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Trace element levels and selenium uptake in cereals grown in lower Austria

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Abstract: Wheat, barley, rye, and maize were grown in field and pot experiments at various non-contaminated soils in order to establish uptake rates for added selenate, and to find baseline concentrations for various soil types. Edible parts (grains) and stalks of the crops were analyzed separately for Se, as well as for Ca, Cu, Fe, Mn, P, S, and Zn. The addition of Na-selenate in admixture with the NPK 20:8:8 fertilizer had no influence on the composition of the other elements investigated. The proportions of added nitrate:selenate, and sulfate:selenate were kept constant. The Se- uptake rate differed among the cereals tested, it was highest for winter wheat. Utilization of added Se in the field ranged from 0,4 – 4,7%, and and in the pots from 3,3 – 5,4%, it was markedly lower in clay soil.

Whereas P and Zn were preferably found in the grains, Ca-Fe-Mn-S got enriched in the stalks. For the fields, the location had some influence upon Fe, Mn, and Zn, whereas it was not important for P, S, Cu, and strikingly, Ca. Pot and field experiments on similar soils led to different results, except for P and S. Maize (whole grains) was significantly lower in Ca, Cu, and Mn, and might even cause trace element deficiencies, if exclusively fed.

Few correlations between the trace elements investigated led to the conclusion that most element contents were governed by plant metabolism. Variations of mobile Fe in the soils were balanced by uptake into the stalks. The data are compared with data from other presumably non-contaminated sites.

1. Introduction

Selenium supply from basic food in Austria is generally low. Whereas farmed animals receive a trace element mix of Se, Cu, Mn, Zn, Co, and Fe, along with their commercial feedstuffs, to meet their nutritional requirements at the optimum, humans are supposed to select food of adequate trace element supply by themselves. Thus, dietary intake of Cu and Se in Europe have been estimated to range at the lower levels of requirements (Van CAUWENBERGH et al. 1995, PFANNHAUSER 1994).

For selenium, the National Research Council of the US recommends a daily intake of 50- 200 µg/day, and the German Society for Nutrition recommends 30 - 70 µg/day. In Austria, the range of daily Se-intake has been estimated to range from 36 to 68 µg/day (PFANNHAUSER 1992 and 1994). The low Se contents in Austrian soils (about 0,2 mg/kg; AICHBERGER, HOFER 1989) results in low Se contents of cereals, which are still used as basic food component for human nutrition.

In order to increase the Se- contents of cereals, addition of Na_2SeO_4 to mineral fertilizers has markedly increased the Se-contents of cereals in Finland (EUROLA et al. 1990), and experiments were needed in order to validate this practice for conventional Austrian farming. Selenium addition as Na_2SeO_3 turned out to be less effective, because it strongly adheres to the pedogenic oxides of the soils (HORAK & LIEGENFELD 1996; SAGER 1993 and 2002). Further on, moderate addition of selenate should not have any effect on the levels of other essential trace elements, yields, plant health etc. Last not least, memory effects of selenate addition had to be checked. Would elevated Se-levels in the edible parts of the crops be still detectable within the next growing season?

A field trial on cambisol in Switzerland showed that nitrogen supply effected the yield of summer wheat, but did not significantly change the composition of the grains with respect to Ca, Cu, Fe, Mn, P, and Zn (FEIL, BÄNZIGER 1993). Similarly, N- supply, Mg-sulfate addition or pesticide application hardly effected Ca, Cu, Fe, Mn, P, and Zn in winter wheat and potatoes (QUINCHE et al. 1987). Mg- sulfate addition did not even change the

Mg- contents in cereals, just in potato - tubers. Thus, no dilution effect due to increase of biomass occurred. Intense N- fertilization (ammonium sulfate or ammonium nitrate) on fields in Bulgaria, however, led to decrease in Ca from a rather high level, and to an increase in Fe and Mn for wheat and maize (PAVLOV, ILCHEV 1997) (see table 11).

Solubility as well as the efficiency of selective extractionss from soils to indicate plant availbals dfractions, are known to be governed by pH. The uptake of Zn/Mn/Ni into summer wheat, of Cd/Ni/Zn/Mn/Cu/Al into potatoes, and Cd/Mn/Zn into carrots showed just weak significant correlations with soil pH ($r< 0,6$), and scattered much (ÖBORN et al. 1995).

Within work it will be tried to point out possible differences in grain and stalk (straw) composition between various locations in different climatic zones and on different soils (Fuchsenbigl, Hirschstetten, Rottenhaus, Zwettl) of Lower Austria, as well as on experimental parameters (field experiment - pot experiment; winter - summer cereals).

2. Material and methods

2.1 Pot experiments

In 1997, 2 pot experiments were designed to investigate selenium uptake in 2 soils. These experiments were continued in the same pots and same soils with other crops in the next year.

As N, S and Se were added from the same fertilizer, the proportions N:Se and S:Se (added sulfate:selenate) remained constant thoughout.

2.1.1 Pot experiment 1

Pots of the Kick- Brauckmann type were filled with 4 kg of test soil + 4 kg of quartz sand. As test soils, a cambisol (non- calcareous, soil pH 5,3 from Zwettl) and chernozem (calcareous, soil pH 7.5 from Hirschstetten) were used (see table 1). For primary fertilization with PK and trace elements, 4 g of a a mineral fertilizer containing 14% P_2O_5, 38% K_2O, 5% MgO, 0,02% B, 0,03% Cu, 0,2% Fe, 0,04% Mn, 0,006% Mo, and 0,005% Zn were added to each pot.

