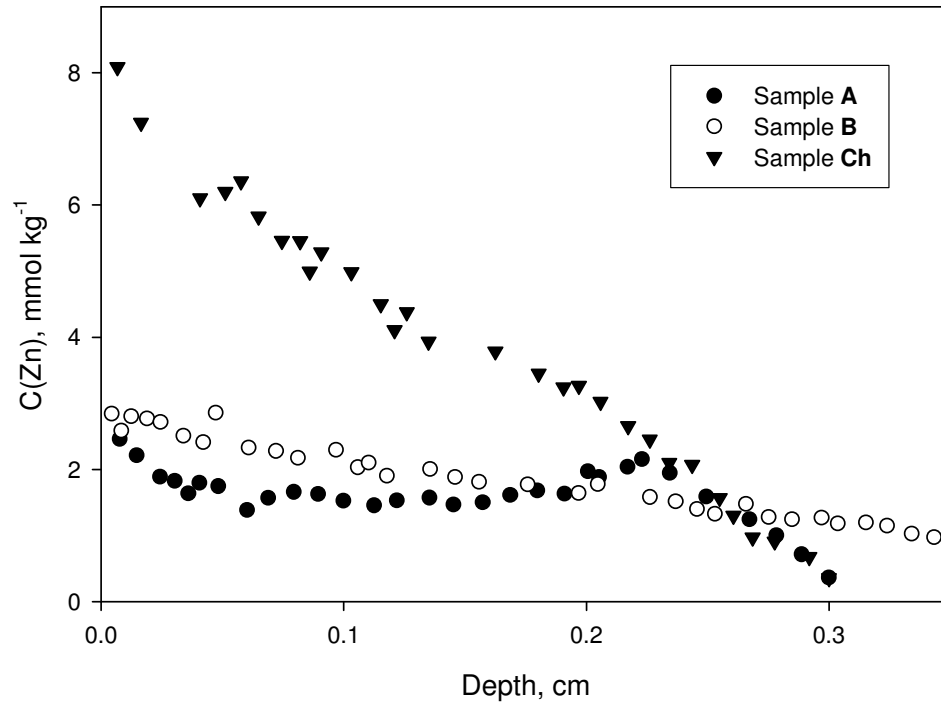
*Figure 3-3. Zink diffusion profiles in luvisol A_l horizon (**A**), B_t horizon (**B**) and A_h horizon of chernozem (**Ch**) soil columns. Cd concentration in solutions was 1 mg l^{-1}, the solution volume was 45 ml and the exposition time was 40 days.*
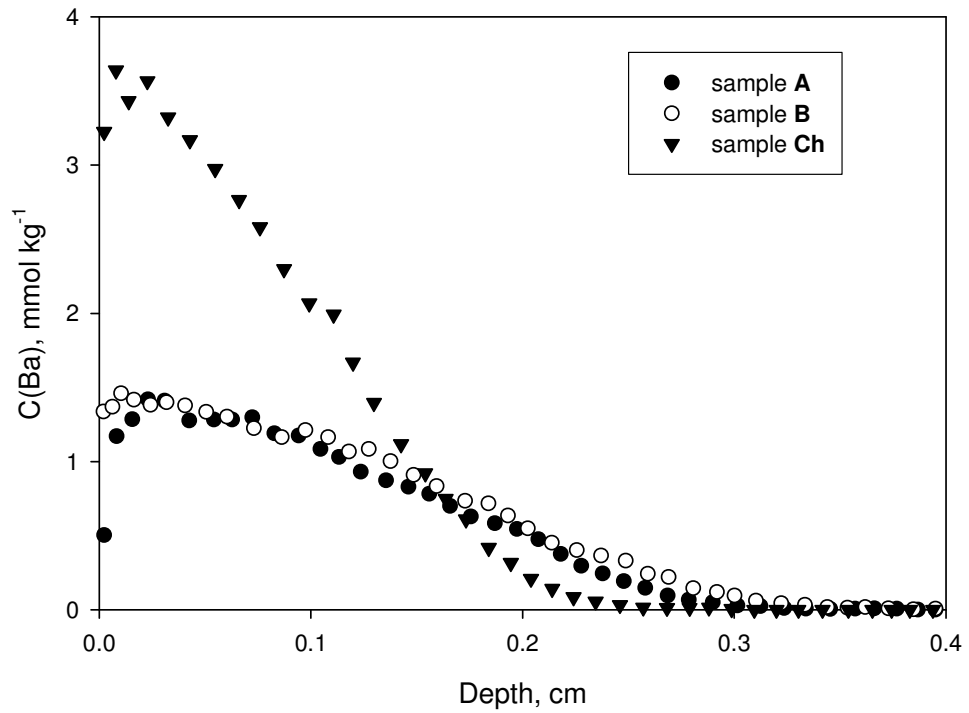
*Figure 3-4. Barium diffusion profiles in luvisol A_l horizon (**A**), B_t horizon (**B**) and A_h horizon of chernozem (**Ch**). Ba concentration in solutions was 10 mg l^{-1}, the solution volume was 45 ml and the exposition time was 4 days.*

The possible explanation may be the higher C_{org} of the chernozem sample when compared to the other soils (Table 3-1). The amounts of heavy metal diffused in samples **A** and **B** are almost equal for Zn and Ba, but different in case of Cd diffusion.
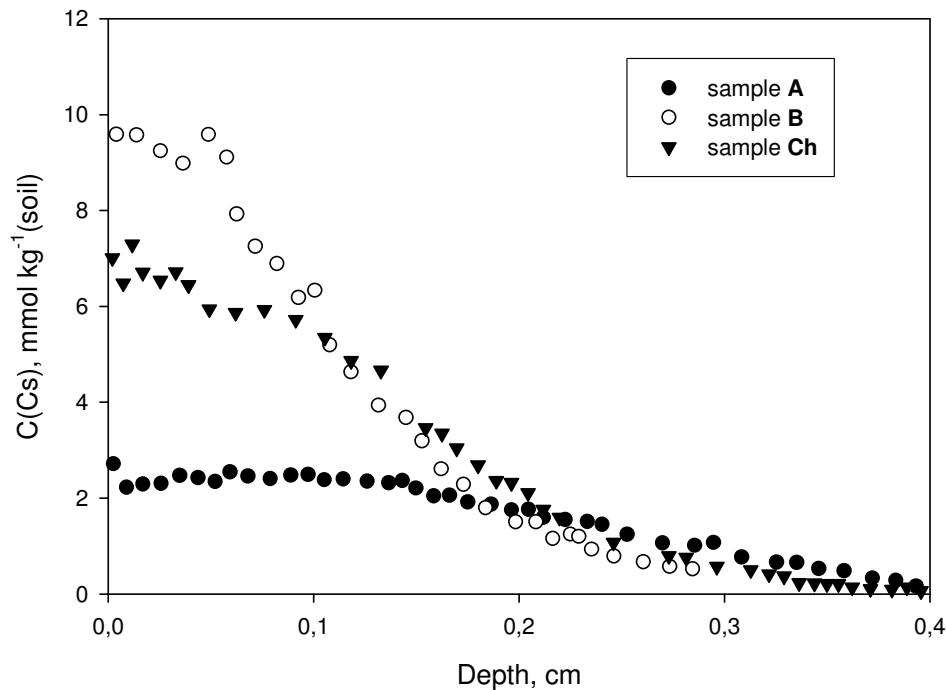
*Figure 3-5. Cesium diffusion profiles in luvisol A_l horizon (**A**), B_t horizon (**B**) and A_h horizon of chernozem (**Ch**). Cs concentration in solution was 40 mg l^1, the solution volume was 45 ml and the exposition time was 4 days.*

In contrast with the other cations, the highest concentration of Cs was in the sample **B**, followed by **Ch** and **A** (Fig. 3-5). I suppose that it can be the consequence of specific formation of interlayer complexes between Cs and smectites, which are common in the B_t-horizon of luvisols.

In general diffusion of heavy metals is not longer than 4 mm (for most concentrated solution – Cs, 40 mg l^1). The profile of Cd diffusion in **Ch** is only 0.15 cm long after 40 days of exposition.

It is also noticeably that in spite of the fact that exposition times differ significantly, the profiles of diffusion for different heavy metals are similar. This indicates that diffusion is rather fast during first hours and then slows down strongly, which is in accordance with decreasing concentration gradients along with time.

3.4.3 *Application of the experiment to real soil systems*

Pinner and *Nye* (1982) were studying effects of soil structure on diffusion. They found the impedance factor – a measure for diffusion path tortuousity in porous media, – is lower in natural soils, than in repacked ones. The difference between impedance factors of natural and sieved soils was reported as "slightly different". *Barraclough* and *Tinker* (1982) reported that sieving and repacking of soils had no great effect on the impedance factor, and "ionic impedance factors obtained with sieved soil will be valid for soils in their natural state." These results allow us to consider laboratory experiments on soil columns as a good approximation of diffusion process in soil aggregates under field conditions.

The experiment under water-saturation has its advantage in simplicity and good reproducibility. These conditions allow to get rid of such effects as preferential flow, uneven water content in different parts of the column, or evaporation of water from the soil, or interfacial resistance by transferring ions to the surface of a soil column (*Pinner* and *Nye*, 1982); diffusion process of ions in soil is the fastest under water-saturation condition. Thus the method will yield maximum diffusion rates. The results obtained with the method from short-term exposition may be extrapolated by means of a mathematical model to not-saturated soils.

3.5   Conclusion

The developed technique of soil column slicing is precise (total error ±2%). Maximum penetration depth of labeled heavy metals into soils was in the range of millimeters even after 40 days of exposition. The results indicate that the diffusion of cations within soil aggregates is limited by their affinity to the soil matrix.

4 Cation diffusion in repacked soils studied by isotopic labeling. II. Influence of organic matter and aggregate coatings

4.1 Abstract

Diffusion of heavy metals in soil aggregates from outer surface into core may affect heavy metal leaching and plant uptake. The aim of our study is to investigate the effect of aggregate skins and soil organic matter on cation diffusion. Soil samples from A_l and B_t horizons of a luvisol and A_h horizon of a chernozem were sieved, packed into columns and exposed from 4 to 30 days to labeled solution of metal chlorides (Cs, Cd, Zn and Ba) under water-saturated conditions. In addition, aggregate skins from the Luvisol B_t horizon were studied. After the experiment soil columns were dried, sliced, and the concentration of heavy metal in each soil slice was determined to obtain concentration distribution of a cation along soil column (diffusion profile). Concentration maxima of the diffusion profiles of Cd, Zn and Ba ions per soil weight correlated with CEC. Apparent diffusion coefficients of cations were calculated from the heavy metal distribution curves. They were in the range from $5.30 \cdot 10^{-10}$ cm^2 s^{-1} for the diffusion of Cd in chernozem to $3.78 \cdot 10^{-8}$ cm^2 s^{-1} for Cs in the soil from the A_l horizon of the luvisol. Differences between diffusion profiles of Cs in different soil samples may be due to different clay mineralogy and C_{org} concentrations. Diffusion profiles of metals in the aggregate skins differ clearly from that of the bulk soil from the same horizon: the retention of Ba in aggregate skins was higher than for the bulk samples, while the retention of Cs was lower.

4.2 Introduction

Industrial activity leads to heavy metals emissions into the air. Atmospheric heavy metals entering the soil with precipitation through inter-aggregate pore network and adsorbed preferentially on the aggregate surfaces (*Wilcke* and *Amelung*, 1996). Heavy metals concentrated on aggregate surfaces are easy achievable for plants and leaching. It has been shown that these concentration gradients are decreasing with time (*Wilcke* and *Kaupenjohann*, 1997, 1998; *Ilg* et al., 2004). The mechanism of the process is not definitely known up to moment. One of the possible explanations is a diffusion of cations, which have been adsorbed first to the aggregate surface, into the core of the aggregate.

There are numerous works dealing with the diffusion of cations in soils. Diffusion rate of cations was found strongly dependent on soil properties, especially those properties, which affect the retention capacity for diffusing ions. Aggregate coatings were intensively studied in last years (*Chen* et al., 1997; *Köhne* et al., 2002; *Gerke* and *Köhne*, 2002). In structured soils external parts of aggregates are exposed to preferential flow paths. This causes preferential weathering of soil minerals on aggregate surfaces (*Horn*, 1987). In addition, aggregate skins provide better conditions for microbiological degradation of soil organic matter than aggregate cores (*Allison*, 1968). As a consequence, physical and chemical properties - such as texture, CEC, amount of Fe oxides, clay and organic content - of an aggregate exterior differ clearly from that of an aggregate interior. These differences will affect also heavy metal binding and diffusion of heavy metals within aggregates. *Wilcke* and *Kaupenjohann* (1997, 1998) concluded from their results on heavy metal speciation and distribution within aggregates that the availability of heavy metals at outer surfaces of aggregates is larger than the availability of heavy metals inside the aggregates. Thus, the process of heavy metal redistribution along aggregates requires information about diffusion in aggregate skins as well as in aggregate cores.

The aim of this work was to study the influence of soil parameters like CEC and C_{org} on cation diffusion in soils and to test whether the diffusion rate in aggregate skins differs from the rate in bulk soil samples.

4.3 Materials and methods

4.3.1 Soil samples

Two different soil types from grassland were sampled for our experiment. Samples were taken from A_l (sample **A**) and B_t (sample **B**) horizons of a luvisol 10 km from the city of Aleksandrov (120 km north-east from Moscow, Russia) and from the A_h horizon (sample **Ch**) of a chernozem near Voronezh city, Russia.

Sampling did not disturb the soil structure. Soil samples were dried in laboratory under room temperature (+20°C). Aggregates of 10-40 mm in

diameter were manually removed from the soil structure, gently ground in mortar and sieved through 1 mm sieve.

In addition, coatings from B_t horizons of the luvisol (sample **C**) were collected. Aggregate from the horizon have been manually peeled by scalpel. The coatings on the soil aggregates could be easily detected and separated, because of the darker color of the coatings compared to the bulk soil. Collected skins were gently grinded in a mortar and then treated like the other sieved soil samples. Concentrations of C_{org} and N, as well as pH and CEC were determined in all soil samples (Table 4-1).

*Table 4-1. Organic carbon (C_{org}) and nitrogen (N) content, pH and cation exchange capacity (CEC) of luvisol soil A_l (sample **A**) and B_t horizons (sample **B**), chernozem A_h horizon (sample **Ch**) and aggregate coatings from luvisol B_t horizon (sample **C**).*

Soil sample	C_{org}, g kg^{-1}	N, g kg^{-1}	pH	CEC, mmol$_c$ kg^{-1}
A	19.9	1.9	6.19	63
B	4.4	0.9	6.02	142
Ch	44.5	2.6	6.54	404
C	7.0	1.1	6.00[*]	290[*]

[*] - data obtained with the less amount of soil as required by the technique

The textures of soil samples were analyzed according to "DIN ISO-11277 / Aug 2002" technique. Soil sample **A** was a silt loam and samples **B** and **Ch** were silty clay loams. Sample **C** was not analyzed because its amount was insufficient for the used technique. The detailed results on the samples' textures are presented in Table 4-2.

*Table 4-2. Texture of luvisol soil A_l (sample **A**) and B_t horizons (sample **B**) and chernozem A_h horizon (sample **Ch**).*

Soil sample	Clay, g kg^{-1}	Silt, g kg^{-1}	Sand, g kg^{-1}
A	175	755	70
B	330	620	50
Ch	374	606	20

4.3.2 Diffusion experiment

Ground and sieved soil samples were mixed with the amount of water necessary to get water-saturated soil. The water content (% of total weight) of the soil samples was 40% for **A** and **C**, 37% for sample **B** and 43% for sample

Ch. This water content was fixed and did not vary from one experiment to the other. The homogenized soil-water mixture was manually packed into plastic columns.

Bulk density of water-saturated soil samples in columns was found equal to that one of water-saturated undisturbed aggregates. Additionally bulk densities of repacked and natural aggregated soils in dry state were compared. The repacked soil samples were dried in columns for 24 hours at 60°C. The difference between the natural aggregated soils and repacked ones was lower than 2% for all samples, what is in the range of measurement error.

Soil columns in plastic cases of 18 mm in diameter and 10 mm height, which were open from one side, were dipped into distilled water for 24 hours to prevent solute mass transfer with water flux. Afterwards each column was immediately dipped separately from the other columns into a 50 ml vessel with 45 ml of labeled chloride salt of one of the studied cations. Cesium concentration was 40 mg l^{-1}, the concentration of Ba and Zn was 10 mg l^{-1} and Cd concentration was 1 mg l^{-1}. The concentrations were chosen to be sufficient for observing diffusion of cations inside the columns on the one hand, but to be abundant high on the other. The concentrations about 10 mg l^{-1} were found optimal. Cesium concentration was higher in order to prevent possible interference with potassium in soil; Cd concentration was chosen 1 mg l^{-1} because normally pollution levels of cadmium in soil are 1 to 3 orders lower compared to zinc. Isotopes ^{65}Zn, ^{109}Cd, ^{133}Ba and ^{137}Cs were used as radioactive labels for corresponding cations.

Vessels with solutions of a single labeled cation and soil columns were closed up tight; nothing was added inside during the whole experiment time. The exposition time was 4 days for Cs and Ba, 7 days for Zn and 40 days for Cd. The lower is the cation concentration the lower is a concentration gradient, and therefore, the slower is diffusion process. This was a reason of choosing different exposition times. After an exposition the columns were carefully removed and dried at 60°C for 24 hours. Due to shrinkage of soils in column after drying, it was possible to easily remove them from plastic cases without disturbing.

