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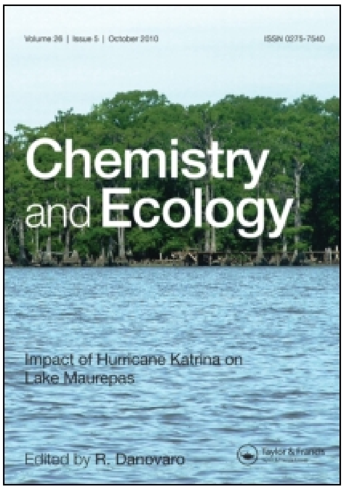

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Behaviour of Chemical Elements in Plants and Soils

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BEHAVIOUR OF CHEMICAL ELEMENTS IN PLANTS AND SOILS

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Neutron activation analysis was used for the determination of the elemental composition of different plants and soils. Variations in concentrations of elements during the day were found. Mean concentrations, standard deviations and relationships between elements in soils and different parts of plants were studied. It was shown that the behaviour of chemical elements in samples from urban and unpolluted areas have significant differences.

KEY WORDS: Trace chemicals, rare earth elements, plants, soils, urban pollution.

INTRODUCTION

The behaviour of trace elements in biological systems has become the subject of numerous investigations in recent years (Adriano, 1986; Markert, 1989; Lobersli and Steinnes, 1990; Liu and Jervis, 1992; Halonen *et al.*, 1993). However, little attention has been given to short-term variations of trace metals in plants (Wills, 1987) or of the relationships between different chemical elements in the environment (Markert, 1987). This may be related to analytical difficulties in the detection of some chemical elements, for example scandium, hafnium, tantalum, rare earth elements (REE) in environmental samples. Moreover, it is believed that variations in trace element concentrations in soils and plants can also cause a change in the concentrations of biologically important elements (Shtangeeva, 1993).

EXPERIMENTAL METHODS

In our research, instrumental neutron activation analysis (INAA) was used to study the behaviour of chemical elements in different plants and soils. The high sensitivity and precision of INAA allowed us to analyse plants and soils in their natural state, without any concentration procedure or ashing of samples.

Two commonly occurring species of plants – couch grass (*Elytrigia repens* (L.) Nevski) and plantain (*Plantago major*), as well as soil samples (from 0–5 cm depth), were collected over several years (from 1986 to 1989) in a large city (St. Petersburg) and in ecologically "clean" (background) areas – forests and parks far from any known pollutant sources.

To select the optimal time of sampling, plants and soils were picked from April to October in 1987 at the same site every ten days. On all dates, the samples were collected (four each hour) through all daylight hours. Subsequently, samples were collected only between 10.00 h and 11.00 h. In total, about 500 plant samples and more than 80 soil samples were studied. After sampling, the plants were washed with water and dried at room temperature (24°C); pieces of glass, brick and plant material were discarded from the soil samples.

Samples and standards (the samples of well-known elemental composition: granite AGV-1, basalt BCR-1 and Russian biological standard SBMT-01) were irradiated for 2 days in a nuclear reactor at a neutron flux density $10^{14}\,\mathrm{n\,cm^{-2}\,s^{-1}}$. Thermal and epithermal irradiations were applied. Measurements were made using two detectors: Ge (Li) (resolution – 2.1 keV for 1332 keV) and hyperpure germanium detector (resolution – 0.35 keV for 122 keV). Standard errors of determination of elements were $< 5\%$ for Na, K, Sc, Cr, Fe, Co, Zn, Br, Rb, Ba, La, Sm, Eu, Hf, Au and U; $< 10\%$ for Ca, As, Sr, Ag, Cd, Sb, Cs, Ce, Tb, Yb, Ta, W, Hg and Th; < 15–20% for Ni, Se, Zr, Sn, Nd and Lu.

RESULTS AND DISCUSSION

Wide variations in elemental composition of plants and soils were found. For example, even during the course of a day, variations in the concentration of chemical elements in different parts of plants were observed. Figure 1 illustrates the variation of cobalt concentration in samples of couch grass that were picked on different dates. Similar variations in element concentrations (to various degrees) are typical of all elements studied, including such essential elements as sodium, potassium and calcium.