Additionally, the nitrogen was added at 3 levels (zero- half- full) as nutrient mineral fertilizer of the 20:8:8 type (20% N + 8% P_2O_5 + 8 % K_2O), which frequently contained 20 mg/kg Se as Na_2SeO_4. The first addition was done before seeding, and the second at germination. Within the first year, winter wheat, summer wheat, summer barley, sommer rye, and durum wheat were planted. In the second year, all pots were seeded with summer barley, and received the same amount of nitrogen and sulfate, except for the zeroes.

2.1.2 Pot experiment 2

This was designed to investigate the effect of the soil: sand proportion on the selenium uptake. 8kg of sand: soil mixture were added to each Kick- Brauckmann Pot. The soils were the same as for pot experiment 1. Type A was sand: soil = 2+6 kg, type B was sand:soil = 4+4 kg, and type C was sand: soil 6+2 kg. Within the first year, summer barley and summer wheat were grown, and in the second year just summer barley. Nutrient supply was the same like in pot experiment 1, but there was just 1 level of selenium addition , besides the zero.

In the second year of the pot experiment (summer barley only), additional fertilization of the pots was done to cope with nutrient limitations, because just 2- 6 kg of soil were available for 2 years of plant growth.

2.2 Field experiments

The experiments were done at 3 experimental sites of different climatic zones and soil types (for soil characteristics see table 1). Winter wheat (WW), winter rye (WR), summer barley (SG), maize (KM) were tested, and the crops were rotated in the second year (WW-KM, WR-K, KM-SG, K-WW, SG-WR). Primary fertilization was done in the first year with a PK-fertilizer containing a selection of trace elements (see above), and in the second year with triple phosphate + KCl. N-supply was exclusively done by the multinutrient fertilizer 20:8:8, with or without Se addition. Trace elements were not added any more.

Table 1. Soil characteristics.

	Soil -pH	Humics content %	Clay size fraction %	Se-contents mg/kg	P-contents mg P/100g	K-contents mg K/100g
cambisol in pots	5,4	2,0	17	0,22	4,0	20,2
chernozem in pots	7,5	3,2	33	0,25	3,2	10,5
calc. phaeozem	7,5	3,4	33	0,35	14,8	14,6
clay soil	6,8	2,3	23	0,15	10,5	13,0
cambisol	5,9	1,9	21	0,28	4,8	10,9

Table 2. Basic and trace element fertilization in the pot experiments (given in mg/ pot).

N	20 %		9% NO_3-N + 11% NH_4-N
P_2O_5	8 %	(3,5 % P)	5% as water soluble phosphate
K_2O	8 %	(6,6 % K)	as water soluble potassium oxide
MgO	3 %	(1,8 % Mg)	as water soluble magnesium oxide
S	4 %		as water soluble sulfur
Se	16 ppm		as water soluble sodium selenate

2.3 Analytical procedure

1 g of dried and ground plant sample was weighed into a 250 ml beaker, mixed with 8 ml of 50% Mg- nitrate solution (50g in 100 ml), dried over 2 nights,, and finally ashed in the muffle furnace at 550°C for 4 hours. The remaining white residue was dissolved with 40 ml 1+1 HCl for 30 min at the boiling water bath, and made up to 100 ml. This converts Se to the quadrivalent form, which can be directly submitted to hydride AAS determination with $NaBH_4$. Each charge consisted of 12 samples + 2 blanks, matching the size of the muffle furnace.

These digest can be submitted to ICP-OES multi-element determination with certain limitations. The elements Ca, Cu, Fe, Mn, P, S, and Zn were evaluated. As, Co, Pb and Ni could not be determined because of background noise from the high Mg- level present, resp. insufficient detection limits. In case of B and Na, the blanks were too high, and Mg was used as a matrix reagent. The lines Cd-228, Cr-205 and Cr-267 could be reasonably read, but the detection limit was insufficient (0,1 mg/kg Cd, resp. 0,8 mg/kg Cr for 1g sample in 100 ml).

For reasons of control, all samples were measured undiluted and 1+3 diluted, and calibrants were matched with respective Mg matrix contents. Salt effects were lowest for Mn and Ca.

The final data were selected to match the anayltical range most properly. P and S were rather high and could only be taken from the diluted solutions. In case of Fe, Mn, and S, the mean results from 2 analytical lines were taken.

The method was checked with a reference grass sample (Austrian ring test of agricultural labs 1995), as well as with occasional alternative digests with $HNO_3/HClO_4$ and flame AAS determinations.

3. Results

3.1 Se- uptake experiment

3.1.1 Pot experiments

Application of the NPK 20:8:8 fertilizer containing Se led to significant increase of Se- concentrations in all 5 kinds of cereals investigated. Addition of 3g mineral fertilizer to each pot raised the mean Se-level from 8 µg/kg up to 86 µg/kg, and double amount addition of the same fertilizer raised the mean Se-level up to 130 µg/kg in the grains. No detectable effects from various soil types and sand:soil proportions used in the pot experiments could be noted. Se- uptake differed among the tested cereals, it was highest for winter wheat.

In the second year, summer barley was seeded to all pots, in order to recognize memory effects. Without previous Se- application, the mean level in summer barley grains was 13 µg/kg. It rose to 29 µg/kg after the 3g NPK fertilizer addition, and to 58 µg/kg after the 6g NPK fertilizer addition. This memory effect did not differ among soil types, or due to previous crops.

Table 3 shows the Se uptake and utilization rates of the supplied fertilizer within the 2 growing seasons. At the first fertilization level (48 µg Se per pot), average transfer to the grain makes 2,0 µg more per pot, with respect to the controls, which aims at a utilization rate of 4%. Adding double amount of fertilizer results in further Se-increase up to 3,8 µg per pot on the average. In this case, utilization rate is about 3%.

