Fate and Plant Uptake of Heavy Metals in Soil-Plant Systems Studied on Soil Monoliths

T. NÉMETH, E. MOLNÁR, J. CSILLAG, K. BUJTÁS, A. LUKÁCS
and G. PÁRTAY

Research Institute for Soil Science and Agricultural Chemistry of the
Hungarian Academy of Sciences, Budapest

Increasing amounts of agricultural, industrial and municipal wastes and waste waters containing a variety of toxic elements are being generated, both in industrialized and developing countries.

In the countries of Eastern Europe, which have no or limited industrial infrastructure for recycling wastes, one of the most economic and efficient means of waste disposal is to use it in agriculture, thereby also utilizing the nutrient content of the wastes. While this type of waste disposal is common practice (Hungarian Standard, 1990), the possibility increases that toxic materials from incorrectly treated or managed wastes will get into the food chain, and pose serious environmental hazards for the population.

The health of terrestrial ecosystems is determined first and foremost by what happens at the soil-plant interface, so more information is needed about the most important transport processes and associated soil and plant properties that affect the behaviour and transport of toxic elements in the soil, their uptake by agricultural crops, and their potential movement through the vadose zone to the underlying groundwater systems.

The aim of the present research is to monitor and model the fate, transport and plant uptake of selected toxic elements applied in sewage sludge to undisturbed cropped soil monoliths.

Specific objectives are

1. To characterize the plant availability of selected toxic elements by quantifying their release into the soil solution from element loadings, and to follow their redistribution in the soil under different soil moisture conditions.
2. To quantify the transport and redistribution of these elements in plants.
3. To identify stress situations in plants as indicated by changes in the composition and/or quantity of different gases generated in plant tissues, and in the solid and liquid phases of the soil, resulting from toxic trace element loadings.
4. To develop a model to predict the transport of the elements in the soil, and their uptake by plants.

In the present paper information is provided about the scientific and technical background of the basic methods to be used in the research; and the results are presented of preliminary experiments concerning the adsorption-release processes of Zn, Pb, Cr and Cd into the liquid phases of two soils having different properties.

Materials and Methods

Soil monolith preparation

Several methods have been used to prepare lysimeters and soil columns without disturbing the structure of the soil. Some of these methods can be used only in situ because of the dimensions of the soil columns involved (ARMIJO et al., 1972), other methods are applicable only to small size columns (MOCHOGE, 1984).

The authors have adapted the method of HOMEYER et al. (1973) for the preparation of undisturbed soil monoliths (40 cm diameter, 150 cm length), and modified this method for application to a large number of soils having different textures (NÉMETH et al., 1991).

The soil around the monolith is excavated, and the monolith remaining in the pit is coated with several layers of glass fibre cloth impregnated with an artificial resin consisting of 3 components. After this coating becomes totally solid, the column can be lifted and transported to any desired place (laboratory, greenhouse, field lysimeter station, etc.), and used for a wide spectrum of studies (NÉMETH et al., 1990; NÉMETH et al., 1991).

The artificial resin coating makes extremely close contact with the soil surface (imbibes the micropores) so there are no "wall effects" in the experiments. The excellent insulating properties of the coating eliminate leaking. Sensors of different instruments can be built into any part of the column through properly sealed holes in the coating (NÉMETH et al., 1991).

Undisturbed soil monoliths prepared according to this method from two soils will be used in experiments carried out in the framework of this research programme.

QMS studies

The working hypothesis for the research is that the composition of the gases originating from air-filled pores and from the liquid phases of the soil, as well as the inner gas composition of plants, which depends on several interacting metabolic processes, respond quickly to stress situations caused by toxic amounts of heavy metals in the root zone.

A method has been developed using mass spectrometry for the qualitative and quantitative measurement of the inner gas composition of plants as well as that in the soil adjacent to the roots (Hung. Patent No. 183.810).