To account for the features of element redistribution between roots and leaves, the ratio (L/R) between the concentration of any element in leaves (L) and its concentration in roots (R) was calculated. As an example, the variations in L/R of chromium and thorium on different dates are shown (Fig. 2). Similar variations in L/R were observed for many other elements. It was found that L/R values were higher at the beginning of May than at the end of May or in August. Furthermore, the variations in L/R in plants sampled on the 1 May have a quite regular character. For most of the elements studied the L/R in couch grass sampled on this day were 1.52 (at 14.00 h) and 0.79 (at 22.00 h); in plantain sampled on the same day and at the same place, L/R was 0.41 (at 22.00 h). Such variations may be reasonably attributed to biorhythmic changes in various biological processes, and to progressive impairment of physiological activity as the plant grows and ages.

Pollution of soils by some heavy metals may influence the behaviour of some biologically important elements (Levitt, 1980; Kauppi and Halonen, 1992). In Table I, mean concentrations of chemical elements are shown for soil and roots and leaves of plantain and couch grass sampled at urban and background sites. Statistically significant differences (*) in concentrations ($P < 0.05$) are observed between urban and background sites for many chemical elements. For example, urban soils are enriched in some elements (Cd, As, Ni, Cr, Se, Zn, Sb, Fe, Co, Sr, Ce, Tb, Au, Ag). It might be expected that such increases in the element concentrations in soils will be reflected in

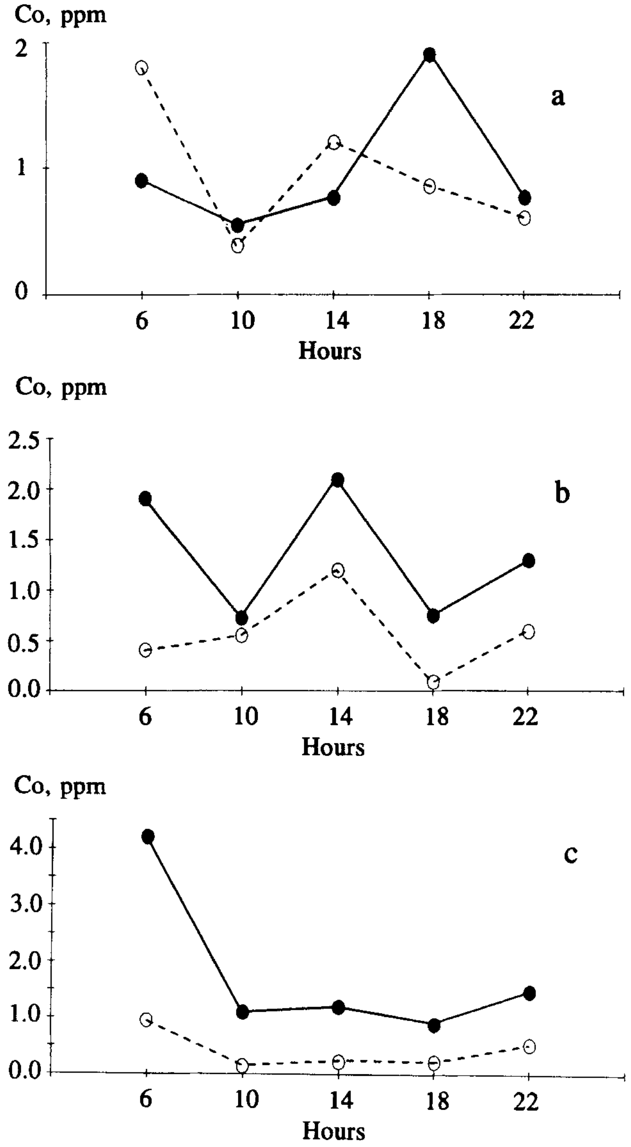

Figure 1 Differences in cobalt concentrations in roots (solid line) and leaves (dashed line) of couch grass during daylight on different dates. a. 1 May 1987, b. 24 May 1987, c. 1 August 1987.

the element concentrations of plants growing on those soils. However, in parts of all urban plant samples higher concentrations of only three elements – iron, nickel and silver – were found.

