Concentrations of 50 Major and Trace Elements in Danish Agricultural Crops Measured by Inductively Coupled Plasma Mass Spectrometry. 3. Potato (*Solanum tuberosum* Folva)

Allan Bibak,† Stefan Stürup,‡ Vagner Haahr,‡ Pernille Gundersen,‡ and Vagn Gundersen*,‡

Risø National Laboratory, Plant Biology and Biogeochemistry Department, PBK-124, P.O. Box 49, DK-4000 Roskilde, Denmark, and Miljø-og Levnedsmiddel Centret, Ved Faurgården 7, DK-4300 Holbæk, Denmark

The multi-element (Ag, Al, Au, Ba, Bi, Ca, Cd, Co, Cr, Cs, Cu, Dy, Er, Fe, Ga, Gd, Ho, In, Ir, La, Lu, Mn, Mo, Nb, Nd, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, Y, Yb, and Zn) concentrations (μg/kg, fresh weight) in potatoes (*Solanum tuberosum*, Folva) were investigated in this study. The potatoes were grown in two fertilization practices; one with pig slurry and one with calcium ammonium nitrate at three levels of N fertilization (0, 60, and 120 kg of N/ha). The experiment field was located at the Risø National Laboratory Agronomy Farms in Roskilde, Denmark. High-resolution−inductively coupled plasma mass spectrometry (HR−ICPMS) was used for analyses of the samples. The effect of three levels of N fertilization on elemental concentrations of the crop are evaluated by use of discriminant partial least-squares regression (PLS). The results provide useful biological and nutritional information on potatoes.

Keywords: *Potato (Solanum tuberosum Folva); HR−ICPMS; major elements; trace elements; multi-element analysis; N fertilizer*

INTRODUCTION

The potato (*Solanum tuberosum*) is important for human foods in many countries. The potato provides a large proportion of the carbohydrate intake of average adults. Daily consumption of the potato by adults is estimated to be 118 g/day in 1995 in Denmark (Levnedsmiddelstyrelsen, 1995b [Danish National Food Agency]), 322 g/day by adult males in Australia (Stenhouse, 1991), and 152 g/day per capita in Finland (*Food Balance Sheet*, 1976). In Australia, potato tubers represent >55% of the total dietary intake of Cd by the average adult man (Stenhouse, 1991). Equivalent figures from the United States indicate that the potato represents about 24% of the daily dietary Cd intake of average U.S. adults (Gartrel et al., 1986). The minimization of the toxic elements and adequate uptake of essential elements by potato are therefore important in those countries in which the potato forms a major component of carbohydrate intake.

Many studies have been conducted in different countries on elemental concentrations of potato tubers in Denmark (Hansen and Andersen,1982; Levnedsmiddelstyrelsen, 1995a [Danish National Food Agency]), Finland (Varo et al., 1980), the United States (Wolnik et al., 1983a,b), England (Ward and Savage, 1994; Ministry of Agriculture, Fisheries and Food, 1994, 1998), Poland (Krelowska-Kulas, 1993), Germany (Brüggemann and Kumpulainen, 1995), and Australia (Jinadasa et al., 1997), but very little information is available on the effect of fertilizer application on its mineral concentrations and especially in relation to trace elements, e.g., noble and rare earth elements.

The objectives of the current study, which is supported financially by the Danish Food Technology and Development Program (FØTEK), were (1) to develop high-quality background values on the level of major and trace elements by routine HR−ICPMS multi-element analysis and (2) to evaluate the elemental concentrations of potato (*Solanum tuberosum* Folva) as affected by application of three levels of N fertilization.

The 50 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 individual elements and may therefore vary from matrix to matrix. These data will be used to relate trace element levels to agricultural production methods and to gain information on levels of mainly trace elements in crops in order to evaluate their role in the food chain.

MATERIALS AND METHODS

Sites. The experimental field was located at the Risø National Laboratory Agronomy Farms in Roskilde, Denmark. It was cultivated and fertilized for more than 50 years. The field experiments were started in the spring of 1995 with the potato (*Solanum tuberosum* Folva) grown using three levels of N fertilizer: 0, 60, and 120 kg of N/ha (0-N, 1-N, and 2-N, respectively). An area of 24 m × 40 m was divided into four plots of 10 m × 24 m. These plots were further divided into 12 subplots of 2.5 × 8 m (4 × 3 N-level). These are used for different crops such as potato and spring types of rye, wheat, and oat. A total of six potato subplots in the experimental area comprises two 0-N levels, two 1-N levels (one fertilized with pig slurry and one fertilized with calcium ammonium nitrate), and two 3-N levels (one fertilized with pig slurry and one

* To whom correspondence should be addressed (telephone +45 4677 4272; fax + 45 4677 4260; e-mail vagn.gundersen@risoe.dk).

† Miljø-og Levnedsmiddel Centret.

‡ Risø National Laboratory.

10.1021/jf980606v CCC: $18.00
Published on Web 06/08/1999

fertilized with calcium ammonium nitrate). The soils in the experimental area have been managed uniformly during the experiments.

