Leaching of Microelement Contaminants: a Long-term Field Study

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A field experiment with microelement loads was set up on loamy textured, calcareous chernozem soil formed on loess. The ploughed layer contained *ca.* 5% $CaCO_3$ and 3% humus. The soil was well supplied with Ca, Mg, Mn and Cu, moderately supplied with N and K, and weakly supplied with P and Zn. The water table is at the depth of 15 m, the water balance of the area is negative, and the site is drought sensitive. Salts of the 13 examined microelements were applied at 4 doses in the spring of 1991.

Treatments were arranged in a split-plot design, in a total of 104 plots with two replications. Loading rates were 0, 90, 270 and 810 kg/ha per element in the form of $AlCl_3$, $NaAsO_2$, $BaCl_2$, $CdSO_4$, K_2CrO_4, $CuSO_4$, $HgCl_2$, $(NH_4)_6Mo_7O_{24}$, $NiSO_4$, $Pb(NO_3)_2$, Na_2SeO_3, $SrSO_4$, $ZnSO_4$. Soil profiles of the control and the 810 kg/ha treated plots were sampled in the 3rd, 6th and 10th year of the trial. The mixed samples, consisting of 5 cores/plot were taken in 30 cm steps to 60 cm (year 1993), 90 cm (year 1996), and 290 cm (year 2000). Ammonium acetate + EDTA-soluble element content was determined. The main conclusions of the study are:

1. In soils contaminated with 810 kg/ha load rates As, Hg, Ni, Cu, Pb, Ba and Sr displayed no significant vertical movement. There is little uptake and translocation in plants of these elements: their concentration in the above-ground plant parts usually remains below 5 – 10 mg/kg dry mass with the exception of Ba and Sr showing a somewhat higher accumulation. Under our conditions the above elements did not behave as dangerous contaminants to the soil, groundwater, or plants.
2. Moderate leaching of Zn and Cd was detected when applied at higher doses. Their accumulation was also moderate in the above-ground plants parts. Zn is not a dangerous pollutant for soil, plants or groundwater at our site. Cd, however, is a very dangerous element because of its high toxicity to mammals, soil life and crops.
3. Cr, Se, and Mo (in the form of chromate, selenate and molybdenate anions) exhibited great mobility in the soil and partly in the soil-plant system. Cr was hardly detectable in the above-ground parts of plants. Still, its rapid leaching can jeopardize groundwater quality. Se was strongly accumulated in all plant organs and was highly toxic for all crops. Mo, too, showed 2 – 3 orders of magnitude greater accumulation in plant parts, resulting in products unfit for animal or human consumption. Under our experimental conditions Cr(VI), Se, Mo can be classified as dangerous contaminants, since the anion forms remained stabile for a long time in this well-aerated calcareous environment.

Key words: Microelements, Leaching, Soil Pollution, Long-term Experiment

Introduction

The aim of our research was to follow the vertical movement of some microelements in the soil profile and characterize their effects on soil pollution and on water quality. Therefore, we set up a long-term field experiment to collect data on the vertical movement and leaching rates of microelements as a function of years and climatic parameters. Mobility and vertical movement of elements depend on the chemical character of the given element and on the soil characteristics, such as pH value, lime content, clay content, humus condition, redox conditions, chelate-forming agents. The movement of anions is relatively fast in soils, as soil colloids bind them only slightly on their negatively charged surfaces. Retention is stronger in the case of metal cations on the specific binding places. At higher loads, however, these places are saturated and leaching is more probable (Chaney *et al.*, 1997).

Earlier studies on plant uptake and leaching of Cd, Cr, Ni, Pb and Zn were carried out on undisturbed soil columns under laboratory conditions. Metal nitrates were mixed with sewage sludge and added to the upper 10 cm layer of the soil column. After 3 months the major part of the applied metals was found at the place of application even

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when the sludge load was a hundred times higher than permissible under watered conditions. The displacement of metals did not exceed 5–10 cm and their concentration was 3 orders of magnitude smaller than in the solid phase. Further studies revealed that the drying out and remoistening of soil decrease the amount of microelements found in the soil solution. In the liquid phase Cr and Pb were less detectable than the more mobile Cd and Zn (Németh, 1993).