The majority of methods for the measurement of gas exchange processes and gas composition changes in plants due to their metabolism require that the plants should be isolated from their natural environment. The present method makes it possible to measure the gaseous components inside the plants without isolating the plant in a closed chamber and, at the same time, it does not cause serious disturbances in the metabolic processes. Continuous in vivo sampling is achieved with special microprobes made of a perforated, stainless steel capillary (diameter about 1.2 mm) covered with a membrane permeable to all gases occurring in plants or soils. This capillary is connected through a flexible stainless steel tube to a quadrupole mass spectrometer (QMS). The sampling capillary can be inserted hermetically into the stem of plants or implanted into the soil surrounding the roots (Fig. 1). The gases in the tissues, liquids and hollow parts of plants, and in the air-filled pores and liquid phase of the soil diffuse across the membrane of the capillary directly into the mass spectrometer, which simultaneously and quickly measures the concentrations of any gases of up to 300 mass units (LANGER et al., 1984a,b).

To test the capabilities of this method, gas concentration changes in several plant species were followed under physical and chemical stress effects, such as

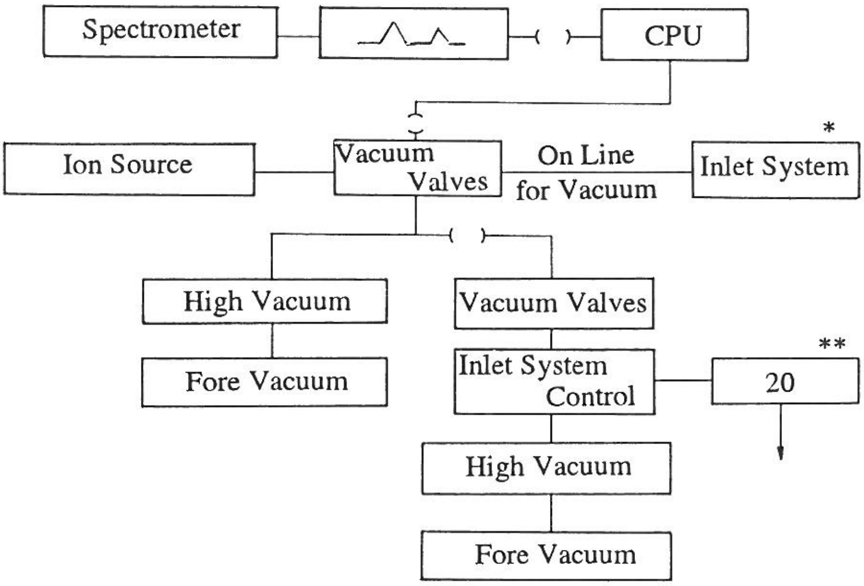

Fig. 1

Block diagram of QMS measuring system. * Single channel inlet system; ** 20 channel inlet system extremely dry or wet soil, temperature changes, salt effects, pesticide application, etc. (BUZÁS et al., 1987; PÁRTAY et al., 1987). In all these instances, rapid changes were observed in the gas composition before the appearance of any visible symptoms. Measurements have been also carried out on the composition of the gas phase in undisturbed soil columns (PÁRTAY et al., 1992).

The measurement of the gas composition in experimental plants and in their root zones will be carried out simultaneously with 20 microprobes on undisturbed soil monolith contaminated with sewage sludge containing heavy metals.

Heavy metal adsorption release measurements on two soils

Model experiments have already been carried out to quantify the heavy metal adsorbing capacity of soils in the case of different loadings of Zn, Pb, Cr and Cd. Aqueous solutions of the nitrate salts of these elements were mixed with air-dried samples of the upper horizons of an acidic brown forest soil (Ragály) and of a calcareous chernozem (Pusztaszabolcs) (Table 1). The metals

Table 1

Some main properties of the two test soils

Soil	pH (H_2O)	$CaCO_3$ %	Organic C, %	SP %	< 0.02 mm, %	CEC, me/100g soil
Ragály	4.3	0	1.6	55	40.8	20.7
Puszta-szabolcs	7.8	6.6	2.8	50	35.8	28.3

SP = saturation percentage; CEC = cation exchange capacity.

