

Leaching of microelement contaminants in a long-term field study

Imre Kádár*

Research Institute for Soil Science and Agricultural Chemistry, Budapest, Hungary

A field experiment with microelement loads was set up on loamy-textured, calcareous chernozem soil formed on loess. The ploughed layer contained about 5% CaCO₃ 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 levels in the spring of 1991.

Treatments were arranged in split-plot design, in a total of 104 plots with two replications. Loading rates were 0, 90, 270 and 810 kg/ha per elements in the form of AlCl₃, NaAsO₂, BaCl₂, CdSO₄, K₂CrO₄, CuSO₄, HgCl₂, (NH₄)₆Mo₇O₂₄, NiSO₄, Pb(NO₃)₂, Na₂SeO₃, SrSO₄, and ZnSO₄. Soil profiles of the control and the 810 kg/ha treatment were sampled in the 3rd, 6th and 10th year of the trial. The mixed samples, consisting of 5 cores/plot, were taken every 30 cm to the depth of 60 (1993), 90 (1996) and 290 (2000) cm. NH₄-acetate + EDTA-soluble element content was determined. The scheme for vertical movement of soluble elements in soil profile as a function of time is shown in Fig. 1. The main conclusions of the study can be drawn as follows:

1. On contaminated soil with 810 kg/ha loading rates, As, Hg, Ni, Cu, Pb, Ba and Sr displayed no significant vertical movement. The movement of these elements is blocked in the soil–plant system: their accumulation in the above-ground plant parts usually remains below 5–10 mg/kg D.M., with the exception of Ba and Sr which showed a somewhat higher accumulation. On this soil the above elements do not seem to be dangerous contaminants either to soil, groundwater or plants. Extreme As and Hg loads, however, resulted in phytotoxicity in some plants.

2. Moderate extent of leaching occurs in the case of Zn and Cd, when they are enriched significantly. Their accumulation was moderate in the above-ground plant parts. Zn is not a dangerous pollutant either for soil, plants or groundwater at this site. Cd, however, is a very dangerous element from the human toxicological point of view and more extreme Cd loads also proved to be toxic for soil life, crops yield and quality.

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 floral parts. Its rapid leaching, however, can jeopardize groundwater quality. Se showed hyperaccumulation in all plant or-

* Corresponding address: Herman Ottó út 15, H-1022 Budapest, Hungary; E-mail: kadar@rissac.hu

gans with high toxicity for all kind of crops. Mo also showed two or three 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 stable for a long time in this well-aerated calcareous environment.

Key words: soil pollution, microelements, long-term experiment, leaching

Introduction

The aim of the presented research was to follow the vertical movement of some microelements in the soil profile and to obtain a picture of the effects of soil pollution on water quality. As it takes a long time to get field data on vertical movement and leaching rate as a function of years and precipitation, long-term field experiments are the most suitable for such investigations. For example, vertical movement of NO₃-N and SO₄-S was first generally estimated in the 12th year of a long-term NPK fertilization experiment, when leaching reached the depth of 3–4 m (Kádár et al. 1987; Németh et al. 1988; Németh 1995). In the 17th and 22nd years of the experiment the leaching of nitrate reached 6 m with a negative water balance. Mobility and vertical movement of elements depend on the chemical character of the given element and on soil characteristics, such as pH, lime content, clay content, humus condition, redox conditions, chelate-forming agents, etc.

The movement of anions or negatively charged ions is relatively rapid in soil, as soil colloids bind them only slightly on their negatively charged surfaces. Retention is stronger in the case of metals and cations on the specific binding places. At higher loads, however, these places are saturated and leaching is more probable (Csathó 1994).

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 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 three orders of magnitude smaller than in the solid phase (Csillag et al. 1994). Further examinations revealed that the drying out and remoistening of soil decreases the amount of elements found in the soil solution. In the liquid phase Cr and Pb were less detectable than the more mobile Cd and Zn (Németh et al. 1993).

Materials and methods

The trial was set up on a calcareous chernozem soil formed on loess, containing 5% CaCO₃ and 3% humus in average in the ploughed layer. Soil texture is loamy with a 20% clay (consisting of illite (~ 50%), chlorite (30%) and smectite) and 40% fine frac-

tion. Soil characteristics of the ploughed layer are: pH(KCl): 7.3, AL-P₂O₅: 80–100, AL-K₂O: 140–160, KCl-Mg: 150–180, KCl+EDTA soluble Mn, Cu and Zn: 80–150, 2–3 and 1–2 mg/kg. Based on the methods and limit values developed by the Hungarian Extension Service (MÉM NAK 1979) 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; 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 nowadays or in the future in the polluted environment of industrial areas, near highways, settlements and in city gardens. The 4 load levels (0, 90, 270 and 810 kg/ha per element) were applied once at initiation in the spring of 1991 under maize in the form of AlCl₃, NaAsO₂, BaCl₂, CdSO₄, K₂CrO₄, CuSO₄, HgCl₂, (NH₄)₆Mo₇O₂₄, NiSO₄, Pb(NO₃)₂, Na₂SeO₃, SrSO₄, and ZnSO₄. Fertilization was carried out yearly with 100–100–100 kg/ha N, P₂O₅ and K₂O active agents, in the form of ammonium nitrate, superphosphate and potash fertilizers. The 13 × 4 = 52 treatments with 2 replications were arranged in a split-plot design, in a total of 104 plots.

