MACRO- AND MICRO ELEMENT LEVELS IN CEREALS GROWN IN LOWER AUSTRIA

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ABSTRACT

In order to study the effects of soil type and site conditions upon essential element levels in cereals, a pilot study of field and pot experiments were carried out on a Dystric cambisol, a Gleyic luvisol, a Calcareous phaeozem, and a Calcareous chernozem in 3 subsequent years. Based on the results of multiemelent analyses, it was evident that P and Zn were found mainly in the grains, and Ca, Fe, and Mn preferably in the straw. Concentrations in the grains were kept rather constant for Fe, Mn, S, and P, whereas the straw acted as a buffer to store excess mobile amounts. Apart from some differences due to cereal species and cultivars, additional supply of nutrient element fertilizer solution and shorter root length led to higher Cu, Fe, Mn, and Zn in cereals grown in pots, and a shift in the grain/straw ratios for Ca. Thus, the results obtained in pot experiments cannot be directly transferred to field conditions.

From at least 5 replicates of each setup, on the average, precision of analytical data obtained for whole grain samples was better than for straw samples, and precision obtained in pot experiments was less than those in field experiments. In pot experiments, increase of the number of replicates from 5 to 10 or 20 did not improve analytical precision.

KEYWORDS: essential element levels, wheat, rye, barley, maize

1. INTRODUCTION

Wheat, barley, rye and maize are basic food for human and animals (e.g.pigs). Their contents in macro- and micro elements depends on plant needs as well as amounts available from the soil. This ssstudy should deliver preconditions for the setup (number of replicates, fertilization practices) and interpretation of future projects of more detailed investigations, as well as establish baseline levels to recognize future contaminations.

A field trial on cambisol in Switzerland showed that nitrogen supply affected 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 [5]. Similarly, N- supply, Mg-sulphate addition or pesticide application hardly effected Ca, Cu, Fe, Mn, P, and Zn in winter wheat and potatoes [4]. Mg- sulphate 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 sulphate 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 [8]

Solubility as well as the efficiency of selective extractions from soils to indicate plant available fractions, 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 [6].

Nutrient supply and genetic strain seem to have low influence upon the essential element contents in the field, 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 [9].Samples were analysed in 5 replicates; summer barley had 9, 12, and 20 replicates, however, this did not improve the accuracy significantly. The abbreviations S, W, and D, stands for summer, winter, and durum, respectively.

In which way do soil type and fertilization practices influence the composition of grains and straw of cereals grown in Austria? A pilot study was set up to get an idea about the precision of the entire setup, to optimize the number of replicates for experimental conditions, and to check the compatibility of field and pot experiments. Interpretations of local differences need to consider the year to year variations on site. Apart from the concentration levels, significant correlations among the elements investigated might be of interest for nutritional aspects.

2. MATERIALS AND METHODS

2.1 Pot experiments

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. A Dystric cambisol (non- calcareous, soil pH 5,3 from Zwettl) and a chernozem (calcareous, soil pH 7.5 from Hirschstetten) were used (see table 1). For primary fertilization with PK and microelements, 4 g of 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. This means the addition of 23 mg P, 158 mg K, 15 mg Mg, 0,10 mg B, 0,15 mg Cu, 1,0 mg Fe, 0,20 mg Mn, 0,03 mg Mo and 0,025 mg Zn to 1 kg of the substrate.

Additionally, nitrogen was added at 2 levels. The upper level was to ensure optimum yields, the lower level was half of it, and zero addition served for comparison as mineral fertilizer of the 20:8:8 type (20% N + 8% P_2O_5 + 8 % K_2O), which contained 16 mg/kg Se as Na_2SeO_4 (see table 1). The first addition was done before seeding, and the second at germination. Within the first year, winter wheat, summer wheat (triticum aestivum (cultivars: Capo and Michael)), summer barley (hordeum vulgare (cultivar: Barke)), summer rye (secrale cereale (cultivar: Sorom)), and durum wheat (triticum durum (cultivar: Helidur) were planted. In the second year, all pots were seeded with summer barley, and received the same amount of nitrogen and sulphate, except for the zeroes.

Selenate addition had no influence upon the levels of other nutrient elements.

2.1.2 Pot experiment 2

This was designed to investigate the effect of the soil: sand proportion on nutrient element uptake. 8 kg 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. In the first year, summer barley and summer wheat were grown, and in the second year only summer barley. Nutrient supply was the same as in pot experiment 1.

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

The macronutrients were given as soluble phosphates, sulfates, and nitrates. The 20% nitrogen in the 20:8:8 fertilizers was composed of 9% nitrate-N and 11% ammonium-N.

