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Soil Monolith Studies with Heavy Metal-Containing Sewage Sludge

G. PÁRTAY, A. LUKÁCS and T. NÉMETH

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

Introduction

One of the most rational and economic ways of disposing waste waters and sewage sludges is to apply them to agricultural fields, thereby utilizing their nutrient contents. Both industrial and communal sludges contain several heavy metals in appreciable quantities. Their level in the sludge is one of the limiting factors of sludge application (LUKÁCS et al., 1984). Despite the strict regulations (Hungarian Technical Directives, 1990), the presence of various toxic components, including heavy metals, in these sludges may pose a potential threat to the ecosystem under changing environmental conditions. Both the plant uptake of these elements and their effects on plant metabolic processes depend on the presence and metabolic behaviour of other trace elements (CHANG et al., 1992). The simultaneous application of subtoxic amounts of several metals present in these sludges may cause unexpected toxic effects in the soil-plant system and consequently in the food chain, when environmental conditions change.

Changes in the gas phase inside the plants were shown to respond characteristically to various stress agents, such as water and temperature stresses, increased concentration of mineral salts, pesticides, etc. (Hungarian Patent, 1982; PÁRTAY et al., 1987). Also, qualitative and quantitative changes in the gas composition in the soil may reflect the extent of stress effects caused by heavy metal pollution (PÁRTAY et al., 1992).

The aim of the present study was to determine the changes in the soil gas phase due to the effect of different treatments (physical and chemical), and also to assess stress situations both in the soil and in plants, caused by the application of metal-enriched sewage sludge onto cropped, undisturbed soil monoliths under laboratory conditions. Changes in the amounts of water vapour, CO_2, O_2 and N_2 in the soil and inside plant stems were measured using quadrupole mass spectrometry. A recently developed experimental set-up (NÉMETH et al., 1993) allowed *in situ* and *in vivo* measurements to be conducted using 20 microprobes simultaneously (Figure 1). These were placed at several depths along the soil profile of monoliths loaded with different amounts of Zn, Ni, Cd, Pb and Cr. Changes in the composition of the gas phase in soils often predict stress situations in growing plants under different kinds of agrotechnical treatments. To model the effect of adding heavy metal-containing sewage sludges to the soil on the soil gas phase, laboratory experiments were carried out with undisturbed soil monoliths. Gas concentrations were measured with a computerized 20 channel Quadrupole Mass Spectrometer (QMS).

Materials and Methods

The quadrupole mass spectrometer (QMS) system used in the experiments was developed in the Research Institute for Nuclear Physics, Hungary. Its specially-designed 20-channel inlet system for 20 microprobes permitted simultaneous, independent measurements in the 1-300 atomic mass range. The microprobes were made of stainless steel capillaries (size No.1 serum needle material) and the tips were covered by a special coating. Gases freely moving in air-filled soil micropores or in the central lumen of plant stems are able to enter through this special coating into the microprobe and reach the inlet port of the mass spectrometer. Also, gases dissolved in the liquid phases in soil and plants can diffuse through the special covering into the microprobe. The concentrations of water vapour, N_2, O_2 and CO_2 were recorded in the present experiment. Automatic, computer-controlled collection of data from the 20 microprobes operated continuously during the whole experiment.

Four undisturbed soil monoliths were used simultaneously under identical environmental and soil physical circumstances. The soil was a strongly leached typical Ramann brown forest soil (Eutrochrept). Its main characteristics are shown in Table 1.

Large undisturbed monoliths of 40 cm diameter and 100 cm height were excavated at a field site, and coated with fibre glass cloth impregnated with a

