



Environmental variations of trace element concentrations in Egyptian cane sugar and soil samples (Edfu factories)

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Abstract

Multielements, Ag, Au, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, and Zn were estimated in the sugar cane plant (green bagasse or cane stalks and leaves), sugar cane, raw juice, mixed juice, in syrup at the different stages of sugar production (10 stages), in sugar (grades A and B), and in soil samples collected from the immediate vicinity of the cane plant roots at surface, 30 and 60 cm depths. The measurements were undertaken on a Pye Unicam SP 1900 Recording Flame Atomic Absorption Spectrophotometer. The results obtained are within the permissible safety baseline levels and in excellent agreement with the previous work done on the sugar cane plant and on the soil of the same area (Edfu) using INAA, ICP-AES and AAS (Awadallah, R. M., Sherif, M. K., Mohamed, A. E., & Grass, F. (1984). Determination of trace elements in Egyptian cane sugar by neutron activation analysis. *Inter. J. Environ. Anal. Chem.*, 19 (1), 41–54; Awadallah, R. M., Sherif, M. K., Mohamed, A. E., & Grass, F. (1985). Determination of trace elements in Egyptian cane sugar by neutron activation analysis. *J. Radioanal. Nucl. Chem.* 92 (1), 7–25; Mohamed, A. E. (1986). Determination of trace elements in sugar cane refuse by instrumental neutron activation analysis. *J. Radioanal. Nucl. Chem., Letters*, 107 (2), 121–128; Mohamed, A. E., Awadallah, R. M., & Hassan, A. A. (1989). Determination of trace elements in Egyptian molasses by instrumental neutron activation analysis. *J. Radioanal. Nucl. Chem. Articles*, 129 (2), 453–457). © 1999 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Trace elements play an important and vital role in metabolism, health and disease. The presence of trace elements in sugar cane plants gives a clear picture of the distribution of these elements in the soil where plants absorb essential and necessary trace elements from soil solution (Bowling, 1976). This gives an idea about the structure and composition of the soil and the presence of elements in crops, vegetables, fruit, sugar cane plant and in sugar products. Sugar cane juice can be freshly utilized as a popular beverage, and for the production of honey commonly employed as a food and in desserts by people in developed countries. Molasses can be employed as a source for the manufacture of some organic solvents (MeOH, EtOH, Me₂CO, etc.) by fermentation. Stalks (bagasse) of sugar cane plants after juice extraction can be utilized as fuel, as well as for the production of some kinds of wood by grinding, compressing, addition of polymers (binding materials) and shaping into flaky forms. Paper pulp and manufactured paper can be produced from bagasse.

Trace elements in sugar cane and in soil have been estimated by neutron activation (NAA), inductively coupled plasma-atomic emission spectrometric and atomic absorption spectrophotometric analyses (Awadallah,

Sherif, Mohamed, & Grass, 1984, 1985; Mohamed, 1986; Mohamed, Awadallah, & Hassan, 1989). The present study is a part of a comprehensive programme planned to follow up the distribution of trace elements' levels in sugar products previously done during the period 1984–1989. The present study is targeted to investigate trace elements in the sugar cane plant (green leaves, bagasse), raw juice, cane sugar products at the different stages and in sugar grades, as well as in the soil of the cultivated area of Edfu district applying atomic absorption spectrophotometric techniques.

