Comparison of Major and Trace Element Concentrations in Danish Greenhouse Tomatoes (*Lycopersicon esculentum* Cv. Aromata F1) Cultivated in Different Substrates

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The concentration of major and trace elements was determined for tomato (*Lycopersicon esculentum* cv. Aromata F1) fruits grown in three different substrate systems. The systems were soil and rockwool irrigated with a normal nutrient solution and rockwool irrigated with a nutrient solution with elevated electrical conductivity (EC). At three harvest times, tomato fruits were analyzed for Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Sr, and Zn by ICP-AES and for Cd, Cr, Mo, Ni, Pb, Sn, and V by HR-ICPMS. The concentrations of Ca, Cd, Fe, Mn, Mo, Na, Ni, Sr, and Zn were significantly different ($p < 0.05$) for tomato fruits grown on the different substrates. Between the harvest times different levels ($p < 0.05$) were shown for Ca, Cd, Fe, Mn Na, Ni, Sr, Zn Cu, K, Mg, P, Sn, and V. The concentration of Cd was >15 times higher and the concentration of Ca was 50−115% higher in soil-grown fruits than in rockwool-grown fruits. Principal component analysis applied on each harvest split the data into two groups. One group includes soil-grown fruits, and the other group includes rockwool-grown fruits with the two different nutrient solutions.

Keywords: *Tomato (Lycopersicon esculentum cv. Aromata F1); major elements; trace elements; soil; rockwool; multielement analysis; principal component analysis; PCA; ICP-AES; HR-ICPMS*

INTRODUCTION

Between April and October most fresh tomatoes (*Lycopersicon esculentum*) consumed in northern Europe are produced in greenhouses. They are almost exclusively cultivated in inert rockwool slabs where the supply of water and nutrients can be precisely controlled. This allows very high and predictable yields per plant. Several studies have shown that consumers consider product quality, in particular aroma and texture, very important for their choice of tomatoes (*1*). Although no objective data are available, the studies also show that a majority of consumers are convinced that vegetables, including tomatoes, grown in soil, are of superior quality to those grown in rockwool and other systems using defined substrates (*2*). Many consumers also believe that the content of vitamins and minerals is substantially higher for vegetables grown in soil. As yields are generally higher in the rockwool system than in soil, partly because it effectively prevents the propagation of soil-borne diseases, this is very unfortunate for the producers, who experience unjustified difficulties in a market with strong price competition. Because the rockwool system provides the best control available over all relevant substrate parameters, it actually has the potential to provide the best quality, as soon as the optimal conditions in the root zone with regard to fruit quality are precisely defined.

It is therefore very important for both tomato growers and producers of rockwool to know which factors are most important for tomato quality. If the type of substrate has no influence, it is important to provide definitive data showing this; if there is an effect, the rockwool product should be adjusted to ensure the best quality possible.

The content of major and trace elements in tomato fruits has been only sparingly investigated. In a number of countries a survey of Cd, Pb, Hg, and sometimes As in tomato fruits has been carried out (*3*). In outdoors soil-grown tomatoes the concentrations of Cd, Pb, and 11 other major and trace elements have been estimated in the United States (*4*). Künsch et al. (*5*) have compared the concentrations of K, Ca, Mg, Na, Pb, and Cd in greenhouse tomatoes cultivated in rockwool and soil and found 5-fold higher concentrations of Cd in the fruits when grown in soil.

The objectives of this work were (1) to develop a reliable analytical method for multielement determination in tomato fruits by routine inductively coupled argon plasma atomic emission spectroscopy (ICP-AES) and high-resolution inductively coupled argon plasma mass spectroscopy (HR-ICPMS) analysis, (2) to evaluate the effect of the growth medium on the content of major and trace elements in tomato fruits, and (3) to investigate whether possible differences in elemental content of tomato fruits from plants grown in soil and rockwool, respectively, are dependent on season.

MATERIALS AND METHODS

Experimental Design. Tomato plants (*L. esculentum* cv Aromata F1) (Rijk Zwaan, Holland) were grown in three different systems in a greenhouse compartment. The experi-

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Table 1. Electrical Conductivity (mS·cm^{-1}) and Nutrient Concentrations (mg/L) in Solutions Used for Rockwool Slab Wetting and Irrigation[a]

			irrigation							
			from March 15		from March 21		from April 10		from May 4	
	slab wet up									
	norm EC	high EC	norm EC and soil	high EC	norm EC and soil	high EC	norm EC and soil	high EC	norm EC and soil	high EC
EC	3.5	5.5	2.5	3.5	2.5	3.5	2.5	3.5	2.5	3.5
N	335	530	230	325	225	320	235	310	225	320
P	40	40	40	40	40	40	30	30	40	40
K	370	585	350	490	340	484	400	530	340	484
Ca	370	585	190	270	187	265	180	240	187	265
Mg	60	94	60	85	58	82	50	66	58	82
S	111	190	102	135	97	143	89	120	86	128
Na	18	21	16	16	17	19	17	19	17	18
Cl	112	188	54	57	97	143	90	132	87	126
Fe	4.00	4.00	4.00	4.00	4.00	4.00	3.00	3.00	3.00	3.00
Mn	0.70	0.70	0.70	0.70	0.70	0.70	0.60	0.60	0.60	0.60
B	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Zn	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Cu	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Mo	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05

[a] Normal (norm) EC for both slab and soil.

mental design was Latin square to take into account the known variation from north to south in the greenhouse and any possible variation from east to west. The three systems were as follows: (1) soil [target electrical conductivity (EC) in soil of 3−4 mS/cm, irrigation with 2.5 mS/cm]; (2) rockwool with normal EC (target EC in slabs of 3−4 mS/cm, irrigation with EC 2.5 mS/cm); and (3) rockwool with relatively high EC (target EC in slabs of 5−6 mS/cm, irrigation with EC 3.5 mS/cm).