Table 3. Se- transfer to the grains for various cereals tested, and utilization rate.

Fertilization with 48 µg Se and 0,6gN per pot					
crop of 1st year	WW	SW	SG	Sr	DW
Se-uptake per pot	2,6	1,6	2,0	2,2	1,6
Se- utilization %	5,4	3,3	4,2	4,2	3,3
Fertilization with 96 µg Se and 1,2g N per pot					
crop of 1st year	WW	SW	SG	SR	DW
Se-uptake per pot	3,9	3,3	3,9	4,4	3,3
Se- utilization %	4,1	3,4	4,1	4,6	3,4

3.1.2 Field experiments

Selenium supply increased concentrations in the grains at all test sites. As the ratio of N:Se was kept constant, the applied Se- amounts varied slightly among the tested crops. For the low addition level, summer barley received 3,2g/ha, winter rye received 3,6 g/ha, and winter wheat received 4,8g/ha. For the high addition level, double amount was taken. Se uptake to the grains markedly differed among the test sites, even for the control group. The overall means of Se found in the grains was 14 µg/kg from the calcareous phaeozem at Fuchsenbigl, 6,6 µg/kg from the clay soil at Rottenhaus, and 5,0 µg/kg for the cambisol at Zwettl. At the calcareous phaeozem at Fuchsenbigl, Se increased from 14 µg/kg to 37,2 µg/kg, and finally to 65,2 µg/kg. At neutral the clay soil at Rottenhaus, Se increased from 6,6 µg/kg to 14,8 µg/kg, and finally to 22,6 µg/kg (table 4). Thus Se- transfer to the grains was significantly less from the clay soil, and the adsorption capacity of the local soil should be considered.

Soil analysis done after 2 years of Se- supply did not show differences in Se- contents. This may be due to the overall low Se amounts applied.

Table 4. Transfer of added Se to the grains, %.

	low addition level	high addition level
calcareous phaeozem	2,8 (2,0-3,8)	2,9 (1,8-4,7)
clay soil	1,0 (0,7-1,6)	0,9 (0,4-1,1)
non- calcareous cambisol	2,4 (2,2 - 2,6)	3,7 (2,8-4,4)

Increased Se-supply resp. Se- uptake within a physiological healthy range did not significantly alter the the composition of the edible parts of the cropped plants (wheat, barley, rye, maize) with respect to the other elements investigated. In case of potato tubers, the number of data was still too small.

3.2 Results sorted for elements

Table 5. Results for the field experiments, means in mg/kg.
cambisol = Zwettl
clay soil = Rottenhaus
phaeozem = Fuchsenbigl

		grains			stalks		
		cambisol	clay soil	phaeozem	cambisol	clay soil	phaeozem
Ca	maize 98	76	53	71			
	maize 99	13	34	29	3991		
	S barley 98	421		398			3974
	S barley 99	395	398	336	2953	3258	
	W wheat 98	372	389			1575	
	W wheat 99	254	288	352	1840	1660	2628
	W wheat 00	314	410	444			
	W rye 98	279	296	320		2362	3132
	W rye 99	195	309	276	1684	1379	
Cu	maize 98	2,3	2,6	2,4			
	maize 99	0,6	1,1	2,2	6,1		
	S barley 98	3,5	6,4	3,7			3,0
	S barley 99	2,8	3,4	5,0	2,4	1,5	
	W wheat 98	3,2	5,7				
	W wheat 99	3,2	4,2	4,4	1,7	2,1	3,1
	W wheat 00	6,2	5,2	5,9			
	W rye 98	3,0	4,0	1,7		< 1,0	1,3
	W rye 99	1,9	3,2	2,6	2,2	2,4	
Fe	maize 98	27,0	20,3	22,6			
	maize 99	22,1	18,4	14,7	229		
	S barley 98	38,5		33,7			67,4
	S barley 99	31,9	32,5	31,1	202	54,1	
	W wheat 98	23	26			103	
	W wheat 99	26	19	19	201	45	116
	W wheat 00	41	37	38			
	W rye 98	24,5	30,8	21,5		36	76
	W rye 99	15,6	36,8	19	172	24,1	
Mn	maize 98	3,6	5,9	4,4			
	maize 99	5,1	7,0	3,5	31,9		
	S barley 98	9,0	13,0	15,0			31,5
	S barley 99	11,3	12,6	15,0	8,7	12,4	
	W wheat 98	24	33			24,7	
	W wheat 99	24	34	39	24	41	22
	W wheat 00	33	35	46			
	W rye 98	14	18,0	15,5		8,8	19,6
	W rye 99				11,8	6,5	
P	maize 98	3006	3456	2590			
	maize 99	2762	3180	1916	669		
	S barley 98	3154	4116	3118			678
	S barley 99	3210	3216	3290	524	848	
	W wheat 98	2720	3667			910	
	W wheat 99	2842	3155	3272	497	525	280
	W wheat 00	3508	3773	3495			
	W rye 98	2419	2994	2730		717	487
	W rye 99	2580	2770	2581	838	745	
S	maize 98	634	735	732			
	maize 99	644	593	452	561		
	S barley 98	871	961	993			906
	S barley 99	779	686	716	917	840	

	W wheat 98	913	944			996	
	W wheat 99	714	763	862	821	730	853
	W wheat 00	899	1427	1319			
	W rye 98	764	647	659		670	656
	W rye 99	604	590	753	578	376	
Zn	maize 98	12,8	15,0	14,1			
	maize 99						
	S barley 98	14,7	21,7	14,7			5,0
	S barley 99						
	W wheat 98	18,1	23,7			9	
	W wheat 99						3,2
	W wheat 00	23,2	34,2	21,7			
	W rye 98	12,6	16,6	7,3		6,2	4,0
	W rye 99						