Table 1

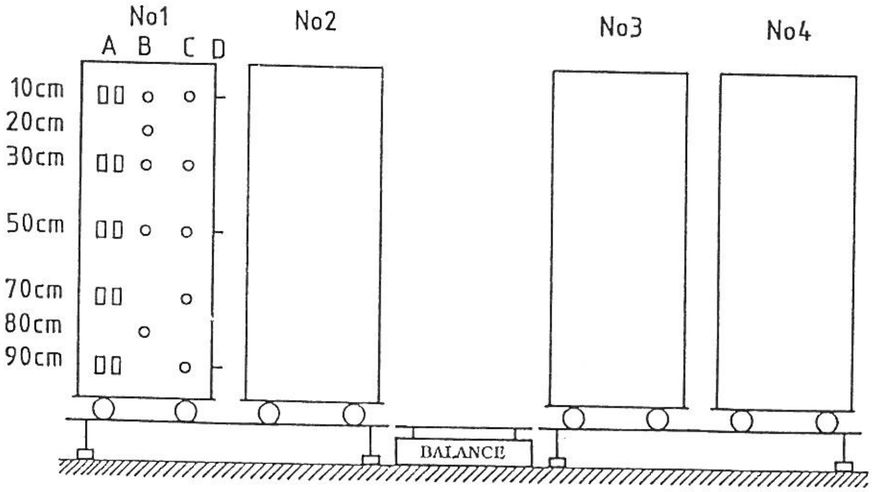
Some characteristic properties of the Ramann brown forest soil

Level	Depth cm	pH_{KCl}	$CaCO_3$ %	Org-C %	CEC meq/100g	Sand % >0.05	Silt % 0.05-0.002	Clay % <0.002
A_{org}	0-8	5.02	0.21	1.05	8.99	74.0	17.8	8.2
A_1	8-16	5.29	0.15	1.24	8.55	74.9	17.1	8.0
B	16-43	5.01	0.13	1.09	8.55	71.0	18.9	10.1
BC	43-66	5.24	0.13	-	10.15	70.1	19.1	10.8
C	66-	5.73	0.13	-	57.97	22.9	42.3	34.8

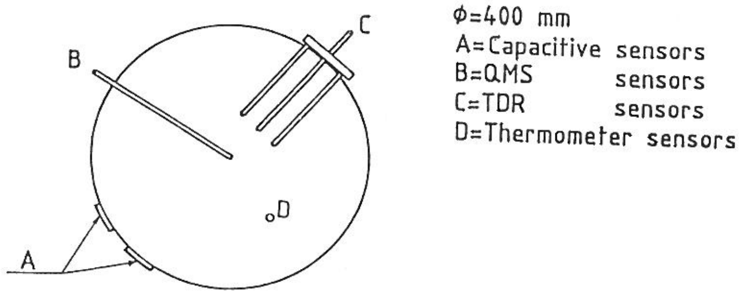
synthetic resin (HOMEYER et al., 1973; NÉMETH et al., 1991). After the coatings solidified, the monoliths were transported to the laboratory, and the QMS microprobes, together with sensors for measuring water content and temperature, were inserted through the coating at several depths along the soil profile.

Uniform soil physical circumstances were obtained by saturating the whole profile with deionized water through a valve built into the bottom of the monoliths, then applying gravitational drainage. After drainage, the soil moisture content was regulated by sprinkler irrigation on the surface.

Nitrate salts of Zn, Ni, Cd, Pb and Cr were added to subsamples of compressed municipal sewage sludge to reach 1, 10, 30 and 100 times their respective maximum permissible limits (MPL) in sludges, as specified by the Hungarian Technical Directives for agricultural sludge application (1990). The MPL values for the specific soil were 25 mg Zn, 1.67 mg Ni, 0.125 mg Cd, 8.3



SIDE VIEW



VIEW FROM ABOVE

Figure 1
Scheme of the experimental set-up

mg Pb and 8.3 mg Cr per kg soil. Identical amounts of the metal-enriched sludges were applied to the top 10 cm layer of the 4 soil monoliths to ensure the same organic matter content at different metal loadings. After sludge application, maize (*Zea mays L.* var. Pioneer 3271) was sown and grown to full maturity on the monoliths.

Figure 1 shows the scheme of the experimental set-up. Three thermometer sensors, six soil moisture probes attached to a TDR multiplexer (a Time Domain Reflectometer was used for moisture measurements) and ten special microsensors for the measurement of gas composition, coupled to the QMS, were built into every soil monolith. In addition, 5 pairs of measuring points for a capacitive soil moisture meter were attached to the coatings. Automatic collection and analysis of QMS and TDR data from the columns operated simultaneously during the experiments.The computer unit also controlled the ion source and vacuum systems of the mass spectrometer itself. Column weights were recorded on a movable scale.

