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The fate of molybdenum contamination in the food chain

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Abstract

A long-term field experiment with different microelement contaminants was set up in 1991 on a calcareous chernozem soil with around 5% $CaCO_3$ and 3% humus in Nagyhörcsök, Hungary. Mo was applied in the form of $(NH_4)_6Mo_7O_{24}$ at 0, 90, 270 and 810 kg/ha rates. The crop sequence was maize, carrot, potato, pea, beetroot, spinach, wheat, sunflower, garden sorrel and winter barley. Mo induced no yield losses or phytotoxic effect on crops. Mo pollution did not result in soil sterility. The Mo displayed a significant downward movement in soil profile, after 10 years reaching the 130-160 cm soil layer. Generally, the Mo exhibited a hyperaccumulation in crop parts, its uptake increased many thousandfold on heavily polluted plots, compared to the control. This element accumulated in plant and animal organs up to one or two orders of magnitude higher concentrations. The high Mo containing feed can impair spermatogenesis in breeding animals and also pose a risk to consumer regarding dietary products of animal origin.

Key words: molybdenum, food chain, contamination

Introduction

Mo is an essential element for plants, animals and human. Above certain critical levels in the diets of animals, particularly ruminant animals, it becomes toxic. The range between deficiency and toxicity in animals is narrow and therefore careful control of Mo in animal diet is essential (Anke et al. 1985). Plants have a flexible capability for tolerating high Mo content in the tissue. Unlike all other microelements, Mo has never reached plant-toxic concentrations in field-grown plants. Mo does not compete with other essential elements for active sites in enzymes. The excess Mo may be immobilized in the plant tissue and so removed (Chaney 1982). Animals require low levels of Mo in their diets for normal growth and development. The toxicity is primarily expressed as a Cu deficiency. It has been generally considered that Mo is not a serious environmental contaminant in term of human health (NAS 1973).The purpose of our work was to evaluate the long-term effect and movement of Mo contaminants in the soil-plant-animal system.

Material and methods

The trial was set up on a calcareous chernozem soil formed on loess, containing 5% $CaCO_3$ and 3% humus in average in the ploughed layer. Soil contains texture is loamy with 20% clay and 40% silt. Soil characteristics of the ploughed layer are: pH(KCl): 7.3, AL-P_2O_5: 80–100 mg 100 g^{-1}, AL-K_2O : 140–160 mg 100 g^{-1}, KCl-Mg: 150–180 mg 100 g^{-1}, KCl+EDTA soluble Mn, Cu and Zn: 80–150, 2-3 and 1-2 mg kg^{-1}. The water table is at a depth of 13–15 m, the area is drought sensitive with 500–550 mm annual precipitation and negative water balance.

The 4 load levels (0, 90, 270 and 810 kg ha^{-1} per element) were applied once in spring 1991 preceeding maize crop, in the form of $(NH_4)_6Mo_7O_{24}$. Fertilization (kg ha^{-1}) was done yearly with 100 N + 100 P_2O_5 + K_2O.
Plant and soil samples were digested with the mixture of cc. HNO_3 + cc. H_2O_2. The soil samples were also extracted by NH_4-acetate + EDTA according to Lakanen and Erviö (1971). The soil profiles were sampled in the 10th year of the trial to the depth of 290 cm, and the NH_4-acetate+EDTA soluble fraction was determined.
The animal feeding experiment was carried out in the University of Veterinary Science. Metabolic experiment was made with 20-day feeding period. A total of 15 male and female New Zealand White rabbits (average body weight of 2300 g) were used. The rabbits were subjected to pathological examination. Samples were taken from the organs, urine and faeces for chemical and histological analyses.

Results and discussion

Table 1. shows the crops cultivated in the first 10 years and their harvested mean yields. Within the 10-year period, two years only (1998 and 1999) had higher rainfall compared to long-term mean (1961-1990). The first grown crop in 1991 (maize) revealed a yield restriction that could be a consequence of NH_4^+ toxicity from ammoniummolibdate. In the following years there was no yield reduction at all in case of any crops.

Table 1. Effect of Mo load on the yield of the harvested crops, 1991-2000.