Table 6. Resultsof pot experiments, means in mg/kg.
cambisol = Zwettl
chernozem = Hirschstetten

		grains		stalks	
		cambisol	chernozem	cambisol	chernozem
Ca	S-barley 197				
	S-barley 198	304	301	5157	
	S-barley 297				
	S-barley 298	291	262	5422	5248
	D-wheat 197				
	S-.wheat 197				
	S- wheat 297				
	W-wheat 197				
	S-rye 197				
Cu	S-barley 197	6,4	5,7	8,1	5,3
	S-barley 198	6,1	6,1	4,2	
	S-barley 297	4,9	7,1	6,7	
	S-barley 298	5,3	6,1	6,0	4,0
	D-wheat 197	8,0	4,8	9,0	6,7
	S-.wheat 197	5,6	5,3	5,7	6,7
	S- wheat 297	7,0	5,9	6,7	10,6
	W-wheat 197	6,9	5,1	6,3	6,3
	S-rye 197	6,7	5,6	8,0	3,2
Fe	S-barley 197	78	39	455	186
	S-barley 198	60	44	202	
	S-barley 297	95	51	229	
	S-barley 298	59	32	394	167
	D-wheat 197	49	21	382	266
	S-.wheat 197	41	28	316	196
	S- wheat 297	47	43	442	318
	W-wheat 197	59	37	174	219
	S-rye 197	59	32	280	160
Mn	S-barley 197	41,8	10,5	458	31
	S-barley 198	28,9	12,4	174	
	S-barley 297	30,7	13,7	180	
	S-barley 298	22,3	11,2	163	25,7

	D-wheat 197	93	8,4	409	21
	S-.wheat 197	87	18	516	27
	S- wheat 297	68	23	240	33
	W-wheat 197	124	14	481	38
	S-rye 197	66	13	560	19
P	S-barley 197	3106	1824	603	311
	S-barley 198	3065	3305	513	
	S barley 297	2453	2736	392	
	S barley 298	2348	3279	419	446
	D-wheat 197	2723	1433	841	373
	S-wheat 197	2518	1929	477	279
	S-wheat 297	2808	3045	495	341
	W wheat 197	3378	2572	760	639
	S rye 197	2795	1979	692	329
S	S-barley 197	1262	740	4663	2134
	S-barley 198	1234	1307	2948	
	S-barley 297	909	700	3061	
	S-barley 298	1140	1040		1995
	D-wheat 197	1123	543	4974	2229
	S-.wheat 197	1002	835	3007	1634
	S- wheat 297	763	818	2324	1858
	W-wheat 197	1450	888	2383	1872
	S-rye 197	1261	647	5760	1938
Zn	S-barley 197			180	126
	S-barley 198	21,0	30,9	27	
	S-barley 297			99	
	S-barley 298	17,2	24,5	39	31,6
	D-wheat 197	47,8	17,5	245	116
	S-.wheat 197	43	24,9	209	124
	S- wheat 297	48,7	33,1	130	118
	W-wheat 197	46,1	34,7	178	155
	S-rye 197	19,5	31,3	149	277

3.2.1 Calcium

Calcium was not added via the fertilizers. It got accumulated in the straw. In the grains, no difference between locations was noted, in spite of different Ca contents of the soils used. The differences among various cereals were larger than between the sites. Ca was markedly low in maize at all 3 sites, also with respect to data found in published databases, especially for the second year of the field experiment.

The kind of plant growth experiment (field experiment - pot experiment) mainly effected the contens of straw. From the pot experiments, Ca in the grains was significantly lower, and in the straw it was significantly higher than from the field experiments (for summer barley). From the pot experiments, Ca in straw was about the same from the calcareous phaeozem soil from Fuchsenbigl, and the acid cambisol soil from Zwettl.

3.2.2 Copper

The low Cu- contents of the crops investigated were found to be in the same range like published in previous papers. Cu distributes about equal between grains and stalks. In the pot experiments, Cu had been added in an available form as a component of the primary fertilizer, but none was added in the field experiments. Plants from pot experiments contained more Cu than from the corresponding field experiments, above all in the stalks, Differences between locations were insignificant.

3.2.3. Iron

For the grains, no significant variations due to cereal type and location were found. Fe was preferably found in the stalks, and differed widely among the various locations. Stalks grown on the acid cambisol at Zwettl contained much more Fe than grown at other sites, which can be reasonably explained by higher mobility and availability in the cambisol.

In the pot experiments, some soluble Fe had been added as a component of the primary PK fertilizer, and thus the levels in grains and stalks got higher than from the open fields, and also concentration ranges increased. For the fields, the proportion grain content / stalk content tended to be higher.

3.2.4 Manganese

The Mn-contents in grains did not vary among the locations. Levels in maize were lowest. Major amounts of Mn moved to the stalks, and differed from site to site. For the acid cambisol, Mn- levels in stalks were highest.

Like in case of Fe, some soluble Mn had been added along with the PK primary fertilizers to the experimental pots. This led to higher Mn levels in both stalks and grains, except for the stalks from the (calcareous) chernozem..

3.2.5 Phosphorus

In the grains, P was accumulated 4-6 fold with respect to the corresponding stalks, and did not vary between locations. Thus, higher experimental P- mobility in the acid soil had no effect on P levels in the grains. Narrow concentration ranges in the grains and extended ranges in the stalks can be explained from balancing variable P-supply.

