Effect of Micropollutants on Soil and Crop on Calcareous Sandy Soil

I. KÁDÁR and B. MORVAI

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

Introduction

The accumulation of potentially dangerous chemical compounds and elements – particularly toxic heavy metals – has decisive sanitary influence and results in irreversible changes in the environment. Industrialization and the intensification of agricultural production have caused adverse *environmental effects* in Hungary: in fact, polluted areas cover about 10% of the country, but affect nearly 40% of the whole population (MOLNÁR, 1995; NÉMETH et al, 1993; VÁRALLYAY, 1990).

The fate of these elements must be followed *in the food chain*. Slow or accumulative changes in the environment may be captured only by long-term studies, following the way they appear in nature. Limited duration of study might miss important results or lead to misinterpretation (KÁDÁR, 1994, 1995). On the other hand, various laboratory model experiments are also necessary to obtain information about the mechanism of processes occurring in either natural or experimental systems. Only the results of an interdisciplinary and complex research work can provide a more detailed and comprehensive understanding of the phenomena.

In order to monitor the *dynamics of heavy metals*, their transformation into different forms, retention within an ecological system, and transfer through biological pathways, a food chain study has been initiated based on long-term field trials with toxic metals. The purpose of this work is to evaluate the movement of some important contaminants in the soil–plant system. The goals of the research are: to study

- the *phytotoxicity* and effects of applied heavy metals on the quantity and quality of the crop,
- their *uptake* by and transport within the plants, accumulation in different organs (shoot, leaves, stalk, grain),
- the *behaviour* of these elements in the soil (fixation, leaching, transformation, availability).

All of the *soil and plant samples* originating from the field trial are analyzed in the same laboratory using identical methodology and conclusions can be drawn after the statistical evaluation and interpretation of these data. Having this principal, the described approach enables us to assess the limit (threshold and trigger) values of micropollutants and to calculate the transfer coefficients of each toxic element via the first part of the food chain.

Material and Methods

A long-term field trial was set up at the Őrbottyán Experimental Station of RISSAC on calcareous sandy soil in 1994. The main characteristics of the soil are as follows: $pH_{(KCl)}$ 7.0, clay content about 5%, $CaCO_3$ 4%, organic C 0.6%. Four levels (0, 30, 90 and 270 kg/ha) of the selected metal salts (Cr(III), Cr(VI), Cu, Pb, Se, Zn, in the form of $Cr_2(SO_4)_3$; $K_2Cr_2O_7$; $CuSO_4$; $Pb(NO_3)_2$; Na_2SeO_3; $ZnSO_4$, respectively) were added to the 35 m² plots once at initiation and were mixed into the 0-20 cm ploughed layer. The treatments were arranged in a split-plot design with triplications. The experimental plots were cultivated with commonly used agrotechnics, mineral fertilizers were added yearly (100 kg/ha N, P_2O_5, K_2O as Ca-ammonium nitrate, superphosphate and 60% KCl) to ensure sufficient macronutrient supply. Different crops were grown each year: carrot in 1995, pea in 1996.

Composite *soil samples* consisting of 20 subsamples were collected yearly from the ploughed layer of each plot. Using 20-40 plants or plant parts per plot randomly, plant samples were taken yearly during the vegetation period at phenophases, i. e. foliage before rooting, root and foliage at harvest in case of carrot, and green and dry grain, and straw at harvest in case of pea.

The „total" amount of the elements in homogenized *soil and plant samples* were measured after microwave digestion using cc. HNO_3+H_2O_2. In the soil samples the so-called „mobile" fraction extracted with ammonium-acetate + EDTA (LAKANEN & ERVIÖ, 1971) was also determined. The composition of prepared samples was analyzed by inductively coupled plasma spectrometry (ICP- AES) detecting 25 elements.