Nine beds were established in the compartment, each ∼9 m in length and ∼95 cm in breadth. Alleys between the beds were ∼90 cm in breadth. The beds were orientated north−south. Each bed was divided into three sections, each consisting of a double row of plants. Twelve plants were planted in each section of the bed at a density of ∼2.3 plants/m^2. The experimental unit (plot) consisted of two neighboring bed sections (i.e., 24 plants).

Propagation. Plants were propagated according to standard practice. Plants to be grown in soil were propagated in 12-cm plastic pots in peat (Grøn Kronmuld, Simontorp A/S, Vallensbæk, Denmark). Plants to be grown in rockwool were sown in Kiem plugs (Grodania A/S, Hedehusene, Denmark) and transferred to Vitagreen DM 6.5G growing blocks (Grodania A/S) 14 days after sowing.

Transplants were placed at final spacing in the experimental greenhouse at Research Centre Årslev on February 24, 2000. Plants to be grown in soil were placed on plastic sheeting covering the soil, and plants to be grown in rockwool were placed on the slabs' plastic coating beside the planting hole prior to planting. All treatments were planted on March 15, 2000. For the soil-grown plants, the plastic pot was removed and plants were planted through holes in the plastic sheeting at spacing corresponding to that used in the rockwool treatments.

Cultivation in Rockwool. Rockwool-grown plants were grown in plastic-wrapped slabs (MAS 2075 A1W, 90 × 20 × 7.5 cm, Grodania A/S). Slabs were placed in plastic-coated metal trays, each 280 cm long and 25 cm wide. Three slabs, each with two plants, were placed in each tray. Excess nutrient solution draining from the slabs was led from the trays to a drain.

Cultivation in Soil. Prior to the present experiment, the upper 25−30 cm layer of greenhouse soil was removed and replaced with fresh soil taken from a field at the Research Center Årslev. Prior to planting, ∼40 L of composted plant material/m^2 and a base dressing comprising 505 g of magnesium nitrate/m^2, 152 g of monopotassium phosphate/m^2, 412 g of potassium nitrate/m^2, and 237 g of potassium sulfate/m^2 were rotovated into the soil. Soil samples taken to a depth of 25 cm after soil amendment showed major element concentrations (mg/L soil) of N, 162; P, 51; K, 390; Ca, 3120; Mg, 130; S, 52; Na, 20; and Cl, 40. Texture analysis characterized the soil as a sandy loam (11% clay, 26% silt, 59% sand, and 4% organic matter).

Fertilization. Throughout the experiment, the soil treatment was irrigated with the same nutrient solutions as used in the normal EC rockwool treatment. Well water was used for the formulation of all nutrient solutions. EC (mS·cm^{-1}) and nutrient concentrations (mg/kg) in solutions used for rockwool slab wetting and irrigation are summarized in Table 1.

Nutrient solutions were supplied to all treatments by a drip-irrigation system (two drippers/plant, each supplying 35 mL/min) connected to an AMI 5000 (DGT-Volmatic, Vallensbæk Strand, Denmark) fertilizer mixer with automatic EC and pH control. Two stock solution tanks were used for each solution formulation (normal EC/soil and high EC), allowing individual adjustment of EC and nutrient solution composition. A common acid stock solution was used for pH control.

Climate. Air temperature setpoints in the greenhouse were adjusted weekly in response to measurements of plant growth and development. The mean air temperature during the entire experimental period was 19.9 °C.

Mean root zone temperatures in the peat and rockwool prior to planting were 17.3 and 18.4 °C, respectively. After planting, mean root zone temperatures were 20.3 and 21.0 °C in the soil and rockwool, respectively.

Venting and increased pipe temperature were begun at a relative humidity of ∼80%. The mean relative humidity for the entire experimental period was 76%.

CO_2 was supplied at 800 mg/kg from 1 h before sunrise to 1 h before sunset when the windows were shut. During venting, CO_2 was supplied at 350 mg/kg.

Sampling. Harvest of tomatoes for element analysis took place three times: at the beginning of May (harvest 1), at the end of May (harvest 2), and finally in the middle of June (harvest 3). First-grade tomatoes of uniform maturity were used for element analysis. All fruit were between 40 and 70 mm in diameter and were free from discoloration, diseases, and deformity. Throughout the harvest the tomato fruits were handled with Nitrile gloves (Nitrile, powder free, Ansell Edmont). For major and trace element analysis one fruit of medium size per plant, from each experimental unit (i.e., 12 fruits) was harvested directly into poly(ethylene terephthalate) (PET) bags to avoid contamination of the fruit. The bagged fruits were placed in boxes and stored at room temperature for 1 or 2 days before further sample preparation. Throughout the harvests the sample size was 12 tomatoes in general. In harvests 2 and 3 the sample size was reduced in a few cases. Sample size was never less than six fruits.

