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Selenium - Occurrence and Cycling in Agricultural Matrices

Abstract

In soils and green plants of Central and Northern Europe, selenium contents is lower than in most parts of the US. Within the Austrian soil monitoring programme, median values for total selenium in aqua regia extracts of soils sieved < 2 mm have been found within the range 0,11 - 0,41 µg/g. No soils enriched in selenium were found. In Austrian diet, daily intake of selenium has been determined within a range of 27-68 µg/day (mea: 48 µg/day), which is rather low. According to the Recommended Daily Allowances in the US, the average daily intake should be 50 - 200 µg/day, and according to the German Society of Nutrition, it should be 20 - 100 µg/day. In order to promote optimum growth and resistance to various illnesses, selenium as sodium selenite is added to commercial animal feedstuffs up to a total contents of 0,5 g/g. Control of this threshold value is one of the main tasks of the Office and Research Centre of Agriculture in Vienna. The selenite may be partially reduced by other components of these mixed diets to non- leachable forms, presumably elementary selenium. Excess selenium is excreted, and can lead to enhanced selenium levels in manure and in sewage sludges. Organic amandments thus cover a wide and still unpredictable source of selenium enrichment for agricultural soils. Under reducing conditions, selenium can be partially volatile on drying. Freeze drying significantly improved selenium regain from liquid manure. The standard method for the analysis of sewage sludges starts from the dried sample, and applies aqua regia. For manure, drying and subsequent ashing in presence of magnesium nitrate has been preferred. In order to study the soil - plant - transfer of selenium in non- contaminated fields, 68 samples of chernozem soils and correponding barley plants were sampled just before harvest at the Parndorfer Platte (Burgenland) in June 1992, just before the construction of the highway. Selenium transfer to the barley grains did not yield a constant ratio versus plant selenium.

Addition of sodium selenate to inorganic fertilizers of the NP or NPK type aiming to enhance selenium levels in cereals, like it has been done in Finnland, has been successfully prevented by the Austrian Ministry of Health. Pot and field experiments showed significant increase of selenium in the eatable parts of wheat, maize and potatoes, without change of the composition of other inorganic constituents. After hydrolization of these cereals with pronase in citrate/phosphate buffer pH 7,3, selenium species were separated on a Hamilton PRP-X100 anion exchange column in citrate buffer pH 5, and detected with ICP-MS. The excess selenium in the plants fertilized with sodium selenate, has been found largely metabolized as seleno-methionine.

In case, sodium selenate would be mixed to some sorts of fertilizers as a micronutrient, like cobalt or molybdenum, prevention of selenium losses because of migration to deeper layers and to the groundwater was investigated in soil columns. From fertilizer solution, selenium was largely fixed, and constantly released to deeper layers as non-selenite selenium. Like for sulfur, drying and aeration periods enhance selenium mineralization, thus increasing its mobility.

For the future, determination of metabolized selenium forms eluting from soil columns with respect to variations in aeration and nitrogen- supplementation conditions (nitrate, ammonia, organic amendments) are planned by HPLC-ICP hyphenated techniques. A further question would be to elucidate reactions of selenite additives with components of feedstuffs on storage.

In soils and green plants of Central and Northern Europe, selenium contents is lower than in most parts of the US. The nutritional status of the Austrian population is regarded to be low, but still adequate. The daily selenium intake has been determined to be within the range 27 - 68 µg/d, with a mean of 48 µg/d (WILPLINGER, PFANNHAUSER 1997). According to the Recommended Daily Allowances in the US, the average daily intake should be 50 - 200 µg/day, and according to the German Society of Nutrition, it should be 20 - 100 µg/day.

Within this brief report, selenium data from the last decade obtained in our Research Centre, are reviewed. More information can be obtained from review papers (SAGER 1994).

