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Food Chemistry 71 (2000) 423–433

Food Chemistry

www.elsevier.com/locate/foodchem

Trace elements in Australian orange juice and other products

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Received 29 February 2000; accepted 17 May 2000

Abstract

The concentrations of 22 trace elements have been determined in 482 samples of Australian and Brazilian orange juices and Australian peel extracts and deacidified juices using inductively coupled plasma–atomic emission spectrometry and inductively coupled plasma–mass spectrometry. Means and ranges of elements have been established over a five year survey. Regional differences were apparent for the levels of one or more trace elements in the juices of Australian origin. These could be related to differences in soil and rootstock. Multivariate analysis of trace elements in Australian and Brazilian juices showed a clear differentiation between them. Peel extracts were also differentiated from Australian and Brazilian juices.

Keywords: Trace elements; ICP; Multivariate analysis; Orange juice; Orange peel extract

1. Introduction

Nutritional and trace element levels in orange juice have been used to monitor quality, authenticity and country of origin (McHard, Foulk & Winefordner, 1979; McHard, Winefordner & Attaway, 1976; McHard, Winefordner & Ting, 1976; Nagy, 1977; Nikdel & Carter, 1986; Nikdel, Nagy & Attaway, 1988). A relationship between elemental concentration and production region was first reported by McHard who noted variations in barium levels in juices from several different countries. Subsequently, using pattern-recognition, target elements such as boron, gadolinium, manganese and rubidium were identified, in addition to barium, as discriminators of geographic origin (Bayer, McHard & Winefordner, 1980). Early investigations used atomic absorption to determine elemental concentrations. The introduction of inductively-coupled plasma–atomic emission spectrometry and inductively-coupled plasma–mass spectrometry (ICP–AES and ICP–MS) allowed a wider range of elements to be analysed economically. Using this larger number of trace and "ultra-trace" elements in juice, and commercially-available chemometric software packages, investigators have been able to further identify geographic origin and detect pulpwash addition to juice (McHard, Foulk, Jorgensen, Bayer & Winefordner, 1980; Nikdel, 1986, 1995; Nikdel & Attaway, 1987, Martin, Fournier, Allain, Mauras & Aguile, 1997). It has been reported that different species of citrus have individual profiles (Nikdel & Barros, 1984), making trace elements potentially useful for controlling citrus products for truth-in-labelling.

In the Australian context, areas of potential adulteration include substitution of orange juice with orange peel extract, labelling of juice as locally grown when in fact it contains a portion of imported product, and substitution of orange juice with juice from other fruits. This paper reports on the results of a survey of trace elements in Australian and Brazilian orange juices and related products such as Australian peel extracts and deacidified concentrates. These have been used to establish a database of authentic values to use in authenticity testing.

2. Materials and methods

2.1. Nature of the orange juice samples

The Australian fresh orange juice survey covered two programs during the years 1992 to 1997. Sampling was

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0308-8146/00/$ - see front matter
PII: S0308-8146(00)00150-3

conducted by Department of Agriculture field inspectors who collected batches of whole fruit weighing approximately 5 kg. Samples were taken between 1992 and 1997 from all of the Australian growing regions except the Northern Territory. Sampling locations included New South Wales Riverina (MIA: Stanbridge, Hillston, Lake Wyangang, Tharbogang, Leeton, Griffith, Beelbangera, Yanco and Hanwood), Victorian Sunraysia region (SUN: Curlwaa, Dareton, Mildura, Redcliffs, Irymple and Monak), South Australian Riverland (SA: Cooltong, Paringa, Renmark, Berri, Loxton, Waikerie, Ramco and Cadell), Western Australia (WA: Gin Gin and Chittering) and Queensland Burnett region (QLD: Mundubberah, Gayndah). Samples from New South Wales Coastal regions (COAST: Gosford, Macleay Valley and Clarence River area) were gathered by the principal author. Fig. 1 shows the location of these production areas. Fruit was taken from trees which had been vegetatively propagated by grafting or budding Navel or Valencia varieties onto rootstocks such as Trifoliata (*Poncirus trifoliata* (L.) Raf.), Troyer and Carizzo citrange (*C. sinensis x P. trifoliata*), sweet orange (*Citrus sinensis* (L.) Osbeck), Cleopatra mandarin (*Citrus reticulata* Blanco), citrumelo (*C. paradisi x P. trifoliata*) and rough lemon. The main rootstocks for the RIV region were sweet orange and rough lemon, because of their tolerance to chloride and the alkalinity of highly calcareous soils there, whilst the trifoliata and citrange varieties predominated in other regions because of their tolerance to heavier soils and better resistance to root rot.

The fresh orange samples were shipped to the laboratory and squeezed within four days of picking. Juice was extracted with a domestic reamer (either hand or electrical), strained to remove seeds and stored in labelled 2 l polyethylene bottles in a freezer at −20°C until analysis. The Australian concentrates (prime orange juice concentrates and water-soluble peel extracts) were sampled during the early part of the program (1992–1994) from regional processing plants. Concentrated juice samples were produced on falling film evaporators such as APV, Wigand or Alfa-Laval types. Generally, Navel concentrates were produced at around 57°Brix, whilst Valencia concentrates were produced at around 63°Brix, because of their lower pectin contents. Peel extracts were made from the waste products of the same fruit used to make the concentrated juices. They were produced from pectinase-degraded orange peels. These had been subjected to enzyme hydrolysis, centrifugation, resin-adsorption using cross-linked styrene-divinylbenzene copolymeric beads to remove bitter ingredients, and then evaporatively concentrated in a similar manner to the juices. Deacidified juices were prepared by using ion-exchange to remove citric acid. The Brazilian samples of juice were supplied as concentrates by Schutzgemeinschaft fur der Fruchtsaft-Industrie (SGF). The concentrated juices and peel extracts were all supplied as finished products and stored in a frozen state at −20°C after receipt until analysis.

