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Mineral Composition of Vegetable Crops Fertilized with Fish-Soluble Nutrients

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Pea, tomato, radish, and lettuce crops were analyzed for 20 elements by atomic absorption spectrometry. Elemental contents of vegetables that had been fertilized with different rates of fish-soluble nutrients were compared to those fertilized with standard Hoagland nutrient solution. The mineral contents of the edible organs were altered by fertilization with fish-soluble nutrients. Pea seeds and tomato fruits responded favorably, with no heavy metal accumulation. Lettuce leaves and radish storage roots showed a greater accumulation of certain mineral elements but no excessive heavy metal accumulation.

Fish and its byproducts have been recognized and used as fertilizer (Aung and Flick, 1980; Ceci, 1975; Emino, 1981; Van Breedveld, 1969). The fish-soluble nutrients are complex mixtures of minerals, amino acids, fats, and vitamins derived from the menhaden industry after oil removal (Soares et al., 1973). The general crop responses of plants fertilized with fish-soluble nutrients have been favorable (Aung et al., 1981). However, the effects of fish-soluble nutrients on possible chemical compositional changes of food crops are not well documented, and the lack of information limits the commercial use of fish solubles as a fertilizer. Since vegetable crops are predominantly consumed to provide essential minerals in the diets (Keane, 1972; Senti and Rizek, 1975), several of the important vegetables were selected for determining the effects of fish-soluble nutrients on the mineral composition of the edible organs. This paper reports the mineral contents of pea, tomato, radish, and lettuce crops fertilized with fish-soluble nutrients.

MATERIALS AND METHODS

Crop Growing. Seeds of pea (*Pisum sativum* L. cv. Little Marvel), tomato (*Lycopersicon esculentum* Mill. cv. Fireball), lettuce (*Lactuca sativa* L. Buttercrunch), and radish (*Raphanus sativus* L. cv. Cherry Belle) were sown in a sand medium contained in pots under greenhouse conditions. Pea, lettuce, and radish were grown during the spring with 18 °C night and 24 °C day temperatures. Tomato was grown in late spring and early summer months at temperatures of 21 °C night and 28 °C day. Pea was

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grown in 9 cm diameter plastic pots, radish was grown in 13 cm diameter clay pots, and tomato and lettuce were grown in 18 cm diameter clay pots. The sand medium (All Star Concrete Co., Blacksburg, VA 24060) used had the following properties: pH 8.1; NO_3–N, 5 ppm; P_2O_5, 4 ppm; K_2O, 11.5 ppm; CaO, 571 ppm; MgO, 30 ppm; 0.1% organic matter; 230 ppm of soluble salts (1:2 soil to water extract). The plants were fertilized at designated intervals (see the tables) with (a) various concentrations of fish solubles (Zapata Haynie Corp., Reedville, VA 22539) and (b) complete nutrient solution 1 prepared according to Hoagland and Arnon (1950) as a reference standard for gauging the relative effectiveness of the fish solubles. A randomized complete design of 8–10 replicates was used. The crops were grown to maturity and the edible parts harvested for determination of mineral nutrients composition.

Sample Preparation. Peas were removed from the pods, sliced in half, and oven-dried for 18 h at 95 °C. Tomato samples were sliced in half, and the seeds were separated from the pulp and then dried for 18 h at 100 °C in a forced draft oven. Radish roots and tops and lettuce leaves were lyophilized for 48 h. The dry samples of the selected crops were ground in a miniblender for 3 min and analyzed for mineral nutrients composition.