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

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

The potatoes collected from a field were stored 6−7 weeks at 5 °C and 99% humidity and then prepared for analysis as follows:

Sample preparation was performed under controlled conditions in three rooms with lock-gate connection. The rooms are classified as R1 (ordinary condition), R2 (fairly clean), and R3 (clean, class 1000 room). Five tubers from one potato plant (representing one sample) were rinsed in tap water and then scrubbed gently in deionized water using a soft nylon brush to remove adhering soil. The washing procedure in deionized water was performed in R1 and was repeated twice. The tubers were then passed through a lock into R2, and the above-described procedure was then repeated once with deionized water and twice with double deionized water under fairly clean laboratory conditions. The washed and clean tubers in R2 were passed through a lock into R3. In R3, the five tubers were cut from both ends (approximately 10−15 mm) with a nitride-hardened titanium knife on a polycarbonate carving board. Then a 20 mm (diameter) longitudinal cylindrical piece was taken from each tuber with a sharp nitride-hardened titanium tube that was pressed through the tuber. The pieces (pure pulp) were then homogenized in the blender (EVA, type 267732, DK) modified with a nitride-hardened titanium cutter. Disposable latex gloves (Gammex, sterile, powder-free, Ansell Edmont) and full laboratory dress (Tyvek) were worn throughout the procedure.

Soils. A composite sample was collected at two depths, 0−25 and 25−100 cm, from all plots (10 m × 24 m area) after the potatoes were harvested as follows: 16 cores of 6.0 cm were taken with a soil probe at each depth, and the 16 cores were mixed. Samples were air-dried, and coarse materials were crushed and then sieved (2 mm) to remove stones and debris. In these materials, texture, pH, total C, and calcium carbonate were determined as described by Bibak et al. (1998).

Multi-element Determination. Approximately 1.5 g of the homogenized material from each sample was accurately weighed (to the nearest 0.0001 g) into each digestion vessel, and 10 mL of redistilled nitric acid (Merck p.a. subboiled in R3) was added. The samples were digested in a microwave oven (MDS 2000 CEM Co., Matthews, NC) equipped with 12 closed Teflon PFA (perfluoro alkoxy) digestion vessels (CEM Co., Matthews, NC). The microwave oven was programmed to run at increasing pressure at 2.8, 5.8, and 12 bar in three steps. The pressure was held constant for 3, 3, and 5 min during each of the three 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 deionized water was added to a final 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 deionized water to 10 g (weighed to the nearest 0.0001 g) for HR−ICPMS measurement. HR−ICPMS (PlasmaTrace2, Micromass, U.K.) was used to determine 50 elements (Ag, Al, Au, Ba, Bi, Ca, Cd, Co, Cr, Cs, Cu, Dy, Er, Fe, Ga, Gd, Ho, In, Ir, La, Lu, Mn, Mo, Nb, Nd, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, Y, Yb, and Zn) in the potato samples. The above elements are those we found possible to measure

Table 1. Instrumental Conditions for the Plasma Trace 2 (HR−ICPMS)

Rf power, W	1350
gas flow rates, L min^{-1}	
plasma	12.5
auxillary	1.5
nebulizer	0.920−0.980 (adjusted daily to max signal intensity)
sample uptake rate, mL min^{-1}	0.7
ion sampling depth	adjusted to max signal intensity
ion lens settings	adjusted to max signal intensity
sampling cone	nickel, 1.0 mm orifice diameter
skimmer cone	nickel, 0.7 mm orifice diameter
Acquisition Parameter	
resolution 400	
peak widths	3
points/peak width	20
dwell time	10 ms
scans	2 (^{85}Rb, ^{88}Sr, ^{89}Y, ^{93}Nb, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{115}In, ^{197}Au, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th)
	1 (^{101}Ru, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{185}Re, ^{193}Ir, ^{238}U)
resolution 4000	
peak width	3
points/peak width	20
scans	2
dwell time (ms)	10 (^{31}P, ^{44}Ca, ^{48}Ti)
	20 (^{45}Sc, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{69}Ga)
	30 (^{27}Al)
resolution 10000	
peak width	5
points/peak width	20

using a routine HR−ICPMS method. The plasma conditions and acquisition parameters are summarized in Table 1. The isotopes chosen for analysis are chosen in order to obtain the best possible sensitivity (highest natural abundance) and to avoid overlap from polyatomic interference. Where overlap from polyatomic ions could not be avoided, a higher resolution (defined as $m/\Delta m$) of either 4000 or 10000 was applied to resolve the analyte peaks from the otherwise interfering polyatomic peaks, e.g., $^{56}Fe^{+}$ can be separated from $^{40}Ar^{16}O^{+}$ ($\Delta m = 0.0049$ amu) using a resolution of 4000. When a higher resolution is applied, the ion transmission is decreased significantly at resolution 4000 and 10000 and the transmission is approximately 15% and 1%, respectively. The quantification was performed using standard addition calibration in order to eliminate interference from the sample matrix. Standard addition calibration was carried out by the addition of six multi-element standard solutions (Perkin-Elmer). Each standard was added at three concentration levels to separate samples. The analyses were performed in a class 1000 room (R3). One standard addition calibration curve was obtained for each element for every 20 samples of potatoes, assuming a similar sample solution matrix for all potato samples digested under the same conditions. 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. 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 50 that were confidently measured by INAA. In Table 2, the results of the INAA measurements are compared with the results of HR−ICPMS analysis of 11 subsamples from the secondary reference material. The precision of the analytical method was determined by 10 subsamples from one potato material. A primary potato CRM material was not commercially available. The best

Table 2. Comparison of Trace Elements in the Secondary Reference Material Prepared In-House[a]

elements	INAA[b]	ICPMS[c]
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[d]	0.45 ± 0.05

[a] Values reported in mg/kg, dry weight. [b] Instrumental neutron activation analysis, three replicates; mean ± SD. [c] High-resolution–inductively coupled plasma mass spectrometry, 11 replicates; mean ± SD. [d] One determination.