Soils were sampled in 1993, 1996 and 2000 at a maximal depths of 60, 90 and 290 cm, respectively. In all cases the control and the maximal rate (810 kg/ha) treatments were checked. The mixed samples (52 in 1993, 72 in 1996 and 108 in 2000) consisted of 5 cores/plot taken every 30 cm to the 60, 90 and 290 cm sampling depth. These samples were dried at 40°C, homogenized and the NH₄-acetate + EDTA-soluble element contents were analyzed using 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. HNO₃ + cc. H₂O₂.

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 the Mo, Cr, Se elements are mobile in the form of molybdate, chromate, and arsenate. Thus for these elements 9 sampling layers were selected to the depth of 290 cm. In the cases of the probably less mobile 9 elements only 3 layers were sampled down to 90 cm. The detailed conditions and the main results of the trial can be found elsewhere (Kádár 1994–1995, 1995; Kádár and Daood 2001).

It has to be emphasized, however, that the examinations have limits, which are due to the experimental-technique as well as the spatial and time scale:

1. No matter how carefully the sampling is done, some contamination of the sub-soil-samples cannot be excluded during the drilling or the preparation of samples.
2. The sampling depth was 90–290 cm, so sampling was limited in space, making it sometimes impossible to expose the entire leaching profile.
3. The 10-year experimental period represents a time limit. Droughty years dominated, and because of the shortage of precipitation the soil often dried out deeply and the cultivated plants suffered drought damage.

4. Changes in soil moisture conditions are not known and there are no actual data about water movement and precise water balance.

According to the above it is obvious that the conclusions drawn can be considered as first information. On the other hand, even though the examination errors cannot be estimated precisely, the vertical movement of some elements can be judged more or less correctly based on trends. As leaching is a slow process and occurs at a different rate in the case of each element, deep sampling must be repeated from time to time. Based on the results of profile sampling which become broader in space and time, our conclusions become more reliable. Leaching can be predicted and modelled more precisely and the necessary soil protective measures can also be made more exactly and cheaply.

Although this is an expensive procedure (the technical difficulties of sampling rise, the number of samples increase, the numbers of analyses are multiplied, etc.), repeated sampling and analyses increase the reliability and scientific value of the evaluation. It is important to determine the “total content” in addition to the mobile fractions, especially at the beginning, because these data may serve as parallels. This type of investigation may become profitable when the information is used in soil and water protection measures on a long run. It must be emphasized that such experiments and their results cannot be adapted from other countries because of the differences in natural conditions.

Results and discussion

Table 1 shows the crops cultivated in the first 10 years, the time of sowing and harvesting as well as rainfall between April and September and the total annual amount of

Table 1
Crop sequence and the amount of precipitation between 1991 and 2000 (Calcareous loamy chernozem soil, Nagyhörcsök)

Sampling year	Cultivated plant	Sowing (day and month)	Harvest	Precipitation (mm)	
				between April and September	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

Note: The annual precipitation sum averaged over 50 years at the Sárbogárd Station was 590 mm.

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 multi-year average. Previously the cultivated plants had dried out the upper 1 m soil layer, up to the harvest of sunflowers in 1998. Following the sunflower harvest, up to the end of 1998 the area received over 200 mm, then during 1999 830 mm precipitation. The garden sorrel in 1999, during its short growing season, utilized about 300–400 mm water. So in the two rainy years (in 1998 and 1999), in theory 400–500 mm surplus moisture could accumulate in the soil, which may cause deeper leaking and leaching. It is known that leaching can also become significant in negative water-balanced arid areas after a heavy shower or rain-storm through soil cracks and animal-made channels. Water may become lost from deeper soil layers through capillary elevation, water vapor and plant uptake, while salts left there can accumulate in the subsoil.

Tables 2 and 3 summarize the 3rd, 6th and 10th year effect of the control and the 810 kg/ha load given in spring 1991 on the NH₄-acetate + EDTA-soluble element contents of the soil profile. We attempt to summarize the main conclusions by element.

The Zn concentration is reduced with increasing depth in the control soil (Fig. 1). After treatment the element Zn remained at the place of application (in the upper 0–30 cm layer) in the first 6 years of the trial. By the end of the 10th year the 30–60 cm subsoil also became enriched. The content of soluble Zn amounts to 40% of the applied quantity. This, however, does not mean water-soluble fraction and is not submitted to quick leaching. In this soil the Zn-load does not endanger soil, groundwater or cultivated plants.