Years	Crops and	Applied Mo (kg ha^{-1}) in spring 1991				LSD
	harvested parts	0	90	270	810	5%
		Yield (t/ha; * yield on air-dried matter basis)				
1991	*Maize grain	8.5	8.4	7.4	4.7	2.5
1992	Carrot root	16.0	11.4	14.2	13.1	4.8
1993	Potato tuber	10.9	8.6	9.1	10.4	3.5
1994	*Peas grain	2.9	3.1	2.9	2.7	0.8
1995	Red beet root	18.7	27.2	24.4	18.3	8.7
1996	Spinach top	18.2	16.8	17.4	19.8	6.5
1997	*W.wheat grain	7.5	7.5	6.9	7.5	1.6
1998	*Sunflower seed	2.4	2.4	2.2	2.4	0.6
1999	Garden sorrel top	40.0	41.2	37.1	38.1	9.9
2000	*W.barley grain	4.6	4.7	4.4	4.2	1.3

Table 2. Effect of Mo load on the Mo content of the soil in plough layer

Sampling time		Applied Mo, kg ha^{-1} in spring 1991				LSD
Month	Year	0	90	270	810	5%
		NH_4-acetate + EDTA soluble (mg kg^{-1}: detection limit = 0.1)				
July	1991	< 0.1	21	27	104	14
August	1991	< 0.1	20	24	63	11
November	1992	< 0.1	12	22	43	16
April	1994	< 0.1	3	7	25	4
July	1997	< 0.1	2	5	8	2
September	2000	< 0.1	4	9	14	4
		cc. HNO_3 + cc. H_2O_2 "total" content (mg kg^{-1})				
April	1994	0.3	10	20	114	24

Table 3. Effect of Mo-load on the crop Mo content, mg kg^{-1} air-dried matter

The growing	Term of	Crop	Applied Mo, kg ha^{-1}, in spring 1991				LSD
season	sampling	parts	0	90	270	810	5%
1991	08. July	Root[1]	<0.1	140	455	990	112
Maize	08. July	Shoot[1]	0.4	107	284	781	16
	08. Aug.	Leaves[3]	<0.1	141	262	404	32
	25. Nov.	Straw[5]	<0.1	35	38	107	8
	25. Nov.	Grain[5]	<0.1	4	7	14	1
1992	29. June	Top[2]	<0.1	442	830	1567	446
Carrot	07. Oct.	Top[5]	<0.1	117	270	434	34
	07. Oct.	Root[5]	<0.1	21	54	99	19
1993	14. June	Leaves[3]	<0.1	71	236	358	13
potato	12. July	Leaves[4]	<0.1	67	131	284	17
	07. Sept.	Tuber[5]	<0.1	11	24	61	12
1994	26. May	Top[3]	<0.1	180	380	502	61
Green peas	14. June	Straw[5]	0.1	262	482	598	80
	14. June	Pods[5]	0.3	100	124	176	44
	14. June	Grain[5]	1.5	89	136	148	42
1995	21. June	Top[2]	0.1	243	459	916	35
Redbeet	07. Sept.	Top[5]	<0.1	182	451	852	15
	11. Sept.	Root[5]	<0.1	37	70	114	8
1996	03. June	Leaves[7]	<0.1	223	412	670	97
Spinach	23. July	Straw[5]	0.1	31	97	132	9
	23. July	Grain[5]	<0.1	13	42	80	6
1997	15. May	Shoot[6]	1.0	166	296	437	82
Winter wheat	24. July	Straw[5]	0.4	46	84	126	38
	24. July	Grain[5]	0.5	22	36	48	19
1998	06. July	Leaves[3]	1.8	48	155	306	25
Sunflower	23. Sept.	Straw[5]	0.4	23	46	87	23
	23. Sept.	Head[5]	0.8	22	58	122	28
	23. Sept.	Grain[5]	0.5	10	23	34	9
1999	09. July	Top[5]	2	41	63	77	28
Garden sorrel							
2000	04. May	Flag leaves[3]	1	124	329	424	50
Winter barley	20. June	Straw[5]	1	96	176	212	58
	20. June	Grain[5]	0.5	18	33	35	5

[1] six leaves stage, [2] before rootbuilding, [3] before flowering, [4] after flowering, [5] at harvest, [6] end of tillering, [7] middle of vegetation period. Note: <0.1 mg kg^{-1} detection limit

In the uncontaminated control soil the NH_4-acetate + EDTA soluble Mo fraction remained under the 0.1 mg kg^{-1} detection limit. After 2.5 months since Mo was mixed into the soil, only about 1/3 of the applied Mo could be detected in this form. During the sampling period there was a drastic drop in soluble Mo content, and large unrevealed fluctuations were found. The cc. HNO_3+cc. H_2O_2 digestable "total" Mo content in 1994 was about 25-30% of the applied four years earlier (Table 2). The downward movement was significant in the soil: Mo could be measured even in the 130-160 cm layer with an average concentration of 5 mg kg^{-1} in 2000, as previously reported (Németh and Kádár 2005). The bulk of the applied Mo in soil was not measurable with the used analytical methods.