Table 3. Precision of HR–ICPMS Method

element	concn (μg/kg)	% RSD
Al	330	14
Au	0.66	26
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
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
Ru	0.163	56
Sb	1.46	24
Sc	0.2	14
Sm	0.02	61
Sn	1.1	35
Sr	200	13
Ta	0.51	49
Th	1.53	17
Ti	13.9	13
Tl	0.69	17
V	1.67	15
Y	0.123	19
Zn	9400	7.1

estimate for the accuracy was therefore obtained from 10 replicate analyses of the NIST 1567a wheat flour reference 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.

Discriminant partial least-squares regression (PLS; *The Unscrambler*, 1966) was used to compare the overall effect of N fertilization on elemental concentrations in potato tubers for each of the two sites fertilized with calcium ammonium nitrate and pig slurry. Analysis of variance (*Statgraphics Plus*, 1995) was used for individual comparison of the elemental concentrations between the tree N fertilization levels for each fertilization practice. For both sites, 9, 10, and 10 samples were used at 0-N, 1-N, and 2-N levels, respectively. These were a less number of samples at the 0 level because of damaged samples.

RESULTS AND DISCUSSION

The elemental mean and standard deviation of 11 replicates by HR–ICPMS and three replicates by INAA analyses of the secondary reference material are shown in Table 2. Comparison of data between the two analytical methods for the five elements (Fe, Co, Zn, Rb, and Mo) listed there shows acceptable agreement. These results validate both the sample digestion and the analytical procedure used and provide a degree of confidence in results obtained by the newly developed HR–ICPMS multi-element analysis method.

Table 4. Quality Control Measurement of NIST 1567A Wheat Flour[a]

elements	certified	measured
Ca	191 ± 4	150 ± 2
P	1340 ± 60	1660 ± 10
Al	5.7 ± 1.3	4.0 ± 0.7
Cd	0.026 ± 0.002	0.031 ± 0.01
Cu	2.1 ± 0.2	1.9 ± 0.2
Fe	14.1 ± 0.5	12.7 ± 0.8
Mn	9.4 ± 0.9	8.1 ± 0.3
Mo	0.48 ± 0.03	0.44 ± 0.07
Zn	11.6 ± 0.4	15.5 ± 2.0
Co	0.006	0.017 ± 0.003
Pb	<0.020	0.019 ±.007
U	0.0003	0.0009 ± 0.00009
V	0.011	0.012 ± 0.002

[a] Values reported in μg/g dry weight.

Table 5. Some Properties of the Soils (0–25 and 25–100 cm) at the Risø Field Fertilized with Calcium Ammonium Nitrate and Pig Slurry[a]

fertilizer	depth (cm)	sand (%)	silt (%)	clay (%)	pH, $CaCl_2$	total C (%)	$CaCo_3$ (%)
calcium ammonium	0–25	50.4	26.6	16.1	7.6	1.86	4.7
nitrate	25–100	47.4	27.3	14.0		1.79	10.4
pig slurry	0–25	53.8	24.9	17.8	7.4	1.43	1.3
	25–100	53.0	25.8	18.8		0.78	1.3

[a] Soil texture: sand (0.063–2 mm), silt (0.002–0.063), and clay (<0.002 mm).

Table 6. Some Properties and Chemical Characteristics of Calcium Ammonium Nitrate and Pig Slurry

fertilizer	% dry matter	pH	% P	% K	% Ca	% Mg	% N NO_3^-	% N NH_4^+	% N total
calcium ammonium nitrate					4.5	2.7	13.5	13.5	27
pig slurry	3.47	6.8	2.4	5.2			0.0001	7.60	12.1

For Zn, there is an apparent positive bias on the HR–ICPMS. The reason for this discrepancy is not fully known, but it is probably due in part to contamination with zinc from the air inlet in our clean room and maybe also contamination with zinc during the sample preparation, which both results in too high values for the HR–ICPMS measurements.

The precision of the HR–ICPMS method for some selected elements is shown in Table 3. All concentrations (μg/kg, fresh weight) are given as the average of the measured concentrations in 10 subsamples taken from the same homogenized potato material from one sample and digested in one run in 10 digestion vessels in a microwave oven. All sample preparation procedures were performed in parallel. In general, the relative standard deviation (% RSD) of the HR–ICPMS is below 15% (Table 3) when the concentration of the element considered is well above the detection limits. 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,