The QMS system - specially developed for such experiments - enabled 20 simultaneous, independent measurements to be made in the 1-300 atomic mass range without any time limitation. In our study the range 17-56 was used for determining nitrogen (28), oxygen (32), argon (40), carbon dioxide (44), resin from the coating (55) and also water vapour (18).

Soil moisture contents in the monoliths were regulated by saturating the columns from the bottom through a special valve, or by sprinkler irrigation at the surface. Water was added on the basis of TDR measurements. Sufficient light was ensured in 12-hour day/night cycles for later plant experiments.

The prepared monoliths were air-dried to constant weight (initial stage, Figure 2) and then gradually filled up to the surface through the bottom tap with deionized water (saturation, Figure 3). The columns were then drained by gravitation to the equilibrium state (drainage, Figure 4).

This was followed by the addition and mixing of compressed sewage sludge, enriched with Cd, Pb, Cr, Ni and Zn nitrates, into the upper 10 cm of the monoliths (sludge addition, Figure 5). The loadings applied were 0, 10, 30 and 100-times the upper limit (MPL) of the Hungarian Standard. (The number of columns in Figures 1 to 7 are: No. 1, No. 4, No. 3 and No. 2, respectively).

Maize (*Zea mays L.*) was sown in the monoliths one week after sludge application. Seven weeks after sowing microprobes were implanted to study the gas metabolism in the plants (Figures 6 and 8, A series).

At the end of the 164-day experiment (Figures 7 and 8, B series) plants were harvested and the upper parts of the the four soil columns were separated into 10 to 30 cm layers. Soil samples were analysed after centrifugation and extraction, plant samples after wet digestion.

Results

Figure 2 shows the gas concentrations of the air-dry soil columns under controlled laboratory conditions (*initial stage* or ground state). All gases in all the four columns show similar concentration levels along the profile.

After saturation with deionized water - compared to the ground state - water vapour had a minimum and CO_2 had a maximum in the 30-50 cm layer. This suggests a more compact soil layer at this depth, which could already be observed in the field, when the monoliths were prepared. The measured anomaly matched the observation. Nitrogen concentration decreased in the upper layers, while O_2 hardly changed (Figure 3).

After drainage the water vapour and oxygen concentrations decreased with depth, while nitrogen was balanced on a lower level along the whole profile. Carbon dioxide was antagonistic to both water vapour and oxygen (Figure 4).

Three weeks *after sludge addition* only water vapour and CO_2 exhibited significant changes in their concentrations: the former decreased, the latter monotonously increased down the monolith profile (Figure 5).

Seven weeks after sowing, 2 months after sludge addition, three microprobes were removed from the 80 cm depths of the monoliths and transferred into the stems of the maize plants. The plant grown on the monolith with 100x loading was too tiny to bear the implantation. The most pregnant change could be observed here at the 80 cm depth: an increase in water vapour and a decrease in nitrogen and carbon dioxide concentrations (Figure 6).

The gas concentrations measured in the stems of the plants differed considerably from the corresponding soil gas concentrations at depths of 10 and 20 cm. It could be ascertained that the RQ value of the plant (CO_2/O_2) was well under 1.0, so no stress status had developed in the plants, even at the 30x loading. At both loadings the N_2 and CO_2 concentrations increased, while the water vapour concentration decreased as compared to the control (Figure 8, A series).

At the end of the experiment (3 months after sowing) the gas distributions in the soil monoliths were simlilar to the state shown in Figure 6, except that at the 10x and 30x loadings, slightly elevated dynamics were apparent for all the gases in the deeper layers (Figure 7).

In the plants the CO_2 concentration was higher and the O_2 concentration lower, compared to the control state (Figure 8, A series), which indicated the gradual development of stress status. In all plants the concentrations of O_2 and N_2 decreased, while the concentrations of CO_2 and water vapour increased (Figure 8, B series).