Every dried soil column was fixed in microtome with paraffin and sliced manually into approximately 0.1 mm slices in the direction parallel to the opened side of the column – normal to the direction of diffusion. Slices were put into plastic test-tubes, and the activity of label in each section was measured using "LKB Wallac Compugamma 1282" gamma-spectrometer.

Soil slices, which activity was already measured, were transferred into crucibles of known weight and were heated for 2 hours at 450°C in order to remove the rest of the paraffin, which has been used for sample fixation in microtome. Each crucible was weighed again afterwards – the difference between two weights gives an exact weight of a soil slice. The activity of each sample was normalized to the sample's weight to yield more precise

concentration values. The questions concerning the precision and accuracy of the method, as well as the validation of the method may be found in *Safronov* et al. (in prep.).

4.3.3   *Apparent diffusion coefficient calculation*

On the basis of thermodynamic laws, *Einstein* (1905) found the relationship between the diffusion coefficient and the mean square run of the particle:

$$D = \frac{\overline{X^2}}{2t} \tag{4.1}$$

where $\overline{X^2}$ - is a mean of the square of the diffusion distance, cm^2 and t - is time, s. Time is the property of the experiment, X can be easily calculated from the diffusion profiles of heavy metals.

4.4   Results and discussion

4.4.1   *Diffusion profiles*

Barium and cesium diffusion were studied in all samples, whereas zink and cadmium diffusion in samples **A**, **B** and **Ch**. Cation distributions along soil columns due to diffusion (diffusion profiles) are exemplary shown for Ba and Cs in Fig. 4-1 and Fig. 4-2.
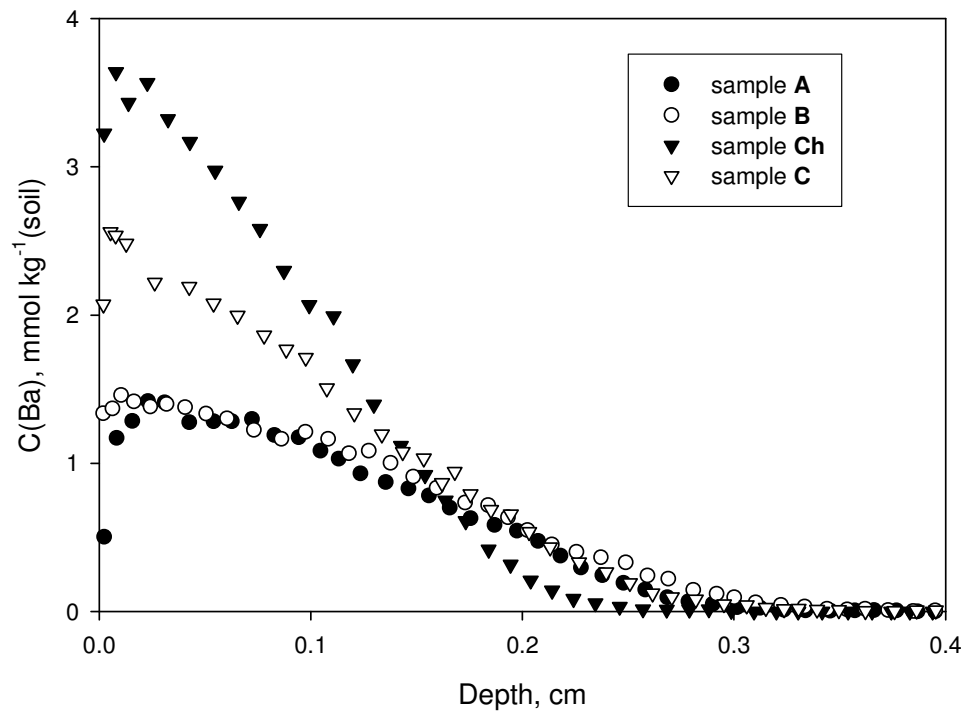
*Figure 4-2. Cesium diffusion profiles in luvisol A$_l$ horizon (**A**), B$_t$ horizon (**B**), chernozem A$_h$ horizon (**Ch**) and in aggregate coatings (**C**). (C(Cs)=40 mg l^1, V=45 ml, t=4 days).*

In general, diffusion patterns of Ba, Zn and Cd are similar, while Cs differs clearly from those metals. Maxima of the diffusion curves of Zn, Cd and Ba are related to the adsorption characteristics of the cation in the soil sample. The concentration maxima of diffusion profiles in samples **A** and **B** are similar, but the concentration maximum of diffusion profile in sample **Ch** is higher. The results are in a good agreement with CEC (Fig. 4-3), and C$_{org}$ (Fig. 4-4) in soil samples for all cations, except Cs.
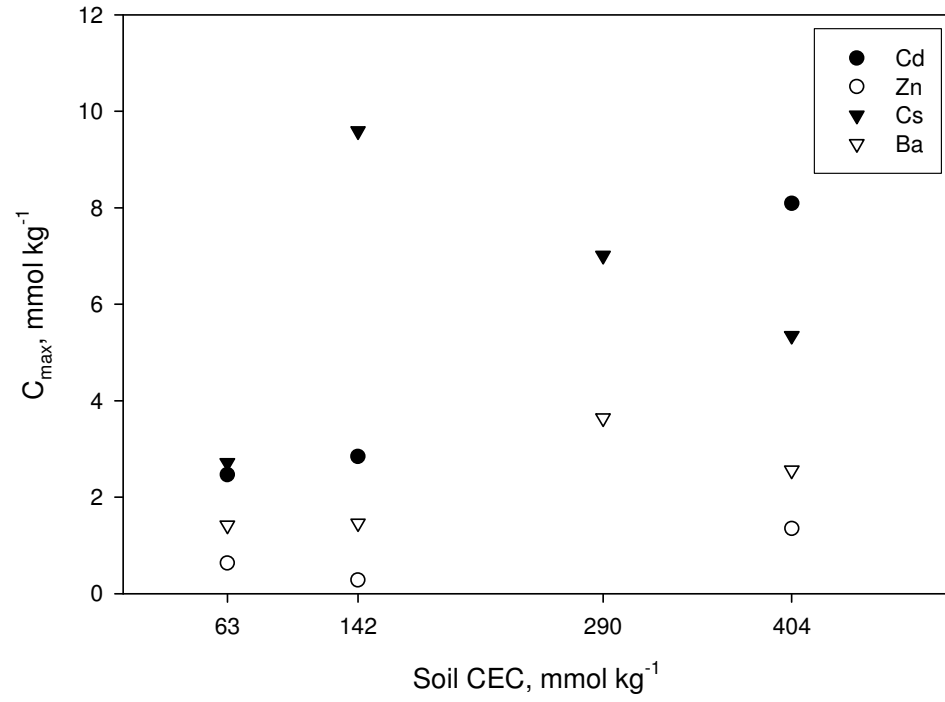
*Figure 4-3. Correlation between the maximum concentration of Zn, Cd, Ba and Cs in diffusion profiles in samples **A, B, Ch** and **C** and CEC of the soils.*
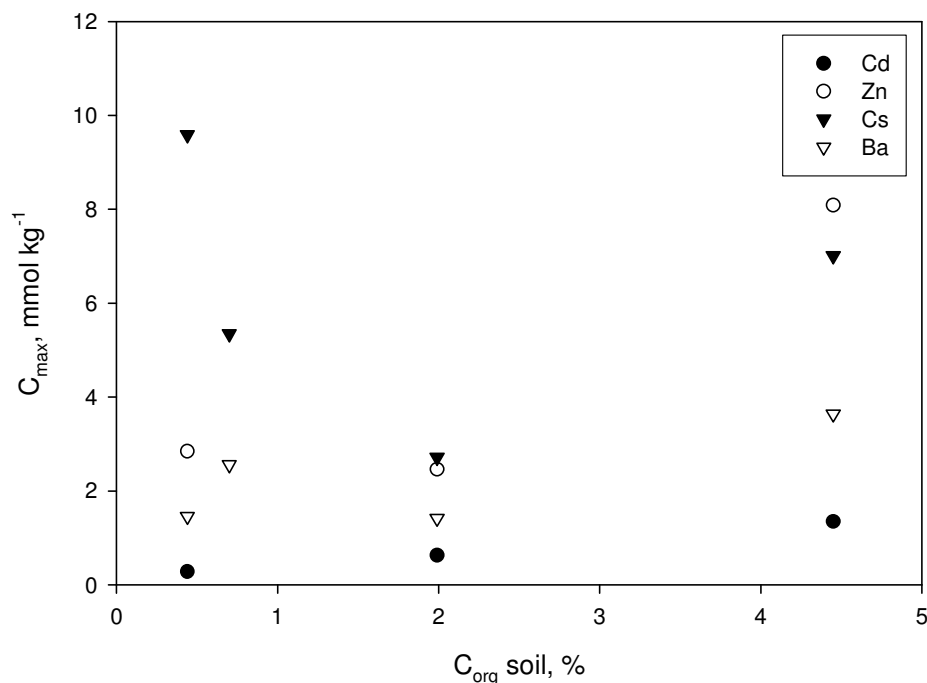
*Figure 4-4. Correlation between the maximum concentration of Zn, Cd, Ba and Cs in diffusion profiles in samples **A**, **B**, **Ch**, and **C** and C_{org} of the soils.*

In contrast, Cs adsorption is the lowest in sample **A**, with the higher adsorption in sample **C**, followed by **Ch** and the highest adsorption maximum is in the sample **B**. Such behavior of cesium in soils may be explained by its specific irreversible adsorption on clay minerals, mostly on the frayed edges of 2:1 phyllosilicates – illite and vermiculite (*Comans* et al., 1991). The soil from B_t horizon contains more clay minerals as the soil from A_l horizon of a luvisol. The importance of clay minerals in Cs retention may be seen from the difference between cesium diffusion profiles in sample **B** and in sample **Ch**. Although sample **Ch** has the highest C_{org} and CEC among all the soil samples, the maximum of the diffusion curve is lower than in sample **B**.

Barium diffusion profile in aggregate skins (sample **C**) has the same length as in sample **B**. This points out on a similar diffusion rate of Ba in aggregate skins and in a bulk soil. However, the higher CEC and C_{org} of aggregate skins are providing more adsorption places for cations than the bulk soil, what can be significant at low heavy metal concentrations. Cesium diffusion in sample **C** is abnormal: although CEC and C_{org} are higher in the sample, the diffusion curve

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goes lower than in the same soil in aggregates (sample **B**). The explanation of the phenomenon may be found in literature. *Maguire* et al. (1992) as well as *Dumat* and *Staunton* (1999) showed that soil organic matter decreases cesium adsorption in soils by binding to the clay particles and preventing access of cesium to specific adsorption sites. Complexes of cesium with fulvic acids or humus are non-specific and may decompose. Thus it can be concluded that the influence of studied aggregate coatings on the retention of cesium diffusion on aggregate scale is negative. Cesium may be adsorbed on the aggregate surface non-specifically by organic matter, where it will be available for plants. This may be a problem in soils with high organic content which are polluted with radioactive [137]Cs.

4.4.2   Calculation of the diffusion coefficient

The negative logarithm of apparent diffusion coefficient was in a good correlation with C_{org} for all cations except Cs (Fig. 4-5) and did not correlate with CEC (Fig. 4-6).
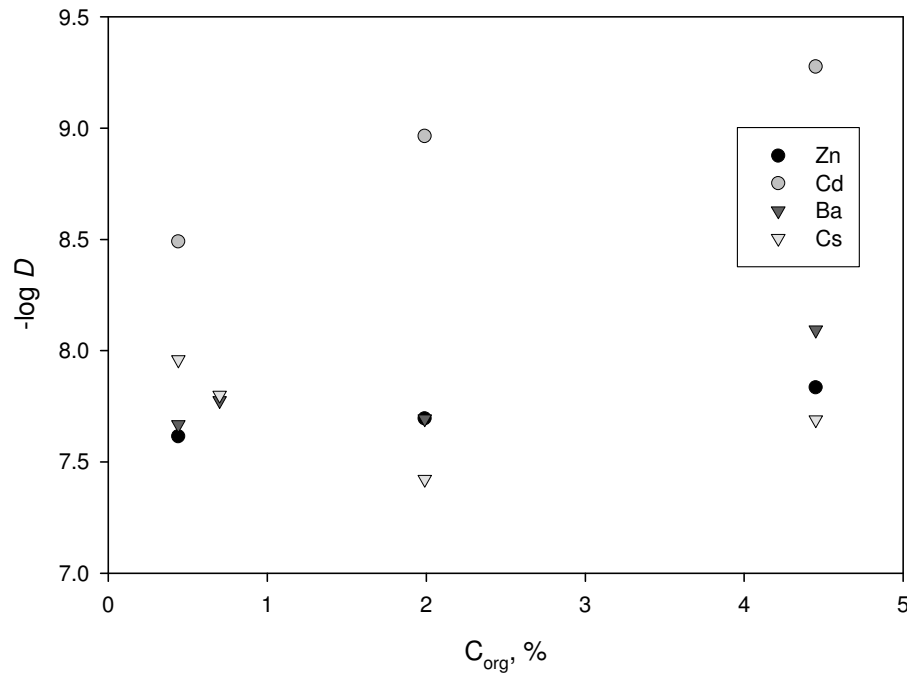
Figure 4-5. Correlation between the negative logarithm of appeared diffusion coefficient -logD and C_{org} of the soils.
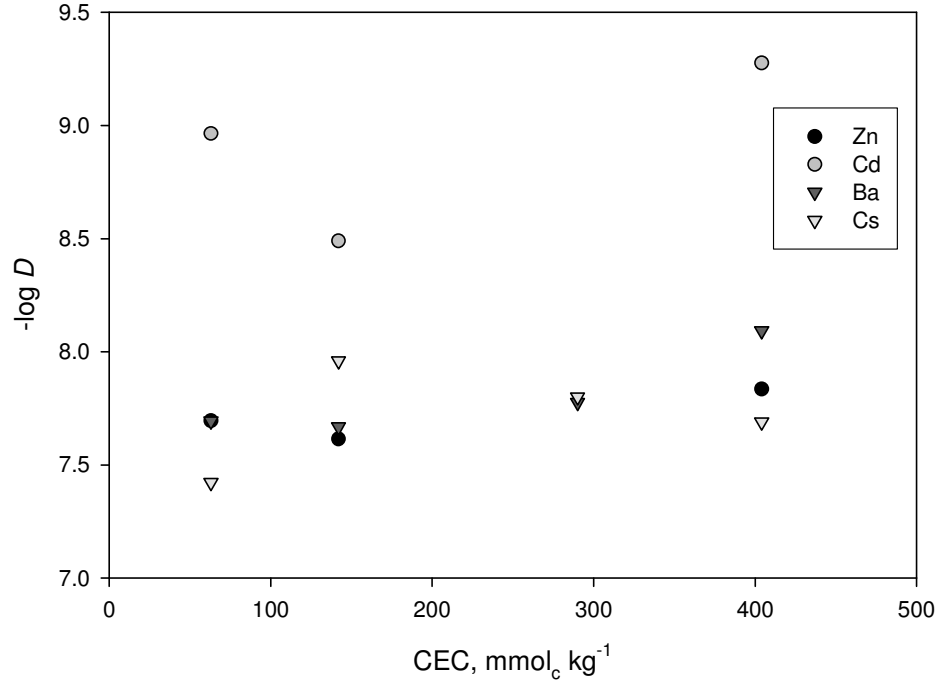
Figure 4-6. Correlation between the negative logarithm of appeared diffusion coefficient of cations –logD and CEC of the soils.

Although the apparent diffusion coefficient D is easy to calculate, it is a poor characteristic of the diffusion process. When D is applied to classic one-dimension diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2},$$

(4.2)

together with the boundaries from our experiment, the resulting curves are totally different compared to the experimental results. Thus proper mathematical model is necessary to predict distribution of cations due to diffusion process along soil aggregates.

4.5   Conclusion

Higher cation exchange capacity and C_{org} content are reducing the diffusion rate of cations in soils. Apparent diffusion coefficients were in a good agreement with C_{org} content of studied soil samples. The higher was the cation exchange capacity and C_{org}, the lower effective diffusion coefficient was observed. Aggregate skins of B_t horizon of a luvisol have higher CEC and C_{org} in comparison with the bulk soil from the same horizon. Thus, the diffusion

rates of cations in aggregate skins may be expected lower then in a bulk soil from the same horizon. However, this is not the case for cesium, which has higher apparent diffusion coefficient in skins than in a bulk soil. This may be explained by indirect influence of the organic matter upon the specific cesium adsorption on 2:1 phyllosilicates edges. From our experimental results it can be concluded that the influence of aggregate skins on heavy metal diffusion is selective and depends on the chemical properties of the diffusing ion.

The negative logarithm of the appeared diffusion coefficient is in a good correlation with the soil organic carbon for all studied heavy metals except cesium. The higher is the C_{org}, the slower is the diffusion process in soil. This shows the importance of soil organic matter in heavy metal retention. The correlation between $-\log D$ of a cation and CEC of soil is not so well pronounced.