Figure 3 shows the distribution of two biologically important elements (potassium and calcium) in roots and leaves of plantain. It is evident that concentrations of both

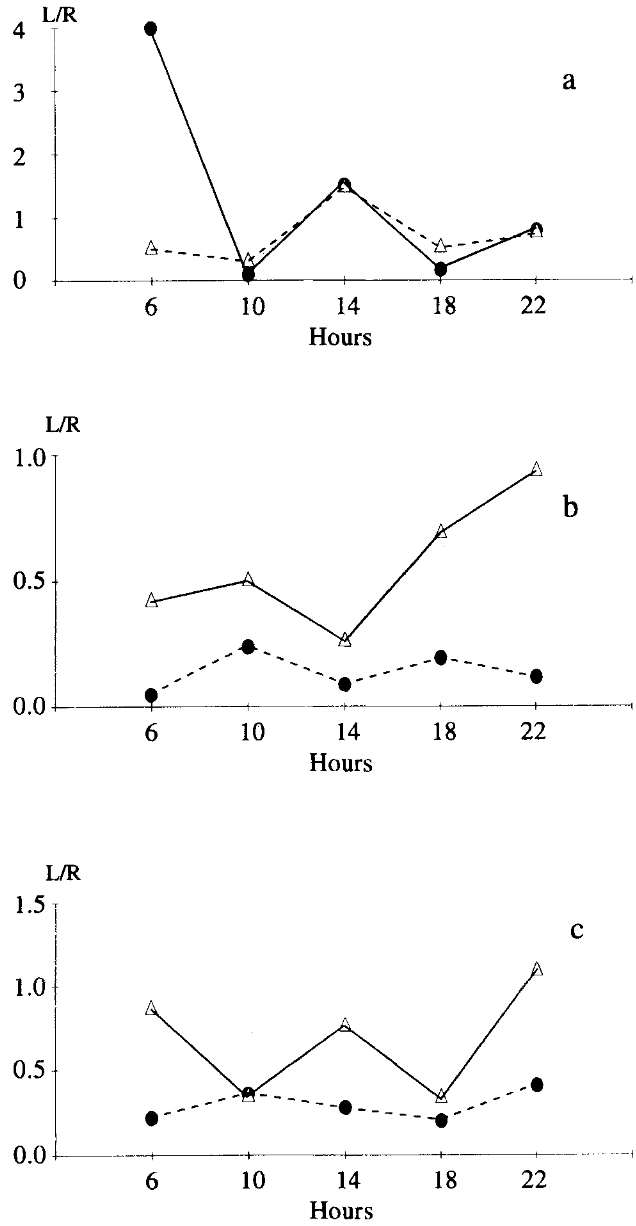

Figure 2 Variations in L/R ratios for couch grass in daylight hours on different dates. Concentrations of thorium (solid line) and chromium (dashed line) in leaves (L) and roots (R). a, b and c are the same as for Figure 1.

elements in plantain roots are higher in the urban plant samples than in background samples. In addition, element concentrations in roots and leaves of plantain and couch grass can be readily distinguished in the background samples, whereas no significant differences were observed between samples of roots and leaves of urban plants.

Table 1 The mean ± SD of chemical element concentrations (as ppm of dry weight) in soils (more than 80 samples) and different parts of plants (about 500 samples). * – differences between background (A) and urban (B) samples are significant at $P < 0.05$. n.d. – element not analysed in these samples.