P had been added as a nutrient both in the field and pot experiments, but this experimental parameter did not effect the P- levels found.

In the grains, major parts of P might be bound as phytate (meso - inosite- hexaphosphate), which contains 28% of its weight as P. Phytate levels in cereals have been reported to range within 0,86 - 1,06% of dry mass (LOTT et al. 2000), which would be equivalent to 2424 - 2987 mg/kg P. Within this work, means in grains ranged within 1433-4116 mg/kg, and in stalks from 373 - 910 mg/kg.

3.2.6 Sulfur

After dry ashing with magnesium nitrate, total sulfur from sulfate and sulfur- containing amino acids was completely regained, and a total sulfur content of the plant samples can be given. Discrimination among sulfur containing compounds, however, would be beyond the scope of this investigation. Both for grains and stalks, the kind of cereal was the primary factor governing the S levels; soil type and location were not important.

Sulfate was supplied along with the nitrogen component, and the experimental conditions largely influenced the sulfur levels in the stalks. Sulfur as a soluble sulfate is readily washed out to deeper soil layers (SAGER 2003), but this was not possible in the pot experiments. Storage capacity for sulfur depends on the turnover of sulfate by soil-micro- organisms.

From the fields, grains and stalks were approximately at the same S-level, whereas from the pots, obviously excess S was found in the stalks. In the second year from the fields, S-levels were significantly lower in grains and stalks for maize, summer barley and winter wheat.

In the second year from the pots, however, S - levels in the grains increased.

3.2.7 Zink

Zn accumulated in the grains, except from the calcareous phaeozem fields (Fuchsenbigl) in the second year. From the fields, Zn levels were about equal for all crops.

In the pot experiments, Zn was added as a component of the primary PK- fertilizer. Thus, Zn in grains from the pots tended to be higher than from the corresponding field experiments. The differences were more pronounced for the acid soils, because of higher mobility therein.

3.3 Results sorted for other parameters

3.3.1 Sorted for crops

Sorting of data according to crops revealed marked differences just for sulfur, for both grains and stalks. Fe and Zn ingrains and stalks, and Mn in the stalks, were in the same range throughout. Maize was significantly lower in Ca, Cu, and Mn than the other cereals.

3.3.2 Locations

Sorting of data according to locations did not show any differences for Ca, Cu, Fe, Mn, P, and S in grains, which leads to the conclusion of strong metabolic influence on the composition of plant organs, which are important for the generative reproduction of annual green plants. Just Zn in samples from the clay soil at Rottenhaus was slightly higher.

3.3.3 Experimental parameters

Contrary to conditions in the open field, pot experiments permit root growth just within a limited space. Further on, it was attempted to achieve trace element supply for the pot experiments at an optimum level, by adding a cocktail of trace elements along with the primary fertilizer. Thus, for seedlings in the pot experiments, additional soluble B, Cu, Fe, Mn, Mo, and Zn was available.

Therefore, higher levels of Cu and Zn were achieved for grains and stalks from the pots. In case of Fe and Mn, differences in Fe and Mn were more pronounced for the (acid) cambisol than for the (calcareous) chernozem. Just in case of Ca, which was not contained in the fertilizers, reverse effects were noted - less Ca in grains, and more Ca in stalks from the pots.

No differences emerged for phosphorus in grainsand stalks, and for sulfur in grains.

Table 7. Summary of effects.

sorted according to		**Ca**	**Cu**	**Fe**	**Mn**	**P**	**S**	**Zn**
crop	grains	*	*	no	*	parts	yes	no
	stalks	Sbarley+	#	no	no	parts	yes	no
location	grains	no	no	no	no	no	no	rye +
	stalks	no	no	yes	no	no		no
pot- field	grains	<	>	>*	>*	no	no	>
	stalks	>	>	>	>*	no	parts	>
precision	grains	~	~	~	>	~	>	>
	stalks	~	~	>	>	~	~	>

*	maize < cereals
#	maize > cereals
parts	partially
~	about constant

3.4 Statistical evaluations

3.4.1 Correlations (data from field experiments only)

In general, for essential elements there are relationships between offer and tissue levels in case of too high and too low supply. Within the range of adequate supply, however, the tissue level is regulated by metabolism of the living cells, when an equilibrium between uptake and excretion can be achieved. For substances which are not submitted to special receptor mechanisms, but enter the living cell by diffusion or dissipation, general relationships between external supply and tissue levels are expectable.

As the conditions in the pots have been changed before seeding by addition of the primary fertilizer containing a cocktail of elements, statistical evaluations were restricted to data from the field experiments.

The data were sorted according to crops, and the concentrations were correlated. (table 8). Just a few significant correlations emerged, like Ca-S, Mn-P, and Zn-P, and Mn-Ca for stalks only. The so-called micronutrient elements were largely independent from one another (or at least less then the analytical precision).

In stalks of winter wheat, the element proportions Fe/Mn - Ca/P significantly correlated with r= 0,819 (N=10). As a proof of this data evaluation, no significant correlations could be obtained with selenium data

Table 8. Significant correlations.