Table 4. Effect of Mo contaminated feed on the Mo content of faeces, urine and different organs of rabbits in 1992 (mg kg^{-1} on dry matter basis)

	Mo intake by feed	Organ of rabbits and Mo contents (Mo mg kg^{-1} in dry matter)					
	Mo mg kg^{-1}	Heart	Lung	Liver	Kidney	Milt	Testis
Control	0.53	0.06	0.03	1.26	0.75	<0.01	0.24
Treated	39.00	1.23	1.21	1.88	3.46	1.08	0.73
		Fat tissue	Muscle	Bone	Hair	Faeces	Urine
Control	0.53	<0.01	<0.01	<0.01	<0.01	0.42	0.42
Treated	39.00	0.06	0.37	1.20	0.41	25.34	6.60

The roots of maize in 1991 accumulated the largest quantities of Mo in 6 leaves stage, reaching a maximum of 990 mg kg^{-1} root dry matter.(Table 3). It was followed by the shoots, then leaves before flowering, then straw and grain at harvest. The grain contained one order of magnitude less Mo in its tissue than the vegetative part, the straw. The carrot in 1992 showed even higher concentrations, which made up to 1567 mg Mo kg^{-1} in the top before root formation at the maximum loading level. At the same time, the edible part of the carrot, the root had 20-25% of that established at harvest. Potato in 1993 and red beet in 1995 showed similar trend of Mo accumulation in its organs. The green peas straw at harvest contained 598 mg Mo kg^{-1} on the heaviest Mo polluted soil, while concentrations in pods and grain reached 176 and 148 mg Mo kg^{-1}, respectively. The young vegetative plant parts like shoots and leaves have had the highest Mo concentration while the straw had less Mo and the grain has had the smallest amounts. During the last four years, the crop parts show measurable Mo concentrations even on the control soil. Contamination of the growing crop with Mo through flying soil dust particles cannot be excluded and the washing of the crop samples before the anayses was not a practice.

Since Mo showed hyperaccumulation, its uptake increased many thousandfold on heavy polluted soil, as compared to the control. The maximum Mo uptake by the harvested crops (main and by-products together) were as follows (Mo ha^{-1}): maize 0.35, carrot 0.68, potato 0.20, green peas 2.85, red beet 1.20, spinach top 2.21, winter wheat 1.13, sunflower 0.71, garden sorrel top 0.22, and winter barley 1.24 kg. During the 10-year period 10.8 kg Mo ha^{-1} was removed from the soil.

The effect of Mo contaminated carrots on the Mo content in the animal organs, faeces and urine is illustrated in Table 4. The Mo showed the highest accumulation in the kidneys, but in all organs it reached one or two orders of magnitude except liver. The bulk of the Mo measured in faeces reached 25.3 mg Mo kg^{-1}, while in the urine it was 6.6 mg Mo kg^{-1}. The contamination of the feed with Mo causes two main problems: it can impair spermatogenesis in breeding animals and pose a risk to the consumers with the products of animal origin.

The rabbits, which consumed Mo-treated carrots received 1.40 mg Mo daily, which was excreted from the body mainly through the urine (54%) and faeces (26%). The accumulation in the tissues, expressed as a proportion of the amount taken up with the feed figured 20%. Histological examination revealed that the rate of spermatogenesis in the testis was reduced in the Mo treted groups as compared to the control. In the same time the body weight of the rabbits in Mo groups did not differ from untreated animals.

Due to the great accumulation of Mo in plant tissues, the flour of grain and all products of edible parts in the Mo treatments should be classified as inadequate for humans orunsuitable for animal consumption.

Conclusions

The soil-applied Mo levels induced no yield losses or phytotoxic effect on crops. Mo pollution did not result in soil sterility. Generally, the Mo exhibited a hyperaccumulation in crop parts, its uptake increased many thousandfold on severely polluted plots, as compared to the control. This element accumulated in plant and animal organs reaching often one or two orders of magnitude higher concentrations. The high Mo containing feed can impair spermatogenesis in breeding animals and also pose a risk to consumer with the products of animal origin.

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References

Anke M., Groppel, B., Grün, M., Kronemann, H. (1985). Molybdenum supply and status in animals and human being. In: Abdulla, M. et al.: Nutrition Research. Suppl. 1. 180-186. Pergamon Press Ltd. USA.

Chaney R.L. (1982). Fate of toxic substances in sludge applies to cropland. In: Proc. Int. Symp. "Land Application of Sewage Sludge". 259-324. Tokyo, Japan.

Kádár I. (1995). Effect of heavy metal load on soil and crop. Acta Agr. Hung. 43:3-9.

Lakanen E., Erviö. R. (1971). A comparison of eight extractants for the determination of plant available micronutrients in soils. Acta Agr. Fenn. 123:223-232.

NAS (1973). National Academy of Sciences: Water quality criteria. Committee on Water Quality Criteria. U.S. Gov. Printing Office. EPA.

Németh T., Kádár I. (2005). Leaching of microelement contaminants: a long-term field study. Z. Naturforsch. 60 (3-4): 261-264.