5 Modeling of adsorption hindered diffusion of cations based on small-scale distribution profiles in soil.

5.1 Abstract

A mathematical model to describe Cs, Cd, Zn and Ba diffusion in repacked soil columns under water saturated conditions has been proposed. In the diffusion experiments soil from aggregates from A_l- (sample **A**) and B_t- (sample **B**) horizons of a luvisol, A_h horizon of a chernozem (sample **Ch**) and aggregate coatings from the B_t horizon of the luvisol (sample **C**) have been used. The mathematical model is based on an assumption, that in a small soil volume a distribution of heavy metal ions between solid and liquid phases occurs instantaneously. Heavy metal ions in liquid phase may diffuse further, whereas adsorbed ions remain attached to the solid phase. I used three different adsorption equations - Langmuir, Freundlich and linear adsorption isotherms to describe relationships between adsorbed and non-adsorbed heavy metal ions and applied them to an equation describing linear diffusion in porous space. Tortuousity of the soil samples was determined by studying diffusion of chloride ion as a conservative tracer. The corresponding impedance factors were 0.57 (samples **A** and **B**), 0.54 (sample **Ch**) and 0.52 (sample **C**). In order to find coefficients in adsorption equations, at which modeled curves fit experimental data the best, Nelder-Mead optimization has been used. The mathematical model of diffusion with Freundlich adsorption isotherm was the best in describing Cs (except sample **A**), Zn and Cd diffusion in the soil samples. Barium diffusion was best described by the model with Langmuir isotherm (except sample **C**). The worst results in the diffusion modeling are produced with the model based on linear adsorption isotherm.

5.2   Introduction

Several studies indicated an ecological relevance of intra-aggregate distribution of pollutants. *Whiteley* and *Dexter* (1983) found plants' roots growing predominantly on aggregate surfaces, but not inside of them. Distribution of heavy metals in structured soils is uneven, with higher concentration on aggregate surfaces then in aggregate cores (*Wilcke* and *Kaupenjohann*, 1997). Thus ecological risks of heavy metal uptake by plants on contaminated sites may be underestimated, if concentrations of heavy metals are analyzed in bulk soil samples (*Hamon* et al., 1998).

Prediction of soil contamination by pollutants is often based on so-called two-region model. One part of the model is related to outer-aggregate space – advection, and the other – to an inter-aggregate space – diffusion (*van Genuchten* and *Wierenga*, 1976). Although the model has successfully predicted heavy metal breakthrough in effluents (*Jardine* et al., 1999), little is known about heavy metal redistribution inside soil aggregates and factors affecting it. The only work in which heavy metal redistribution along aggregates has been studied is by *Tokunaga* et al. (2001). They investigated Cr(IV) diffusion in soil columns by means of X-ray adsorption near edge structure (micro-XANES) spectroscopy. The technique is not widely available; therefore a simple method based on γ-spectroscopy measurements of labeled heavy metal ions in different soil column parts has been developed (*Safronov* et al., in prep.). We found that diffusion of Cs, Ba, Cd and Zn in soil columns did not exceed 0.4 cm even after 40 days of exposure to water solutions of the heavy metals. Studied soils showed high affinity to the cations.

In this work I try to apply a mathematical model for Cs, Zn, Ba and Cd diffusion in four different soils by introducing Freundlich, Langmuir and linear adsorption isotherm equations into the partial differential equation of diffusion process. The model was first introduced by *Darrah* (1991) to describe diffusion of rhizosphere exudates in soil. He fitted coefficients of Langmuir and linear adsorption isotherms to experimental distributions of diffusing substances along soil column – diffusion profiles – of organic acids and found good agreement between the theory and the experiment. Although the model with Langmuir adsorption was more complicated, the better results were obtained with linear adsorption isotherm. Heavy metal adsorption, however, is best described by means of Langmuir and Freundlich isotherms. I applied both of them together with linear adsorption isotherm into the partial differential equation of diffusion to fit experimental data on cation diffusion in soil samples.

The aim of our study was to describe diffusion profiles of cations in studied soils in terms of adsorption and diffusion. The profiles can not be described by means of the classic diffusion theory – they have different shape and concentration maxima (*Safronov* et al., in prep.). A proper mathematical model is necessary to compare diffusion rates of different cations in soil samples and to

identify soil properties which govern diffusion rates. The data obtained from the modeling may be used for an estimation of heavy metal distribution along soil aggregates and for an estimation of contamination risks in structured soils.

5.3 Materials and Methods

5.3.1 Soil samples

Soil samples were taken from A_l- (sample **A**) and B_t- (sample **B**) horizons of a luvisol 10 km from the city of Aleksandrov (120 km north-east from Moscow, Russia) and from A_h horizon (sample **Ch**) of a chernozem near Voronezh city, Russia.

Sampling did not damage the soil structure. The samples were dried in the laboratory at room temperature, 10-40 mm aggregates were manually removed from the soil structure. We considered mineral content and chemical properties of the aggregates as representative for all aggregates in the soil. The chosen aggregates were gently ground in mortar so that clay minerals were not damaged, and then plant residues and stones were sieved out from the soil material on a 1 mm sieve.

An additional sample **C** was represented by aggregate coatings of B_t horizon of a luvisol soil. A difference between inner aggregate part and coatings was clearly visible because the coatings were darker compared to bulk soil. The coatings were gently ground in mortar and then treated like the other samples. Cation exchange capacity (CEC), C_{org}, N and pH of the soil samples are given in Table 4-1.*Carey, et al.*, (2002)

5.3.2 Chloride diffusion study

Disposable plastic syringes of 2 ml were used for chloride ions diffusion study in soils. The tip of a syringe for needle fixation has been removed so that only plastic cylinder and plunger remained (Fig. 5-1).

The studied soil samples were saturated with water and properly packed into the cylinder. The amount of water in samples (% of total weight) was 40% for samples **A** and **C**, 37% for sample **B**, 43% for sample **Ch**. They were collected by manual peeling aggregates with scalpel. Before an exposition to labeled chloride ions soil columns were left under water for 24 hours for the equilibration to exclude ion transfer with water flux.

Soil columns were exposed to 600 ml of $3.5 \cdot 10^{-3}$ M NaCl solution labeled with ^{36}Cl isotope from 18 to 22 hours. The vessel was closed during experiment time, so there were no changes in chloride concentration due to evaporation. The concentration of chloride ion in the solution may be considered as constant, because chloride is not adsorbing on soil minerals, and the dilution of the chloride solution by the water from the soil columns is neglible.
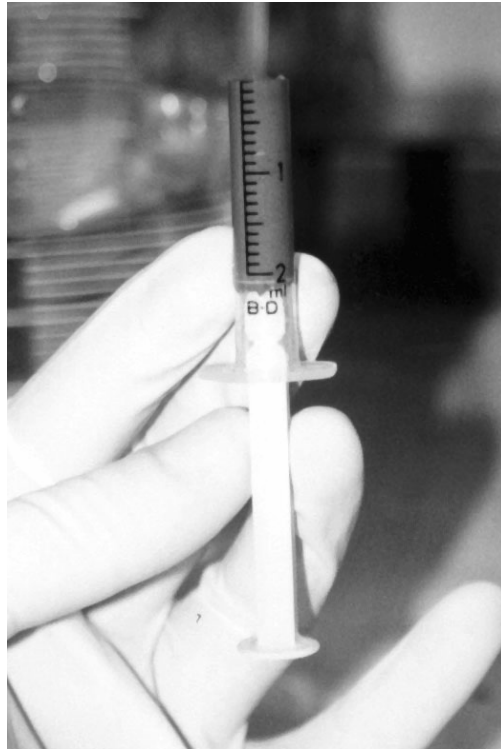
Figure 5-1. Modified syringe with repacked soil for chloride diffusion studies

Soil columns were immediately sliced when exposition was finished. The slices were about 0.83 mm; their thickness was controlled using side marks on a syringe. Soil slices was weighed and placed into plastic test tubes. Approximate weight of each soil slice was about 0.09 g. Afterwards 0.5 ml deionized water was added into the test-tube, mixed with a soil slice to homogenized suspension, left for 1 day and then centrifuged 5 minutes at 5000 rpm. The centrifugate (0.5 ml) was separated from soil and mixed with "Eco Plus" liquid scintillator (0.5 ml). The mixture of solution and scintillator was homogenized by shaking, followed by the measurement of radioactivity using "LKB Wallac 1219 Rackbeta" scintillation counter. The activity and the thickness of each soil slice were normalized to its weight in order to obtain more precise diffusion profiles.

5.3.3   Heavy metal diffusion study

Soil samples **A**, **B**, **Ch** and **C** were sieved and mixed with water to form the same soil-water proportion as in the experiment with chloride diffusion. Mass water content was 40% for sample **A**, 37% for **B**, 43% for **Ch** and 40% for **C**. The homogenized soil samples were packed into plastic cylinders of 18 mm in diameter and 10 mm height, which were opened from one side, and dipped into water for 24 hours for equilibration. Afterwards an equilibrated column was

exposed to one of the cation solutions: CsCl (Cs concentration was 40 mg l^{-1}, the exposition time was 96-100 hours), BaCl$_2$ (10 mg l^{-1}, 96 hours), ZnCl$_2$ (10 mg l^{-1}, 7 days) and CdCl$_2$ (1 mg l^{-1}, 40 days). After the exposition the columns were dried at 60°C for 24 hours. We suppose that drying procedure did not affect cation distribution in columns, because the majority of the cations are adsorbed to soil matrix and could not be transferred with soil solution. The soil was removed from the plastic case, fixed with paraffin in microtome and sliced manually in the direction parallel to the opened side into approximately 0.1 mm slices. The activity of the label in each slice was measured using "LKB Wallac Compugamma 1282" gamma-spectrometer. The slices were collected in crucibles, heated for 2 hours at 400°C to get rid of paraffin and then weighed. The weight of each slice was 0.037 ± 0.002 g (P=0.95; n=60). As there were differences in weight of the slices, the thickness of each slice was normalized to its weight to get more precise diffusion profiles.

The recovery of labeled heavy metal in each diffusion experiment was checked by comparing the loss of activity in the solution and the total activity in soil slices. The recovery of heavy metal was always complete, the difference did not exceed 2%. The questions concerning precision and accuracy of the method are described more detailed in the work by *Safronov* et al. (in prep.).

5.4 Mathematical model of diffusion processes

Diffusion is a process of spontaneous transfer of a matter by thermal molecular motion. The mathematical theory of diffusion is based on the first Fick's law: diffusion flux of a substance is proportional to its concentration gradient. One-dimensional diffusion equation is derived directly from the Fick's law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} ; \tag{5.1}$$

C is the substance concentration, t - time and D - a diffusion coefficient.

Nye (1979) proposed to consider an effective diffusion coefficient of non-adsorbing solutes in soil as

$$D = D_L f , \tag{5.2}$$

where D_L is the diffusion coefficient of the solute in free solution and $f \in [0;1]$ is an impedance factor, the coefficient inversely related to the tortuousity of a diffusion path in porous media. The impedance factor is a peculiar constant of a soil sample.

5.4.1 Determination of soil tortuousity

Crank in his book (1979) gives an analytical solution of a diffusion problem, when a diffusion coefficient is constant, a boundary of the semi-infinite media is

kept at constant concentration and an initial concentration of diffusing substance in media is zero.

If we assume diffusion into soil column is planar along X-axis and set the surface of the column as 0, $x < 0$ will refer to the external solution and $x > 0$ - to the soil column. Boundary conditions for the diffusion problem are: 1) $C = C_{ex}$ for $x < 0$, $t = (0, +\infty)$, where C is a concentration of a conservative tracer, C_{ex} is a concentration of the solute outside of the soil column, t - time; 2) $C = 0$ for $x > 0$, $t = 0$.

The solution of the problem for the boundaries is

$$C(x) = C_{ex} erfc \frac{x}{2\sqrt{Dt}} . \qquad (5.3)$$

A shape of the $C(x)$ curve for the predefined C_{ex} and t is unambiguously defined by the effective diffusion coefficient D and hence, according to the equation (5.2), by the impedance factor f. Accepting that Cl⁻ is a conservative solute in our experiment, f was determined by fitting Eq. (5.3) to the chloride profiles (Fig. 5-2).

Reproducibility of the method was experimentally proved. Diffusion profiles of chloride in two soil columns with sample **B** were obtained (Fig. 5-3) and fitted with the model (Fig. 5-4). Corresponding impedance factors of the profiles were 0.568 and 0.571.
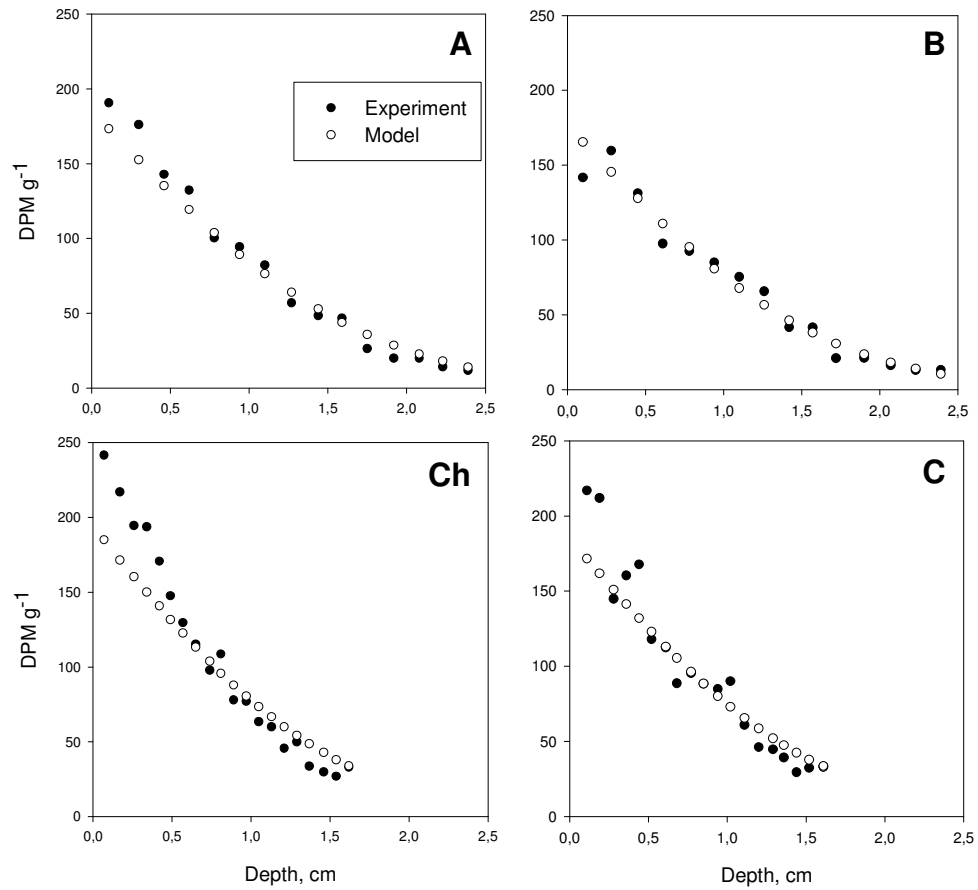
*Figure 5-2. Chloride diffusion profiles in samples **A, B, Ch** and **C** (t=20 h.): experimental points (black) and the best fitting model (white).*
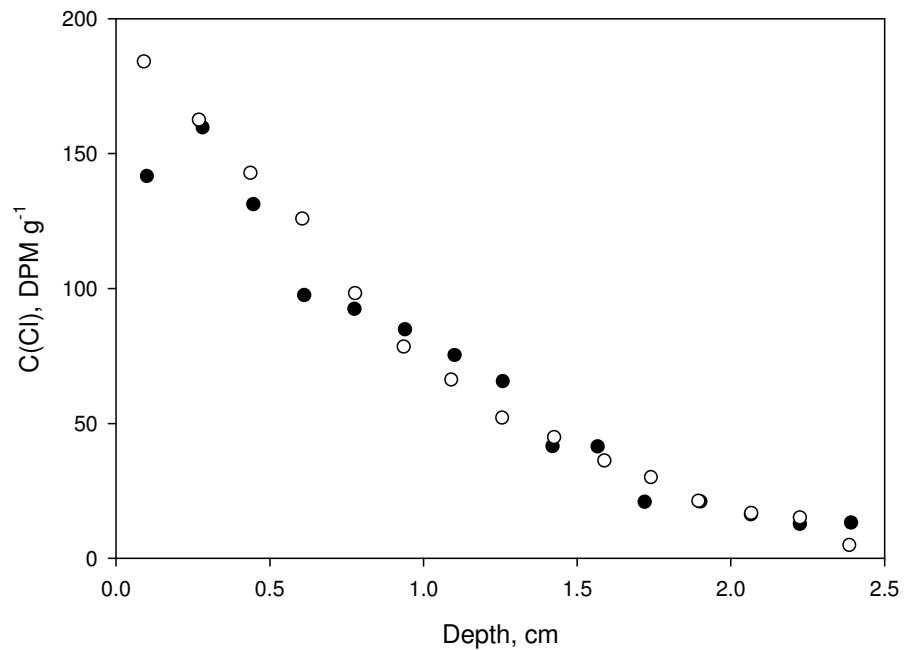
*Figure 5-3. Reproducibility of the experiment on chloride diffusion in soil samples; chloride distribution along soil samples **B** in two parallel experiments after 18 hours of exposition to Cl solution*
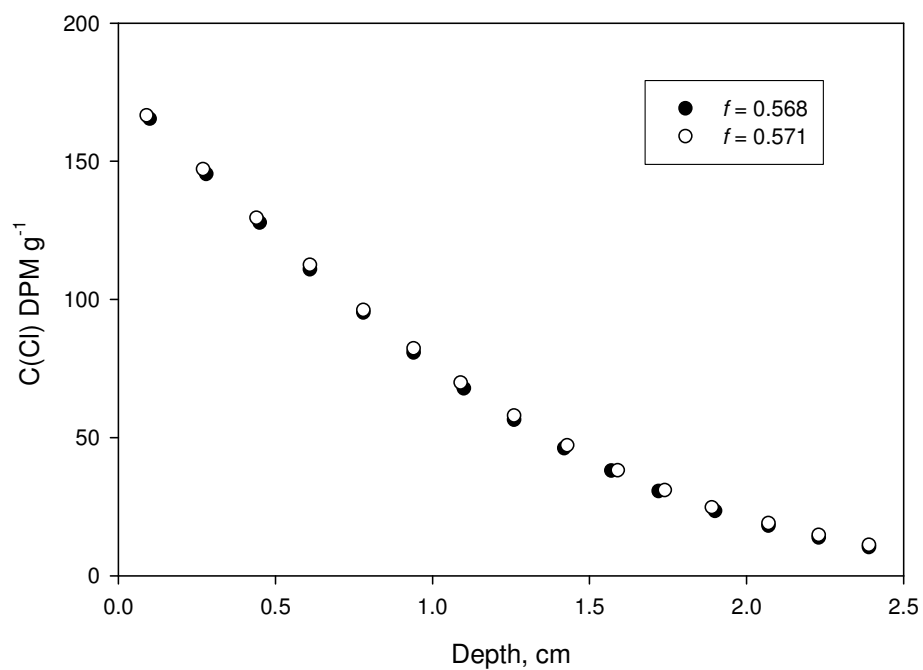
Figure 5-4. Comparison of the best-fitting curves for chloride diffusion profiles from Fig. 5-3 and corresponding impedance factors

5.4.2 *Application of adsorption process to cation diffusion in soil*

Nye and *Tinker* (1977) proposed to use an effective diffusion coefficient for adsorbing substances in form:

$$D = D_L f \theta \frac{dC_L}{dC},$$ (5.4)

where θ is the volumetric moisture content and $\frac{dC_L}{dC}$ is the reciprocal buffer power, usually denoted as Z. Diffusion coefficient in water D_L is a tabulated value, θ can be measured experimentally and f can be found from the diffusion experiment with non-sorbing substance. The only unknown reciprocal buffer power Z can be found from a relationship between substance concentration in solid and in liquid phases of soil, which is usually described by means of adsorption isotherms.

