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FATE AND PLANT-UPTAKE OF TOXIC ELEMENTS IN CROPPED SOIL PROFILES

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3. EXECUTIVE SUMMARY

Fate, transport, plant-uptake, and stress effects of selected toxic elements (Cd, Cr, Ni, Pb, and Zn) were monitored in large undisturbed cropped soil monoliths.

Most of the metals were found in the upper 10 cm of the monoliths after application of metal-enriched sewage sludge to the same top 10 cm soil layer. Concentrations of the elements in the soil liquid phase were 10^1-10^5 times lower than those in the solid phase, depending on mobilities of the metals. However, availability of the more mobile Cd, Ni, and Zn increased substantially in the uncontaminated soil layers directly below the application zone at the highest applied contamination. Downward movement of the elements, their release into the soil solution, and their calculated availability was higher in a slightly acidic sandy soil, than in a brown forest soil.

Composition of the gas phase *in situ* in the soil and *in vivo* in the plants was followed by quadrupole mass spectrometry. Composition of soil gas phase in the root zone was clearly different from gas composition inside the plants. Concentrations of the biologically important gases, O_2 and CO_2, altered in the whole profile depending on soil moisture conditions or after application of the metal-enriched sewage sludge; and also in the plants at elevated metal levels.

Concentrations of the metals in the above-ground parts of corn and tomato test plants were generally lower than reported phytotoxic concentrations, except at the highest metal loading level. This was in agreement with the growth (dry matter accumulation) and inner CO_2 and O_2 concentrations of the plants. Concentration ratios of the metals between shoots and roots and between the reproductive and vegetative parts indicated a greater mobility of Cd, Ni, and Zn in the plants, than of Cr and Pb. Tomato was more tolerant to elevated metal levels than corn, as indicated by the lack of stress effects in the gas composition and also of strong phytotoxic effects in the growth as compared to corn.

Joint evaluation of the results obtained for release of the metals into soil solution fractions available for plants + their plant uptake and distribution + their stress effects in the test plants gives a complex, and in many aspects new approach of the transfer of heavy metals in the biogeosphere.

The project enabled substantial developments of experimental facilities (upgrading of the QMS system and TDR equipment of RISSAC), ensuring comprehensive and cost-effective measurements with potentially significant applications for various environmental problems.

4. RESEARCH OBJECTIVES

The main objectives of the project were:

1. To characterize the plant-availability of selected toxic metals (Cd, Cr, Ni, Pb, and Zn) by quantifying their release into the soil solution of undisturbed soils from element loadings similar to or exceeding their permissible levels in wastes applied to agricultural lands, and to follow their redistribution in the solid and liquid phases under different soil moisture conditions,

2. To quantify the transport of these elements to, and their distribution in, different parts of plants as a function of changing element loadings,

3. To identify stress situations in plants as indicated by changes in the composition and/or quantity of different gases (O_2, CO_2, N_2, water vapor) generated in plant tissues and the soil as a result of toxic trace elements loadings; using a quadrupole mass spectrometer equipped with microsensors suitable also for *in vivo* measurements.

4. To provide information needed for simulating the movement and plant uptake of heavy metals at ecologically important field soil moisture contents.

Background and rationale

The amounts of agricultural, industrial and municipal wastes, waste waters, and sewage sludges are rapidly increasing in many developing countries. Hungary currently produces approximately 22 millions tons of communal wastes per year. Source-control of these wastes is very poor, and the industrial infrastructure for recycling wastes is limited (Szenes, 1990).

A rational and economic way to dispose of waste waters and sludges is to apply them to agricultural fields. This practice is of increasing importance also in developed countries. However, heavy metals are characteristic contaminants of industrial and municipal waste waters and sewage sludges and their addition to agricultural soils may cause environmental hazards (Berglund et al.,1984; Chang *et al.*, 1984; Juste and Mench, 1992; McBride, 1995).

Sludge application in Hungary is officially regulated in order to prevent or limit the pollution of soils, surface water and groundwater. The upper limits of the toxic elements selected for our studies are specified as 15 mg Cd, 1000 mg Cr, 200 mg Ni, 1000 mg Pb, and 3000 mg Zn per kg sludge dry matter (Hungarian Technical Directive, 1990). Using these values and assuming an average sludge application practice (500 t/ha sewage sludge with 5 % dry matter content is incorporated into a 20-cm surface soil layer) the loadings (L) of the elements are 0.375 kg Cd, 25 kg Cr, 5 kg Ni, 25 kg Pb, and 75 kg Zn/ha, respectively. The cumulative amount of these metals from a prolonged application of sludge or any other sources must not exceed their maximum acceptable concentrations in the soil, i.e. 6.4 kg Cd, 320 kg Cr, 64 kg Ni, 320 kg Pb, and 800 kg Zn per ha, for soils with adsorption capacity of 15-25 me/100 g soil. In comparison, U.S. Environmental Protection Agency standard cumulative loading limits are 18 kg Cd, 530 kg Cr, 78 kg Ni, 125 kg Pb, and 172 kg Zn per hectare, under the most restrictive conditions of land use (USEPA, 1989; see also Chang et al., 1992), and the maximum permitted metal loadings are 39 kg Cd, 3000 kg Cr, 420 kg Ni, 300 kg Pb, and 2800 kg Zn per ha (McBride, 1995). Despite the lower Hungarian loading limits, improper or

illegal deposition of sludges and industrial wastes may lead to serious contamination of the environment with toxic substances.

Potentially toxic heavy metals are especially hazardous for the environment when they enter the liquid phase of the soil: they may move through the vadose zone towards underlying groundwater systems (Kabata-Pendias and Pendias, 1992) and they may also enter the food chain via plant roots, since water-soluble forms of an element are generally the most easily and immediately available for plant uptake (Petruzzelli, 1989).

The concentration of heavy metals in the soil solution is regarded as an indicator of the mobile pool of metals in soils (Kabata-Pendias and Adriano, 1995). Generally a larger proportion of the soil's total Cd, Ni and Zn content occurs in the liquid phase than of the less mobile Cr and Pb (Kabata-Pendias and Pendias, 1992). The storage capacity of the soil for the heavy metals, the bioavailability and mobility of the stored elements and their concentrations in the soil solution are influenced by environmental changes (periods of drought and flooding, changes in redox conditions, soil acidification as a consequence of atmospheric pollution, etc.) (Brümmer, 1986; Stigliani, 1991; Vernet, 1991; Salomons 1992).

Data concerning heavy metal concentrations in the soil solution are available in the literature (Campbell and Beckett, 1988; Linehan et al., 1989; cit.in Alloway, 1990), but the energy status of the liquid phase in contaminated soils is generally not taken into account. Since -1500 kPa (=pF 4.2; conventional wilting point) is regarded as the upper limit of the suction exerted by plant roots, soil solution fractions retained in the soil with potentials not reaching -1500 kPa may represent the liquid phase available for plant uptake at natural field soil moisture contents. These soil solution fractions may be separated from the soil by centrifugation with a speed corresponding to -1500 kPa water potential (Csillag et al., 1995). We applied this method in the present project for quantitative determination of the metals in that fraction of the soil solution which is energetically available to plant roots.

In a specific soil-plant system the real measure of the availability of the elements is their actual amount taken up by the plants. This depends on both soil and plant factors. Uptake and transport of the elements in the plants are mostly metabolism-dependent, active physiological processes (Sze, 1985; Møller and Lin, 1986) influenced by environmental factors such as temperature, water supply, pH, light, and presence of other elements; and greatly varying during the developmental stages of the plant and among plant species and cultivars (Bowen, 1987; Marschner, 1991). Mechanism and regulation of the transport of the major nutrients, especially of potassium are much studied issues. In contrast, there is still lacking an acceptable model for the uptake mechanisms of trace cations (Kabata-Pendias, 1995)

Plants have generally two strategies for dealing with excess concentrations of the various elements: excluding them from plant tissues by limited uptake/translocation (Kuiper et al., 1987); or accumulating them in specific compartments (cell walls, cell vacuole, bound in specific chelates, etc.) thus excluding them from the metabolic processes (Grill et al., 1987; Grignon and Sentenac, 1991). Occurrence of these two strategies depend on which elements are needed/tolerated by the plants. Among the metals selected for our studies, Zn is an essential microelement (Bergmann, 1993), the essentiality of Ni at very low concentrations is still debated (Pais, 1990; Körös, 1990), and Cd -although not essential- may be taken up by the plants similarly as Zn, accumulating in the plant vacuoles in concentrations high enough to cause later troubles in the food-chain (Wagner, 1993). In contrast, the low plant toxicity of

Cr and Pb (Page et al., 1992) may be at least partly due to their strong binding to the reactive groups in the cell walls (Lehn and Bopp, 1987).

Phytotoxicity is an intoxication of living plants by substances present in the growth medium, when these substances are taken up and accumulated in plant tissues (Chang et al., 1992) or better to say - in plant compartments available for the metabolic processes. Above a certain critical tissue level of the metals toxicity symptoms appear. Growth inhibition which is a plausible and easily evaluated toxicity symptom, is generally the consequence of earlier damage of other metabolic processes such as regulation of plant water relations (Poschenrieder et al., 1989), uptake and utilization of other nutrients (Bujtás and Cseh, 1981; Zaccheo et al., 1982), photosynthesis (Siedlecka et al., 1994), etc.

Excess but less than toxic metal levels present a stress situation for the plants which may impair yields without severe visible symptoms. One of the hypotheses to be tested in our project was that such stress may be indicated and followed by determining the qualitative and quantitative composition of the gas phase inside the plants and also in the soil, with special emphasis on the biologically important gases (O_2, CO_2, water vapor). Several experimental technologies exist for measuring the composition of the gas phase both in the laboratory and in field conditions (Hack, 1956; Robertson and Bracewell, 1979; Glinski and Stepniewski, 1985). Major problems of these methods involve the sampling techniques, preservation of undisturbed conditions, and preservation or simulation of field conditions. The experimental technology developed in the 1980's in a joint effort of RISSAC and the Institute for Nuclear Research of the Hungarian Academy of Sciences allowed qualitative and quantitative determination of gases in plants by mass spectrometry (Hung.Pat., 1982; Langer et al., 1984). This instrumentation was upgraded in the frame of the present PSTC project to ensure simultaneous, computer-controlled measurements and data evaluation in 20 channels. Also, the scope of the measurements was extended to assess the gases in the soil at several depth.

To fulfill the research objectives, we measured in laboratory experiments

- release of the selected metals (Cd, Cr, Ni, Pb, and Zn) into the soil solution and their redistribution in the solid and liquid phases;
- their transport to, and their distribution in, different parts of plants;
- and stress situations in the soil and inside the plants as indicated by changes in the composition of the gas phase (quantity of O_2, CO_2, N_2, water vapor);
- with the metals applied in sewage sludge to cropped, undisturbed, large soil monoliths representing selected Hungarian soil types typically used for agricultural production.

To improve the reliability and cost-effectiveness of the experimental work on the large, undisturbed soil monoliths, several batch and pot experiments were first carried out on disturbed soil samples. These experiments involved the application of metal salt solutions to air-dried samples of three Hungarian soils different in pH and texture in order to reach sufficiently high metal levels in the soil solution to allow differentiation among different soil types. These experiments were also used to assess the impact of soil moisture content, sorption time, rate of metal application, drying-rewetting period and acidification on the ratio of the metals recovered in solution and adsorbed on the solid phase of the soil. Several studies (cit. in Chang et al., 1992; McBride, 1995) have shown differences in the behavior and biological effectiveness of metals when applied as metal salt solutions, as sludges enriched artificially with metals, or as sludges having high metal content. These differences for our experimental conditions were also assessed in preliminary experiments.

5. METHODS AND MATERIALS

The main physical and chemical properties of the soils are listed in Table 1.

The metals were applied as aqueous multicomponent solutions of Cd, Cr, Ni, Pb and Zn nitrates or as communal sewage sludge enriched with these metal salts. Dry matter content of the compressed sludge was 20.6 %, inorganic matter content was 48.2 %. Original concentrations of the metals in the sludge were: 12.3 mg Cd, 217 mg Cr, 109 mg Ni, 210 mg Pb and 3026 mg Zn per kg d.m. These values are comparable to or less than the limits in the Hung. Techn. Dir. (1990). Additions of metal nitrates to this sludge were calculated to give metal loadings in the soil equivalent to 10x, 30x and 100x the permitted loading levels (L-values) resulting from an average sludge application practice (500 t/ha sewage sludge with 5 % dry matter content is incorporated into a 20-cm surface soil layer). Loadings corresponding to 1xL were 0.125 mg Cd, 8.33 mg Cr, 1.67 mg Ni, 8.33 mg Pb, and 25 mg Zn per kg soil. Identical amounts of the metal-spiked sludges were applied in the various treatments in order to obtain uniform sludge (organic matter) loading levels.

Cd, Cr, Ni, Pb and Zn concentrations of all solid and solution samples, from plants and soil, were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Soils No. 1, 3 and 4 were included in the ***preliminary soil chemical experiments***. All soil samples were air-dried and ground to pass a 2.0-mm sieve. To study the effects of *loading rate, soil water content and adsorption time* on the composition of the soil liquid phase, subsamples were contaminated with aqueous multicomponent solutions of the metals at rates of 1x, 10x and 100xL. Water contents of the soil samples (θ) resulting from the application of the metal salt solutions were in the water potential range between -250 and -0.1 kPa. Soil solution was separated by centrifugation with a rotor speed corresponding to -1500 kPa water potential; saturation paste and soil suspensions with soil : metal salt solution ratios of 1:1, 1:2, 1:2.5, 1:5, 1:10 were also prepared. The liquid phases were obtained immediately after the contamination, or after equilibration periods of 1 week and 1 month. Effects of *drying-rewetting and acidification* were studied on contaminated samples dried for 1 month, rewetted with distilled water or with 0.001, 0.1 and 1.5mol/L HNO_3 solutions to soil water potentials of -20 and -0.1 kPa (field and maximum water capacities) and incubated for 1 week. Detailed description of the methodology is found in Németh et al. (1993), Csillag et al. (1994) , and Németh et al. (1994). Studies were also carried out to compare the amounts of Cd, Cr, Ni, Pb and Zn entering the liquid phases of soil or sludge contaminated with multicomponent nitrate salt solution in batch experiments; or the liquid phase of soil loaded with *metal-enriched sewage sludge* both in batch and in soil column experiments.

The adsorption of the heavy metals in the soil was calculated from concentrations measured in the soil solution (c_s), and in the applied metal salt solution (c_m), as $\% = 100\ (c_m - c_s) / c_m$. Recovery of the metals in the acidification experiments was calculated in terms of percentages of the applied amounts ($\% = 100\ c_s / c_m$).

Soil monolith experiments

Undisturbed, 40-cm diameter, 100-cm long soil monoliths were prepared according to the method of Homeyer et al. (1973) modified by Németh et al. (1991). The monoliths were excavated at the selected field sites and the cylindrical surfaces were coated with fiber glass cloth impregnated with a synthetic resin. After the coatings solidified, the monoliths were

lifted, the bottoms were similarly coated, and the monoliths were transported to the laboratory. The coatings made extremely close contact with the soil surface by imbibing the outer micropores, thus eliminating possible "wall effects" during the experiments. The excellent insulating properties of the coating also eliminated leakage from the monoliths.

Experimental set-up

Two soils and two plant species were included in three series of experiments, each one with four monoliths, in the following arrangement:

	soil type	test plant	
1st exp.	brown forest soil, Gödöllő;	corn	(*Zea mays* L. cv. Favea),
2nd exp.	brown forest soil, Gödöllő;	tomato	(*Lycopersicon esculentum* MILL.cv. Kecskeméti bőtermő)
3rd exp.	slightly acidic sandy soil, Somogysárd;	corn	(*Zea mays* L. cv. H-3893 Pioneer)

Various sensors were inserted into the monoliths through holes drilled in the coatings to follow changes in temperature, soil moisture content and gas composition along the soil profile:

- 5 pairs of measuring points attached to the coatings for a capacitive soil moisture meter at 10, 30, 50, 70 and 90 cm depths,
- 4 soil moisture probes at 10, 30, 55 and 85 cm depths, attached to the multiplexer of a time-domain reflectometric soil moisture meter (TDR),
- 5 special microprobes (microsensors) for sampling the gas phase in the soil at 10, 20, 30, 50 and 80 cm depths, coupled to the 20-channel inlet system of a computer-controlled quadrupole mass spectrometer (QMS),
- 3 thermometer sensors at 10, 50 and 90 cm depths.

The scheme of the experimental set-up is shown on Fig. 1.

Soil moisture contents were regulated along the soil profile by saturating the columns from the bottom through a special built-in valve using a hanging water-column; or by sprinkler irrigation at the soil surface. Water was added on the basis of TDR measurements and/or weighting.

The 20-channel inlet system of the QMS system enabled simultaneous, independent measurements in the 1-300 atomic mass range. The microsensors were made of stainless steel capillaries with the tips covered by a special coating. Gases moving freely in air-filled soil micropores or dissolved in the liquid phases in soil and plants could diffuse through this special coating into the microsensor and reach the inlet port of the mass spectrometer. Concentrations of water vapor (18), N_2 (28), O_2 (32) and CO_2 (44) were recorded in the present experiment. Automatic, computer-controlled collection of data from the 20 microprobes operated continuously during the whole experiment.

Supplementary light was ensured in 12 hours day/night cycles. Temperature was recorded daily. Ambient temperature during the experiments was about 25 C°. Variation of temperatures inside the monoliths was less than 2.0 C°. Changes in weights of the columns during stages of the experimental procedure were recorded on a movable scale.

Experimental procedure

The monoliths were air-dried to constant weight (initial stage), then via the bottom-valve gradually filled up to the surface with deionized water (saturation). This step was followed immediately by drainage by gravitation through the bottom-valve (drainage).

When gas composition and soil moisture data remained constant for several days after completion of drainage, sewage sludge spiked with Cd-, Cr-, Ni-, Pb- and Zn- nitrates was mixed into the upper 10 cm of the soil. Metal loadings corresponded to 10x, 30x and 100xL. Original sludge was used as control treatment (about 1xL metal loading). This arrangement proved to be in accordance with literature data suggesting that additional factors (organic matter, nutrients) in the sludges necessitate a control treatment with a low-metal sludge for yield comparison (McBride, 1995).