Table 2. Instrumental Conditions for the Varian Vista (ICP-AES) and the PlasmaTrace 2 (HR-ICPMS)

	ICP-AES	HR-ICPMS
rf power	1200 W	1350 W
plasma gas flow	15 L min^{-1}	12.5 L min^{-1}
auxiliary gas flow	1.5 L min^{-1}	2.0 L min^{-1}
nebulizer gas flow	0.9 L min^{-1}	0.9 L min^{-1} (optimized daily)
sample uptake rate	0.7 mL min^{-1}	0.7 mL min^{-1}
ion sampling depth		optimized daily for maximum intensity
ion lens settings		optimized daily for maximum intensity and optimum resolution
nebulizer type	concentric	concentric
spraychamber	cyclonic	Scott-type maintained at 5 °C
sampler/skimmer cone	nickel	copper
scans		2
replicates	2	2
peak widths		5(^{51}V, ^{52}Cr, ^{60}Ni, ^{208}Pb) 3 (^{98}Mo, ^{111}Cd, ^{120}Sn)
points per width		20
dwell time		20 ms (^{51}V, ^{52}Cr, ^{60}Ni) 10 ms (^{98}Mo, ^{111}Cd, ^{120}Sn, ^{208}Pb)
resolution 400	Ca, 396.847	^{98}Mo, ^{111}Cd, ^{120}Sn, ^{208}Pb
resolution 4000	Cu, 327.395	^{51}V, ^{52}Cr, ^{60}Ni
selected wavelengths	Fe, 238.204 nm K, 766.491 nm Mg, 279.553 nm Mn, 257.610 nm Na, 589.592 nm P, 213.618 nm S, 181.972 nm Sr, 407.771 nm Zn, 213.857 nm	

Sample Preparation. To minimize the risk of contamination, all sample preparations were 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). Double-deionized water (resistance > 18.2 MΩ cm) from an Elgastat Maxima Analytical System (Elga, Blocks, U.K.) was used throughout the sample preparation.

Tomato. The fruits were rinsed and scrubbed gently with a soft nylon brush in double-deionized water under fairly clean laboratory conditions (R2). The tomato fruits were packed in PET bags and then passed through the lock into R3.

All sample preparations after the initial cleaning procedures were carried out in the class 1000 environment (R3). Disposable surgical latex gloves (Gammex, sterile and powder free, Ansell Edmont) and full laboratory dress (Tyvex) were worn throughout the procedure. Laboratory wares were stored in a clean air environment (R3).

In R3 the tomato fruits were rinsed once more in double-deionized water and then wiped with clean-room tissues. The samples of tomato fruits were homogenized in a blender (Büchi Mixer B 400, Flawil SCH) equipped with zirconium oxide ceramic cutters. From the homogenized tomato samples a ~500 g subsample was taken out and freeze-dried. The freeze-dried sample was homogenized again. Eight subsamples of ~0.5 g each were selected from the homogenized sample. The subsamples were 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) and 2 mL of double-deionized water were added. The samples were digested in a microwave oven (MDS 2000, CEM Co., Matthews, NC) equipped with 12 closed Teflon PFA (perfluoroalkoxy) digestion vessels (CEM Co.). The microwave oven (power level = 535 W) was programmed to run at increasing pressures at 1.5, 3, 6, 9, and 12 bar in five steps. The times of each step were 5, 5, 10, 10, and 10 min, respectively. The clear, light yellow digest without any residue was then cooled to room temperature and transferred quantitatively with double-deionized water to a polyethylene flask, and double-deionized water was added to a final mass of 50 g (weighed to the nearest 0.0001 g). These sample solutions were stored at 5 °C until analysis.

The dry matter contents of the tomato samples were determined from the mass of fresh and freeze-dried samples.

Soil and Rockwool. Samples of soil with and without compost amendment were taken at a depth of 0−25 cm for analyses. From each homogenized soil sample three subsamples and from an unused rockwool slab four subsamples were taken for analyses. The sample preparation and digestion with 33% nitric acid in a microwave oven was performed as described by Larsen et al. (*6*). The dry matter content of the soil samples was determined by heating 50 g of each sample at 120 °C for 8 h. Water samples were sucked from the rockwool slabs irrigated with high and normal EC nutrient solutions at the time of the third harvest. The samples were analyzed after dilution with double-deionized water.

Multielement Determination. The tomato sample solutions and the soil and rockwool sample solutions were diluted with double-deionized water before analyses for major and trace elements. ICP-AES (Vista CCD simultaneous ICP-AES, Varian Mulgrave, AUS) was used for the determination of Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Sr, and Zn in the tomato samples, and HR-ICPMS (PlasmaTrace 2, Micromass Manchester, UK) was used to determine Cd, Cr, Mo, Ni, Pb, Sn, and V. In the soil samples Fe, K, Mg, Mn, Na, Ni, P, Sr, V, and Zn were analyzed by ICP-AES and Cd and Mo were analyzed by HR-ICPMS. For the elements analyzed by HR-ICPMS quantification was performed using standard addition calibration including correction with a reagent blank. For determinations by ICP-AES external calibration was applied.