Mineral Nutrients Determination. A wet ashing procedure was used for atomic absorption spectrometry (AAS) analyses (Simpson and Blay, 1966). A Perkin-Elmer Model 403 atomic absorption spectrophotometer was used. A 4-in. burner head and standard air–acetylene flame were used for determination of calcium, copper, chromium, iron, magnesium, manganese, nickel, potassium, sodium, zinc, and the heavy metals cadmium, cobalt, lead, mercury, and silver. For barium, boron, molybdenum, phosphorus, and the heavy metal tin, a nitrous oxide–acetylene burner and flame were used. Approximately 1-g samples were weighed

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into 250-mL Erlenmyer flasks and 25 mL of 26% (v/v) HCl was added. The solutions were brought to a boil and simmered for 5 min. The samples were then cooled and transferred to 50-mL volumetric flasks. The volume was made up with distilled water and mixed thoroughly by shaking. The solutions were filtered through Whatman No. 1 paper before analyses by AAS for all listed elements except calcium, magnesium, and phosphorus. For calcium, magnesium, and phosphorus, it was necessary to dilute the samples with distilled deionized water to obtain AAS readings in a suitable range. A 1/5 dilution was needed to read calcium and magnesium in the samples. To dampen potential anionic interferences, a 1% (w/v) lanthanum solution was added to samples for analysis of calcium and magnesium. Phosphorus was determined by the indirect molybdenum determination of Parker (1972). A sample containing up to 0.13 mg of phosphorus in the form of soluble orthophosphate was placed in a separatory funnel. Aliquots of 10 mL of tomato and radish solutions, 2.5 mL for pea, and 2 mL for lettuce were used. Molybdophosphoric acid was separated from molybdosilicic acid by the use of hydrochloric acid, a 1:10 ammonium molybdate solution, and diethyl ether. Excess molybdenum was discarded from the ether extract by washing with a 1:10 HCl solution. A buffer consisting of ammonium chloride and ammonium hydroxide was used to further wash the ether extract. The aqueous layers from the buffer washings were combined, and the molybdenum content was determined by AAS. A calibration curve using several concentrations of phosphorus standard was prepared, and the amount of phosphorus vs. molybdenum concentration was plotted. The nitrogen content of pea seeds was determined by AOAC Kjeldahl procedures (Association of Official Analytical Chemists, 1980).

The accuracy of the atomic absorption spectrometry procedure was evaluated by using a Standard Reference Material from the National Bureau of Standards (1982). Citrus leaves, SRM 1572, were analyzed by the same method as the vegetable samples. The percent variation from the certified value for several elements is given below.

element	% variation from NBS
Mg	+1.7
K	-4.1
Cu	-14.5
Fe	0
Pb	-18.8
Mn	0
Na	+4.3
Zn	-3.0

These values show acceptable variation for the given elements. Other elements for which comparisons to certified values could not be made are useful for comparisons between vegetable samples since precision within repetitions was good.

RESULTS AND DISCUSSION

Tomato fruits fertilized with fish-soluble nutrients (FSN) had significantly lower levels of K, Mg, Ca, Zn, and Cu than fruits from plants fertilized with a complete inorganic Hoagland nutrient solution (HNS). However, Na and Ni contents of fruits fertilized with FSN were higher than those of fruits of HNS plants (Table I). No excessive accumulation of heavy metals was observed.

The mineral compositions of peas from plants fertilized with different rates of FSN were generally higher, except K and Cu, than those of peas from plants fertilized with HNS (Table II). The levels of N, P, Ca, and Mn were significantly increased with FSN fertilization. The Na level

Table I. Mineral Composition of Tomato Fruit Flesh (Dry Weight Basis)[a]

	ppm	
element	HNS	FSN 2×
P	640	700
K	30300	14900[b]
Mg	1200	800[b]
Ca	800	420[b]
Na	1200	4200[b]
B	c	c
Zn	22	18[b]
Fe	39	30
Cu	6	3[b]
Mn	12	13
Ni	6	10
Ba	c	c
Cd	1	1
Co	c	c
Cr	2	c
Hg	c	c
Pb	c	c
Sn	c	c
Ag	c	c
Mo	c	c

[a] HNS = full strength Hoagland's nutrient solution 1; FSN 2× = 30 mL of fish-soluble nutrients/3.8 L of water; all samples were fertilized once a week. [b] Significance at the 5% level of probability by the least significant difference test. [c] Element below the detection limit of the AAS instrument: 700 ppm for B, 88 ppm for Ba, 1 ppm for Co, 2 ppm for Cr, 89 ppm for Hg, 9 ppm for Pb, 32 ppm for Sn, 2 ppm for Ag, and 8 ppm for Mo.