Materials and Methods

The trial was set up in Nagyhörcsök (Hungary) in 1991 on a calcareous chernozem soil formed on loess, containing 5% $CaCO_3$ and 3% humus in average in the ploughed layer. Soil texture is loamy with 20% clay [consisting of illite (*ca.* 50%), chlorite (*ca.* 30%) and smectite] and 40% fine fraction. Soil characteristics of the ploughed layer are: pH (KCl): 7.3, AL-P_2O_5 (ammonium lactate-soluble P_2O_5): 80–100, AL-K_2O (ammonium lactate-soluble K_2O): 140–160, KCl–Mg: 150–180, and KCl + EDTA soluble Mn, Cu and Zn are 80–150, 2–3 and 1–2 mg/kg, respectively. The soil is well supplied with Mn, sufficiently supplied with Mg and Cu, moderately supplied with N and K, and weakly supplied with P and Zn. The water table is at a depth of 13–15 m, which practically excludes its contamination by leaching. The climate is dry and the area is drought sensitive with 500–550 mm annual precipitation and a negative water balance.

The applied treatments simulate soil contamination conditions that may occur in industrial areas, near highways, settlements and in city gardens. The 4 load levels (0, 90, 270 and 810 kg element/ha) were applied as a single dose in the spring of 1991 in the form of $AlCl_3$, $NaAsO_2$, $BaCl_2$, $CdSO_4$, K_2CrO_4, $CuSO_4$, $HgCl_2$, $(NH_4)_6Mo_7O_{24}$, $NiSO_4$, $Pb(NO_3)_2$, Na_2SeO_3, $SrSO_4$, and $ZnSO_4$. Fertilization was done yearly with 100–100–100 kg/ha N, P_2O_5 and K_2O active agents, in the form of ammonium nitrate, superphosphate, and potash fertilizers. The $13 \times 4 = 52$ treatments with 2 replications were arranged in a split-plot design in altogether 104 plots.

Soils were sampled in 1993, 1996 and 2000 at the maximal depths of 60, 90 and 290 cm, respectively. In all cases the control and the maximal rate (810 kg/ha) treatments were analyzed. The samples (52 in 1993, 72 in 1996, and 108 in 2000) consisted of 5 cores/plot taken in 30 cm steps to the 60 cm, 90 cm, and 290 cm sampling depths. The samples were dried at 40 °C, homogenized and the ammonium acetate + EDTA-soluble element contents were analyzed by the method of Lakanen and Erviö (1971). In some cases the so-called “total” element contents were also determined for 20–24 elements by digestion with cc. HNO_3 + cc. H_2O_2.

The depth of sampling in 2000 was determined from the data of the earlier sampling and previous soil chemical analysis and plant uptake data. In this soil Mo, Cr, Se are mobile in the form of molybdate, chromate, and selenate. Thus for these elements 9 sampling layers were selected to the maximal depth of 290 cm. For the less mobile 9 elements only 3 layers were sampled to the depth of 90 cm.

Results and Discussion

Table I shows the crops cultivated in the first 10 years, the time of sowing and harvesting, the

Table I. Crop sequence and the amount of precipitation between 1991 and 2000 (Calcareous loamy chernozem soil, Nagyhörcsök).

Year	Cultivated plant	Sowing (day.month.)	Harvest (day.month.)	Precipitation [mm]* Between April and September	Precipitation [mm]* Annual total amount
1991	Maize	22.05.	25.11.	308	522
1992	Carrots	08.04.	02.11	217	471
1993	Potatoes	06.04.	06.09.	205	487
1994	Peas	11.03.	18.07.	242	370
1995	Beetroot	25.04.	11.09.	287	483
1996	Spinach	17.04.	23.07.	316	407
1997	Winter wheat	15.10.	24.07.	183	319
1998	Sunflower	23.04.	23.09.	458	682
1999	Sorrel	30.03.	19.07.	564	830
2000	Winter barley	30.09.	20.06.	180	384

* The annual precipitation sum averaged over 50 years at the Sárbogárd Station is 590 mm.

