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Levels of 44 elements in organically grown potatoes (*Solanum tuberosum*, Sava)

Allan Bibak, Stefan Stürup, and Vagn Gundersen

Abstract The multielement (Ag, Al, Au, Ba, Ca, Cd, Co, Cr, Cs, Cu, Dy, Er, Fe, Ga, Gd, Ge, Hf, Ho, La, Mn, Mo, Nb, Nd, P, Pb, Pr, Pt, Rb, S, Sb, Sc, Si, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, V, Y, Zn, and Zr) levels in Potatoes (*Solanum tuberosum*, Sava) are presented in this paper. The potatoes were collected from seven background areas, on South East Jutland and South Jutland, Denmark, with organic farming method. High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS) was used for analyses of the samples. The results provide useful biological, nutritional and background level information on organically grown potatoes.

Contents

Preface

The total area of organic farmland in Denmark was 44.991 ha at 1996, an increase of 17% from 1995 (Plant Directorate, 1996) and the trend is accelerating. Plant analysis is based on the principle that the concentration of elements within the plant integrates all of the factors affecting plant growth and availability of elements in the soil (Munson and Nelson, 1990). Plant analysis can also be used to evaluate the elemental status of plant in order to assess the adequacy of elements and the safety of human food chain resources.

High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS) is a powerful technique for trace and ultratrace analysis of biological materials offering rapid multi-element analysis with excellent detection limits (Begerow and Dunemann, 1996). The 44 elements measured in this study are those for which a routine HR-ICPMS method could be applied. The number of elements possible to measure is dependent on the composition of the sample matrix and on the concentration of the individual element and may therefore vary from matrix to matrix.

The present study is a part of an ongoing Danish Food and Technology Development Program (FØTEK). The purpose of our study is to develop high-quality data on the levels of trace and major elements in potatoes produced by organic farming. Secondly, correlation between element levels in potatoes and soil properties such as contents of clay, organic matter and pH that may influence the elements uptake are being considered.

1 Materials and Methods

1.1 Sites

Potato samples were collected from 7 production areas on South East Jutland and South Jutland in Denmark. The sites were selected to avoid contamination from human activities, such as highway, big cities, and factories, since they may affect trace element levels in soils and the crops. The sites were therefore more than 10 km from industries with extensive emission, at least 15 km from high ways, 3 km from major roads and 3 km from cities with more than 10.000 inhabitants. The criterion for site selection was to use with as wide variations in soil properties as possible with use of organic farming and with use of the same sorts of potatoes so big differences in sites areas occur.

1.2 Potato

A total of 50 undamaged, healthy, and average-sized potato tubers from 10 potato plants (5 tubers per plant) were collected by hand digging in even spread over each sites. All potato samples were collected with Nitrilite gloves (Nitrilite, powder free, Ansell Edmont). Tuber cultivars were noted and tubers were placed in polyethylene tissue bags with closing tape and transported to the laboratory for analysis.

1.3 Sample Preparation

Laboratory modification, special equipment for sample preparation, digestion, laboratory ware cleaning procedures, and deionised water (DW) and double deionised water (DDW) supply are described in Bibak et al. (1998a,b).

1.4 Soils

A composite sample was collected at each site after potatoes were harvested as follows: Ten cores (7.5 cm diameter and 25 cm deep) were taken from each site and mixed. Samples were air-dried and coarse materials crushed, then sieved (2 mm) to remove stones and debris. In these materials texture, pH, total C, and calcium carbonate were determined. The particle size distribution was determined by combined sieving and sedimentation analysis (Gee and Bauder, 1986). A 1:2.5 soil:0.1 M $CaCl_2$ suspension was used in the pH determination. Total carbon was determined by dry combustion.

1.5 Multi-element Determination

The homogenized samples were digested with HNO_3 (Merck p.a., subboiled in clean room class 1000) in a microwave oven (MDS 2000, CEM Co.) equipped with 12 closed Teflon PFA (per fluoro alkoxy) digestion vessels (CEM Co.). In these digests 44 elements (Ag, Al, Au, Ba, Ca, Cd, Co, Cr, Cs, Cu, Dy, Er, Fe, Ga, Gd, Ge, Hf, Ho, La, Mn, Mo, Nb, Nd, P, Pb, Pr, Pt, Rb, S, Sb, Sc, Si, Sn,

Sr, Ta, Tb, Te, Th, Ti, Tl, V, Y, Zn, and Zr) were measured by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS). The above elements are the elements that we found possible to measure using a routine HR-ICPMS method. The microwave oven was programmed to run at increasing pressure at 80, 80 and 80 psi in 3 steps. The pressure was held constant for 3, 3 and 5 minutes during each of the 3 steps, respectively. The clear, light yellow, residue-free digest was then cooled to room temperature and transferred quantitatively to a 50-ml polyethylene flask, and double deionised water was added to a mass of approximately 30 g (weighted to the nearest 0.0001 g). These sample solutions were stored at 5°C until analysis.