The subsequent table contains substrate, correlation coefficient and the number of paired data one below the other Data from field experiments only, and given correlations are restricted to > 0,5

	Cu	Mn	P	S	Zn
Ca	maize grains 0,538 28	barley stalks 0,943 15 rye stalks 0,736 20	barley grains 0,628 30	barley grains 0,631 30 wheat grains 0,901 25 wheat stalks 0,529 16 rye stalks 0,856 20	wheat grains 0,871 13
Cr			wheat stalks 0,643 15	barley grains -0,612 30	
Cu	X		barley grains 0,639 30 wheat stalks 0,658 15		wheat grains 0,832 13 wheat stalks 0,940 6
Fe					rye grains 0,615 20
Mn		X	maize grains 0,709 31 wheat grains 0,729 25 rye grains 0,585 30		rye grains 0,594 21
P		rye stalks -0,598 20	X	maize grains 0,662 31	maize grains -0,680 19 wheat stalks 0,973 6 rye grains 0,647 21
S		rye stalks 0,564 20		X	barley stalks 0,618 5 wheat grains 0,812 13
Se				rye grains 0,505 23	

3.4.2 Factor analyses

In order to look for relations which are beyond a simple linear function between 2 concentrations, factor analysis was separately done with data from each crop. The obtained factors differed for each dataset, and no general interpretation can be given at the moment (see table 9). The presumable anions P and S, and chemically related Fe-Mn, or S-Se were not necessarily seen in the same factors.

Table 9. factor analysis.

Factor	**maize grains**	**W-rye grains**	**W-wheat grains**	**W-rye stalks**	**W-wheat stalks**
1	P-S-Mn	Fe-P-Zn	Ca-S	S-Ca-Mn	S-Ca-Se
2	Ca-Cu	S-Se	Mn-P-Cu	P- (-Zn)	Cu-P
3		Cu-Ca	Se	Zn –(-Mn)	Fe- (-Mn)

3.5 Nutritional aspects

The investigated crops investigated in this work are main components of the meals for men and farmed animals. Thus, another aspect of current investigations is to ensure adequate supply with trace elements. Table 10 shows the daily needs of men for these trace elements, recommended by the German Society of Nutrition DGE (simplified after RADKE 1992)), together with the loads obtained from exclusive feeding on cereals and maize from the field experiments (means). The figures for selenium refer to the grains not supplemented with selenium.

Table 10. Nutritional Aspects.

	human daily needs mg	cereals mg/kg (field)	maize mg/kg (field)	kg cereals containing daily needs	kg maize containing daily needs
Ca	1000	250 –470	13 – 76	2 – 4	13 – 77
Cu	1,5 – 3,0	1,7 – 6,4	0,6 – 2,6	0,2 – 1,8	0,6 – 5,8
Fe	10 – 15	19 – 39	15 – 27	0,3 – 0,8	0,4 – 1,0
Mn	2,0 – 5,0	9 – 39	3,5 – 7,0	0,05 – 0,5	0,3 – 1,4
Zn	12 – 15	7 – 24	13 – 15	0,5 – 2,1	0,8 – 1,2
Se	0,02 – 0,1	<0,004-0,01	<0,004-0,007	2 - > 25	3 - > 25

According to the recommendations of the DGE (after RADKE 1992), exclusive feeding with maize would lead to severe deficiencies in Se, Cu, and Ca, and possibly also in Mn (table 10). The cereals lead to deficiencies in Ca and Se. They supply adequate amounts of Cu, Mn, and Zn, but mind that whole grains have been taken into account. Se- deficiency is not predicted in case the cereals have been fertilized with the seleniferous NPK 20:8:8 (20 mg/kg as Na_2SeO_4).

Wheat, barley, rye and maize are basic food for men and pigs, and have been investigated in the past quite often. Table 11 shows some data about the same elements, published elsewhere.

Nutrient supply and genetic strain seem to have low influence upon the essential element contents, because this seems strictly regulated by plant metabolism. Thus, from the sandy soils of northern Poland, which are extremely low in Cu and Zn, crops with about the same Cu-Zn levels were produced like elsewhere (Ruszkowska et al. 1996)

Table 11. Some published data about trace elements in cereals - means from field experiments.

mg/kg	Ca	Cu	Fe	Mn	P	Zn		Lit.
S wheat	250	6,1	41,9	39,7	3650	30,4	0 kgN/ha	Feil 1993
	242	6,4	41,3	40,1	3630	28,8	50	
	256	5,6	40,3	39,8	3650	28,2	100	
	272	6,2	37,6	39,4	3610	26,9	0	
	240	5,3	40,3	38,5	3600	28,7	50 (late)	
	236	6,6	45,6	41,7	3720	31,7	100 (late)	
W wheat	480	4,0	37,3	53,2	4200	29,2		Quinche 1987

	400	3,6	40	56,0	3950	25,3		
	410	3,7	36	54,5	3960	26,3		
potatoes	470	6,1	43	6,4	270	15,6		
	380	6,9	40	10,1	260	18,4		
wheat	7200	4	64	24	1700	24	0	Pavlov 1997
	5200	5	94	28	2100	26	NH_4NO_3	
	5700	4	95	36	1800	27	$NH_4(SO_4)_2$	
maize	5300	6	132	45	2210	33		
S barley		6,0		15		47	130-230 kgN/ha	Ruszkowska 1996
W wheat		6,4		22		24	130-230 kgN/ha	
rye grains		4,0				24,5		Horak 2000
rye stalks		2,3				9,0		
wheat grains		2,0				18,8		
wheat grains		2,3				24,1		
wheat grains		4,8				27		

Another approach of data interpretation might be table 12, presenting data from the International Plant Exchange (IPE) analytical program of Wageningen Agricultural University /The Netherlands, and also data from the ALVA (Austrian Society of Agricultural Labs). These data are very safe with respect to analytical precision (in some cases more than 100 labs have analyzed these samples), but fertilization mode and soil types are unknown to the user. Most of the samples were probably grown in the Netherlands.