Elem.	*Soil*	*Couch grass*		*Plantain*		
		Roots	*Leaves*	*Roots*	*Leaves*	
Na (%)	1.03 ± 0.31	0.09 ± 0.04	0.04 ± 0.02	0.08 ± 0.03*	0.02 ± 0.01*	A
	1.17 ± 0.39	0.11 ± 0.07	0.06 ± 0.03	0.24 ± 0.10	0.04 ± 0.02	B
K (%)	1.75 ± 0.59	0.69 ± 0.31*	3.42 ± 1.36	1.67 ± 0.68*	4.74 ± 1.84	A
	2.19 ± 0.95	1.07 ± 0.44	3.83 ± 0.72	2.37 ± 0.78	3.99 ± 1.43	B
Ca (%)	4.14 ± 1.40*	0.33 ± 0.14	0.44 ± 0.12	0.41 ± 0.16*	2.68 ± 1.08	A
	2.85 ± 0.86	0.30 ± 0.16	0.37 ± 0.13	0.56 ± 0.22	2.29 ± 0.92	B
Sc (%)	3.97 ± 1.71	0.20 ± 0.10*	0.04 ± 0.03*	0.10 ± 0.06*	0.02 ± 0.01*	A
	3.82 ± 1.65	0.30 ± 0.11	0.12 ± 0.11	0.20 ± 0.07	0.12 ± 0.04	B
Cr (%)	5.41 ± 1.87*	3.45 ± 1.45	1.93 ± 0.68*	2.86 ± 1.18*	2.24 ± 0.97*	A
	34.6 ± 18.9	10.9 ± 77.7	5.28 ± 2.30	5.69 ± 1.92	4.83 ± 1.52	B
Fe (%)	11440 ± 4500*	760 ± 317*	214 ± 69*	539 ± 331*	137 ± 48*	A
	15460 ± 5940	1790 ± 1570	723 ± 140	1070 ± 360	659 ± 224	B
Co (%)	3.42 ± 1.31*	0.57 ± 0.23	0.11 ± 0.03*	0.24 ± 0.13*	0.11 ± 0.04	A
	4.80 ± 1.88	1.10 ± 1.18	0.39 ± 0.19	0.52 ± 0.15	0.36 ± 2.01	B
Ni (%)	6.10 ± 2.59*	0.20 ± 0.29*	0.36 ± 0.15*	0.20 ± 0.26*	0.27 ± 0.11*	A
	13.7 ± 5.2	1.19 ± 0.67	0.90 ± 0.13	0.77 ± 0.26	0.79 ± 0.24	B
Zn (%)	37.0 ± 15.6*	44 ± 332	19.3 ± 6.9*	27 ± 102	25.5 ± 21.8*	A
	158 ± 65	145 ± 46	54.4 ± 20.3	55.6 ± 56.7	46.0 ± 16.7	B
As (%)	4.42 ± 1.75*	0.99 ± 0.32*	0.28 ± 0.11*	0.68 ± 0.27*	0.23 ± 0.09	A
	6.05 ± 2.37	1.91 ± 1.00	0.51 ± 0.35	1.64 ± 0.83	0.33 ± 0.51	B
Se (%)	0.76 ± 0.28*	0.22 ± 0.07	0.07 ± 0.02	0.09 ± 0.03*	0.04 ± 0.05*	A
	2.92 ± 0.78	0.24 ± 0.07	0.11 ± 0.09	0.18 ± 0.07	0.1 ± 0.1	B
Br (%)	5.67 ± 2.17	4.64 ± 2.15	8.91 ± 3.79*	1.13 ± 0.41*	5.86 ± 3.30*	A
	5.81 ± 2.02	5.13 ± 1.54	6.10 ± 1.33	2.41 ± 2.07	10.5 ± 4.3	B
Rb (%)	89.3 ± 29.8	14.7 ± 6.8*	43.8 ± 19.1*	17.0 ± 10.7	32.5 ± 17.5*	A
	79.4 ± 34.8	9.57 ± 2.99	16.3 ± 4.3	12.5 ± 4.6	16.8 ± 6.0	B
Sr (%)	133 ± 50*	44.3 ± 47.4	18.6 ± 5.6*	34.7 ± 31.7*	40.5 ± 44.5*	A
	190 ± 74	55.2 ± 21.3	44.2 ± 18.1	89.5 ± 37.0	167 ± 70	B
Zr (%)	252 ± 82	9.01 ± 3.25*	6.03 ± 2.17*	7.43 ± 2.57*	7.71 ± 3.28*	A
	214 ± 78	21.2 ± 6.3	13.7 ± 5.4	18.8 ± 7.2	17.8 ± 7.0	B
Ag (%)	0.17 ± 0.09*	0.15 ± 0.06*	0.07 ± 0.03*	0.05 ± 0.03*	0.03 ± 0.02*	A
	0.7 ± 0.3	0.32 ± 0.19	0.14 ± 0.08	0.18 ± 0.06	0.12 ± 0.04	B
Cd (%)	2.58 ± 0.94*	2.02 ± 0.56*	1.03 ± 0.51	1.33 ± 0.57*	0.91 ± 0.54	A
	5.83 ± 2.34	8.73 ± 2.74	1.26 ± 5.46	2.50 ± 1.83	1.52 ± 2.67	B
Sn (%)	2.56 ± 1.01	n.d.	n.d.	n.d.	n.d.	A
	1.95 ± 0.88	0.23 ± 0.05	0.15 ± 0.12	0.19 ± 0.05	0.20 ± 0.05	B
Sb (%)	0.42 ± 0.46*	0.29 ± 0.10	0.13 ± 0.04*	0.14 ± 0.05*	0.08 ± 0.04*	A
	2.27 ± 0.87	1.3 ± 3.5	0.38 ± 0.33	0.66 ± 0.26	0.31 ± 0.12	B

Table 1 (*continued*)