Two grams (weighed to the nearest 0.0001 g) of the sample solution was diluted with double deionised water to 10 g (weighed to the nearest 0.0001 g) for HR-ICPMS measurement. Each batch consisted of 10 samples, a reagent blank and a secondary reference material (a homogenized potato material prepared in house). The reagent blank was used to check for contamination from digestion vessels, whereas the secondary reference material was used to check the efficiency of the digestion to secure uniformity of the sample matrix from batch to batch. The accuracy was not determined because a primary potato CRM material was not commercially available. To validate the newly developed HR-ICPMS method for multi-elements analysis, the analytical procedure was compared with Instrumental Neutron Activation Analysis (INAA) for five elements (Fe, Co, Zn, Rb, and Mo) in the secondary reference material. The selected elements are the elements among the forty-four which were confidently measured by INAA. In Table 1 the results of the INAA measurements are compared with the results of HR-ICPMS analysis of eleven subsamples from the secondary reference material. The precision of the analytical method was determined by 10 subsamples from one potato material. Element concentrations for some of the samples were estimated in analytical combination with different spiked samples to verify that the sample solution matrix is similar for different potatoes, when digestion conditions are the same.

Instrumental parameters for the HR-ICPMS analysis, quantification, cleaning procedures, and data processing have been described by Bibak et al. (1998a).

The results were analyzed statistically using simple correlation coefficient (r) in the Statgraphics statistical software package (Statgraphics Plus, 1995).

2 Results and Discussion

The mean and standard deviation of 11 replicates by HR-ICPMS and 3 replicates by INAA analyses for Fe, Co, Zn, Rb, and Mo in the secondary reference material are shown in Table 1. For the five elements listed there is an acceptable agreement obtained between the two analytical methods. These results validate both the sample digestion and the analytical procedures applied and provide a degree of confidence in results obtained by the newly developed HR-ICPMS multi-elements analyses method.

The precision of the HR-ICPMS method for some selected elements is shown in Table 2. All concentrations (μg/kg, fresh weight) are given as the average of the measured concentrations in 10 subsamples taken from the homogenized potato material. All sample preparation procedures were performed in parallel. In general, the relative standard deviation (%RSD) for the HR-ICPMS is below 15%, when the concentration of the element considered is well above the detection limit. There are, however, a few exceptions, e.g. Cr for which the %RSD is

somewhat higher (24%). This may be due to the fact that even in clean rooms, it is very difficult at these low concentrations to completely avoid contamination from chemical and sample containers. The large deviation is a result of variations in Cr background level. Also Sb, Sn and Ta have higher %RSDs than expected. For Sb and Sn it is due to tailing, which is very difficult to overcome using even a long washing time between samples. For Ta the high %RSD is due to small electrical spikes in the mass spectrum. The mass spectrum at the masses of Ta is prone to electrical spikes, which is not seen in the rest of the mass range. The reasons for that are unknown for us. When the concentration of an element is close to the detection limit the %RSD raises as expected: see Au, Ga, Gd, Hf, Ho, Pt, Sb, Sn, Ta, and Te for which the %RSD is higher than 20. Overall levels of precision for the elemental values measured in homogenized potato material are acceptable, keeping in mind that the determination is an multi-element analysis.

The 44 elements (Ag, Al, Au, Ba, Ca, Cd, Co, Cr, Cs, Cu, Dy, Er, Fe, Ga, Gd, Ge, Hf, Ho, La, Mn, Mo, Nb, Nd, P, Pb, Pr, Pt, Rb, S, Sb, Sc, Si, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, V, Y, Zn, and Zr) concentrations in potatoes taken from seven background areas and measured by HR-ICPMS multi-elements analyses method are shown in Table 3. From the data materials outliers were omitted. For some elements it was necessary to remove 1 to 5 estimations after spiking on high levels due to tailing. Therefore the number of samples (n) in Table 3 are different. The detection limits (µg/kg) are calculated as 3 times the standard deviation of 10 replicates of the blank determination. The elemental concentrations within the sites were uniform. The mean, median, minimum, and maximum values in Table 3 are calculated from all samples from the 7 sites. For most of the elements the mean exceeds the median (Table 3) because a few sites have very high values. Some elements have concentration levels below the mean of 10 consecutive blank determination, these are listed as b > c in Table 3. In these cases the negative values (c - b) are included in the statistical calculations.