2. Materials and methods

All chemicals used were of A.R. grade (99.9%) and purchased from BDH, Aldrich, Sigma and E. Merck. Nine groups of sugar cane plant samples (three sugar cane plant stalks of each group) were taken from three locations of the cultivated fields of Edfu area (Edfu belongs to Aswan, Upper Egypt). In addition the soil samples were collected from the immediate vicinity of the roots of the sugar cane plant at surface, 30 and 60 cm depths in the same area. Three crude juice samples and syrup samples were withdrawn from the progressive

stages of sugar industry. Molasses and sugar (grades A, B) samples were also taken and analysed. The successive processing stages of the sugar cane industry can be summarised as follows: stage 1: mixed or principle juice; stage 2: mixed juice + $\text{Ca}(\text{OH})_2$ (slaked lime is added as a flocculant to precipitate the very fine suspended particles); stage 3: juice + super phosphate (which is added to enhance complete precipitation of the suspended materials); stage 4: juice + sulphur dioxide; stage 5: clear juice; stage 6: turbid juice; stage 7: syrup (concentrated juice); stage 8: syrup without SO_2 ; stage 9: syrup + SO_2 ; stage 10: molasses and sugar A (99.7% purity) and sugar B (down to 99.3% purity).

Certified atomic absorption spectroscopic standard solutions (1 mg/ml) for Ag, Au, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn were purchased from BDH (UK). Working standard solutions were prepared by appropriate dilution of the stock solutions, biological standards (Backer, Veglia, & Schmidt, 1974) [Bown's Kale (BK), Orchard Leaves (OL), and Tomato Leaves (TOML)], and geological standards (Taskaev & Apostolov, 1982) [coal fly ash (CFA), and Granite (USG₂)] as well as the certified atomic absorption spectroscopic standards were used to check the accuracy of the results.

2.1. Plant samples

Cane samples (green leaves) were washed separately with tap, deionised and tridistilled water. The samples were dried in an electrical furnace at 105°C for 3 h. The dried samples were blended with a stainless steel blender. The dried cane plant samples were powdered in an agate mortar and kept in polyethylene bottles. One gram of plant sample was wet-ashed in Teflon beaker using 20 ml (1:1) of concentrated HNO_3 – HClO_4 acids mixture, followed by the addition of three drops of hydrofluoric acid. The content was evaporated on a sand bath near to dryness. The residue was cooled, then it was dissolved in 5ml of concentrated HCl, and made up to 100 ml using thrice distilled water.

2.2. Juice, molasses and sugar samples

One liter of the original juice, crude juice, juice (syrup) from the different stages of sugar products, molasses and sugar (A and B) were evaporated on a hot plate down to a homogeneous state. Four gram portions of the dried samples were ashed using 40 ml concentrated HNO_3 in a Teflon beaker. The beaker was covered with a watch glass and placed on a sand bath until a clear solution was obtained. The solution was then made up to 100 ml using tridistilled water.

2.3. Soil samples

The representative soil (which was prepared by the quartering method) (Awadallah, 1971) sample was dried

at 105°C for 3 h in an electrical furnace; thereafter, it was ground and powdered using a mechanical agate mortar and kept in a polyethylene bottle. 0.5 g of soil sample was hydrofluorized using 3 ml of super pure HF, then it was dissolved in a mixture of 10 ml concentrated HNO_3 and 10 ml concentrated HCl acids in a Teflon beaker. The beaker was placed on a sand bath and evaporated until dryness. The residue was dissolved in an equal mixture of (1:1) HNO_3 –HCl acids (10 ml). The reaction mixture was heated until dryness; thereafter, 10 ml of 2N HCl were added and heated. The solution was cooled and filtered. The filtrate was made up to 100 ml using tridistilled water.

2.4. Analytical determinations

A SP 1900 Pye Unicam Recording Flame Atomic Absorption Spectrophotometer was utilised to measure the concentrations of Ag, Au, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn using Pye Unicam single element hollow cathode lamps.