Table 2

The maximum permissible amount of heavy metals in waste waters and sewage sludges for use on agricultural lands (Hungarian Standard MI-08-1735-1990)

Element	mg/kg dry material	mg/kg soil*
Zn	3000	25.00
Pb	1000	8.33
Cr	1000	8.33
Cd	15	0.125

* Calculated for 20 cm soil layer; 500 t sewage sludge/ha; (sewage sludge contains 5% dry material)

were used in amounts equivalent to 1, 10 and 100 times the upper limits allowed by the Hungarian Standard for the deposition of sewage sludges (Table 2, Hung. Standard, 1990).

Soil solutions obtained by the centrifugation method, using a rotor speed corresponding to 1500 kPa pressure, i.e. the wilting point of plants (Fig. 2) (CSILLAG et al., 1991), saturation extract, and aqueous extracts with different soil:model solution ratios were prepared in order to study the effect of soil moisture content on the heavy metal concentration in the liquid phase of the soil. The adsorption of the elements in the soil was calculated from the soil solution (c) and the added model solution concentration (c_m) using the equation:

$$adsorption(\%) = (c_m - c_\theta) \times \frac{100}{c_m}$$

The Zn, Pb, Cr and Cd concentrations in the solutions were determined with a Jarrel Ash ICP spectrometer.

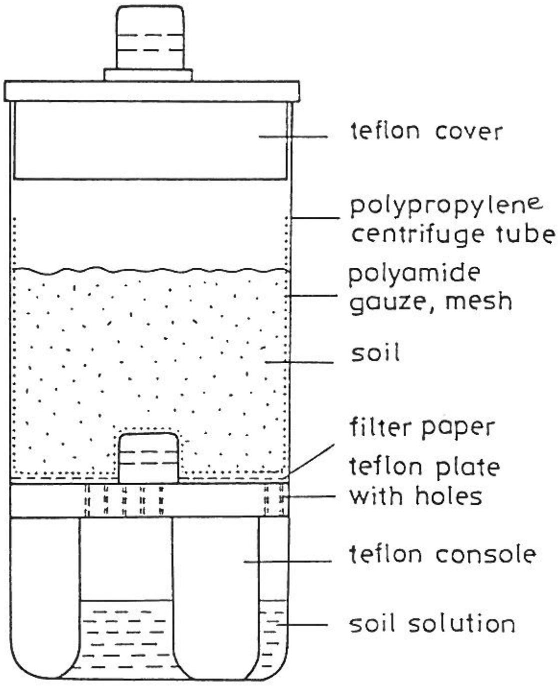

Fig. 2
Centrifuge tube for obtaining soil solution

Table 3

Heavy metal concentrations in the soil solution after treating the forest soil (from Ragály) with solutions containing the allowed quantity of toxic elements

Heavy metals	Zn			Pb			Cr			Cd		
$\theta_{w.\%}$	37.5	28.2	19.5	37.5	28.2	19.5	37.5	28.2	19.5	37.5	28.2	19.5
kPa	0.13	10.0	251	0.13	10.0	251	0.13	10.0	2541	0.13	10.0	251
A	19.3	18.1	19.9	9.3	9.8	9.8	11.5	11.7	11.9	0.16	0.09	0.12
B	51.4	64.0	101.9	24.8	34.7	50.0	30.6	41.4	61.1	0.44	0.34	0.61
C	1.7	1.3	1.6	0	0.12	0.05	0.04	0.04	0.04	0.01	0.01	0.02

$\theta_{w.\%}$: soil moisture content (expressed as weight percentage); kPa: soil moisture potential; A: actual load of the soil with heavy metals calculated on the basis of the max. permissible level in the Hungarian Standard (1990), mg/kg soil; B: concentrations in the model solutions, mg/L; C: concentrations in the soil solution after treating the soil with the model solutions, mg/L

Results and Discussion

The Pb, Cr and Cd concentrations in the liquid phase of the original, uncontaminated soil samples were below the detection limit, while the Zn concentration was negligible.