Welp and *Brümmer* (1998) found concentrations of Mg, Sr, Co Zn, Ni, Cd, Cu and Pb in soil solution are controlled by adsorption process. The same conclusion was made for low concentrations of Cd in soil-water suspension (*Street* et al., 1977). So, if an adsorption is the main and the only process controlling heavy metal concentration in soil solution, then an appropriate adsorption isotherm would unambiguously define Z value.

5.4.3 *Langmuir adsorption isotherm*

An adsorption isotherm represents a relation between an amount of substance in solid and in liquid phases. Adsorption of substances in soil is often described by means of Langmuir (*John*, 1972; *Olsen* and *Watanabe*, 1957) or Freundlich (*Garcia-Miragaya* and *Page*, 1978) isotherms.

Langmuir isotherm may be described as

$$C_{ads} = \frac{C_{ads\,max} K C_L}{1 + K C_L},$$ (5.5)

where $C_{ads\,max}$ is maximum amount of substance which can be adsorbed, K is a coefficient, related to the energy of adsorption, C_L is a concentration of substance in liquid phase. The equation may be transformed in form

$$C_{ads} = \frac{C_{ads\,max} C_L}{Q + C_L},$$ (5.6)

where Q is the reciprocal of K.

Langmuir isotherm was successfully applied to describe an adsorption of Cd in 30 various surface soils (*John*, 1972). Langmuir partition coefficient was found more precise for the description of Pb and Zn adsorption, compared with Freundlich (*Diatta* et al., 2003).

The total amount of substance in soil is distributed between liquid and solid phases:

$$C = C_{ads} + C_L^*$$ (5.7)

The asterisk at C_L^* shows that the concentrations in liquid and in solid phases are equidimensional: g kg^{-1} (soil), in contrast to C_L dimension (g l^{-1}) in the adsorption equations (5.5) or (5.6). If we assume, that the density of soil minerals in studied samples is equal to the density of silicate minerals (2.65 g cm^{-3}), and the whole pore space is filled with water, the relation between C_L^* and C_L will be

$$C_L^* = \frac{C_L \theta}{2.65(1-\theta)}.$$ (5.8)

For the simplicity of the following calculations, I designated $\frac{\theta}{2.65(1-\theta)} \equiv R$.

The reciprocal of Z in the diffusion equation (5.4) may be presented as

$$\frac{1}{Z} = \frac{dC}{dC_L}$$ (5.9)

The equation may the transformed using the adsorption equation (5.6) and equations (5.7) and (5.8) into

$$\frac{1}{Z} = \frac{dC_{ads}}{dC_L} + \frac{dC_L^*}{dC_L} = \frac{C_{ads\,max}Q}{(Q+C_L)^2} + R \, ;$$ (5.10)

or

$$Z = \left[\frac{C_{ads\,max}Q}{(Q+C_L)^2} + R\right]^{-1}$$ (5.11)

The only unknown in (5.11) C_L can be found from the equations (5.6) and (5.8) when applied to (5.7):

$$C = C_{ads\,max}C_L + RC_L(Q+C_L).$$ (5.12)

The equation can be solved with respect to C_L:

$$C_L = \frac{-(RQ + C_{ads\,max}) + \sqrt{(RQ + C_{ads\,max})^2 + 4RC}}{2R}.$$ (5.13)

5.4.4   Freundlich adsorption isotherm

The adsorption equation proposed by *van Bemmelen* (1888) and widely known as Freundlich isotherm, was the first equation describing adsorption processes:

$$C_{ads} = AC_L^B,$$ (5.14)

where $A, B \in R_+$.

The principal difference from the Langmuir isotherm is theoretical absence of adsorption limit: the higher is the concentration of adsorbate in liquid phase, the higher will be the amount of adsorbed substance. Most of the scientist considered parameters A and B as empirical, but *Sposito* (1980) proved, that the equation can be derived rigorously for binary exchange reactions, where one of the components is adsorbed in trace amounts. Coefficients A and B can be related to nonuniformity in the surface characteristics. *Benjamin* and *Leckie* (1981) found adsorption of Cu, Zn, Cd and Pb traces in soil in good agreement with Freundlich isotherm. *Street* et al. (1977) reported the relationship between adsorbed and dissolved cadmium in soil-water suspension is better described by Freundlich, than Langmuir isotherm. *Welp* and *Brümmer* (1999) found Cd adsorption well described by Freundlich isotherm in four different soils. Moreover, 19 of 40 experimental adsorption isotherms were fitted over a wide concentration range by means of Freundlich equation.

The equation (5.7) can be modified according to (5.14) as

$$C = AC_L^B + C_L^*$$ (5.15)

Then the buffer power should be

$$\frac{1}{Z} = \frac{dC_{ads}}{dC_L} + \frac{dC_L^*}{dC_L} = ABC_L^{B-1} + R,$$ (5.16)

or

$$Z = \left(ABC_L^{B-1} + R\right)^{-1}.$$ (5.17)

The equation (5.17) requires explicit C_L value to find the reciprocal buffer power. The obvious complicacy is to resolve the equation

$$C = AC_L^B + RC_L.$$ (5.18)

with respect to C_L for any positive A and B.

This, however, may be done by means of numerical methods. The functions AC_L^B and RC_L are not negative for all C_L values and monotone increasing, C is a not-negative constant. That means the function

$$f(C_L) = AC_L^B + RC_L - C$$ (5.19)

is monotone increasing as well. At $C_L = 0$ the function $f(C_L)$ is negative. According to the first Bolzano-Cauchy theorem $f(C_L)$ has only one root (such C_L value at which $f(C_L) = 0$). The root may be found with any predetermined degree of accuracy by means of Bolzano method (bisection), or, more effective, using the *regula falsi* procedure (*Mathews* and *Fink*, 1999).

5.4.5 Linear adsorption isotherm

The linear adsorption isotherm is known for its simplicity and has been used widely to describe the relationship between the amount of heavy metal in liquid and solid phases in terms of "distribution coefficient". The amount of substance adsorbed is in direct proportion to the amount of substance in liquid phase:

$$C_{ads} = K_d C_L \tag{5.20}$$

The reciprocal buffer power Z may be found directly from the equation. Total concentration in soil sample is

$$C = C_{ads} + C_L^* = K_d C_L + R C_L = C_L (K_d + R) \tag{5.21}$$

and

$$Z = (K_d + R)^{-1}. \tag{5.22}$$

Reciprocal buffer power is a constant for all C_L values, what makes the calculation of diffusion profile and the optimization procedure much simpler.

5.4.6 Numerical solution of the diffusion equation

When the reciprocal buffer power Z and hence, the effective diffusion coefficient are known, it is possible to use it in the appropriate partial differential equation. When applied to the diffusion equation, the effective diffusion coefficient (5.4) produces:

$$\frac{\partial C}{\partial t} = D_L f \theta \frac{\partial}{\partial x} \left(Z \frac{\partial C}{\partial x} \right) \tag{5.23}$$

The diffusion equation (5.1) is the typical parabolic partial differential equation and can be solved numerically by means of finite-difference approach. Transformation of the equation (5.23) with finite-difference method is described in the work of *Darrah* (1991). When $\Delta t = const$ and $\Delta x = const$,

$$C(x, t+\Delta t) = \frac{D_L f \theta \Delta t}{\Delta x^2} [Z_a (C(x+\Delta x, t) - C(x,t)) - Z_b (C(x,t) - C(x-\Delta x, t))] + C(x,t) \tag{5.24}$$

$$Z_a = \frac{Z(x+\Delta x, t) + Z(x,t)}{2}; \text{ and } Z_b = \frac{Z(x,t) + Z(x-\Delta x, t)}{2}.$$

Equation (5.24) allows calculating the required diffusion curve $C_t(x)$ if an initial condition $f_{init} = C(x,0)$ and boundaries are known. In the model it is postulated that 1) a distribution of diffusing cations between solid and liquid phases in soil occurs instantly, and 2) the diffusion take place after the local equilibrium is achieved.

Since Z is the function of two parameters: $C_{ads\,max}$ and Q for the Langmuir-type adsorption, or A and B for the Freundlich-type adsorption, the result of the diffusion equation function $C_t(x)$ - depends on two parameters as

well. The criterion of modeled diffusion profile fitting to the profile with n experimental points is the function

$$F = \sum_i \left(C_{\exp}(x_i) - C_t(x_i) \right)^2 . \tag{5.25}$$

It should be mentioned here that the experimental points $C_{\exp}(x_i)$ are distributed unevenly along the diffusion profile (*Safronov* et al., in prep.), whereas $C_t(x)$ are distributed evenly with predetermined Δx step. Cubic spline interpolation has been used to find $C_t(x_i)$ - the values of final function $C_t(x)$ in points x_i.

Pairs of the parameters (C_{adsmx}, Q) in Langmuir equation and (A, B) in Freundlich equation for which F is minimal are the problem's solution. Effective procedure to solve such tasks was proposed by *Nelder* and *Mead* (1965). This is a direct search method of optimization which is based on evaluating a function of n variables at the $(n+1)$ vertexes of a simplex, then iteratively shrinking the simplex as better points are found until some desired bound is obtained.

Darrah (1991) had also proved there is only one pair of $(C_{ads\,max}, Q)$ values, which is the solution of the problem. The same approach may be applied to prove that there is only one pair of Langmuir isotherm coefficients (A, B) for which the final curve fits the experimental curve the best. It does not prevent from obtaining local minima during the optimization procedure. Therefore additional calculations and results comparing were made to prove that the calculated values are true minima of function F.

The fitting of the diffusion profile in case of linear adsorption isotherm is the simplest. Equation (5.24) is reduced to

$$C(x, t + \Delta t) = \frac{D_L f \theta \Delta t}{\Delta x^2} Z \left[C(x + \Delta x, t) - 2C(x, t) + C(x - \Delta x, t) \right] + C(x, t) \tag{5.26}$$

Thus the only unknown parameter affecting the final diffusion curve is the distribution coefficient K_d, which can be found by means of linear optimization procedure.

5.5   Results and discussion

5.5.1   *The tortuousity of the diffusion path in soil columns*

Diffusion of chloride ion was successfully described by the mathematical model. Figure 5-5 represents diffusion profiles of chloride along the soil columns and the best fitting curves. The shape of the best-fitting curve is determined by the impedance factor f, related to tortuousity. The least tortuous soil samples were **A** and **B** ($f = 0.57$), followed by **Ch** ($f = 0.54$)

and **C** ($f = 0.52$). These results are in a good agreement with the theory. A_h horizon of chernozem contains higher amount of OM compared to both luvisol samples (Table 3-1). Organic matter in soil leads to the better binding of soil particles, and thus it is responsible for more tortuous soil structure of the sample **Ch** compared with **A** and **B**. Aggregate coatings are enriched with clay particles compared to the bulk soil. Under water-saturated conditions clays have a tendency to swelling (*Hillel*, 1998), reducing pore size, and hence, increasing tortuousity of diffusion paths.

There were reports on lower amount organic matter on aggregate surfaces compared to bulk soil (*Wilcke* and *Kaupenjohann*, 1997). The explanation of the difference between our results and the results of the authors is that B_t horizon of a luvisol can accumulate organic matter and clays, which are washed away from upper soil horizons.

5.5.2   Results on heavy metal diffusion modeling

Mathematical model of adsorption hindered diffusion produced good results in modeling heavy metal diffusion profiles (Fig. 5-5). Although mathematical model based on the linear adsorption isotherm produced good results, they were in any case worse than the results based on Langmuir and Freundlich isotherms (Table 5-2). This was expected because two-parameter equations of Langmuir and Freundlich are more "flexible" in describing nonlinear isotherms. Mathematical model based on Langmuir isotherm was the best in describing barium diffusion in all soil samples except the sample **C**. It was also the best in describing cesium diffusion in sample A. The model based on Freundlich isotherm was the best in most cases: in modeling Cd and Zn diffusion, Cs diffusion except the sample **A** and the diffusion of Ba in sample **C**.
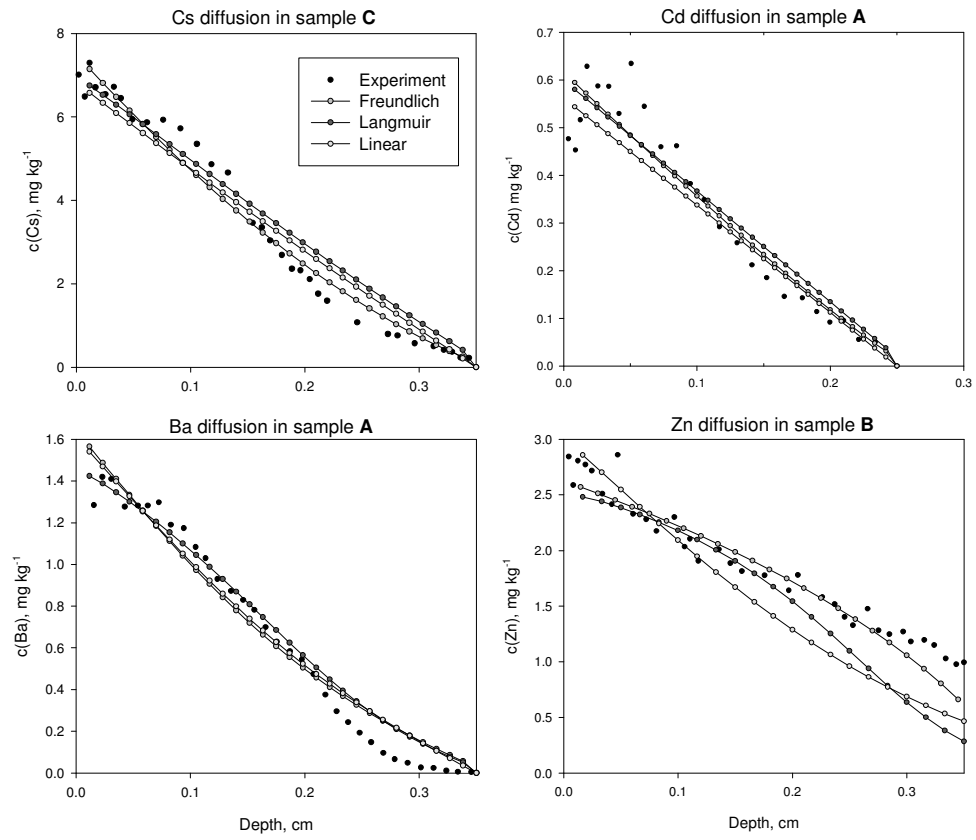
Figure 5-5. Some of the heavy metal diffusion profiles in soil columns and their approximation with different models

Table 5-1. Difference between experimental results and the mathematical model calculated as F function (Eq. 4.25). The best approximations are marked with bold font.

Diffusing cation	Soil sample	Error of the model, F, mg² kg⁻²		
		Freundlich	Langmuir	Linear
Cesium	A	1.3255	**1.0334**	2.9604
	B	**19.8013**	27.0131	30.0387
	Ch	**4.6244**	9.0415	7.7911
	C	**1.9267**	8.3815	8.049
Cadmium	A	**0.0962**	0.1	0.1141
	B	**0.0118**	0.0119	0.0573
	Ch	**0.5778**	0.7115	0.6713
Zinc	A	**3.3355**	57.77	10.4785
	B	**1.0953**	4.9856	4.5861
	Ch	**11.498**	39.4653	25.4673
Barium	A	0.3303	**0.2282**	0.3
	B	0.4543	**0.0371**	0.5096
	Ch	1.225	**0.2061**	1.6519
	C	**0.2841**	0.6017	0.9765

Diffusion of Cs in samples **B**, **Ch**, **C** and the diffusion of Cd in samples **A** and **Ch** was best described when the adsorption parameter B in Freundlich isotherm was more then 1. In case of Cs such result may be explained by specific adsorption of the ions on clay minerals. There were some reports in the literature on the Freundlich adsorption of heavy metals in soil with the parameter $B > 1$ (*O'Connor* et al., 1984). That was probably because of relative long time used for the equilibration of heavy metal solutions and soil. In our experiment the time of heavy metal redistribution between liquid and solid phases is limited by the diffusion process, and the effects of specific soil-ion interaction may be observed better compared to batch adsorption experiments. It is also interesting to notice that soil-metal pairs for which the adsorption parameter B in Freundlich isotherm is more then 1 are not possible to describe with the mathematical model based on Langmuir equation: it approaches results of the model based on linear adsorption isotherm.