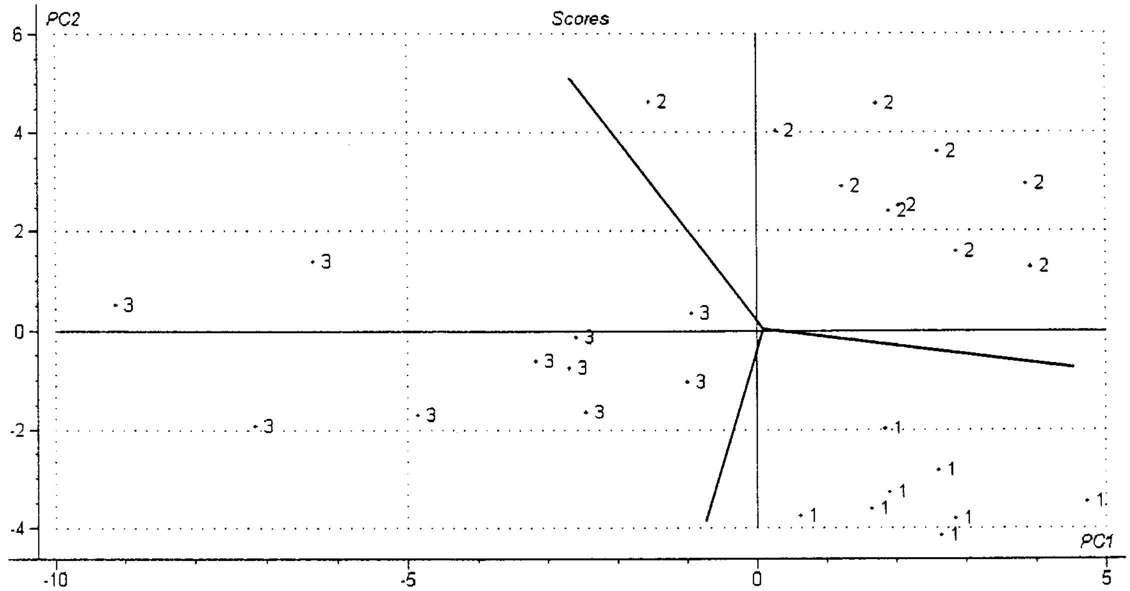

Figure 1. Score plot of the PLS regression for potatoes fertilized with calcium ammonium nitrate. PC1 explains 24% and PC2 explains 15% of the variation in *X*. The lines in the plot indicate that the three levels of N fertilization tends to split in the groups.

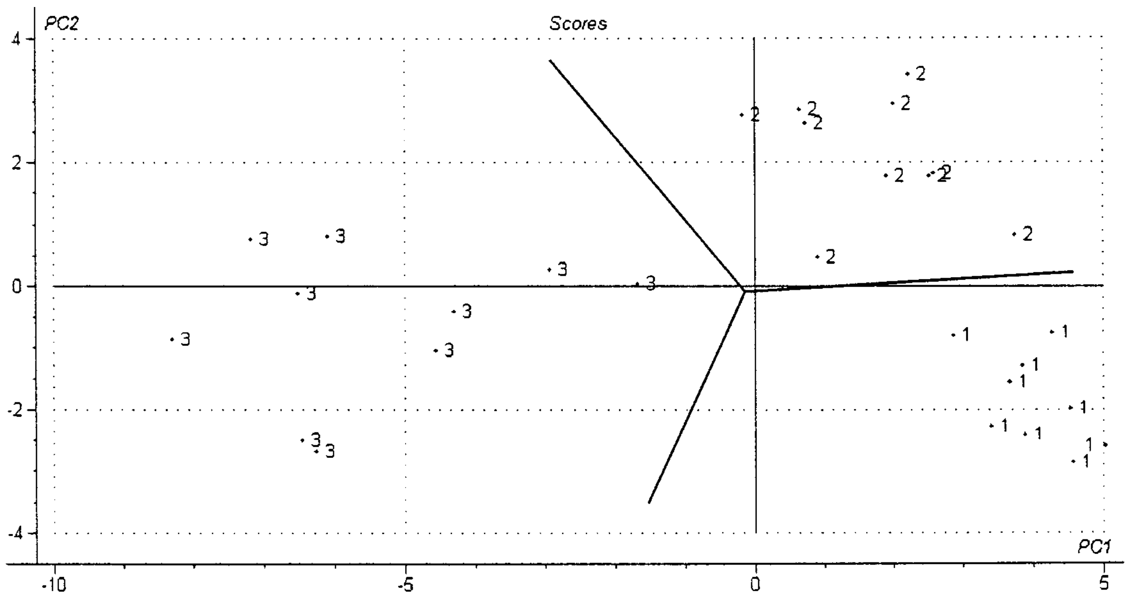

Figure 2. Score plot of the PLS regression for potatoes fertilized with pig slurry. PC1 explains 35% and PC2 explain 7% of the variation in *X*. The lines in the plot indicate that the three levels of N fertilization tend to split in the groups.

Sn, and Ta have higher % RSD values 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 reason for that is 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, Ru, Sb, Sm, Sn, and Ta for which the % RSD is higher than 20. Overall levels of precision for the elemental values measured in the homogenized potato material are acceptable, keeping in mind that the determination is a multi-element analysis where the instrument settings are a compromise between the optimum setting for the 50 elements. Also the change of mass resolution during a run contributes to the overall precision since a better precision can be obtained if the mass resolution is kept constant, as it is when analyzing one element at the time.

The elemental mean and 95% confidence interval (μg/g, dry weight) of 10 replicate analyses of the NIST 1567a wheat flour reference material are shown in Table 4. For the 13 elements, nine certified (Ca, P, Al, Cd, Cu, Fe, Mn, Mo, and Zn) and four noncertified elements (Co, Pb, U, and V) listed there, an acceptable order of accuracy was obtained using HR−ICPMS taking into account the 95% confidence interval and the multi-element method.

The physical and chemical soil characteristics of the agricultural practices investigated are given in Table 5. The soil is sandy loam. The pH levels of the top soils are 7.6 and 7.4 (Table 5). In the top soil, the contents of total carbon (C) are from 1.86% to 1.43% and decrease to 1.79% and 0.78% at the 100 cm depth (Table 5). The chemical characteristics of the fertilizers are given in Table 6. The analyses of soil and fertilizers were

Table 8. Elements in Potatoes (μg/kg, Fresh Weight) with Three Levels of Pig Slurry N Fertilization[a]