From the maximum waste loading permissible on one occasion (1-time loading), 97-100% of the heavy metals were adsorbed by both soils in the field moisture range (Table 3). The negligible amount entering the liquid phase of the soil may not pose an immediate environmental hazard.

In the forest soil, at the 10-times loading, even at lower soil moisture contents, the only concentration which was not negligible in the liquid phase of the soil was that of Zn (Fig. 3). This high adsorption can probably be attributed to the fairly high clay content (14.7%) of this soil.

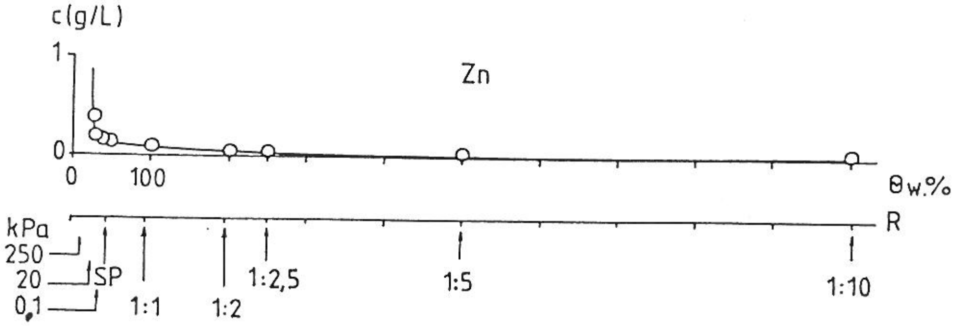

Fig. 3
The dependence of Zn concentration in the liquid phase of an acidic brown forest soil (Ragály) on soil moisture content ($\theta_{W.\%}$). (Loading: 10 times the allowed upper limit; R: soil:water ratio; SP: saturation percentage; kPa: moisture potential)

For the 100-times loading the concentrations (c) were found to increase rapidly with decreasing soil moisture content (θ) (Fig. 4) in the field soil moisture content range. The c-θ relationships were approximated by hyperbolic equations. The parameters of the linearized equations are given in Table 4. The slopes of the lines (b) characterize the change in element concentrations in the soil solution with changing soil moisture content. The goodness of fit of the regressions increases significantly, with the exception of Cr, if a quadratic member is included.

When adsorption was studied as a function of loading it was found that smaller amounts of Zn and Cd are adsorbed in the soil as compared to Pb and Cr (Fig. 5). This is in accordance with literary data (KABATA-PENDIAS & PENDIAS, 1992). The relative adsorbing capacity increased at all loadings with de-

Table 4

The parameters of the hyperbolic relationships 1: $c = a + b\left\{1/\left(\theta_w - \theta'_w\right)\right\}$ and 2. $c = a + b\left\{1/\left(\theta - \theta'_w\right)\right\} + d\left\{1/\left(\theta - \theta'_w\right)\right\}^2$ obtained from the data of centrifuged soil solutions (in the potential range of 250-0.1 kPa), as well as of saturation extracts and of aqueous soil extracts (having soil to model solution ratios of 1:1; 1:2; 1:2.5; 1:5 and 1:10) (Ragály, acidic brown forest soil)

Statistical Index	Elements							
	Zn		Pb		Cr		Cd	
	1.	2.	1.	2.	1.	2.	1.	2.
a	$1.2.10^3$	282	89	48	104	106	5.0	0.7
b	$7.9.10^4$	$1.7.10^5$	$4.1.10^3$	$8.0.10^3$	$2.9.10^3$	$2.7.10^3$	400	805
d	0	$-6.2.10^5$	0	$-2.7.10^4$	0	$1.1.10^3$	0	$-2.8.10^3$
r^2	0.909	0.997	0.920	0.980	0.804	0.801	0.922	0.995

Loading: 100 times the allowed upper limit; c: ion concentration, mg/L; θ_W: soil moisture content expressed as weight percentage; θ'_W: soil moisture content at 1500 kPa potential.

