

Elemental concentration in fruits and leaves of chicku and mango under natural environmental conditions

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Abstract. A knowledge of the distribution patterns of stable elements in the environment is an essential pre-requisite for understanding the problems of radioactive pollution. In this paper the data obtained under natural conditions of the environment in the case of potassium, calcium, magnesium, iron, copper, zinc, cobalt, manganese, strontium, lithium and uranium are presented. A method for elimination of the interference from phosphate in the estimation of calcium and strontium in plant materials is also described.

Keywords. Elements; atomic absorption spectrophotometry; soil-plant relationship; concentration; discrimination.

1. Introduction

The increasing use of nuclear fission in power production calls for an assessment of potential environmental contamination (Unsear 1972) and in the eventual distribution of radionuclides along food chains in natural environmental systems and the potentialities for transfer of radionuclides from one system to another through food chains.

Soil, which is the direct mineral substrate for terrestrial plants, is an extremely heterogeneous medium, varying in important chemical, physical and biological properties from place to place, depending on parent material, climate, topography, age and biological factors. Many factors operate or restrict the availability of elements to plants. Changes may be effected directly by the root system altering the pH or oxidation-reduction potential of the soil immediately adjacent to it or indirectly by microflora associated with the root system (Bowen 1966; Thompson and Troech 1973; Brady 1974).

Soil biology or plant growth has not been affected to any significant extent by fallout because of the addition of far too little radioactivity. The behaviour of radioactive elements in the soil-plant system may be expected to be similar to that of stable nuclides of the same elements except for the fact that radioactive elements decay with time. Thus a knowledge of the distribution patterns of the stable elements may be helpful for a deeper understanding of radioactive pollution.

Much of the data on the uptake and concentration/discrimination of elements from the soil have been derived from green house experiments which are carried out under controlled conditions. The data presented in this paper were obtained under undisturbed conditions of the environment. The elements studied include potassium, calcium, magnesium, iron, copper, zinc, cobalt, manganese, strontium, lithium and uranium. A method for the elimination of the interference from phosphate in the estimation of calcium and strontium through atomic absorption spectrophotometry in plant materials is also described.

Seasonal fruits like chicku (*Achras sapota*) and mango (*Mangifera indica*) grow in abundance at Trombay (19° 02' N, 72° 53' E). The area selected for this study does not bear an impression of any recent mechanical disturbance. The uptake of elements by plants from soil is difficult to assess unless the samples are collected from the same place. The elements mentioned above were determined in leaves and fruits of chicku and mango trees and also the soil in which these trees have grown.

Most of the elements chosen in this study have comparatively long-lived radioisotopes either naturally occurring or produced as a result of activation or fission (table 1). Mg and Cu do not have appreciably long-lived radioisotopes but because of their essentiality to plants they have been included. Very little work has been carried out on the uptake of Li from soil by plants and it is therefore of great scientific interest.

Table 1. Table of long-lived radioisotopes*.

Isotope	Natural abundance percentage	Lifetime
⁴⁰ K	0.0118	1.28 × 10 ⁹ Y
⁴⁵ Ca		165 d
⁵⁴ Mn		303 d
⁵⁵ Fe		2.6 Y
⁵⁹ Fe		45.1 ± 0.5 d
⁵⁷ Co		270 d
⁵⁸ Co		71.3 d
⁶⁰ Co		5.26 ± 0.01 Y
⁶⁵ Zn		243.6 ± 0.1 d
⁸⁹ Sr		52 d
⁹⁰ Sr		28.1 Y
²³⁴ U	0.0054	2.47 × 10 ⁵ Y
²³⁵ U	0.7110	7.1 × 10 ⁸ Y
²³⁸ U	99.2830	4.51 × 10 ⁹ Y

* Weast 1975.

d = days. Y = years.

2. Experimental

2.1. Sample collection and preparation

2.1a. *Leaves*: The leaves were plucked manually, depetiololed and weighed. They were freed of extraneous matter by holding under running tap water first and then rinsing with distilled water. Around 250 g of leaves were taken for each set of experiments (wet weight basis).

2.1b. *Fruits*: After collecting the fruits from the tree, 500–1000 g of the pulp were taken for each set of experiments (wet weight basis). In all nine samples of leaves and fruits each of chicku and mango trees were collected.