Fig. 1. Principal orange growing areas in Australia. 1 = Riverina-Murrumbidgee Irrigation Area (MIA); 2 = Sunraysia (SUN); 3 = Riverland (RIV); 4 = Chittering River (WA); 5 = Burnett District (QLD); 6 = NSW Coastal Areas (COAST).

2.2. Sample preparation

Prior to analysis, samples were brought to room temperature and thoroughly mixed. Concentrates were reconstituted to 10° Brix. Fresh juices were tested at their natural Brix. The samples were not centrifuged or filtered, other than to remove large particles of cellular material from fresh juices by passing through a small strainer having a mesh size of 0.5 square millimetres.

Samples were prepared for ICP analysis using a method based on that of Nikdel and Temelli (1987). About 15.00 g of juice were accurately weighed into an acid washed teflon digestion tube (Prolabo Floyd Inc., USA). Redistilled concentrated nitric acid (4 ml) was added, and the tube was heated in a microwave oven (Prolabo Floyd Inc., USA, Model RMS-150) at power setting 50% for 12 min. The process was repeated if the digest was not completely clear. This digest was transferred into a 50 ml acid washed graduated polypropylene tube and made up to 40 ml. One ml of this solution was diluted with deionised water to 10 ml for determination of potassium and the remaining undiluted digest was used to determine other elements. Three water blanks were run with each batch of samples.

2.3. Method of analysis

The orange juices were analysed by inductively coupled plasma–atomic emission spectrometry (Perkin

Table 1
Operating conditions for elements

Element	Symbol	ICP–MS isotope (amu)	ICP–AES spectral line (nm)
Aluminium	Al		396.152
Barium	Ba	137,138	455.4
Boron	B		208.96
Calcium	Ca		422.67
Cobalt	Co	59	
Copper	Cu	63,65	324.75
Iron	Fe		259.94
Lithium	Li	7	
Lutetium	Lu		291.139
Magnesium	Mg		279.08
Manganese	Mn	55	257.61
Molybdenum	Mo	98	
Nickel	Ni	60,62	
Phosphorus	P		178.29
Potassium	K		766.49
Rubidium	Rb	85	
Silicon	Si		251.61
Sodium	Na		589.59
Strontium	Sr		407.77
Tin	Sn	118,120	
Titanium	Ti		336.12
Vanadium	V	51	
Zinc	Zn	66	213.8

Elmer OPTIMA 3100DV) and by inductively coupled plasma–mass spectrometry (Perkin Elmer SCIEX ELAN 5100). ICP–AES was used for aluminium, boron, calcium, iron, magnesium, phosphorus, silicon, sodium, potassium, strontium and titanium and ICP–MS was used for other elements. All elements showing high concentrations by ICP–MS were confirmed by ICP–AES. Where possible, two isotopes were used for ICP–MS and if the results were different, the lower result was reported. Instrument operating conditions and measurement parameters are listed in Tables 1 and 2.

2.4. Standard preparation

Mixed (multi-element) working standard solutions were made from stock solutions (1000 mg/l) supplied by Plasma Chem Corp, USA. Three concentrations covering the range of metal concentrations in the orange juice digest were prepared for ICP–MS (at μg/L levels) and for ICP–AES (at mg/l levels).

2.5. Internal standards

Internal standards were prepared as follows: for ICP–AES a lutetium stock solution (1000 mg/l) was made from lutetium oxide (99.99%, supplied by Aldrich Chem. Co.) dissolved in 4% hydrochloric acid. An appropriate volume of this stock solution was dispensed into standard and sample solutions using a micropipette, so that all contained 2 mg/l of lutetium. For ICP–MS, an indium stock solution (1000 mg/l) was made from indium (supplied by Johnson Matthey, Australia) dissolved in 4% nitric acid. An appropriate volume of this stock solution was dispensed into standard and sample solutions using a micropipette, so that all contained 5 mg/l of indium.

2.6. Calculations

The final results were calculated by using a spreadsheet containing a macro to perform blank correction, matrix effect correction, and results comparison

Table 2
Manual settings for spectrometers

Settings	ICP–MS	ICP–AES
Argon plasma/coolant gas flow (l/min)	15	15
Argon nebulizer gas flow (l/min)	0.8–1.0	0.8
Argon auxiliary flow (l/min)	1.0	1.0
Power (kW)	1.0	1.2
RF power (kW)	< 5	< 5
Sample uptake rate (ml/min)	0.8	1.0
Spray chamber	Cyclonic	Cyclonic
Nebuliser type	Meinhard	Meinhard
Dwell time (ms)	100	
Replicates	3	

between different isotopes or instruments. The final averaged results were reported in mg/kg.