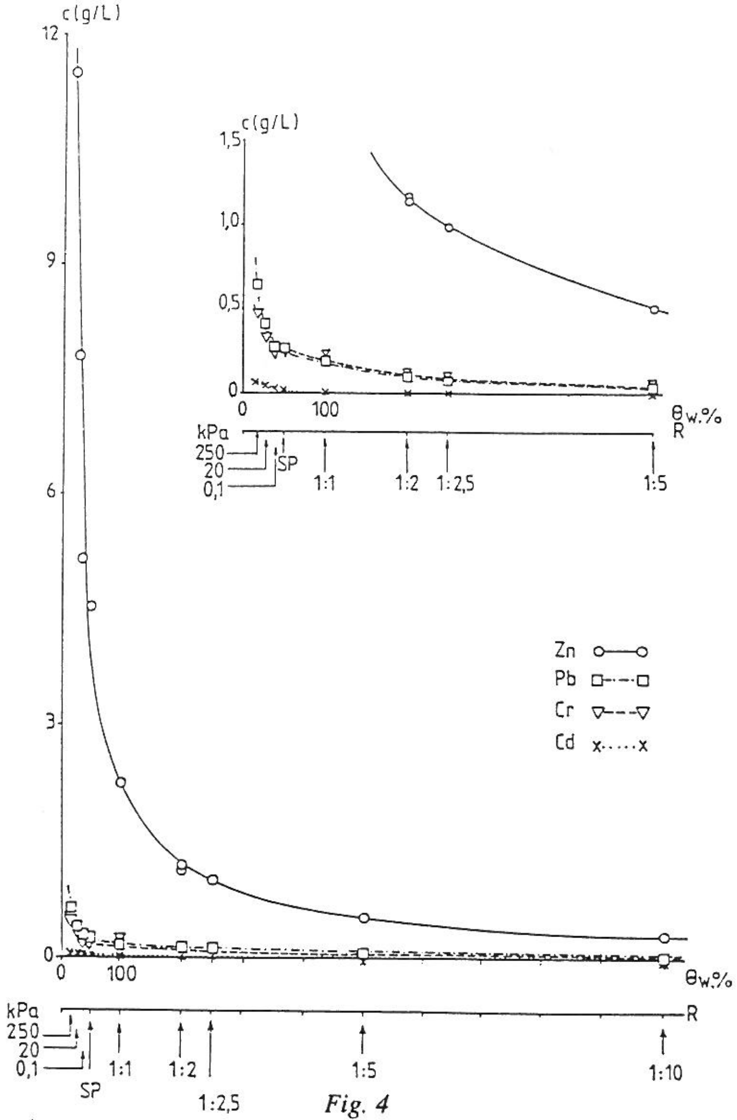

Fig. 4

The dependence of heavy metal ion concentrations in the liquid phase of an acidic brown forest soil (Ragály) on soil moisture content ($\theta_{w.\%}$). (Loading: 100 times the allowed upper limit, R: soil:water ratio; SP: saturation percentage; kPa: moisture potential)

creasing soil moisture content, in the case of all studied elements with the exception of Cr. The parallel increase in adsorption and element concentrations in the liquid phase with decreasing soil moisture content (θ) might be explained by the fact that it was necessary to use model solutions with increasing metal