The physical and chemical soil characteristics of the seven agricultural practices investigated are given in Table 4. The composition of the soils differs greatly (Table 4). Thus the organic carbon and clay contents range from 1.1% organic C to 4% organic C and from 3.7% clay to 6.9% clay, respectively. Accordingly, the pH varies from 4.8 to 5.9. Because only one genotype of potato was grown on the range of soils, the variation in elements concentrations are probably related to soil properties and agricultural practices. These variations in properties, therefore, may be responsible for the variations in contents of the elements in potatoes. Since the soil composition or soil parameters (pH, clay contents, and organic matter) may influence elemental distribution between soil and soil solution and different soils may show different affinities for elements at comparable soil solution composition. Correlations between these parameters and the elemental concentrations of the potatoes can be helpful tool to improve our understanding of the role of soil parameters on the availability of the elements to the crop.

The results of correlation analysis are shown in Table 5. Simple correlation between clay contents and concentrations of the elements show significantly positive ($P < 0.05$) with Dy, Co, Cs, Cu, S; ($P < 0.01$) Mn, Te; ($P < 0.001$) Ba, Sr and significantly negative ($P < 0.05$) with V (Table 4). Organic carbon correlated significantly positive ($P < 0.05$) with Sn; ($P < 0.01$) Cr, Tl, Zn and significantly negative ($P < 0.01$) with Fe, Rb; ($P < 0.001$) Co, Cu and Mn (Table 4). The correlation between the elemental concentration and pH were significantly positive ($P < 0.01$) with Si, V; ($P < 0.001$) Sn and significantly negative ($P < 0.05$) with Fe, Ge, Pr; ($P < 0.01$) Ba, Co; ($P < 0.001$) Cu, Mn, Sr and Te (Table 4). These are in good agreement with many investigations showing the importance of clay minerals, showing that the pH and organic matter are the

main factors influencing the solubility, and showing the availability of trace elements in arable soils (Bibak, 1994; McKenna et al., 1993; Alloway, 1995; Öborn et al., 1995; Miner et al., 1997; Jinadasa et al., 1997).

3 Conclusions

The methodology used in this study may be efficiently employed to study a wide range of elements in agricultural crops. Results are important in providing nutritional information on the background levels of trace elements in organically grown potatoes. The variation in contents of some elements in potatoes is due to variation in soil properties.

4 Acknowledgment

5 References

Alloway, B.J. 1995. *Individual elements*. pp. 122-303. IN: Heavy Metals in Soils. B.J. Alloway (Eds.), Blackie, Glasgow.

Begerow, J.and Dunemann, L. 1996. *Mass spectral interfaces in the determination of trace levels of precious metals in human blood using quadrupole magnetic sector field and inductively coupled plasma mass spectrometry*. J. Anal. At. Spectrom. 303-306.

Bibak, A. 1994. *Retention of cobalt, copper, manganese and molybdenum by soils and soil components*. Ph.D. Thesis, The Royal Veterinary and Agricultural University, Copenhagen, Denmark.

Bibak, A., Behrens, A., Stürup, S., Knudsen, L., and Gundersen, V. 1998a. *Concentration of 63 major and trace elements in Danish agricultural crops measured by inductively coupled plasma mass spectrometry.1. Onion* (Allium cepa Hysam). J.Agric. Food Chem. (in press).

Bibak, A, Stürup, S., Haahr, V., Gundersen, P., and Gundersen, V. 1998b. *Concentration of 54 major and trace elements in Danish agricultural crops measured by inductively coupled plasma mass spectrometry.4. Potato* (*Solanium tuberosum*, Folva). J.Agric. Food Chem. (sumitted).

Gee, G. W. and Bauder J.W. 1986. *Particle -size analysis*. pp. 383-412 IN: Methods of Soil Analysis A. Klute (Eds.), part 1. American Society of Agronomy, Madison, Wisconsin.

Jinadasa, K.B.P.N., Milham, P.J., Hawkins, C.A., Cornish, P.S., Williams, P.A., Kaldor, C.J., and Conroy, J.P. 1997. *Heavy metals in the environment: Survey of cadmium levels in vegetables and soils of greater Sydney, Australia.* J. Environ. Qual. **26:** 924-933.

McKenna, I. M., Chaney, R. L., and Williams, F.M. 1993. *The effects of cadmium and zinc interactions on the accumulation and tissue distribution of zinc and cadmium in lettuce and spinach.* Environ. Pollut. **79**: 113-120.