3. Results

The results obtained from the analysis of the sugar cane plant, juice, samples taken at respective stages of the sugar industry and soil samples picked up from immediate vicinity of plant roots at surface, 30 and 60 cm depths are recorded in Tables 1–5. The data show that Co, Na and Pb are present at higher concentrations in juice than in the cane plant. Also, juice contains higher concentrations of Co, Cr, Cu, Fe, K, Na, Pb, Sr and Zn than sugar. The successive stages of sugar products (successive stages of sugar productions) exhibit higher levels of Cr, Fe, Mn, Na, Ni and Pb than in juice (higher concentrations of these metals may come as a

Table 1
Trace element concentrations in sugar cane plant samples (Edu factories)

Element	Plant 1	Plant 2	Plant 3	Mean	SD ^a	RE % ^b
Ag (ppb)	4.0	5.5	3.5	4.0	2.78	1.61
Au (ppb)	14.0	13.0	12.0	13.0	11.0	6.36
Ca %	0.77	0.23	0.47	0.49	0.271	0.156
CO (ppb)	26.0	30.0	26.0	27.3	2.310	1.33
Cr (ppm)	0.29	0.23	0.20	0.24	0.046	0.026
Cu (ppb)	106	81.0	61.0	82.7	27.8	11.1
Fe (ppm)	2.7	5.3	5.2	4.4	1.473	0.850
K (ppm)	1010	1395	1130	1178.3	197	13.7
Mg (ppm)	20.8	21.6	21.8	21.4	0.529	0.306
Mn (ppm)	0.58	0.56	0.46	0.53	0.179	0.103
Na (ppm)	3.0	2.5	6.0	3.83	7.654	4.42
Ni (ppb)	72.0	80.0	60.0	70.7	21.2	12.2
Pb (ppb)	32.0	25.0	26.0	24.3	18.0	10.4
Sr (ppb)	50.0	50.0	42.0	37.3	16.2	9.333
Zn (ppm)	0.71	0.25	0.30	0.42	0.476	0.275

^a SD, standard deviation.

^b RE, relative error.

result of contamination by juice). This is consistent with the previous findings by Awadallah et al. (1984) done on the same studied area (Edfu factories). Higher concentrations of these metals in the successive stages of sugar production may result from evaporation, corrosion of the plant containers or by the effect of additives [Ca(OH)₂, superphosphate and SO₂].

The results of the soil samples (Table 5) reveal that the subsamples taken from 30 cm depth exhibit lower concentrations of most elements, while the subsamples taken from surface and 60 cm depth contain higher concentrations. This indicates that the plant takes up most of its needs of trace elements from the soil at 30 cm depth. The presence of lower concentrations of trace elements in this depth agrees with the presence of the same elements at higher concentrations in the cane plant. This is concordant

with the results reported by Awadallah et al. (1984, 1985, 1986) in the sugar cane plant, and in subsamples of soil at 30 cm depth in the same area. The sensitivity, accuracy and precision of the results depend on the techniques applied for the dissolution of the samples, and on the tools utilised for measurements. The results of trace elements in Egyptian cane sugar of Edfu factories by AAS analysis are in good agreement with the results of the previous work conducted on the sugar cane plant, juice, etc., and the soil samples of the same area using INAA, ICP-AES and AAS analyses (Awadallah et al., 1984). The relative error (RE%) of this work by (AAS) reaches 0.026–13% in the case of the cane plant, 0.00–13.4% in crude juice, 0.02–14.7% in the products at different stages of sugar industry, 0.00–5.0% in the pure sugar (grades A and B), and 0.021–8.22% in the soil samples.

Table 2

Trace element concentrations in sugar cane juice samples (Edfu factories)

Metal	J ₁ ^a	J ₂	J ₃	Mean	SD ^b	RE% ^c
Ag (ppb)	2.0	2.0	2.0	2.0	0.00	0.0
Au (ppb)	12.0	14.0	16.0	14.0	2.0	8.21
Ca(%)	0.79	0.22	0.17	0.393	0.344	5.80
Co (ppb)	34.0	26.0	34.0	31.3	4.62	8.52
Cr (ppm)	0.22	0.21	0.19	0.207	0.015	4.33
Cu (ppb)	52.0	52.0	120	74.7	39.3	9.60
Fe (ppm)	2.6	5.04	1.6	3.08	1.77	12.1
K (ppm)	560	815	605	660	136	11.9
Mg (ppm)	15.8	11.4	10.0	12.4	3.03	10.3
Mn (ppm)	0.10	0.10	0.09	0.097	5.77 × 10 ⁻³	3.00
Na (ppm)	30.6	13.4	13.6	19.2	9.87	13.2
Ni (ppb)	46.0	56.0	46.0	49.3	5.77	6.71
Pb (ppb)	30.0	56.0	28.0	38.0	15.6	10.0
Sr (ppb)	20.0	36.0	24.0	26.7	8.33	8.13
Zn (ppb)	72.0	26.0	44.0	47.33	23.2	1.02