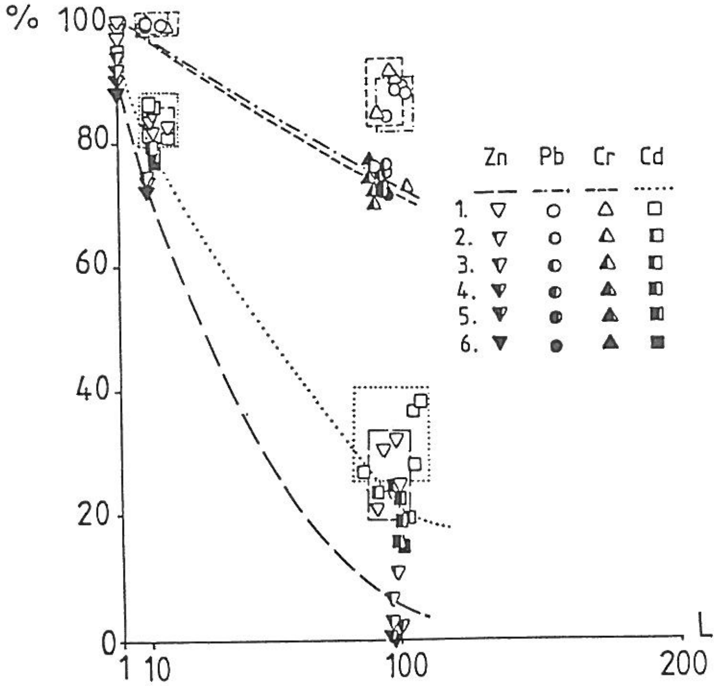

Fig. 5

Adsorption of heavy metals in an acidic brown forest soil (Ragály) as a percentage of the concentrations of model solutions, as a function of loading (L) and soil moisture content (θ: weight percentage). 1: Soil solutions obtained from soils at θ=17, 27, 38% (adsorption time 1 week); saturation extract, θ=49%) (adsorption time 24 h); 2-6: soil extracts with 1:1, 1:2, 1:2.5, 1:5, 1:10 soil:solution ratios (adsorption time 1 h)

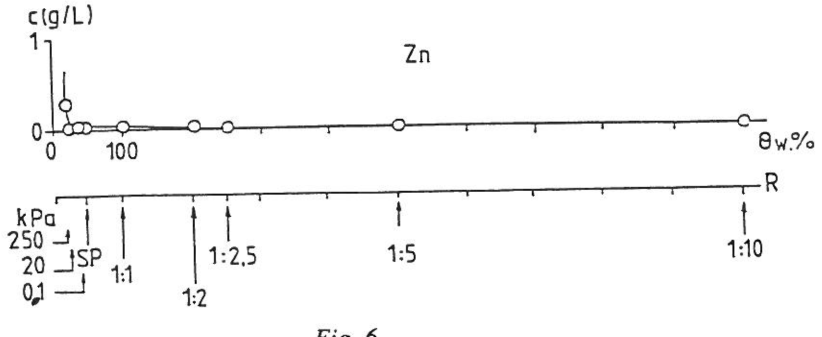

Fig. 6

The dependence of Zn concentration in the liquid phase of a calcareous chernozem soil (Pusztaszabolcs) on soil moisture content ($\theta_{W.\%}$). (Loading: 100 times the allowed upper limit; R: soil:water ratio; SP: saturation percentage; kPa: moisture potential) concentrations at the decreasing soil moisture contents in order to apply constant metal loads at all θ values.

The calcareous chernozem soil adsorbed practically all the toxic metals, even at the 100-times loading. Only Zn was detectable in the soil solutions, but only at lower moisture contents (Fig. 6).

Conclusions

The amount of Zn, Pb, Cr and Cd entering the liquid phase of the two soils was negligible after the application of a one-time maximum loading. However, an abrupt overload may raise the concentration of these metals in the soil solution, and in consequence increase their availability to plants and their leaching into the groundwater.

The moisture content of the soils affects the amount of metals entering the soil solution. Although at constant loading an increased adsorption of these metals occurred with decreasing soil moisture content, this was not enough to decrease their concentration in the liquid phase of the soils.

Summary

The present paper provides information about a research programme aimed at monitoring and modelling the fate, transport, and plant uptake of selected toxic elements, applied in sewage sludge to undisturbed cropped soil monoliths.