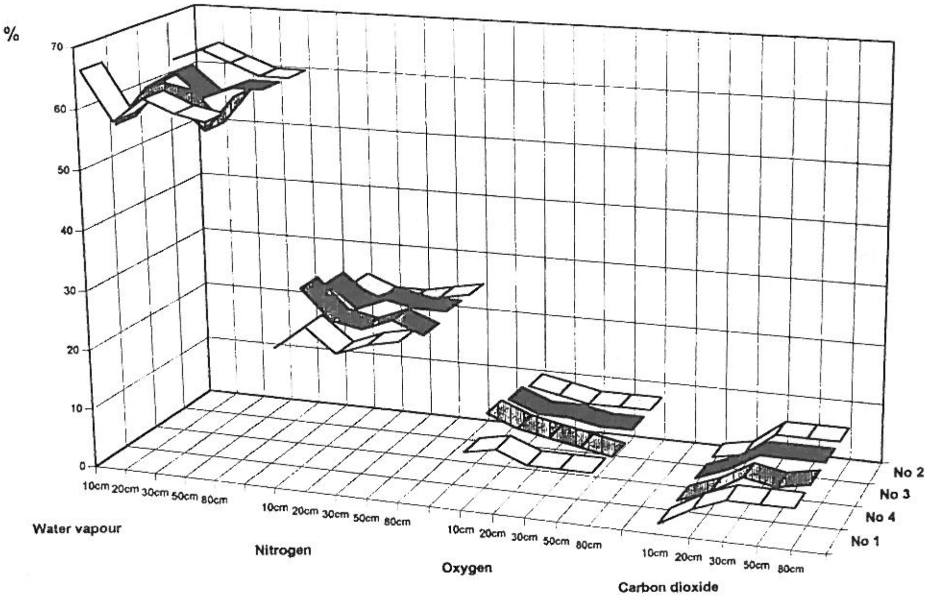


Figure 2
Gas concentrations in the air-dry soil columns

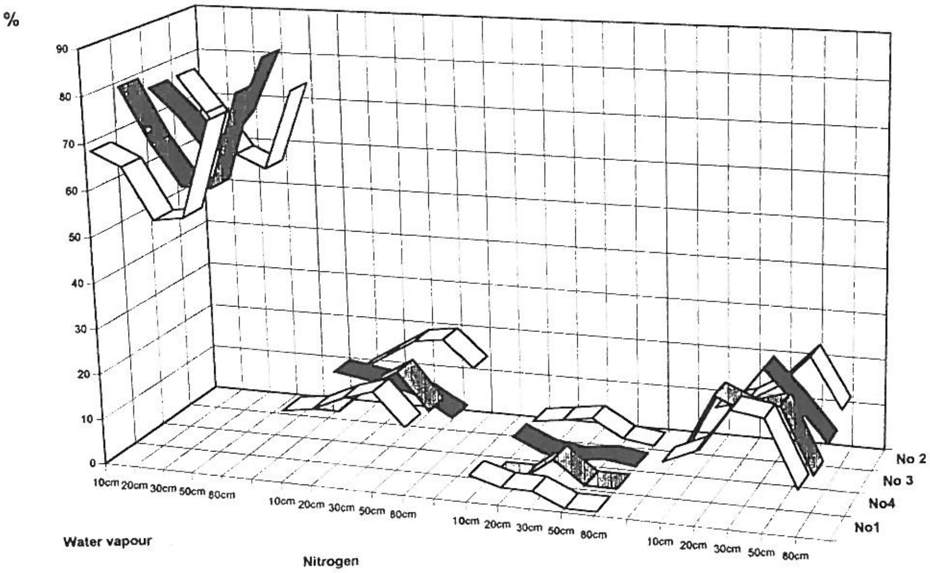


Figure 3
Gas concentrations in the monoliths after saturation with deionized water