2.2 Field experiments

Table 1: Macro- and micro element fertilization in the pot experiments (given in mg/kg soil)

	Pot experiment 1 Treatment (mg/kg soil)					**Pot experiment 2** Treatment (mg/kg soil)			
	1st year			2nd year		1st year		2nd year	
Fertilization level →	N0	N1	N2	N0	N1	N0	N1	N0	N1
N	0	75	150	0	112,5	0	150	0	112,5
P2O5	70	100	130	70	70	70	130	70	700
K2O	190	220	250	190	190	190	250	190	190
MgO	25	36,3	47,5	25	25	25	47,5	25,0	25,0
S	0	15,0	30,0	0	0	0	30,0	0	0
Se	0	0,006	0,012	0	0	0	0	0	0
B	0,10	0,10	0,10	0,475	0,475	0,10	0,10	0,48	0,475
Cu	0,15	0,15	0,15	1,15	1,15	0,15	0,15	1,15	1,15
Fe	1,00	1,00	1,00	6	6	1,0	1,00	6	6
Mn	0,20	0,20	0,20	2,05	2,05	0,20	0,20	2,05	2,05
Mo	0,03	0,03	0,03	0,041	0,041	0,03	0,03	0,04	0,04
Zn	0,025	0,025	0,025	0,713	0,713	0,025	0,025	0,71	0,71

The experiments were conducted at 3 experimental sites of different agro-ecological regions and soil types (for soil characteristics see table 2). Winter wheat, winter rye, summer barley, maize and potatoes (data not given) were studied and the crops were rotated in the second year. Primary fertilization was done in the first year with a PK-fertilizer containing several mineral elements (see above), and in the second year with triple phosphate + KCl. N-supply was exclusively done by the NPK fertilizer 20:8:8, micro elements were not added.

2.3 Analytical procedure

Traditional dry- ashing was to be modified in order to obtain digests suitable for Se- determination by hydride-AAS. Our continuously operating mills usually provide samples of 100-150 µm mean grain size. Statistical treatment of grain size distributions revealed that less than 1 g sample weight might not be representative for determinations at the mg/kg level [1].

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. Dry ashing with magnesium nitrate enabled also the complete regain of total sulphur from sulphate and sulphur- containing amino acids. These digest can be submitted to ICP-OES (Perkin Elmer Optima 3000 XL) multi-element determination with Mg matrix matched calibrants, to measure the amounts of elements Ca, Cu, Fe, Mn, P, S, and Zn. The digests can be used for the determination of As, Se, and Sb by hydride generation methods. In the ICP instrument, 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 from the glass beakers were too high, and Mg was used as a matrix reagent. The lines Se-196, Cd-228, Cr-205 and Cr-267 could be reasonably read, but the detection limit was insufficient for the cereal samples. Calibrants for the pure and diluted sample solutions were matched with respective Mg matrix contents. Salt effects were lowest for Mn and Ca. 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 Precision

In order to obtain information about the precision of the various field and pot trials, the relative standard deviations from the 5 (or more) replicates were calculated and compiled in tables 4AB. Experiments of 9/12/20 replicates in the pots had no better precision than from 5 replicates only. Thus, increasing the number of replicates will not improve the precision of the given method.

Table 2. Main characteristics of experimental soils

Soil type	Location	Soil—pH CaCl2	Humus content %	CaCO3 % (Scheibler)	Clay size fraction %	P * mg /kg	K * mg /kg	Cu** mg/kg	Zn** mg/kg
Dystric cambisol in pots	Zwettl	5.4	2.0	0	17	40	202	29	64
chernozem in pots	Hirschstetten	7.5	3.2	25,8	33	32	105	20	62
Calcaric phaeozem	Fuchsenbigl	7.5	3.4	16,8	33	148	146	23	60
Gleyic luvisol	Rottenhaus	6.8	2.3	0	23	105	130	22	83
Dystric cambisol	Zwettl	5.9	1.9	0	21	48	109	29	64

- Nutrient P and K were (traditionally) determined in CAL extract, (0.05M Ca-lactate + 0.05 M Ca-acetate pH 4,1)

** in aqua regia extract

Precisions for the grain sample data were better than for the straw throughout. Among the micro- elements, precision was best for manganese. Second, precision obtained from the pots was less than from the fields, except for Ca-Cu-Fe in grains, for which some field data were near the detection limit. Sorting due to soil types did not show trends, except that again straw data were less precise than grain data.

3.2 Macro elements

In the subsequent tables, the abbreviations S, W, and D stand for summer, winter, and durum, respectively.

Though calcium was not contained in the fertilizers, Ca uptake from the acid Dystric Cambisol and the Calcareous Phaeozem into the grains was largely overlapping, whereas more differences among the straw samples appeared. In particular, the high Ca in straw obtained from pots is noteworthy. Ca content of crops may differ significantly from year to year. Ca was markedly low in maize grains and maize straw at all 3 sites, also with respect to data found in published databases, especially for the second year of the field experiment (table 5). From the pot experiments, Ca in the grains was significantly lower, and in the straw it was significantly higher than from the fields (summer barley).