	0-N				1-N				2-N			
elements	*n*	min	max	mean	*n*	min	max	mean	*n*	min	max	mean
Ag	9	b > c	0.185	b > c	10	b > c	0.50	b > c	8	b > c	0.45	0.054
Al	9	195	450	320	10	115	810	370	10	125	390	230
Au***	9	0.55	1.09	0.82e	10	0.33	1.46	0.70e	10	0.72	2.8	1.59f
Ba	9	43	106	79	10	49	110	82	10	61	89	76
Bi***	9	b > c	b > c	b > ce	10	b > c	b > c	b > ce	9	b > c	b > c	b > cf
Ca	9	31000	46000	36000	9	28000	53000	39000	10	25000	53000	39000
Cd*	9	37	58	45e	10	39	78	55f	10	47	78	59f
Co***	9	7.2	9.9	8.7e	10	6.6	12.4	9.2e	10	10.3	14.9	12.1f
Cr***	9	2.5	5.4	4.1e	10	5.2	14.5	8.4f	10	3.2	8.0	4.6e
Cs***	9	0.169	0.60	0.38e	9	0.114	0.60	0.31e	10	6.5	21	10.5f
Cu**	9	940	1370	1110e	10	1070	1570.0	1230e	10	1150	1580	1390f
Dy***	9	b > c	0.134	0.036e	10	b > c	0.101	0.020e	8	0.025	0.164	0.104f
Er**	9	b > c	0.078	b > cf	10	b > c	0.00061	b > cf	10	b > c	b > c	b > ce
Fe***	9	2300	4300	3100e	10	3600	5900	4500f	10	6100	10900	8100g
Ga	9	0.0075	0.20	0.111	10	0.033	0.29	0.126	10	0.024	0.29	0.114
Gd*	9	b > c	0.194	0.096e	10	b > c	0.150	0.079e	10	0.086	0.21	0.142f
Ho	9	b > c	0.0087	0.00084	9	b > c	0.0160	0.0055	10	0.00	0.0076	0.00143
In***	9	b > c	b > c	b > ce	10	b > c	b > c	b > ce	9	b > c	b > c	b > cf
Ir*	9	b > c	b > c	b > ce	10	b > c	b > c	b > ce	10	b > c	0.089	b > cf
La	9	0.26	0.89	0.44	10	0.156	0.40	0.26	10	0.185	0.87	0.34
Lu	9	b > c	0.0134	b > c	10	b > c	0.0045	b > c	10	b > c	0.0050	b > c
Mn**	9	1450	1990	1730e	10	1380	2500	2000ef	10	1780	2700	2300f
Mo***	9	290	450	370g	10	159	314	230.0f	10	123	192	161e
Nb*	9	2.4	5.7	3.2f	9	0.95	5.4	2.5ef	10	0.055	3.3	1.41e
Nd	9	0.122	0.58	0.37	10	0.027	0.46	0.21	10	0.070	0.61	0.27
P***	9	660000	880000	760000g	10	530000	810000	670000f	10	490000	620000	540000e
Pb	9	2.0	16.2	4.1	10	1.41	7.9	3.4	10	1.84	11.2	4.6
Pd**	9	b > c	b > c	b > cf	10	b > c	b > c	b > cf	10	b > c	b > c	b > ce
Pr***	9	b > c	0.0088	b > cf	10	b > c	b > c	b > ce	10	b > c	b > c	b > ce
Pt***	9	b > c	0.116	0.0179e	10	b > c	0.151	0.045e	8	0.107	0.57	0.26f
Rb	9	650	1360	1030ef	10	630.0	1300.0	970.0e	10	920	1660	1200f
Re***	8	b > c	0.0157	b > cf	10	b > c	b > c	b > ce	9	b > c	b > c	b > ce
Rh**	9	b > c	b > c	b > cf	10	b > c	b > c	b > cf	10	b > c	b > c	b > ce
Ru***	9	b > c	b > c	b > ce	10	b > c	0.00082	b > ce	10	0.145	0.41	0.27f
Sb	9	0.80	2.6	1.67	10	0.93	3.2	1.76	10	1.05	3.7	1.6
Sc	9	0.101	0.24	0.175	10	0.054	0.97	0.24	9	0.027	0.94	0.45
Sm	9	b > c	0.055	0.0077	10	b > c	0.131	0.044	10	b > c	0.085	0.025
Sn**	9	0.85	7.3	2.6e	10	3.0	12.0	6.4e	10	3.9	25	10.7f
Sr**	9	107	196	166e	9	147	183	167e	10	101	166	131f
Ta	9	1.01	3.8	2.3ef	10	0.58	8.9	2.9f	10	0.46	2.6	1.08e
Tb	9	b > c	0.029	0.0127	10	b > c	0.020	0.0074	9	b > c	0.033	0.0100
Th***	9	0.47	2.3	1.15e	10	b > c	2.6	0.80e	9	0.058	6.2	3.7f
Ti	8	9.7	45	23	6	5.2	37	24	9	6.8	47	19.2
Tl***	9	0.025	0.130	0.070e	10	0.177	0.35	0.27f	10	0.74	1.85	1.23g
Tm	9	b > c	0.0088	b > c	10	b > c	0.0163	0.00085	10	b > c	0.0034	b > c
U	9	b > c	0.048	b > c	10	b > c	b > c	b > c	9	b > c	0.024	b > c
V**	9	1.51	2.7	2.0f	10	1.03	2.6	1.81f	10	0.89	2.0	1.29e
Y*	7	0.186	0.32	0.22f	10	0.127	0.30	0.21f	10	0.103	0.29	0.158e
Yb**	9	b > c	0.029	b > ce	9	b > c	0.041	b > ce	10	0.0068	0.033	0.0169f
Zn***	9	2400	4400	3300e	10	3600	7300	4600f	10	3800	6400	4800f

[a] 0, 60, and 120 Kg/Ha (0-N, 1-N, and 2-N, respectively). b > c = element concentration below the mean of 10 blanks. *, **, and *** mean significant at $P < 0.05$, 0.01, and 0.001, respectively. Mean values followed by same letter (e, f, andg) are not statistically different at $P < 0.05$, according to Duncan multiple range.

performed according to The Danish Government's Directions. The distribution of pig slurry to the different N levels is based on the total % N.