One week after sludge application nine corn seeds were sown or seven young tomato plants were planted per monolith. When the plants reached a suitable developmental stage, microsensors of the QMS system were implanted into the stems (one per monolith) to study the gas metabolism *in vivo* inside the plants. By the end of the experiment the plants have already entered the reproductive stage, or even finished their vegetation period. There were small cobs on some corn plants, and most fruits on the tomato plants reached full ripeness.

At the end of the experiment soil samples were taken from the four consecutive soil layers at the 0-10, 10-15, 15-20 and 20-30 cm depth intervals. Soil water contents were measured to determine the water potential of the samples. The roots from each layer and above-ground parts were collected, fresh weight and dry matter accumulation as well as some morphological parameters (length of the plants, shape of the fruits, etc.) were determined. Total potentially available metal concentrations in soil (after 2 mol/L HNO_3 extraction, as described by Andersson, 1976), directly plant-available concentration of the metals in the soil solution (obtained by immediate centrifugation of the soil samples), and in samples of the various plant parts (after wet digestion by HNO_3+H_2O_2 in a microwave oven) were determined. Soil solution samples were obtained from each layer of the monoliths in triplicates, and the data show the average value. For the determination of the plant-uptake of the metals each monolith represented a single replicate.

Availability of the metals, i.e. their transfer between the solid and liquid phases in the soil, was also characterized by the soil availability factor, *SA*, which is analogous to the recovery value calculated in the preliminary experiments:

$SA = 100\ c_s / c_m$, where

c_s = concentrations in the soil solution and
c_m = potentially available concentrations in 2 mol/L HNO_3 soil extracts.

6. RESULTS AND DISCUSSION

Preliminary studies

Effects of loading rate, soil properties, water content, and adsorption time

Cd, Cr, Ni and Pb concentrations in the liquid phase of the uncontaminated acidic brown forest soil (No.3. in Table 1.), of the light-textured brown forest soil (A_1 level of No.1)and of the $CaCO_3$-containing chernozem soil (No.4.) were below the detection limit of the ICP spectrometer. Zn concentrations were also very small.

In all three soils only a negligible transfer of Cd, Cr, Ni, Pb and Zn to the soil solution occurred when the 1xL quantities were applied. The metal ion concentrations in the soil solutions of the chernozem soil were lower than, and in the forest soils were comparable to the limits allowed for underground and drinking waters (Csillag and Lukács, 1992).

Practically all metals were adsorbed or precipitated in the $CaCO_3$-containing chernozem, even when applied in amounts 100xL, with the exception of Zn which was found in appreciable concentration in the soil solution.

In the liquid phase of the forest soils the concentrations increased with increasing loading and decreasing soil water content. For the acidic brown forest soil the concentration - soil water content relationships were approximated by hyperbolic equations in the range between -250 kPa potential and 1 : 10 soil:solution ratio. The hyperbolic relationships were established for different adsorption periods (1 hour, 1 week and 1 month) at the 10x and 100xL loading rates (Németh et al., 1993; Csillag et al., 1994) Soil solution concentrations were found to decrease with increasing adsorption time and increasing θ values. Loading rate and soil water content had greater impact on the release of the elements into the soil solution than the duration of application (Csillag et al.,1994; Németh et al., 1994).

With the exception of Cr the adsorbed amounts of the metals decreased at higher soil water contents. This effect was more pronounced at higher metal application levels (100xL). Longer adsorption periods somewhat increased the adsorbed amounts of the elements, while higher loading rates significantly decreased it. The adsorption % - soil water content (θ) relationships gave curves of similar shapes in the two forest soils, but the degree of adsorption was higher in the light-textured non-acidic ($pH \cong 6$) soil (A_1 level of soil No.1). A likely explanation of this finding may be a greater mobility of the elements in the other brown forest soil (soil No.3.) in consequence of its more acidic character ($pH \cong 4$). In both brown forest soils the sorption of the more mobile Cd, Ni and Zn was smaller than that of Cr and Pb. This is in agreement with literature data (Kabata-Pendias and Pendias, 1992; Kabata-Pendias and Adriano, 1995)

Effect of sludge application

When the soil was contaminated with multicomponent solutions of inorganic forms of the metals, metal concentrations in the soil solution reflected the loading rates with the exception of Ni whose concentration exceeded that of Cr (Table 2.a.). Element concentrations in the liquid phase were higher at field capacity than at maximum water capacity. In a similar experiment, when the metals were applied to the soil in communal sewage sludge, the

concentrations in the solution were significantly smaller (Table 2. c.). Generally higher adsorption was found in the 'pure' sludge (Table 2.b.) than in the soil (Table 2.a.), with the exception of Ni. Cr and Pb were adsorbed by the sludge to such a high extent (Table 2.b.) that their adsorption hardly increased any more when soil and sludge were present together (Table 2. c.).

Effect of drying-rewetting procedure

In the acidic brown forest soil at 10xL loading, concentrations of the metals in the liquid phase were 50-70 % lower after a drying-rewetting procedure than in samples not subjected to drying (Németh et al., 1993). At maximum water capacity the drying-rewetting procedure had less impact on the compositon of the liquid phase than at field capacity. The light textured forest soil at 100xL loading rate adsorbed hardly more metals during the drying-rewetting procedure, but the relatively small adsorbed amounts were still significant in absolute value. Cr was an exception, adsorbing strongly (about 90 %) during the drying-rewetting cycle.

Effect of soil acidification

Acidic treatment of the previously contaminated forest soils promoted the release of the elements into the soil solution. Acidic desorption, characterized by element concentrations in the liquid phase, expressed as mg/L or mg/kg, were proportional to the loading rates (Zn>Pb= Cr>Ni>Cd) with the exception of the strongly adsorbed Cr both in the absence and presence of sludge (in samples from batch and column experiments, resp.). In contrast, recoveries of the elements expressed as percentage of the applied amounts, were more closely related to their mobilities, being higher for the more mobile Cd, Ni and Zn than for Cr and Pb. Recovery increased with increasing acidity for Cd, Ni and Zn, while Cr and Pb entered the liquid phase in appreciable amounts (15 and 30 %, resp., in soil No.1.) only after desorption with strong acid (1.5mol/L HNO_3). In contrast, 80-90% of Cd, Ni and Zn present in the sludge-treated soil were released after this treatment. For more details see Németh et al. (1993), and Csillag et al. (1994).

Soil monolith experiments

Total, potentially available (2 mol/L HNO_3-extractable) concentrations

In both soil types (light-textured brown forest soil, No.1., and slightly acidic sandy soil, No.2.) most of the applied heavy metals were adsorbed in the upper 10 cm, sludge containing layer (Table 3). In the brown forest soil the element concentrations in the top 10 cm reflected well the differences in the applied rates at the extremely high contamination level. No increases in concentrations were found in the deeper layers, even at the higher metal application rates, with the exception of Ni and Zn which had slightly elevated concentrations in the 10-15 cm depth interval at the highest contamination level. In the slightly acidic sandy soil a somewhat higher downward movement of the elements was observed below 10 cm at both higher loading rates (30x and 100xL). There are contradictory views in the literature about the leaching of sludge-borne metals in the soil. For instance, Legret et al. (1988) found significant migration of Ni and especially of Cd , but small or no movement of Pb and Cr in a field experiment on a sludge-treated, coarse-textured soil. In contrast, Dowdy and Volk (1983), Chang et al. (1984) and Alloway (1990) reported retention of these elements within

the zone of sludge incorporation in column and field experiments. These discrepancies can be explained mostly by the different properties of the soils and sludges included in the various experiments.

Soil solution concentrations

Concentrations of the metals in soil solution fractions energetically available for plant uptake were mostly several orders of magnitudes lower than the total potentially available (2 mol/L HNO_3 extractable) concentrations, with the exceptions of Cd, Ni, and Zn in the sandy soil and of Ni and Zn in the brown forest soil at the highest loading (Tables 3 and 4). Cr and Pb entered the liquid phase of the soil in negligible amounts even at the highest metal loadings. Release of the more mobile Cd, Ni and Zn into the soil solution increased substantially at higher metal application rates in the top 10 cm and also in the originally uncontaminated soil layers directly below the application zone. Cd was found in much lower concentrations in the soil solution than Ni or Zn. The low Cd concentrations were consistent with the relatively low application rates of this metal as compared to the other four elements. Release of the metals into the soil solution at all metal application rates was significantly higher in the sandy soil than in the brown forest soil.

It is difficult to compare our data, referring to soil solution fractions available for the plant uptake, with the greatly varying literature data which were obtained using very different experimental conditions and methodology (Campbell and Beckett, 1988; Kabata-Pendias and Pendias, 1992). Our results show similar tendencies as cited by Kabata-Pendias and Adriano (1995).

Soil availability

The soil availability factor (*SA*) of the metals in the soil system is a conventional parameter for estimation the bioavailability of various elements (Coughtrey et al., 1985). *SA* calculations (Table 5) indicated a very low availability of Pb and mainly of Cr, and some decrease in their available amounts at the higher application rates since only negligible amounts of these elements were released into the soil solution. In contrast, availability of Cd, Ni and Zn were much more higher and increased in the upper soil layers when the application rate increased. At the highest application rate *SA* values for these mobile elements increased more than one order of magnitude, as compared to the availability observed after application of the original sludge. Such increase was observed not only in the application zone of the metal-enriched sludge, but also in the originally uncontaminated 10-15 cm depth interval.

The calculations indicated a substantially higher availability of the elements in the sandy soil, than in the brown forest soil. The acidic character of the sandy soil may be responsible for this observation. This explanation is in agreement with literature data concerning the effect of acidification on the availability and mobility of heavy metals (Brümmer, 1986; Marschner, 1991) and also with the findings of our preliminary experiments where the recovery of the elements (which is numerically the same as SA value) increased with increasing acidity, but more so for the more mobile Zn and Cd than for Pb and Cr (Németh et al., 1993; Csillag et al., 1994).

Plant growth

Growth of plants during the experiment was much affected by the metal loading rates. Application of the lower metal rates did not inhibit substantially the growth and development of tomato plants, while biomass accumulation of corn was increased at the 10x and 30xL (Table 6). The highest applied metal rate caused severe harm, only one corn (in the first experiment) and one tomato plant survived this treatment. These plants grew very slowly, and a small improvement in their performance at the end of the experiment may coincide with the extension of their roots below the contaminated soil layer. The amount of dry matter in the roots collected from the top 30 cm was generally very small compared to the biomass accumulation of the shoots. This may be due to a restricted root growth into the undisturbed soil under the specific laboratory conditions (sufficient water supply from above by sprinkling irrigation), since the most part of the root system was recovered from the top 10 cm. Also, inhibition of root growth by metal contamination cannot be excluded even in the control sludge treatment. Growth inhibition is one of the most general symptoms of heavy metal toxicities, and it is much more expressed in the roots than in the shoots (Breckle and Kahle, 1992; Punz and Sieghardt, 1993).

Metal uptake by and distribution in the plants

Metal concentrations in the plants generally reflected the application rates (Table 7.). However, great differences in the uptake of the various elements and also in their transport into the above-ground parts were observed. These differences reflected the mobility and the essentiality of the metals. The concentrations of Zn, Cd, and Ni in the roots and shoots were much greater as compared to their applied amounts, than the concentrations of Cr and Pb. (We must stress that data for the 100xL application rates are based on measurements of single plants showing strong toxicity, and they were included as comparisons.)

The dependence of root and shoot metal concentrations on the applied rates show substantial increases at the higher metal levels, especially at 100xL. Mechanisms of selective sorption and transport of trace cations can be broken down under an excessive concentration of mobile species of trace metals (Kabata-Pendias and Pendias, 1992; Ernst et al., 1992). Concentrations of Cd, Ni and Zn in the soil solution (Table 4.) and their soil availability index (*SA*, Table 5.) indicate substantial increases in plant-available forms of these metals at the higher application rates, which may enhance the metabolism-dependent uptake processes and/or cause an aspecific sorption.

Critical tissue concentration levels of the metals for plant growth depend on the plant species, developmental stage, plant part, etc., and vary greatly in the literature. Reported values for the selected metals [mg/kg d.m.] are for instance:

	a	b	c	d
Cd	5-10	10-70	5-30	
Cr	1-2	1-10	5-30	5.9
Ni	20-30	10-150	10-100	3.0
Pb	10-20	-	30-300	
Zn	150-200	100-450	100-400	2200

a Kloke et al. (1984), threshold values for sensitive species
b MacNicol and Beckett (1985)
c Kabata-Pendias and Pendias (1992)
d Chang et al. (1992), PT_{50} values for corn

Values measured in the above-ground parts of our test plants generally do not exceed the above critical concentrations, except at the highest metal loading level where the values are comparable to the literature data, indicating phytotoxicity. This is in agreement with the growth data.

Metal concentrations in the roots were substantially higher than those measured in the above-ground parts (Tables 7 and 9). This was even more pronounced when the parts of the root system separated from the different soil layers were analysed separately. Much higher concentrations were found in that part of the root system which at the time of harvest was in contact with the originally contaminated layer, than in those parts which grew below 10 cm depth (see Table 8. for corn in the first experiment).
Some contamination of the root samples by soil particles cannot be excluded despite the thorough washing. However, the ratios among the root concentrations of the metals from such a contamination would have been similar to the ratios among the applied rates. This was not the case, Pb and Cr were relatively less sorbed by the roots, than Cd, Ni, and Zn:

	Cd	Cr	Ni	Pb	Zn
application ratio	1	67	13	67	200
root concentration ratios (tomato, 30xL)	1	15	8	17	142

Similar trends were observed also for corn and for the lower metal application rates.

Transport of Cr and Pb to the shoots was less than that of the more mobile Cd, Ni and Zn as shown by the shoot/root concentration ratios (Table 9.a.). According to literature data these elements can be adsorbed very strongly to the negatively charged groups in the cell walls, and thus may remain in the apoplast of the roots, fairly inaccessibly to further transport into the shoot (Lepp, 1981; Zaccheo et al., 1982). Further decrease was observed in the transport of these elements into the reproductive organs (Table 9.b). Fruits, grains, etc. generally contain less heavy metals than the leaves or stems (Coughtrey, 1985). However, in our experiments concentration ratios greater than 1 were observed between the reproductive/vegetative parts of the shoot for Cd (corn), Ni (corn and tomato) and Zn (corn), indicating a relative accumulation of these more mobile metals in the edible parts. These concentration ratios decreased strongly at the higher metal application rates, indicating retention of the metals in the vegetative parts at high tissue concentrations.

Comparison of the two plant species shows that tomato was more tolerant to elevated metal levels than corn, as indicated by the lack of strong phytotoxic effects in the growth of the tomato plants.

Gas concentration measurements in the soil

Some general remarks:

When evaluating the QMS data we had to consider several important factors other than heavy metal loadings, such as: irrigation water (quantity and frequency), ambient air temperature and air temperatures in the soil columns at different depths, atmospheric air movements and soil heterogeneity. Despite the fact, that we tried to collect soil monoliths from sites where soil physical, chemical and biological parameters were presumably uniform, some

unavoidable heterogeneity was found in the monoliths and later consequently in the higher plants as well.

Before this project started, we had only experience with the single channel QMS unit with manual operation. The funds of this project provided us the possibility to work with the new 20-channel QMS unit with computer controlled operation. The lack of experience with the measuring parameters of the new QMS system at the beginning caused some problems such as the overrunning of CO_2 and water vapor at the later stages of the first experiment. As principle we did not want to change the operational parameters on the course of the 5 months long experiment, but with this knowledge in mind we corrected this problem in the subsequent experiments.

All three expriments were preceded by control gas measurements of ambient air for all 20 microsensors. In addition, control gas measurements were made before implanting the sensors into the plants. Such control measurements of the third experiment are shown in Fig. 6. The gas concentration values of the air measurements showed very good agreement in the three sensors, indicating that the QMS measuring system was faultless even after long uninterrupted use.

The following gas components were measured: water vapor, N_2, O_2, CO_2. (Water vapor is not discussed in the following summary). Automatically two measurements were saved daily: at 6 am and at 6 pm. The periodical day-night air temperature changes appeared in sinusoidal curves for N_2, CO_2 (and water vapor) concentrations if continuously measured and can be seen in the figures as "saw-tooth"- like curves showing daily low and high values.

The microsensors were implanted at 10, 20, 30, 50 and 80 cm depths in the soil monoliths. In this report we discuss only the data measured by the upper four sensors because the fifth sensor (at 80 cm depth) was later used for measurements in the plant on the same monolith. In our experience the replacement of this sensor caused the least error in later evaluation of QMS data.

In the figures (Fig. 2a to Fig. 6) relative intensities (I/I_0) of gas concentrations are shown versus time (x12h). The time interval between two measurements is 12 hours.

First experiment (Fig 2a, 2b, 2c and 2d):
Saturation of the monoliths was made between measurement points No. 13 and 25, which is indicated by well defined peaks in the CO_2 curves. This phenomenon is characteristic for all depths and loadings. Saturation was made by filling up the monoliths from the bottom, so CO_2 peaks are higher in the deeper layers. An overrunning in the CO_2 curves can be observed at the 30 and 50 cm depths. The width of these peaks (i.e. the length of this phenomenon) grows paralel with the depth, caused probably by the changing profile of the saturated zone in the monoliths. At 10 cm, where saturation was quickly followed by drying up, the change in CO_2 concentration takes the form of a sharp peak and lasts only a few measurement periods.

Sewage sludge was mixed into the top 10 cm of the soil at measurement point No. 51. This also was followed by significant increase of CO_2 concentration. In the deeper layers this reaction was delayed (e.g. at 30 cm it started between measurement point No. 61. and 73.) and its duration was longer.

After sludge-mixing and sowing, germination and root growth is characterized by smaller but wider peaks on the CO_2 curves. This is followed by a relatively smoother period. At measurment point No. 181. the end of the vegetation period and the death of the plant is indicated by the increase of CO_2 concentration.

Summary of the first experiment:

1./ CO_2 was the most mobile gas in the soil columns, its concentration changes reflected the changes in the soil physical, chemical and biological properties.
2./ The changes in the gas concentrations - as a result of different kind of treatments -could be measured both time and space dependent (along the whole depth of the monoliths).
3./ No changes in gas concentrations of the gas phase of the soil could be attributed to the heavy metal loadings.
4./ The germination of the seeds sown in the monoliths, as well as the growing of the roots and the final stage of the vegetation period could be followed by the measuring of the gas concentrations in the root zone.
5./ In the root zone, the changes in the gas concentrations - as consequence of the various treatments - could be linked to the stress status of the plants.