P had been added as a nutrient both in the field and pot experiments. In the grains, P has been found at about the same levels for all locations and cereal types, and the replicates were within a narrow range. It was more variable in the straw samples. Contrary to many other parameters investigated, P was at the same level obtained from pot and field experiments. The annual variation was low (table 6).

With respect to the sulphur contents of both grains and straw, soil type and location were not important, and the annual variation was larger than the variation among cereal types. From the fields, grains and stalks were approximately at the same S-level, whereas from the pots, obviously excess S was found in the straw. The data range of replicates was much closer from the field than from the pot experiments (table 7).

3.3 Micro - elements

Cu got distributed about equal between grains and stalks, just maize grains may be extremely low. In the pot experiments, Cu was added in an available form as a component of the primary fertilizer, thus plants from pot experiments contained more Cu than from the corresponding field experiments, above all in the stalks, Differences between locations were less than year to year variations (table 8).

With respect to iron, no significant variations due to cereal type and location were found for the grains. The

Table 3. Some parameters of the ICP-OES determination in the Mg-nitrate digests for 1g/100 ml (detection limits 2 s; precision of Cu was low, because it was near detection limit)

Element	Detection limit from Std. Dev. of 4 blanks in one run	Detection limit from repeatability of pairs of blanks	Repeatability from 66 double determinations in cereal samples
Ca	23 mg/kg	66 mg/kg	X
Cd	0,11	0,15	X
Cr	0,42	0,32	X
Cu	0,05	1,87	23 ,2 %
Fe	5,0	1,4	10,8 %
Mn	0,46	0,18	5,4 %
P	16,5	16,7	7,3 %
S	28	10	3,3 %
Se	0,86	1,27	X
Zn	0,56	1,13	6,1 %

Table 4A. Range of % precisions of analytical data, sorted for number of replicates

Element	Grains from fields (5 replicates)	Straw from fields (5 replicates)	Grains from pots (5 replicates)	Grains from pots (more than 5 replicates)	Straw from pots (5 replicates)	Straw from pots (more than 5 replicates)
Ca	9,3 ± 6,4 *	8,6 ± 4,5 *	X	14,6 ± 5,1	X	12,0 ± 5,5
Cu	30,0 ± 16,9	50,9 ± 22,5	19,2 ± 14,6	21,8 ± 10,8	21,4 ± 15,2	41,6 ± 10,5
Fe	23,4 ± 17,0	23,0 ± 12,7	15,2 ± 8,0	19,7 ± 13,4	16,0 ± 5,4	24,9 ± 9,2
Mn	10,2 ± 4,5	14,3 ± 3,5	10,2 ± 5,0	15,1 ± 9,5	20,2 ± 7,9	23,6 ± 9,9
P	6,5 ± 3,7	16,6 ± 8,5	11,4 ± 5,6	15,8 ± 11,2	19,3 ± 5,2	24,2 ± 8,9
S	9,6 ± 5,1	15,1 ± 6,6	17,5 ± 9,4	12,2 ± 5,1	11,2 ± 4,9	14,0 ± 9,1
Zn	13,5 ± 10,3	27,1 ± 4,3	15,0 ± 5,3	18,4 ± 12,1	14,6 ± 6,6	22,3 ± 10,1

* without maize data; as Ca was at the limits of determination in the maize samples, precision was significantly worse.

Table 4B. Range of % precisions of analytical data, sorted for soil types

Element	Grains from fields Cambisol	Straw from fields Luvisol	Grains from fields Phaeozem	Grains from pots Cambisol	Grains from pots Chernozem	Straw from pots Cambisol	Straw from pots Chernozem
Ca	9,8 ± 9,7 *	7,9 ± 2,3 *	10,5 ± 5,8	X	X	X	X
Cu	24,5 ± 19,5	32,4 ± 15,5	33,4 ± 16,2	23,0 ± 13,3	17,7 ± 12,5	23,9 ± 18,3	32,6 ± 14,7
Fe	19,7 ± 12,3	17,9 ± 11,1	21,2 ± 12,6	19,5 ± 13,5	15,0 ± 6,9	24,6 ± 12,1	16,4 ± 8,7
Mn	12,4 ± 2,7	10,1 ± 4,3	7,9 ± 5,6	9,4 ± 3,6	12,4 ± 7,5	21,3 ± 8,4	21,7 ± 9,4
P	7,9 ± 3,9	5,5 ± 2,4	6,2 ± 4,6	11,3 ± 5,5	15,4 ± 10,7	21,6 ± 8,2	20,5 ± 5,6
S	7,8 ± 2,4	11,1 ± 4,3	9,8 ± 7,8	14,7 ± 6,6	15,1 ± 8,0	10,4 ± 4,4	14,7 ± 8,5
Zn	11,8 ± 7,3	14,9 ± 16,0	13,7 ± 6,3	16,5 ± 11,3	16,5 ± 6,1	16,6 ± 10,4	18,7 ± 6,4

straw, however, contained more Fe and differed widely among the various locations. The high Fe contents from the acid cambisol can be reasonably explained by higher mobility and availability. For the fields, the proportion grain content / stalk content tended to be higher (table 9).

