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Copper Content of South African Fruits and Vegetables

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Although copper is an essential trace element required by living organisms, the range between required and toxic levels is small (Wolnik et al. 1983; Zaroogian and Johnson 1983). Increased levels of copper as a result of industrial activities have been found in the environment and in living organisms (e.g. Aulio 1980). The use of fungicides and fertilizers may significantly affect the trace element content of agricultural crops (Rao Maturu 1980). High levels of elements such as copper may be present in harvested crops if excessive dosages of pesticide were applied or if the crops were harvested too soon after application of chemicals.

Fungicides based on copper salts have been applied for many years to certain agricultural crops in South Africa. Although legal limits to pesticide residues have been laid down, including some for copper in foodstuffs, the effects of the prolonged and widespread use of these fungicides on levels of copper residues in crops was not known before this study was undertaken. This was regarded as a serious deficiency, and the monitoring of fresh vegetables for copper residues was listed as of high priority for investigation by the Working Group on Pesticide Residues (Van Dyk et al. 1982).

The main objective of the work reported here was to determine residue levels of copper in raw samples of fresh commercial fruit and vegetables and to see how these levels compared with the legal maximum permissible residue limit of 20 mg/kg laid down for these products for local consumption and for export (in Bot et al. 1984). This would reveal whether any problem existed regarding high concentrations of copper in the particular crops. Further aims were to determine to what extent copper occurred in certain crops that had been treated experimentally with a fungicide and how concentrations of the element declined in the crop during the compulsory witholding period between application and harvest (given in Bot et al. 1984).

MATERIALS AND METHODS

Samples of export fruit and vegetables were obtained from the

Division of Agricultural Product Standards in Pretoria and from the Department of Health in Cape Town. Samples on the domestic market were obtained from the Fresh Produce Market in Pretoria. The samples, each consisting of several fruits or vegetables, were representative of all the major growing areas in the country and were produced by many different growers. Where possible, several cultivars of a fruit were collected. All these samples were collected during the growing seasons within the period January 1983 to June 1984, and were prepared for analyses as described below.

Copper oxychloride wettable powder (850 g/kg or 500 g Cu/kg), was obtained from Agrihold Ltd. for experimental spraying of peach trees and bean plants. In November 1983, three out of six selected peach trees (cultivar Rhodes Swellengrebel), standing in a row in an orchard near Pretoria, were treated at the recommended concentration of 5 g/l water. A full cover spray was applied to the foliage and fruit. The remaining three trees were left unsprayed. These six trees had not been treated with a copper containing pesticide for at least four years prior to this experiment. Samples of fruit were taken from the sprayed and control trees immediately before spraying and then at 1 h and at 1, 3, 7 and 14 days after spraying (the witholding period for harvest after application of the fungicide on peach trees, is 14 days). Each sample consisted of 10 randomly picked peaches per tree, which were placed in a plastic bag. On day 14 the fruits were generally just beginning to ripen.

In February 1984, one half of a plot (3 x 4 m) planted with green beans (stem type) was sprayed with copper oxychloride at the recommended concentration of 4g/l water. The other half of the plot was screened off and remained unsprayed. The plot and its surrounding area had not previously been treated with any chemical containing copper for at least 8 years. Samples of pods on both halves of the plot were taken immediately before spraying and then at 1 h and 1, 3 and 6 days (The witholding period for harvest of beans is 6 days). Pods of all sizes were picked randomly, and three replicates of about 200 g each were taken per treatment during each sampling and kept in plastic bags. At the time of sampling the pods varied in size from initial stage to fully developed.

Warm and sunny weather prevailed throughout the peach and bean spraying experiments. Only 4 mm rain fell on the peach trees three nights before day 14. The soil underneath the bean plants was gently watered daily, as no rain fell during the 6-day trial.

The fruit or vegetables of each market and experimental sample were cut into small pieces and homogenized to a smooth pulp by means of a liquidizer. Whole fruit or vegetable units were taken as the sample matrix, except in the case of stone-fruits and mangoes, of which the pips were discarded. The pulp of each sample was put in a plastic bag and kept in a freezer. Sample preparation for analysis was done on a principle similar to that used by Aulio (1980). Ten grammes of pulp was oven-dried at 80°C for 18 h and 0.50 g samples of dried and ground material were dry ashed at 500°C for 3 h. The ash was covered with 0.5 ml nitric acid (65%), evaporated on a water bath, and then dissolved in 10 ml of 5% HNO_3, before filtering and making up to a final volume of 25 ml with deionized water. Recoveries of copper through the extraction process were checked by running some duplicate samples which were fortified with 1 ml of a standard containing 10 µg/ml copper.

A stock solution for analytical standards of copper was prepared from powdered metallic copper (99.7%, Merck) dissolved in concentrated nitric acid and made up to 1000 µg/ml. From this stock solution the final standards for analytical work were made up in distilled deionized water at Cu concentrations ranging from 0.02 to 0.20 µg/ml. The pH of standards, samples and blanks were matched.

Samples were analysed on a Varian AA-475 atomic absorption spectrophotometer with a CRA-90 graphite furnace. The furnace was operated with parameters almost the same as those used for Cu in multivitamins by Culver (1975) and were as follows: drying at 100°C for 30 s., ashing at 700°C for 30 s., and atomizing at 2000°C for a 2-s. hold time, while the ramp rate for temperature increase to atomizing was 500°C/s. The wavelength setting for the hollow cathode lamp was 324.7 nm. The calibration curve quantitation technique was used, and the mean of two to four determinations per sample was taken as the analytical result. The detection limit for Cu was 0.025 ng. All results on residues were converted to wet weight, for direct comparison with the applicable maximum residue limit.