Results and Discussion

Phytotoxicity and plant uptake

Carrot was grown in the first experimental year. Cr(VI) and Se treatments already showed drastic phytotoxic effects *early in the vegetation period*, even at the 90 kg/ha load, which resulted in the dying out of almost all plants. In addition to these toxic elements, Zn also proved to decrease the growth of carrot. On the treated plots plants partly perished or did not spring and the rest of the population remained at a lower stage of development. In case of Se load the increasing average root weight could just partly compensate the decrease in plant density. The phytotoxic effects of applied elements on carrot at *harvest* are characterized in Table 1. At the end of the vegetation period even the amount of green canopy yield indicated the extreme, strong and moderate phytotoxicity of Cr(VI), Se and Zn, respectively. Although, due to bad weather conditions, the crop yields in the region were generally low (about 20 t/ha), the root production was similarly reduced to 90%, 80% and more than 50% over the control by the 90 kg/ha load of the above-mentioned elements, respectively. At the highest dose of Cr(VI) and Se the harvest was found to be negligible. The rate of root

Table 1

Phytotoxic effects of applied elements on carrot at harvest
(Calcareous sandy soil, Őrbottyán, 1995)

Element applied	Load (kg/ha) in 1994				$LSD_{5\%}$	Average
	0	30	90	270		
			Root yield, t/ha			
Cr(VI)	15.9	6.4	1.5	0.1		6.0
Se	18.5	12.5	3.3	0.2	13.0	8.6
Zn	22.9	22.7	9.6	6.6		15.5
			Canopy yield, t/ha			
Cr(VI)	6.3	2.3	0.7	0.1		2.3
Se	5.8	3.0	1.3	0.1	2.9	2.4
Zn	4.0	4.4	4.2	3.4		4.0
			Rate of root and canopy yield			
Cr(VI)	2.5	2.8	2.1	1.0		2.1
Se	3.2	4.2	2.5	2.0	1.1	3.0
Zn	5.7	5.2	2.3	1.9		3.8
			Dry matter content of root, %			
Cr(VI)	13.3	14.6	14.8	9.4		13.0
Se	15.1	14.7	13.2	4.4	4.2	11.8
Zn	14.4	14.8	13.1	13.2		13.9
			Dry matter content of canopy, %			
Cr(VI)	20.1	22.6	24.5	14.3		20.4
Se	25.3	25.0	18.9	6.8	9.2	19.0
Zn	25.9	26.9	20.6	19.3		23.2
			Fresh weight of root, g/pieces			
Cr(VI)	29	22	22	7		20
Se	29	56	62	9	22	39
Zn	36	37	34	31		34

Remark: The Cr(III), Cu and Pb treatments were ineffective and canopy yield decreased meaningfully on the plots with higher contamination, so the depression mainly concerned the root, the edible part of carrot. The dry matter content of root and canopy was reduced significantly only by the highest (270 kg/ha) dose of Cr(VI) and Se.

The uptake of toxic elements by carrot can be followed in Table 2. The canopy showed high element accumulation *early in the vegetation period* (6 June). Since the leaves were not washed, their contamination by dust can be considerable. Considering this fact, the origin of the overwhelming Se content of canopy samples from control plots is questionable. *At harvest* (11 September), these samples were undusted mechanically and rinsed with water. This time, the Se concentation in the canopy was detected to be about 2 mg/kg. Generally, it can be summarized that the amount of each applied toxic element in the canopy decreased by 30-50% at maturation as compared to the previously studied phenophase. The root composition at harvest reflected the treatments well. Selenium was found to be the most mobile element in this plant part, it accumulated in amounts two orders of magnitude higher on plots with the

Table 2

Effect of treatments on the total element content of carrot, mg/kg, on dry matter base (Calcareous sandy soil, Őrbottyán, 1995)

Element applied	Load (kg/ha) in 1994				$LSD_{5\%}$	Average
	0	30	90	270		
			Canopy in early June			
Cr(III)	10	31	71	78	30	47
Cr(VI)	12	27	21	64	30	31
Cu	7	14	61	89	16	43
Pb	4	15	31	179	15	57
Se	1	29	48	56	18	34
Zn	23	32	48	102	17	51
			Canopy in mid-September at harvest			
Cr(III)	2	7	15	36	5	15
Cr(VI)	2	6	14	22	5	10
Cu	9	14	44	47	3	29
Pb	2	5	9	25	2	10
Se	1	58	149	-	23	69
Zn	30	38	50	48	9	42
			Root in mid-September at harvest			
Cr(III)	3	8	12	31	3	13
Cr(VI)	4	6	8	11	3	7
Cu	7	9	19	24	2	15
Pb	3	6	9	39	2	14
Se	1	27	56	103	9	35
Zn	20	36	46	66	7	42

maximum Se load (270 kg/ha) than on control plots. Cr and Pb also showed high accumulations, reaching an order of magnitude higher values as compared to the control. Concerning regulation, root yields from plots with the highest loads of Cr, Pb and Se became non-permissible for human consumption. It is noticeable that the concentration of these elements in carrot grown on calcareous chernozem with similar treatments were 1/2-1/3 of the values obtained in this experiment. Obviously, the buffering capacity of a sandy soil poor in colloid fraction is much lower than that of a loamy soil.