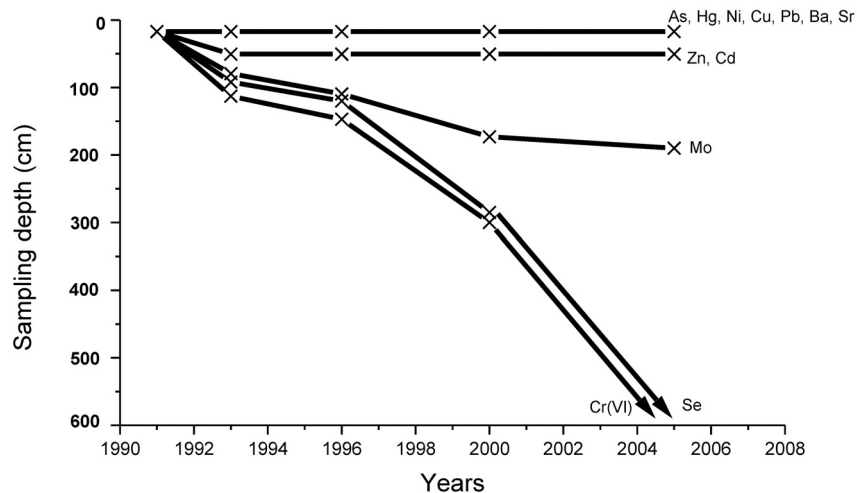


Fig. 1 Scheme for vertical movement of NH₄-acetate + EDTA soluble element content in soil profile as a function of time (Calcareous chernozem loamy soil, Nagyhörösök)

Table 2
The control and the 3rd, 6th and 10th year effect of the 810 kg/ha treatment on the NH₄-acetate + EDTA-soluble element content in the soil profile (Calcareous loamy chernozem soil, Nagyhörcsök)

Sampling depth (cm)	Zn mg/kg				Cu mg/kg			
	Ø	1993	1996	2000	Ø	1993	1996	2000
0–30	1.3	213.0	96.0	93.5	3.4	270.5	108.1	98.2
30–60	.4	4.5	1.8	23.1	1.6	6.9	2.9	2.4
60–90	.6	x	.9	.6	1.1	x	1.2	1.4
100–130	.3	x	x	x	.8	x	x	x
130–160	.4	x	x	x	.9	x	x	x
160–190	.5	x	x	x	.9	x	x	x
200–230	.7	x	x	x	.9	x	x	x
230–260	.6	x	x	x	.8	x	x	x
260–290	.6	x	x	x	.8	x	x	x

Sampling depth (cm)	Ni mg/kg				Pb mg/kg			
	Ø	1993	1996	2000	Ø	1993	1996	2000
0–30	3.7	223.5	45.6	52.7	3.9	280.5	121.0	112.0
30–60	1.1	4.4	.8	.9	1.6	23.2	2.5	2.1
60–90	.5	x	.5	.6	1.5	x	1.6	1.8
100–130	.5	x	x	x	1.6	x	x	x
130–160	.6	x	x	x	1.8	x	x	x
160–190	.6	x	x	x	2.0	x	x	x
200–230	.7	x	x	x	2.0	x	x	x
230–260	.7	x	x	x	1.9	x	x	x
260–290	.8	x	x	x	1.9	x	x	x

Sampling depth (cm)	Ba mg/kg				Sr mg/kg			
	Ø	1993	1996	2000	Ø	1993	1996	2000
0–30	17	285	60	61	36	257	142	131
30–60	22	44	22	24	42	51	36	54
60–90	21	x	20	20	55	x	48	62
100–130	21	x	x	x	85	x	x	x
130–160	21	x	x	x	113	x	x	x
160–190	21	x	x	x	128	x	x	x
200–230	20	x	x	x	137	x	x	x
230–260	18	x	x	x	126	x	x	x
260–290	17	x	x	x	125	x	x	x

Note: x: no sampling

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

Table 3
The control and the 3rd, 6th and 10th year effect of the 810 kg/ha treatment on the NH₄-acetate + EDTA soluble element content in the soil profile (Calcareous loamy chernozem soil, Nagyhörösök)

Sampling depth (cm)	Mo mg/kg				Cr mg/kg			
	Ø	1993	1996	2000	Ø	1993	1996	2000
0–30	–	43.3	13.6	11.3	.1	7.2	2.4	1.8
30–60	–	2.0	1.9	1.0	.2	14.3	1.4	1.0
60–90	–	x	1.3	1.3	.2	x	2.0	1.0
100–130	–	x	x	1.2	.3	x	x	1.0
130–160	–	x	x	.5	.3	x	x	1.1
160–190	–	x	x	.1	.2	x	x	1.2
200–230	–	x	x	–	.2	x	x	1.5
230–260	–	x	x	–	.2	x	x	1.5
260–290	–	x	x	–	.2	x	x	1.8