In the pot experiments, the Fe-levels in grains and stalks got higher than from the open fields, because some soluble Fe had been added as a component of the primary PK fertilizer.

Among the micro– elements investigated, the Mn data show high precision. Mn in grains from the fields increased within the sequence maize < barley < rye < wheat, whereas annual variations and site variations were insignificant. Whereas straw from the fields was at the same level than the grains, excess soluble Mn added along with the PK primary fertilizers to the experimental pots, from the acid cambisol clearly moved to the straw (table 10).

Results of field experiments showed that Zn accumulated in the grains, whereas it was significantly higher in the straw in pot experiments. Differences between soil types and year to year variation were higher than between types of cereals. In the pot experiments, Zn was added as a component of the primary PK- fertilizer, which had more effect in the acid than in the calcareous soil (table 11).

Table 5. Ca in cereals from fields and pots (mg/kg); N = number of replicates

	Fields	Grains			Straw		
N		Cambisol	Luvisol	Phaeozem	Cambisol	Luvisol	Phaeozem
5	maize 98	76 ± 24	53 ± 11	71 ± 17			
5	maize 99	13 ± 5	34 ± 25	29 ± 18	3991 ± 352		
5	S barley 98	421 ± 24	469 ±19	398 ± 13			3974 ± 224
5	S barley 99	395 ± 20	398 ± 31	336 ± 28	2953 ± 198	3258 ±249	
5	W wheat 98	372 ± 36	389 ± 34			1575	
5	W wheat 99	254 ± 15	288 ± 32	352 ± 30	1840 ± 145	1660 ± 231	2628 ± 501
5	W wheat 00	314	410	444			
5	W rye 98	279 ± 9	314 ± 25	338 ± 47		2526 ±137	2923 ± 31
5	W rye 99	195 ± 57	309 ± 24	276 ± 51	1684 ± 96	1379 ± 51	

	Pots	Grains		Stalks	
N		Cambisol	Chernozem	Cambisol	Chernozem
20	S-barley 198	304 ± 46	301 ± 64	5157 ±693	5248 ± 308
12	S-barley 298	291 ± 27	262 ± 33	5422 ± 906	

Table 6. P in cereals from fields and pots (mg/kg); N = number of replicates

	Fields	Grains			Straw		
N		Cambisol	Luvisol	Phaeozem	Cambisol	Luvisol	Phaeozem
5	maize 98	3006 ± 295	3456 ± 323	2590 ± 177			
5	maize 99	2762 ± 40	3180 ± 263	1916 ± 103	669 ± 209		
5	S barley 98	3154 ± 176	4116 ± 168	3118 ± 71			678 ± 50
5	S barley 99	3210 ± 160	3216 ± 110	3290 ± 73	524 ± 149	848 ± 81	
5	W wheat 98	2720 ± 271	3667 ± 251			910	280 ± 45
5	W wheat 99	2842 ± 199	3155 ± 153	3272 ± 152	497 ± 59	525 ± 28	
1	W wheat 00	3508	3773	3495			
5	W rye 98	2419 ± 339	3104 ± 74	2197 ± 347		766 ± 145	441 ± 50
5	W rye 99	2580 ± 267	2770 ± 130	2581 ± 167	838 ± 200	745 ± 135	

	Pots	Grains		Straw	
N		Cambisol	Chernozem	Cambisol	Chernozem
5	S-barley 197	3106 ±171	1824 ± 240	603 ± 128	311 ± 40
20	S-barley 198	3065 ± 280	3305 ± 180	513 ± 67	446 ± 76
9	S barley 297	2453 ± 356	2736 ± 862	392 ± 99	
12	S barley 298	2348 ±251	3279 ± 229	419 ± 92	
5	D-wheat 197	2723 ± 537	1433 ± 95	841 ± 218	373 ± 88
5	S-wheat 197	2518 ± 455	1929 ± 203	477 ± 112	279 ± 62
9	S-wheat 297	2808 ± 375	3045 ± 1063	495 ± 185	341 ± 104
5	W wheat 197	3378 ± 144	2572 ± 336	760 ± 68	534 ± 99
5	S rye 197	2795 ± 174	1979 ± 330	692 ± 120	329 ± 63