Distribution coefficients K_d obtained by means of mathematical model from the diffusion profiles of Cs, Zn and Ba were found well correlating with CEC of studied soils (Fig. 5-6). Distribution coefficient of cadmium correlated also well with C_{org} (Fig. 5-7).
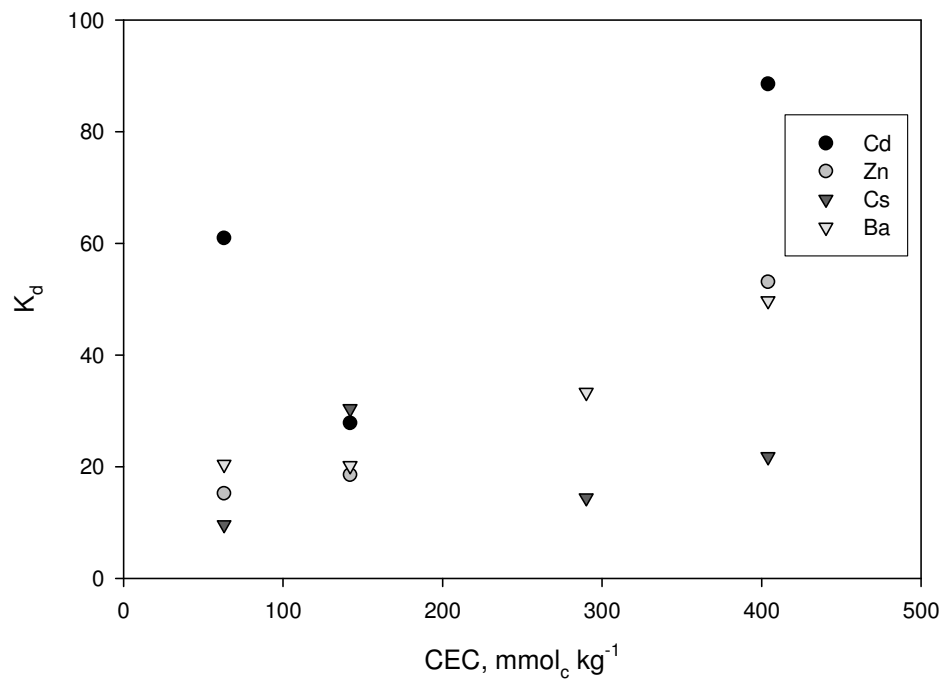
Figure 5-6. Correlation between CEC of the soils and the distribution coefficient of linear adsorption K_d obtained with the help of mathematical model.
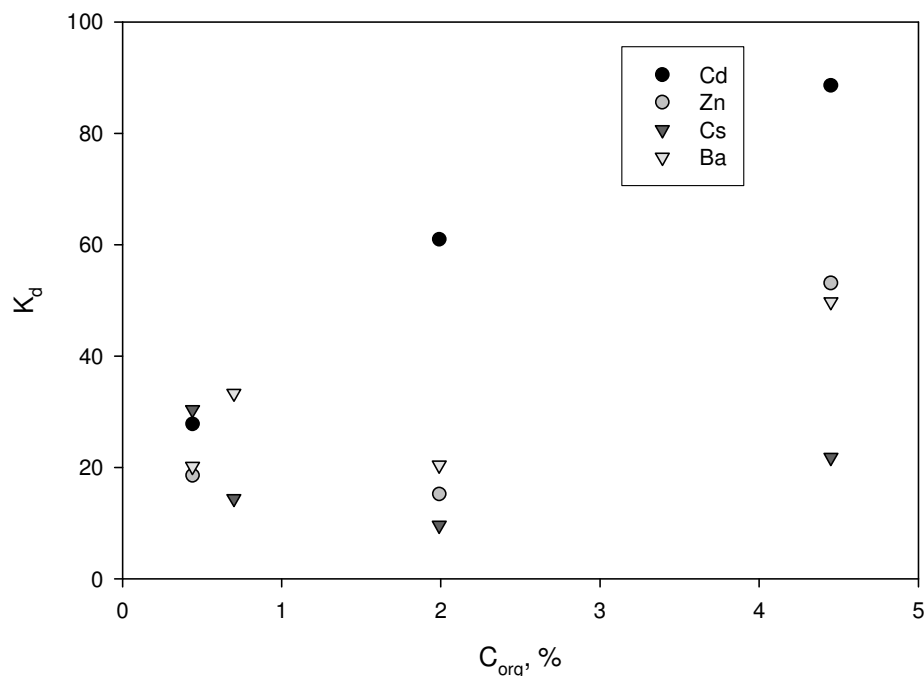
Figure 5-7. Correlation between C_{org} of the soils and the distribution coefficient of linear adsorption K_d obtained with the help of mathematical model.

5.6 Conclusions

The mathematical model has successfully described diffusion profiles of heavy metals in repacked soil columns. The best results on Cs (except sample **A**), Zn and Cd diffusion were obtained with mathematical model based on Freundlich adsorption isotherm. Barium diffusion was best described by mathematical model with Langmuir adsorption isotherm (except sample **C**). The worst results in the diffusion modeling were obtained when the mathematical model based on linear adsorption isotherm has been used.

Clays and organic matter are making diffusion path of solutes more tortuous and thus slowing down diffusion mechanically. Clays and organic matter are also retarding diffusion chemically: they are providing adsorption sites for heavy metal ions. Adsorbed ions do not take part in a formation of a concentration gradient. The effect of clays on tortuousity of a diffusion path in studied soils was more pronounced than the effect of soil organic matter.

The coefficient of linear adsorption isotherm obtained by means of mathematical model is correlating well with soil CEC (Fig. 5-6). This is expected: the higher CEC of a soil, the more pronounced will be adsorption. It

is however important, that the distribution coefficient in our model is used as a "retention factor" for diffusion process, and this factor is growing up with increasing CEC (for Zn, Cd, Ba) and C_{org} (for Cd). This is the direct evidence that higher CEC and C_{org} are slowing down the diffusion of cations.

6 General discussion and conclusions

6.1 Method for studying diffusion profiles in soil columns

The method of studying diffusion profiles of heavy metals in soil columns allows high-resolution observation of heavy metal diffusion profiles and suitable for the study of diffusion process in soil columns. It is simpler in comparison to micro-XANES technique, but requires working with radioactive isotopes for high precision measurements.

The data obtained with the method were precise and reproducible. The diffusion profiles obtained are suitable for the following mathematical treatment. The method has several limitations. First of all, it is suitable only for studying the diffusion of cations labeled by γ-rays emitters with high energy of γ-quanta. The interaction of such γ-rays with soil matrix in analyzed samples may be considered as negligible. However, the application of the method for studying diffusion of β-emitters, like ^{90}Sr, or especially α-emitters is doubtful. β- and α-rays has lower penetration ability, making results of radioactivity measurements dependent on configuration of studied samples. Extraction of α- and β-labeled ions from soil into liquid phase followed by their determination is too complicated and high-risk. The second limitation of our method is that the diffusion studies may be provided only for limited period. Soil minerals left for a long time under water-saturated conditions undergo structural changes. This may lead to an incorrect interpretation of results on macro-scale diffusion study.

Obvious incorrigible disadvantage of the technique is that the method is destructive. The soil column can not be recovered after obtaining diffusion profile from it. The other disadvantage was manual processing of exposed soil columns. This made slices unevenly thick, producing additional errors and making the mathematical data processing more complicated. The improvement of the method could be an automated slicing process. The same refer as well to the method of impedance factor determination by studying the diffusion of non-adsorbing chloride ions.

6.2 Influence of soil properties on ion diffusion

Diffusion of cations in soil can be affected by soil composition in two ways: mechanically and chemically. Soil matrix forms a porous space in which diffusion occurs. Studying diffusion of conservative tracer in a soil allows determination of diffusion path tortuousity. The corresponding parameter – impedance factor was found dependent on soil properties. I found sample **C** (aggregate coatings from B_t horizon of a luvisol soil) the most tortuous and diffusion-resistant, followed by the sample **Ch** (chernozem). This is in a good agreement with theory: sample **C** is rich in clays, sample **Ch** – in organic matter. Under water-saturated conditions clays are swelling, reducing the pore size and

thus increasing the tortuousity of ion diffusion. Organic matter binds the soil particles, making the diffusion path more tortuous as well.

Soil chemical properties have auxiliary effect on cation diffusion, mainly through the adsorption process. Cations in soil are distributed between solid and liquid phases. The ratio of the adsorbed and dissolved ions is controlled by the adsorption process (*Welp* and *Brümmer*, 1998). Cation diffusion on macro-scale level is possible only if the ions are in dissolved state. Our mathematical model produced adsorption isotherms from the observed diffusion curves. From the coefficients of the isotherms, it is clear that the majority of cations are in adsorbed state. This means, that the most of heavy metal ions in soil are retarded by adsorption.

The reverse process - desorption of the adsorbed ions - is slower than adsorption. Hysteresis effect is often observed in adsorption-desorption experiments in soils. Significant desorption of heavy metals occurs in nature only if the soil properties are abruptly changed, e.g. acidification of soil by acid rains. Furthermore, adsorbed heavy metal ions may slowly diffuse into crystal lattice of soil minerals, forming very stable inner-sphere complexes. For example, in batch experiments on adsorption-desorption of Cr, Cd and Hg on different soils significant fractions of the metals adsorbed was not released into solution and was not exchangeable, indicating irreversible sorption (*Amacher* et al., 1986). *Almås* et al. (2001) found the initial adsorption of Zn and Cd very fast, followed by the slow transfer of ions into an irreversibly adsorbed fraction as well.

The correlation of CEC and C_{org} with distribution coefficient K_d (Fig. 5-6, 5-7) and also the correlation between effective diffusion coefficient and C_{org} (Fig. 5-5) confirm that adsorption playing an important role in cation diffusion in soil. The higher is sorption, the slower diffusion can be expected. Thus, the higher CEC or C_{org} of a soil make diffusion slower.

6.3   Influence of aggregate coatings on heavy metal diffusion

The study of cation diffusion in aggregate skins has been performed with the coatings from B_t horizon of a luvisol soil (sample **C**). The coatings had the same pH, but significantly higher C_{org} and CEC when compared to the bulk. This is probably because of the accumulation of clay minerals and organic matter on aggregate surfaces in B_t horizon. The experiment on cation diffusion in aggregate skins has been provided with Ba and Cs.

An apparent diffusion coefficient of Ba in aggregate skins fit well to the regularity $-\log D$ vs C_{org} and $-\log D$ vs CEC. This, however, was not the case for cesium. The explanation of this specific behavior is probably the specific sorption of Cs on 2:1 phyllosilicates.

Experiments on conservative tracer diffusion showed that aggregate skins are the most tortuous amongst all soil samples. The impedance factor of

coatings $f = 0.52$ was smaller than in chernozem $f = 0.54$, followed by soil from A_l and B_t horizons of luvisol with $f = 0.57$. This means that the retardation of ion diffusion in aggregate skins occur not only because adsorption, but because of more tortuous structure than the bulk soil has. This is in agreement with results from *Gerke* and *Köhne* (2002) who found water diffusivity in skins several times lower than in corresponding bulk soil samples. It should be however mentioned that this work dealt with homogenized aggregate coatings, while *Gerke* and *Köhne* (2002) studied undisturbed skins. Considering their findings, we can estimate higher retardation of cation diffusion from aggregate coatings as predicted in this work.

6.4   Mathematical model of adsorption hindered diffusion

Mathematical model of adsorption hindered diffusion has successfully described observed diffusion profiles of cations. Firstly, the model explained S-shape of the profiles, whereas the classic diffusion theory produces only L-shaped curve. Secondly, the model was able to explain the maximum of diffusion profile, which is much higher than predicted by classic model.

Among three different types of adsorption isotherms, the best results were obtained with the help of Freundlich equation. Ten of fourteen diffusion profiles were better described by means of Freundlich adsorption isotherm, than with the help of linear or Langmuir isotherms. However, Langmuir isotherm was more suitable in describing barium diffusion.

6.5   Application of the results to the real systems

The advantage of the mathematical model is that it includes the basic parameters affecting cation diffusion: diffusion coefficient of cation in water, water content of soil and the soil impedance factor. The first value is a predetermined constant, the second can be easily measured and the third could be obtained experimentally. Furthermore a linear regression between volumetric moisture content and impedance factor was found (*Olesen* et al., 1999, 2001). The results obtained by *Olesen* et al. (2001) and *Barraclough* and *Tinker* (1982) are justifying extrapolation of the results from water-saturated soil column onto unsaturated field soil.

If we consider, that even in contaminated areas the annual atmospheric deposition of heavy metals is only several grams per hectare (*Nicholson* et al., 2003), it becomes clear that the adsorption process should completely retard diffusion process on macroscale level. The findings of *Hagedorn* and *Bundt* (2002) on the stability of radiotracer gradients in preferential flow paths over decades are confirming the immobilization of diffusing heavy metals in soil. The mathematical model developed during this study was also predicting insignificant redistribution of heavy metal cations along aggregates during months.

All the facts are pointing out that <u>any redistribution of heavy metals along aggregates in contaminated soils due to diffusion process is unlikely</u>. Heavy metal concentration gradients in soil are disappearing because of decomposition and formation of soil aggregates.

6.6 Further possible studies

This work shows that disappearing of heavy metal concentration gradient due to diffusion is unlikely. The possible reason of the process is decomposition of old and formation of new soil aggregates. If it is true, than in a limited period after contamination the local heterogenity of contaminants with pronounced concentration gradients should be observed inside aggregates. The more cycles of decomposition-formation of aggregates occur, the more diffused will be the local contamination zones inside them. Investigation of detailed contamination patterns inside aggregates with µ-XANES from the areas with recent, continuing and old contamination could reveal one of the soil science problems: a lifetime of single aggregate. There could be different investigations on the dependence of the aggregate lifetime from their size, soil type, climate, SOM and clay content etc. Some of these questions, if answered, should be very useful in soil management and protection, in agriculture and in soil science.

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*Table A-1. Reproducibility of the experiment on heavy metal diffusion in soil samples; distribution of cesium along soil columns with sample **B** in two parallel experiments after 4 days of exposition to 40 mg L^{-1} Cs solution.*

Slice Nr.	Sample Nr. 1		Sample Nr. 2	
	X,cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}
1	0.003892	2.010378	0.003017	2.574035
2	0.011119	2.54517	0.008728	2.396164
3	0.017183	2.570141	0.014187	2.723229
4	0.024488	2.459647	0.021596	2.6055
5	0.033862	2.423047	0.031265	2.477022
6	0.042202	2.383666	0.041677	2.405356
7	0.052468	2.198778	0.052454	2.267027
8	0.065436	1.979925	0.06194	2.127339
9	0.076775	1.812649	0.070878	2.018435
10	0.088037	1.559025	0.081894	1.69975
11	0.0986	1.34119	0.092867	1.53304
12	0.109202	1.119497	0.104023	1.260239
13	0.119597	0.906327	0.115628	1.069687
14	0.128971	0.770141	0.126882	0.865457
15	0.140103	0.577755	0.138136	0.690319
16	0.151934	0.541053	0.148731	0.578978
17	0.164294	0.410008	0.159255	0.47155
18	0.174185	0.358292	0.169162	0.413689
19	0.183766	0.321128	0.179799	0.328214
20	0.192959	0.277529	0.191615	0.295099
21	0.200225	0.246954	0.201409	0.349759
22	0.211332	0.213362	0.210376	0.225709
23	0.224209	0.169641	0.221097	0.185691
24	0.237889	0.130643	0.232435	0.147785
25	0.250624	0.091838	0.242146	0.223984
26	0.26067	0.06463	0.250481	0.118603
27	0.270277	0.040421	0.260192	0.085479
28	0.280918	0.033017	0.272975	0.058936
29	0.291313	0.122854	0.28444	0.049291
30	0.301308	0.005693	0.293631	0.024658
31	0.311962	0.009502	0.303552	0.024252
32	0.320779	0.012087	0.312547	0.007673
33	0.328809	0.008046	0.323366	0.004113
34	0.336463	0.004026	0.335546	0.005348
35	0.344932	0.015756	0.345552	0.00334

*Table A-2.Experimental data on reproducibility of the chloride diffusion experiment in soil samples. Provided on soil samples **B**, exposition time was 18 hours.*

Slice Nr.	X, cm	C(Cl), DPM g^{-1}	X, cm	C(Cl), DPM g^{-1}
1	0.09	184.1057	0.1	141.6512
2	0.27	162.4889	0.28	159.6506
3	0.44	142.8079	0.45	131.2041
4	0.61	125.8447	0.61	97.5145
5	0.78	98.181	0.78	92.4387
6	0.94	78.4884	0.94	84.8546
7	1.09	66.2168	1.1	75.2757
8	1.26	52.158	1.26	65.5508
9	1.43	44.857	1.42	41.5495
10	1.59	36.2438	1.57	41.4355
11	1.74	30.0337	1.72	20.8835
12	1.89	21.3101	1.9	21.0508
13	2.07	16.783	2.07	16.2336
14	2.23	15.1247	2.23	12.7958
15	2.39	4.868	2.39	13.1481

*Table A-3. Experimental results on chloride diffusion in samples **A**, **Ch** and **C***