2.7. Uncertainty

A number of analytical quality control procedures were put into place to reduce uncertainty. Internal standards were used to compensate for possible variations in instrument performance during the determination. External standards used for calibration were regularly reinjected after every ten samples to monitor possible shift of initial calibration. The protocol for conducting analyses of batches of up to ten samples involved an instrument calibration using one blank and three standard solutions, followed by analysis of independant check standard solutions, sample blanks, blank spikes and finally the samples themselves. At the end of the analysis sequence, at least two standards, sample blanks and blank spikes, were then run again. A dilute nitric acid wash was carried out for a 30 s period between samples. Some elements, such as aluminium, boron, barium, copper, strontium, titanium, and zinc, were analysed by both ICP–AES and ICP–MS. Ten percent of samples were analysed in duplicate. One or two orange juices in each batch were spiked with mixed elements at above 50% of their natural concentration.

The uncertainty of estimates, based on recovery data and duplicate analyses, varied by ± 10% for the major elements, such as potassium, calcium and magnesium, and up to ± 20% for minor elements, such as sodium, iron and aluminium. The limits of detection for those elements which were not detected are set out in the tables of results.

3. Results and discussion

3.1. Summary of results for each element

The elemental concentrations of the samples of fresh and concentrated juices and peel extracts tested in this survey are summarized in Tables 3–5. Results (mg/kg) are presented as mean or average (Avg), standard deviation (Std Dev), minimum (min) and maximum (max) values for each of the categories tested. The data for fresh juices are given on an "As Squeezed" basis. Australian oranges are currently processed almost exclusively for fresh juice production, and for this purpose must not be diluted other than by blending with other fresh orange juices. The values for concentrates (also in mg/kg) are reported after their reconstitution to 10°Brix (the industry-accepted minimum strength for reconstituted juices) using distilled water.

3.2. Regional differences within Australia

Out of the 23 elements that were determined in Australian juices, seven varied significantly between regions. These were sodium (higher in some of the Riverland samples), rubidium and cobalt (higher in some WA samples), calcium and boron (higher in MIA and RIV samples), potassium (somewhat lower in the Riverland

Table 3
Elemental composition of fresh Australian juices at natural Brix (mg kg^{-1})

	Navel (90 samples)				Valencia (200 samples)			
Element	Avg	Std Dev	Min	Max	Avg	Std Dev	Min	Max
Aluminium	0.09	0.09	0.001	0.55	0.15	0.16	0.001	0.97
Barium	0.16	0.07	0.007	0.41	0.15	0.08	0.01	0.44
Boron	1.5	0.37	0.75	2.91	1.39	0.35	0.57	2.37
Calcium	80.3	22.5	35	131	82.8	21.4	46.1	160
Cobalt	0.003	0.003	< 0.001	0.02	0.003	0.002	< 0.001	0.015
Copper	0.36	0.2	0.04	0.9	0.35	0.12	0.06	0.84
Iron	0.61	0.21	0.02	1.5	0.72	0.27	0.32	1.8
Lithium	0.004	0.002	< 0.002	0.034	0.003	0.004	< 0.002	0.041
Magnesium	114.1	15.6	82	145	106.6	17.4	55.1	170
Manganese	0.19	0.06	0.1	0.44	0.22	0.07	0.11	0.47
Molybdenum	0.003	0.003	< 0.001	0.01	0.003	0.004	< 0.001	0.026
Phosphorus	179	28.3	110	270	183	27.3	78	266
Nickel	0.03	0.09	< 0.001	0.18	0.03	0.02	0.004	0.16
Potassium	1696	269	930	2320	1676	293	777	2345
Rubidium	0.91	0.99	0.18	5.24	0.96	1.37	0.15	11
Silicon	0.54	0.34	< 0.1	1.68	0.88	0.53	< 0.001	4.53
Sodium	9.4	11.1	1.4	71	8.69	10.09	0.58	66
Strontium	0.63	0.32	0.07	1.47	0.71	0.38	0.07	2.6
Tin	0.002	0.001	< 0.001	0.14	0.002	0.001	< 0.001	0.004
Titanium	0.005	0.005	< 0.001	0.02	0.01	0.01	< 0.001	0.004
Vanadium	0.001	0.001	< 0.001	0.01	0.001	0.001	< 0.001	0.006
Zinc	0.34	0.1	0.21	0.68	0.33	0.11	0.12	0.67

Table 4
Elemental composition of orange juice concentrates reconstituted to 10° Brix (mg kg^{-1})