The overall effects of three levels of N fertilization on elemental concentrations of potato in each field site are evaluated by the use of discriminant partial least-squares (PLS) regression. The *X* matrixes used in the PLS regressions comprise the concentrations of 50 elements in 29 potato samples; 9 concentrations of each element at 0-N level, 10 at 1-N level, and 10 at 2-N level resulting in two 29 × 50 matrixes. The data used in the PLS regressions are range normalized. From the 0-N level in the field site fertilized with calcium ammonium nitrate, one sample was omitted as outlier. All 50 elements (Ag, Al, Au, Ba, Bi, Ca, Cd, Co, Cr, Cs, Cu, Dy, Er, Fe, Ga, Gd, Ho, In, Ir, La, Lu, Mn, Mo, Nb, Nd, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, Y, Yb, and Zn) were included in both regressions. The score plots for PLS regressions of *X* are shown in Figures 1 and 2 for the field site fertilized with calcium ammonium nitrate and pig slurry, respectively. Each N fertilizer level is given the code of 1 for 0 kg of N/ha, 2 for 60 kg of N/ha, and 3 for 120 kg of N/ha.

The score plots show that 0, 60, and 120 kg of N/ha split the samples in three groups separated by the three lines (Figures 1 and 2). The PLS component 1 (PC1) explains 24%, and the PLS component 2 (PC2) explains 15% of the variation in *X* in Figure 1. In Figure 2, PC1 explains 35% and PC2 explains 7% of the variation in *X*. Mean-normalized and not normalized data give a similar splitting in the score plots. The explanation for this can be that only few elements in low concentrations have important influence on the regression. The score

Table 7. Elements in Potatoes (μg/kg, Fresh Weight) with Three Levels of Calcium Ammonium Nitrate N Fertilization[a]

	0-N				1-N				2-N			
elements	*n*	min	max	mean	*n*	min	max	mean	*n*	min	max	mean
Ag***	6	b > c	0.038	b > ce	10	b > c	b > c	b > ce	9	b > c	1.44	0.42 f
Al***	8	100	180	131e	10	143	510	290f	9	290	980	610g
Au**	9	0.61	2.3	1.26f	10	0.47	1.36	0.71e	9	0.99	2.6	1.66f
Ba	8	54	80	66	10	49	86	63	10	47	84	65
Bi	9	b > c	b > c	b > c	10	b > c	b > c	b > c	9	b > c	b > c	b > c
Ca***	8	46000	63000	55000f	10	28000	54000	36000e	10	39000	77000	56000f
Cd*	9	3.9	68	49e	10	34	83	67f	10	43	75	62ef
Co	8	8.6	12.2	10.7	10	6.1	17.1	11.2	10	7.6	13.2	9.3
Cr*	8	6.5	18.0	11.2f	10	3.9	10.4	6.6e	10	4.1	15.6	8.9ef
Cs***	9	0.196	2.1	0.98e	10	3.8	6.5	5.0g	10	0.65	2.3	1.29ef
Cu	8	1220	1540	1370	10	1120	1750	1480	10	1000	1640	1300
Dy**	8	b > c	0.028	b > ce	10	b > c	0.135	0.068f	9	b > c	0.082	0.021e
Er*	9	b > c	0.062	0.0104ef	10	b > c	0.056	b > ce	10	b > c	0.127	0.032f
Fe***	8	2400	3500	2900e	10	4700	8600	6400g	10	4600	6900	5500f
Ga	7	0.0181	0.28	0.169	9	0.027	0.20	0.096	10	0.085	0.73	0.23
Gd***	8	0.00125	0.130	0.058e	10	0.091	0.20	0.142f	8	0.0140	0.141	0.066e
Ho	9	0.00163	0.026	0.0108	10	b > c	0.024	0.0063	9	b > c	0.025	0.0095
In	8	b > c	b > c	b > c	10	b > c	b > c	b > c	9	b > c	b > c	b > c
Ir	9	b > c	b > c	b > c	10	b > c	b > c	b > c	8	b > c	b > c	b > c
La	8	0.109	0.70	0.24	9	0.174	0.50	0.29	8	0.192	0.73	0.41
Lu	9	b > c	0.0147	0.000095	10	b > c	0.0054	b > c	10	b > c	0.0163	0.0021
Mn	8	1820	2400	2000	10	1470	3000	2200	10	1400	2400	1910
Mo	9	15.8	330	220	10	164	330	220	10	149	270	220
Nb**	8	0.169	3.2	1.11e	10	0.095	0.81	0.49e	10	0.34	27	8.0f
Nd**	8	0.032	0.22	0.120e	9	0.135	0.42	0.27e	8	0.124	0.87	0.44f
P**	8	430000	680000	540000f	10	420000	690000	540000f	10	360000	520000	440000e
Pb	9	2.9	9.1	5.7	10	2.9	15.6	5.6	10	2.3	13.8	5.3
Pd**	9	b > c	b > c	b > cf	10	b > c	b > c	b > ce	10	b > c	b > c	b > cf
Pr**	8	b > c	b > c	b > ce	9	b > c	b > c	b > cf	8	b > c	0.090	b > cf
Pt	8	b > c	0.23	0.102	10	b > c	0.158	0.056	8	b > c	0.51	0.151
Rb***	9	200	940	600e	10	1200	2100	1510g	10	920	1690	1270f
Re	9	b > c	b > c	b > c	10	b > c	b > c	b > c	10	b > c	b > c	b > c
Rh	8	b > c	b > c	b > c	10	b > c	b > c	b > c	10	b > c	b > c	b > c
Ru***	9	b > c	b > c	b > ce	10	b > c	0.191	0.065g	10	b > c	0.048	b > cf
Sb***	9	0.63	4.8	3.1f	10	0.80	1.45	1.09e	10	0.50	1.45	0.95e
Sc	8	b > c	0.65	0.20	10	b > c	0.27	0.133	8	0.052	0.74	0.32
Sm*	9	b > c	0.046	0.0036e	9	b > c	0.131	0.059f	9	b > c	0.132	0.034ef
Sn***	7	0.63	2.9	1.33e	10	4.5	13.5	8.6g	10	3.1	7.7	4.9f
Sr	8	121	174	146	10	95	158	121	10	91	161	125
Ta***	8	0.043	0.82	0.29e	10	b > c	0.65	0.29e	10	0.27	10.6	4.8f
Tb	9	b > c	0.029	0.0092	10	b > c	0.024	0.0110	8	b > c	0.038	0.0151
Th	8	b > c	1.80	0.66	10	b > c	1	0.28	7	b > c	4.1	1.06
Ti	9	5.2	52	20	10	6.3	29	16.4	9	11.5	41	19.7
Tl***	9	0.048	0.28	0.171e	10	0.53	0.82	0.69g	10	0.23	0.67	0.37f
Tm	9	b > c	0.0103	b > c	10	b > c	b > c	b > c	9	b > c	0.0114	0.00036
U	8	b > c	0.047	b > c	10	b > c	b > c	b > c	9	b > c	0.194	b > c
V**	7	0.59	1.74	1.28e	10	1.20	2.7	1.94f	10	1.34	3.6	2.3f
Y**	9	0.044	0.171	0.120e	10	0.100	0.32	0.188f	9	0.147	0.30	0.23f
Yb	9	b > c	0.055	0.0036	9	b > c	0.056	0.0121	10	b > c	0.034	0.0119
Zn*	8	3300	7600	5500f	10	3500	6800	5000f	9	2900	5200	3800e