Sample **A**		Sample **Ch**		Sample **C**	
X, cm	C(Cl), DPM g^{-1}	X, cm	C(Cl), DPM g^{-1}	X, cm	C(Cl), DPM g^{-1}
0.11	190.631	0.07	241.4591	0.03	359.9803
0.3	176.0553	0.17	216.7897	0.11	216.9495
0.46	142.818	0.26	194.3587	0.19	211.8871
0.62	132.255	0.34	193.5012	0.28	144.8289
0.78	100.3381	0.42	170.5066	0.36	160.3893
0.94	94.3019	0.49	147.4534	0.44	167.7584
1.1	82.1066	0.57	129.5031	0.52	117.9084
1.27	56.8898	0.65	115.0634	0.61	112.3548
1.44	48.457	0.74	97.8123	0.68	88.6634
1.59	46.6775	0.81	108.5567	0.77	95.4853
1.75	26.2773	0.89	77.856	0.85	88.361
1.92	20.0272	0.97	76.9494	0.94	84.7191
2.08	19.8042	1.05	63.4331	1.02	90.0046
2.23	14.2144	1.13	59.9699	1.11	60.9307
2.39	11.6854	1.21	45.5908	1.2	46.1177
		1.29	49.9206	1.29	44.5591
		1.37	33.65	1.36	39.1821
		1.46	29.7136	1.44	29.3896
		1.54	26.9053	1.52	32.1993
		1.62	32.9974	1.61	33.0757

*Table A-4. Experimental data on Cs diffusion in samples **A, B, Ch** and **C***

Slice Nr.	Sample **A**		Sample **B**		Sample **Ch**		Sample **C**	
	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}
1	0.0026	2.7145	0.0040	9.5890	0.0021	7.0082	0.0034	5.2098
2	0.0090	2.2247	0.0139	9.5744	0.0074	6.4817	0.0104	5.3483
3	0.0169	2.2919	0.0255	9.2454	0.0118	7.2945	0.0185	5.1031
4	0.0258	2.3028	0.0364	8.9847	0.0168	6.7061	0.0275	4.9330
5	0.0349	2.4702	0.0488	9.5846	0.0255	6.5389	0.0370	4.6825
6	0.0438	2.4232	0.0577	9.1108	0.0329	6.7153	0.0466	4.5534
7	0.0521	2.3441	0.0626	7.9252	0.0391	6.4441	0.0539	4.3816
8	0.0594	2.5464	0.0716	7.2545	0.0492	5.9392	0.0661	4.1279
9	0.0681	2.4580	0.0822	6.8939	0.0620	5.8668	0.0815	3.5666
10	0.0789	2.4065	0.0927	6.1841	0.0761	5.9266	0.0928	3.3236
11	0.0889	2.4756	0.1007	6.3332	0.0913	5.7211	0.1017	2.9516
12	0.0973	2.4909	0.1079	5.1971	0.1056	5.3478	0.1118	2.6493
13	0.1052	2.3804	0.1182	4.6314	0.1183	4.8643	0.1244	2.4860
14	0.1144	2.3994	0.1316	3.9393	0.1328	4.6600	0.1347	4.0031
15	0.1261	2.3486	0.1450	3.6802	0.1545	3.4615	0.1442	1.8122
16	0.1366	2.3201	0.1528	3.1906	0.1625	3.3486	0.1548	1.6288
17	0.1432	2.3646	0.1621	2.6071	0.1697	3.0391	0.1652	1.4488
18	0.1499	2.2066	0.1730	2.2837	0.1800	2.6858	0.1750	1.3272
19	0.1585	2.0408	0.1837	1.7953	0.1889	2.3589	0.1856	1.1890
20	0.1662	2.0544	0.1984	1.5033	0.1963	2.3194	0.1957	1.0402
21	0.1751	1.9142	0.2083	1.5037	0.2044	2.1068	0.2058	0.8592
22	0.1864	1.8700	0.2164	1.1573	0.2118	1.7594	0.2158	0.8403
23	0.1964	1.7539	0.2250	1.2455	0.2197	1.5921	0.2236	0.7169
24	0.2046	1.7623	0.2292	1.1984	0.2460	1.0746	0.2333	0.5676
25	0.2119	1.5942	0.2353	0.9299	0.2729	0.7945	0.2442	0.4892
26	0.2225	1.5487	0.2462	0.7920	0.2813	0.7587	0.2534	0.3834
27	0.2332	1.5088	0.2605	0.6712	0.2963	0.5719	0.2629	0.2971
28	0.2404	1.4492	0.2734	0.5719	0.3128	0.5000	0.2726	0.2350
29	0.2526	1.2439	0.2845	0.5230	0.3217	0.4122	0.2821	0.1390
30	0.2699	1.0615			0.3290	0.3686	0.2935	0.0886
31	0.2855	1.0126			0.3363	0.2282	0.3036	0.0243
32	0.2947	1.0722			0.3438	0.2200	0.3125	0.0077
33	0.3084	0.7654			0.3499	0.2074	0.3234	0.0041
34	0.3254	0.6616			0.3555	0.2077	0.3355	0.0053
35	0.3352	0.6545			0.3621	0.1379	0.3456	0.0033
36	0.3460	0.5287			0.3710	0.1040		
37	0.3582	0.4803			0.3815	0.0919		
38	0.3720	0.3306			0.3888	0.1382		
39	0.3834	0.2781			0.3957	0.0650		
40	0.3933	0.1591						

Table *A-5. Experimental data on Ba diffusion in samples **A**, **B**, **Ch** and **C**.*

Slice Nr.	Sample **A**		Sample **B**		Sample **Ch**		Sample **C**	
	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}
1	0.0023	0.5033	0.0020	1.3362	0.0023	3.2233	0.0020	2.0716
2	0.0083	1.1693	0.0063	1.3676	0.0079	3.6395	0.0053	2.5595
3	0.0156	1.2844	0.0104	1.4586	0.0139	3.4318	0.0077	2.5364
4	0.0231	1.4190	0.0165	1.4160	0.0228	3.5663	0.0128	2.4818
5	0.0309	1.4086	0.0242	1.3827	0.0325	3.3219	0.0263	2.2189
6	0.0426	1.2760	0.0318	1.3984	0.0428	3.1687	0.0425	2.1905
7	0.0541	1.2813	0.0406	1.3782	0.0548	2.9730	0.0541	2.0767
8	0.0627	1.2812	0.0506	1.3337	0.0660	2.7643	0.0654	1.9953
9	0.0723	1.2965	0.0604	1.3012	0.0759	2.5811	0.0779	1.8627
10	0.0828	1.1894	0.0731	1.2242	0.0873	2.2976	0.0884	1.7658
11	0.0943	1.1733	0.0862	1.1641	0.0993	2.0663	0.0976	1.7110
12	0.1045	1.0827	0.0975	1.2110	0.1108	1.9912	0.1076	1.5055
13	0.1133	1.0289	0.1082	1.1639	0.1199	1.6669	0.1205	1.3362
14	0.1236	0.9292	0.1181	1.0669	0.1298	1.3950	0.1336	1.1933
15	0.1355	0.8720	0.1274	1.0827	0.1426	1.1173	0.1435	1.0761
16	0.1462	0.8294	0.1377	1.0020	0.1540	0.9207	0.1534	1.0328
17	0.1559	0.7816	0.1485	0.9090	0.1638	0.7484	0.1620	0.8665
18	0.1657	0.6986	0.1595	0.8327	0.1732	0.6082	0.1680	0.9416
19	0.1756	0.6281	0.1729	0.7348	0.1840	0.4178	0.1755	0.7908
20	0.1869	0.5837	0.1839	0.7156	0.1944	0.3160	0.1852	0.6851
21	0.1974	0.5436	0.1931	0.6351	0.2040	0.2081	0.1945	0.6556
22	0.2075	0.4736	0.2025	0.5472	0.2141	0.1405	0.2032	0.5353
23	0.2181	0.3751	0.2139	0.4511	0.2241	0.0848	0.2131	0.4309
24	0.2278	0.2952	0.2257	0.4012	0.2345	0.0559	0.2267	0.3325
25	0.2379	0.2429	0.2371	0.3652	0.2460	0.0316	0.2397	0.2635
26	0.2479	0.1920	0.2488	0.3311	0.2570	0.0145	0.2508	0.1913
27	0.2580	0.1471	0.2591	0.2412	0.2683	0.0125	0.2615	0.1217
28	0.2686	0.0955	0.2690	0.2195	0.2789	0.0116	0.2706	0.0968
29	0.2785	0.0661	0.2808	0.1434	0.2882	0.0140	0.2820	0.0794
30	0.2899	0.0482	0.2918	0.1175	0.2988	0.0047	0.2953	0.0480
31	0.3015	0.0265	0.3002	0.0949	0.3095	0.0000	0.3060	0.0402
32	0.3125	0.0235	0.3103	0.0588	0.3200	0.0000	0.3151	0.0235
33	0.3237	0.0111	0.3222	0.0429	0.3303	0.0000	0.3238	0.0153
34	0.3339	0.0051	0.3334	0.0331	0.3417	0.0000	0.3305	0.0187
35	0.3455	0.0038	0.3440	0.0167	0.3540	0.0000	0.3393	0.0114
36	0.3571	0.0066	0.3535	0.0136	0.3653	0.0000	0.3496	0.0084
37	0.3663	0.0070	0.3619	0.0164	0.3744	0.0000	0.3622	0.0027
38	0.3768	0.0068	0.3729	0.0075	0.3830	0.0000	0.3759	0.0018
39			0.3847	0.0019	0.3940	0.0000	0.3863	0.0062
40			0.3951	0.0048			0.3955	0.0063

*Table A-6. Experimental data on Zn diffusion in samples **A**, **B** and **Ch***

Slice Nr.	Sample **A**		Sample **B**		Sample **Ch**	
	X, cm	C(Zn), mmol kg^{-1}	X, cm	C(Zn), mmol kg^{-1}	X, cm	C(Zn), mmol kg^{-1}
1	0.0078	2.4606	0.0044	2.8428	0.0068	8.0855
2	0.0147	2.2137	0.0084	2.5879	0.0165	7.2441
3	0.0244	1.8885	0.0124	2.8052	0.0408	6.0997
4	0.0304	1.8269	0.0190	2.7706	0.0512	6.1972
5	0.0360	1.6391	0.0245	2.7165	0.0577	6.3610
6	0.0406	1.7951	0.0340	2.5089	0.0649	5.8246
7	0.0483	1.7468	0.0422	2.4140	0.0746	5.4605
8	0.0602	1.3871	0.0473	2.8591	0.0821	5.4547
9	0.0689	1.5697	0.0609	2.3284	0.0861	4.9927
10	0.0794	1.6604	0.0722	2.2797	0.0908	5.2847
11	0.0894	1.6261	0.0811	2.1742	0.1031	4.9840
12	0.0998	1.5261	0.0969	2.2980	0.1153	4.4997
13	0.1126	1.4568	0.1058	2.0338	0.1209	4.1099
14	0.1220	1.5319	0.1104	2.1030	0.1260	4.3793
15	0.1354	1.5717	0.1178	1.9049	0.1350	3.9354
16	0.1453	1.4668	0.1356	2.0080	0.1625	3.7863
17	0.1573	1.5023	0.1459	1.8849	0.1804	3.4511
18	0.1686	1.6140	0.1558	1.8135	0.1906	3.2406
19	0.1798	1.6797	0.1758	1.7754	0.1970	3.2647
20	0.1911	1.6347	0.1969	1.6406	0.2058	3.0237
21	0.2006	1.9740	0.2048	1.7788	0.2173	2.6543
22	0.2052	1.8867	0.2262	1.5819	0.2262	2.4554
23	0.2170	2.0398	0.2369	1.5174	0.2342	2.0986
24	0.2229	2.1555	0.2457	1.4021	0.2436	2.0701
25	0.2344	1.9481	0.2530	1.3277	0.2550	1.5688
26	0.2495	1.5899	0.2657	1.4760	0.2606	1.2994
27	0.2672	1.2457	0.2752	1.2823	0.2686	0.9706
28	0.2784	1.0048	0.2847	1.2466	0.2776	0.9126
29	0.2888	0.7151	0.2970	1.2694	0.2919	0.6782
30	0.3000	0.3661	0.3036	1.1822	0.3000	0.3581
31			0.3153	1.1957		
32			0.3240	1.1497		
33			0.3341	1.0291		
34			0.3434	0.9767		
35			0.3500	0.9952		

*Table A-7. Experimental data on Cd diffusion in samples **A**, **B** and **Ch***

Slice Nr.	Sample **A**		Sample **B**		Sample **Ch**	
	X, cm	C(Cd), mmol kg^{-1}	X, cm	C(Cd), mmol kg^{-1}	X, cm	C(Cd), mmol kg^{-1}
1	0.0035	0.4761	0.0016	0.2301	0.0146	1.3489
2	0.0090	0.4525	0.0055	0.2839	0.0315	0.4156
3	0.0125	0.5161	0.0109	0.1854	0.0363	0.6809
4	0.0175	0.6283	0.0181	0.2275	0.0404	0.6743
5	0.0257	0.5869	0.0249	0.2007	0.0438	0.7920
6	0.0338	0.5864	0.0339	0.1731	0.0489	0.6186
7	0.0416	0.5294	0.0433	0.1964	0.0555	0.6868
8	0.0507	0.6342	0.0524	0.1991	0.0625	0.4691
9	0.0604	0.5444	0.0636	0.1815	0.0696	0.5261
10	0.0730	0.4595	0.0738	0.1757	0.0779	0.3984
11	0.0847	0.4613	0.0855	0.1793	0.0897	0.3071
12	0.0951	0.3826	0.0979	0.1727	0.1052	0.2019
13	0.1053	0.3487	0.1083	0.1876	0.1184	0.1744
14	0.1168	0.2920	0.1176	0.1819	0.1279	0.0913
15	0.1300	0.2579	0.1258	0.1819	0.1373	0.0458
16	0.1413	0.2120	0.1353	0.1666	0.1549	0.0385
17	0.1523	0.1851	0.1475	0.1681	0.1769	0.0120
18	0.1655	0.1459	0.1597	0.1751	0.1905	0.0056
19	0.1792	0.1430	0.1703	0.1684	0.1997	0.0037
20	0.1899	0.1140	0.1791	0.1595	0.2087	0.0008
21	0.1998	0.0922	0.1895	0.1428	0.2185	0.0012
22	0.2101	0.0956	0.2016	0.1555	0.2293	0.0016
23	0.2214	0.0557	0.2138	0.1452	0.2380	0.0010
24	0.2337	0.0503	0.2278	0.1822	0.2449	0.0009
25			0.2403	0.1343	0.2529	0.0008
26			0.2522	0.1429	0.2628	0.0002
27			0.2638	0.1213	0.2727	0.0147
28			0.2738	0.1072	0.2837	0.0004
29			0.2834	0.1218	0.2941	0.0007
30			0.2940	0.1182	0.3013	0.0013
31					0.3073	0.0009

*Table A-8. Results on mathematical modeling of chloride diffusion in reproducibility experiment in sample **B**.*

Slice Nr.	X, cm	C(Cl), DPM g^{-1}	X, cm	C(Cl), DPM g^{-1}
1	0.1	165.3333	0.09	166.5589
2	0.28	145.4127	0.27	147.1339
3	0.45	127.7713	0.44	129.4682
4	0.61	110.9108	0.61	112.4262
5	0.78	95.2336	0.78	96.1689
6	0.94	80.7046	0.94	82.2704
7	1.1	67.7174	1.09	69.862
8	1.26	56.4567	1.26	57.9065
9	1.42	46.145	1.43	47.1705
10	1.57	38.0041	1.59	38.1536
11	1.72	30.6594	1.74	30.9626
12	1.9	23.4418	1.89	24.7463
13	2.07	18.0719	2.07	19
14	2.23	13.8587	2.23	14.6886
15	2.39	10.3554	2.39	11.166

Table A-9. Results on mathematical modeling of chloride diffusion in samples **A, Ch** *and* **C.**

Sample **A**		Sample **Ch**		Sample **C**	
X, cm	C(Cl), DPM g^{-1}	X, cm	C(Cl), DPM g^{-1}	X, cm	C(Cl), DPM g^{-1}
0.11	173.3267	0.07	184.8489	0.11	171.5811
0.3	152.5457	0.17	171.3353	0.19	161.7849
0.46	135.1619	0.26	160.1776	0.28	150.8899
0.62	119.2907	0.34	149.9152	0.36	141.3631
0.78	103.7068	0.42	140.7061	0.44	132.026
0.94	89.3168	0.49	131.4739	0.52	122.9154
1.1	76.4043	0.57	122.6194	0.61	112.9793
1.27	63.9319	0.65	113.1445	0.68	105.5074
1.44	52.8408	0.74	103.851	0.77	96.2618
1.59	43.7568	0.81	95.7012	0.85	88.4091
1.75	35.8009	0.89	87.8389	0.94	80.0108
1.92	28.6171	0.97	80.4227	1.02	72.9493
2.08	22.7231	1.05	73.4629	1.11	65.4728
2.23	18.0155	1.13	66.7111	1.2	58.4999
2.39	14.0008	1.21	59.9501	1.29	52.0333
		1.29	54.167	1.36	47.352
		1.37	48.5938	1.44	42.3703
		1.46	42.8045	1.52	37.7735
		1.54	37.8947	1.61	33.0485
		1.62	33.8978		

Table A-10. Cesium diffusion in soil samples calculated with mathematical model based on linear adsorption isotherm.