Second experiment (Fig 3a, 3b, 3c and 3d):
Saturation, which was made between measuring points No.16 and 31.had induced significant CO_2 growth. The level of this concentration change is nearly the same at all depths, but its duration is longer in the lower soil layers where saturation lasted longer. The shorter saturation period is characterized by narrowing peaks towards the higher layers. The dynamics of saturation and drying can be seen in the asymmetry of the CO_2 curves. The steeper, increasing part indicates fast saturation, while the extended decreasing part indicates the slow drying phase.

Sewage sludge addition was made at measurment point No. 106. indicated by immediate and significant elevation of CO_2 concentration. The tomato seedlings were planted at measurement point No. 121. The growing phase of plants (roots) was accompanied by continuously decreasing CO_2 concentration. In this experiment the tomato plant proved to be very stress tolerant, which can be seen from the lack of the increase of CO_2 concentration at the end of the experiment (see also *measurements in the plants*, later in this section). Although we extended the duration of the measurements by more than two months, the experiment had to be finished before the end of the vegetation period.

The tendency of the changes of N_2 concentration is similar to CO_2 , but the extent of these changes are much smaller. Concentration changes of O_2 are always antagonistic to concentration changes of CO_2 .

Summary of the second experiment

1./ CO_2 was the most mobile gas in the soil columns, its concentration changes reflected the changes in the soil physical, chemical and biological properties.
2./ The changes in the gas concentrations - as a result of different kind of treatments - could be measured both time and space dependent (along the whole depths of the monoliths).
3./ No changes in gas concentrations of the gas phase of the soil could be attributed to the heavy metal loadings in the 10 to 30 cm upper layer of the monoliths. However, at 50 cm depth the high concentration of CO_2 returned to the base line level only at the later stages:
   0x loading (control)..... at measurement point No.185
   10x loading..... at measurement point No.196

30x loading..... at measurement point No. 211
100x loading..... at measurement point No. 271

4./ The stress status of the tomato plants as consequence of the planting procedure could be followed both in time and depth in the soil columns.

Third experiment (Fig. 4a, 4b, 4c and 4d):
The reactions found in the soil gas phase were considerably different from those observed in the previous two experiments, as expected, because of the different soil type.
Saturation was made between measurement points No. 37 and 49. In the 50 cm layer hardly any reaction could be measured due to the high CO_2 concentration. Unambiguous concentration changes as a result of saturation can be observed only at 30 cm and above. Both the saturation and drying phase was very short (caused probably by the lighter soil texture), which is shown in the steepness of the peaks.
Sewage sludge addition and sowing was made between measurement points No. 97. and 109. These procedures did not cause any reaction in the soil gas phase, however, many random concentration changes of all three measured gases could be observed possibly as a result of local, isolated soil movements.
No plant was growing in the soil column with 100x loading and plant development was poor also in the other treatments.

Summary of the third experiment

1./ CO_2 was the most mobile gas in the soil columns, its concentration changes could be followed through the whole soil profile.
2./ No changes in gas concentrations of the gas phase of the soil could be attributed to the different heavy metal loadings.
3./ Anaerobic conditions were dominating throughout the experiment, except at 10 cm. The concentration of CO_2 was three times higher at the 50-80 cm depth, than in the 10-30 cm layer.
4./ No changes in the gas concentrations could be attributed to sowing, germination or plant root development.

Gas concentration measurements in the plants

Some general remarks:

Previously we had measured the concentration changes of CO_2 and O_2 in various test plants "in situ" and "in vivo" both with the first test model apparatus of QMS and with the later developed one-channel QMS instrument. The treatments applied in these experiments were various mechanical, physical and chemical influences. The test plants gave stress responses upon these influences (Pártay and Buzás, 1985). Measuring the gas concentrations before and after the treatments we found that stress status was characterized by elevated CO_2 and lowered O_2 concentrations. The stress response was very fast: it could be measured already 10-15 minutes after the treatment. The level of stress is characterized by the value of $[CO_2]/[O_2]$ (=RQ (respiration quotient)).

The RQ value was always below 1 at normal - physiological - state of the plant. RQ values above 1 became closer to 1 in those plants which had survived the stress status and went below 1 when normal physiological state was recovered. If stress had been so high, that the plant could not survive, RQ values were high (about 4 - 5, depending on species) and later

had dropped well below 1 and became close to the value of gas concentrations of ambient air, indicating the death of plant cellular system.

First experiment, corn (Fig. 5)
The microsensors were implanted at the 6-leaf- stage of the corn in the control, 10x and 30x loadings. Implantation of a microsensor was impossible into the very poorly developing plant at the 100x loading.
The characteristic RQ values found on the basis of continuous QMS measurements were:

0x loading (control) ..... below 1
10x loading ..... below 1
30x loading ..... above 1

On the basis of the tendency of the concentration changes of CO_2 at the 30x loading it seems that even this high loading was tolerable by the plant, although the plant was in a slight stress status throughout the studied phase of the vegetation period (after implanting the sensor).

Second experiment, tomato (Fig. 5)
The microsensors were implanted six weeks after planting of the tomato seedlings in the soil columns. Both the control and the 10x and 30x loadings showed physiologically stress free status, indicating the excellent heavy metal tolerance of the tomato plant. The only exception was the soil column with 100x loading, where only one of the plants survived the stress status, but because its development was much delayed, the implantation of the microsensor was not possible.

Third experiment, corn (Fig. 6)
The microsensors were implanted at the 6-leaf- stage of the corn in the control, 10x and 30x loadings. No plant survived the 100x loading.
The characteristic RQ values found on the basis of continuous QMS measurements were:

0x loading (control) ..... below 1
10x loading ..... above 4
30x loading ..... above 5

After implantation of the sensors little or no stress was found at the 0x loading (control), while at 10x loading at the measurement point No. 35. the CO_2 concentration was close to the limit value for withering and at the 30x loading between the measuring points No. 45. and 49. this limit value was exceeded. Then the values of CO_2 and O_2 concentrations were approaching the concentrations of these gases measured previously in air. Both plants at the 10x and 30x loading were in serious stress status.

Final conclusions of the QMS measurements:

The quadrupole mass spectrometer equipped with the new 20-channel inlet system proved to be suitable for continuous measurement of the changes in the soil gas phase. During the three 5-month long experiments water vapor and CO_2 levels showed the highest sensitivity to the changes in the chemical and physical properties in the soil profile, N_2 and O_2 responded less. Composition of soil gas phase in the root zone was clearly different from gas composition inside the plants. After application of metal-enriched sewage sludges the concentrations of these biologically important gases altered in the whole profile as compared to the initial status before sludge application. The observed changes were different from those observed after water saturation or after drainage. Gas concentrations in soil and plants were not proportionally dependent on metal loading rates applied to the top soil layers. Stress effects of heavy metals at the 10x and 30x times loadings were apparent in the corn plant both in sandy soil and in the brown forest soil. No stress effect was found in the tomato plant.

7. IMPACT, RELEVANCE AND TECHNOLOGY TRANSFER

The project is resulting in a unique database of information on the fate and transport of heavy metals in the soil-plant system. Joint evaluation of the results obtained in various scientific fields (release of the metals into soil solution fractions available for plants + their plant uptake and distribution + their stress effects in the test plants) gives a complex and in many aspects new approach of problems of the transfer of heavy metals in the biogeosphere.

The project enabled substantial developments of methodology, both technologically and theoretically. The TDR equipment of RISSAC, for measuring soil moisture content in the soil monoliths was upgraded by the manufacturer, Soilmoisture Equipment Corp. (US, CA), by a multiplexer for 64 channels. This was a technological development also for the manufacturer. The quadrupole mass spectrometric system of RISSAC was upgraded by the manufacturer, ATOMKI, (Hungary) by a 20-channel inlet system and by developing the hardware and software for controlling the different parts of the mass spectrometer, for collecting and processing data. A relatively high proportion of project funds was spent to prepare additional 30 modified centrifuge tubes which served to obtain soil solution fractions at the same time from numerous soil samples by a special technique.

These technological developments and investments increased not only the instrumental capacities in RISSAC, but made the measurement programs much more comprehensive and cost-effective. The accuracy of the measurements was increased and their variability decreased to the level of the inherent differences in the structure of the monoliths, by the possibilities of simultaneous measurements in several soil monoliths under the same experimental circumstances.

As far as we know, our study is the first ever in which a multiple inlet quadrupole mass spectrometric system was used for determining soil gas composition in undisturbed soils. Important scientific aspects of the project were a better understanding of the physical and chemical backgrounds of this new experimental technique, since the project permitted a detailed study of the QMS system itself under different experimental circumstances.

New research skills were acquired during operation of the multichannel systems of the QMS and TDR equipments. Handling of the vast amount of data necessitated adaptation of certain data-processing programs to the specific needs of selecting specific groups of data on the basis of various criteria. Development of software for these purposes was made in RISSAC. Use of such software promoted development of new skills of several team members. Additional skills in word processing, computer modeling, and the use of graphics software for visualization and preparation of results in papers or for presentations were also acquired, in co-operation with the US Salinity Laboratory, Riverside, CA.

Detailed results of the project were presented at several Hungarian and international conferences and symposia, with the abstracts published. Also, several full papers documenting project results were published in peer-reviewed international and Hungarian scientific journals, and also in edited conference proceedings (see Section 7). A detailed English monograph on the overall achievements of the project is under preparation.

8. PROJECT ACTIVITIES/OUTPUTS

Collaboration and training:

visit of Dr. M.Th.van Genuchten (US Salinity Laboratory) in RISSAC, August 25-28, 1991.
to get acquainted with team members, facilities and experimental plans;

visit of Dr. M.Th.van Genuchten (US Salinity Laboratory) in RISSAC, July 1-Sept. 10, 1992,
to discuss theoretical aspects and experimental parts, with special emphasis on the importance of having preliminary data and conceptual understanding of plant uptake processes;

visit of Drs. K.Bujtás, J.Csillag, and E.Molnár (RISSAC) in US Salinity Laboratory, November 21-December 10, 1992.
to get acquainted with the experimental and modeling techniques used at USSL in studies on water management and salinity (toxic element) problems in Californian soils;

visit and training of Drs. K.Bujtás, I.Buzás, and T.Németh (RISSAC) in US Salinity Laboratory, August 1-29, 1994, June 26-July 29, and May 9-August 29, 1994, resp.
to review and analyse the results so far achieved, discuss the need for additional experiments to fill gaps in current database, and prepare material for publication;

visit of Drs. M.Th.van Genuchten and F.J.Leij (US Salinity Laboratory) in RISSAC, October 8-12, 1995 (joint workshop)
to discuss and evaluate the overall achievements of the project prior to the preparation of the Final Report.

Seminars held in the frame of the project:

December 3, 1992, U.S.Salinity Laboratory, USDA/ARS, Riverside, CA.
Bujtás, K.: Problematic points in studies on heavy metal transport processes of plants.
Csillag,J.: Changes in the liquid phase of soils as a consequence of chemical degradation processes.
Molnár,E.: Salinity and heavy metal pollution problems in Hungary.

August 19, 1994. U.S. Salinity Laboratory, USDA/ARS, Riverside, CA.
Bujtás,K.: Preliminary results of the PSTC project: Fate and plant-uptake of selected toxic elements in cropped soil profiles.

PSTC workshop, October 10, 1995, RISSAC, Budapest
van Genuchten,M.Th.: Issues and opportunities in vadose zone hydrologic research
Leij,F..J.: Formulation and application of a stream-tube model for field scale solute transport.
Németh,T.: Fate and plant uptake of toxic elements in cropped soil profiles
Csillag,J.: Effect of heavy metal contamination of disturbed and undisturbed soils on the composition of the soil solution.
Bujtás,K.: Plant uptake and distribution of the selected metals.
Lukács,A.: Results of the soil gas measurements by QMS and soil moisture measurements by TDR.
Pártay,G.: Video demonstration of the 3 soil monolith experiments.

*Meetings, conferences attended (L=lecture, P=poster, *=abstract published in proceedings)*

1st Symposium on Measurement of Water Quality, May 21-24, 1991. Balatonvilágos, Hungary.
P: Csillag,J., Lukács,A., Molnár,E., Pártay,G. and Rajkai,K.: The estimation of the release of Zn, Pb, Cr, Cd from wastes to soil solution.*

33rd IUPAC Congress, Aug 17-22, 1991. Budapest, Hungary.
P: Lukács,A., Fodor,P., Csillag,J., Pártay,G. and Molnár,E.: Determination of heavy metals in the soil solution.*

EUROENVIRONMENT '92 "Chemistry for the Protection of the Environment", 170th event of the Federation of European Chemical Societies (FECS), May 10-14, 1992. Budapest, Hungary.
P: Csillag,J., Lukács,A., Molnár,E. and Pártay,G.: Modeling the release of Zn, Pb, Cr, Cd from wastes to soil solution fractions available to plants.*

Conference of Hungarian Chemists, July 6-8, 1992. Szombathely, Hungary.

P: Molnár,E., Koncz,J., Csillag,J. and Baczó,Gné: Comparison of the heavy metal concentrations of different soil extracts, as well as those of the soil solution. (In Hungarian)*

P: Csillag,J., Lukács,A., Molnár,E. and Pártay,G.: Model experiment for determination of soil solution concentration of Zn, Pb, Cr, Cd originating from sewage sludge. (In Hungarian)*

Symposium on Soil Resilience and Sustainable Land Use, Sept 28-Oct 2, 1992. Budapest, Hungary.

P: Németh,T., Molnár,E., Csillag,J., Bujtás,K., Lukács,A. and Pártay,G.: Fate and plant-uptake of some heavy metals in soil-plant systems studied on soil monoliths.*

Heavy Metals. Problems and Solutions. Workshop organised by SETAC-Europe, Oct 11-17, 1992. Libice Castle, Czechoslovak Federal Republic.

L: Molnár,E., Németh,T. and Pálmai,O.: Problems of heavy metal pollution in Hungary - "state-of-the-art".

Conference on Physical Chemistry and Mass-exchange Processes in Soils. Oct 12-16, 1992. Puschino, Russia.

L: Csillag,J. and Lukács,A.: The soil as a buffer for heavy metals: analysis of the soil solution for Zn, Pb, Cr, Cd in a model experiment.*

V. Environmental Protection Conference, Oct. 27-29, 1992. Székesfehérvár, Hungary.

L: Németh,T., Molnár,E., Csillag,J., Bujtás,K. and Lukács,A.: Studies on the fate of selected toxic heavy metals in a soil-plant system, on undisturbed soil monoliths. (In Hungarian)*

P: Csillag,J., Lukács,A., Molnár,E. and Pártay,G.: Model experiment to study the Zn, Pb, Cr and Cd sorption ability of soils. (In Hungarian)*

P: Molnár,E., Koncz,J., Csillag,J. and Baczó,Gy.: Environmental evaluation of the concentration of different heavy metal forms in soils measured by several extractants and in the soil solution. (In Hungarian)*

International Conference on Water Protection, May 5-7, 1993. Siófok, Hungary.

L: Pártay G., Németh T., Lukács A., Molnár E., Bujtás K., Csillag J. and Bohátka S.: Application of a 20-channel quadrupole mass spectrometric measuring system to environmental protection measurements. (In Hungarian)

Second International Conference on the Biogeochemistry of Trace Elements. Sept 5-10, 1993. Taipei, Taiwan, Republic of China.

P: Németh,T., Molnár,E., Csillag,J., Lukács,A., Bujtás,K. and van Genuchten,M.Th.: Model experiments to assess the fate and plant uptake of heavy metals applied in sewage sludge.*

P: Németh,T., Pártay,G., Bujtás,K., Lukács,A.: Use of quadrupole mass spectrometry to assess in soils and plants the toxic effects of several heavy metals applied simultaneously in sewage sludge.*

National Conference for Environmental Protection, Sept 7-9, 1993. Siófok, Hungary.

L: Csillag, J., Lukács, A. and Molnár,E.: Studies on binding of Zn, Pb, Cr and Cd in soils. (In Hungarian)

L: Pártay,G., Lukács,A. and Németh,T.: Gas analytical studies on soil monoliths loaded with heavy metals, using quadrupole mass spectrometry. (In Hungarian)

First International Specialized Conference on Diffuse (Nonpoint) Pollution: Sources, Prevention, Impact and Abatement. International Association on Water Quality. Sept 20-24, 1993. Chicago, Illinois, USA.

L: Németh,T., Molnár,E., Csillag,J., Bujtás,K., Lukács,A., Pártay,G., Fehér,J. and van Genuchten,M.Th.: Mobility of some heavy metals in soil-plant systems studied on soil monoliths.

II. International Conference and Exhibition on Environmental Protection, May 4-6, 1994. Kecskemét, Hungary.

P: Pártay,G. and Bohátka,S.: Measurement and prediction of stress situations by means of *in situ* and *in vivo* gas analysis.

SECOTOX, 3rd Regional CCEE Meeting, May 14-19, 1994. Balatonaliga, Hungary.

P: Lukács,A., Bujtás,K., Csillag,J., Pártay,G. and Németh,T.: Column experiment for measuring the distribution of Zn, Pb, Cd, Cr and Ni in a sewage sludge-soil-plant model system.*

XXIV. Membrane-Transport Conference, May 24-27, 1994. Sümeg, Hungary.

L: Bujtás K. Interactions in plant uptake of the heavy metals. (In Hungarian)*

Biostress '94- Bioexpo '96. Workshop on Plant Responses to Environmental Stress. July 11-12, 1994. Szeged, Hungary

P: Pártay,G., Bohátka,S., Buzás,I., Bujtás,K. and Németh,T.: Measurement and prediction of stress status in plants by direct gas analysis.*

V. Hungarian Congress of Plant Physiology. July 13-15, 1994. Szeged, Hungary.

L: Bujtás K., Lukács A. and Csillag J.: Plant uptake and toxicity of heavy metals in the presence of several metals simultaneously. (In Hungarian) *

15th World Congress of Soil Science, July 10-16, 1994. Acapulco, Mexico.

P: Csillag,J., Lukács,A. and Molnár,E.: Study of heavy metal overloading of soils in a model experiment.*

P: Pártay,G., Lukács,A. and Németh,T.: Soil monolith studies with heavy metal containing sewage sludge.*

P: Koncz,J., Molnár,E., Csillag,J. and Baczó, Gy.: Comparison of different extractants for the determination of heavy metals in the soil. *

3rd International Symposium on Environmental Geochemistry, Krakow, Poland, September 12-15, 1994.