	Australian prime concentrate (83 samples)				Brazilian concentrate (42 samples)			
Element	Avg	Std Dev	Min	Max	Avg	Std Dev	Min	Max
Aluminium	0.13	0.1	0.01	0.49	0.13	0.1	0.03	0.4
Barium	0.12	0.03	0.08	0.33	0.34	0.18	0.08	0.78
Boron	1.14	0.2	0.3	1.7	0.56	0.18	0.28	0.95
Calcium	79	16.7	37.8	125	67.8	10.1	51.7	100
Cobalt	0.002	0.001	< 0.001	0.004	.001	0.001	< 0.001	0.006
Copper	0.29	0.05	0.131	0.51	0.24	0.04	0.16	0.33
Iron	0.75	0.25	0.33	1.51	0.61	0.11	0.3	0.95
Lithium	0.002	0.001	< 0.002	0.006	0.001	< 0.001	< 0.002	0.004
Magnesium	97.8	16.9	41.1	153	96.2	8.9	84	120
Manganese	0.19	0.03	0.13	0.29	0.26	0.07	0.14	0.5
Molybdenum	0.003	0.003	< 0.001	0.007	0.001	0.002	< 0.001	0.007
Nickel	0.04	0.02	0.008	0.033	0.01	0.01	0.003	0.035
Phosphorus	165	33.7	98.1	242	149	13.7	119	190
Potassium	1645	254	1061	2250	1626	144	1350	2030
Rubidium	0.56	0.23	0.24	1.01	2.05	0.5	0.9	3.1
Silicon	1.17	0.81	0.339	6.11	1.93	1.98	0.585	8.27
Sodium	17.7	14.7	3.5	94.7	2.8	3	0.4	13.4
Strontium	0.65	0.19	0.358	1.45	0.42	0.17	0.192	1
Tin	0.002	0.001	< 0.001	< 0.001	0.004	0.003	< 0.001	0.037
Titanium	0.001	0.001	< 0.001	0.012	0.003	< 0.001	< 0.001	0.007
Vanadium	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zinc	0.25	0.06	0.12	0.38	0.27	0.07	0.14	0.38

samples), and strontium (lower in WA than other regions). Smaller regional differences were evident in the average and spread of results in other elements as well. Fig. 2 shows a comparison of each of the trace elements in Australian juices from each of the regions, as well as reconstituted Australian prime concentrates and reconstituted Brazilian concentrates. The spread of results for the fresh Australian juices is noticeably wider than for

Table 5
Elemental composition of other samples reconstituted to 10 °Brix (mg kg $^{-1}$)

	Australian peel extract (49 samples)				Deacidified concentrate (18 samples)			
Element	Avg	Std Dev	Min	Max	Avg	Std Dev	Min	Max
Aluminium	0.38	0.48	0.06	2.77	0.12	0.11	0.018	0.41
Barium	0.6	0.21	0.11	1.1	0.13	0.04	0.06	0.2
Boron	1.88	0.49	0.96	2.87	0.41	0.22	0.18	1.18
Calcium	302	101.7	84.9	510	87.6	18.4	55.8	130
Cobalt	0.002	0.001	< 0.001	0.005	0.002	0.001	< 0.001	0.003
Copper	0.38	0.17	0.18	1.22	0.28	0.05	0.18	0.4
Iron	1.53	1.1	0.63	8.35	0.36	0.24	0.03	1.14
Lithium	0.008	0.004	< 0.002	0.017	0.002	0.001	< 0.002	0.005
Magnesium	97.3	20.1	36.2	144	98.8	9.4	73.9	119
Manganese	0.39	0.12	0.16	0.81	0.14	0.01	0.13	0.15
Molybdenum	0.003	0.003	< 0.001	0.02	0.001	0.001	< 0.001	0.002
Nickel	0.07	0.03	0.03	0.15	0.05	0.01	0.03	0.07
Phosphorus	138	29.3	92.2	208	138	24.7	86.6	194
Potassium	1348	237	703	1991	2017	233	1390	2390
Rubidium	0.53	0.21	0.17	0.95	0.85	0.11	0.6	1.01
Silicon	3.9	1.79	0.68	8.76	1.38	0.32	0.78	2.16
Sodium	153	79	7.4	381	94.8	41.8	8.9	180
Strontium	3.72	1.69	0.48	7.03	0.58	0.1	0.36	0.73
Tin	0.001	0.001	< 0.001	0.007	0.002	0.001	< 0.001	0.012
Titanium	0.03	0.09	< 0.001	0.349	< 0.001	< 0.001	< 0.001	0.003
Vanadium	0.001	0.001	< 0.001	0.007	0.001	0.001	< 0.001	0.002
Zinc	0.29	0.1	0.15	0.74	0.18	0.06	0.12	0.35