Table 7. S in cereals from fields and pots (mg/kg); N = number of replicates

	Fields	Grains			Straw		
N		Cambisol	Luvisol	Phaeozem	Cambisol	Luvisol	Phaeozem
5	maize 98	634 ± 38	735 ± 115	732 ± 37			
5	maize 99	644 ± 47	593 ± 84	452 ± 13	561 ± 136		
5	S barley 98	871 ± 47	961 ± 61	993 ± 61			906 ± 67
5	S barley 99	779 ± 55	686 ± 48	716 ± 44	917 ± 165	840 ± 97	
5	W wheat 98	913 ± 80	944 ± 130			996	853 ± 206
5	W wheat 99	714 ± 83	763 ± 72	862 ± 103	821 ± 143	730 ± 166	
1	W wheat 00	899	1427	1319			
5	W rye 98	764 ± 42	687 ± 42	658 ± 171		735 ± 40	678 ± 84
5	W rye 99	604 ± 65	590 ± 96	753 ± 79	578 ± 78	376 ± 37	

	Pots	Grains		Straw	
N		Cambisol	chernozem	cambisol	Chernozem
5	S-barley 197	1262 ± 321	740 ± 95	4663 ± 419	2134 ± 344
20	S-barley 198	1234 ± 100	1307 ± 182	2948 ± 223	1995 ± 146
9	S-barley 297	964 ± 196	700 ± 100	3061 ± 609	
12	S-barley 298	1140 ± 99	1040 ± 56	2074 ± 254	
5	D-wheat 197	1123 ± 208	543 ± 76	4974 ± 376	2229 ±305
9	S-.wheat 197	1002 ± 145	835 ± 58	3316 ± 397	1516 ± 53
5	S- wheat 297	763 ± 130	818 ± 78	2324 ± 172	1858 ± 551
5	W-wheat 197	1570 ± 72	888 ± 245	2383 ± 301	1872 ± 253
5	S-rye 197	1261 ± 194	647 ± 226	5760 ± 291	1938 ± 374

Table 8. Cu in cereals from fields and pots (mg/kg); N = number of replicates

	Fields	Grains			Straw		
N		Cambisol	Luvisol	Phaeozem	Cambisol	Luvisol	Phaeozem
5	maize 98	2,4 ± 0,8	2,6 ± 1,2	2,4 ± 0,5			
5	maize 99	0,6 ± 0,1	1,1 ± 0,4	2,2 ± 1,2	6,1 ± 2,1		
5	S barley 98	3,5 ± 0,3	6,4 ± 1,5	3,7 ± 0,7			3,0 ± 1,1
5	S barley 99	2,8 ± 1,2	3,4 ± 0,8	5,0 ± 2,2	2,4 ± 1,9	1,5 ± 0,3	
5	W wheat 98	3,2 ± 0,8	5,7 ± 0,5				3,1 ± 0,9
5	W wheat 99	3,2 ± 0,1	4,2 ± 2,4	4,4 ± 2,3	1,7 ± 1,3	2,1 ± 1,3	
5	W wheat 00	6,2	5,2	5,9			
5	W rye 98	3,0 ± 0,2	5,1 ± 1,2	2,9 ± 0,7		2,2 ± 1,0	2,1 ± 0,6
5	W rye 99	1,9 ± 1,1	3,2 ± 1,3	2,6 ± 0,5	2,2 ± 1,6	2,4 ± 1,8	

	Pots	Grains		Straw	
N		Cambisol	Chernozem	Cambisol	Chernozem
5	S-barley 197	6,4 ± 0,9	5,7 ± 0,6	8,1 ± 0,6	5,3 ± 0,9
20	S-barley 198	6,1 ± 0,7	6,1 ± 0,8	4,2 ± 0,9	4,0 ± 1,5
9	S-barley 297	4,9 ± 0,9	7,1 ± 3,1	6,7 ± 3,5	
12	S-barley 298	5,3 ± 1,2	6,1 ± 1,9	6,0 ± 2,7	
5	D-wheat 197	8,0 ± 3,8	4,8 ± 0,3	9,0 ± 0,9	6,7 ± 1,9
5	S-.wheat 197	5,6 ± 0,8	5,3 ± 0,3	5,7 ± 1,0	6,7 ± 3,7
9	S- wheat 297	7,0 ± 1,3	5,9 ± 0,9	6,7 ± 3,0	10,6 ± 4,7
5	W-wheat 197	6,9 ± 1,1	5,1 ± 1,0	6,3 ± 0,6	6,3 ± 1,2
5	S-rye 197	4,8 ± 2,1	5,6 ± 0,8	8,0 ± 0,6	3,2 ± 0,7