2.1c. *Ashing*: An electric muffle furnace was used for this purpose. The temperature was used around 400° C in order to avoid loss of volatile elements like Zn. Unburnt carbon was ashed with conc. HNO₃ until a white residue was obtained. The weight of the acid used was noted in order to apply correction for the blank. The sample ash was dissolved in aqua regia. The insoluble residue, if any, was given HClO₄-HF treatment (Rao and Shah 1971). Aqua regia was evaporated to dryness and HNO₃ was removed by repeated evaporation with HCl. The final solution was diluted to 250 ml and made N/5 with respect to HCl. Aliquots were taken from these.

2.1d. *Soil*: Soil samples were taken around each tree from where the leaves and fruits were collected for analysis. Care was taken to see that no roots accompanied the soil samples. The samples were dried at 105°–110° C and then ground with a pestle and mortar and fractions passing through 100 mesh (US Standard Sieve Series aperture 149 μm) were taken for analysis. They were then heated to 400° C in a muffle furnace to remove organic matter (Rao *et al* 1970).

For the determination of absorbed cations, the choice of extractant must be guided by the required degree of displacement. Various extractants such as 1N ammonium acetate for Cu and Zn (Epstein 1972), 0.05 N HCl for Mg (Hesse 1971), dil CaCl₂ (0.02 M) for plant available Al and Mn (Hoyt and Nyborg 1972), 0.2% hydroquinone in 1N ammonium acetate (pH 7.0) for exchangeable Mn (Safo and Lowe 1973), 0.005 M DTPA, 1M MgCl₂, 0.01 M CaCl₂ to extract Zn (Maclean 1974) have been used by different workers. We have used 0.05 N HCl for extracting elements from the soil and the results are based on this extractant.

25 g of processed soil samples were leached with 2.5 litres of 0.05 N HCl for a period of 16 hr and then filtered through Whatman No. 42 filter paper. The leaching process was repeated thrice. The leachates were then evaporated to dryness and dissolved in HCl. Any insoluble residue formed during evaporation and drying was given HClO₄-HF treatment. The final solution was diluted to 250 ml and made 0.2 N with respect to HCl.

3. Analyses

Except U, all other elements were determined by using a single beam atomic absorption spectrophotometer. Wherever necessary, further dilutions of the sample solutions were made. In the case of Ca and Sr from plants, the samples were freed

of phosphate by a procedure described below. U was determined fluorometrically after initial concentration with ethyl acetate (Sandell 1959).

3.1. Elimination of phosphate interference

An anion exchange technique has been used for elimination of phosphate (Joseph *et al* 1967). This technique is time-consuming and where excessive phosphate is present, very long columns are needed. In the present study it was found that if citrate is used as a complexing agent, then Ca and Sr can be precipitated as oxalate in the presence of phosphate. 5 ml of sample solution was taken. The pH was adjusted to 4 by adding 1:4 ammonium hydroxide (methyl orange indicator test) followed by 5 ml of 3 N citric acid and heated to 80° C. Excess of saturated solution of oxalic acid was added (the quantity depending on the amount of Ca present but roughly about 10 ml) to precipitate Ca and Sr as oxalates. The oxalate precipitates were allowed to settle overnight and then centrifuged. The precipitate was dissolved in minimum quantity of HCl and the pH was adjusted to 4. Ca and Sr were then reprecipitated as oxalate in the presence of citric acid. After overnight settling, the solution was centrifuged and the oxalates separated were dissolved in minimum quantity of HCl and diluted to 10 ml. This solution is free of phosphate and can be taken for analysis. This method is very simple and can also be used for determination of ⁹⁰Sr in biological samples such as fish where one can expect considerable amount of phosphate which interferes in the estimation.

4. Results and discussion

Tables 2 and 3 give the elemental concentrations in soils, leaves and fruits of chicku and mango plants respectively. Wherever the values followed Gaussian distribution, the mean value is accompanied by standard deviation of the distribution; otherwise, instead of the mean value, the most probable value is mentioned in the tables.

The ratio of ash: dry: wet weights was calculated and given at the bottom of tables 2 and 3 for chicku and mango respectively. It is observed from these tables that the uptake of U by plants analysed is below detectable limits, even though significant amount of U is found in the soil. This is of considerable interest in view of the radioactivity of this element.