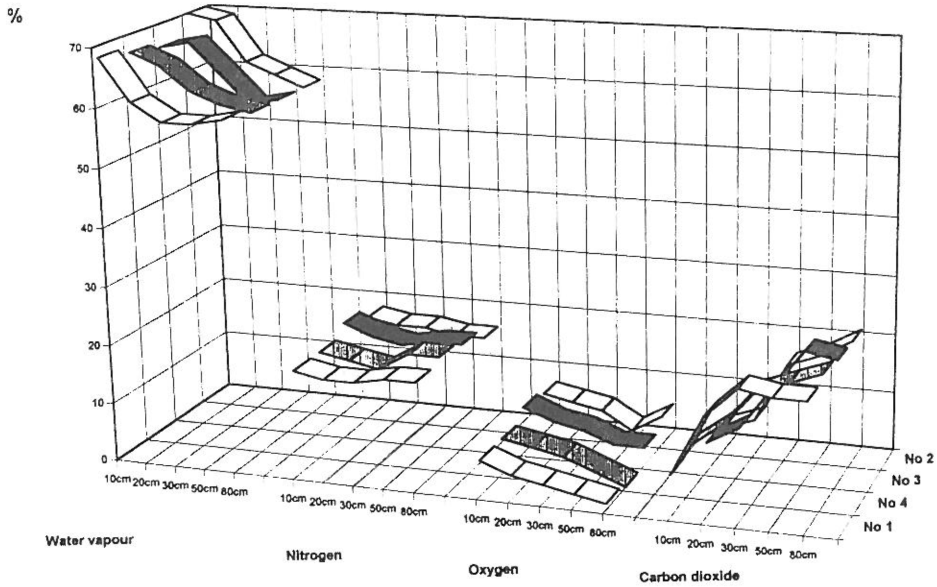


Figure 4
Gas concentrations in the monoliths after drainage

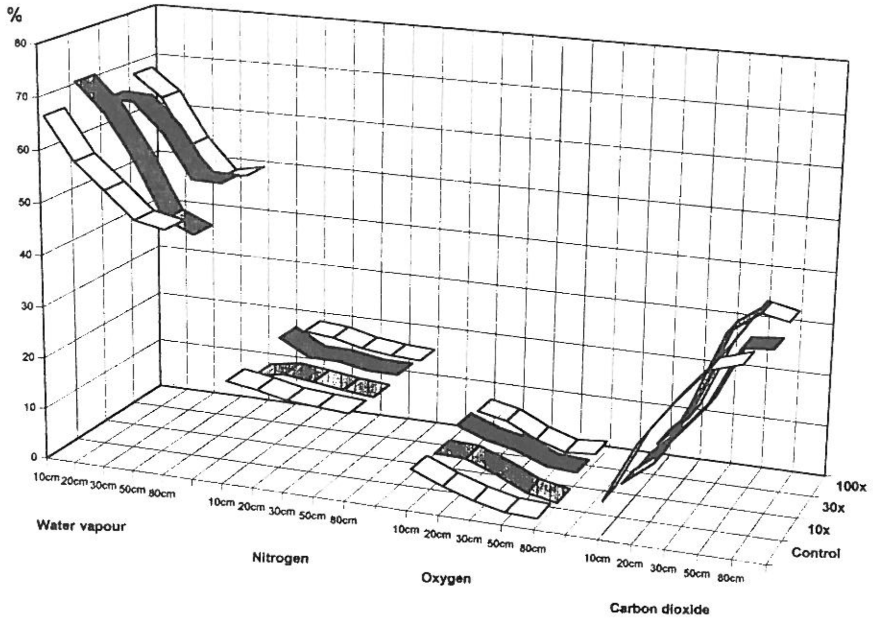


Figure 5
Gas concentrations in the monoliths three weeks after sludge addition

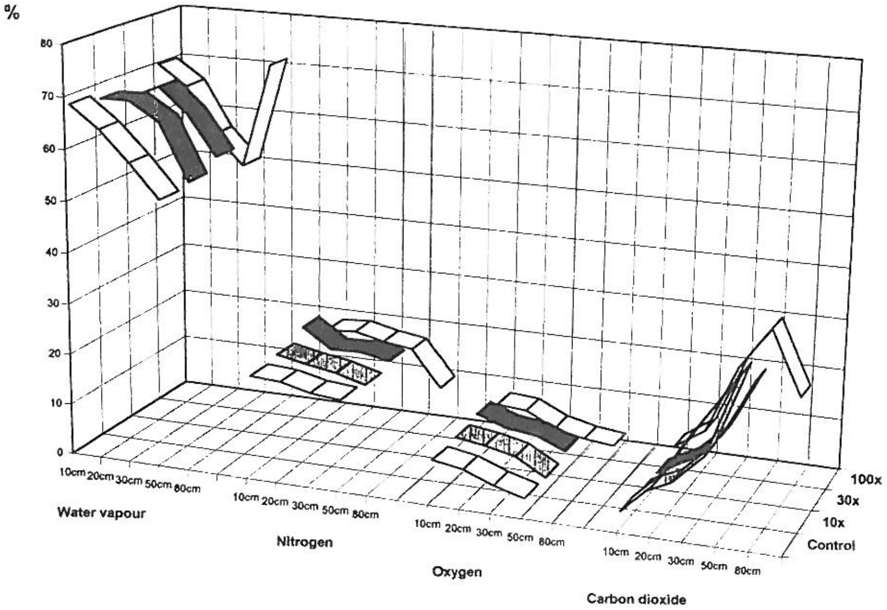


Figure 6

Gas concentrations in the monoliths two months after sludge addition (seven weeks after sowing)

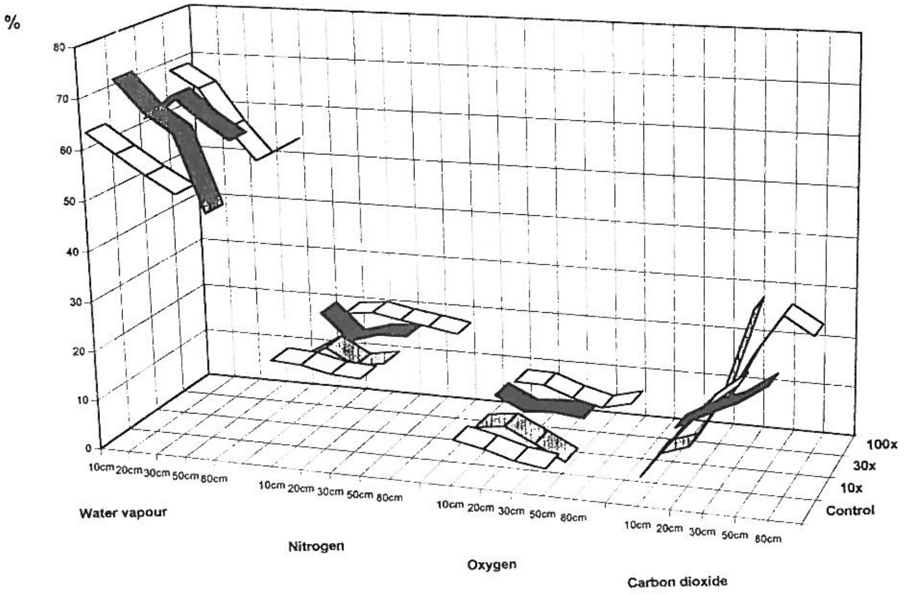


Figure 7

Gas concentrations in the monoliths at the end of the experiment

The distribution of heavy metals in the upper 30 cm of the soil monoliths was determined after separation and analysis of the upper 30 cm sections of the monoliths.

No movement of Pb, Cr and Cd was found down the soil profile - below the upper 10 cm layer of the monoliths, and Zn and Ni also showed very little movement even at the highest loading rate (Table 2)

Table 2