Table 9. Fe in cereals from fields and pots (mg/kg); N = number of replicates

	Fields		Grains			Straw	
N		Cambisol	Luvisol	Phaeozem	Cambisol	Luvisol	Phaeozem
5	Maize 98	27,0 ± 4,7	20,3 ± 2,9	22,6 ± 5,8			
5	Maize 99	22,1 ± 6,3	18,4 ± 4,3	14,7 ± 9,4	229 ± 27		
5	S barley 98	38,5 ± 10,5	31,1 ± 1,1	33,7 ± 7,4			67,4 ± 8,7
5	S barley 99	31,9 ± 2,2	32,5 ± 1,8	31,1 ± 1,9	202 ± 49	54,1 ± 12,8	
5	W wheat 98	22,6 ± 1,3	26,0 ± 4,4			103	116 ± 36
5	W wheat 99	26,0 ± 2,0	19,3 ± 6,3	19,1 ± 3,9	201 ± 68	44,5 ± 8,9	
1	W wheat 00	41	37	38			
5	W rye 98	24,5 ± 5,9	30,8 ± 8,9	17,3 ± 1,9		39,8 ± 7,4	72,6 ± 5,6
5	W rye 99	15,6 ± 6,2	36,8 ± 24,1	19,0 ± 8,0	172 ± 28	24,1 ± 12,8	

	Pots	Grains		Straw	
N		Cambisol	Chernozem	Cambisol	Chernozem
5	S-barley 197	77,8 ± 10,7	39,0 ± 4,4	455 ± 69	186 ± 21
20	S-barley 198	60,0 ± 10,6	44,4 ± 4,3	202 ± 47	169 ± 19
9	S-barley 297	94,6 ± 46,9	44,1 ± 9,9	229 ± 51	
12	S-barley 298	59,2 ± 5,3	31,9 ± 3,4	394 ± 139	
5	D-wheat 197	49,0 ± 8,2	21,4 ± 2,3	382 ± 57	266 ± 68
5	S-.wheat 197	41,0 ± 13,8	28,0 ± 6,7	316 ± 47	196 ± 19
9	S- wheat 297	47,2 ± 6,4	43,2 ± 10,7	442 ± 230	318 ± 101
5	W-wheat 197	58,8 ± 6,4	37,0 ± 2,5	174 ± 37	219 ± 33
5	S-rye 197	58,8 ± 6,1	31,6 ± 4,6	280 ± 63	182 ± 18

Table 10. Mn in cereals from fields and pots (mg/kg); N = number of replicates

	Fields		Grains			Straw	
N		Cambisol	Luvisol	Phaeozem	Cambisol	Luvisol	Phaeozem
5	maize 98	3,6 ± 0,4	5,9 ± 0,9	4,4 ± 0,5			
5	maize 99	5,1 ± 0,5	7,0 ± 0,7	3,5 ± 0,2	31,9 ± 3,6		
5	S barley 98	9,0 ±1,2	13,0 ± 2,2	15,0 ± 0,8			31,5 ± 2,1
5	S barley 99	11,3 ± 1,7	12,6 ± 0,6	15,0 ± 0,5	8,7 ± 1,5	12,4 ± 2,2	
5	W wheat 98	24,1 ± 4,0	32,9 ± 3,2			24,7	22,2 ± 4,4
5	W wheat 99	24,3 ± 2,6	34,2 ± 2,6	39,0 ± 2,8	23,8 ± 3,0	40,7 ± 5,6	
1	W wheat 00	33	35	46			
5	W rye 98	14,7 ± 1,3	18,0 ± 1,0	15,3 ± 2,9		10,0 ± 1,3	17,7 ± 2,8
5	W rye 99	16,6 ± 2,3	18,7 ± 2,1	21,1 ± 0,7	11,8 ± 1,6	6,5 ± 0,5	

	Pots	Grains		Straw	
N		Cambisol	chernozem	cambisol	chernozem
5	S-barley 197	41,8 ± 2,4	10,5 ± 1,2	458 ± 75	31,0 ± 4,5
20	S-barley 198	28,9 ± 3,7	12,4 ± 0,9	174 ± 29	25,7 ± 2,6
9	S-barley 297	30,7 ± 4,0	13,7 ± 2,1	180 ± 69	
12	S-barley 298	22,3 ± 3,4	11,2 ± 1,1	163 ± 36	
5	D-wheat 197	93,4 ± 6,8	8,4 ± 1,2	409 ± 84	21,0 ± 4,9
5	S-.wheat 197	87,4 ± 14,3	18,3 ± 2,9	516 ± 51	26,5 ± 4,2
9	S- wheat 297	68,4 ± 6,9	23,2 ± 8,7	240 ± 72	33,2 ± 8,1
5	W-wheat 197	124,0 ± 7,2	14,3 ± 2,9	481 ± 98	38,4 ± 14,9
5	S-rye 197	65,6 ± 5,9	13,4 ± 0,9	560 ± 96	19,1 ± 4,8