Abstract: Csillag,J., Lukács,A. and Bujtás,K.: Zn, Pb, Cr, Cd mobilization due to acidification in a contaminated soil.*

Budapest '94. Second International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe. Sept 20-23, 1994. Budapest, Hungary.

P: Csillag,J., Lukács,A., Bujtás,K. and Németh,T.: Assessment of heavy metals in soil solution fractions.*

P: Pártay,G., Bujtás,K., Lukács,A., Németh,T. and Bohátka,S.: Quadrupole mass spectrometry technique in environmental studies.*

COST 8.21. Workshop on Arbuscular Mycorrhizas in Sustainable Soil-Plant Systems. Oct 21-23, 1994. Weihenstephan, Germany

P: .Biró,B., Bujtás,K., Pártay,G., Köves-Péchy,K. and Vörös,I.: Endomycorrhizal infection of maize affected by heavy metals.

Third International Conference on the Biogeochemistry of Trace Elements, Symposium A3 "Mobilization: biological processes". May 15-19, 1995. Paris, France.

L: Németh,T., Csillag,J., Lukács,A., Pártay,G., Molnár,E. and Bujtás,K.: Soil - soil solution - plant transfer of selected metals in undisturbed soil profiles.*

III. International Conference for Environmental Protection. May 24-26, 1995. Kecskemét, Hungary.

P: Bujtás,K., Lukács,A., Csillag,J., Pártay,G., Molnár,E. and Németh,T. Fate in the soil and plant-uptake of toxic elements of sewage sludge (Cd, Cr, Ni, Pb, Zn) in undisturbed soil columns. (In Hungarian)

The soil as a strategic resource: Degradation processes and conservation measures. July 11-15, 1995. Canary Islands, Spain.

P: Csillag,J., Lukács,A. and Bujtás,K.: Zn, Pb, Cr, Cd mobilization as a consequence of acidification in a contaminated soil.*

XXVth Annual Meeting of ESNA, Sept 15-19, 1995. Castelnuovo Fogliani(Piacenza), Italy.

L: Bujtás, K., Csillag,J., Pártay,G. and Lukács,A.: Distribution of selected metals in a soil-plant experimental system after application of metal-spiked sewage sludge.*

ISEAC 26, 26th International Symposium on Environmental Analytical Chemistry, April 9-12, 1996. Vienna, Austria.

P: Pártay,G., Lukács,A: Bujtás, K. and Németh,T.: Use of quadrupole mass spectrometry for soil and plant gas analysis in heavy metal polluted soil columns.*

Int.Workshop on Water Pollution and Protection in Agricultural Practice. May 20-24, 1996. Zagreb, Croatia.

L: Molnár,E., Németh,T., Csillag,J. and Bujtás,K.: Studies for estimating groundwater pollution by heavy metals and nitrate in Hungary.

Full publications

Németh,T., Molnár,E., Csillag,J., Bujtás,K., Lukács,A. and Pártay,G. (1993) Fate and plant-uptake of some heavy metals in soil-plant systems studied on soil monoliths. *Agrokémia és Talajtan* **42**, 195-206.

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9. PROJECT PRODUCTIVITY

The proposed goals were generally accomplished. The inherent variability in the physical and chemical properties of the undisturbed soil monoliths (which is a well-known feature also in the literature) and the consequent + additional variability in plants' responses to metal loadings made full comparisons among treatments difficult and detailed statistical analyses unreasonable. Despite these problems, the results provide information needed for simulating the movement of the selected metals in soil-plant systems.

Many important issues (impact of soil moisture contents, drying-rewetting periods, duration of contamination, differences between the fate of metals applied as inorganic salts or in sludge, interactions among the metals in the plant transport processes, etc.) could not be addressed in the experiments on the undisturbed monoliths. These problems were dealt with in additional batch and pot experiments. The informations obtained in these additional experiments were essential for proper evaluation of the findings observed on the monoliths.

10. FUTURE WORK

Several scientific issues outside the scope of the project have arisen during the experimental work. Successful research work on these issues much depends on the possibility of financial support from various sources.

Studies were initiated during the project in co-operation with staff members of the Soil Biology Department of RISSAC with the aim to investigate interactions between the selected elements and possible vesicular-arbuscular mycorrhizal infection of the test plants, and the likely beneficial effects of such interactions on the plants. These studies continue between 1995 and 1998 in the frame of a project supported by the Hungarian National Scientific Research Fund (OTKA) with an annual support of 1,000,000 HUF. This project comprises also a part of the European joint research program COST 821 (Arbuscular mycorrhizas in sustainable soil-plant systems)

Also, the project results support views stressing the importance of acidification of the environment in (re)mobilization of metal contaminants in the soil. Two projects were submitted in 1996 to the Hungarian National Scientific Research Fund addressing the following issues: Impact of heavy metal contamination and soil acidification on the mobility of the metals in the soil-plant system (PI: J.Csillag), and Impact of soil contamination and soil acidification on plant-uptake and phytotoxicity of Cd, Cr, Ni, and Pb (PI: K.Bujtás). Decision on these projects is expected early 1997.

Also, the experimental technique and the expertise developed in the PSTC project may have potentially significant applications for many environmental studies. Example of this are the project proposals submitted in 1996 to the Hungarian Academy of Sciences on studies of the fate and stress effects of herbicides in the soil-plant system (partly in controlled experiments on undisturbed soil monoliths with multichannel QMS measurements) (PI: K. Bujtás); and on adsorption and mobilization of Cd, Pb, and Zn in typical Hungarian soils (PI: Prof. G. Filep, Agricultural University, Debrecen; participant: J.Csillag, RISSAC). Decisions are expected in July 1996.

Further co-operation is planned with the U.S. Salinity Laboratory, involving joint research on movement of contaminants in regional field scale (in varied landscapes). A project proposal for such co-operation submitted in 1995 to the US-Hungarian Joint Fund (PI: T.Németh and M.Th.van Genuchten) obtained favourable decision, but no financial support for the present.

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APPENDIX

Tables and Figures

Table 1. Some chemical and physical properties of the soils

soils	depth [cm]	horizon	pH		$CaCO_3$ [%]	organic matter [%]	CEC [me/100g soil]	SP	<0.02 mm [%]
			H_2O	KCl					
No.1.	0-8	A_p	5.90	5.02	0	1.0	9.0	25	19.5
	8-16	A_1	6.26	5.29	0	1.2	8.5	28	18.9
	16-43	B	5.85	5.01	0	1.1	8.5	28	20.5
	43-66	BC	6.51	5.24	0	*	10.1	28	23.3
	66-	C	7.15	5.75	0.1	*	58.0	74	54.4
No.2.	5-15	A_p	5.63	4.48	0	1.3	6.7	27	20.2
	40-50	B	6.07	4.84	0	0.3	4.7	30	12.2
	80-90	C	6.38	5.56	0	0.1	2.3	24	5.0
No.3.	5-15	A_1	4.35	3.21	0	1.6	20.7	55	40.8
No.4.	0-20	A	7.72	6.98	6.6	2.8	28.3	50	35.8

No.1.: brown forest soil (Ramann-type), Ochrept (Gödöllő)
No.2.: slightly acidic sandy soil, Psamment (Somogysárd)
No.3.: acidic brown forest soil (Ragály)
No.4.: calcareous chernozem (Pusztaszabolcs)
* no measurements

Table 2. Heavy metal concentrations [mg/L] in the liquid phases of and adsorption [%] in metal-contaminated (L = 100x) brown forest soil (A_1 level of soil No.1.), sludge, and soil + sludge

water potential [kPa]	Cd		Cr		Ni		Pb		Zn	
	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%
a. soil										
-20 (FC)	75	33	937	87	970	33	1392	82	15420	26
-0.3 (MC)	30	54	337	92	580	32	495	89	9310	27
b. sludge										
~ -20	5.3	95.2	3.7	99.95	1023	31	17	99.80	10590	52
~ -0.1	*	*	1.9	99.96	596	30	2.2	99.95	3960	69
c. soil + sludge										
-25 (FC)	3.8	96.6	0.8	99.99	417	72	5.6	99.92	4598	79
-1.6 (MC)	0.2	99.6	0.4	99.99	175	79	0.7	99.98	1206	91

% = $100 \times (c_m - c_s)/c_m$, where c_s = metal concentrations in the liquid phases and c_m = metal concentrations in the applied metal salt solutions

FC = field water capacity
MC = maximum water capacity
* = concentration in liquid phase below determination limit

Table 3. Metal concentrations in the 2 mol/L HNO_3-extracts [mg/kg dry soil]

depth [cm]	brown forest soil (1st exp.)				slightly acidic sandy soil (3rd exp.)			
	loading				loading			
	control	10x	30x	100x	control	10x	30x	100x
Cd								
0-10	1.3	3.3	5.8	11.4	1.8	2.8	3.8	9.5
10-15	0.8	0.9	0.9	1.0	1.6	1.6	1.5	1.9
15-20	0.7	0.9	1.0	1.0	1.5	1.5	1.3	1.4
Cr								
0-10	13.6	130	292	687	10.6	74.0	158	533
10-15	8.5	11.2	9.6	10.9	7.7	10.5	11.1	35.9
15-20	8.0	9.0	8.8	10.3	7.2	7.2	6.8	7.7
Ni								
0-10	15.5	47.0	74.7	150	10.7	24.1	39.8	115
10-15	12.0	11.0	12.4	19.3	9.1	9.9	9.7	20.3
15-20	10.8	10.8	11.7	13.8	8.5	8.8	8.0	9.2
Pb								
0-10	15.9	138	310	736	7.9	73.9	166	574
10-15	11.8	14.3	14.3	13.4	4.5	8.2	9.7	35.4
15-20	11.1	12.3	11.9	13.2	4.5	4.8	4.5	4.9
Zn								
0-10	100	503	1011	2092	76.6	293	556	1740
10-15	34.7	39.0	36.8	49.7	33.5	37.4	41.6	157
15-20	34.6	30.2	30.3	38.1	25.5	26.0	23.9	32.4

Table 4. Concentrations of the metals in the soil solution [µg/kg dry soil]

depth [cm]	brown forest soil (1st exp.)				slightly acidic sandy soil (3rd exp.)			
	loading				loading			
	control	10x	30x	100x	control	10x	30x	100x
Cd								
0-10	*	0.4	1.2	90.2	2.1	2.0	16.5	357
10-15	*	*	*	11.6	1.7	1.4	2.2	13.2
15-20	*	*	*	*	0.7	1.0	1.1	1.2
Cr								
0-10	1.9	1.4	0.7	7.0	0.4	2.9	7.2	10.7
10-15	0.6	3.0	*	2.3	3.0	17.4	4.8	10.8
15-20	*	2.4	3.7	*	3.2	2.9	1.7	6.0
Ni								
0-10	4.3	12.9	39.2	2600	24.5	49.3	375	9197
10-15	2.1	4.9	6.8	225	27.0	23.6	39.0	623
15-20	5.6	3.5	11.3	13.7	17.0	12.8	22.5	29.4
Pb								
0-10	*	5.9	*	7.8	18.2	10.4	14.1	154
10-15	*	3.3	6.1	11.5	20.1	30.1	16.9	33.6
15-20	*	6.5	2.8	*	34.3	14.0	9.7	28.1
Zn								
0-10	50.8	120	219	28600	283	500	3492	106200
10-15	81.0	82.6	127	761	395	273	342	6249
15-20	130	140	125	232	184	78	168	266

* concentrations below determination limit

Table 5. Soil availability factors ($SA = 100\ c_s / c_m$) of the heavy metals

depth [cm]	brown forest soil (1st exp.)				slightly acidic sandy soil (3rd exp.)			
	loading				loading			
	control	10x	30x	100x	control	10x	30x	100x
Cd								
0-10	*	0.012	0.021	0.791	0.114	0.070	0.432	4.07
10-15	*	*	*	1.22	0.107	0.089	0.149	0.679
15-20	*	*	*	*	0.048	0.066	0.086	0.084
Cr								
0-10	0.014	0.001	0.0002	0.001	0.004	0.004	0.004	0.002
10-15	0.007	0.027	*	0.021	0.039	0.166	0.043	0.030
15-20	*	0.027	0.042	*	0.044	0.041	0.025	0.078
Ni								
0-10	0.028	0.027	0.052	1.73	0.228	0.205	0.941	7.61
10-15	0.018	0.045	0.055	1.17	0.297	0.239	0.401	3.07
15-20	0.052	0.032	0.097	0.099	0.200	0.146	0.280	0.321
Pb								
0-10	*	0.004	*	0.001	0.232	0.014	0.008	0.026
10-15	*	0.023	0.043	0.086	0.446	0.367	0.175	0.095
15-20	*	0.053	0.024	*	0.763	0.293	0.214	0.574
Zn								
0-10	0.051	0.024	0.022	1.37	0.369	0.170	0.628	5.83
10-15	0.233	0.212	0.346	1.53	1.18	0.730	0.821	3.98
15-20	0.375	0.463	0.412	0.608	0.720	0.298	0.702	0.822

* concentration in the soil solution below determination limit

c_s = metal concentrations in the soil solution [mg/kg dry soil]

c_m = metal concentrations in the 2 mol/L HNO_3 extracts [mg/kg dry soil]

Table 6. Biomass accumulation in the plants, dry weight [g/plant]

	loading	tomato	corn1	corn2
reproductive parts	control	1.7	0.9	
	10x	0.9	1.9	
	30x	2.4	2.6	
above-ground vegetative parts	control	24.3	6.3	
	10x	18.3	11.2	
	30x	18.8	11.8	
total shoot	control	25.9	7.2	3.0
	10x	19.2	13.1	5.6
	30x	21.3	14.4	5.4
root (0-30 cm)	control	0.32	0.35	0.39
	10x	0.22	0.46	0.12
	30x	0.22	0.98	0.19
number of plants	control	6	6	5
	10x	7	7	3
	30x	7	5	4
	100x	1	1	1*

*Plant died before harvest.

Table 7. Concentrations of the applied metals in the experimental plants [mg/kg d.m.]

	loading	a. above-ground parts			b. roots (0-30 cm depth)		
		tomato	corn1	corn2	tomato	corn1	corn2
Cd	control	1.07	0.38	0.68	2.38	n.d.	3.14
	10x	1.41	0.60	0.88	3.20	n.d.	3.44
	30x	2.49	0.82	1.11	4.69	n.d.	6.11
	100x	2.32	1.77	n.d.	7.20	n.d.	n.d.
Cr	control	2.52	1.20	5.00	12.3	4.81	15.2
	10x	2.29	4.06	1.46	26.9	20.4	32.1
	30x	2.06	1.62	2.10	70.0	38.4	85.3
	100x	20.6	2.49	n.d.	69.8	163	n.d.
Ni	control	2.91	1.41	3.50	17.1	12.0	26.6
	10x	3.23	2.20	2.80	20.5	29.3	37.5
	30x	6.56	2.34	5.60	38.5	59.4	86.5
	100x	21.8	29.4	n.d.	105	118	n.d.
Pb	control	3.13	1.26	4.82	14.6	3.38	8.08
	10x	3.68	0.24	0	32.5	22.0	17.5
	30x	9.03	0.95	0	81.4	46.0	65.0
	100x	22.9	4.48	n.d.	84.3	90.4	n.d.
Zn	control	95.8	68.5	171	370	144	431
	10x	124	158	355	502	165	383
	30x	132	220	264	665	427	542
	100x	285	798	n.d.	1504	1356	n.d.

n.d. = not determined

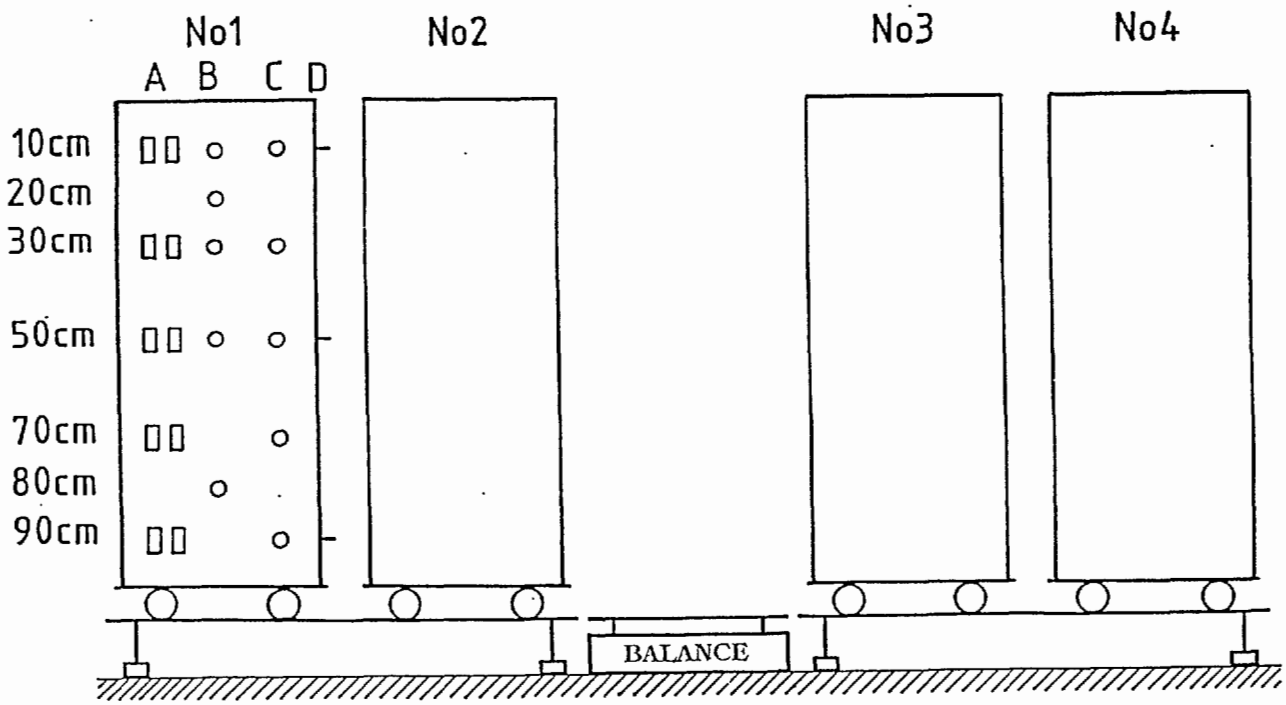
Table 8. Distribution of the metals in the root system of corn on the brown forest soil
Metal concentrations [mg/kg d.m.]