The mass resolution ($m/\Delta m$) of the PlasmaTrace2 instrument can be varied between 400 and 10000. Throughout this study only mass resolution settings of 400 and 4000 were applied. At mass resolution 4000 the ion transmission is ~20% of that of low-mass resolution (400). The instrumental parameters for the ICP-AES and HR-ICPMS instruments are summarized in Table 2. A primary tomato CRM material was not commercially available. The best estimate for the accuracy was therefore obtained for 12 replicate analyses of the GBW 08504 cabbage certified reference material (Food Detection Science Institute Ministry of Commerce, Bejing, China). The precision of the analytical method was determined by analysis of eight subsamples from one tomato sample.

Statistical Analysis. The results from the major and trace element determinations are analyzed as a complex split plot design, with randomization of treatments to the whole plots and harvest time to the subplots. Whole plots are conducted

Table 3. Quality Control Measurement of GBW 08504 Cabbage[a]

element	certified	measured	*n*
K[b]	14500 ± 800	11000 ± 390	12
Na[b]	7570 ± 160	6480 ± 180	12
Ca[b]	7920 ± 360	8250 ± 210	12
Mg[b]	1840 ± 40	1650 ± 70	12
Cu[b]	3.00 ± 0.20	2.45 ± 0.07	12
Zn[b]	26.7 ± 1.7	30.6 ± 1.9	12
Mn[b]	22.0 ± 1.0	20.4 ± 0.6	12
Fe[b]	52.0 ± 3.2	47.5 ± 1.5	12
Cd[c]	0.029 ± 0.006	0.037 ± 0.002	12
Sr[b]	45.2 ± 2.6	39.2 ± 1.0	12
Pb[c]	0.28 ± 0.09	0.29 ± 0.05	12
P[b]	3400 ± 200	3590 ± 140	12

[a] Mean values reported in μg/g dry weight. Uncertenty given as 2 times the standard deviation. [b] Measured by ICP-AES. [c] Measured by HR-ICPMS.

Table 4. Precision of the ICP-AES and HR-ICPMS Methods

major elements (ICP-AES)	concn (mg/kg)	%RSD
Ca	113	2.1
Cu	0.37	3.1
Fe	2.7	6.5
K	1380	3.1
Mg	77	3.9
Mn	0.62	7.9
Na	2.4	12.0
P	313	3.6
S	111	5.5
Sr	0.169	1.80
Zn	1.27	6.2
minor elements (HR-ICPMS)	**concn (μg/kg)**	**%RSD**
Cd	24	7.3
Cr	1.30	59
Mo	44	5.0
Ni	8.1	23
Pb	1.40	28
Sn	0.78	38
V	0.07	46

as an incomplete Latin square (*7*). Analysis of the mixed model was performed using *proc mixed* (SAS ver. 6.12, Cary, NC). Principal component analysis (PCA) (*8*) was performed using Unscrambler (CAMO A/S ver. 7.5 Oslo, Norway).

RESULTS AND DISCUSSION

Evaluation of the Analytical Method. The elemental mean and 2 times the standard deviation of 12 replicates of the reference material are shown in Table 3. Ca, Cd, Fe, Mn, P, and Pb are in good agreement with the certified values. The measured values of Zn, Mg, and Sr are close to the certified values. Mg and Sr have a small and Cu, Na, and especially K a pronounced negative bias. The relatively great deviations from the certified values of Cu, Na, and K are still below 17%.

The precision of the method is evaluated by the relative standard deviation (%RSD) of eight repeated measurements, that is, performed on eight individual subsamples taken from a homogenized tomato sample and digested in one run. All sample preparation procedures were performed in parallel. In general, the relative standard deviation (%RSD) is below 12% when the concentration of the element considered is well above the detection limit (Table 4). Cr, Ni, and V are estimated with a resolution of 4000, where the signal intensity is ~20% of the intensity with a resolution of 400. In addition to the low concentrations of these elements, the rather high %RSD may be explained by the very low signal.

From these facts it can be concluded that the applied ICP-AES and HR-ICPMS methods possess an acceptable accuracy for the analysis of major and trace elements in tomato, keeping in mind that the determination is a multielement analysis in which the instrument settings are a compromise between the optimum settings for the individual elements.

Comparative Statistical Tests. The 18 element concentrations in tomato are given in Tables 5 and 6. The mean values of the concentrations of major and minor components are reported in separate tables in milligrams per kilogram of fresh weight (fw) and in micrograms per kilogram of fw, respectively. The dry matter content in the samples varied from 4.38 to 6.86% (harvest 1), from 5.50 to 7.19% (harvest 2), and from 7.31 to 7.78% (harvest 3). Analyses based on dry matter gave no differences in the conclusions presented below.