Pea was cultivated in our field trial in 1996. In this year only Se and Zn treatments resulted in considerable phytotoxicity, while Cr(VI), which caused serious depression in the carrot yield the year before, was found to be ineffective. The crop results of pea are summarized in Table 3. The green grain yield decreased by more than 50% over the control in plots treated with 90 and 270 kg/ha Zn, as well as with 90 kg/ha Se. The highest Se load (270 kg/ha) resulted in a nearly total reduction of pea production. Similar trends were observed in the pod yield. The depression was found to be less effective on straw yield, so it can be concluded that contamination with Zn and Se, first of all, inhibited the growth of the generative part of peas.

Evaluating the results of plant composition (Table 4) it was clear that element accumulation in pea straw reflected better the presence of each contaminant in soil. The concentration of Cr(III), Cr(VI), Pb and Zn in straw was found to be 4-10 times higher at higher loads than in the control. The uptake of

Table 3

Phytotoxic effects of applied elements on pea at harvest (Calcareous sandy soil, Őrbottyán, 1996)

Element applied	Load (kg/ha) in 1994				$LSD_{5\%}$	Average
	0	30	90	270		
			Grain yield, t/ha			
Se	0.70	0.63	0.23	0.02	0.21	0.40
Zn	0.97	0.94	0.40	0.45		0.69
			Pod yield, t/ha			
Se	0.45	0.51	0.22	0.04	0.19	0.31
Zn	0.68	0.68	0.32	0.28		0.49
			Straw yield, t/ha			
Se	2.62	2.05	0.99	0.22	0.32	1.47
Zn	2.91	3.02	1.73	1.91		2.39
			Pod number, 1000 pieces/ha			
Se	712	645	307	64	171	432
Zn	772	868	557	496		673

Remark: The Cr(III), Cr(VI), Cu and Pb treatments were ineffective.

Table 4

Effect of treatments on the total element content of pea, mg/kg, on dry matter base (Calcareous sandy soil, Őrbottyán, 1996)

Element applied	Load (kg/ha) in 1994				$LSD_{5\%}$	Average
	0	30	90	270		
			Grain			
Cr(III)	0.2	0.2	0.1	0.1	0.1	0.1
Cr(VI)	0.1	0.1	0.2	0.2	0.1	0.1
Cu	9.0	10.6	11.0	10.8	2.1	10.4
Pb	0.1	0.4	0.3	0.6	1.3	0.4
Se	0.6	100.9	167.3	169.7	24.6	109.6
Zn	58.9	82.4	79.8	98.0	10.5	79.8
			Straw			
Cr(III)	0.5	0.8	1.0	1.7	0.7	1.0
Cr(VI)	0.4	0.8	1.3	4.0	0.7	1.6
Cu	5.3	6.0	7.4	8.8	1.6	6.9
Pb	2.0	3.6	4.7	8.4	1.5	4.7
Se	1.0	69.4	168.7	213.3	18.2	113.0
Zn	17.3	29.6	36.8	70.6	13.2	38.6

Se was extreme at nearly the similar rate by both examined plant parts. Additionally, in grain only Zn accumulation was enhanced slightly (maximum by 50% over the control) by rising loads and the concentration of Cu remained on the same level (10 mg/kg on the average). Cr and Pb remained unchanged in the treatments with an average content of 0.1-0.3 mg/ kg.