Sampling depth (cm)	Se mg/kg				As mg/kg			
	Ø	1993	1996	2000	Ø	1993	1996	2000
0–30	.3	81.0	45.5	17.2	–	92.6	44.6	34.4
30–60	.2	1.1	6.2	13.4	–	–	2.5	.4
60–90	.1	x	1.0	12.5	–	x	–	–
100–130	.1	x	x	8.7	–	x	x	x
130–160	.1	x	x	4.2	–	x	x	x
160–190	.1	x	x	4.0	–	x	x	x
200–230	–	x	x	4.0	–	x	x	x
230–260	–	x	x	3.9	–	x	x	x
260–290	–	x	x	4.0	–	x	x	x

Sampling depth (cm)	Hg mg/kg				Cd mg/kg			
	Ø	1993	1996	2000	Ø	1993	1996	2000
0–30	–	60.9	12.8	10.0	.2	227.5	141.0	118.0
30–60	–	.4	2.0	.1	.1	6.6	.3	2.9
60–90	–	x	.1	–	.1	x	.1	.3
100–130	–	x	x	x	.1	x	x	x
130–160	–	x	x	x	.1	x	x	x
160–190	–	x	x	x	.1	x	x	x
200–230	–	x	x	x	.1	x	x	x
230–260	–	x	x	x	.1	x	x	x
260–290	–	x	x	x	.3	x	x	x

Note: – means under 0.1 mg/kg detectable limit; x: no sampling

The leaching of Ni can also be excluded on similar soil and at similar load levels. Not even the layer below 30 cm shows any accumulation. 17–20% of the given 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 and there was no pollution of the groundwater. The behavior of Pb was similar, with the difference that 40% of

the load was detectable in soluble form. In the control plots the content of both elements decreased to one-half.

The concentration of Ba shows a relatively even distribution in the 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, and it can occur only in a geologic or soil-forming sense as in the case of other bivalent alkali soil metals (Ca, Mg). These 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 elements in the untreated soil. In contaminated plots Mo was leached to the 60–90 cm layer after the 3rd year of the experiment, 90–130 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 downward 15–20 cm/year toward the groundwater and became strongly diluted. Mo was extremely enriched, by two to three orders of magnitude, in plant tissues. Although plants were not injured and yields did not decrease, the crops became unsuitable for human or animal consumption. Under similar conditions it can be a dangerous contaminant for soil, plant and groundwater.

Similarly to nitrate, Cr(VI) also shows a rapid 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 the entire depth of leaching could not be followed. The data of the 10th year sampling indicate that not only the upper 1–1.5 m rooted layer was contaminated: leaching can also reach layers deeper than 3 m. In the future limits of vertical movement must be controlled with deepening drills. When the vertical movement of Cr follows that of nitrate, leaching may reach the depth of 4 m.

According to our previous examinations, 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 NH₄-acetate + EDTA-soluble, and 1% was in 0.01 M CaCl₂-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 CaCl₂-soluble form (Kádár and Prokisch 2000).

Se occurs in mobile Ca-selenate form in calcareous soils and it is weakly adsorbed. Plant uptake was characterized by hyper-accumulation: a thousand-fold increase occurred during the first decade in different plant parts (including generative ones, like grains) 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 the toxic form also endangers groundwater. It is important to note that nodule-forming and atmospherical N-binding soil life was in fact stopped in the 4th year of the trial on pea roots in the case of more extreme Se-treatments and partly in As-treatments. Endomycorrhizal symbiosis suffered damage in polluted soil. To some extent higher Cd loads had a similar effect (Kádár et al. 2001).

Similarly to Hg, As was not mobile in the soil–plant system. Contamination of the subsoil could not be verified beyond doubt: 13% and 4% of the given As and Hg is found in NH₄-acetate + EDTA-soluble form at the place of input, in the 0–30 cm layer. The excess As load often caused yield decrease and blocked the microbiological activity (nodule-forming of peas, mycorrhization). As and Hg were hardly detectable in the above-ground plant parts and significant accumulation occurred only in the roots. Under our experimental conditions these two elements seem to be moderately dangerous pollutants. Temporarily they can cause yield decrease, but the crops and the entire food chain will hardly be contaminated. Contamination of the groundwater can be excluded.

45% of Cd remained in NH₄ acetate + EDTA-soluble form in the rooted topsoil even after 10 years. Its movement is undoubtedly limited: the subsoil is not or hardly contaminated after a decade. Its negligible effect on soil-life is also 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-life in the human organism. Some crops reacted to high Cd-loads with a slight yield decrease.

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