Nine of the 18 elements analyzed were significantly different ($p < 0.05$) between the substrates, and 14 differed between harvest times. The elements Ca, Cd, Ni, Sr, and Zn have higher concentration and Mn, Mo, and Na have lower concentration in soil-grown tomato fruits. The most remarkable result is the relatively high level of Cd in tomatoes from the soil treatment. The level is 15−30 times higher in tomatoes from soil, compared to those from rockwool with normal EC and high EC treatments. The mean values (harvests 1−3) of Cd in the fruits are 14.7 μg/kg of fw in soil-grown and 0.70 μg/kg of fw in rockwool-grown tomatoes. The great difference cannot be explained by the substrate data given in Table 7. The mean values of Cd are 0.34 mg/kg in the soil used in the cultivation and 0.44 mg/kg in the rockwool slab (Table 7). From a comparison of the Cd content in the substrates with the concentrations in the fruits it may be concluded that Cd is more accessible in the soil than in the rockwool slabs as they both have been irrigated with the same normal EC nutrient solution. There is no obvious explanation for the observed differences in Cd, but some proposals are given below.

1. Cd may be incorporated in a more accessible form in the soil than in the rockwool structure.

2. The microbiological activity in the soil is more intensive and interactive in the uptake of Cd in the plant by leaching the mineral from the substrate or by a symbiotic uptake mechanism.

3. The root system is more bulky in the soil than in the rockwool and in that way it is possible to utilize the Cd resources from a greater quantity of substrate.

The uptake of Cd in roots, shoots, leaves, and seedlings of tomatoes has been intensively investigated, but there is nothing reported in the literature on how different substrates affect the concentration in the fruits. Several investigations concerned with Cd uptake from substrates such as contaminated soil and sewage sludge with high Cd concentrations have concluded that the availability of Cd is greater in acid than in calcareous soil and that the speciation of Cd is not important to the uptake (*9*). Checkai et al. (*10*) investigated the uptake of Cd and micronutrient metals in tomatoes in the presence and absence of a complexing agent (EDTA) and found that accumulation of Cd, Zn, Mn, and Cu in

Table 5. Concentrations of Major Elements in Tomato Fruits[a]

treatment	harvest	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Sr	Zn
soil norm EC	all	110a	0.34	2.6ab	1640	90	0.71a	5.5a	330	118	0.175a	1.25a
rockwool norm EC	all	71b	0.35	2.4a	1510	85	0.93b	7.3b	320	108	0.153b	1.01b
rockwool high EC	all	51c	0.37	2.8b	1530	87	0.89b	7.8b	310	113	0.115c	1.08b
p value		*<0.0001*	*0.3654*	*0.0487*	*0.2592*	*0.1424*	*<0.0001*	*0.0002*	*0.5477*	*0.1387*	*<0.0001*	*0.0203*
all	1	89a	0.39a	2.8a	1400a	80a	0.69a	3.0a	310a	110	0.175a	1.23a
all	2	67b	0.34b	2.5b	1500a	79a	0.83b	8.4b	300a	114	0.119b	0.85b
all	3	76c	0.34b	2.5b	1780b	104b	1.01c	9.1b	360b	116	0.148c	1.26a
p value		*<0.0001*	*0.0291*	*<0.0001*	*0.0034*	*<0.0001*	*<0.0001*	*<0.0001*	*0.0122*	*0.4404*	*<0.0001*	*<0.0001*
treatment × harvest *p* value		*0.1949*	*0.4895*	*0.9252*	*0.8790*	*0.9501*	*0.0003*	*0.4758*	*0.4175*	*0.8902*	*0.0124*	*0.8520*

[a] Mean values in mg/kg of fw. Values followed by the same letter (a−c) are not significantly different ($p < 0.05$).

Table 6. Concentrations of Trace Elements in Tomato Fruits[a]

treatment	harvest	Cd	Cr	Mo	Ni	Pb	Sn	V
soil norm EC	all	14.7a	1.20	29a	9.4a	1.01	0.91	0.124
rockwool norm EC	all	0.63b	1.09	62b	5.2b	1.48	0.91	0.126
rockwool high EC	all	0.77b	1.35	80c	4.9b	1.65	0.87	0.090
p value		*<0.0001*	*0.9069*	*0.0003*	*0.0089*	*0.4721*	*0.8394*	*0.7248*
all	1	6.5a	0.75	60	3.6a	1.42	0.72a	0.024a
all	2	5.4b	1.78	58	7.5b	1.89	1.42b	0.169b
all	3	5.0b	1.20	60	8.7b	1.93	0.63a	0.149ab
p value		*0.0008*	*0.3510*	*0.9430*	*0.0012*	*0.5777*	*0.0195*	*0.0562*
treatment × harvest *p* value		*0.0002*	*0.9614*	*0.5792*	*0.3269*	*0.8110*	*0.9710*	*0.7064*

[a] Mean values in μg/kg of fw. Values followed by the same letter (a−c) are not significantly different ($p < 0.05$).

Table 7. Elements in Soil and Rockwool (mg/kg of Dry Weight) and Elements in Water from Slabs (μg/kg)

	soil				rock-wool	norm EC	high EC
	bed 1	bed 6	bed 8	pure			
Ca	9600	9500	4900	4900	45000	330000	460000
Cd	0.35	0.35	0.32	0.31	0.44	0.31	0.31
Cr	15.5	16.2	17.2	10.2	171	6.4	1.87
Cu	8.2	7.3	8.4	7.3	26	300	350
Fe	9600	10400	11700	7900	14900	1220	2200
K	2400	2400	2800	1390	4300	350000	490000
Mg	1920	1930	2300	1280	53000	92000	119000
Mn	260	300	350	300	630	320	480
Mo	0.43	0.25	0.55	0.131	1.04	69	113
Na	84	82	94	50	6100	46000	47000
Ni	9.8	9.0	14.0	8.8	120	30	18.4
P	1050	1110	1380	820	640	21000	29000
Sr	31	31	29	16.5	280	1390	1980
V	27	28	30	18	118	3.3	1.60
Zn	56	59	83	53	176	640	870

shoots appears to be related to their respective ionic activities rather than their concentrations in hydroponic solution, where the activity ratios of the mentioned ions were controlled with chelating resin. Furthermore, they found that efficiencies of Cd uptake calculated from shoots, roots, and whole plants all conform to the pattern of decreased efficiency with increased activity of Cd ion, indicating that Cd is taken up by metabolically active uptake mechanisms.