^a J, juice.

^b SD, standard deviation.

^c RE, relative error.

4. Discussion

The existence of trace elements, Ag, Au, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn in the investigated cane plant samples indicates their valuable, important and essential vital roles for plant growth, animals and humans (Russell, 1973). The presence of some elements such as Co, Na and Pb, in juice at higher concentrations than in the cane plant, may be ascribed to corrosion effects of juice by additives [Ca(OH)₂, Ca₃(PO₄)₂, SO₂], heat and mass transfer (Awadallah et al., 1985) of juice and syrup by containers during the sugar product processes. Increase of some trace elements at the successive stages of sugar products may be related to the concentration of juice, treatment processes, such as the addition of Ca(OH)₂, superphosphate, passage of SO₂, evaporation and corrosion effects on juice boilers. Decrease of trace elements may be ascribed to filtration and purification processes.

Table 3

Trace element levels in different stages of sugar production in Edfu factories

Metal	Stage										Mean	SD	RE(%)
	1	2	3	4	5	6	7	8	9	10			
Ag (ppb)	2.0	2.0	2.0	2.0	2.0	2.0	4.0	4.0	2.0	4.0	2.6	0.966	11.7
Au (ppb)	18.0	18.0	16.0	24.0	24.0	26.0	22.0	26.0	26.0	56.0	25.6	11.3	13.9
Ca(%)	0.28	0.13	0.32	0.27	0.62	0.16	0.46	0.38	0.42	1.13	0.417	0.289	11.9
Co (ppb)	24.0	30.0	36.0	38.0	34.0	28.0	30.0	32.0	28.0	42.0	32.2	5.37	5.2
Cr (ppm)	0.15	0.17	0.016	0.10	0.12	0.10	0.12	0.11	0.12	0.22	0.137	0.038	8.7
Cu (ppb)	162	40.0	60.0	14.0	22.0	18.0	16.0	46.0	90.0	54.0	52.2	45.5	2.7
Fe (ppm)	7.00	2.50	1.10	0.86	1.50	1.06	1.18	1.24	1.22	3.40	2.106	1.891	2.8
K (ppm)	1010	1000	1295	1075	1110	1020	990	1535	1090	3310	1344	71.5	12.7
Mg (ppm)	18.0	17.0	7.0	17.0	15.6	15.4	16.4	19.4	18.6	43.4	18.78	9.306	15.6
Mn (ppm)	0.22	0.14	0.06	0.07	0.06	0.07	0.07	0.08	0.07	0.22	0.106	0.064	9.9
Na (ppm)	21.0	18.0	18.0	13.8	14.6	14.0	15.0	18.8	21.6	33.0	18.8	5.73	9.6
Ni (ppb)	50.0	52.0	38.0	40.0	64.0	52.0	38.0	46.0	42.0	84.0	50.6	14.2	8.9
Pb (ppb)	18.0	24.0	24.0	32.0	20.0	24.0	22.0	28.0	20.0	38.0	25.0	6.13	7.8
Sr (ppb)	58.0	54.0	28.0	70.0	80.0	56.0	64.0	82.0	54.0	190	73.6	43.7	8.7
Zn (ppb)	30.0	40.0	82.0	64.0	72.0	60.0	26.0	42.0	48.0	150	59.6	36.3	9.1

The cane plant takes up its needs of trace elements from the surrounding soil solutions. The presence of large concentrations of these elements before planting, and lower concentrations after planting in soil samples at 30 cm depth indicate that the trace elements were taken up by the plant at this depth. This may be ascribed to the release of the exchangeable cations and anions from the soil solutions at this depth and their adsorption by the plant (Bowling, 1976).