[a] 0, 60, and 120 Kg/Ha (0-N, 1-N, and 2-N, respectively). b > c = element concentration below the mean of 10 blanks. *, **, and *** mean significant at $P < 0.05$, 0.01, and 0.001, respectively. Mean values followed by same letter (e, f, and g) are not statistically different at $P < 0.05$, according to Duncan multiple range.

plot of a PLS regression, for a 58 × 50 *X* matrix for combined data from the two sites, tend to split the samples into the three groups given by the N levels. The separation is not as distinct as for the two sites when separated. This can be explained if the regressions are influenced by elements by different loading in the PLS of separated data (Figures 1 and 2). An inspection of loading plots show differences, but it is difficult to quantify.

Analysis of variance (one-way ANOVA and Duncan multiple range) was performed for each set of data as used in the PLS regressions (calcium ammonium nitrate and pig slurry). The results of the analysis of variance together with the mean, minimum, and maximum elemental concentrations (μg/kg, fresh weight) of potato (*Solanum tuberosum* Folva) as affected by the three levels of N fertilization are shown in Tables 7 and 8 for the sites fertilized with calcium ammonium nitrate and pig slurry, respectively.

By comparing the two tables, it is confirmed what was already expected from the PLS regressions, that N fertilization effects elemental concentrations in a different pattern dependent on the fertilization practice. Although the elements Au, Cd, Cr, Cs, Dy, Er, Fe, Gd, Nb, P, Pr, Pd, Pr, Ru, Sn, Tl, V, Y, and Zn have a significant variation ($P < 0.05$) between the three levels of N fertilization for both sites, the variations of elemental concentrations between the three N levels are different for the two sites.

The content of P and Mo were reduced ($P < 0.001$) by the addition of N fertilizer as pig slurry. With addition of calcium ammonium nitrate, the contents of P ($P <$ 0.01) and Zn ($P < 0.05$) were reduced from level 1-N to level 2-N. A similar response for P was recorded for potato (Huett and Dettmann, 1992). The content of Al with calcium ammonium nitrate fertilization and the contents of Fe and Tl with pig slurry fertilization were increased ($P < 0.001$) by increasing N levels (Tables 7 and 8). For pig slurry fertilization, the contents of Gd, Ir ($P < 0.05$), Cu, Sn, Sr, Yb ($P < 0.01$), and Au, Bi, Co, Cs, Dy, In, Pt, Ru, and Th ($P < 0.001$) and for calcium ammonium nitrate fertilization the content of Nb, Nd ($P < 0.01$), and Ag and Ta ($P < 0.001$) were increased from level 1-N to 2-N. From level 0-N to 1-N, the content was increased for Cd ($P < 0.05$), Cr, and Zn ($P < 0.001$) with pig slurry fertilization and for Pr, V, and Y ($P < 0.01$) with calcium ammonium nitrate fertilization. A reduced content from 1-N to 2-N to 0-N level was observed for the elements Fe, Rb, Ru, Sn, and Tl ($P < 0.001$) with calcium ammonium nitrate fertilization. A reduced content from level 0-N to 1-N and 2-N was observed for Pr and Re ($P < 0.001$) with pig slurry fertilization and for Sb ($P < 0.001$) with calcium ammonium nitrate fertilization. Y ($P < 0.05$), Er, Pd, Rh, and V ($P < 0.01$) show an increased content from level 2-N to 1-N and 0-N with pig slurry fertilization. Effect of N on elemental uptake by plants has been inconsistent and depends on a number of factors such as source and amount of the element, presence of micronutrients as impurities in fertilizers, secondary effect on soil pH, secondary influence due to dilution through increased plant growth, preference for the elements, and others (Logan et al., 1997; Faria-Marmol et al., 1997).