RESULTS AND DISCUSSION

Copper was found at detectable levels (>0.04 mg/kg) in all 645 market samples analysed (Table 1). It is clear that none of these samples had any residue concentrations exceeding or even nearly approaching the maximum residue limit of 20 mg/kg. The vast majority of samples (82.8%) had less than 1 mg/kg Cu, while only 1.4% contained Cu in excess of 3 mg/kg, with none higher than 6 mg/kg. Considerable variation was found between residue levels in different crops and between levels of different samples of the same crops. These variations are probably not unusual, as the trace-element content of crops is likely to vary according to numerous factors, such as inherent qualities of plants, trace element content of soil, geographical location and fertilizers and fungicides used (Rao Maturu 1980). Much variation was also found for background values of copper in peanuts, potatoes, soybeans, sweet corn and wheat by Wolnik et al. (1983). The levels of mineral copper reported by these authors and also by Erdman and Moul (1982), who studied residues of mineral copper in wheat, barley and oats, led to the conclusion that a significant part of

TABLE 1. Copper residues found in samples of raw commercial fruit and vegetables.

Crop	Number of samples	Copper concentration (mg/kg wet mass)	
		Mean	Range
Apples	120	0.46	0.15 - 2.61
Apricots	18	0.47	0.19 - 1.11
Beans (green)	33	1.19	0.25 - 3.39
Cabbage	21	0.52	0.15 - 1.13
Citrus*	60	0.78	0.16 - 2.57
Gem Squash	18	0.51	0.29 - 0.82
Grapes (table)	110	0.63	0.18 - 2.27
Mangoes	31	1.85	0.14 - 5.98
Peaches**	72	1.18	0.20 - 3.01
Pears	64	0.68	0.28 - 1.15
Peppers	19	0.68	0.08 - 1.52
Plums	31	0.51	0.13 - 1.29
Tomatoes	48	0.46	0.06 - 1.17

* Samples of oranges, lemons and grapefruit.
** Including nectarines.

the residues in Table 1 could be due to the presence of copper as natural trace element. However a small minority of the samples had relatively high concentrations, which could possibly have originated partly from preharvest treatment with a fungicide, but even their levels were very low.

Mean percentages of copper recovered from 85 fortified market samples of all crops, ranged from 81 to 109, with an overall mean of 92%.

The effects of copper oxychloride sprays on copper residues in harvested peaches and beans are illustrated in Tables 2 and 3.

TABLE 2. Copper in fruit samples from fungicide-treated and untreated peach trees

Time sampled	Copper concentration (mg/kg wet mass)			
	Sprayed trees		Unsprayed trees	
	Mean**	Range	Mean**	Range
Before spraying	0.76	0.65-0.82	0.88	0.82-1.08
1 h*	23.10	20.54-26.87	0.85	0.67-1.01
1 day*	20.99	18.80-22.77	0.89	0.85-0.92
3 days*	18.16	15.50-22.20	0.93	0.82-1.01
7 days*	13.82	6.70-17.59	0.78	0.69-0.88
14 days*	7.95	4.85-12.83	0.82	0.81-0.84

* After spraying
** Mean of 3 samples of 10 peaches, each taken from one tree.

Mean copper concentrations above or near the maximum residue limit were found in peaches collected at 1 h and 1 and 3 days after fungicide treatment of the trees, but marked declines of residue content occurred at 7 and 14 days (Table 2). These decreases could be partly due to the dilution effect of increase in fruit size. It is also possible that the 4 mm rain that fell on Day 11 could have removed some residues; however, deposits of fungicide were still clearly visible on the fruits collected on Day 14.

Residues of copper found in peaches from unsprayed trees (Table 2) were not much lower than the mean level found in peaches from market samples (Table 1)

TABLE 3. Copper in samples of green beans from fungicide-treated and untreated plants

Time sampled	Copper concentration (mg/kg wet mass)			
	Sprayed plants		Unsprayed plants	
	Mean**	Range	Mean**	Range
Before spraying	0.81	0.76-0.89	0.70	0.66-0.72
1 h *	22.91	21.60-23.94	0.79	0.72-0.87
1 day*	20.40	18.90-21.90	0.79	0.66-0.90
3 days*	22.28	21.20-23.35	0.63	0.50-0.84
6 days*	21.88	20.25-23.28	0.49	0.41-0.59

* After spraying

** Mean of 3 samples of about 200 g each per time sampled.

Spraying of bean plants with fungicide led to copper concentrations in the pods that were higher than the maximum residue limit (20 mg/kg), and the copper content persisted at approximately the same level for at least 6 days (Table 3). Since the minimum time allowed between application of copper oxychloride and harvest of beans is only 3 days, it is difficult to explain why copper residues in market samples of beans were not much higher than those actually found (Table 1). The mean copper concentration in beans in Table 1 was, however, somewhat higher than copper levels found in beans from unsprayed plants in Table 3.

From the studies reported here it is evident that spraying of peach trees and bean plants with a fungicide could cause levels of over 20 mg/kg copper in the crop. Yet such levels were not found in any market samples of these and various other fruit and vegetable crops analysed. In fact, most of the market samples contained copper levels that were probably not very different from the normally occuring levels of copper as trace element.

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