Selenium in soils

Within the Austrian soil monitoring programme, median values for total selenium in aqua regia extracts of soils sieved < 2 mm have been found within the range 0,11 - 0,41 µg/g (Tab. 1). No significant differences between soils developed on various geological facies, have been observed. There might be some depletion in older soils, like this has been markedly observed in case of zinc. No locations enriched in selenium up to toxic levels were found.

Geological unit	Sample number	Median mg/kg Se
Postglacial sediments	173	0,30
Glacial sediments	179	0,25
Loess	280	0,21
Molasse	78	0,26
Flysch	94	0,30
Limestone of Northern Alpine Zone	80	0,31
Schists and gneisses of Bohemian Crystalline	102	0,23
Granites of Bohemian Crystalline	113	0,16

Tab. 1: Selenium background values in soilsLower Austria and Burgenland 0-20 cm aqua regia, air - dried soil < 2 mm

Selenium transfer from soil to crops

In order to study the soil - plant - transfer of selenium in non - contaminated fields, 68 samples of haplic chernozem soils at the Parndorfer Platte /Burgenland with corresponding barley plants sampled before harvest in the middle of June have been investigated. The site is unique for Central Europe, because there has been no settlement after retreat of the Romans at the begin of the 5th century, and all trace elements at background levels. There are no surface waters at an area of 25x40 km, and soils of the same type throughout. Topsoils and subsoils were not significantly different. There was no significant correlation between barley grain selenium - soil selenium (r = 0,202). Wheat and maize samples grown without the addition of selenate to the fertilizers, have later been found 10 times lower than barley, i e. within the range 4-10 µg/kg Se.

		median	range	n
Soil 0 - 25 cm	selenium	0,23 mg/kg	0,17-0,34	68
	humic substances	2,9 %	2,3-3,8	
	carbonates	0,5%	< 0,2 - 4,8	
	clays	27%	23-29	
Soil 40 - 60 cm	selenium	0,26 mg/kg	0,21-0,35	6
Barley grains	selenium	0,046 mg/kg	0,024 - 0,088	68

Tab. 2. Soils from Parndorfer Platte before construction of the highway Vienna – Budapest corresponding barley samples before harvest, 15.-17.6. 1992

Selenium in animal feedstuffs

In order to promote optimum growth and resistance to various illnesses, selenium as sodium selenite is usually added to commercial animal feedstuffs up to a total contents of 0,5 mg/kg. Control of this threshold value is one of the main tasks of the Office and Research Centre of Agriculture in Vienna. During storage, the selenite may have been partially reduced by other components of these mixed diets to non-leachable forms, presumably elementary selenium. (Leaching was done with 0,001M formic acid). Separation of eluted selenium species was done on an anion exchange column, operated via HPLC with element- sensitive detection by ICP-MS.

	Median	Max	Min
Total Selenium µg/kg	929	3932	524
Selenite µg/kg	347	1104	70
Selenate µg/kg	34	71	0
Residue µg/kg	503	2810	291
% Selenite	28,3	53,5	13,4
% Selenate	0,0	3,7	0,0
% Residue	53,6	75,8	33,7

Tab. 3. Selenium speciation in Animal Feedstuffs after Storage

Selenium in excrements

From farmed animals, excess selenium is excreted, and ean lead to enhanced selenium levels in manure and in sewage sludges (CAPPON 1991: Se in US-sewage sludges was 0,4-9,6 mg/kg d.w.). Organic amendments thus cover a wide and still unpredictable source of selenium enrichment for agricultural soils. Whereas there have been no problems with plant material, animal feedstuffs and animal tissues, under reducing conditions, selenium can be partially volatile on drying; the boiling point of the metabolite dimethylselenide is only 58 °C. Data found in the literature or in reports and certificates, however, have been got always from the dried samples. Addition of aqua regia to dried and wet samples can thus lead to different results in both directions; too much water prevents oxidation of elementary selenium and selenides. Addition of solid sodium thiosulfate led to an almost complete regain of selenium in the drying procedure, but as the speciation of selenium in these materials is still unknown, the mechanism is not understood yet. Freeze drying significantly improved selenium regain from liquid manure, but methylated species are still lost. The standard method for the analysis of sewage sludges starts from the dried sample, and applies aqua, regia. For reasons quoted above, however, we have changed our standard procedure for the analysis of manure and organic amendments towards drying and subsequent ashing in presence of magnesium nitrate (Tab. 4).