Table 11. Zn in cereals from fields and pots (mg/kg); N = number of replicates

	Fields		Grains			Straw	
N		Cambisol	Luvisol	Phaeozem	Cambisol	Luvisol	Phaeozem
5	maize 98	12,8 ± 0,8	15,0 ± 1,6	14,1 ± 1,2			
5	S barley 98	14,7 ± 1,2	21,7 ± 2,8	14,7 ± 1,2			5,0 ± 1,3
5	W wheat 98	18,1 ± 2,3	23,7 ± 1,5			9,0	3,2 ± 0,9
1	W wheat 00	23,2	34,2	21,7			
5	W rye 98	12,9 ± 1,0	19,5 ± 0,4	10,3 ± 1,8		6,8 ± 2,2	4,1 ± 0,9
5	W rye 99	19,9 ± 4,8	41,3 ± 17,6	46,8 ± 9,7			

	Pots	Grains		Straw	
N		Cambisol	Chernozem	cambisol	Chernozem
5	S-barley 197	33,5 ± 2,8	18,2 ± 4,7	180 ± 16	126 ± 18
20	S-barley 198	21,0 ± 2,1	30,9 ± 2,9	26,8 ±11,2	31,6± 4,6
9	S-barley 297	30,3 ± 4,3	27,6 ± 5,6	99 ± 20	
12	S-barley 298	17,2 ± 7,9	24,5 ± 5,5	39 ±6,8	
5	D-wheat 197	47,8 ± 7,2	17,5 ± 2,6	245 ± 37	116 ± 19
5	S-.wheat 197	43,0 ± 7,0	24,9 ± 3,3	209 ± 19	124 ± 13
9	S- wheat 297	48,7 ± 5,7	33,1 ± 4,3	130 ± 21	118 ± 28
5	W-wheat 197	46,1 ± 6,1	34,7 ± 2,8	178 ± 23	155 ± 36
5	S-rye 197	31,5 ± 4,3	19,5 ± 4,1	277 ± 21	149 ± 42

3.4 Correlations among field data

Data from the field experiments were sorted according to crops, and the concentrations were correlated. Correlations might indicate a common uptake mechanism, or a common source, and a lack of metabolic regulation (excretion of excess). Just a few significant correlations emerged, like Ca-S, Mn-P, and Zn-P, and Mn-Ca for stalks only.

In straw of winter wheat, the element ratios Fe/Mn - Ca/P significantly correlated r= 0,819 (N=10). Micronutrient elements were rather independent from one another (or at least less then the analytical precision).

3.5 Dilution effects with sand

In the standard setup of pot experiments, 4 kg of soil were diluted with 4 kg of sand. The effect of the sand: soil proportion was investigated in the first experimental year with 3 replicates each, utilizing 2 kg of soil + 6 kg of sand, 4 kg of soil + 4 kg of sand, and 6 kg of soil + 2 kg of sand.

Beneath dilution of the nutrients bound to the solid phase of the soil, addition of sand caused changes in aeration and water capacity. Only few trends were noted. Dilution of the acid soil increased zinc content in the grains and Mn in the straw, and decreased P in the straw, possibly an effect of increasing aeration. Dilution of the alkaline soil decreased Cu in the barley grains, as well as Cu+S+Zn in the wheat straw. Within the pots, the roots utilize the entire volume, whereas in the fields, dilution with sand would mean lower water storage capacity, as well as the necessity to grow longer roots.

4. DISCUSSION

Within the range of adequate supply of essential elements, the tissue level is regulated by metabolism of the living cells, when an equilibrium between uptake and excretion can be achieved. For substances (i.e. non-essentials) 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.

Surely as a result of metabolism, in most cases, the annual variation was larger than the differences between the species or cultivars of cereals. On the other hand, Ca, Cu and Mn content of maize was significantly (tables 5,6,8) lower than in the other crops. Only in case of Mn in grains, the order was as follows: maize > summer barley > winter wheat < winter rye. Thus, the elemental composition in grains, which are important for the generative reproduction of annual crops, become equalized during the plant metabolic processes. The straw (and probably also the roots) act as a buffer towards excess or lack of available fractions. Sorting of the field data according to locations revealed a significant increase of Fe (and maybe

Table 12. Dilution effects with sand

Increasing sand:	S-wheat grains	S-barley grains	S-wheat straw	S-barley straw
Dystric cambisol	Zn ↑	Zn ↑, P ↓	Mn ↑	Fe, Mn ↑; P ↓
Calcareous chernozem		Cu ↓	Cu, S, Zn ↓	

Table 13. Nutritional Aspects

	human daily needs mg	Cereals mg/kg (field)	maize mg/kg (field)	kg of cereals containing daily needs	kg of 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**

Zn) in straw from luvisol < phaeozem < cambisol, which can be explained by increased availability.

From the pot experiments, due to lack of washout to deeper soil layers, and additional fertilization with trace elements (soluble B, Cu, Fe, Mn, Mo, and Zn), concentrations in grains and straw from pot experiments were higher for Cu, Fe, Mn, S, and Zn. Calcium was not added via the fertilizers. More Ca in grains at the field, and less Ca in straw from the field might be explained from different root length – the Ca may be taken from deeper soil layers, which are lacking in the pots.