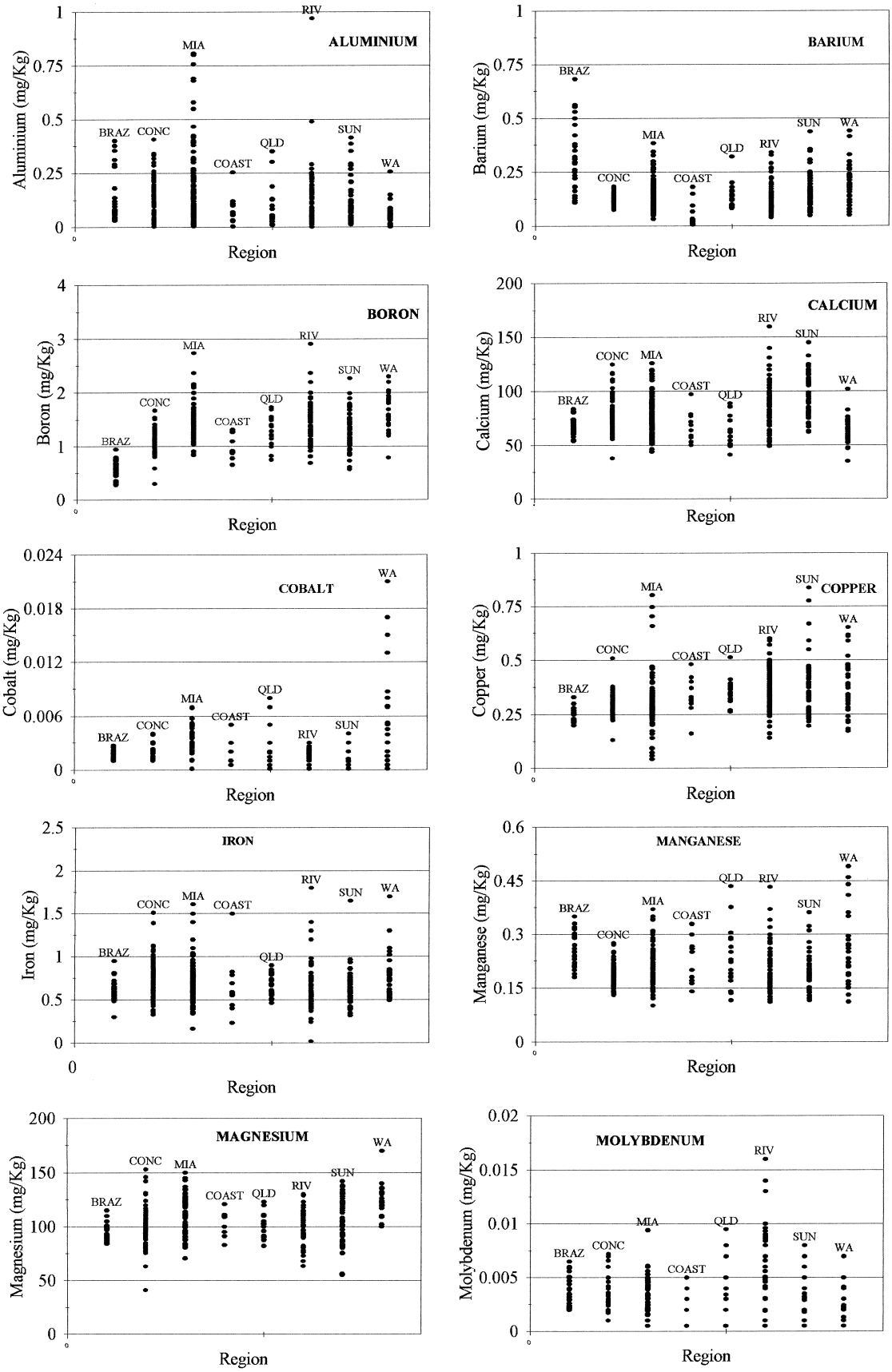

Fig. 2. Distributions of trace elements in reconstituted juice concentrates from Brazil (BRAZ), Australia (CONC) and fresh juices squeezed from oranges from different Australian regions (see Fig. 1 for codes) *(continued on next page)*.