Potassium is an essential nutrient and has an important role in growth of plants and in the synthesis of amino acids and proteins (Malik & Srivastava, 1982). Ca and Mg play a significant role in photosynthesis, carbohydrate metabolism, nucleic acids and chlorophyll syntheses, and binding agents of cell walls. Iron and cobalt cause substantial catalytic activity and have been shown to be essential elements for nitrogen fixation in addition to their usefulness for the formation of vitamin

B₁₂ (Russell, 1973). Iron is an essential activator for enzymes catalysing reactions involved in chlorophyll synthesis and for ferredoxin nitrate reductase (Bowling, 1976). Chromium is an essential element for increasing glucose tolerance. It also serves as a cofactor and activator for several enzymes involving the synthesis of fatty acids, DNA and RNA, and cholesterol from acetate (Gibbs, 1978). The taste, colour and smell of juice and molasses may be attributed to the presence of Mn (Gibbs). The dark colour of molasses and brown honey may be related to the existence of Fe, Co, Cu, Ni and Mn. Relative error in the data of soil, cane plant, juice, and products at the different processes of sugar industry is acceptable, comparing these results with those obtained by INAA and ICP-AES (Awadallah et al., 1985). RE% is a little higher because INAA and ICP-AES are more accurate and sensitive than the AAS technique.

4.1. Statistical analysis of data

Multielement correlation coefficient (*r*) values in cane sugar plant, juice, products of successive stages of sugar production, sugar and soil samples were evaluated. Positive and significant correlations are found to equal 0.908–0.998 (sugar cane plant), 0.945–1.00 (juice), 0.947–0.965 (syrup) and soil 0.988–0.999 (surface), 0.900–1.00 (30 cm depth), and 0.904–0.999 (60 cm depth). The results give a new picture of significant (due to proportionality, i.e. as one element increases the others increase) and negative (ion antagonism) correlation coefficients in the sugar cane plant, arising from ion absorption and uptake of convenient and essential trace elements by the plant from the surrounding soil solution.

Negative correlations (–0.305 to –0.945) in sugar cane plants are observed. Negative correlations are exhibited and give new information about the ion

Table 4
Trace element levels: sugar levels in sugar of Edfu factories

Metal	Sugar A	Sugar B	Mean	SD	RE(%)
Ag (ppb)	2.0	2.0	2.0	0.0	0.0
Au (ppb)	6.0	4.0	5.0	1.41	6.9
Ca(%)	0.15	0.14	0.145	7.07×10^{-3}	3.4
Co (ppb)	10.0	12.0	11.0	1.41	8.3
Cr (ppm)	0.014	0.006	0.01	5.66×10^{-3}	5.8
Cu (ppb)	14.0	22.0	18.0	5.66	7.6
Fe (ppm)	0.16	0.30	0.23	0.099	11.1
K (ppm)	33.0	36.0	34.5	2.121	4.3
Mg (ppm)	0.96	1.06	1.01	0.071	4.9
Mn (ppm)	0.012	0.018	0.015	4.24×10^{-3}	2.0
Na (ppm)	1.70	1.50	1.60	0.141	6.2
Ni (ppb)	4.0	10.0	7.0	4.24	9.8
Pb (ppb)	4.0	12.0	8.0	5.66	10.1
Sr (ppb)	20.0	30.0	25.0	7.07	13.4
Zn (ppb)	4.0	4.0	4.0	0.0	0.0