Wheat and barley grains grown in Lower Austria had just half of the Zn of the samples from the Netherlands,

Wheat and barley grains grown in Lower Austria were at the same level with respect to Cu, Mn and Fe like the samples from the Netherlands, but had just half of the Zn. For maize, just one reference value has been available, because within the IPE program, whole plants were analyzed. This maize was also very low in Cu and Ca.

Table 12. Data from the International Plant Exchange Program, Wageningen/ The Netherlands, and other ring tests.

Medians	**test run**	**Cu**	**Mn**	**Fe**	**Zn**	**Cr**	**Se**	**Ca**	**P**	**S**
barley	ALVA 92	5,0	17,3	31	25,5	0,21	X	640	3980	X
summer barley	IPE 93.1	5,8	16,6	60	39,5	0,307	X	520	3410	X
summer barley	IPE 93.5	6,0	X	8	43,9	0,313	X	400	3286	X
barley	ALVA 95	4,6	18,1	37,6	26,3	0,111	0,020	540	4120	1190
barley	IPE 96.2	5,08	21,3	50	52,3	0,26	0,020	580	3782	1395
barley	IPE 96.3	5,57	38	52	54,6	X	0,013	400	3565	X
barley grains	IP3 97.5	4,81	20,8	47,5	51,5	0,159	0,016	592	3751	1350
barley grains	IPE 98.1	5,3	16,1	41,9	50,8	0,173	0,012	536	3013	1414
barley grains	IPE 98.3	5,44	36	53,5	54,2	0,23	0,022	500	3813	1478
barley grains	IPE 98.4	4,6	20,6	47,8	51,5	0,179	0,016	532	3813	1370
barley grains	IPE 99.1	5,34	16,2	43,6	52	0,213	0,020	516	3035	1427
barley grains	IPE 99.5	5,35	36	52	54	0,118	0,015	440	3534	1440
barley grains	MÜHLE	4,1	17	39,5	23,2	0,23	X	X	X	X
barley grains	Ostautobahn	2,4	X	X	16	X	0,046	X	X	X
barley stalks	IPE 96.5	2,22	19	103	11,9	0,495	0,038	2800	896	X
barley stalks	IPE 98.5	2,06	19,2	103	11,6	0,433	0,039	3072	905	1411
barley stalks	IPE 99.3	2,16	19,2	105	12	0,452	0,040	2764	899	1408
potatoes	IPE 92.2	6,0	5,7	54	16	0,5	X	X	X	X
potatoes	IPE 99.3	4,15	5,74	66,6	16	0,203	0,026	1628	3013	1283
potato leaves	IPE 99.6	5,47	44,6	1088	36,8	2,18	0,054	26720	1823	2474
maize	IPE 98.5	3,7	27	410	48,1	1,406	0,038	4120	1996	1456
maize	IPE 94.3	3,76	27	420	49	1,416		4000	2009	XX

maize plants	IPE 96.3	5,6	94	171	76,4	0,68	0,031	3000	1934	X
maize plants	IPE 96.5	11	178	510	62,3	1,315	0,036	2600	1392	X
maize plants	IPE 98.2	4	74	100	64,8	0,437	0,022	3304	2660	1155
maize plants	IPE 98.4	5,22	91,5	168	75,9	0,657	0,028	3104	1941	X
maize plants	IPE 99.2	4,00	74	100	65,1	0,488	0,026	3292	2700	1168
maize plants	IPE 99.3	4,41	27,8	51,7	30,1	1,079	0,044	3612	1789	1024
maize plants	IPE 97.6	3,7	27	421	49,3	1,325	0,020	4080	1987	1482
maize	IPE 99.4	11,1	178	500	61,2	1,189	0,037	2696	1398	1107
maize	IPE 99.5	6,49	121	185	47,7	0,55	0,025	1840	1500	928
maize flour	IPE 94.1	2,39	6,49	28	21,8	0,321	X	120	2846	X
rye	ALVA 98	4,09	36,6	34,3	28,5	X	0,011	420	3440	1300
straw	ALVA 96	1,8	32,5	132	10,5	0,42	0,070	X	830	X
wheat	IPE 93.1	5,0	52	45	52	0,362	X	440	3906	X
wheat grains	IPE 98.1	4,69	36,8	51,3	42	0,114	0,056	428	3658	1354
wheat grains	IPE 98.2	3,2	19,1	34,9	23	0,197	0,068	327	3844	970
wheat grains	IPE 99.1	4,85	36,8	53,7	41,9	0,193	0,059	368	3658	1382
wheat grains	IPE 99.2	3,3	18,9	34	23,1	0,212	0,075	364	3906	976
wheat grains	MÜHLE	3,51	30,9	32,1	22,5	0,24	X	X	X	X
summer wheat	IPE 97.2	5,85	67,9	46,2	55,8	0,157	X	400	3286	X
summer wheat	IPE 94.2	5,73	69,4	46	56,1	X	X	420	3286	X
wheat stalks	IPE 97.6	2,18	21,2	112	10,5	X	0,033	3120	840	1485

The dataset labelled as „Mühle“ refers to a ring test to evaluate contaminations from milling and grinding of cereals (SAGER, MITTENDORFER 1997). The dataset „Ostautobahn“ presents the measn from 44 samples taken between Parndorf and the Hungarian border, before the construction of todays highway between Vienna and Budapest (SAGER 1992).

Conclusions

Current investigations clearly show marked effects of the applied mineral fertilizers on the Se- concentrations of the tested crops. In the pot experiment, these effects remained for the second year also. It is possible to raise Se levels to the range which is regarded as the optimum for human nutrition. From the significant increases caused by even low additions it may be concluded that storage of Se in the soils will be rather marginal, and precautions have to be considered to avoid exceeding the physiological optimum range.