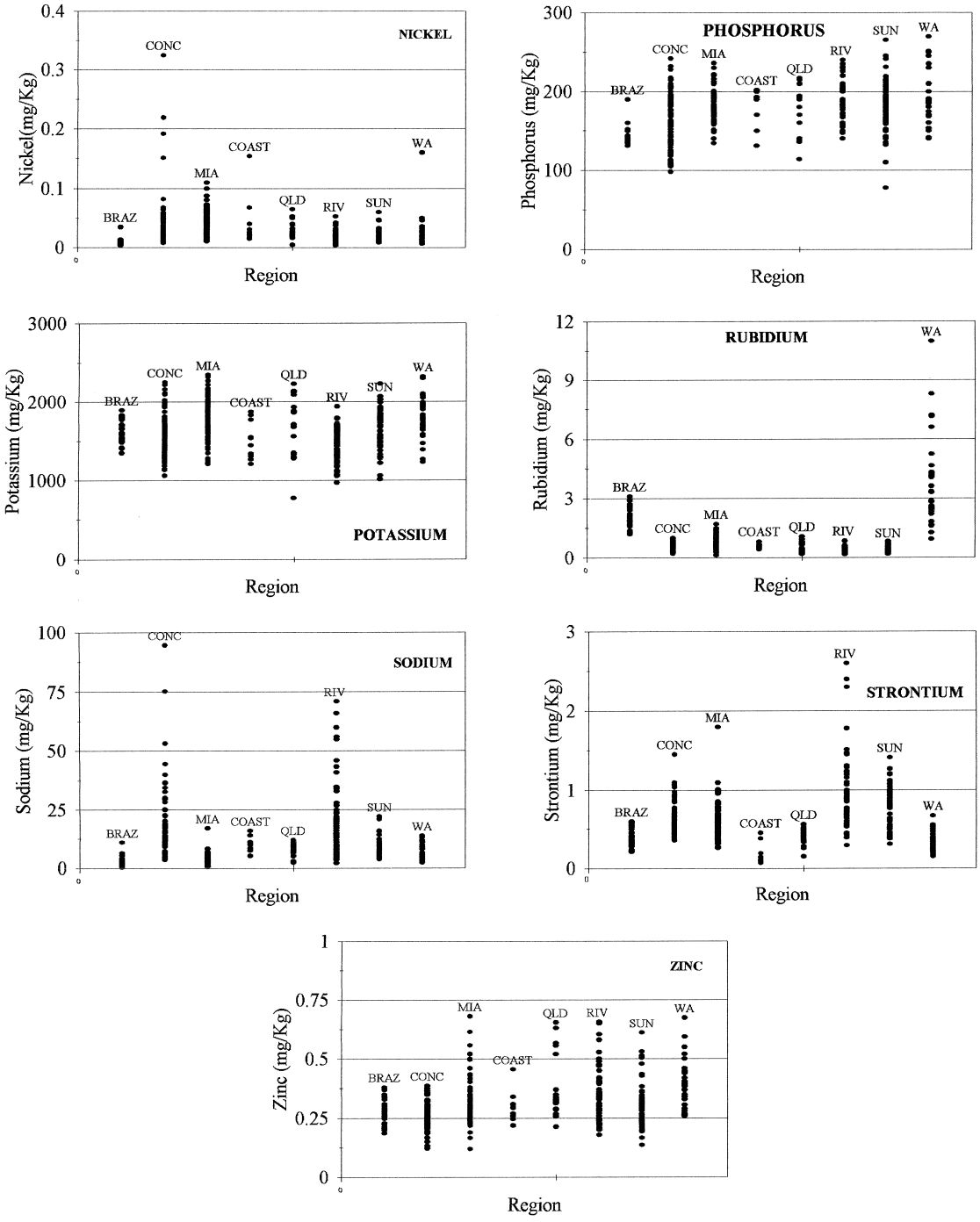

Fig. 2. *(continued)*

the concentrates, most likely because of the relatively small samples sizes (~5 kg) used in their preparation. The concentrates generally came from an intermixture of juices from several tonnes of fruit.

A search of the available literature indicates that there may be several factors which contribute to these regional variations in trace element levels. First and foremost, amongst these, is the availability of the element for uptake by the plant. Availability depends on the soil's cation exchange capacity which can vary considerably between soil types, depending on pH and the mineral composition. There are also other factors, such as fertilizer application, irrigation water, mycorrhizal fungi in the root zone and even rootstock variety (Chapman, 1968) which are also known to contribute to trace element differences in plants. In Australia, citrus fruits are grown on soils with divergent chemical qualities. Relating citrus districts to Prescott's Soil Map of Australia (Prescott, 1931; Bettenay, 1983) and more recent treatises on soil composition, it can be seen that

several Great Soil groups and many soil types are encountered. On the one hand, citrus fruit is grown in the acid podzolic soils of the humid coastal districts and, on the other, in the neutral to alkaline soils of the Mallee, as well as in the soils of the red Brown Earth group, which are neutral to slightly acid (Bettenay, 1983; Bowman, 1956). Of course these soil classifications can only be general and, within quite small areas, a range of soil sub-types is likely to be used in agriculture. Citrus fruit has a preference for sands and sandy loams which enable good moisture penetration and drainage and have a pH between 5 and 8.

Most of the regional differences that we found could be linked to underlying differences in soil type. The high sodium levels found in many of the RIV samples are due to the well documented increase in salinity in Murray River water as it progresses downstream, accumulating run-off from the irrigation areas where it is extensively used (Gutteridge, Hoskins & Davey, 1970). The highest sodium value came from the Waikerie area, and is typical of many of the Mallee soils. These soils are mostly deep loose-drift sands of varying depths, overlying limestone marl subsoils which are impermeable and prevent excess irrigation water from draining away. The often shallow water table, containing dissolved salts laid down from the late Ternary and Quaternary period, when the Mallee area was a sea-bed, has the tendency to rise up into the root zone. Indeed, salination is a problem of major concern to many inland areas of Australia.

The calcium levels in RIV, SUN and MIA samples were higher than in other regions. This may be linked to the abundant limestone subsoils in these areas.

Boron is also concentrated in marine evaporites and sediments. The MIA and RIV samples contained more boron than other regions, although there was no marked correlation with sodium. Elevated boron levels are also a characteristic of many Australian soils, and toxicity associated with shallow water tables is a problem for agriculturalists in many inland areas of South Australia (Cartwright, Zarcinas & Mayfield, 1984).

The rubidium levels were highest in a large number of the WA samples. The rubidium content of soils is largely inherited from parent rocks, as indicated by soils over granites (Kabata-Pendias & Pendias, 1984). Many farmers in the WA region have chosen soils on some of the basic dykes that cut through granite.

The potassium levels of fruit from RIV were lower than in all of the other regions. This might be a result of orchards having been planted on highly leached sandy loams, although it would be expected that, if this were the case, farmers would make up for any potassium deficit with the application of fertilizer. It appears more likely that rootstock may have an important influence on potassium levels. Rough lemon and sweet orange rootstock are predominantly grown in the South Australian region vs. mostly trifoliata in the rest of Australia. An association between potassium levels and rootstock variety has long been known (Haas, 1948).

3.3. Brazilian concentrates

Australian and Brazilian concentrates differ considerably in the levels of several trace elements. This can be seen from a visual inspection of the data in Fig. 2. These differences are sufficiently large to allow multivariate analysis to distinguish between countries of origin. Principal components analysis (PCA) of the results for these two regions, after auto-scaling to preprocess the data, was able to clearly separate them into two distinct clusters (see Fig. 3) within the first two principal components. The contribution of each element can be seen in the loadings plot (see Fig. 4), with rubidium, barium and boron making the strongest contribution to the first two factors.

