Measuring techniques for contaminant hydrology

Lubomir LICHNER – Andrea CIPAKOVA – Miloslav SIR
Institute of Hydrology, Slovak Academy of Sciences, Bratislava, Slovakia
State Institute of Public Health, Kosice, Slovakia
Institute of Hydrodynamics, Czech Academy of Sciences, Prague, Czech Republic

ABSTRACT

Three original measuring techniques are presented in this paper. Radioactive tracer techniques can be used for in-situ measurements of the solute (contaminant) velocity, longitudinal dispersion coefficient and bypassing ratio, as well as for laboratory measurements of the solute (contaminant) sorption, distribution coefficient and partitioning among individual fractions of studied soil. Retardation factor of a contaminant can be estimated from the breakthrough curves measured in a laboratory on the undisturbed soil column with the System of European Water Monitoring (SEWING) developed in the 5th EC Framework Programme Project IST-2000-28084.

INTRODUCTION

The water issue is set to become one of the major questions of the 21st century. The world's water problems arise not so much from a shortage of freshwater as from its uneven distribution, from ever-increasing demand and from practices detrimental to water quality (Falkenmark et al., 1999). The aim of this contribution is to present three original measuring techniques that can serve to measure the quantities connected with a contaminant transport in water.

MATERIAL AND METHODS

The Danubian Lowland is a large (1260 km^2) agriculturally utilized area, with shallow (0.5–3 m) underlying aquifer containing about 10 km^3 of freshwater. Three soils from this region were used in this study. The light soil was sampled in Kalinkovo (loamy-sand soil, Calcaric Fluvisol (WRB, 1998)), the medium heavy soil in Macov (loamy soil, Calcari-Haplic Chernozem (WRB, 1998)), and the heavy soil in Jurova (clay soil, Calcari-Mollic Fluvisol (WRB, 1998)). Basic characteristics of the soils used in this study are presented in Table 1 (Fulajtar et al., 1998). Quality of humus is assessed by the ratio of humic acids to fulvic acids content (HA/FA).

Radioactive tracer technique can be used to measure freshwater contaminant relative concentration vs. depth distributions in a soil. Radioactive iodide $^{131}I^-$ was used as the tracer of non-reactive fertilizer transport, and radioactive cadmium $^{115}Cd^{2+}$ as the tracer of cadmium transport in studied soil. The probe (Fig. 1) consists of a duralumin tube (3) in which a Geiger-Mueller (G-M) detector and analog interface unit (1), connected to the nuclear analyser (2) with coaxial cable, can be placed in any desired position. The tubes (10-mm O.D., 8-mm I.D., and 1500-mm length) are inserted vertically from the soil surface into the holes made by a 10-mm-diam. steel rod into the soil below the 1-m^2 square infiltrometer (4). Conical soil sealing (5) made for each vertical probe prevents water from bypassing past the probe, as it was proved by a dye test with Methylene Blue. Owing to its small size (21-mm length and 6.3-mm O.D.) the G-M detector can be considered as a point detector. Bypassing ratio (partition of water and solutes between the macropore domain and the matrix domain) and an impact of land-use change on nutrient fluxes in a structured soil (Lichner, 1997; Lichner et al., 1999).

The conventional (Cipakova and Mitro, 1997) and modified batch technique (Lichner and Cipakova, 2002) serve to measure the sorption of contaminant on soil particles and to estimate the distribution coefficient K_d. In this contribution, the results of Cd sorption and its relation to the duration of Cd-soil interaction is presented. The radioactive cadmium ^{109}Cd was used as a tracer of cadmium behaviour in soil for its easier and faster detection. Each sorption experiment involved 10 g of soil, passed through a 2-mm sieve before use, 40 ml of distilled water, and cadmium ^{109}Cd (in the form of $CdCl_2$) with concentration of 50.9 $mg.l^{-1}$ and specific activity a_0.

Table 1: Particle size distribution, mineral composition of the clay fraction and selected chemical properties of the soils used in this study (Fulajtar et al., 1998).

Soil studied	Kalinkovo	Macov	Jurova
≥ 0.25 mm (%)	6.04	0.86	1.54
0.25–0.05 mm (%)	55.77	36.14	11.35
0.05–0.01 mm (%)	22.48	28.84	27.84
0.01–0.001 mm (%)	10.22	19.94	37.32
≤ 0.001 mm (%)	5.49	14.22	21.92
≤ 0.01 mm (%)	15.71	34.16	59.27
Illite (%)	60–80	60–80	50–70
Chlorite (%)	10–20	10–20	10–20
Smectites (%)	5–10	10–20	10–20
Calcite (%)	2–5	2–5	2–5
Dolomite (%)	1–3	1–3	1–2
Quartz (%)	2–5	1–3	1–3
pH (H_2O)	7.8	8.0	8.6
pH (KCl)	7.4	7.7	7.4
$CaCO_3$ (%)	27	26	16
C_{ox} (%)	0.78	1.38	2.20
Humus (%)	1.35	2.38	3.79
HA/FA	0.62	1.58	1.77