The crop exhibited specific preferences for the toxic elements (Cd and Pb), and the order of uptake was generally Cd > Pb in all three levels of N fertilization for both fertilization practices. This compares with patterns obtained by Wolnik et al. (1983a), Varo et al. (1980), Logan et al. (1997), and Ministry of Agriculture, Fisheries and Food (1998). Only minor differences occur in the concentrations of Cd and Pb between potato tubers from the two sites with different fertilization practice.

The methodology used in this study may be efficiently employed to study a wide range of elements in agricultural crops. Application of three levels N fertilizer split the potatoes into three groups with different element profiles. The pattern of uptakes is very dependent on the fertilization practice.

ACKNOWLEDGMENT

The authors wish to thank Lis Vinther Kristensen, Jette Bruun Nielsen, and Anette Møller, who did the sample preparation and the analyses.

LITERATURE CITED

Bibak, A.; Behrens, A.; Stürup, S.; Knudsen, L.; Gundersen, V. Concentration of sixty-three major and trace elements in Danish agricultural crops measured by inductively coupled plasma mass spectrometry. 1. Onion (*Allium cepa* Hysam). *J. Agric. Food Chem.* **1998**, *46*, 3139−3145.

Brüggemann, J.; Kumpulainen, J. The status of trace elements in staple foods from the former Federal Republic of Germany. 1. Contents of 11 trace elements. *Z Lebensum Forsch.* **1995**, *201*, 1−6.

Faria-Marmol, J.; Morillo, D. E.; Caraballo, A.; McDowell, L. R. Effect of defoliation and nitrogen and phosphorus fertilization on Andropogon gayanus Kunth. III. Microelement concentrations. *Commn. Soil Sci. Plant Anal.* **1997**, *28*, 875−883.

Food balance sheet 1976. Agricultural Economics Research Institute: Helsinki, 1977.

Gartrel, M. J.; Cran, J. C.; Podrebarac, D. S.; Gunderson, E. L. Pesticides, selected elements, and other chemicals in adult total diet samples, October 1980−March 1982. *J. Assoc. Off. Anal. Chem.* **1986**, *69*, 146−161.

Hansen, H. H.; Andersen, A. *Bly, cadmium, kobber og zink i frugt og grøntsager 1977−1980*; International publication of the National Food Institute: Søborg, Denmark. 1982.

Huett, D. O.; Dettmann, B. Nutrient uptake and partitioning by zucchini squash, head lettuce and potato in response to nitrogen. *Aust. J. Agric. Res.* **1992**, *43*, 1653−1665.

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

Krelowska-Kulas, M. Determination of the level of certain trace elements in vegetables in differently contaminated regions. *Die Nahrung* **1993**, *37*, 456−462.

Levnedsmiddelstyrelsen. *Overvågningssystem for Levnedsmidler 1988−1992*; Publication No. 232; 1995a; 204−223.

Levnedsmiddelstyrelsen. *Danskernes kostvaner 1995 hovedresultater*; Publication No. 235; May 1995b.

Logan, T. J.; Goins, L. E.; Lindsay, B. J. Field assessment of trace element uptake by six vegetables from N-Viro soil. *Water Environ. Res.* **1997,** *69*, 28−33.

Ministry of Agriculture, Fisheries and Food. *1991 Total diet study*; Publication No. 34; July 1994.

Ministry of Agriculture, Fisheries and Food. *1994 Total diet study*; Publication No. 149; May 1998.

Stenhouse, F. *The 1990 Australian marked basket survey report*. National Health and Medical Research Council/National Food Authority; Australian Government Printing Service: Canberra, 1991.

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

The Unscrambler, version 6.11, User Guide; Camo A/S: Norway, 1996.

Varo, P.; Lähelmä, O.; Nuurtamo, M.; Saari, E.; Koivistoinen, P. Mineral element composition of Finnish foods. VII. Potato, vegetables, fruits, berries, nuts and mushroom. *Acta Agric. Scand. Suppl.* **1980**, *22*, 90−113.

Ward, N. J.; Savage, J. M. Metal dispersion and transportational activities using food crops as biomonitors. *Sci. Total Environ.* **1994**, *146*/*147*, 309−319.

Wolnik, K. A.; Fricke, F. L.; Capar, S. G.; Braude, G. L.; Meyer, W.; Satzger; R. D.; Bonnin, E. Elements in major raw agricultural crops in the United States. 1. Cadmium and lead in lettuce, peanuts, potatoes, soybeans, sweet corn, and wheat. *J. Agric. Food Chem.* **1983a**, *31*, 1240−1244.

Wolnik, K. A.; Fricke, F. L.; Capar, S. G.; Braude, G. L.; Meyer, W.; Satzger; R. D.; Kuennen, R. W. Elements in major raw agricultural crops in the United States. 2. Other elements in lettuce, peanuts, potatoes, soybeans, sweet corn, and wheat. *J. Agric. Food Chem.* **1983b**, *31*, 1244−1249.

Received for review June 8, 1998. Revised manuscript received December 21, 1998. Accepted April 21, 1999. The investigation has been supported financially by the Danish Food and Technology Development (FØTEK) Program. We gratefully acknowledge this support.

JF980606V