Li tolerance of 11 plant species noted by growing plant in soil treated with Li salt has shown (Bigham *et al* 1964) that when the Li content on dry weight basis is less than 5 ppm in the plant tissue analysed, no injury was noticed. On the other hand, the results of a survey of trace elements in 43 citrus groves in Southern California (Sauchelli 1969) showed that Li when present in amounts ranging from 5 to 40 ppm produced visual toxicity symptoms varying from slight to severe. Our results in tables 2 and 3 show that the Li content in fruits varies between 0.04 and 0.06 ppm and in leaves between 0.04 and 1.0 ppm. These figures may be considered quite low compared to the toxicity level. The exact role of Li in plants is yet to be demonstrated.

The uptake of elements from the soil by plants can be better understood if we consider the concentration ratio, *i.e.*,

Table 2. Elemental concentrations in soil, chicku leaf and chicku fruit.

Element	Soil µg/g (dry wt.)		Leaf µg/g (dry wt.)		Fruit µg/g (dry wt.)	
	Range	Average or most probable value (9 samples)	Range	Average or most probable value (9 samples)	Range	Average or most probable value (9 samples)
	K	300-325	313 ± 12	3280-4200	3950	2273-3300
Ca	6000-7000	6000	16000-19270	16600	300-550	500
Mg	2850-4000	3000	4100-5125	4912	515-580	525
Fe	4000-6000	5225	270-400	299	13-16	13
Cu	175-400	205	6-8	7 ± 1	2-3	2.3 ± 0.18
Zn	687-900	723	25-37	27	6-13	7.5
Co	34-36	35 ± 1.2	0.5-1.0	0.5	ND	ND
Mn	1000-1250	1230	20-50	25	2-4	2
Sr	40-42	41 ± 1.2	73-82	79 ± 5.2	2-3	2.3 ± 0.18
Li	1-2	1	0.5-1.0	0.8 ± 0.29	0.04-0.05	0.046 ± 0.018
U	1-2	1	ND	ND	ND	ND

ND = Not detectable.

Chicku leaf Ash : dry : wet weight = 1 : 13 : 33.

Chicku fruit Ash : dry : wet weight = 1 : 54 : 167.

Table 3. Elemental concentrations in soil, mango leaf and mango fruit.

Element	Soil µg/g (dry wt.)		Leaf µg/g (dry wt.)		Fruit µg/g (dry wt.)	
	Range	Average or most probable value (9 samples)	Range	Average or most probable value (9 samples)	Range	Average or most probable value (9 samples)
	K	300-550	312	3532-6588	5914	7956-10100
Ca	3375-6248	6248	8332-17260	10166	426-1263	497
Mg	2625-5000	4250	2034-2424	2200	700-738	719 ± 18
Fe	7750-7950	7830 ± 104	387-766	530	177-227	177
Cu	532-588	550 ± 33	6-7	6.6 ± 0.6	6-7	6.3 ± 0.56
Zn	700-800	766 ± 57	112-163	121	157-199	157
Co	34-34.5	34.2 ± 0.3	0.39-1.3	1.07	0.28-0.50	0.41 ± 0.12
Mn	1075-1400	1087	30-68	66	7-13	10
Sr	40-42	41.3 ± 1.1	34-39	36 ± 2.6	0.6-1.6	1.16 ± 0.51
Li	0.9-1.8	1.2 ± 0.6	0.04 ± 0.13	0.12	0.05-0.06	0.05 ± 0.01
U	1-2	1	ND	ND	ND	ND

ND = Not detectable.

Mango leaf Ash : dry : wet weight = 1 : 19 : 44.

Mango fruit Ash : dry : wet weight = 1 : 24 : 204.

Elemental content ($\mu\text{g/g}$) of dry plant materialElemental content ($\mu\text{g/g}$) of dry soil

The concentration ratios for all the elements analysed are listed in table 4. The values in table 4 have been rearranged in table 5 in three ranges of concentration ratio (> 10 , $1-10$ and < 1) so that one can easily find out the extent to which a particular element is concentrated or excluded.

From table 4 it is noticed that concentration ratios for chicku and mango fruits vary from 0.003 to 0.02 for Fe, below detectable limit to 0.01 for Co and 0.002 to 0.01 for Mn. From these values one may infer that the uptake of radioisotopes of these elements through consumption of chicku and mango fruits would be low.