Table 5
Trace element concentrations in soil (Edfu area) as function of depth

Element	Sample 1			Sample 2			Sample 3			Mean	SD	RE%
	Surface	30 cm	60 cm	Surface	30 cm	60 cm	Surface	30 cm	60 cm			
Ag(PPb)	40.0	40.0	30.0	20.0	10.0	30.0	20.0	20.0	10.0	24.4	11.30	4.77
Au(PPb)	320	520	330	280	310	340	330	350	320	344	68.8	11.92
Ca(%)	1.80	1.20	1.53	2.34	2.88	2.52	2.56	2.34	2.16	2.150	0.538	0.179
Co(PPm)	0.59	0.97	0.57	0.52	0.61	0.55	0.59	0.61	0.58	0.62	0.134	0.045
Cr(PPm)	0.98	1.66	1.04	0.99	1.21	1.15	1.08	1.11	1.15	1.15	0.205	0.068
Cu(PPm)	0.89	1.4	0.89	0.95	0.99	0.91	1.29	1.27	1.22	1.09	0.202	0.067
Fe(PPm)	61	780	608	595	644	658	628	639	644	645	54	8.16
K(PPm)	36	52	29	43	47	49	46	42	37	42.3	7.2	2.4
Mg(PPm)	226	309	229	245	260	256	242	245	239	250	24	8.22
Mn(PPm)	9.5	15.2	10.2	9.08	10.4	9.80	10.2	10.4	10.1	10.5	1.80	0.600
Na(PPm)	7.22	10.4	7.4	10.7	16.4	17.4	13.7	15.1	16.3	12.7	3.9	1.3
Ni(PPm)	0.965	1.58	0.91	0.93	1.04	1.02	0.98	0.93	0.89	1.03	0.214	0.071
Pb(PPm)	0.20	0.41	0.25	0.23	0.28	0.22	0.26	0.30	0.29	0.27	0.062	0.021
Sr(PPm)	0.58	0.53	0.51	0.46	0.55	0.39	0.43	0.49	0.37	0.48	0.072	0.024
Zn(PPm)	1.19	1.42	1.18	1.15	1.25	1.29	1.37	1.22	1.30	1.26	0.090	0.030

antagonism (anticorrelations) and the deficiency or excess of some elements in the soil solution. Negative correlations may be ascribed to a result of counteraction, blocking, stunting, interlocking or due to the effect of some elements on the mobility and on the absorption (uptake) of the other elements remaining in the surrounding soil solution.

Some reviews (Bowling, 1976) have cited an antagonism between the elements assayed in sugar cane plant samples. Negative correlations may be attributed to opposition or counteraction which takes place between trace elements in the soil as well as in the sugar cane plant.

Juice shows good positive (significant) correlation coefficient values ($r = 0.958–1.00$). Correlation coefficients between trace elements existing in the products of the different industrial stages exhibit positive values ($r = 0.944–0.965$). Significant correlation coefficient values between trace elements in juice and in different stages of sugar products may be related to proportional relations as a result of the addition of $\text{Ca}(\text{OH})_2$, superphosphate, passage of SO_2 and corrosion effect on machinery, tanks or containers by juice and additives.

Soil at different depths shows significant correlation coefficient values ($r = 0.908–0.999$) between the estimated elements existing at the surface of soil.

In the case of samples taken from 30 cm depth, positive and significant correlation coefficient values ($r = 0.90–1.0$) are also observed, while at 60 cm depth, the database of the statistical analysis shows positive correlation values ($r = 0.904–0.999$). Variations in correlation coefficient values shown at different depths of the soil may be attributed to variable mineralogical, chemical compositions of the soil and texture and structure of the soil, and also due to the variations of geochemical and biogeochemical behaviour of the elements existing in the soil. Significant correlations may also be ascribed to proportional relationships between

trace elements (as one element increases, the others increase together), leading to increase the mobility of these elements which facilitate their uptake into the plants. However, some of these elements (K, Fe, Mn) are good indicators of plant behavior.

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