	loading	roots in the 0-10 cm layer	roots in the 10-30 cm layer
Cr	control	4.7	6.5
	10x	21.6	7.2
	30x	39.0	19.4
	100x	283	9.1
Ni	control	12.2	9.6
	10x	28.7	34.6
	30x	60.5	25.8
	100x	199	12.2
Pb	control	3.6	0
	10x	24.0	0
	30x	47.5	0
	100x	160	0
Zn	control	150	59.3
	10x	179	6.8
	30x	441	0
	100x	2392	14.5

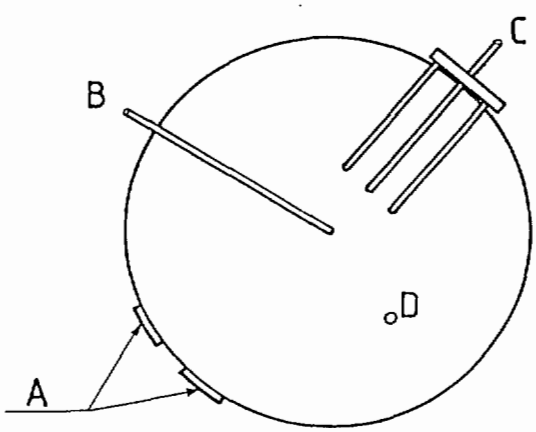
Table 9. Concentration ratios between plant parts

	loading	**a.** shoot/root ratio(*SRR*)		**b.** reproductive/vegetative part ratio in the shoot *(RVR)*	
		tomato	corn1	tomato	corn1
Cd	control	0.45	n.d.	0.49	15
	10x	0.44	n.d.	0.64	1.87
	30x	0.53	n.d.	0.39	1.43
	100x	0.32	n.d.	0.28	0.85
Cr	control	0.20	0.25	0.24	2.67
	10x	0.085	0.20	0	0.61
	30x	0.029	0.042	0.03	1.06
	100x	0.30	0.015	0.02	0.81
Ni	control	0.17	0.12	3.69	1.91
	10x	0.16	0.075	1.11	1.13
	30x	0.17	0.039	4.27	1.73
	100x	0.21	0.25	0.97	0.61
Pb	control	0.21	0.37	0.18	n.c.
	10x	0.11	0.011	0.15	n.c.
	30x	0.11	0.021	0.09	0.38
	100x	0.27	0.050	0.05	0.64
Zn	control	0.26	0.48	0.50	1.59
	10x	0.25	0.96	0.47	1.13
	30x	0.20	0.52	0.38	0.95
	100x	0.19	0.59	0.14	0.50

n.d. = not determined
n.c. = not calculated because of concentration values less than limits of measurement



SIDE VIEW



ϕ=400 mm
A=Capacitive sensors
B=QMS sensors
C=TDR sensors
D=Thermometer sensors

VIEW FROM ABOVE

Fig. 1 Scheme of the experimental set-up

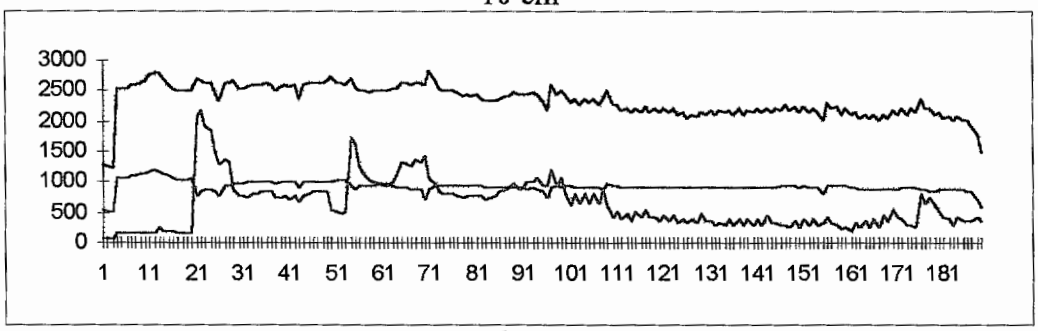
(the position of the sensors shown in column No. 1 was the same in all four soil monoliths and in all three experiments)

Soil type: Ramann brown forest soil, Gödöllő Plant: maize Loading: **0x**

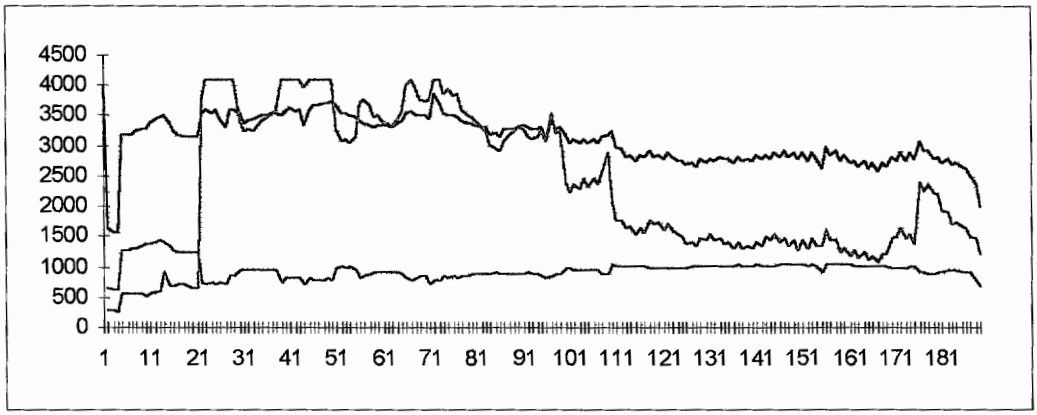
---------- Nitrogen ---------- Oxygen ---------- Carbon dioxide

I/I_0

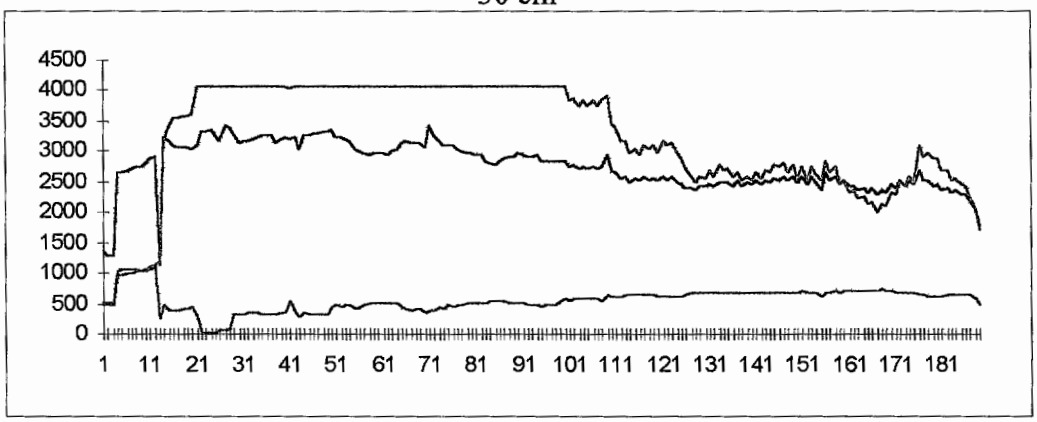
10 cm



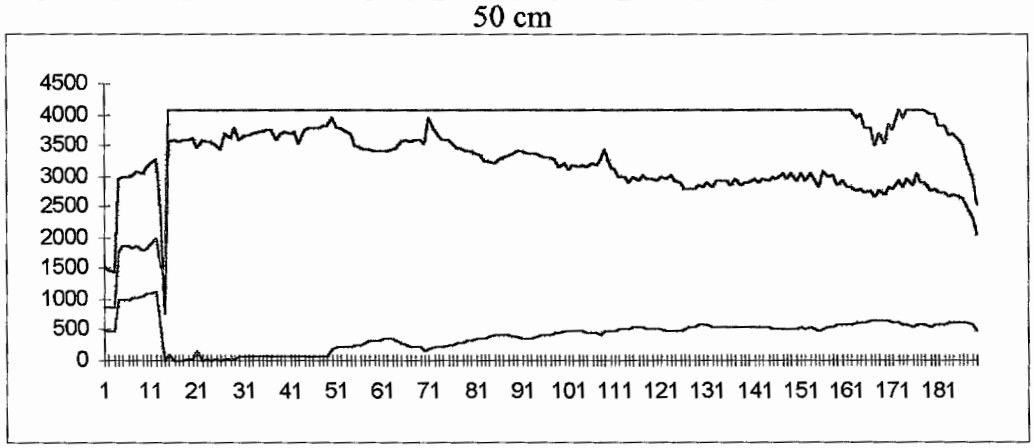
20 cm



30 cm



50 cm



x12h

Fig. 2a

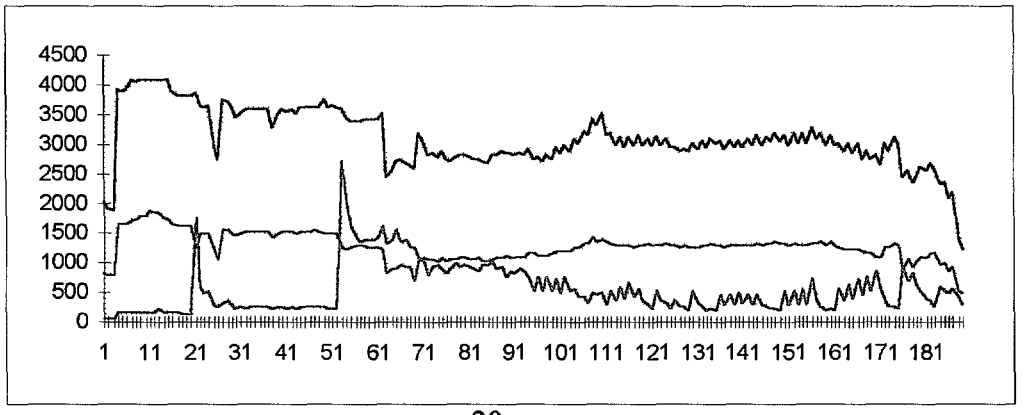
34

Soil type: Ramann brown forest soil, Gödöllő Plant: maize Loading: **10x**

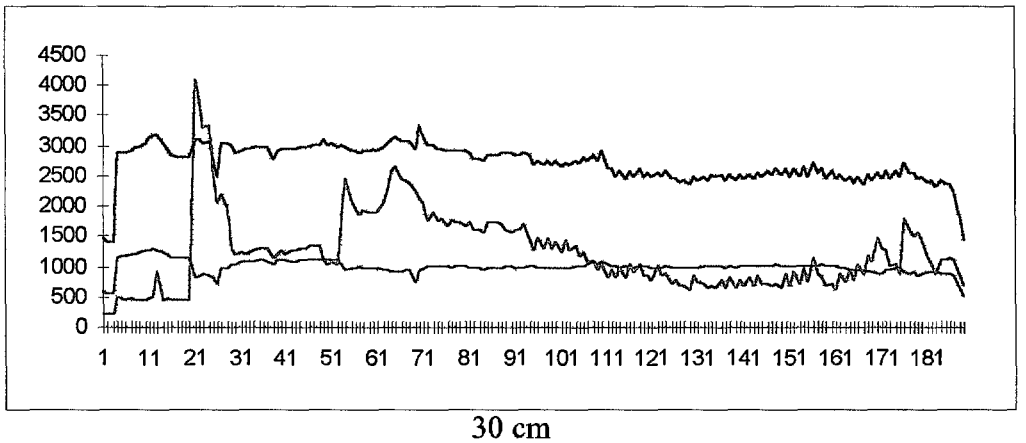
---------- Nitrogen ---------- Oxygen ---------- Carbon dioxide

I/I_0

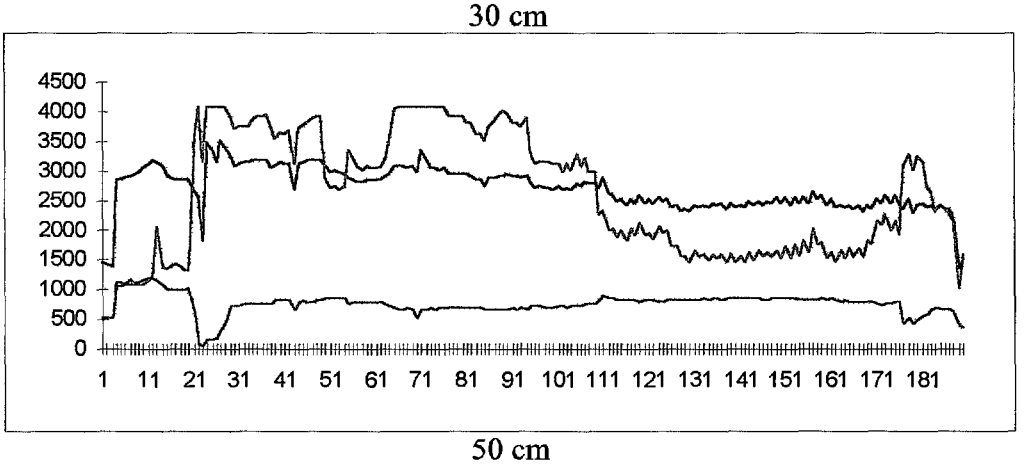
10 cm



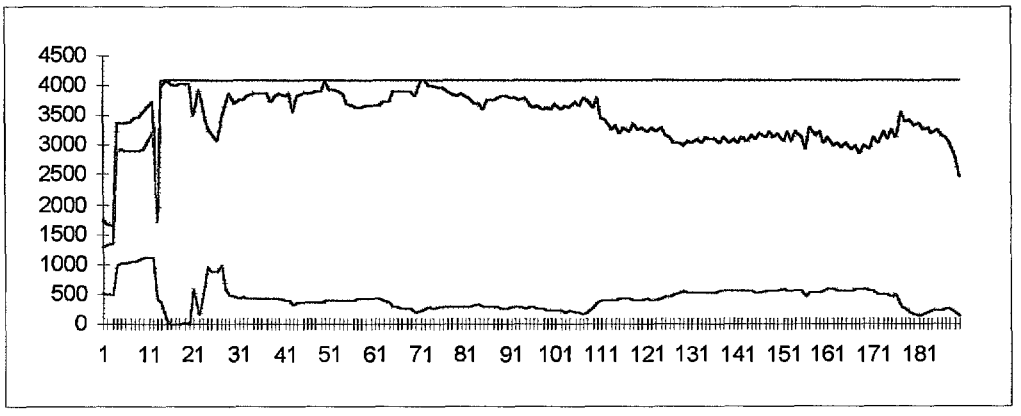
20 cm



30 cm



50 cm



x12h

Fig. 2b

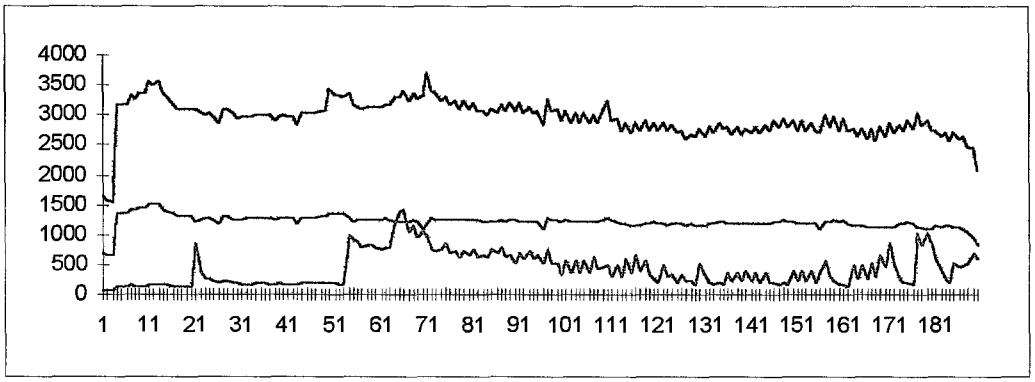
35

Soil type: Ramann brown forest soil, Gödöllő Plant: maize Loading: **30x**

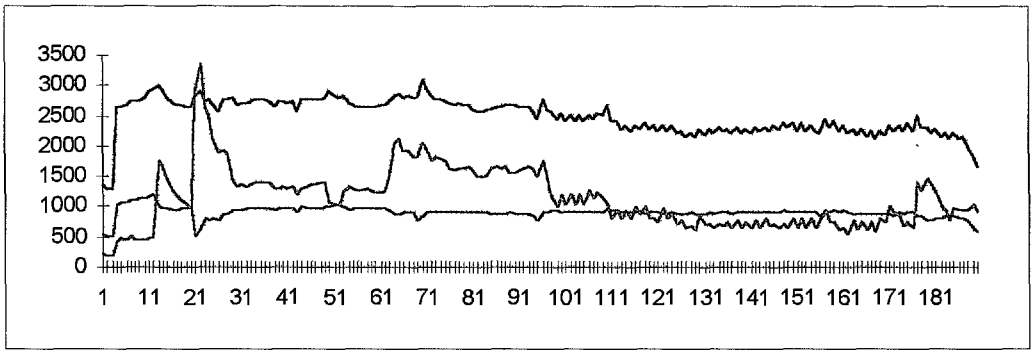
--------- Nitrogen --------- Oxygen --------- Carbon dioxide