	median mg/kg	range	year	n
Manure after biogas production	0,74	-	1998/99	1
Solid manure from pigs	3,09	1,08-7,7	1998/99	25
Liquid manure from pigs	1,31	1,16-1,41	1998/99	4
poultry dung	1,33	0,54-1,78	1998/99	6
liquid manure from fattening cattle	0,125	0,12-0,13	1998/99	2
liquid manure from dairy cows	0,825	0,804 - 0,846	1998/99	2
sewage sludge dried	1,25	0,33-10,8	1992/93	16
sewage sludge wet	1,89	0,41-30,1	1992/93	18

Tab. 4. Selenium in organic amendmentmanure dried in presence of $Mg(NO_3)_2$ - muffle fumace 560 °C sewage sludge dried without additive, aqua regia wet sewage sludge + aqua regia, calculated for dried sample

Selenium in fertilizers

Addition of sodium selenate to inorganic fertilizers of the NP or NPK type (16 mg/kg Se or 30 mg/kg Se) aiming to enhance selenium levels in cereals, like it has been done in Finnland, has been successfully prevented by the Austrian Ministry of Health. Pot and field experiments showed significant increase of selenium in the edible parts of wheat, maize and potatoes, without change of the composition of other inorganic constituents. After hydrolization of these cereals with pronase in citrate/phosphate buffer pH 7,3, soluble selenium species were separated on a Hamilton PRP-X100 anion exchange column in citrate buffer pH 5, and detected with ICP-MS. The excess selenium in the plants fertilized with sodium selenate, has been found largely metabolized as seleno-methionine.

Vertical, transport of selenium in soil columns.In case, sodium selenate would be mixed to some sorts of fertilizers as a micronutrient, like cobalt or molybdenum, prevention of selenium losses because of migration to deeper layers and to the groundwater was investigated in soil columns. From artificial fertilizer solution, selenium was largely fixed. Daily addition of water to the soil columns of

about 0,1 pore volumes simulated rain events. The eluates were dried and ashed in presence of magnesium nitrate and potassium permanganate to yield total selenium contents, which were much higher than selenite. Like for sulfur, there was a constant release of selenium from the column, which was enhanced after drying and aeration perlods (Tab. 4).

Perspectives

Future projects speciation of mobile selenium forms eluting from soil columns with respect to variations in aeration and nitrogen - supplementation conditions (nitrate, ammonia, organic amendments) are planned to be performed by HPLC-ICP hyphenated techniques. A further problem to be worth while investigated would be to elucidate reactions of selenite additives with components of feedstuffs on storage. The last and most difficult task will finally be to investigate the selenium species and turnover reactions in organic amendments and sewage sludges.

Nutrient salts per hectare		absolute amounts
160 kg/ha N as NH_4NO_3		
320 kg/ha P_2O_5 as $Ca(H_2PO_4)2{\cdot}H_2O$	113 mg Ca	175 mg PO_4-P
200 kg/ha K_2O as K_2SO_4 + KCl	208 mg K	17 mg SO_4-S
2 g/ha B		2,5 mg B
0,8 g/ha Mo and V		1,0 mg Mo and V
0,4 g/ha As and Se		0,5 mg As and Se

Tab. 5. Selenium mobility in the soil column 4 times 3 soils, 5 kg each; haplic - calcic - gleyic chernozems non-saturated flow from top to bottom in the dark 2 times each day 0,1 pore volwnes = 150 ml = annual precipitation within 2 months Pore volume determination: peak of Cl of KCl Addition of selenite in NPK - fertilizer

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