In the pot experiments, the soil type did not effect the Se transfer to the grains. The rather small amount of 4 kg soils per pot might have been too low to develop differences. Effects of pH, clay grain size and humics contents on the Se-transfer found in published references (JOHNSSON 1991; HORAK and LIEGENFELD 1996), were confirmed in the field experiments. They have to be considered to achieve optimum application rate.

Crops from pot experiments contained higher levels of trace elements than crops from field experiments done with the same soils, except for P and Ca. Pot experiments thus do not necessarily reflect conditions in the field.

Trace element levels in crops obtained in grains from 3 locations which were different in climate and soil type, were equal.

Trace element levels for maize have been low enough to provoke deficiencies in Ca, Cu and Mn, if fed exclusively. Besides the known low selenium contents of Austrian crops, also Zn turned out to be lower with respect to reference data from other sources.

References

EUROLA M., EKHOLM P., YLINEN M., KOIVISTOININEN P., VARO P.: Effects of selenium fertilizations on the selenium content of cereal grains, flour and bread produced in Finland. Cereal Chem, 67, 334-337 (1990)

FEIL B., BÄNZIGER M.: Nitrogen and Cultivar Effects on the MIneral Element Concentration in the Grain of Spring Wheat. Eur. J. Agron. 2(3), 205-212 (1993)

GISSEL NIELSEN, G., UMESH, C. G., LAMAND, M. und WESTERMARCK, T., 1984: Selenium in soils and plants and its importance in livestock and human nutrition. Advances in Agronomy, 37, 397-460, 1984.

HALDIMANN M., DUFOSSÉ K, ZIMMERLI B.. Vorkommen von Selen in schweizerischen Cerealien. Mitt. Gebiete Lebensm. Hyg. 87, 267-295 (1996)

HOESCH J.: Steigerung der Selenaufnahme bei Getreide durch den Einsatz eines Mehrnährstoffdüngers mit Selenzusatz im Gefäßversuch. VDLUFA-Schriftenreihe, 52,

115-118, Kongressband 1999.

HORAK, O. und LIEGENFELD, R., 1996: Untersuchungen zum Selentransfer Boden-Getreide. VDLUFA-Schriftenreihe, 44, 687-690, Kongressband 1996.

JOHNSSON, L., 1991: Selenium uptake by plants as a function of soil type, organic matter content and pH. Plant and Soil, 133, 57-64, 1991.

LOTT N.A., OCKENDEN I., RABOY V., BATTEN G.D.: Phytic acid and phosphorus in crop seeds and fruits: a global estimate. Seed Sci. Res. 10, 11-33 (2000)

ÖBORN I., JANSSON G., JOHNSSON L.: A Field Study on the Influence of Soil pH on Trace Element Levels in Spring Wheat, Potatoes and Carrots. Water, Air and Soil Poll. 85, 835-840 (1995)

QUINCHE J.P., MAILLARD A., REUST W.: Teneurs en fer, manganese, cuivre, zinc, bore et lithium dans les grains du ble d'automne et dans les tubercules de pommes de terre (resultats preliminaires). Dev. Plant Soil Sci. 29, 202-217 (1987)

PAVLOV D., ILCHEV A.: Content of Nitrogen and Mineral Substances of the Winter Pea- Cereal Mixture, Maize and Sunflower with Intensive Utilization of the Soil. Plant Science (Sofia) 34 (9-10), 88-92 (1997)

PFANNHAUSER W.: Das essentielle Spurenelement Selen: Bedeutung, Wirkung und Vorkommen in der Nahrung. Ernährung/ Nutrition 16, 1992

PFANNHAUSER W.: Der Versorgungsstatus mit dem essentiellen Spurenelement Selen in Österreich. Lebensmittelchemie 48, 123-123 (1994)

RADKE M.: Neue Nährstoffempfehlungen der DGE. Ernährung/Nutrition 16 (4), 219-221 (1992)

RUSZKOWSKA M., SYKUT ST., KUSIO M.: Stan zaopatrzenia roslin w mikroelementy w warunkach zroznicowanego nawozenia w wieloletnim doswiadczeniu lizymetrycznym, Zesz. Probl. Postepow Nauk Roln. 434, 43-47 (1996)

SAGER M., MITTENDORFER J.: Influence of Milling or Cutting Procedures on Trace Element Contents of Plant Samples. Int. Journal of Environmental Analytical Chemistry 67, 59-71 (1997)

SAGER M.: Bericht über Schadstoffbelastungen der Parndorfer Platte vor dem Bau der Ostautobahn. Bericht der LCBA 1992.

SAGER M.: Selenium, in: Environmental Contamination, J.P. Vernet ed., Elsevier Amsterdam

1993, pp. 403-476

SAGER M.: Vertical mobility of selenium, arsenic and sulfur in model soil columns. Die Bodenkultur 53(2), 83-103 (2002)

STADLOBER M., SAGER M., IRGOLIC K.J.: Effects of Selenate Supplemented Fertilization on the Selenium Level of Cereals - Identification and Quantification of Selenium Compounds by HPLC – ICP-MS, Food Chem. 73, 357-366 (2001)

STADLOBER M., SAGER M., IRGOLIC K.J.: Identification and Quantification of Selenium Compounds in Sodium Selenite Supplemented Feed by HPLC-ICP-MS, Die Bodenkultur 52(4), 313-322 (2001)

Van CAUWENBERGH R., HENDRIX P., ROBBERECHT H., DEELSTRA H.A.: Daily dietary Cu- intake in Belgium, using duplicate portion sampling. Z. Lebensm. Unters. Forsch. 200, 301-304 (1995)