SELENIUM UPTAKE IN CEREALS GROWN IN LOWER AUSTRIA

M. Sager, J. Hoesch

Austrian Agency for Food and Safety, Agricultural Researches Vienna, Austria, manfred.sager@ages.at

Manuscript received: February 11, 2006; Reviewed: February 23, 2006; Accepted for publication: March 9, 2006

ABSTRACT

In order to ensure optimum trace element supply via cereals, the uptake of selenium from a selenate containing NPK fertilizer (20:8:8, with 20 mg/kg selenate Se) was tested. A series of field and pot experiments were run on a cambisol, a clay soil, a calcareous phaeozem, and a chernozem within the physiologically feasible range in 3 subsequent years. Selenate addition led to a significant increase in all kinds of cereals investigated, and the memory in subsequent years was poor. The transfer of added selenium to the grains ranged between 0,7 and 4,7% in the field conditions, and between 1,6 and 5,4 % from the pots. In the grains, selenium was specified mainly as seleno-methionine. The selenium addition did not affect the contents of the other essential trace elements. Uptake from pot and field experiments was different.

Keywords: selenium, wheat, rye, barley, maize

1. INTRODUCTION

Selenium supply from basic food in Austria is generally low. Farmed animals are usually fed with feedstuffs to which Se has been added up to 0,5 mg/kg, in order to fulfil requirements to obtain optimum growth and health. 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 and 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). Prior to the introduction of a similar mineral fertilizer in Austria (containing 16 mg/kg Se as sodium selenate), the Austrian Ministry of Health insisted to have a respective study performed at local conditions and farming practice.

Selenium addition as Na_2SeO_3 turned out to be less effective, because it strongly adheres to the pedogenic oxides of the soils (Horak and 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?

In order to monitor the effects of the application of a selenate containing mineral fertilizer upon the composition of cereals, field and pot experiments were carried out at the soil types most common in Austria within 3 subsequent years. Field experiments are laborious, and can be done just in a limited number, but do the results of pot experiments really reflect the conditions in the field? Are there memory effects in the field?

Besides selenium uptake and utilization rate, the great number of samples was used to investigate other total element contents, which were possible to determine reliably by ICP-OES spectrometry from the sample digests prepared for selenium analysis (see part 2).

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

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 sulphate, except for the zeroes.

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; soil pH was done in 0,01M $CaCl_2$)). Winter wheat, winter rye, summer barley, maize and potatoes (data not given) were tested, and the crops were rotated in the second year. 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 (table 2). Trace elements were not added any more.

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

Table 1. Soil characteristics

	Location	Soil -pH	Humics content %	Clay size fraction %	Se-contents mg/kg	P-contents mg P/100g	K-contents mg K/100g
Dystric cambisol in pots	Zwettl	5,4	2,0	17	0,22	4,0	20,2
Calcaric chernozem in pots	Hirschstetten	7,5	3,2	33	0,25	3,2	10,5
Calcaric phaeozem	Fuchsenbigl	7,5	3,4	33	0,35	14,8	14,6
Gleyic luvisol	Rottenhaus	6,8	2,3	23	0,15	10,5	13,0
Dystric cambisol	Zwettl	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 sulphur
Se	16 ppm		as water soluble sodium selenate

Table 3. Se concentrations from the pot experiments

Cereal	**Soil**	**Grains**			**Straw**			
			+48 µg Se	+96 µg Se		+48µg Se	+96 µg Se	
Durum wheat	Cambisol	< 5	102	151	58	144	247	
Durum wheat	Chernozem	11	76	135	51	130	232	
Summer barley	Cambisol	<5	57	111	59	196	319	
Summer barley	Cambisol	< 4	34	48	23		96	memory
Summer barley	Chernozem	< 5	91	112	28	150	232	
Summer barley	Chernozem	7	18	42				memory
Summer rye	Cambisol	9	82	152	74	245	393	
Summer rye	Chernozem	<5	58	102	46	133	175	
Summer wheat	Cambisol	10	49	104	46	150	282	
Summer wheat	Chernozem	7		98	38	112	177	

with $NaBH_4$. Each charge consisted of 12 samples + 2 blanks, matching the size of the muffle furnace. From the resultant sample solution, up to 15 ml sample could be taken for determination of selenium by hydride AAS on a Perkin Elmer 3030 / MHS 20 in the batch technique, without further sample preparation. The detection limit was obtained from the repeatability of two blank solutions, and went down to 4 µg/kg, if no high selenium samples are analyzed within the same period of time.

The sample digests were also submitted to ICP-OES determinations, to get information about other elements, like Cu, Mn, Fe, Zn, P, S, and Ca, which were not influenced by the Se-uptake experiment.

Some high- selenium grains were checked for Se-speciation by HPLC- ICPMS using an anion exchanger column, after hydrolysis of proteins with pronase. The main fraction of Se- containing compounds was identified as seleno-methionine (Stadlober et al. 2001).

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, approximately linear with addition. In the second year, summer barley was seeded to all pots, and some memory effect could be noticed, which did not differ among soil types, or due to previous crops.

Table 3 shows the average concentrations of selenium (µg/kg) found in grains and straw from pot experiments. The straw contained significantly more selenium, and the transfer from the cambisol was higher than from the chernozem. Some memory in the subsequent year was noted in the crops, but not in the soil itself. Table 4 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 made 2,0 µg more per pot, with respect to the controls, which aimed at a utilization rate of 4%. Adding double amount of fertilizer resulted in a further average Se- increase of 3,8 µg per pot, resulting in a utilization rate of about 3%.

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 Se- transfer to the grains was significantly less from the clay soil, which may be explained from adsorption capacity (table 5). 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. The transfer of added selenium to the edible parts, however, was rather low (table 6).