In the conventional batch technique, the soil, water and cadmium were placed into a 100-ml polyethylene bottle and shaken for 5 s. Then 5-ml sample of eluate was taken in 1 min after shaking, centrifuged, and the specific activity a of the ^{109}Cd in aqueous phase was measured with a multichannel gamaspectrometer with Ge/Li detector. The measurements took for 10–60 minutes depending on the measured specific activity. The Cd sorption S on all the soil particles, and the distribution coefficient K_d were calculated from the equations:

$$S = (a_0 - a)/\, a_0 \qquad /1/$$

$$K_d = (V/m)\,(a_0 - a)/\, a \qquad /2/$$

The same procedure was chosen for the 2-, 3-, 5-, 10-, 30-, and 60-min duration of Cd-soil interaction.

In the modified batch technique, the soil, water and cadmium were placed into a 100-ml polyethylene bottle and shaken for 5 s. Then, 5-ml sample of solution (where ^{109}Cd in aqueous phase and that adsorbed on the soil particles <10^{-5} m occur) was taken in 1 min after shaking, and the specific activity a' was measured for 90 seconds with a multichannel gamaspectrometer with Ge/Li detector. Cadmium sorption S' on the clay particles <10^{-5} m, which did not settle on the bottom of a polyethylene bottle in one minute after shaking, and the modified distribution coefficient K_d' were calculated as follows:

$$S' = (a' - a)/\, a_0 \qquad /3/$$

$$K_d' = (V/m)\,(a_0 - a')/\, a' \qquad /4/$$

Similar procedure was chosen for the 2-, 3-, 5-, 10-, 30-, and 60-min duration of Cd-soil interaction with one change that 1 min before taking the sample of eluate the mixture was shaken for 5 s. Time t = 1 min, in which all the particles >10^{-5} m settle on the bottom of a bottle, was calculated according to the Stokes law:

$$v = l/t = 2\, g\, r^2\, (\rho_s - \rho_w)/9\, \eta \qquad /5/$$

where: v – velocity of the soil particle in water, l – path, t – time, g – acceleration of gravity, r – radius of the soil particle, ρ_s – density of the soil-water mixture, ρ_w – density of water, η – dynamic viscosity of water.

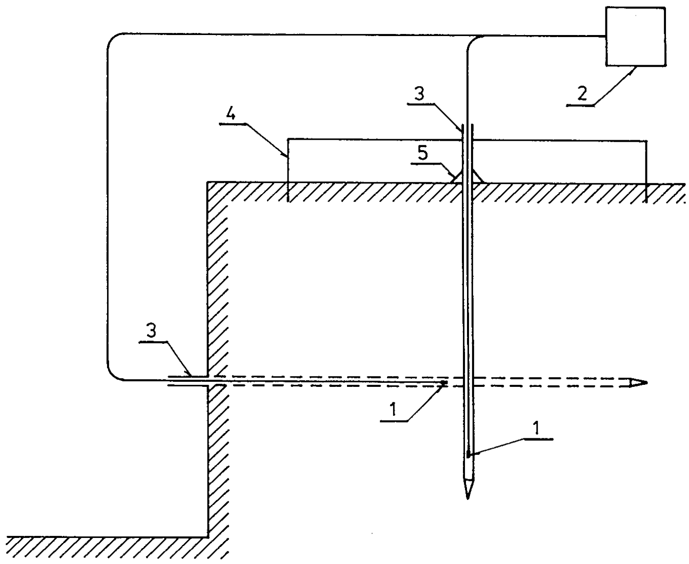

Fig. 1: Schematic arrangement for radioactive tracer technique.

Retardation factor R equals to the ratio of time which a reactive and non-reactive solute needs to travel a given distance in the soil. It is related to the distribution coefficient K_d by

$$R = 1 + \rho\, K_d / \Theta \qquad /6/$$

where ρ is soil dry bulk density and Θ is volumetric water content.

Retardation factor R can be estimated from the breakthrough curves of the studied reactive and non-reactive solute. The breakthrough curves could be measured in a laboratory on the undisturbed soil column with the System of European Water Monitoring (SEWING) developed in the 5th EC Framework Programme Project IST-2000-28084 (Filipkowski, 2001). Sensors of this system, based on the ion sensitive field effect transistor (ISFET) or chemically-modified field effect transistor (CHEMFET), are able to measure simultaneously concentrations of 5 selected inorganic ions in the column outflow water.