Distribution of heavy metals (μg/g) in the upper 30 cm of the soil monoliths after harvesting the maize plant

Treatment	Cd	Cr	Ni	Pb	Zn
Control					
0-10 cm	1.34	13.6	15.5	15.9	100
10-15 cm	0.77	8.5	12.0	11.8	34.7
15-20 cm	0.73	8.0	10.8	11.1	34.6
20-30 cm	0.75	7.9	11.0	11.4	27.6
10x loading					
0-10 cm	3.30	1.30	47.0	138	503
10-15 cm	0.91	11.2	11.0	14.3	39.0
15-20 cm	0.89	9.0	10.8	12.3	30.2
20-30 cm	0.84	9.0	11.3	12.5	29.6
30x loading					
0-10 cm	5.8	292	74.7	310	1011
10-15 cm	0.89	9.6	12.4	14.3	36.8
15-20 cm	0.95	8.8	11.7	11.9	30.3
20-30 cm	0.88	9.1	11.7	11.8	29.0
100x loading					
0-10 cm	11.4	687	150	736	2092
10-15 cm	0.95	10.9	19.3	13.4	49.7
15-20 cm	0.99	10.3	13.8	13.2	38.1
20-30 cm	0.97	9.2	11.9	12.8	30.0

(three months after sewage sludge application - spiked with different amounts of heavy metals - to the upper 10 cm of the monoliths). Digestions were made by 2N nitric acid on 100 °C. Analysis: by ICP spectrometry.