3.4. Peel extracts

In addition to high calcium, which is well-known to concentrate in citrus peel, we found that the peel extracts contained, on average, more copper, iron,

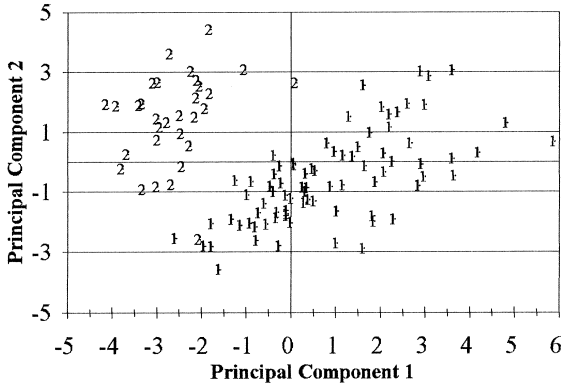

Fig. 3. Scores for principal components analysis of trace elements in reconstituted (1) Australian and (2) Brazilian juices.

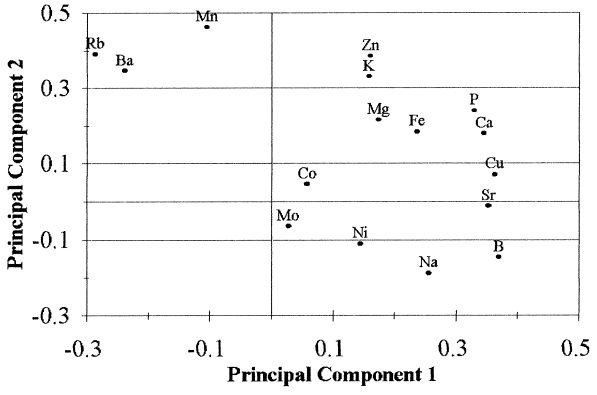

Fig. 4. Loadings for trace elements used in PCA of Australian and Brazilian reconstituted juices.

manganese, sodium, nickel, silicon, strontium and boron, and less potassium and phosphorus than the juice from the same batches of fruit (both reconstituted to same °Brix). PCA of the data for peel extract, after auto-scaling, showed that it clearly differed from that of Australian and Brazilian concentrates, except for two samples of reconstituted Navel juice, which just overlapped the distribution for the peel extracts. Navel peels can sometimes partially disintegrate during juice extraction. In such cases, some peel water could contaminate the juice. If this had happened during the preparation of these juices, it would explain their similarity to peel extract. The scores plot of the PCA of peel and prime concentrates is shown in Fig. 5. Here, the best visual separation can be seen in the second and third components. The loadings plot (see Fig. 6) shows that rubidium, barium, sodium, calcium, strontium and boron make the strongest contribution to the factors.

3.5. Deacidified juices

The deacidified juices were prepared commercially from the same bulk juices as the concentrates in this survey. A comparison of trace elements shows that sodium levels have increased fivefold, presumably because of residual sodium in the ion-exchange resin used in deacidification and the transition elements manganese, iron, cobalt, nickel, copper and zinc decreased by about 10%, perhaps as a result of chelation with organic acids such as citrate and pectate which adhere to the resin. Boron and molybdenum both decreased markedly. Since these exist as borate and molybdate they are adsorbable by anion-exchange resins.

3.6. Commercial juices

All concentrates in the database were reconstituted in the laboratory using deionised water which was metal-free. However, commercial juices based on reconstituted concentrates may contain some elements from the tap-water used in their manufacture. Commonly these include aluminium, calcium, strontium, copper, iron, magnesium, sodium and silicon.

3.7. Other citrus types

A limited survey was carried out to compare other types of citrus juice and peel to orange. The samples (mandarin, lemon, grapefruit, lime, tangello, Seville orange, pummelo) were purchased from local green-groceries. Juices were expressed on a hand-reamer. The flavedo was thinly removed with a vegetable peeler, and the remaining albedo was comminuted in a food processor with about twice its weight of water. The pectolytic enzyme Pectinex Ultra (Novo Nordisk) was added, and the slurry was maintained at about 45°C for 24 h. The remaining solid portion was then removed by filtering the liquid portion through a fine cloth. The °Brix of these peel extracts were all around 3–4. Analytical procedures were the same as for orange juice. Results for all the peel extracts have been normalised to 10 °Brix.

Results are set out in Tables 6 and 7. The profiles of other citrus juices and peel extracts appear to be similar to the corresponding orange juice component.

3.8. Adulteration detection

Most economic adulterations of Australian juices are likely to involve their intermixture with small to intermediate amounts of peel extract or imported juice. The trace element profile of the adulterated juice may then become sufficiently skewed to allow easy identification of the extender. In some cases, adulteration may be evident from other markers. Phlorin for example is strongly concentrated in the peel (Johnson, Htoon & Shaw, 1995). In other cases, however, detection of adulterants will require multivariate statistical analysis. A thorough investigation of these issues is currently being conducted and will be reported upon completion.

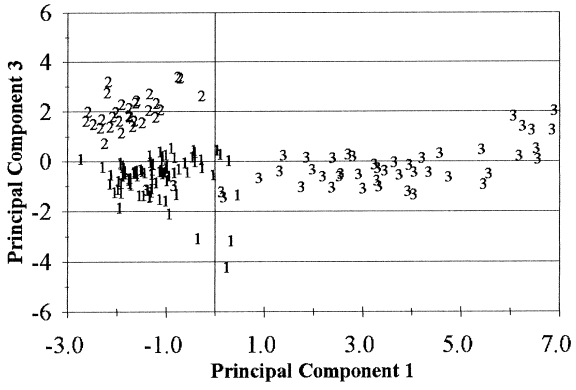

Fig. 5. Scores for principal components analysis of trace elements in (1) Australian (2) Brazilian reconstituted juices and (3) Australian peel extract.