Miner, G.S., Gutierrez, R., and King, L.D. 1997. *Soil factors affecting plant concentrations of cadmium, copper, and zinc on sludge-amended soils.* J. Environ. Qual. **26:** 989-994.

Munson, R.D. and Nelson, W.L. 1990. *Principles and practices in plant analysis.* IN: Soil Testing and Plant Analysis. R.L. Westerman (Eds.), Third Edition. Soil Science Society of America, Madison, Wisconsin.

Öborn, I., Jansson, G., and Johnsson, L. 1997. *A field study on the influence of soil pH on the trace element levels in spring wheat (Triticum asetivum), potatoes (Salanum tuberosum) and carrots (Daucus carota).* Water, Air and Soil Pollution. **85:** 835-840.

Plant Directorate. 1996. *Annual Report*.

The Statgraphics Plus. 1995. *User Guide, Statistical Graphics Corp version 2.1.*

Table 1. Comparison of trace elements in the secondary reference material prepared in house; values reported in mg/kg dry weight.

Elements	INAA[a]	ICPMS[b]
Fe	23 ± 0.66	25 ± 1.4
Co	0.018 ± 0.001	0.026 ± 0.003
Zn	12.0 ± 2.2	20 ± 3.6
Rb	4.6 ± 0.05	6.0 ± 0.2
Mo	0.49[c]	0.45 ± 0.05

[a] Instrumental neutron activation analysis, 3 replicates; mean ± S.D.
[b] High resolution inductively coupled plasma mass spectrometry, 11 replicates; mean ± S.D. [c] One determination.

Table 2. Precision of HR-ICPMS method.

Element	Concentration (µg/kg)	%RSD
Al	330	14
Ba	50	7.9
Ca	11000	13
Cd	23	9.0
Co	8.3	11
Cr	15	24
Cs	3.2	8.0
Cu	1930	5.5
Er	0.177	12
Fe	6300	11
Ga	0.39	36
Gd	0.05	66
Ge	20	27
Hf	0.56	31
Ho	0.01	29
La	0.183	19
Mn	1880	5.9
Mo	73	4.3
Nd	0.159	16
P	1510000	8.9
Pb	6.7	15
Pt	0.09	63
Rb	1400	8.3
S	1110000	7.4
Sb	1.46	24
Sc	0.2	14
Si	14800	6.9
Sn	1.1	35
Sr	200	13
Ta	0.51	49
Te	1.79	21
Th	1.53	17
Ti	13.9	13
Tl	0.69	17
V	1.67	15
Y	0.123	19
Zn	9400	7.1

Table 3. Elements in potatoes (µg/kg, fresh weight).

Elements	n	Min	Max	Mean	Median
Ag	63	b>c	10.6	0.23	0.00140
Al	64	80	650	230	198
Au	66	0.097	3.4	1.25	1.10
Ba	66	5.3	53	18.3	15.7
Ca	66	16900	76000	36000	34000
Cd	68	6.0	40	18.1	15.4
Co	66	1.41	13.0	4.3	3.4
Cr	63	1.61	34	8.6	7.6
Cs	68	0.38	12.3	3.6	3.6
Cu	68	370	1510	870	860
Dy	68	b>c	0.108	0.0085	0.0020
Er	67	b>c	0.146	0.034	0.035
Fe	67	2800	5900	4000	3900
Ga	64	0.0187	0.41	0.118	0.087
Gd	68	b>c	0.21	0.040	0.036
Ge	66	7.1	40	16.9	16.3
Hf	59	b>c	4.2	0.38	0.20
Ho	67	b>c	0.022	0.0047	0.00190
La	65	0.0149	0.99	0.194	0.138
Mn	68	830	2800	1480	1470
Mo	68	39	136	63	59
Nb	65	0.0047	13.1	2.8	1.81
Nd	66	b>c	0.72	0.145	0.101
P	68	400000	660000	500000	490000
Pb	66	2.5	24	7.7	6.3
Pr	68	b>c	0.27	0.0074	b>c
Pt	53	0.0031	0.69	0.189	0.154
Rb	49	580	3100	1870	1940
S	68	380000	700000	500000	490000
Sb	68	0.41	5.4	1.34	1.15
Sc	58	b>c	0.87	0.169	0.082
Si	49	14100	172000	68000	63000
Sn	67	0.0078	21	5.8	4.7
Sr	68	23	99	59	59
Ta	67	0.32	12.6	3.1	2.3
Tb	68	b>c	0.037	0.0089	0.0054
Te	59	0.099	4.6	1.72	1.34
Th	47	b>c	2.9	0.77	0.45
Ti	67	1.19	46	13.4	10.8
Tl	62	0.48	11.9	3.4	2.6
V	67	0.39	2.3	1.00	0.87
Y	67	0.0133	0.40	0.100	0.088
Zn	66	1980	7500	3800	3600
Zr	49	0.38	21	4.91	2.25

b>c = elements concentration below the mean of 10 blank.