Elem.	*Soil*	*Couch grass*		*Plantain*		
		Roots	*Leaves*	*Roots*	*Leaves*	
Cs (%)	1.62 ± 0.56	0.19 ± 0.08*	0.09 ± 0.04	0.09 ± 0.04	0.07 ± 0.03	A
	1.72 ± 0.54	0.13 ± 0.05	0.07 ± 0.05	0.08 ± 0.03	0.07 ± 0.03	B
Ba (%)	512 ± 201	50.0 ± 15.2*	22.8 ± 7.9*	58.9 ± 27.9*	60.4 ± 24.4*	A
	619 ± 246	129 ± 62	71.4 ± 35.3	92.3 ± 25.0	99 ± 34	B
La (%)	19.4 ± 8.7	1.05 ± 0.42	0.37 ± 0.13*	0.88 ± 0.75	0.40 ± 0.15*	A
	19.2 ± 6.9	1.61 ± 1.61	0.79 ± 0.38	0.88 ± 0.50	0.66 ± 0.24	B
Ce (%)	27.0 ± 10.2*	2.9 ± 1.0	0.77 ± 0.32*	1.60 ± 2.27	0.61 ± 0.53*	A
	35.7 ± 12.9	3.32 ± 2.21	1.88 ± 0.78	2.29 ± 0.80	1.43 ± 1.68	B
Nd (%)	14.2 ± 13.4	n.d.	n.d.	n.d.	n.d.	A
	19.4 ± 7.0	3.17 ± 1.07	2.52 ± 0.65	3.89 ± 1.52	3.05 ± 1.08	B
Sm (%)	2.85 ± 1.04	0.46 ± 0.23	0.09 ± 0.07*	0.22 ± 0.38	0.10 ± 0.04*	A
	3.01 ± 1.14	0.50 ± 0.19	0.17 ± 0.08	0.23 ± 0.08	0.15 ± 0.05	B
Eu (%)	0.77 ± 0.30	0.10 ± 0.06	0.03 ± 0.05*	0.05 ± 0.08*	0.04 ± 0.07*	A
	0.85 ± 0.39	0.13 ± 0.06	0.11 ± 0.06	0.13 ± 0.07	0.13 ± 0.08	B
Tb (%)	0.38 ± 0.15*	0.031 ± 0.013*	0.012 ± 0.004	0.018 ± 0.012*	0.012 ± 0.004*	A
	0.52 ± 0.19	0.05 ± 0.01	0.02 ± 0.03	0.04 ± 0.01	0.03 ± 0.01	B
Yb (%)	1.40 ± 0.55	0.07 ± 0.02*	0.03 ± 0.01*	0.04 ± 0.04*	0.03 ± 0.02*	A
	1.32 ± 0.56	0.18 ± 0.13	0.10 ± 0.08	0.15 ± 0.05	0.14 ± 0.04	B
Lu (%)	n.d.	0.010 ± 0.006*	0.007 ± 0.002*	0.013 ± 0.004*	0.006 ± 0.002*	A
	n.d	0.052 ± 0.016	0.028 ± 0.008	0.031 ± 0.008	0.03 ± 0.01	B
Hf (%)	4.75 ± 1.92	0.39 ± 0.16	0.28 ± 0.11*	0.41 ± 0.12	0.38 ± 0.12*	A
	5.20 ± 2.07	0.47 ± 0.17	0.38 ± 0.07	0.46 ± 0.19	0.51 ± 0.20	B
Ta (%)	0.45 ± 0.18	0.05 ± 0.02	0.02 ± 0.09	0.04 ± 0.01	0.03 ± 0.01*	A
	0.43 ± 0.17	0.06 ± 0.02	0.04 ± 0.01	0.05 ± 0.02	0.05 ± 0.02	B
W (%)	2.68 ± 0.91	1.88 ± 1.01	1.39 ± 3.22	1.96 ± 0.71	2.44 ± 0.66	A
	2.88 ± 1.23	2.48 ± 1.07	2.0 ± 1.0	2.33 ± 3.67	2.74 ± 3.41	B
Au (%)	0.006 ± 0.002*	0.06 ± 0.02	0.02 ± 0.01	0.015 ± 0.006	0.012 ± 0.005	A
	0.010 ± 0.006	0.05 ± 0.02	0.02 ± 0.04	0.02 ± 0.06	0.009 ± 0.012	B
Hg (%)	2.36 ± 0.83	n.d.	n.d.	n.d.	n.d.	A
	0.11 ± 0.06	0.05 ± 0.14	0.12 ± 0.04	0.06 ± 0.11		B
Th (%)	6.47 ± 1.46	0.31 ± 0.10	0.10 ± 0.03*	0.18 ± 0.33	0.08 ± 0.03*	A
	5.93 ± 2.23	0.38 ± 0.19	0.24 ± 0.19	0.28 ± 0.09	0.22 ± 0.23	B
U (%)	1.33 ± 0.85	n.d.	n.d.	n.d.	n.d.	A
	1.39 ± 0.53	n.d.	n.d.	n.d.	n.d.	B