The Ca concentration in tomatoes from the high EC treatments is remarkably low in view of fact that the Ca concentration in the high EC solution sucked from the slabs is higher than the respective normal EC solution (Table 7). Again, the highest concentration is in the soil-grown fruits. Part of the explanation may be the last two proposals given for Cd, but it cannot be the whole explanation. Competition from other elements in high concentrations in the high EC solution and the method of distribution Ca in the plant may also be part of the explanation. A decreased Ca uptake with increasing salinity is well described in several studies (*11*−*13*). The decreased Ca content from normal EC to high EC in our experiment is in good agreement with these observations. The explanation for the Ca concentration in the soil-grown fruits is higher than in the rockwool-grown fruits with normal EC solution may be a less effective salinity in the soil caused by a higher degree of ion sorption in the soil than in the rockwool.

The concentration of Sr in the fruits shows a tendency similar to that of Ca as could be expected from the chemical similarities of the two elements.

For the two other elements (Ni and Zn) with highest concentration in soil-grown tomatoes the explanation may be the same as for Cd.

For the elements Mn, Mo, and Na the higher concentration in fruits from rockwool-grown tomato plants can be related to a higher concentration in the substrate.

Harvest date had generally less influence on the content of elements than the substrates. Most pointedly is the influence observed in the concentrations of K, Ni, and Na with increasing concentrations from the first to the second and third harvests, Mg and P with increasing concentrations from harvests 1 and 2 to harvest 3, and Mn with continually increasing concentrations through all three harvests. Cd, Cu, and Fe have declining concentrations from harvest 1 to harvests 2 and 3, and Ca, Sr, and Zn have declining concentrations from harvest 1 to harvest 2 and increasing concentrations from harvest 2 to harvest 3.

In Table 8 concentrations of some elements from this study are compared with the results reported by Künsch et al. (*5*). A higher content of Ca and Cd in soil-grown tomato fruits found in our study is in good agreement with their investigation, but the difference in the Cd content in our study is 4 times the difference reported by Künsch et al. Remarkable differences between the two investigations are the concentrations of K, Na, and Pb, which are severalfold lower in our study. It is not possible to explain the differences with the available information.

The high concentrations of Cd in soil-grown tomato fruits (14.7 μg/kg) call for an assessment of eating soil-

Table 8. Comparison of Mean Values (mg/kg of Fresh Weight) Reported by Künsch et al. (1994) and in This Study

	Künsch et al.		this study	
	soil	rockwool	soil	rockwool
Ca	99[a]	71[a]	110[b]	61[b]
K	2520[a]	2160[a]	1330	1240
Mg	84[a]	61[a]	90	86
Na	110	99	5.5	7.6
Cd	0.0075	0.0015	0.0147[b]	0.00070[b]
Pb	0.0065	0.0061	0.00101	0.00157

[a] Values reported are significant different at $p < 0.001$. [b] Values reported are significant different at $p < 0.0001$.

grown tomatoes cultivated in Denmark. In Danish cultivated soil (0−25 cm) the mean value of Cd is 180 μg/kg. 95% of Danish cultivated soil has a concentration below 430 μg/kg at 0−25 cm (*6*). Compared to this, the substrate used in this study has a relatively high content of Cd (340 μg/kg). There are no Danish maximum allowable values of Cd in tomato fruits, but values above 100 μg/kg in vegetables and 30 μg/kg in fruits will give rise to remarks in the Danish surveys carried out to monitor the safety and nutrient value of food (*14*). Despite the relatively high level of Cd in the soil-grown tomatoes, it does not give rise to concern about soil-grown tomatoes in Denmark in general.

Principal Component Analysis (PCA). PCA was applied to the 18 elements measured in the 216 individual tomato subsamples (8 sample replicates × 3 treatments × 3 replications × 3 harvests) to investigate the relevant and interpretable structure in the data. The data set consisted of a table containing the results of the elemental analysis performed on the 216 samples, that is, 216 objects and 18 variables. The variables were weighted with the inverse of the standard deviation of all objects before the PCA. This was done to compensate for the different scales of the variables. It was found that three principal components (PCs) explained only 61% of the variation in the data set (PC1, 24%; PC2, 23%; and PC3, 14%). However, as it appears from Figure 1, the tomato samples split into partially separated groups according to the growth medium when the scores of the first and second PCs are plotted against each other.

In Figure 2 the loadings for the first and second PCs are shown. In general, the elements with high numerical loadings are the elements of most importance for the model.