Table 4. Some Properties of the Surface Soil (0-25 cm) at 10 Sites. Soil Texture:
sand (0.063-2.0 mm), silt (0.002-0.063 mm) and clay (< 0.002 mm).

sites	field texture of surface			pH (CaCl$_2$)	organic C
	sand	silt	clay		
		%			%
1	84.8	3.4	5.1	5.7	4.0
2	88.9	4.2	4.2	5.1	1.5
3	81.3	8.6	5.8	5.2	2.6
4	70.9	18.9	6.5	5.3	2.2
5	84.5	6.6	5.3	5.9	2.2
6	79.2	12.1	6.9	4.8	1.1
7	88.6	4.3	3.7	5.9	2.0

Table 5. Simple correlation coefficients (r) between soil properties and the elemental concentrations (µg/kg) in potatoes.

Elements	Clay (%)	Org. C (%)	pH
Ag	0.0715	-0.2629	0.0676
Al	0.1702	0.0742	0.0655
Au	0.1765	0.0372	-0.0947
Ba	0.6927[c]	-0.2416	-0.4274[b]
Ca	0.2071	0.1016	0.1336
Cd	0.1886	-0.2708	-0.0403
Co	0.3417[a]	-0.5251[c]	-0.4253[b]
Cr	0.2547	0.4091[b]	-0.0483
Cs	0.3156[a]	0.2192	0.1830
Cu	0.2862[a]	-0.7677[c]	-0.7244[c]
Dy	0.2993[a]	-0.2414	-0.1456
Er	-0.1612	0.0072	0.1326
Fe	0.1454	-0.3818[b]	-0.3384[a]
Ga	-0.1036	-0.0705	0.0179
Gd	0.1671	0.1382	0.1055
Ge	0.1585	-0.2471	-0.3090[a]
Hf	0.0564	0.0855	0.0729
Ho	0.0605	0.1186	-0.0278
La	0.2542	-0.0194	-0.0589
Mn	0.4035[b]	-0.5578[c]	-0.6596[c]
Mo	0.0532	-0.0044	0.0870
Nb	0.0650	-0.0169	0.1552
Nd	0.0268	-0.2956	-0.0661
P	0.1599	-0.3204	-0.3449
Pb	-0.3079	0.0938	0.2374
Pr	0.1385	-0.1779	-0.4291[a]
Pt	0.3038	0.3808a	0.1722
Rb	-0.1728	-0.5293[b]	-0.1743
S	0.4691[a]	-0.2830	-0.2420
Sb	0.2717	-0.3989[a]	-0.3045
Sc	-0.1084	0.0758	0.1919
Si	0.1921	0.3041	0.5254[b]
Sn	-0.1421	0.4662[a]	0.6901[c]
Sr	0.6237[c]	-0.1746	-0.6479[c]
Ta	-0.0457	-0.1089	0.1306
Tb	0.2783	0.0964	-0.3016
Te	0.5333[c]	-0.0219	-0.7032[c]
Th	0.2556	-0.3192	-0.1493
Ti	0.0707	0.3211	0.0570
Tl	0.1878	0.4679b	0.1050
V	-0.3681[a]	0.2232	0.5576[b]
Y	0.3443	-0.2384	-0.3119
Zn	-0.0702	0.5220[b]	0.1000
Zr	-0.2527	-0.0392	0.3139

a,b,c, significance at P < 0.05, 0.01 and 0.001 levels, respectively

Title and authors

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Abstract (max. 2000 characters)

The multielement (Ag, Al, Au, Ba, Ca, Cd, Co, Cr, Cs, Cu, Dy, Er, Fe, Ga, Gd, Ge, Hf, Ho, La, Mn, Mo, Nb, Nd, P, Pb, Pr, Pt, Rb, S, Sb, Sc, Si, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, V, Y, Zn, and Zr) levels in Potatoes (*Solanum tuberosum*, Sava) are presented in this paper. The potatoes were collected from seven background areas, on South East Jutland and South Jutland, Denmark, with organic farming method. High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS) was used for analyses of the samples. The results provide useful biological, nutritional and background level information on organically grown potatoes.

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