rainfall between April and September, and the total annual amount of precipitation. The annual precipitation sum averaged over fifty years at the nearby meteorological station in Sárbogárd was 590 mm. Within the 10-year period only two years (1998, 1999) had a higher rainfall than the many-year average. Following the sunflower harvest, up to the end of 1998 the area received plus 200 mm then, during 1999, 830 mm precipitation. The garden sorrel in 1999, during its short growing season utilized about 300–400 mm water. Thus, during the two rainy years (in 1998 and 1999) theoretically 400–500 mm surplus moisture reached the soil, causing microelement leaching. It is known that after a heavy shower or a rainstorm leaching through soil cracks and animal-made channels may be significant even in negative water-balanced arid areas. From deeper soil layers water may become lost through capillary elevation and plant uptake during which salts accumulate in the subsoil.

Tables II and III summarize the 3rd, 6th and 10th year effects on the control and the 810 kg/ha doses on the ammonium acetate + EDTA-soluble element contents of the soil profile.

The Zn concentration is reduced with increasing depth in the control soil. After treatment the Zn remained at the place of application (in the upper 0–30 cm layer) during the first 6 years of the study. However, by the end of the 10th year the 30–60 cm subsoil also became enriched in Zn. Although the content of soluble Zn amounts to 40% of the applied quantity it is not submitted to quick leaching. Thus, under our conditions even high Zn concentrations do not endanger the soil, the groundwater or the cultivated plants.

Cu is not displaced to deeper layers: the mobile content of Cu in the 30–60 cm layer is similar to the non-treated control soil. After 10 years the soluble Cu content amounts to about 37% of the applied load. Cu is bound in the topsoil and plant uptake is moderate. The excess Cu load did not cause decrease in crop yields or deterioration in the quality of the soil. It can be stated that under similar conditions such Cu load does not threaten the productivity of the soil or the groundwater.

The leaching of Ni can also be excluded in similar soils and at similar load levels. 17–20% of the given Ni load was detectable in soluble form in the 6th and 10th year of the trial. Ni cannot be considered as a dangerous pollutant in this soil. No decrease occurred in the yield or the quality of cultivated plants, plant uptake was hardly influenced by excess Ni and there was no pollution of

Table II. The control and the 3rd, 6th and 10th year effect of the 810 kg/ha treatment on the ammonium acetate + EDTA-soluble element content in the soil profile (Calcareous loamy chernozem soil, Nagyhörcsök).

Sampling	Zn [mg/kg]				Cu [mg/kg]				Sr [mg/kg]			
depth [cm]	∅	1993	1996	2000	∅	1993	1996	2000	∅	1993	1996	2000
0– 30	1.3	213.0	96.0	93.5	3.4	270.5	108.1	98.2	36	257	142	131
30– 60	0.4	4.5	1.8	23.1	1.6	6.9	2.9	2.4	42	51	36	54
60– 90	0.6	n.d.*	0.9	0.6	1.1	n.d.	1.2	1.4	55	n.d.	48	62
100–130	0.3	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	n.d.	85	n.d.	n.d.	n.d.
130–160	0.4	n.d.	n.d.	n.d.	0.9	n.d.	n.d.	n.d.	113	n.d.	n.d.	n.d.
160–190	0.5	n.d.	n.d.	n.d.	0.9	n.d.	n.d.	n.d.	128	n.d.	n.d.	n.d.
200–230	0.7	n.d.	n.d.	n.d.	0.9	n.d.	n.d.	n.d.	137	n.d.	n.d.	n.d.
230–260	0.6	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	n.d.	126	n.d.	n.d.	n.d.
260–290	0.6	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	n.d.	125	n.d.	n.d.	n.d.