By simultaneous evaluation of Figures 1 and 2, it appears that the tomato grown in soil (coded S) are placed in the left part of the scores plot, corresponding to relatively high levels of the elements Ca, Cd, Sr, Zn, Ni, and Fe. Correspondingly, tomatoes grown in rockwool (coded N or H) are placed in the lower part of the scores plot, corresponding to relatively high levels of the elements Mo, Na, Mn, Pb, Cr, Sn, Cr, and V. No clear grouping between the two rockwool treatments is seen. The separation of the soil and rockwool treatments becomes clearer if the tomato samples are sorted according to harvest before modeling.

In the scores plot for harvest 3 (Figure 3) a clear grouping between soil and rockwool is seen, and furthermore a grouping between the two rockwool treatments is apparent. In individual score plots for harvests 1 and 2 (not shown) a clear grouping between soil and rockwool treatments is seen, but no clear grouping between the two rockwool treatments is evident.

The results from the PCA models are in agreement with the comparative statistical tests.

In an overview of the results of this study it can be concluded that the Cd concentration in soil-grown tomato fruits is 15−20 times greater than in rockwool-grown fruits. The great difference between the Cd concentrations in fruits from soil-grown and rockwool-grown tomatoes treated with the same normal EC solution calls for further investigation to clarify the

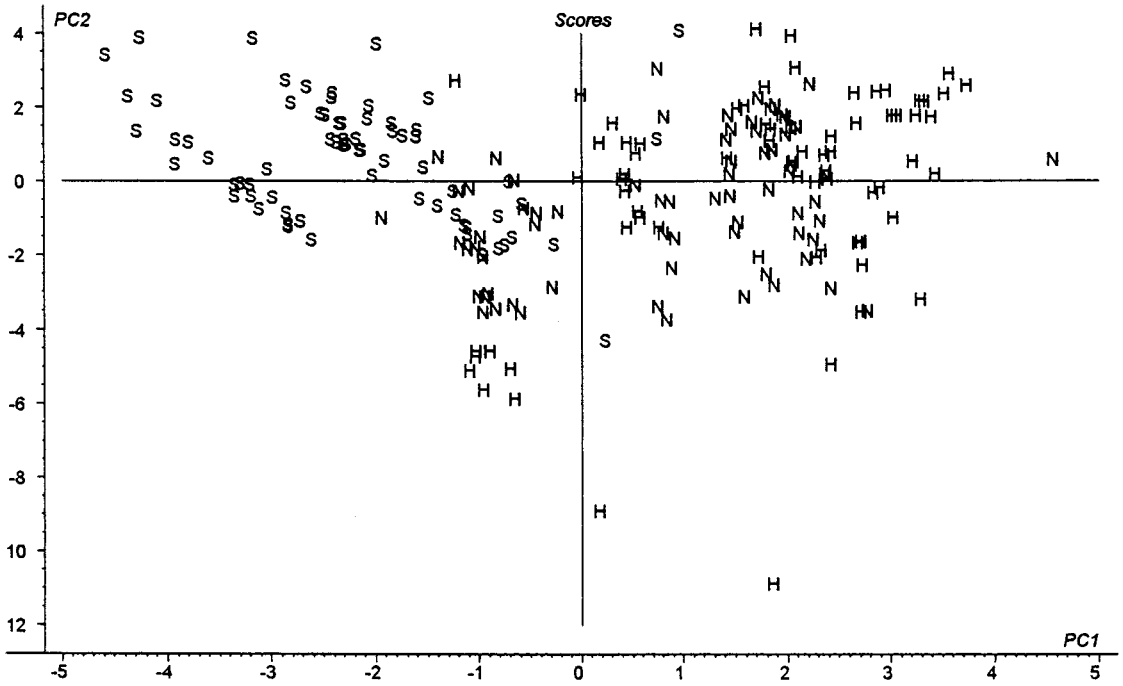

Figure 1. PCA scores plot for trace elements (fresh weight). The letters in the plot refer to the treatment (S, soil; N, rockwool normal EC; H, rockwool high EC).