I/I_0

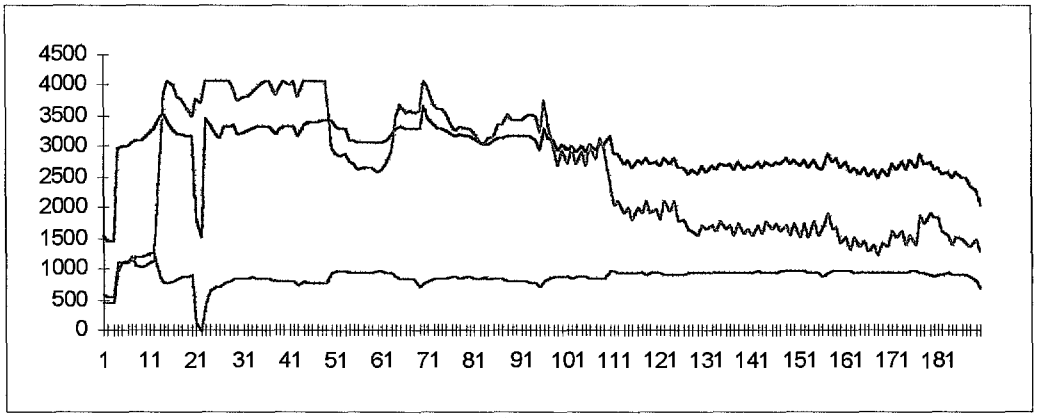
10 cm



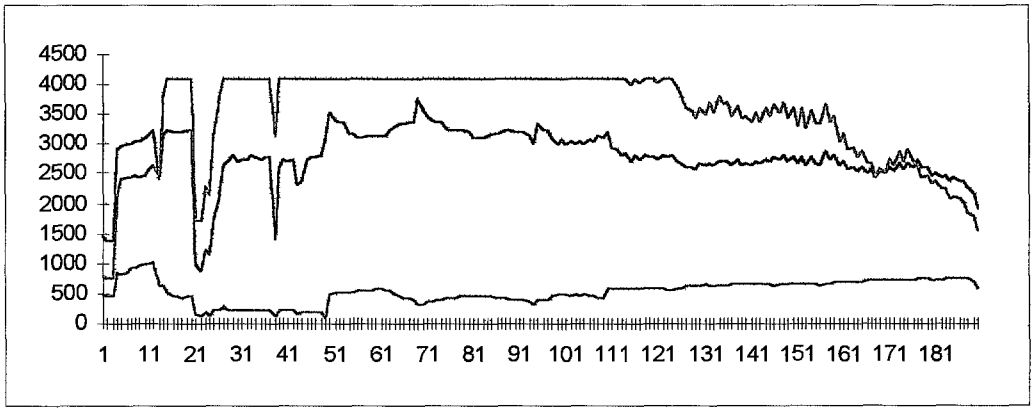
20 cm



30 cm



50 cm



x12h

Fig. 2c

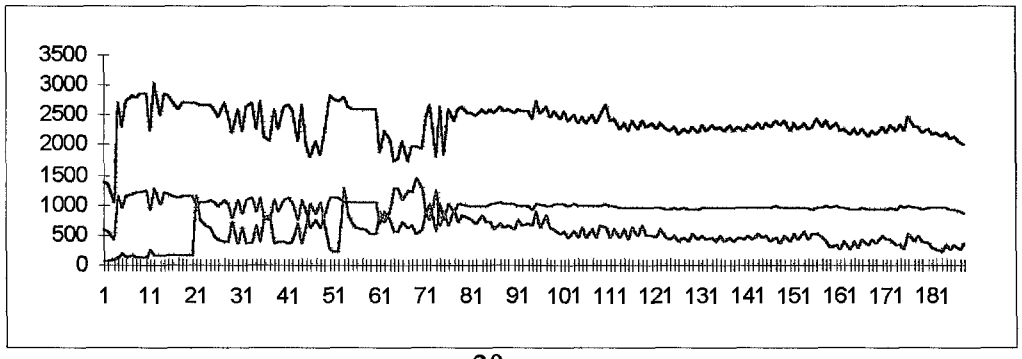
36

Soil type: Ramann brown forest soil, Gödöllő Plant: maize Loading: **100x**

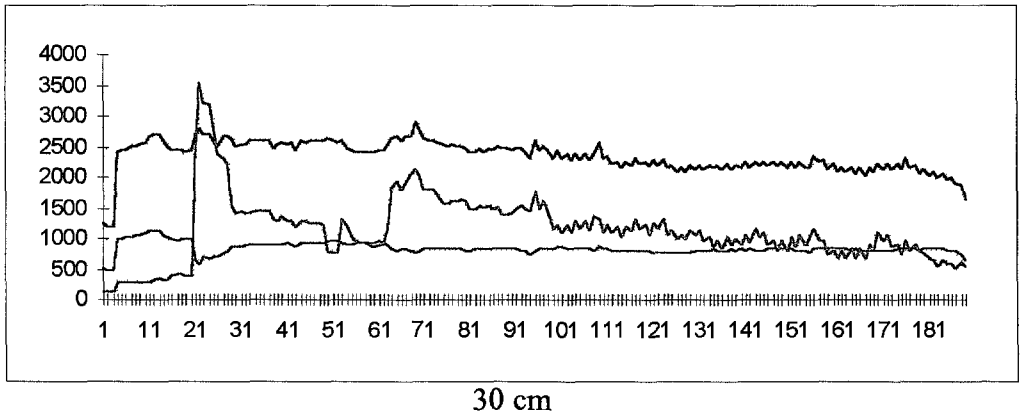
---------- Nitrogen ---------- Oxygen ---------- Carbon dioxide

I/I_0

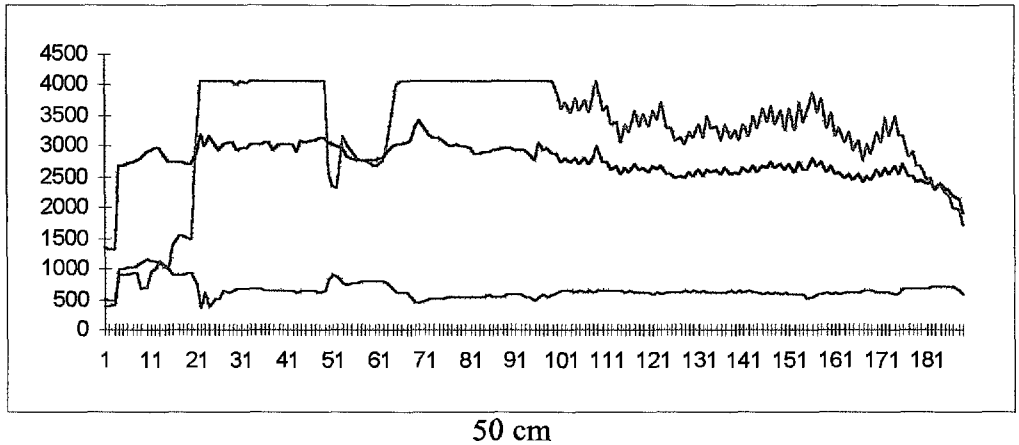
10 cm



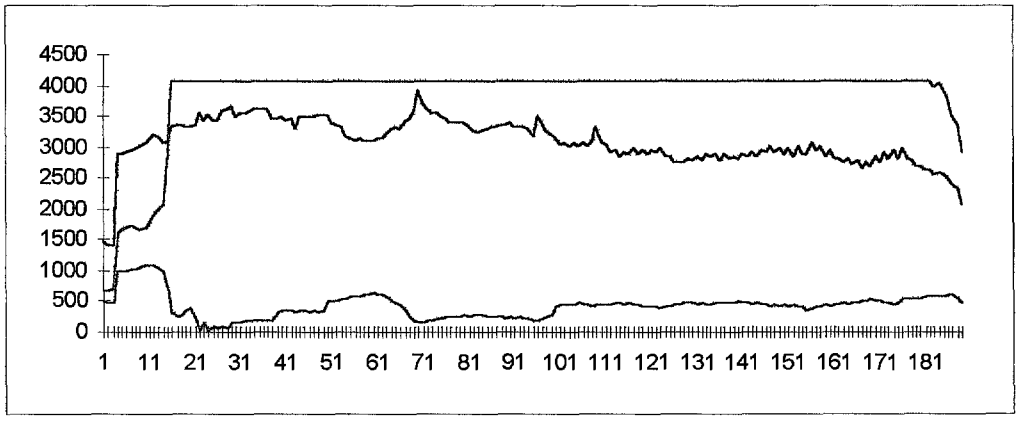
20 cm



30 cm



50 cm



x12h

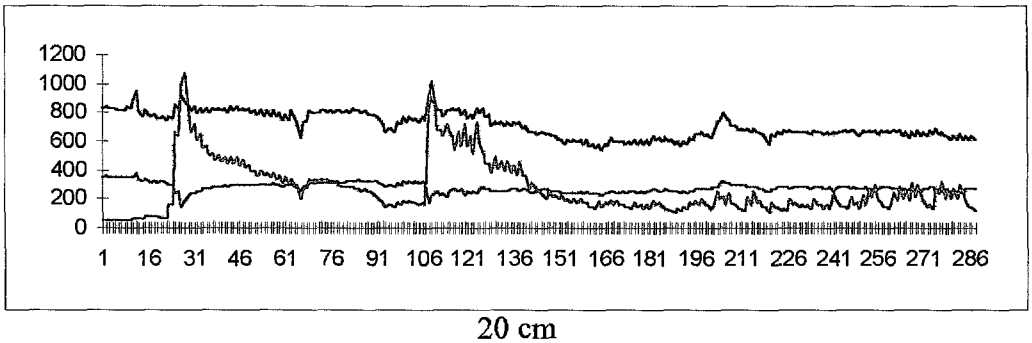
Fig. 2d

Soil type: Ramann brown forest soil, Gödöllő Plant: tomato Loading: **0x**

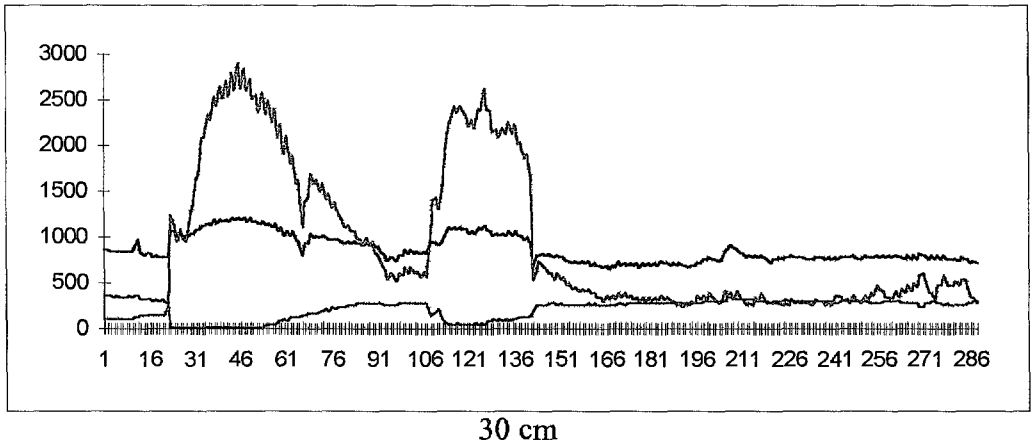
--------- Nitrogen --------- Oxygen --------- Carbon dioxide

I/I_0

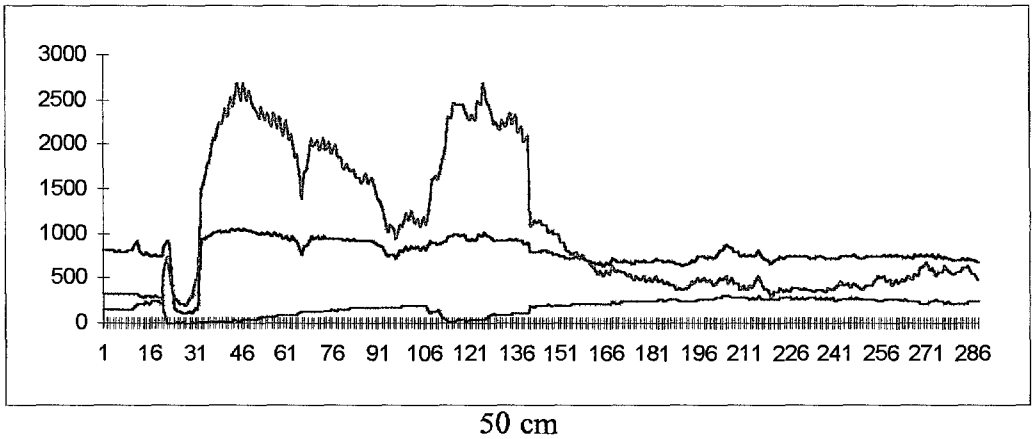
10 cm



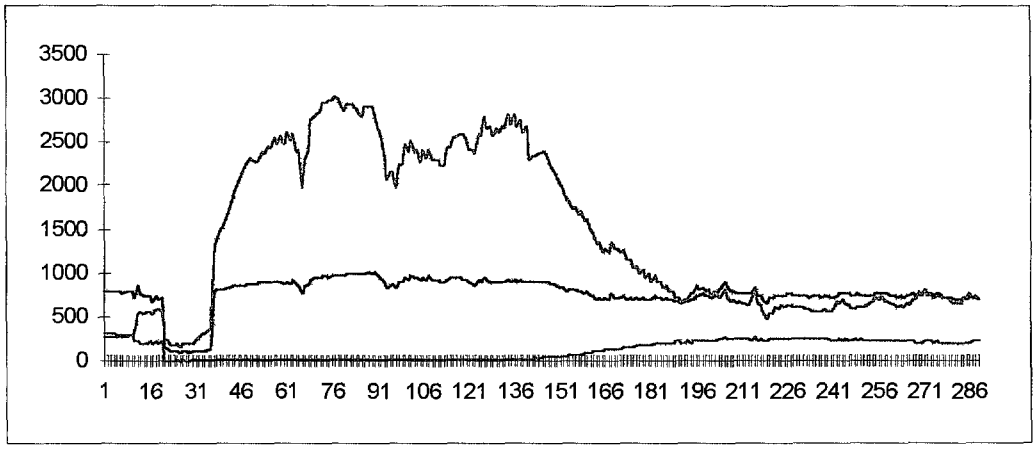
20 cm



30 cm



50 cm



x12h

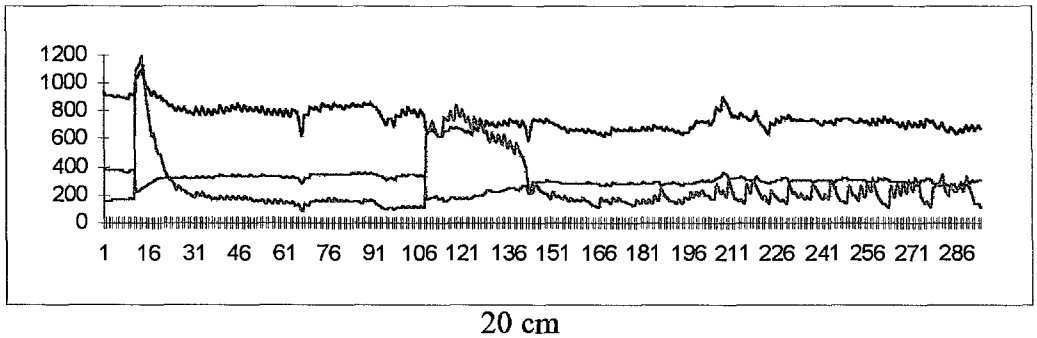
Fig. 3a

Soil type: Ramann brown forest soil, Gödöllő Plant: tomato Loading: **10x**

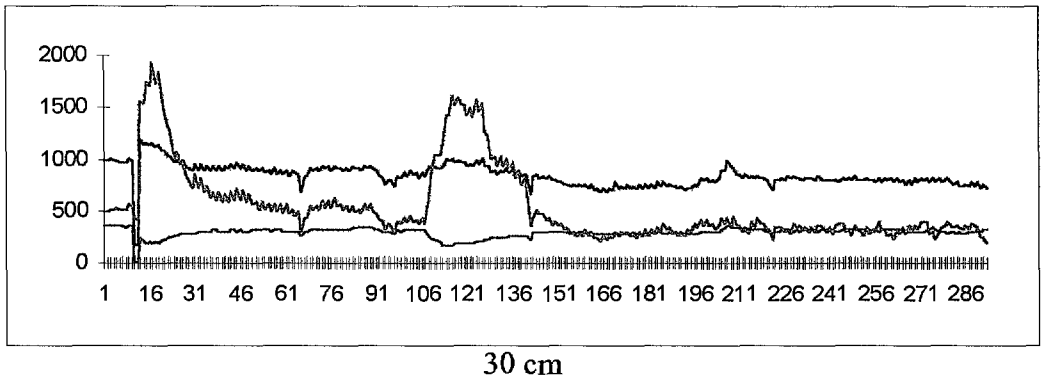
--------- Nitrogen --------- Oxygen --------- Carbon dioxide