Sampling	Ni [mg/kg]				Pb [mg/kg]				Ba [mg/kg]			
depth [cm]	∅	1993	1996	2000	∅	1993	1996	2000	∅	1993	1996	2000
0– 30	3.7	223.5	45.6	52.7	3.9	280.5	121.0	112.0	17	285	60	61
30– 60	1.1	4.4	0.8	0.9	1.6	23.2	2.5	2.1	22	44	22	24
60– 90	0.5	n.d.	0.5	0.6	1.5	n.d.	1.6	1.8	21	n.d.	20	20
100–130	0.5	n.d.	n.d.	n.d.	1.6	n.d.	n.d.	n.d.	21	n.d.	n.d.	n.d.
130–160	0.6	n.d.	n.d.	n.d.	1.8	n.d.	n.d.	n.d.	21	n.d.	n.d.	n.d.
160–190	0.6	n.d.	n.d.	n.d.	2.0	n.d.	n.d.	n.d.	21	n.d.	n.d.	n.d.
200–230	0.7	n.d.	n.d.	n.d.	2.0	n.d.	n.d.	n.d.	20	n.d.	n.d.	n.d.
230–260	0.7	n.d.	n.d.	n.d.	1.9	n.d.	n.d.	n.d.	18	n.d.	n.d.	n.d.
260–290	0.8	n.d.	n.d.	n.d.	1.9	n.d.	n.d.	n.d.	17	n.d.	n.d.	n.d.

* n.d., not determined.

Table III. The control and the 3rd, 6th and 10th year effect of the 810 kg/ha treatment on the ammonium acetate + EDTA soluble element content in the soil profile (Calcareous loamy chernozem soil, Nagyhörcsök).

Sampling depth [cm]	Mo [mg/kg]				Cr [mg/kg]				Cd [mg/kg]			
	∅	1993	1996	2000	∅	1993	1996	2000	∅	1993	1996	2000
0– 30	–*	43.3	13.6	11.3	0.1	7.2	2.4	1.8	0.2	227.5	141.0	118.0
30– 60	–	2.0	1.9	1.0	0.2	14.3	1.4	1.0	0.1	6.6	0.3	2.9
60– 90	–	n.d.**	1.3	1.3	0.2	n.d.	2.0	1.0	0.1	n.d.	0.1	0.3
100–130	–	n.d.	n.d.	1.2	0.3	n.d.	n.d.	1.0	0.1	n.d.	n.d.	n.d.
130–160	–	n.d.	n.d.	0.5	0.3	n.d.	n.d.	1.1	0.1	n.d.	n.d.	n.d.
160–190	–	n.d.	n.d.	0.1	0.2	n.d.	n.d.	1.2	0.1	n.d.	n.d.	n.d.
200–230	–	n.d.	n.d.	–	0.2	n.d.	n.d.	1.5	0.1	n.d.	n.d.	n.d.
230–260	–	n.d.	n.d.	–	0.2	n.d.	n.d.	1.5	0.1	n.d.	n.d.	n.d.
260–290	–	n.d.	n.d.	–	0.2	n.d.	n.d.	1.8	0.3	n.d.	n.d.	n.d.

Sampling depth [cm]	Se [mg/kg]				As [mg/kg]				Hg [mg/kg]			
	∅	1993	1996	2000	∅	1993	1996	2000	∅	1993	1996	2000
0– 30	0.3	81.0	45.5	17.2	–	92.6	44.6	34.4	–	60.9	12.8	10.0
30– 60	0.2	1.1	6.2	13.4	–	–	2.5	0.4	–	0.4	2.0	0.1
60– 90	0.1	n.d.	1.0	12.5	–	n.d.	–	–	–	n.d.	0.1	–
100–130	0.1	n.d.	n.d.	8.7	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.
130–160	0.1	n.d.	n.d.	4.2	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.
160–190	0.1	n.d.	n.d.	4.0	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.
200–230	–	n.d.	n.d.	4.0	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.
230–260	–	n.d.	n.d.	3.9	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.
260–290	–	n.d.	n.d.	4.0	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.

* Below detection limit (0.1 mg/kg); ** n.d., not determined.

the groundwater. The behavior of Pb in the soil was similar, with the difference that a higher load was detectable in soluble form. In the control plots the content of both elements decreased to one half or so in subsoil.

The concentration of Ba shows a relatively even distribution on control soil. There was no significant accumulation in the subsoil. The soluble Sr content increases in the loess layer, similarly to the total element content. Significant leaching cannot be demonstrated, since it can occur only in geological or soil-forming sense as in the case of other bivalent alkaline-earth metals (Ca, Mg). The elements Ba and Sr represent no danger to the soil, groundwater, or to plants at this site.