Sample A		Sample B		Sample Ch		Sample C	
X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}
0.0026	3.00338	0.004	8.92234	0.0021	6.77046	0.0034	4.45999
0.009	2.95489	0.0139	8.60296	0.0074	6.66261	0.0104	4.35471
0.0169	2.89471	0.0255	8.22988	0.0118	6.57117	0.0185	4.2316
0.0258	2.82748	0.0364	7.87971	0.0168	6.4674	0.0275	4.0955
0.0349	2.75828	0.0488	7.48293	0.0255	6.2865	0.037	3.95281
0.0438	2.69075	0.0577	7.20045	0.0329	6.135	0.0466	3.80772
0.0521	2.62746	0.0626	7.04265	0.0391	6.00612	0.0539	3.69766
0.0594	2.57191	0.0716	6.75749	0.0492	5.79825	0.0661	3.51235
0.0681	2.50578	0.0822	6.42338	0.062	5.53493	0.0815	3.28027
0.0789	2.42416	0.0927	6.09283	0.0761	5.24588	0.0928	3.11009
0.0889	2.34806	0.1007	5.84206	0.0913	4.93443	0.1017	2.9758
0.0973	2.28432	0.1079	5.6182	0.1056	4.64384	0.1118	2.8229
0.1052	2.22452	0.1182	5.29869	0.1183	4.38751	0.1244	2.6343
0.1144	2.15493	0.1316	4.88734	0.1328	4.09726	0.1442	2.33572
0.1261	2.06645	0.145	4.48016	0.1545	3.66724	0.1548	2.17635
0.1366	1.98643	0.1528	4.24215	0.1625	3.50825	0.1652	2.02015
0.1432	1.93659	0.1621	3.96287	0.1697	3.36782	0.175	1.87213
0.1499	1.88607	0.173	3.63731	0.18	3.16758	0.1856	1.71325
0.1585	1.8205	0.1837	3.32153	0.1889	2.99511	0.1957	1.56233
0.1662	1.76219	0.1984	2.88955	0.1963	2.852	0.2058	1.40973
0.1751	1.695	0.2083	2.60293	0.2044	2.69608	0.2158	1.25983
0.1864	1.60946	0.2164	2.36786	0.2118	2.55543	0.2236	1.14406
0.1964	1.53363	0.225	2.12255	0.2197	2.40433	0.2333	0.99863
0.2046	1.47218	0.2292	1.99984	0.246	1.90897	0.2442	0.83449
0.2119	1.41662	0.2353	1.82711	0.2729	1.40975	0.2534	0.69702
0.2225	1.33647	0.2462	1.51695	0.2813	1.25472	0.2629	0.55456
0.2332	1.25578	0.2605	1.10997	0.2963	0.9789	0.2726	0.41039
0.2404	1.20125	0.2734	0.74624	0.3128	0.67684	0.2821	0.26799
0.2526	1.1097	0.2845	0.43565	0.3217	0.51495	0.2935	0.09768
0.2699	0.97892			0.329	0.38154		
0.2855	0.86118			0.3363	0.24935		
0.2947	0.79187			0.3438	0.11261		
0.3084	0.68872						
0.3254	0.5608						
0.3352	0.48739						
0.346	0.4064						
0.3582	0.31445						
0.372	0.21027						
0.3834	0.12466						
0.3933	0.05043						

Table A-11. Cesium diffusion in soil samples calculated with mathematical model based on Langmuir adsorption isotherm.

Sample A		Sample B		Sample Ch		Sample C	
X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}
0.0026	2.66449	0.004	6.57959	0.0021	6.92352	0.0034	4.75749
0.009	2.64405	0.0139	6.38561	0.0074	6.82805	0.0104	4.64901
0.0169	2.61677	0.0255	6.14799	0.0118	6.74562	0.0185	4.52192
0.0258	2.58399	0.0364	5.919	0.0168	6.65049	0.0275	4.38113
0.0349	2.54747	0.0488	5.65743	0.0255	6.48057	0.037	4.23338
0.0438	2.51062	0.0577	5.46953	0.0329	6.33409	0.0466	4.08308
0.0521	2.47561	0.0626	5.36395	0.0391	6.20896	0.0539	3.96901
0.0594	2.44437	0.0716	5.17203	0.0492	6.00594	0.0661	3.77693
0.0681	2.40651	0.0822	4.9453	0.062	5.74654	0.0815	3.53631
0.0789	2.35877	0.0927	4.71899	0.0761	5.45922	0.0928	3.35987
0.0889	2.3132	0.1007	4.54597	0.0913	5.14699	0.1017	3.22067
0.0973	2.27425	0.1079	4.39054	0.1056	4.85366	0.1118	3.06222
0.1052	2.23701	0.1182	4.16713	0.1183	4.59362	0.1244	2.86686
0.1144	2.19282	0.1316	3.87679	0.1328	4.29812	0.1442	2.55784
0.1261	2.13525	0.145	3.58641	0.1545	3.85922	0.1548	2.39306
0.1366	2.08181	0.1528	3.41533	0.1625	3.69687	0.1652	2.23167
0.1432	2.04784	0.1621	3.21333	0.1697	3.55354	0.175	2.07884
0.1499	2.01285	0.173	2.97619	0.18	3.34937	0.1856	1.91493
0.1585	1.9666	0.1837	2.7445	0.1889	3.17381	0.1957	1.75934
0.1662	1.92463	0.1984	2.42495	0.1963	3.02839	0.2058	1.60214
0.1751	1.87528	0.2083	2.21133	0.2044	2.8703	0.2158	1.44783
0.1864	1.81084	0.2164	2.03521	0.2118	2.72802	0.2236	1.32872
0.1964	1.75217	0.225	1.85055	0.2197	2.57557	0.2333	1.17918
0.2046	1.70352	0.2292	1.75785	0.246	2.07903	0.2442	1.01047
0.2119	1.65864	0.2353	1.627	0.2729	1.58401	0.2534	0.86925
0.2225	1.59237	0.2462	1.39099	0.2813	1.43135	0.2629	0.72294
0.2332	1.52376	0.2605	1.07933	0.2963	1.16079	0.2726	0.57491
0.2404	1.47629	0.2734	0.7989	0.3128	0.86571	0.2821	0.43047
0.2526	1.39446	0.2845	0.5661	0.3217	0.70788	0.2935	0.22175
0.2699	1.27278			0.329	0.58009		
0.2855	1.15807			0.3363	0.45728		
0.2947	1.08813			0.3438	0.2494		
0.3084	0.98053						
0.3254	0.84092						
0.3352	0.75751						
0.346	0.66255						
0.3582	0.55079						
0.372	0.41878						
0.3834	0.31171						
0.3933	0.15762						

Table A-12. Cesium diffusion in soil samples calculated with mathematical model based on Freundlich adsorption isotherm.

Sample **A**		Sample **B**		Sample **Ch**		Sample **C**	
X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}	X, cm	C(Cs), mmol kg^{-1}
0.0026	2.73777	0.004	10.19927	0.0021	7.42274	0.0034	7.36231
0.009	2.70661	0.0139	9.70676	0.0074	7.27062	0.0104	7.13347
0.0169	2.66773	0.0255	9.14263	0.0118	7.14228	0.0185	6.86827
0.0258	2.62402	0.0364	8.62411	0.0168	6.99734	0.0275	6.57809
0.0349	2.57875	0.0488	8.05072	0.0255	6.74648	0.037	6.27751
0.0438	2.53428	0.0577	7.65216	0.0329	6.53814	0.0466	5.97597
0.0521	2.4923	0.0626	7.43324	0.0391	6.36228	0.0539	5.75013
0.0594	2.45523	0.0716	7.04448	0.0492	6.08132	0.0661	5.37586
0.0681	2.4108	0.0822	6.60057	0.062	5.7304	0.0815	4.91826
0.0789	2.35552	0.0927	6.17407	0.0761	5.35191	0.0928	4.59098
0.0889	2.30349	0.1007	5.85912	0.0913	4.95235	0.1017	4.33787
0.0973	2.25955	0.1079	5.58438	0.1056	4.58763	0.1118	4.05535
0.1052	2.21801	0.1182	5.20274	0.1183	4.27261	0.1244	3.71539
0.1144	2.16928	0.1316	4.72985	0.1328	3.92373	0.1442	3.19709
0.1261	2.10667	0.145	4.28234	0.1453	3.63233	0.1548	2.93067
0.1366	2.04939	0.1528	4.0303	0.1545	3.42273	0.1652	2.67659
0.1432	2.01339	0.1621	3.74349	0.1625	3.24243	0.175	2.44238
0.1499	1.97663	0.173	3.42138	0.1697	3.08546	0.1856	2.19822
0.1585	1.92851	0.1837	3.12145	0.18	2.86539	0.1957	1.97337
0.1662	1.8853	0.1984	2.73103	0.1889	2.67945	0.2058	1.7532
0.1751	1.835	0.2083	2.48455	0.1963	2.52773	0.2158	1.54416
0.1864	1.77016	0.2164	2.28989	0.2044	2.36517	0.2236	1.38781
0.1964	1.71186	0.225	2.09391	0.2118	2.22102	0.2333	1.19789
0.2046	1.66403	0.2292	1.99858	0.2197	2.06884	0.2442	0.99267
0.2119	1.6203	0.2353	1.86754	0.246	1.59039	0.2534	0.82877
0.2225	1.55636	0.2462	1.64128	0.2729	1.14262	0.2629	0.66722
0.2332	1.49089	0.2605	1.36219	0.2813	1.01139	0.2726	0.51319
0.2404	1.446	0.2734	1.13002	0.2963	0.78811	0.2821	0.37342
0.2526	1.36932	0.2845	0.94495	0.3128	0.56038	0.2935	0.1889
0.2699	1.25666			0.3217	0.44667		
0.2855	1.15164			0.329	0.35968		
0.2947	1.08799			0.3363	0.28104		
0.3084	0.99036			0.3438	0.15171		
0.3254	0.86359						
0.3352	0.78734						
0.346	0.69965						
0.3582	0.59432						
0.372	0.46485						
0.3834	0.35163						
0.3933	0.18015						

Table A-13. Barium diffusion in soil samples calculated with mathematical model based on linear adsorption isotherm.

Sample **A**		Sample **B**		Sample **Ch**		Sample **C**	
X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}
0.0156	1.5158	0.0020	1.5933	0.0023	3.9177	0.0020	2.6644
0.0231	1.4702	0.0063	1.5667	0.0079	3.7879	0.0053	2.6177
0.0309	1.4223	0.0104	1.5415	0.0139	3.6473	0.0077	2.5849
0.0426	1.3511	0.0165	1.5040	0.0228	3.4427	0.0128	2.5143
0.0541	1.2816	0.0242	1.4565	0.0325	3.2193	0.0263	2.3281
0.0627	1.2300	0.0318	1.4099	0.0428	2.9860	0.0425	2.1074
0.0723	1.1732	0.0406	1.3562	0.0548	2.7219	0.0541	1.9524
0.0828	1.1120	0.0506	1.2960	0.0660	2.4804	0.0654	1.8038
0.0943	1.0462	0.0604	1.2370	0.0759	2.2748	0.0779	1.6447
0.1045	0.9884	0.0731	1.1616	0.0873	2.0497	0.0884	1.5162
0.1133	0.9402	0.0862	1.0856	0.0993	1.8248	0.0976	1.4068
0.1236	0.8843	0.0975	1.0216	0.1108	1.6218	0.1076	1.2935
0.1355	0.8216	0.1082	0.9617	0.1199	1.4699	0.1205	1.1534
0.1462	0.7670	0.1181	0.9084	0.1298	1.3156	0.1336	1.0208
0.1559	0.7185	0.1274	0.8589	0.1426	1.1320	0.1435	0.9271
0.1657	0.6711	0.1377	0.8060	0.1540	0.9824	0.1534	0.8383
0.1756	0.6249	0.1485	0.7523	0.1638	0.8662	0.1620	0.7659
0.1869	0.5732	0.1595	0.6995	0.1732	0.7622	0.1680	0.7183
0.1974	0.5273	0.1729	0.6377	0.1840	0.6545	0.1755	0.6613
0.2075	0.4847	0.1839	0.5897	0.1944	0.5614	0.1852	0.5925
0.2181	0.4415	0.1931	0.5506	0.2040	0.4840	0.1945	0.5313
0.2278	0.4033	0.2025	0.5126	0.2141	0.4102	0.2032	0.4782
0.2379	0.3646	0.2139	0.4686	0.2241	0.3440	0.2131	0.4229
0.2479	0.3278	0.2257	0.4254	0.2345	0.2829	0.2267	0.3546
0.2580	0.2914	0.2371	0.3857	0.2460	0.2220	0.2397	0.2981
0.2686	0.2549	0.2488	0.3473	0.2570	0.1700	0.2508	0.2550
0.2785	0.2216	0.2591	0.3154	0.2683	0.1215	0.2615	0.2186
0.2899	0.1842	0.2690	0.2863	0.2789	0.0791	0.2706	0.1908
0.3015	0.1473	0.2808	0.2536	0.2882	0.0438	0.2820	0.1601
0.3125	0.1133	0.2918	0.2245	0.2988	0.0044	0.2953	0.1292
0.3237	0.0791	0.3002	0.2036			0.3060	0.1077
0.3339	0.0483	0.3103	0.1794			0.3151	0.0918
0.3455	0.0134	0.3222	0.1523			0.3238	0.0782
		0.3334	0.1281			0.3305	0.0686
		0.3440	0.1062			0.3393	0.0571
		0.3535	0.0871			0.3496	0.0451
		0.3619	0.0708			0.3622	0.0323
		0.3729	0.0499			0.3759	0.0198
		0.3847	0.0281				
		0.3951	0.0090				

Table A-14. Barium diffusion in soil samples calculated with mathematical model based on Langmuir adsorption isotherm.

Sample **A**		Sample **B**		Sample **Ch**		Sample **C**	
X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}
0.0156	1.4118	0.0020	1.4260	0.0023	3.5123	0.0020	2.3550
0.0231	1.3886	0.0063	1.4222	0.0079	3.4919	0.0053	2.3492
0.0309	1.3605	0.0104	1.4173	0.0139	3.4532	0.0077	2.3435
0.0426	1.3161	0.0165	1.4080	0.0228	3.3733	0.0128	2.3270
0.0541	1.2706	0.0242	1.3933	0.0325	3.2568	0.0263	2.2618
0.0627	1.2351	0.0318	1.3757	0.0428	3.1233	0.0425	2.1479
0.0723	1.1943	0.0406	1.3519	0.0548	2.9509	0.0541	2.0562
0.0828	1.1480	0.0506	1.3241	0.0660	2.7693	0.0654	1.9573
0.0943	1.0954	0.0604	1.2946	0.0759	2.5928	0.0779	1.8371
0.1045	1.0468	0.0731	1.2533	0.0873	2.3720	0.0884	1.7274
0.1133	1.0044	0.0862	1.2070	0.0993	2.1182	0.0976	1.6236
0.1236	0.9529	0.0975	1.1637	0.1108	1.8570	0.1076	1.5046
0.1355	0.8924	0.1082	1.1191	0.1199	1.6407	0.1205	1.3396
0.1462	0.8371	0.1181	1.0754	0.1298	1.4041	0.1336	1.1637
0.1559	0.7859	0.1274	1.0312	0.1426	1.1053	0.1435	1.0276
0.1657	0.7342	0.1377	0.9795	0.1540	0.8567	0.1534	0.8906
0.1756	0.6823	0.1485	0.9218	0.1638	0.6685	0.1620	0.7746
0.1869	0.6227	0.1595	0.8595	0.1732	0.5101	0.1680	0.6966
0.1974	0.5686	0.1729	0.7788	0.1840	0.3624	0.1755	0.6031
0.2075	0.5178	0.1839	0.7102	0.1944	0.2528	0.1852	0.4911
0.2181	0.4659	0.1931	0.6504	0.2040	0.1768	0.1945	0.3953
0.2278	0.4202	0.2025	0.5893	0.2141	0.1181	0.2032	0.3169
0.2379	0.3743	0.2139	0.5151	0.2241	0.0771	0.2131	0.2416
0.2479	0.3315	0.2257	0.4399	0.2345	0.0486	0.2267	0.1607
0.2580	0.2902	0.2371	0.3701	0.2460	0.0283	0.2397	0.1055
0.2686	0.2503	0.2488	0.3041	0.2570	0.0165	0.2508	0.0716
0.2785	0.2154	0.2591	0.2514	0.2683	0.0093	0.2615	0.0485
0.2899	0.1782	0.2690	0.2062	0.2789	0.0052	0.2706	0.0343
0.3015	0.1438	0.2808	0.1598	0.2882	0.0032	0.2820	0.0219
0.3125	0.1140	0.2918	0.1233	0.2988	0.0004	0.2953	0.0126
0.3237	0.0857	0.3002	0.1004			0.3060	0.0079
0.3339	0.0629	0.3103	0.0772			0.3151	0.0053
0.3455	0.0230	0.3222	0.0558			0.3238	0.0036
		0.3334	0.0405			0.3305	0.0026
		0.3440	0.0294			0.3393	0.0017
		0.3535	0.0219			0.3496	0.0011
		0.3619	0.0166			0.3622	0.0006
		0.3729	0.0114			0.3759	0.0003
		0.3847	0.0074				
		0.3951	0.0027				

Table A-15. Barium diffusion in soil samples calculated with mathematical model based on Freundlich adsorption isotherm.