I/I_0

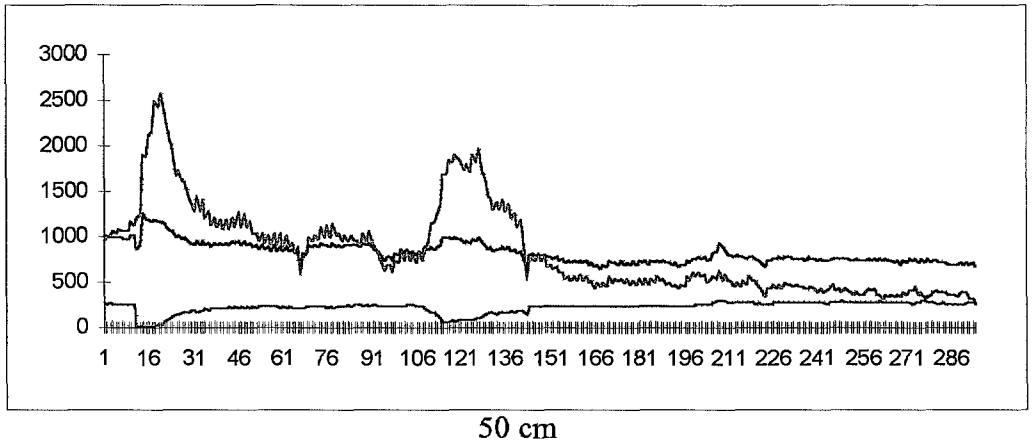
10 cm



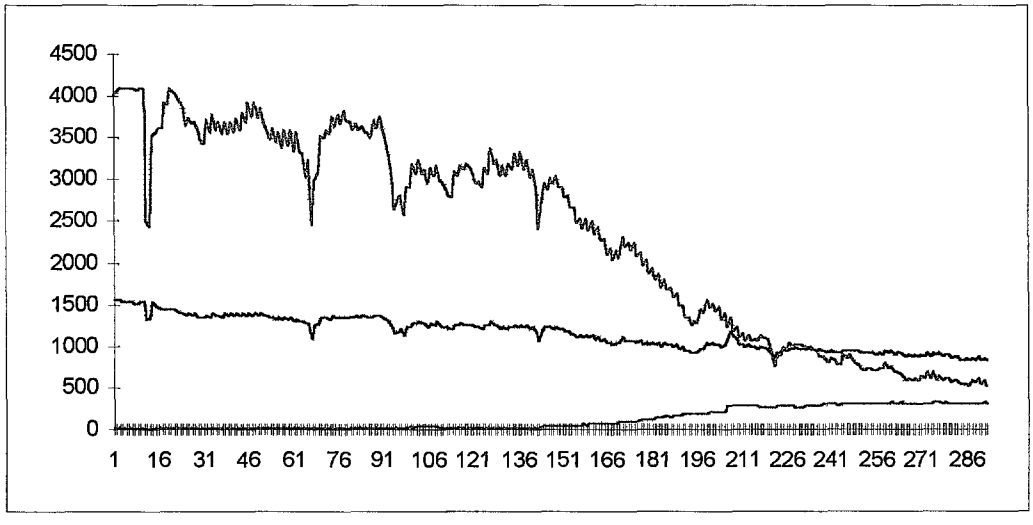
20 cm



30 cm



50 cm



x12h

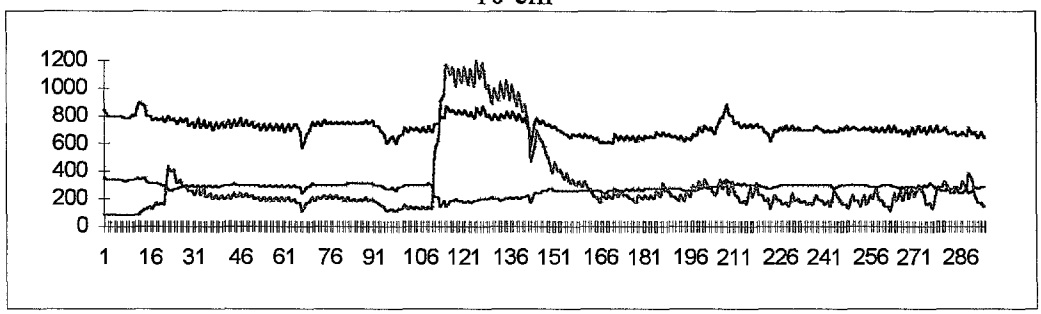
Fig. 3b

Soil type: Ramann brown forest soil, Gödöllő Plant: tomato Loading: **30x**

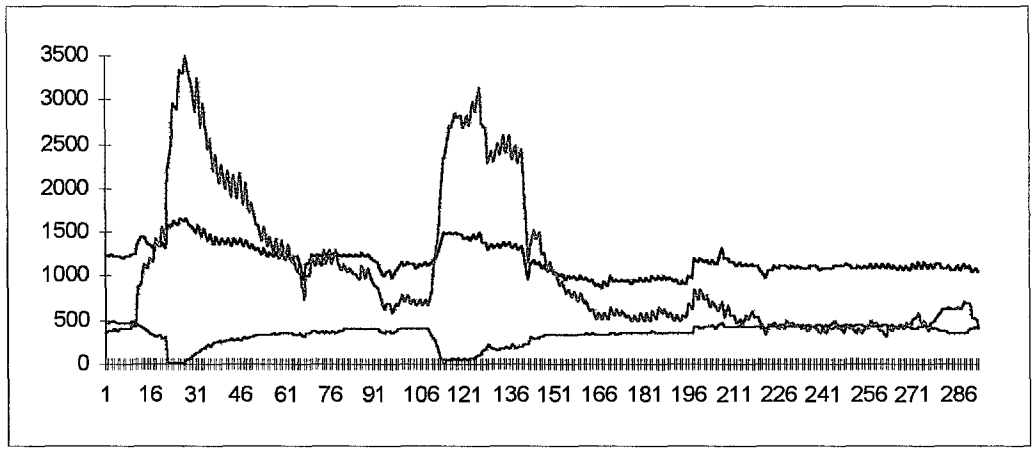
--------- Nitrogen --------- Oxygen --------- Carbon dioxide

I/I_0

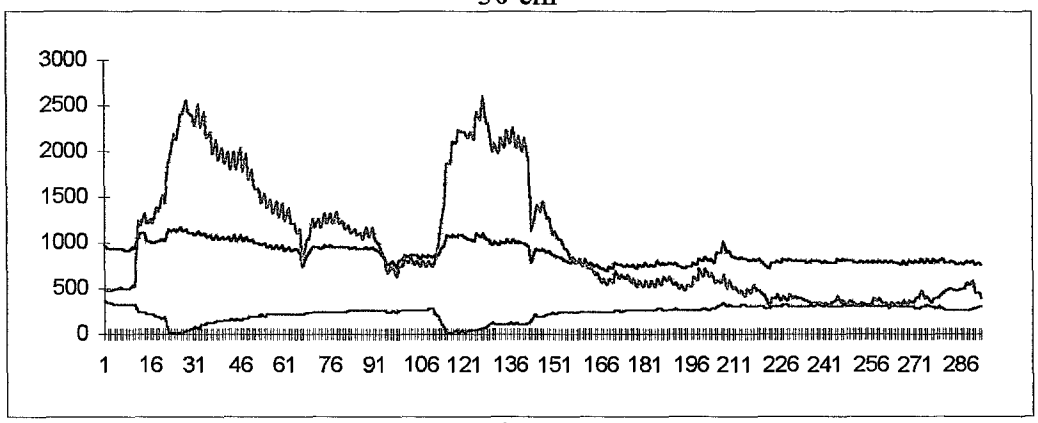
10 cm



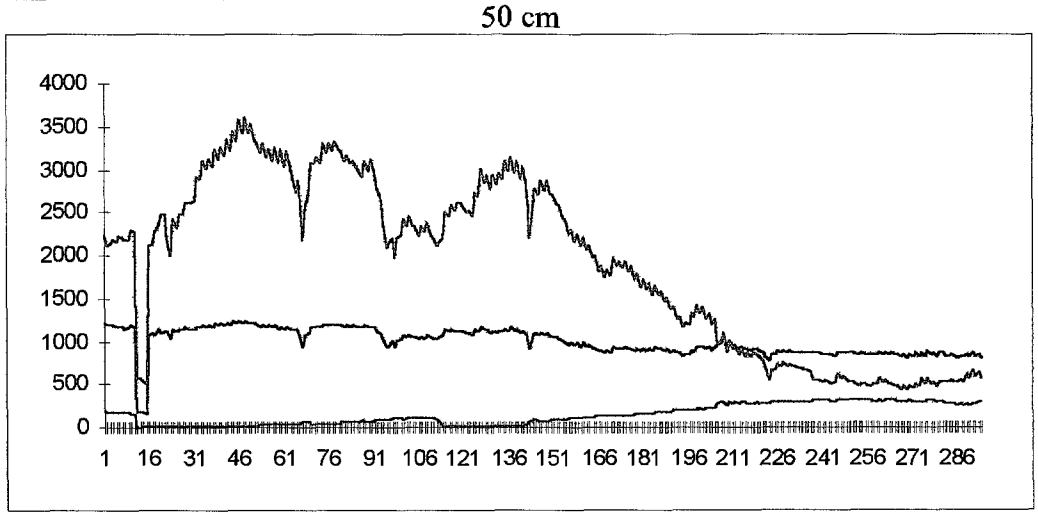
20 cm



30 cm



50 cm



x12h

Fig. 3c

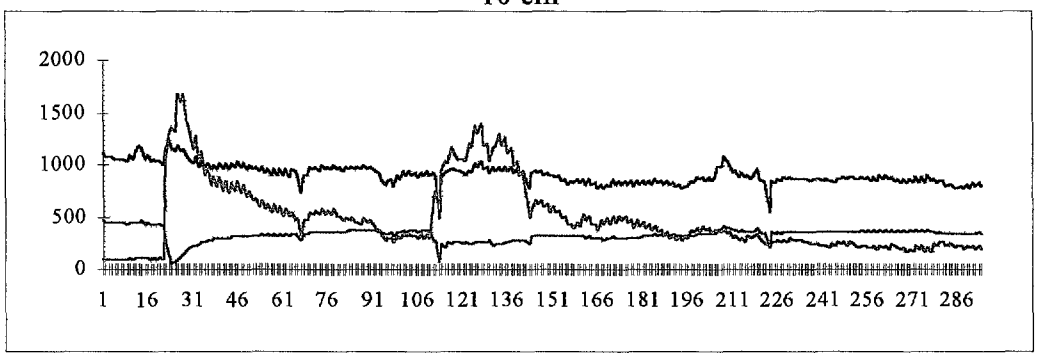
40

Soil type: Ramann brown forest soil, Gödöllő Plant: tomato Loading: **100x**

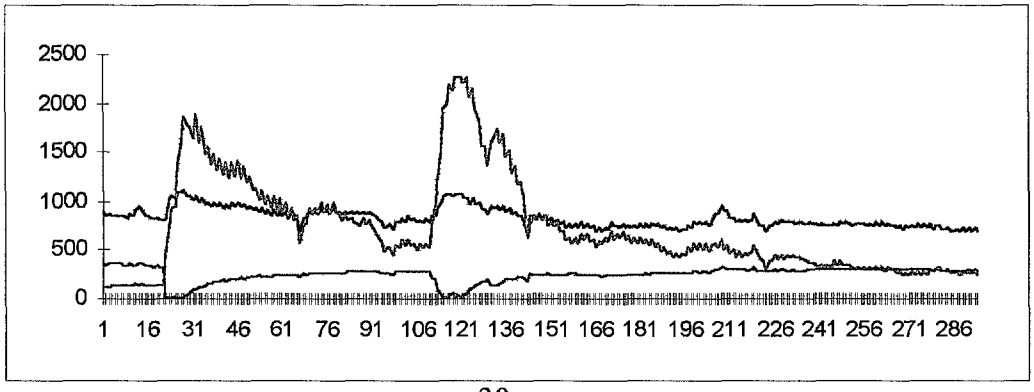
---------- Nitrogen ---------- Oxygen ---------- Carbon dioxide