It is evident from tables 4 and 5 that K is the element strongly concentrated in leaves and fruits of both chicku and mango. Since ^{40}K is a naturally occurring radio-

Table 4. Concentration ratios.

Element	Chicku leaf	Chicku fruit	Mango leaf	Mango fruit
K	12.6	10.4	18.9	26.9
Ca	2.8	0.08	1.6	0.08
Mg	1.6	0.17	0.5	0.2
Fe	0.06	0.003	0.07	0.02
Cu	0.03	0.01	0.01	0.01
Zn	0.04	0.01	0.2	0.2
Co	0.01	ND	0.03	0.01
Mn	0.02	0.002	0.06	0.01
Sr	1.9	0.06	0.9	0.03
Li	0.80	0.05	0.1	0.04
U	ND	ND	ND	ND

ND = Not detectable.

Table 5. Relative concentration of elements in chicku and mango.

Sample	Strongly concentrated (CR* > 10)	Slightly concentrated (CR* = 1-10)	Not concentrated (CR* < 1)
Chicku leaf	K	Ca, Mg, Sr	Fe, Cu, Zn, Co, Mn, Li, U,
Chicku fruit	K	..	Ca, Mg, Fe, Cu, Zn, Co, Mn, Sr, Li, U
Mango leaf	K	Ca, Sr (0.87)	Mg, Fe, Cu, Zn, Co, Mn, Li, U,
Mango fruit	K	..	Ca, Mg, Fe, Cu, Zn, Co, Mn, Sr, Li, U

*CR = Concentration ratio (as defined above).

isotope of K, high K intake may have some relevance from the point of view of internal radiation dose from ^{40}K . K content of the soil is a very important factor upon which depends on the availability of ^{137}Cs to plants. The uptake of ^{137}Cs by plants decreases with increasing K content in the soil (Scott Russel 1966).

From table 5 it is evident that Ca is concentrated in the mango leaf while Ca, Mg and Sr are concentrated in chicku leaf. The differential behaviour of Mg and Ca in relation to soil properties and plant growth may be due to interspecific differences between various plant species. Ion exchange equilibrium with Ca and Mg revealed that there are a number of exchange sites with higher specific affinity for Ca and lower for Mg (Paliwal *et al* 1975).

An important factor in the migration of Sr or Mg with respect to Ca from soil to plant is the possible discrimination against one of these elements. A quantitative assessment of this discrimination is given by the discrimination factor, defined by the ratio

$$DF_{\text{sample-precursor}} = \frac{\text{Sr or Mg/Ca content of sample}}{\text{Sr or Mg/Ca content of precursor}}$$

In order to calculate the discrimination factors, the average values of Sr, Mg and Ca in soil, leaves and fruits are taken from tables 2 and 3. The discrimination factors are presented in tables 6 and 7. From these tables the following conclusions may be made.

There is discrimination with respect to Ca when Sr and Mg are absorbed from soil by plants. Plants discriminate against Sr in favour of Ca. This is also true for Mg when it is absorbed from soil to leaf. The present data compare well with the values of $DF_{\text{Sr-Ca (plant-soil)}}$ ranging from 0.47 to 0.88 reported in

Table 6. Discrimination factor* when Sr and Ca are absorbed.

	$DF_{\text{leaf-soil}}$	$DF_{\text{fruit-soil}}$
Chicku tree	0.70	0.67
Mango tree	0.54	0.35
*(Sr/Ca in sample) \div (Sr/Ca in precursor).		

Table 7. Discrimination factor* when Mg and Ca are absorbed.

	$DF_{\text{leaf-soil}}$	$DF_{\text{fruit-soil}}$
Chicku tree	0.59	2.10
Mango tree	0.32	2.13
*(Mg/Ca in sample) \div (Mg/Ca in precursor).		

the literature (Fredriksson *et al* 1958; Rao *et al* 1970). It is interesting to note (table 7) that both chicku and mango fruits discriminate against Ca in favour of Mg. The studies indicate that if soils are contaminated by ^{90}Sr or ^{89}Sr , due to discrimination in favour of Ca, the transfer of these radionuclides to the plants and consequently to the fruit will be low. This discrimination is almost independent of the Ca content of the soil so long as the soil exchange complex is not Ca saturated (Fredriksson *et al* 1958). At a Ca content exceeding the soil exchange capacity the discrimination factor increases and exceeds 1.

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