RESULTS AND DISCUSSION

In our previous study on the cadmium transport (Lichner, 1998), a deep Cd penetration up to 60 cm was measured in a loam soil under meadow using the radioactive tracer technique (Fig. 1). Using the equilibrium distribution coefficient K_d^{eq} and convective-dispersion equation it was predicted that all the Cd would remain in the 10-cm thick top layer. In spite of that prediction it was found that more than 40 % of Cd penetrated deeper than predicted.

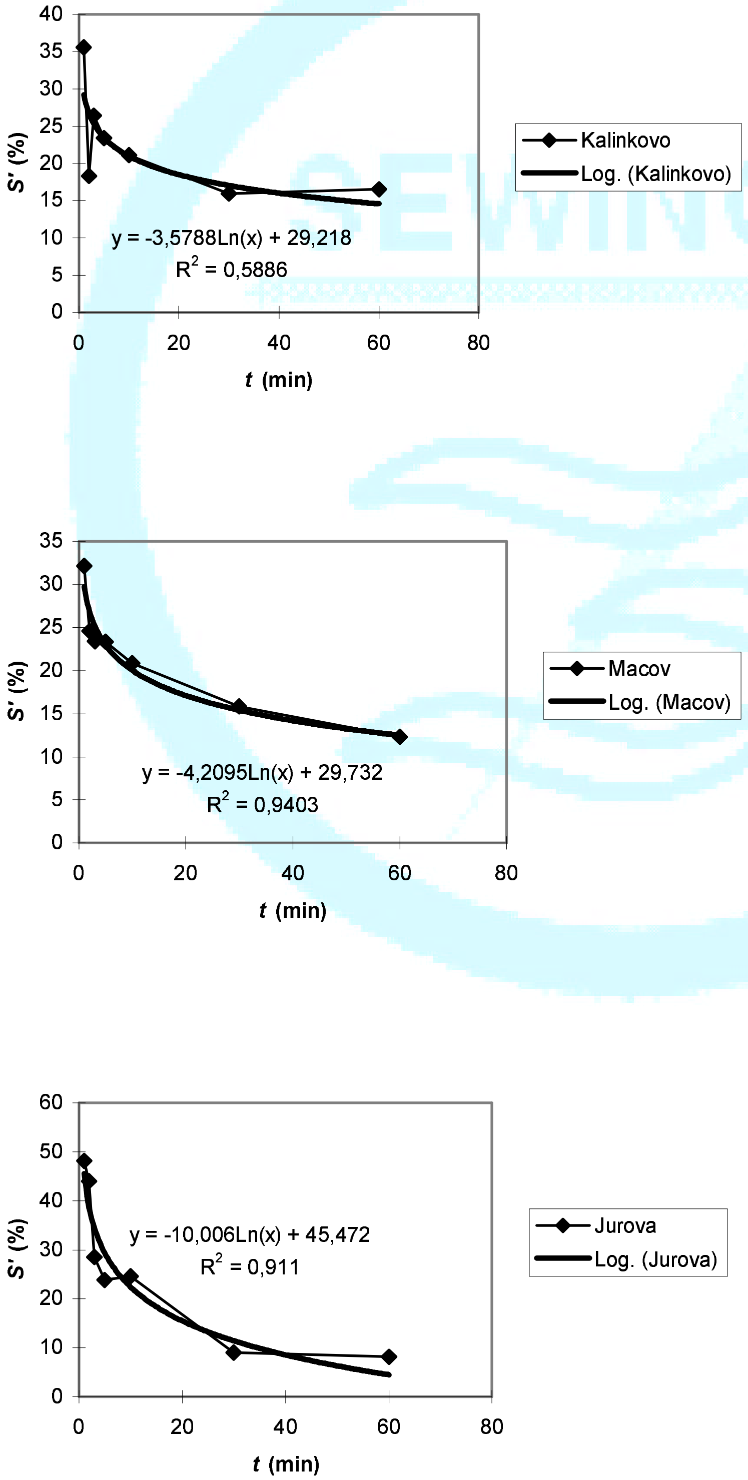

Fig. 2: Sorption *S'* of cadmium on the soil particles $<10^{-5}$ m, which did not settle on the bottom of a bottle in one minute after shaking, vs. duration *t* of the Cd-soil contact.

This discrepancy could be explained by the particle-facilitated Cd transport (transport of Cd sorbed on clay particles) via soil macropores (Jacobsen et al., 1997) which was studied on three various soils. It was found for the Cd-soil contact lasting 1 min that more than 35 %, 32% and 48% of Cd was adsorbed on the particles $<10^{-5}$ m of the soil from Kalinkovo, Macov, and Jurova, respectively. It should be mentioned that the percentage of Cd adsorbed on the particles <10^{-5} m decreased with an increase in contact time (Fig. 2). Surprisingly, after the 30-min and 60-min lasting Cd-soil interaction, 9.0 and 8.2 % of cadmium only was adsorbed on the particles <10^{-5} m forming >59 % of all the particles in the soil from Jurova.