I/I_0

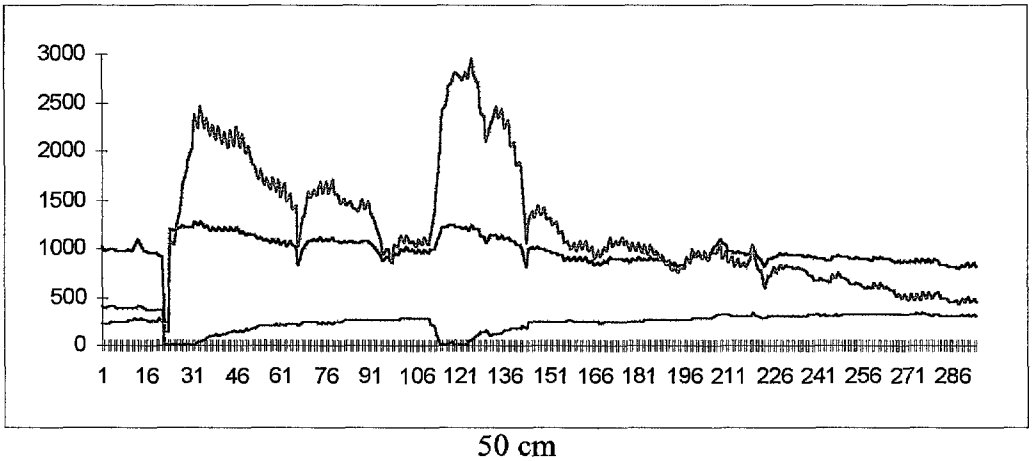
10 cm



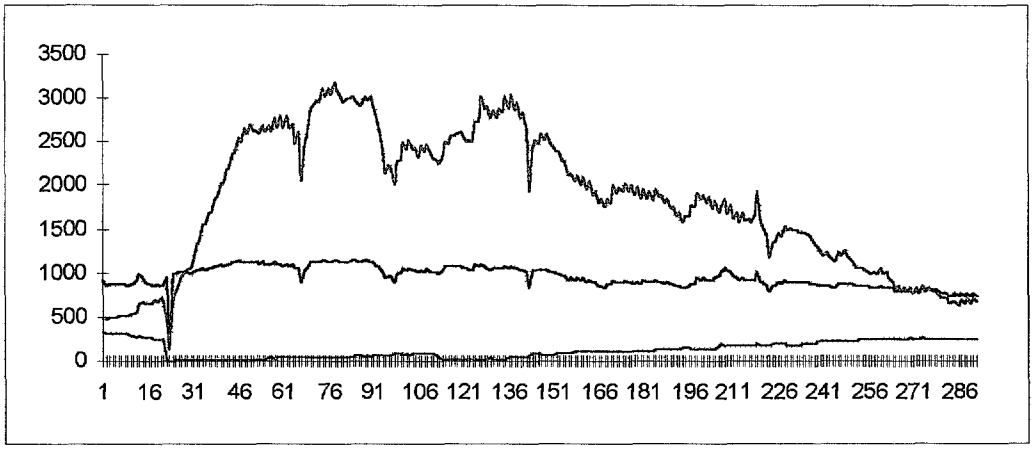
20 cm



30 cm



50 cm



x12h

Fig. 3d

Soil type: Sandy soil, Somogysárd Plant: maize Loading: **0x**

---------- Nitrogen ---------- Oxygen ---------- Carbon dioxide

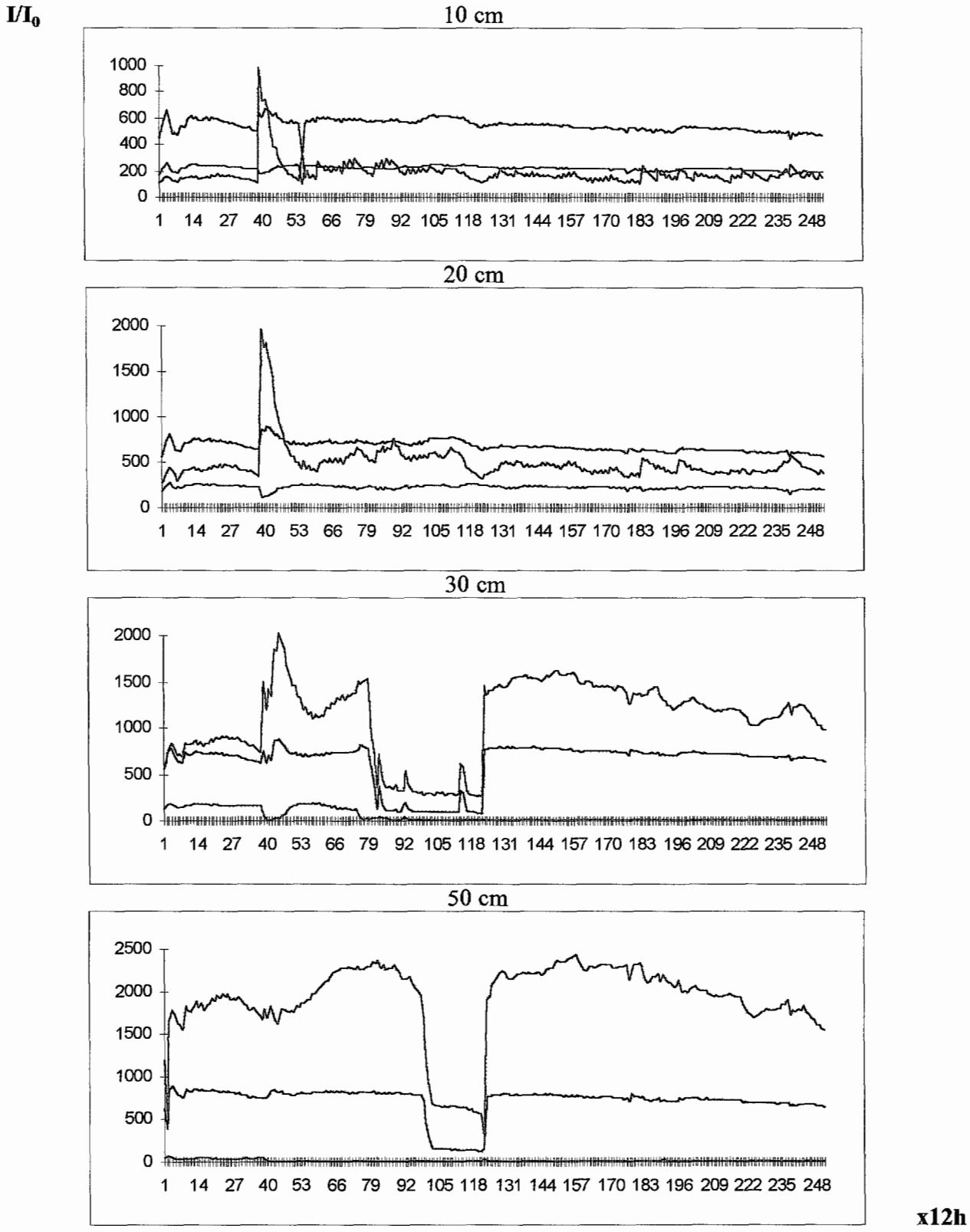


Fig. 4a

Soil type: Sandy soil, Somogysárd Plant: maize Loading: **10x**

---------- Nitrogen ---------- Oxygen ---------- Carbon dioxide

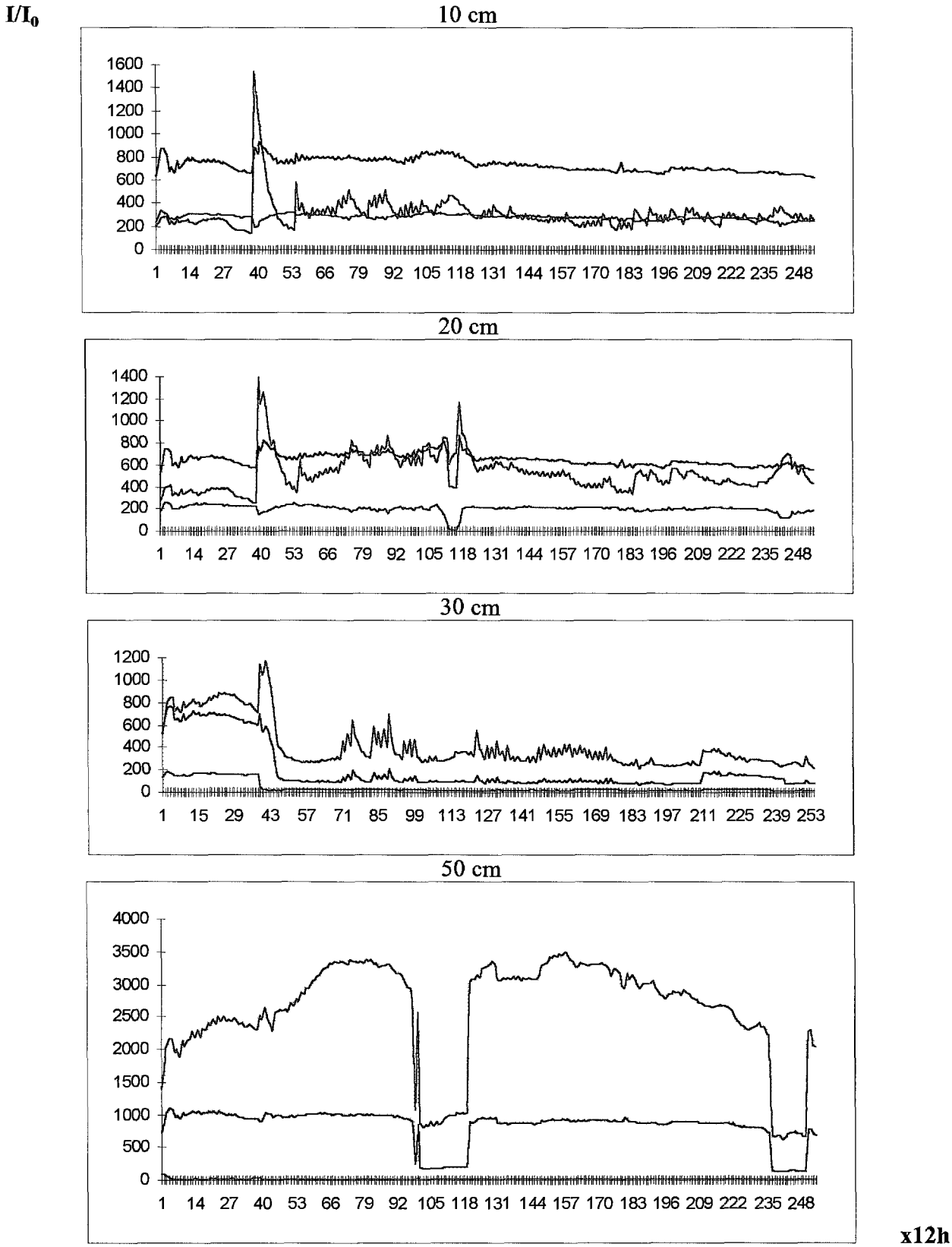


Fig. 4b

43

Soil type: Sandy soil, Somogysárd Plant: maize Loading: **30x**

--------- Nitrogen --------- Oxygen --------- Carbon dioxide

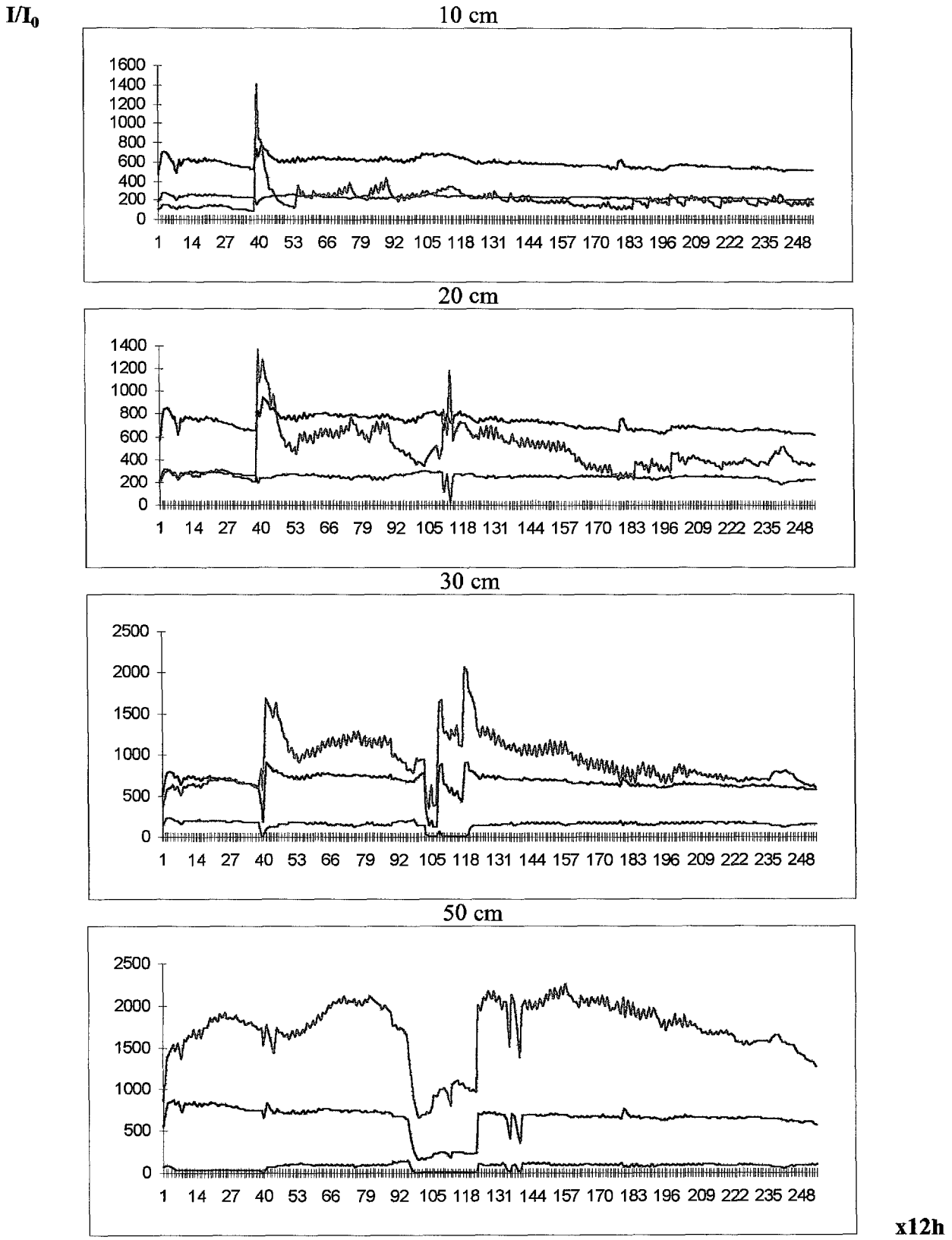


Fig. 4c

Soil type: Sandy soil, Somogysárd Plant: maize Loading: **100x**

--------- Nitrogen --------- Oxygen --------- Carbon dioxide

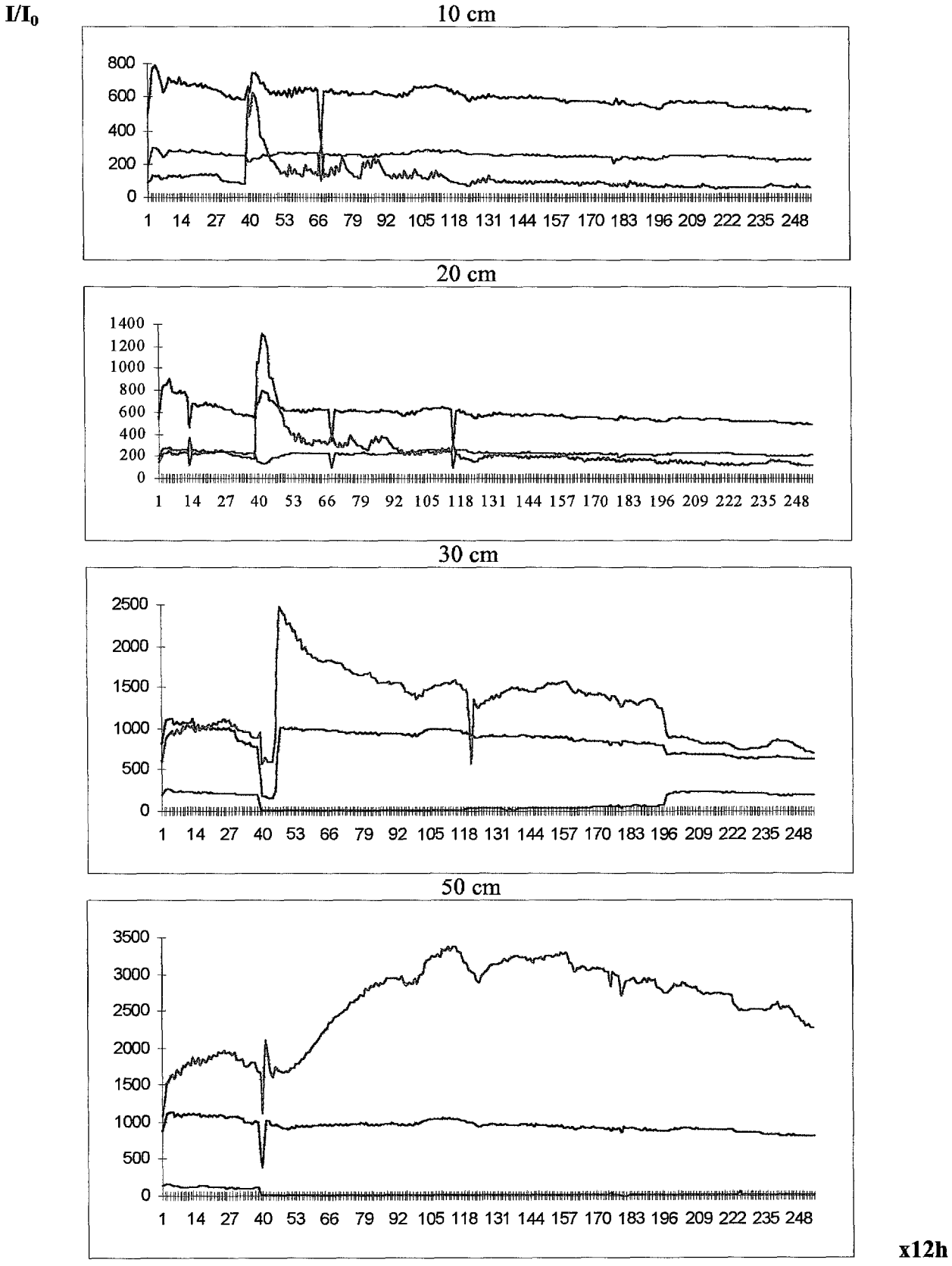


Fig. 4d

Soil type: Ramann brown forest soil, Gödöllő | Microsensor in plant | --------- Nitrogen --------- Oxygen --------- Carbon dioxide

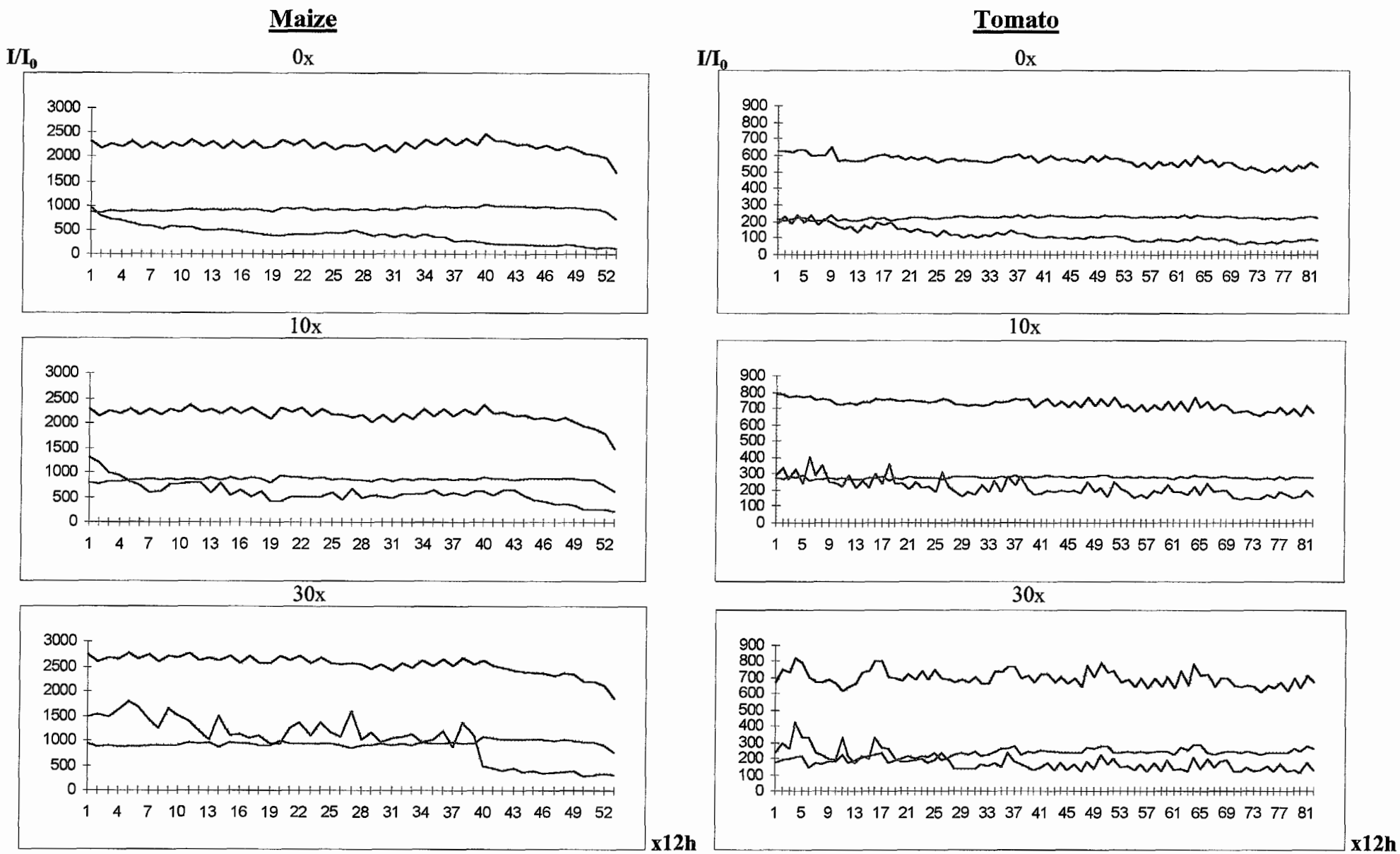


Fig. 5

Soil type: Sandy soil, Somogysárd Plant: maize |Microsensor in air| |Microsensor in plant|
-------- Nitrogen -------- Oxygen -------- Carbon dioxide

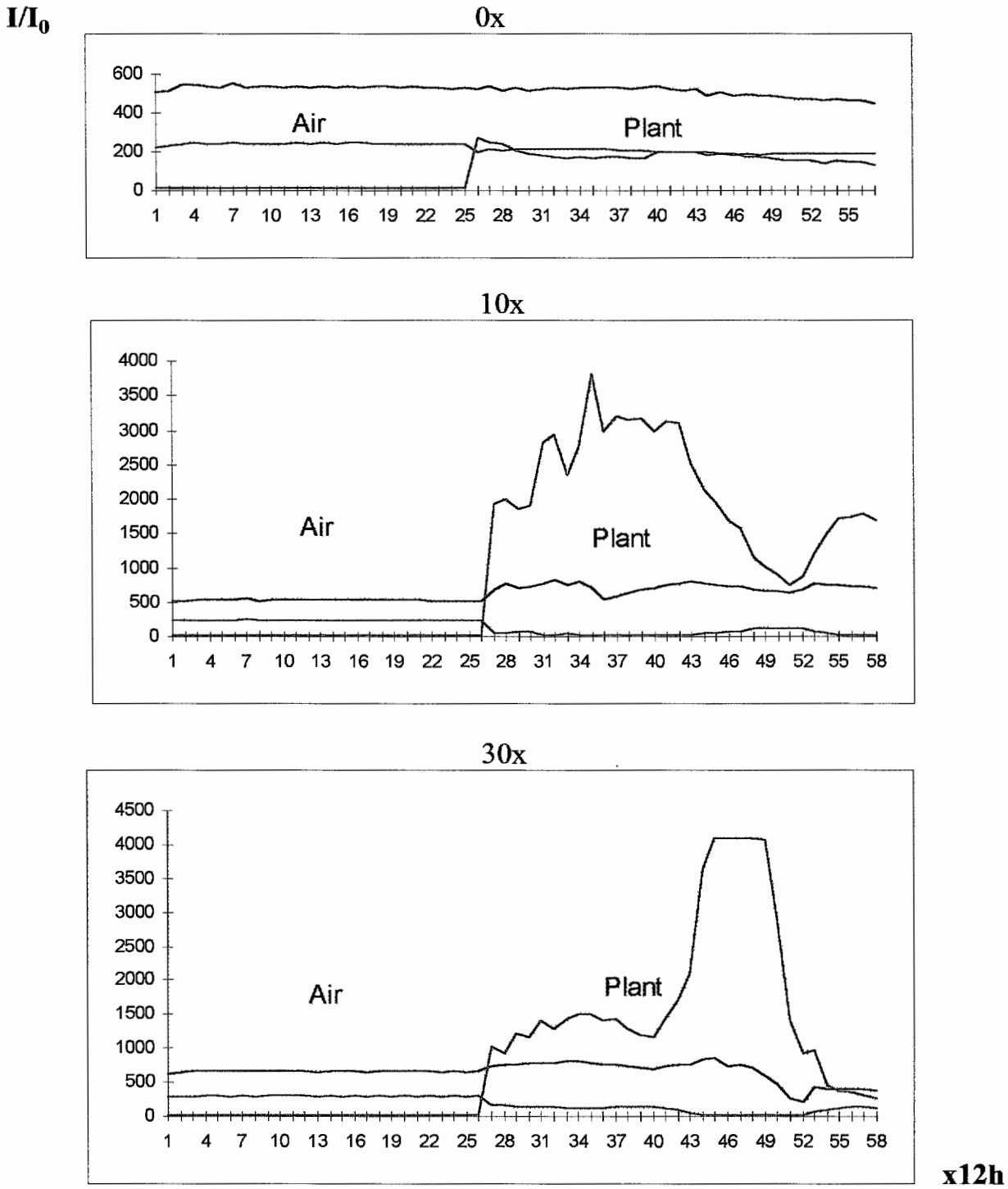


Fig. 6