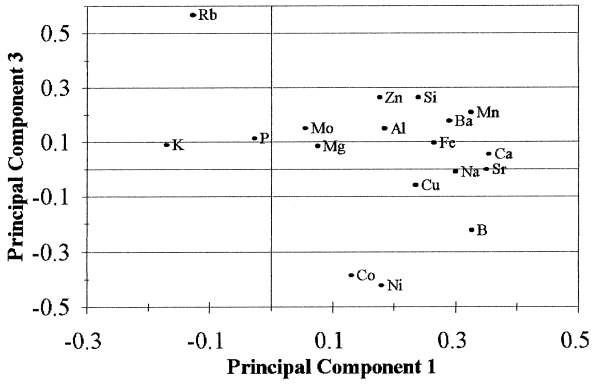

Fig. 6. Loadings for trace elements used in PCA of Australian and Brazilian reconstituted juices and Australian peel extract.

Table 6
Elemental composition of juice from other citrus types at natural °Brix (mg kg^{-1})

Element	Mandarin	Lemon	Grapefruit	Lime	Tangello	Seville orange	Pummelo
Aluminium	0.42	0.01	0.02	0.05	0.03	0.26	0.07
Barium	0.02	0.19	0.01	0.23	0.26	0.21	0.03
Boron	0.32	1.67	0.7	0.5	1.33	1.07	0.65
Calcium	79.3	116	57.2	58.2	129	108	104
Cobalt	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001
Copper	1.37	0.22	0.37	0.26	0.19	0.3	0.19
Iron	0.98	0.98	0.69	0.46	0.63	0.71	0.76
Lithium	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Magnesium	122	114	86.6	67.1	104	87.1	75
Manganese	0.34	0.23	0.17	0.34	0.18	0.13	0.08
Molybdenum	< 0.001	< 0.001	0.01	0.01	< 0.001	< 0.001	0.01
Nickel	0.08	0.01	0.02	0.03	0.03	0.02	0.01
Potassium	2290	1450	1370	1370	1670	1470	1560
Phosphorus	181	191	182	150	173	133	185
Rubidium	0.71	0.68	0.21	1.65	0.37	0.28	2.37
Silicon	1.2	< 0.1	0.8	< 0.1	< 0.1	0.8	0.8
Sodium	10	18.2	11.8	4.2	18.4	10.4	4.2
Strontium	0.11	0.35	0.04	0.16	1.55	0.96	0.06
Tin	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Titanium	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Vanadium	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zinc	0.47	0.48	0.54	0.59	0.38	0.82	0.46

4. Conclusions

This investigation into the trace element profiles of Australian and Brazilian orange juices and Australian peel extracts and deacidified juices has established the mean and ranges of twenty two elements in 482 samples. Regional differences were apparent in orange juices sampled from different growing regions within Australia. These could be linked to elemental differences in the soil where the fruit was grown and also to different types of rootstock. Multivariate analysis of trace elements in Australian and Brazilian reconstituted concentrates showed a clear differentiation. Peel extracts were also differentiated from Australian and Brazilian juices.

Table 7
Elemental composition of peel extract from other citrus types normalised to 10°Brix (mg kg^{-1})

	Mandarin	Lemon	Grapefruit	Lime	Tangello	Seville	Pummelo
Aluminium	0.2	0.09	0.1	0.19	0.07	0.12	0.09
Barium	3.28	1.15	0.57	4.41	1.41	1.2	0.15
Boron	3.56	2.1	2.34	2.88	2.74	2.67	2.26
Calcium	659	507	305	546	450	402	402
Cobalt	0.003	0.005	0.003	0.006	< 0.001	< 0.001	< 0.001
Copper	0.96	0.57	0.38	5.06	0.49	2.78	1.64
Iron	1.02	0.55	0.62	3.16	0.86	1.19	0.45
Lithium	< 0.002	< 0.002	0.01	0.01	0.01	0.01	< 0.002
Magnesium	144	38.3	71.0	98.4	81.2	100	116
Manganese	0.33	0.69	0.25	2.14	0.28	0.26	0.13
Molybdenum	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Nickel	0.2	0.13	0.4	0.18	0.05	0.04	0.05
Phosphorus	71.6	48.1	98.7	88.4	65.9	57.2	61.1
Potassium	1509	773	1410	1097	624	783	1151
Rubidium	0.33	0.34	0.41	1.35	0.16	0.15	1.84
Silicon	2.19	1.43	2.05	1.25	0.48	0.87	0.57
Sodium	136	65.4	18.2	180	102	46.5	50.3
Strontium	8.25	5.74	5.46	3.81	9.43	8.41	0.68
Tin	< 0.001	< 0.001	< 0.001	0.16	0.02	0.04	0.03
Titanium	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.0010
Vanadium	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zinc	1.90	0.88	1.13	1.19	0.42	0.28	0.23

Acknowledgements

The authors wish to thank Dr. Seif Nikdel of Florida Department of Citrus for advice on methodology during the inception of this survey. Financial assistance for funding to carry out the project was provided by the Australian Citrus Industry Council, The Horticultural Research and Development Corporation and the Australian Government Analytical Laboratory's Public Interest Program.

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