As an exception, there was no difference for P between field and respective pot experiments, though P had been added as a nutrient. Exact balance of variable P-supply leads to narrow P-concentration ranges in the grains and extended ranges in the straw. 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 [2], which would be equivalent to 2424 - 2987 mg/kg P, similar to most of the data presented here.

Sulphate was supplied in the nitrogen fertilizer (S content 4% as soluble sulphur). The experimental conditions largely influenced the sulphur levels, especially in the straw. The storage capacity for sulphur depends on the turnover of soluble sulphate versus fixed sulphur by soil-micro- organisms. Whereas in the field, sulphur is readily washed out to deeper soil layers [3], this is not possible in the pot experiments, resulting in higher sulphur levels.

5. COMPARISON WITH DATA FROM OTHER SOURCES

Wheat, barley, rye and maize are basic food for human and animals (e.g.pigs), and have been investigated in the past quite often [4, 5, 6, 7, 8]. The presented data fit well within the range of other published data; it may be advantageous to have soil type, fertilization conditions together with nutrient elements.

Another approach of data interpretation might be to compare data from ring tests, 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 practices, rates and soil types are unknown to the user. Wheat and barley grains grown in Lower Austria (this work) had just half of the Zn of the samples from the Netherlands, but were at the same level with respect to Cu, Mn and Fe. 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.

The data from a ring test to evaluate contaminations from milling and grinding of barley and wheat [10] were also within the current ranges. The mean of 44 barley samples taken between Parndorf and the Hungarian border, before the construction of todays highway between Vienna and Budapest [11], was slightly lower for Cu (2,4 mg/kg) and Zn (16 mg/kg).

6. NUTRITIONAL ASPECTS

The crops studied in this work are main components of food for human consumption and in fodder for domestic animals. Thus, another aspect of current investigations is to ensure adequate supply with nutrient elements. Table 13 shows the daily needs of men for several nutrient elements, recommended by the German Society of Nutrition DGE (simplified after [12]), together with the loads obtained from exclusive feeding on cereals and maize from the field experiments (means).

According to the recommendations of the DGE (after [12]), exclusive feeding with maize would lead to severe deficiencies in Se, Cu, and Ca, and possibly also in Mn (table 13). 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.

7. CONCLUSIONS

Crops from pot experiments contained higher levels of most of essential elements than crops from field experiments carried out on the same soils, except for P and Ca. Pot experiments thus do not necessarily reflect conditions in the field, because mineral elements had been additionally added to ensure optimum plant growth. Results of pot and field experiments should never be mixed.

Macro- and micro- element levels in maize grains were found low enough to provoke deficiencies in Ca, Cu and Mn in men and animals, if fed exclusively.

Annual variations in essential element levels in grains obtained from 3 locations different in climate and soil type, were larger than differences between cereal types in most cases. Plant yield, microbial soil life, and weather conditions may contribute. Increase in the number of replicates to more than 5 did not improve the precision of the resulting data.

REFERENCES

[1] Sager M., Strelec H., Getreidevermahlung und Statistik, ALVA Jahrestagung 1998 in Hollabrunn, 183-186

[2] Lott N.A., Ockenden I., Raboy V., Batten G.D., Phytic acid and phosphorus in crop seeds and fruits: a global estimate, Seed Science Research (2000) 10: 11-33.

[3] M. Sager, Vertical mobility of Selenium, Arsenic and Sulfur in Model Soil Columns, Die Bodenkultur (2002), 53(2): 83-103

[4] 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. (1987) 29: 202-217.

[5] Feil B., Bänziger M., Nitrogen and Cultivar Effects on the mineral element concentration in the grain of spring wheat, European Journal of Agronomy (1993) 2(3): 205-212.

[6] 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 Pollution (1995) 85: 835-840.

[7] Horak O., Liegenfeld R., Untersuchungen zum Selentransfer Boden-Getreide. VDLUFA-Schriftenreihe (1996) 44: 687-690.

[8] 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) (1997) 34 (9-10): 88-92.

[9] Ruszkowska M., Sykut St., Kusio M., Stan zaopatrzenia roslin w mikroelementy w warunkach zroznicowanego nawozenia w wieloletnim doswiadczeniu lizymetrycznym, Zeszity Problemow Postepow Nauka Rolniczej (1996) 434: 43-47.

[10] Sager M., Mittendorfer J., Influence of milling or cutting procedures on trace element contents of plant samples, International Journal of Environmental Analytical Chemistry (1997) 67: 59-71.

[11] Sager M., Bericht über Schadstoffbelastungen der Parndorfer Platte vor dem Bau der Ostautobahn, Bericht der Landwirtschaftlich Chemischen Bundesanstalt (Wien 1992).

[12] Radke M., Neue Nährstoffempfehlungen der DGE. Ernährung/Nutrition (1992) 16(4): 219-221.