The soluble concentration of Mo remained below the 0.1 mg/kg detection limit together with As, Hg and partly with Se in the untreated soil. In contaminated plots Mo was leached to the 60–90 cm layer after the 3rd year of the experiment, 100–430 cm after the 6th year, and 160–190 cm after the 10th year. Nevertheless, the largest part of the mobile fraction remained in the ploughed layer. Mo – in the form of molybdate – moved downwards 15–20 cm/year and became strongly diluted. Mo was enriched very strongly in plant tissues. Although plants were not injured and yields did not decrease, the crops became unsuitable for human or animal consumption. Thus, Mo can be a dangerous contaminant for soil, plant and groundwater.

Similarly to nitrate Cr(VI) shows a fast downward movement. After the 3rd year of the trial the largest part of the soluble Cr-content was already leached into the subsoil. After the 6th year all three examined soil layers (0–30, 30–60, 60–90 cm) were contaminated, but because of the 90 cm sampling depth limit the leaching could not be followed further. The data of the 10th year sampling indicate that not only the upper 1.0–1.5 m layer was contaminated. If the vertical movement of Cr follows that of nitrate, leaching may easily reach the depth of 4 m. According to our previous examinations (Kádár, 1995) the ratio of different Cr-forms changes with depth. At the end of the 3rd year in the 0–20 cm layer 6% of the total Cr content was ammonium acetate + EDTA-soluble, and 1% was in 0.01 M $CaCl_2$-soluble form. In the 20–40 cm layer this rate increased to 14% and 5%, and in the 40–60 cm layer the total Cr content was mainly in 0.01 M $CaCl_2$-soluble form.

Se occurs in mobile Ca-selenate form in calcareous soils and it is weakly adsorbed. Plant uptake was characterized by hyperaccumulation: a thousand-fold increase occurred in different plant parts (including generative ones) together with a crop yield decrease. Se is a dangerous pollutant, as it can accumulate in plants, animals, or humans at toxic levels. Leaching of Se endangers groundwater. It is important to note that nodule-forming and atmospherical N-binding soil life was completely inhibited in the 4th year of the trial in the case of high Se doses and partly in treatments with As. Endomycorrhizal symbiosis was also damaged. Higher Cd loads had a similar effect.

Similarly to Hg, As was not mobile in the soil-plant system. There was no contamination of the subsoil: 13% and 4% of the given As and Hg were found in ammonium acetate + EDTA-soluble form at the place of input, in the 0–30 cm layer. Higher As load often caused yield decrease and blocked the microbiological activity (nodule-forming of peas and mycorrhization). As and Hg were hardly detectable in the above-ground plant parts but significant accumulation occurred in the roots. Under our experimental conditions these two elements seem to be moderately dangerous pollutants. They can cause yield decrease but will not contaminate the groundwater, the crops, or the food chain.

45% of Cd remained in ammonium acetate + EDTA-soluble form in the rooted topsoil even after 10 years. The movement of Cd is slow: the subsoil is not or hardly contaminated even after a decade. The negative effect of Cd on soil-life is evident at higher loads. Although little Cd was accumulated in above-ground plant parts, the vegetative parts of crops and the seeds of oil plants were unsuitable for animal or human consumption. Considering human toxicity Cd can be dangerous because of its long half-time in the human organism. Some crops reacted to high Cd loads with a slight yield decrease.

Conclusion

It has to be emphasized that these studies are complicated by unavoidable contamination during sampling and limitations in time as well as in sampling depths. Therefore, the results obtained cannot be easily extrapolated to other climatic and environmental conditions. Still, the vertical movement of several elements can be judged with high certainty based on the trends observed. Since leaching is a relatively slow process and occurs at different rates, deep sampling must be repeated from time to time. As the database becomes broader in space and time the conclusions drawn will become more and more reliable. As a result, microelement leaching will be predictable with significantly higher precision and soil protective measures will be less expensive and more reliable. Although this study involves a very expensive procedure (technical difficulties of sampling and costs of analysis rise with the increasing number of samples and the increasing depth of sampling) our approach is the only one to gather reliable scientific data on the behavior of microelements under field conditions. This type of basic research provides a solid foundation for practical applications and the information collected will be useful in the design of soil and water protection measures.

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