Afterwards, the distribution coefficient K_d for 60-min lasting Cd-soil contact was set to be equal to the matrix distribution coefficient K_{dm}, and the distribution coefficient K_d' for 1-min lasting Cd-soil contact was set to be equal to the macropore distribution coefficient K_{dM}. It was found that using the coefficient K_{dm} instead of K_{dM} would underestimate a penetration of the part of Cd transported in the macropores about 255-times in the loamy-sand soil in Kalinkovo, 20-times in the loam soil in Macov, and 122-times in the clay soil in Jurova. Fasko (Lichner et al., 1999) gave evidence from 10-year-lasting observations that macropore flow can appear 24-times in the average in the south-western Slovakia during vegetation season. This flow can be the cause of rapid Cd transport from the soil surface to the depth well below the root zone.

CONCLUSION

Ease and speed of measurements are the most significant advantages of the radioactive tracer techniques presented. When used in a field soil, the radioactive tracer technique is non-destructive, able to locate heterogeneities in a field soil, and does not influence solute transport. The duration of the measurement of each point in a breakthrough curve or in tracer concentration distribution was only one minute. Installation or removal required about 10 minutes per probe. The time reduction is profitable in the studies of spatial variability of transport properties in the field soils where an extensive set of values is required for statistical processing. The dose of radioactive tracer necessary for one measurement is very small and in the case of $^{131}I^-$ it is one sixth of the dose used in thyroid gland therapy (Lichner, 1995).

The SEWING system is intended for solute concentration measurement (in the first variant NO_3, NH_4, Ca, Na, and H) in industrial and municipal waste water, irrigation water, fresh water, groundwater, and surface water (e.g., in the studies on a fertilizer washout from hill fields into the rivers or brooks), for solute breakthrough curve measurement in a soil-physical laboratory, for an early warning in the rivers near a factory or other contaminant producer, etc.

ACKNOWLEDGEMENT

The financial support from the Slovak Scientific Grant Agency Project 2/7065/20 and 5th EC Framework Programme Project IST-2000-28084 is gratefully acknowledged.

REFERENCES

Cipakova, A., Mitro, A. (1997): Influence of agrochemical characteristics on ^{85}Sr and ^{137}Cs sorption in soil samples from the localities around nuclear power plants in Slovak Republic. J. Radioecology, **5**(2), 3–8.

Falkenmark, M., Andersson, L., Castensson, R., Sundblad, K. (1999): Water – a reflection of land use. Swedish Natural Science Research Council, Stockholm, 128 p.

Filipkowski, A. (2001): System for European Water Monitoring (SEWING). IST-2000-28084. Project Presentation. Brussels, 4 p.

Fulajtar, E., Barancikova, G., Curlik, J., Sedlakova, B., Surina, B. (1998): An impact of the water work Gabcikovo on agricultural soils (in Slovak). VUPU, Bratislava, 204 p.

Jacobsen, O. H., Moldrup, P., Larsen, C., Konnerup, L., Petersen, L. W. (1997): Particle transport in macropores of undisturbed soil columns. J. Hydrol., **196**, 185–203.

Lichner, L. (1995): A nuclear tracer technique for investigation of solute transport in the unsaturated zone of soil. In: Leibundgut, Ch. (ed): Proc. Int. Symp. Tracer technologies for hydrological systems, Boulder 1995. IAHS Publication No. 229, Wallingford, p. 109–116.

Lichner, L. (1997): In-situ measurement of bypassing ratio in macroporous soil. J. Hydrol. Hydromech., **45**(5), 365–376.

Lichner, L. (1998): Cadmium transport in a loamy soil as influenced by macropore flow (in Slovak). J. Hydrol. Hydromech., **46**(3), 207–217.

Lichner, L., Cipakova, A. (2002): Cadmium distribution coefficients and Cd transport in structured soils. Rostlinna Vyroba (Plant Production), **48**(3), 96–100.

Lichner, L., Meszaros, I., Germann, P., Alaoui, A. M., Sir, M., Fasko, P. (1999): Impact of land-use change on nutrient fluxes in structured soils. In: Heathwaite, L. (ed): Proc. Int. Symp. Impact of land-use change on nutrient loads from diffuse sources, Birmingham 1999. IAHS Publication No. 257, Wallingford, p. 171–177.

WRB (1998): World reference base for soil resources. World Soil Resources Reports, No. 84. FAO, Rome, 88 p.