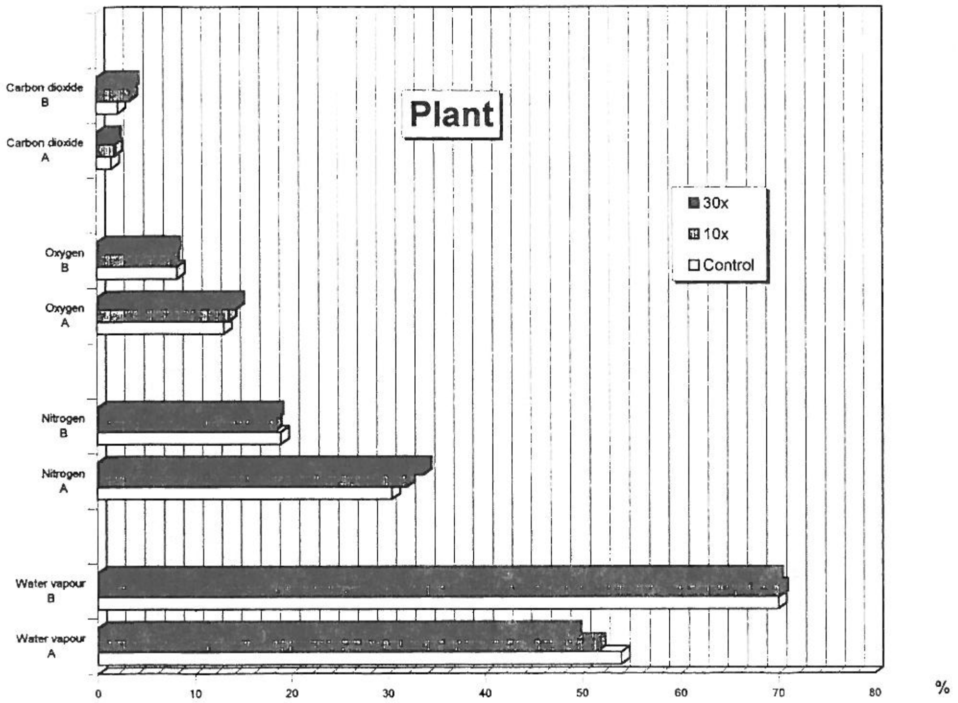


Figure 8
Gas concentrations in the maize plants seven weeks after sowing ("A series) and at the end of the experiment ("B" series)

Conclusions

The quadrupole mass spectrometer equipped with a new 20-channel inlet system proved to be suitable for continuous (uninterrupted) measurement of the changes in the soil gas phase. During the 164-day experiment, water vapour and carbon dioxide levels showed the highest sensitivity to changes in the chemical and physical properties in the soil profile; nitrogen had less response and oxygen the least. The composition of the soil gas phase in the root zone was clearly different from the gas composition inside the plants. After the 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. The gas concentrations in soil and plants were not proportionally dependent on the metal loading rates applied to the top soil layers. This may have been the result of an adaptation of the relatively slowly changing gas concentration values to the elevated metal levels.

Further research

The results shown in this article covered only a quarter of the planned research period. Problems to study in the future are the following:

- Further clarification of the relationship between soil gas phase and heavy metal loadings;
- Finding the causes of concentration changes in the deeper layers of the soil monoliths;
- Study on the simultaneous and periodic alterations in the concentrations of all gases over the whole length of the monoliths;
- Changes in soil physical and chemical properties (by testing substantially different soil types in the forthcoming experiment);
- Use of other test plants;
- Detailed study on the gas phase of the root zone;
- Effect of soil and air temperatures (± 2 °C) and air pressure.

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