The scientific and technical background of the basic methods to be used in the research, and the results of preliminary experiments on the adsorption-release processes of Zn, Pb, Cr and Cd into the liquid phases of two soils with different properties are presented.

Model experiments have already been carried out to quantify the heavy metal adsorbing capacity of soils in the case of different loadings of Zn, Pb, Cr and Cd in air-dried samples of the upper horizons of an acidic brown forest soil (Ragály) and of a calcareous chernozem (Pusztaszabolcs). Metals were used in amounts of 1, 10 and 100 times the allowed upper limits determined by the Hungarian Standard for the deposition of sewage sludges.

The amount of Zn, Pb, Cr and Cd entering the liquid phase of the two soils was negligible upon application of a one-time maximum loading. The moisture content of the soils affects the amount of metals entering the soil solution.

References

ARMIJO, J. D. et al., 1972. A large undisturbed weighing lysimeter for grassland studies. Trans. Am. Soc. Ag. & Eng. **15.** 837-840.

BUZÁS I. et al., 1987. Quadrupole mass spectrometer and microsonde studies on the NO_3 poisoning of maize. Proc. Joint Conference on Protection of Water Quality from Harmful Emissions with Special Regard to Nitrate and Heavy Metals, 1-4 September, 1987. Balatonfüred. 361-364.

CSILLAG, J., SILYEVA, T. M. & RÉDLY, M., 1991. Comparison of methods for obtaining soil solution from salt affected soils. In: Genesis and Control of Fertility of Salt Affected Soils. 181-186. Dokuchaev Soil Institute, Moscow.

HOMEYER, B. et al., 1973. Herstellung von Lysimetern mit Boden in naturlicher Lagerung (Monolith-Lysimeter) als Durchlauf-, Unterdruck- oder Grundwasserlysimeter. Z. Pflanzernähr. Bodenkd. **136.** 242-245.

Hungarian Patent No. 183.810, 1982. Eljárás és elrendezés növényekben lejátszódó élettani folyamatok nyomonkövetésére [Procedure and arrangegment to follow physiological processes in plants] 1982. 02. 03.

Hungarian Standard, 1990. Land- and forest application of waste waters and sewage sludges. MI-08-1735-1990.

KABATA-PENDIAS, A. & PENDIAS, H., 1992. Trace Elements in Soils and Plants. CRC Press, Boca Raton, Florida.

LANGER, G. et al., 1984a. Studies on the internal gas composition of the wheat stalk. Wissenschaftliche Zeitschrift der Humboldt Universität zu Berlin, Math.-Nat. R. **XXXIII.** 302-303.

LANGER, G. et al., 1984b. Mass spectrometric in vivo measurements of gases in plants. Vacuum, 1984. 747-758.

MOCHOGE, B. O., 1984. Simulation of nitrate movement in undisturbed soil columns. Agric. Ecosyst. Environment. **11.** 105-115.

NÉMETH, T. et al., 1990. Movement and distribution of ^{15}N labelled nitrogen in undisturbed soil columns. In: Extended Synopsis of Int. Symp. on the Use of Stable Isotopes in Plant Nutrition, Soil Fertility and Environmental Studies. 1-5 Oct., 1990, Vienna Austria. 104-106.

NÉMETH, T. et al., 1991. Bolygatatlan szerkezetű talajoszlopok készítése. [Preparation of undisturbed soil monoliths]. Agrokémia és Talajtan. **40.** 236-242.

PÁRTAY, G., PÁTKAI, T. & BUZÁS, I., 1987. Uses of QMS-microsonde system in agroenvironmental studies. EUROANALYSIS VI., 7-11 September, 1987, Paris, France. 324.

PÁRTAY, G. et al., 1992. A gázfázis vizsgálata bolygatatlan szerkezetű talajoszlopban, kvadrupol tömegpsektrométerrel. [Analysis of the gas phase in undisturbed soil columns, using a quadrupole mass spectrometer.] Agrokémia és Talajtan. **41.** 299-321.