Table II. Mineral Composition of Pea Seeds (Dry Weight Basis)[a]

ele-ment	ppm				
	HNS	FSN 1×1W	FSN 2×1W	FSN 1×2W	FSN 2×2W
N	38800	46000[b]	47800[b]	48400[b]	49800[b]
P	900	900	1100[b]	1000[b]	1100[b]
K	16200	15100[b]	14700[b]	14400[b]	14100[b]
Mg	1300	1300	1300	1200	1300
Ca	600	800[b]	700	700	600
Na	80	100	80	80	120[b]
Zn	67	92[b]	72	64	60
Fe	100	122	109	129[b]	103
Cu	11	11	8[b]	9[b]	8[b]
Mn	20	40[b]	36[b]	33[b]	32[b]
B	c	c	c	c	c
Ni	c	c	c	c	c
Ba	c	c	c	c	c
Cd	c	c	c	c	c
Co	c	c	c	c	c
Cr	c	c	c	c	c
Hg	c	c	c	c	c
Pb	c	c	c	c	c
Sn	c	c	c	c	c
Ag	c	c	c	c	c
Mo	c	c	c	c	c

[a] HNS = full strength Hoagland's nutrient solution 1 applied once a week; FSN = fish-soluble nutrients; 1× = 15 mL of FSN/3.8 L of water; 2× = 30 mL of FSN/3.8 L of water; 1W = once-a-week fertilization; 2W = twice-a-week fertilization. [b] Significantly different from the HNS treatment at the 5% level of probability by the least significant difference test. [c] Element below the detection limit of the AAS instrument: 700 ppm for B, 6 ppm for Ni, 88 ppm for Ba, 1 ppm for Cd, 1 ppm for Co, 2 ppm for Cr, 89 ppm for Hg, 9 ppm for Pb, 32 ppm for Sn, 2 ppm for Ag, and 8 ppm for Mo.

of peas was high only in plants fertilized with a high rate of FSN given biweekly. The heavy metals in peas were all below the level of detection in the FSN- or HNS-fertilized plants.

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Table III. Mineral Composition of Lettuce Leaves (Dry Weight Basis)[a]

element	ppm		
	1/4 HNS	1/3 FSN	1/6 FSN
P	4200	4600	3900
K	65200	36800[b]	37100[b]
Mg	3800	4400	3700
Ca	11100	13000	12800
Na	2900	9000[b]	8600[b]
B	c	c	c
Zn	90	149[b]	128
Fe	299	439[b]	545[b]
Cu	9	11	11
Mn	128	99[b]	78[b]
Ni	17	22	21
Ba	c	c	c
Cd	8	11	12
Co	10	11	10
Cr	c	c	c
Pb	c	c	c
Hg	c	c	c
Sn	c	c	c
Ag	c	c	c
Mo	c	c	c

[a] 1/4 HNS = 1/4-strength Hoagland's nutrient solution 1; 1/3 FSN = 5 mL of fish-soluble nutrients/3.8 L of water; 1/6 FSN = 2.5 mL of fish-soluble nutrients/3.8 L of water; all samples were fertilized once a week. [b] Significantly different from the HNS treatment at the 5% level of probability by the least significant difference test. [c] Element below the detection limit of the AAS instrument: 580 ppm for B, 130 ppm for Ba, 1 ppm for Cr, 15 ppm for Pb, 245 ppm for Hg, 125 ppm for Sn, 12 ppm for Ag, and 12 ppm for Mo.

In lettuce leaves, the contents of macronutrients except K and the micronutrients except Mn of plants fertilized with FSN were higher than those of leaves fertilized with HNS (Table III). The Na level in leaves receiving FSN fertilization was increased by 3-fold over that of leaves fertilized with HNS. The levels of heavy metals did not differ between plants fertilized with FSN and HNS.