3.2 Statistical treatment of field data

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 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 7). The presumable anions P and S, and chemically related Fe-Mn, or S-Se were not necessarily seen in the same factors.

4. Discussion

Farmed animals are usually fed with feedstuffs to which Se has been added up to 0,5 mg/kg, in order to fulfil requirements to obtain optimum growth and health. In order to raise the Se- uptake rate via nutrition for men, the application of selenate containing mineral fertilizers led to increased selenium levels in both cereal grains and straw, up to a range which can be regarded as the optimum for human nutrition. Transfer to maize grains was lowest.

Marked differences between pot and respective field experiments appeared. In the pot experiments, washout to deeper soil layers is not possible, and there cannot be roots to deeper soil layers. Increase of selenium concentration from the pots was higher, and selenium preferably moved to the straw. The rather small amount of 4 kg soils per pot might have been too low to develop marked differences between soil types. With respect to edible parts of the farmed cereal, Se- utilization rate was about 2 % of added Se, and some memory remained for the subsequent year.

In the field, plants grown at the cambisol had the highest selenium concentrations, and at the high adsorptive clay soil, the lowest, though the mobility of anions should be higher at higher pH. Some 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. Differences between pots and open fields, like the proportion of selenium uptake between grains and straw, cannot be explained by washout only. In respective column experiments with chernozem soils

Table 4. 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	W-wheat	S-wheat	S-barley	S-rye	Durum-wheat
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	W-wheat	S-wheat	S-barley	S-rye	Durum-wheat
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

Table 5. Concentrations of selenium from the field experiments

Cereal	Soil	Grains			Straw			Se - addition
Maize	Luvisol	6,6	10,9	13,1				
Maize	Cambisol	< 4	10,4	19,9	8,5	14,0	24,7	
Summer barley	Phaeozem	23	41,6	52	23,6	41,0	62	3,2 / 6,4 g per ha
Summer barley	Luvisol	< 4	7,9	10,1	5,5	8,0	13,2	
Summer barley	Cambisol	< 4	17,5	68,2	9,2	33,6	56,4	
Winter rye	Phaeozem	15,1	21,8	46	11,9	17,1	36,4	3,6/ 7,2 g per ha
Winter rye	Luvisol	6,1	9,7	13,2	4,4	12,1	15	
Winter rye	Cambisol	<4	20,2	69,2	6,3	23,5	39,1	
Winter wheat	Phaeozem	9,4	24,6	37,5	12,4	38,2	74	4,8 / 9,6 g per ha
Winter wheat	Luvisol	7	10,8	18,8	7,3	12,3	20,3	
Winter wheat	Cambisol	< 4	26,8	59,6	5,8	23,3	46,5	

Table 6 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)
Gleyic luvisol	1,0 (0,7-1,6)	0,9 (0,4-1,1)
Dystric cambisol	2,4 (2,2 - 2,6)	3,7 (2,8-4,4)

Table 7 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)

Table 8. 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**

(Sager 2002), most of selenium added together with a fertilizer solution, got adsorbed at the topsoil, and washout was low. Significant increases caused by even low additions and rather linear increase of selenium levels show plant needs to exceed soil adsorption. But precautions may be considered to avoid exceeding the physiological optimum range.

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 8 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.

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 15). 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 (16 mg/kg as Na_2SeO_4), because Se concentrations can easily be raised 5 to 10 fold in the field.

5. CONCLUSIONS

In most cases, year to year variations in essential element levels in crops obtained in grains from 3 locations which were different in climate and soil type, were larger than differences between cereal types. Plant yield, microbial soil life, and weather conditions may contribute.

Crops from pot experiments contained higher levels of most of essential elements included Se 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, because trace elements had been additionally added to ensure optimum plant growth. Results of pot and field experiments should never be mixed.

Trace element levels in maize grains have been low enough to provoke deficiencies in Ca, Cu and Mn in men and animals, if fed exclusively.

REFERENCES

Eurola M., Ekholm P., Ylinen M., Koivistoininen P., & Varo P. 1990. Effects of selenium fertilizations on the selenium content of cereal grains, flour and bread produced in Finland. Cereal Chemistry 67: 334-337.

Horak, O. & Liegenfeld R. 1996. Untersuchungen zum Selentransfer Boden-Getreide. VDLUFA-Schriftenreihe 44: 687-690.

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

Pfannhauser W. 1992. Das essentielle Spurenelement Selen: Bedeutung, Wirkung und Vorkommen in der Nahrung. Ernährung /Nutrition16(11), 642-646.

Pfannhauser W. 1994. Der Versorgungsstatus mit dem essentiellen Spurenelement Selen in Österreich. Lebensmittelchemie 48: 123-123.

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

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

Sager M. 1993. Selenium. In: Vernet J.P (ed.). Environmental Contamination, Elsevier Amsterdam. p. 403-476.

Sager M. 2002. Vertical mobility of selenium, arsenic and sulphur in model soil columns. Die Bodenkultur

53(2): 83-103.

Stadlober M., Sager M., & Irgolic K.J. 2001. Effects of selenate supplemented fertilization on the selenium level of cereals - identification and quantification of selenium compounds by HPLC – ICP-MS. Food Chemistry 73: 357-366.

Stadlober M., Sager M., & Irgolic K.J. 2001. Identification and quantification of selenium compounds in sodium selenite supplemented feed by HPLC-ICP-MS. Die Bodenkultur 52(4): 313-322.

Van Cauwenbergh R., Hendrix P., Robberecht H., & Deelstra H.A. 1995. Daily dietary Cu- intake in Belgium, using duplicate portion sampling. Zeitschrift für Lebensmittel Untersuchung und Forschung 200: 301-304.