„Mobile" and „total" fractions of applied elements in soil

The so called „mobile" fraction of applied elements was determined in both experimental years, while their „total" amount only in 1995. These results are presented in Table 5. The values of „total" amount – extracted using the mixture of concentrated nitric acid and peroxide with microwave digestion – reflected more or less the amount of applied elements. It is practically estimated that the plough layer weighs 3 million kg/ha, so a 3 kg/ha load of each element makes a 1 mg/kg concentration increase in soil. The „mobile", i. e. available fraction – extracted with the mixture of ammonium acetate and EDTA – varied widely for the different examined elements. The rate of „mobile" fraction as compared to the „total" amount was 1-2% in case of Cr, 30-40% in case of Se and Zn, and about 60% in case of Cu and Pb. Comparing the results of the determination of AAc+EDTA-extractable fractions in 1995 and in 1996 a con-

Table 5

Effect of treatments on the element content of soil, mg/kg, on dry weight base (Calcareous sandy soil, Őrbottyán)

Element applied	Load (kg/ha) in 1994				$LSD_{5\%}$	Average
	0	30	90	270		
	„Total" amount, 1995					
Cr(III)	10	24	44	138	12	54
Cr(VI)	10	15	35	109	12	42
Cu	5	23	49	156	16	58
Pb	8	18	36	85	10	37
Se	0	6	17	43	3	16
Zn	20	34	57	103	15	53
	„Mobile" fraction, 1995					
Cr(III)	0.1	0.4	0.6	1.2	0.6	0.6
Cr(VI)	0.1	0.3	1.1	3.2	0.6	1.2
Cu	1.2	13.0	40.9	116.1	17.0	42.8
Pb	2.4	9.7	24.8	63.8	4.5	25.2
Se	0.2	1.9	6.8	20.5	2.0	7.4
Zn	2.0	7.3	20.3	54.9	8.4	21.2
	„Mobile" fraction as a percentage of the „total" amount, 1995					
Cr(III)	1	2	1	1	-	1
Cr(VI)	1	2	3	3	-	2
Cu	24	57	83	74	-	60
Pb	30	54	69	75	-	57
Se	50	32	40	48	-	42
Zn	10	21	36	53	-	30
	„Mobile" fraction, 1996					
Cr(III)	0.1	0.3	0.4	0.8	0.3	0.4
Cr(VI)	0.1	0.3	0.6	1.5	0.3	0.6
Cu	1.2	3.8	16.1	93.6	25.6	28.7
Pb	3.2	5.8	14.0	29.6	9.0	13.2
Se	0.4	3.1	5.7	14.4	1.0	5.9
Zn	1.6	5.0	26.9	51.9	15.7	21.4

Remark: „Total" amount was extracted with cc HNO_3 + cc H_2O_2, the „mobile" fraction was extracted with AAc-EDTA

siderable transformation of applied elements into less available forms during one year can be proved. The decrease was about 30% in case of Se, Cu and Cr(III) and about 50% for Cr(VI) and Pb. In case of Cr(VI), as it exists in anionic form, leaching can be taken into account as one reason of loss. However, according to the absolute values changes can be assumed significant only in the case of Pb and Cu.

Summary

Long-term field trials were set up in 1994 on calcareous sandy soil to examine the plant uptake of some toxic elements. Cr(III), Cr(VI), Cu, Pb, Se, Zn loads were 30, 90 and 270 kg/ha in form of soluble salts. The „total" amount – determined after microwave digestion using cc. HNO_3+H_2O_2 – and „mobile" fraction – extracted with AAc+EDTA – of these elements in soil were determined. The composition of different parts of carrot in 1995 and pea in 1996 was also obtained. Plants were grown on experimental plots cultivated with commonly used agrotechniques. Phytotoxic effects were followed by examining the development of these plants during the vegetation period and the crop results.

Se was found to be extremely phytotoxic each year even at a dose of 90 kg/ha, while the effect of Zn was more moderate, presumably because of leaching. Cr(VI) caused depression only in the first experimental year in the case of carrot. The toxicity of Cu, Cr(III) and Pb could not be proven on this soil. According to its effect, the accumulation of Se was most enhanced in both plants. Additionally, the concentration of Cr, Cu, Pb and Zn rose considerably in carrots and significant accumulation of Zn was found in pea. Soil tests indicated that the „mobile", available fraction of elements varied widely and did not follow the observed plant uptake, and decreased significantly during one year.

At present, we are at the early stage of understanding the movement of microelement pollutants through the soil–plant–animal food chain. Only the results of complex investigation can be useful, since the phenomena should be studied in the way it appears in nature. Presented results and conclusions are meaningful parts of such a comprehensive research.

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