The K, Ca, and Mn levels in the storage roots of radish fertilized with FSN were lower than those of radish fertilized with HNS (Table IV). The P and Mg contents of radish roots receiving FSN fertilization compared favorably with those of plants fertilized with HNS. On the other hand, the Na and Fe levels of radish roots fertilized with FSN were significantly higher than those of plants fertilized with HNS. A low rate of FSN tended to increase Zn, Cu, and Ni levels of radish roots while a higher rate resulted in a lower level of these elements compared to those of plants fertilized with HNS. In radish tops, the P level was higher in plants fertilized with a high rate of FSN applied twice a week (Table V). However, the K, Mg, Ca, and Mn levels were lower in radish tops fertilized with FSN compared to levels in plants fertilized with HNS. Zn and Mn levels of plants fertilized with high rates of FSN and at greater frequency were lower than those of plants receiving a low rate of FSN applied at lesser frequency. This suggests that a high FSN rate fertilization may be counterproductive. It may be observed that while the levels of heavy metals present in radish roots and tops differ, the levels found in plants fertilized with FSN were not excessive compared to those of plants fertilized with HNS.

CONCLUSIONS

The fertilization with fish-soluble nutrients altered the mineral contents of different crops. The degree of alteration in mineral contents depended upon the edible organs of the crops grown for consumption: storage roots of radish, leaves of lettuce, seeds of peas, or fruits of tomato.

Table IV. Mineral Composition of Radish Storage Roots (Dry Weight Basis)[a]

element	ppm				
	HNS	FSN 1×1W	FSN 2×1W	FSN 1×2W	FSN 2×2W
P	500	500	500	500	500
K	29500	22400[b]	21500[b]	20100[b]	18900[b]
Mg	2100	2200	2200	2200	1900[b]
Ca	2600	2100[b]	2000[b]	2000[b]	1800[b]
Na	4200	5000[b]	5600[b]	5600[b]	5200[b]
B	c	c	c	c	c
Zn	209	172[b]	214	264[b]	164[b]
Fe	1005	1699[b]	1365[b]	1206[b]	1272[b]
Cu	11	13[b]	9[b]	9[b]	7[b]
Mn	287	247[b]	169[b]	120[b]	104[b]
Ni	25	38[b]	26	28	19[b]
Ba	c	c	c	c	c
Cd	2	3	3	3	3
Co	4	5	4	4	4
Cr	12	28[b]	8[b]	20[b]	16[b]
Pb	c	c	c	c	c
Hg	c	c	c	c	c
Sn	c	c	c	c	c
Ag	c	c	c	c	c
Mo	c	c	c	c	c

[a] HNS = full-strength Hoagland's nutrient solution 1 applied once a week; FSN = fish-soluble nutrients; 1× = 15 mL of FSN/3.8 L of water; 2× = 30 mL of FSN/3.8 L of water; 1W = once-a-week fertilization; 2W = twice-a-week fertilization. [b] Significantly different from the HNS treatment at the 5% level of probability by the least significant difference test. [c] Element below the detection limit of the AAS instrument: 770 ppm for B, 90 ppm for Ba, 9 ppm for Pb, 90 ppm for Hg, 145 ppm for Sn, 2 ppm for Ag, and 8 ppm for Mo.

Table V. Mineral Composition of Radish Tops (Dry Weight Basis)[a]

element	ppm				
	HNS	FSN 1×1W	FSN 2×1W	FSN 1×2W	FSN 2×2W
P	400	400	400	500	600[b]
K	15200	10400[b]	7700[b]	8900[b]	11600[b]
Mg	6600	6700	6200	6000[b]	5400[b]
Ca	31900	31400	25800	27300	13800[b]
Na	4500	6500[b]	7400[b]	7500[b]	8100[b]
B	c	c	c	c	c
Zn	403	417	507[b]	544[b]	338[b]
Fe	264	290	342[b]	231	237
Cu	9	10	9	9	9
Mn	1358	1513	1120[b]	812[b]	531[b]
Ni	44	47	47	47	42
Ba	c	c	c	c	c
Cd	13	16	15	14	14
Co	12	12	10	12	9
Cr	2	2	3	1	2
Pb	9	9	9	9	9
Hg	c	c	c	c	c
Sn	440	440	440	440	440
Ag	c	c	c	c	c
Mo	c	c	c	c	c

[a] HNS = full-strength Hoagland's nutrient solution 1 applied once a week; FSN = fish-soluble nutrients; 1× = 15 mL of FSN/3.8 L of water; 2× = 30 mL of FSN/3.8 L of water; 1W = once-a-week fertilization; 2W = twice-a-week fertilization. [b] Significantly different from the HNS treatment at the 5% level of probability by the least significant difference test. [c] Element below the detection limit of the AAS instrument: 1200 ppm for B, 145 ppm for Ba, 265 ppm for Hg, 2 ppm for Ag, and 8 ppm for Mo.