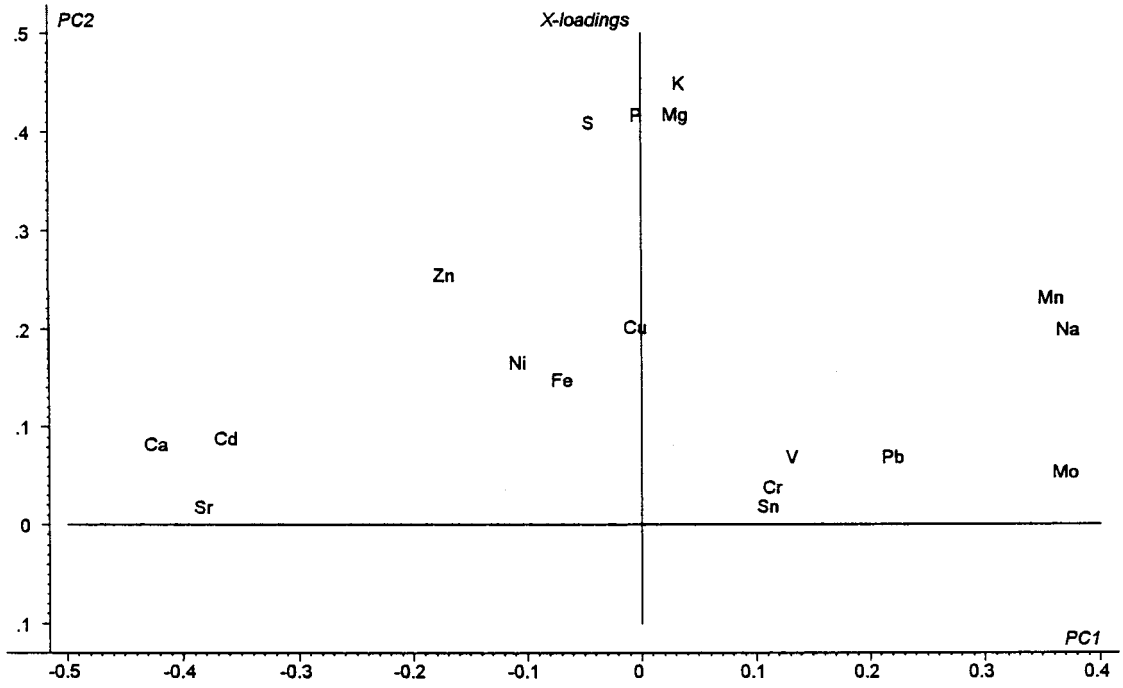

Figure 2. PCA loading plot for trace elements (fresh weight).

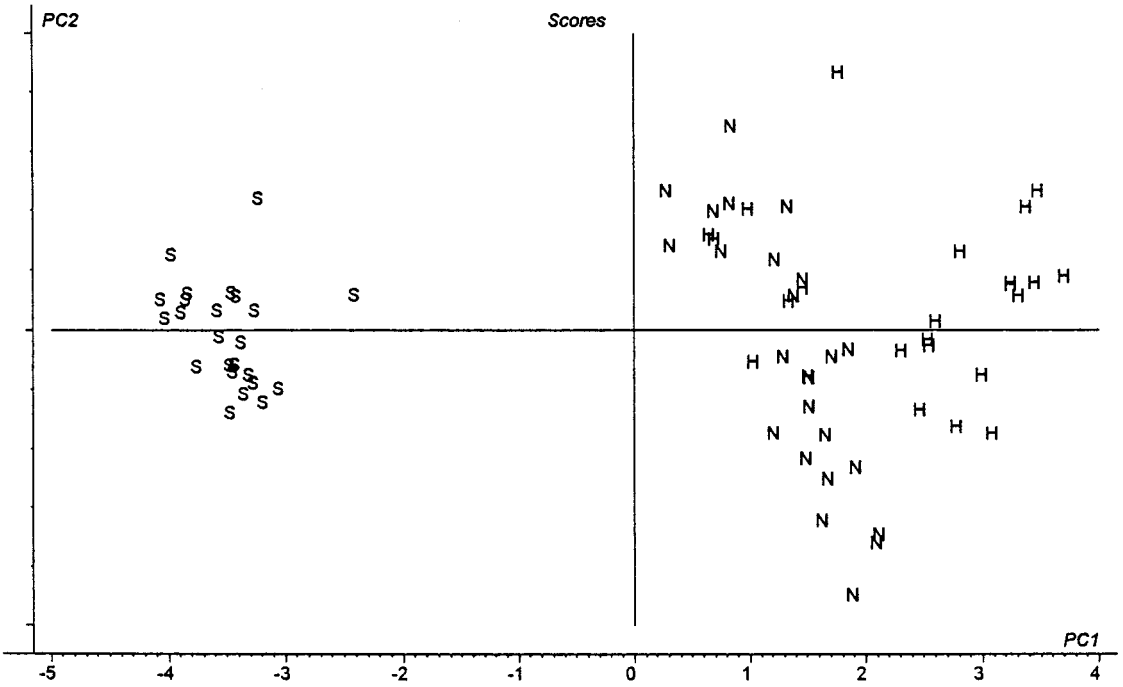

Figure 3. PCA scores plot, trace elements, harvest 3. The letters in the plot refer to the treatment (S, soil; N, rockwool normal EC; H, rockwool high EC).

reason. The concentration profiles of tomatoes grown in soil and rockwool are different as verified by the comparative statistical tests and the PCA of the data. None of the observed differences between the two media can be explained by differences in fruit dry matter content.

The growth medium, within limits relevant to the industry, has an effect on the level of 9 of 18 of the major and trace elements measurable in tomato fruit that is of a magnitude that can be identified by chemical analysis even though both media are irrigated with the same nutrient solution.

Cultivation conditions have a significant effect on the uptake of elements, but there is no overall trend; each element is affected according to its own specific properties.

The limitation of this study must be remembered. The tomato fruits are represented by only one variety. Other varities may have another elemental concentration profile when cultivated in the three substrates and more or less extreme difference in the uptake of Cd compared to this study.

The possible influence of the observed differences in element composition between the two media on taste

or content of vitamins, flavonoids, and sensorically important components will be evaluated in separate papers.

ABBREVIATIONS USED

EC, electrical conductivity; HR-ICPMS, high-resolution inductively coupled argon plasma mass spectroscopy; ICP-AES, inductively coupled argon plasma atomic emission spectroscopy; PC, principal component; PCA, principal component analysis.

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