Sample **A**		Sample **B**		Sample **Ch**		Sample **C**	
X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}	X, cm	C(Ba), mmol kg^{-1}
0.0156	1.5377	0.0020	1.54709	0.0023	3.76006	0.0020	2.49247
0.0231	1.4882	0.0063	1.52578	0.0079	3.66741	0.0053	2.46345
0.0309	1.4364	0.0104	1.50549	0.0139	3.56577	0.0077	2.44287
0.0426	1.3595	0.0165	1.4752	0.0228	3.41546	0.0128	2.39824
0.0541	1.2849	0.0242	1.43655	0.0325	3.24786	0.0263	2.27751
0.0627	1.2298	0.0318	1.3984	0.0428	3.06833	0.0425	2.12884
0.0723	1.1694	0.0406	1.35403	0.0548	2.85858	0.0541	2.02009
0.0828	1.1047	0.0506	1.30391	0.0660	2.65958	0.0654	1.91174
0.0943	1.0354	0.0604	1.25411	0.0759	2.48393	0.0779	1.79042
0.1045	0.9751	0.0731	1.18969	0.0873	2.28391	0.0884	1.68783
0.1133	0.9249	0.0862	1.12368	0.0993	2.0748	0.0976	1.59666
0.1236	0.8672	0.0975	1.06719	0.1108	1.87676	0.1076	1.49806
0.1355	0.8029	0.1082	1.01354	0.1199	1.72196	0.1205	1.36933
0.1462	0.7473	0.1181	0.96497	0.1298	1.55814	0.1336	1.23924
0.1559	0.6982	0.1274	0.91928	0.1426	1.35324	0.1435	1.14156
0.1657	0.6506	0.1377	0.86967	0.1540	1.17725	0.1534	1.04373
0.1756	0.6044	0.1485	0.81839	0.1638	1.03438	0.1620	0.95982
0.1869	0.5533	0.1595	0.76723	0.1732	0.90162	0.1680	0.90236
0.1974	0.5081	0.1729	0.70605	0.1840	0.75897	0.1755	0.83075
0.2075	0.4666	0.1839	0.65764	0.1944	0.63183	0.1852	0.74016
0.2181	0.4248	0.1931	0.61763	0.2040	0.52367	0.1945	0.65515
0.2278	0.3882	0.2025	0.57818	0.2141	0.41931	0.2032	0.57755
0.2379	0.3514	0.2139	0.53178	0.2241	0.3262	0.2131	0.49283
0.2479	0.3167	0.2257	0.48551	0.2345	0.2423	0.2267	0.38204
0.2580	0.2826	0.2371	0.44236	0.2460	0.16353	0.2397	0.28523
0.2686	0.2489	0.2488	0.40024	0.2570	0.10346	0.2508	0.20902
0.2785	0.2184	0.2591	0.36486	0.2683	0.05693	0.2615	0.14419
0.2899	0.1847	0.2690	0.33239	0.2789	0.02672	0.2706	0.09606
0.3015	0.1519	0.2808	0.29578	0.2882	0.01074	0.2820	0.04698
0.3125	0.1222	0.2918	0.26323	0.2988	0.00065	0.2953	0.01103
0.3237	0.0929	0.3002	0.23991			0.3060	0.00127
0.3339	0.0687	0.3103	0.21306			0.3151	0.00007
0.3455	0.0253	0.3222	0.18338			0.3238	0.00001
		0.3334	0.15728			0.3305	0
		0.3440	0.13403			0.3393	0
		0.3535	0.11419				
		0.3619	0.09737				
		0.3729	0.07609				
		0.3847	0.0545				
		0.3951	0.02161				

*Table A-16. Zinc diffusion in soil samples **A, B** and **Ch** calculated
with mathematical model based on linear adsorption isotherm.*

Sample **A**		Sample **B**		Sample **Ch**	
X, cm	C(Zn), mmol kg^{-1}	X, cm	C(Zn), mmol kg^{-1}	X, cm	C(Zn), mmol kg^{-1}
0.0078	2.3641	0.0044	2.9417	0.0068	8.2883
0.0147	2.3068	0.0084	2.9047	0.0165	7.8586
0.0244	2.2267	0.0124	2.8661	0.0408	6.7928
0.0304	2.1768	0.0190	2.8034	0.0512	6.3483
0.0360	2.1305	0.0245	2.7515	0.0577	6.0714
0.0406	2.0926	0.0340	2.6625	0.0649	5.7718
0.0483	2.0287	0.0422	2.5848	0.0746	5.3786
0.0602	1.9307	0.0473	2.5369	0.0821	5.0810
0.0689	1.8590	0.0609	2.4100	0.0861	4.9248
0.0794	1.7727	0.0722	2.3052	0.0908	4.7449
0.0894	1.6901	0.0811	2.2227	0.1031	4.2845
0.0998	1.6048	0.0969	2.0795	0.1153	3.8550
0.1126	1.5003	0.1058	1.9999	0.1209	3.6631
0.1220	1.4237	0.1104	1.9592	0.1260	3.4943
0.1354	1.3147	0.1178	1.8937	0.1350	3.2079
0.1453	1.2343	0.1356	1.7399	0.1625	2.4157
0.1573	1.1368	0.1459	1.6530	0.1804	1.9691
0.1686	1.0455	0.1558	1.5711	0.1906	1.7368
0.1798	0.9553	0.1758	1.4099	0.1970	1.5998
0.1911	0.8650	0.1969	1.2469	0.2058	1.4202
0.2006	0.7885	0.2048	1.1876	0.2173	1.2035
0.2052	0.7520	0.2262	1.0326	0.2262	1.0471
0.2170	0.6575	0.2369	0.9585	0.2342	0.9137
0.2229	0.6109	0.2457	0.8985	0.2436	0.7658
0.2344	0.5193	0.2530	0.8499	0.2550	0.5965
0.2495	0.3999	0.2657	0.7665	0.2606	0.5169
0.2672	0.2593	0.2752	0.7060	0.2686	0.4074
0.2784	0.1708	0.2847	0.6472	0.2776	0.2868
0.2888	0.0884	0.2970	0.5724	0.2919	0.1024
0.3000	0	0.3036	0.5327	0.3000	0.0000
		0.3153	0.4646		
		0.3240	0.4144		
		0.3341	0.3575		
		0.3434	0.3055		
		0.3500	0.2691		

*Table A-17. Zinc diffusion in soil samples **A**, **B** and **Ch** calculated with mathematical model based on Langmuir adsorption isotherm.*

Sample **A**		Sample **B**		Sample **Ch**	
X, cm	C(Zn), mmol kg⁻¹	X, cm	C(Zn), mmol kg⁻¹	X, cm	C(Zn), mmol kg⁻¹
0.0078	0.4476	0.0044	2.5497	0.0068	6.7969
0.0147	0.4033	0.0084	2.5447	0.0165	6.7033
0.0244	0.3753	0.0124	2.5383	0.0408	6.2356
0.0304	0.3822	0.0190	2.5255	0.0512	5.9861
0.0360	0.3859	0.0245	2.5128	0.0577	5.8187
0.0406	0.3845	0.0340	2.4877	0.0649	5.6255
0.0483	0.3820	0.0422	2.4610	0.0746	5.3518
0.0602	0.3803	0.0473	2.4431	0.0821	5.1279
0.0689	0.3787	0.0609	2.3941	0.0861	5.0039
0.0794	0.3768	0.0722	2.3504	0.0908	4.8554
0.0894	0.3749	0.0811	2.3137	0.1031	4.4459
0.0998	0.3728	0.0969	2.2444	0.1153	4.0225
0.1126	0.3701	0.1058	2.2025	0.1209	3.8198
0.1220	0.3679	0.1104	2.1800	0.1260	3.6342
0.1354	0.3646	0.1178	2.1421	0.1350	3.3044
0.1453	0.3619	0.1356	2.0445	0.1625	2.3055
0.1573	0.3584	0.1459	1.9832	0.1804	1.7130
0.1686	0.3548	0.1558	1.9209	0.1906	1.4112
0.1798	0.3509	0.1758	1.7835	0.1970	1.2383
0.1911	0.3466	0.1969	1.6218	0.2058	1.0225
0.2006	0.3425	0.2048	1.5566	0.2173	0.7821
0.2052	0.3405	0.2262	1.3690	0.2262	0.6256
0.2170	0.3346	0.2369	1.2708	0.2342	0.5063
0.2229	0.3315	0.2457	1.1871	0.2436	0.3902
0.2344	0.3246	0.2530	1.1172	0.2550	0.2791
0.2495	0.3140	0.2657	0.9932	0.2606	0.2350
0.2672	0.2982	0.2752	0.9012	0.2686	0.1830
0.2784	0.2858	0.2847	0.8111	0.2776	0.1360
0.2888	0.2719	0.2970	0.6973	0.2919	0.0836
0.3000	0.2534	0.3036	0.6384	0.3000	0.0629
		0.3153	0.5404		
		0.3240	0.4724		
		0.3341	0.4002		
		0.3434	0.3398		
		0.3500	0.3009		

*Table A-18. Zinc diffusion in soil samples **A, B** and **Ch** calculated with mathematical model based on Freundlich adsorption isotherm.*

Sample **A**		Sample **B**		Sample **Ch**	
X, cm	C(Zn), mmol kg^{-1}	X, cm	C(Zn), mmol kg^{-1}	X, cm	C(Zn), mmol kg^{-1}
0.0078	1.90588	0.0044	2.6084	0.0068	7.1583
0.0147	1.89387	0.0084	2.5940	0.0165	6.9360
0.0244	1.87674	0.0124	2.5789	0.0408	6.3586
0.0304	1.86587	0.0190	2.5541	0.0512	6.1043
0.0360	1.8556	0.0245	2.5333	0.0577	5.9410
0.0406	1.84707	0.0340	2.4970	0.0649	5.7595
0.0483	1.83244	0.0422	2.4646	0.0746	5.5129
0.0602	1.80931	0.0473	2.4444	0.0821	5.3191
0.0689	1.79183	0.0609	2.3893	0.0861	5.2147
0.0794	1.77007	0.0722	2.3422	0.0908	5.0919
0.0894	1.74852	0.0811	2.3041	0.1031	4.7642
0.0998	1.72536	0.0969	2.2352	0.1153	4.4384
0.1126	1.69567	0.1058	2.1953	0.1209	4.2855
0.1220	1.67287	0.1104	2.1745	0.1260	4.1469
0.1354	1.6387	0.1178	2.1401	0.1350	3.9020
0.1453	1.61209	0.1356	2.0556	0.1625	3.1466
0.1573	1.57788	0.1459	2.0052	0.1804	2.6563
0.1686	1.54374	0.1558	1.9556	0.1906	2.3782
0.1798	1.50758	0.1758	1.8517	0.1970	2.2059
0.1911	1.46861	0.1969	1.7362	0.2058	1.9700
0.2006	1.43293	0.2048	1.6912	0.2173	1.6699
0.2052	1.41499	0.2262	1.5647	0.2262	1.4431
0.2170	1.36498	0.2369	1.4990	0.2342	1.2436
0.2229	1.33818	0.2457	1.4429	0.2436	1.0171
0.2344	1.28031	0.2530	1.3954	0.2550	0.7556
0.2495	1.19072	0.2657	1.3094	0.2606	0.6340
0.2672	1.05052	0.2752	1.2429	0.2686	0.4708
0.2784	0.92232	0.2847	1.1744	0.2776	0.3009
0.2888	0.72214	0.2970	1.0816	0.2919	0.0866
0.3000	0	0.3036	1.0292	0.3000	0.0207
		0.3153	0.9341		
		0.3240	0.8589		
		0.3341	0.7675		
		0.3434	0.6776		
		0.3500	0.6098		

*Table A-19. Cadmium diffusion in soil samples **A**, **B** and **Ch** calculated with mathematical model based on linear adsorption isotherm.*

Sample **A**		Sample **B**		Sample **Ch**	
X, cm	C(Cd), mmol kg^{-1}	X, cm	C(Cd), mmol kg^{-1}	X, cm	C(Cd), mmol kg^{-1}
0.0035	0.55557	0.0016	0.25567	0.0146	0.75669
0.009	0.54534	0.0055	0.25281	0.0315	0.68745
0.0125	0.53873	0.0109	0.24891	0.0363	0.66785
0.0175	0.52923	0.0181	0.24356	0.0404	0.6512
0.0257	0.51384	0.0249	0.23856	0.0438	0.63741
0.0338	0.49862	0.0339	0.23201	0.0489	0.61662
0.0416	0.48399	0.0433	0.2251	0.0555	0.58945
0.0507	0.46701	0.0524	0.21845	0.0625	0.56092
0.0604	0.44864	0.0636	0.21019	0.0696	0.53208
0.073	0.42503	0.0738	0.20273	0.0779	0.49822
0.0847	0.40316	0.0855	0.19411	0.0897	0.44994
0.0951	0.38363	0.0979	0.185	0.1052	0.387
0.1053	0.36436	0.1083	0.17738	0.1184	0.33283
0.1168	0.34284	0.1176	0.17057	0.1279	0.29419
0.13	0.31799	0.1258	0.16454	0.1373	0.25595
0.1413	0.29687	0.1353	0.1576	0.1549	0.18401
0.1523	0.27627	0.1475	0.1486	0.1769	0.09423
0.1655	0.25149	0.1597	0.13967	0.1905	0.03879
0.1792	0.22588	0.1703	0.13191	0.1997	0.00103
0.1899	0.20579	0.1791	0.12544		
0.1998	0.18737	0.1895	0.11778		
0.2101	0.16805	0.2016	0.1089		
0.2214	0.14694	0.2138	0.09992		
0.2337	0.12384	0.2278	0.08964		
		0.2403	0.08048		
		0.2522	0.07174		
		0.2638	0.06326		
		0.2738	0.05595		
		0.2834	0.0489		
		0.294	0.04113		

*Table A-20. Cadmium diffusion in soil samples **A**, **B** and **Ch** calculated with mathematical model based on Langmuir adsorption isotherm.*

Sample **A**		Sample **B**		Sample **Ch**	
X, cm	C(Cd), mmol kg^{-1}	X, cm	C(Cd), mmol kg^{-1}	X, cm	C(Cd), mmol kg^{-1}
0.0035	0.5908	0.0016	0.2143	0.0146	0.7437
0.009	0.5784	0.0055	0.2144	0.0315	0.6780
0.0125	0.5704	0.0109	0.2141	0.0363	0.6594
0.0175	0.5587	0.0181	0.2133	0.0404	0.6436
0.0257	0.5397	0.0249	0.2121	0.0438	0.6305
0.0338	0.5210	0.0339	0.2099	0.0489	0.6108
0.0416	0.5029	0.0433	0.2075	0.0555	0.5850
0.0507	0.4819	0.0524	0.2051	0.0625	0.5579
0.0604	0.4591	0.0636	0.2021	0.0696	0.5305
0.073	0.4299	0.0738	0.1992	0.0779	0.4983
0.0847	0.4027	0.0855	0.1957	0.0897	0.4525
0.0951	0.3785	0.0979	0.1918	0.1052	0.3927
0.1053	0.3546	0.1083	0.1884	0.1184	0.3413
0.1168	0.3279	0.1176	0.1852	0.1279	0.3046
0.13	0.2970	0.1258	0.1823	0.1373	0.2683
0.1413	0.2708	0.1353	0.1788	0.1549	0.2001
0.1523	0.2453	0.1475	0.1740	0.1769	0.1150
0.1655	0.2146	0.1597	0.1690	0.1905	0.0637
0.1792	0.1829	0.1703	0.1643	0.1997	0.0024
0.1899	0.1580	0.1791	0.1603		
0.1998	0.1353	0.1895	0.1552		
0.2101	0.1114	0.2016	0.1490		
0.2214	0.0853	0.2138	0.1423		
0.2337	0.0568	0.2278	0.1340		
		0.2403	0.1260		
		0.2522	0.1177		
		0.2638	0.1091		
		0.2738	0.1011		
		0.2834	0.0929		
		0.2940	0.0831		

*Table A-21. Cadmium diffusion in soil samples **A**, **B** and **Ch** calculated with mathematical model based on Freundlich adsorption isotherm.*

Sample **A**		Sample **B**		Sample **Ch**	
X, cm	C(Cd), mmol kg^{-1}	X, cm	C(Cd), mmol kg^{-1}	X, cm	C(Cd), mmol kg^{-1}
0.0035	0.6070	0.0016	0.2179	0.0146	0.5657
0.009	0.5925	0.0055	0.2169	0.0315	0.5159
0.0125	0.5831	0.0109	0.2154	0.0363	0.5018
0.0175	0.5697	0.0181	0.2134	0.0404	0.4898
0.0257	0.5480	0.0249	0.2115	0.0438	0.4799
0.0338	0.5267	0.0339	0.2090	0.0489	0.4649
0.0416	0.5062	0.0433	0.2063	0.0555	0.4454
0.0507	0.4827	0.0524	0.2036	0.0625	0.4248
0.0604	0.4573	0.0636	0.2003	0.0696	0.4041
0.073	0.4249	0.0738	0.1972	0.0779	0.3797
0.0847	0.3952	0.0855	0.1935	0.0897	0.3449
0.0951	0.3689	0.0979	0.1896	0.1052	0.2996
0.1053	0.3431	0.1083	0.1861	0.1184	0.2605
0.1168	0.3145	0.1176	0.1830	0.1279	0.2327
0.13	0.2820	0.1258	0.1802	0.1373	0.2051
0.1413	0.2546	0.1353	0.1769	0.1549	0.1531
0.1523	0.2282	0.1475	0.1725	0.1769	0.0882
0.1655	0.1969	0.1597	0.1679	0.1905	0.0489
0.1792	0.1652	0.1703	0.1638	0.1997	0.0019
0.1899	0.1408	0.1791	0.1603		
0.1998	0.1188	0.1895	0.1560		
0.2101	0.0962	0.2016	0.1508		
0.2214	0.0723	0.2138	0.1453		
0.2337	0.0471	0.2278	0.1386		
		0.2403	0.1323		
		0.2522	0.1258		
		0.2638	0.1191		
		0.2738	0.1129		
		0.2834	0.1064		
		0.2940	0.0986		