The mineral composition of pea seeds and to a lesser extent tomato fruits was favorably altered with no detectable heavy metal accumulation. The Na, Zn, and Fe contents of lettuce leaves and the Na, Fe, and Cr contents of radish

storage roots showed a greater amount of accumulation with FSN fertilization. Thus, the absorption patterns of these elements for the two vegetable crops require further study.

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Stability of Sorbic Acid in Orange Squash

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Degradation of sorbic acid (SA) in orange squash was appreciable when stored in polypropylene pouches but very slight when stored in laminate pouches and glass bottles. In model systems also, the degradation of SA was high in polyethylene and polypropylene pouches but negligible in saran-coated cellopoly and laminate pouches. Metabisulfite and fruit acids acted as prooxidants while sucrose above 5% decreased the rate of degradation.

Use of sorbic acid (SA) as an antimicrobial food additive is permitted in many countries, and it is extensively used in preserving fruit juices, bakery, and dairy products. Though information on the physiological harmlessness of SA is well documented, literature on its stability in foods during processing and storage is at variance. Arya (1980) reported that in aqueous solution SA undergoes autoxidative degradation, forming malonaldehyde and other carbonyls. The degradation was found to be influenced by a number of factors such as temperature, pH, and the presence of salts, trace metal ions, glycerol, and amino acids. Bolin et al. (1980) have also reported degradation of SA during storage of raisins, the losses being related with storage temperature and moisture content. Heintze (1973), however, reported that autoxidation of SA was not appreciable even after 48 h of intensive aeration. Heintze (1971) had reported that degradation of SA was appreciable in fish sausages but insignificant in fruit juices. In none of these studies has the role of packaging material on the rate of degradation of SA been evaluated. In the present paper the stability of SA in orange squash and the role of packaging materials and squash ingredients are described.

MATERIALS AND METHODS

Reagents. Sorbic acid and potassium sorbate were from E. Merck. All other chemicals were of analytical reagent grade and used as such without further purification. Methyl alcohol and ethyl alcohol were refluxed with aluminum dust and potassium hydroxide for 2 h and distilled in an all-glass apparatus to free them from traces of carbonyls.

Orange Squash. Good-quality mandarin oranges (*Citrus reticulata*) procured from a local market were washed under running water and peeled, and the rag sticking to the segments was removed by hand. The segments were passed through a laboratory model stainless steel screw-type juice extractor (Raylon Metal Works, Bombay, India). Freshly extracted juice had a Brix of 9° and titratable acidity of 0.63%. The orange squash was prepared by mixing cane sugar (8.0 kg), citric acid (177 g), and water (2 L) with 10 kg of freshly extracted juice. Freshly prepared squash on analysis gave 45 °Brix and 1.2% titratable acidity. The squash was pasteurized by heating it in a stainless steel vessel for 10 min in a thermostatically controlled water tank maintained at 80 ± 2 °C. The juice was continuously stirred during the heating operation and attained bath temperature in 8 min. After pasteurization the juice was cooled, divided into four lots, and separately treated with (a) 0.061% potassium metabisulfite (350 ppm of SO_2), (b) 0.035% potassium metabisulfite (200 ppm of SO_2) plus 0.268% potassium sorbate (0.2% SA), (c) 0.134% potassium sorbate (0.1% SA), and (d) 0.268% potassium sorbate (0.2% SA).

Storage Tests. The treated squash samples were stored in hermetically sealed pouches (6 in. × 4 in.) of polypropylene (60 μm) and paper (60 g)–Al foil (40 μm)–