It was found that under stable conditions over a long period of growth, plant tissues maintain a relatively constant proportion between concentrations of potassium and sodium (Baker and Hall, 1975). It is of interest to look at this relationship (K/Na) as well as the concentrations of rubidium, which has physical and chemical properties similar to those of potassium and sodium. Figure 4 shows that K/Na ratios in plants from

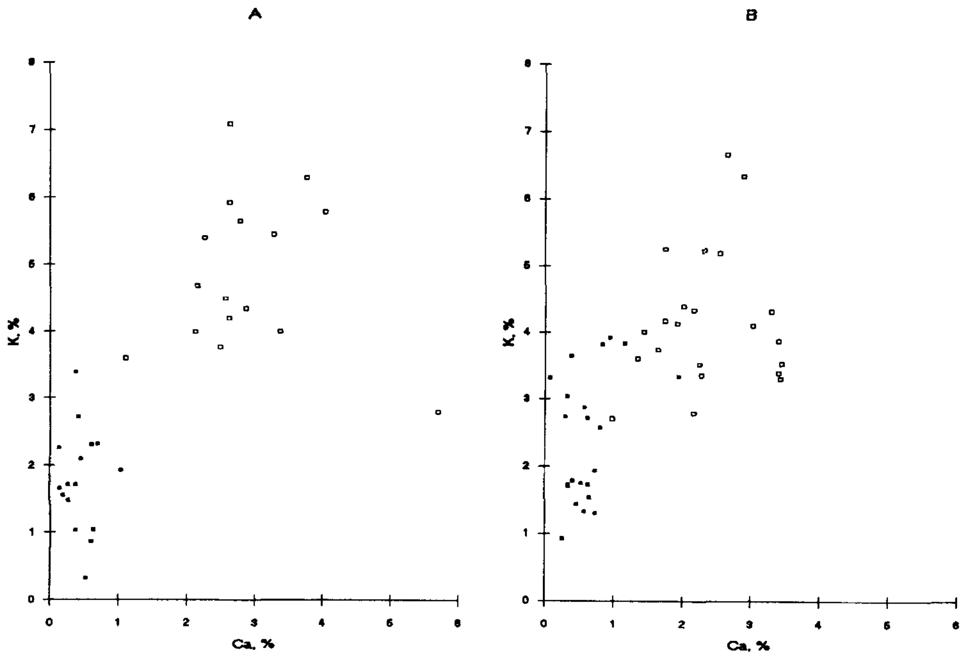

Figure 3 Relationship between potassium and calcium in roots (■) and leaves (□) of plantain. A. background, B. city.

urban sites were much lower overall than those of plants from background areas; this is typical for both couch grass and plantain. In addition, urban plant samples have lower rubidium concentrations than those from background sites and the leaves and roots in samples from the background sites differ, while in urban plant samples no such distinct difference is found.

It has been shown in many experiments that a decrease in mineral nutrient content affects several metabolic processes, including photosynthesis (Kirchgebner and Roth, 1982; Natr, 1987; Chatterjee *et al.*, 1994), and also leads to different genetic responses (Sanderman, 1984). Although no visible (external) changes in the urban plants studied were observed, it is suggested that the variations in relative concentrations might initiate such changes.

It is also of interest to compare the different relationships of chemical elements in background and urban samples. Correlation coefficients between all elements analysed were calculated. It was found that the number of all statistically significant relationships ($P < 0.05$) was different for urban and background samples. In Figure 5 this has been demonstrated for some elements (Fe, Sc, Co, Ta); for example, in background plants, statistically significant relationships between cobalt and other elements number 4, while in urban plants they are 25. In contrast, in background soil statistically significant relationships for cobalt are 9, while in urban soil they are 4.

It is clear that urban soil consists not only of the natural soil, but a variable debris component as well. The presence of foreign materials may change the natural relationships between elements. On the other hand, plants are more highly organised than soils

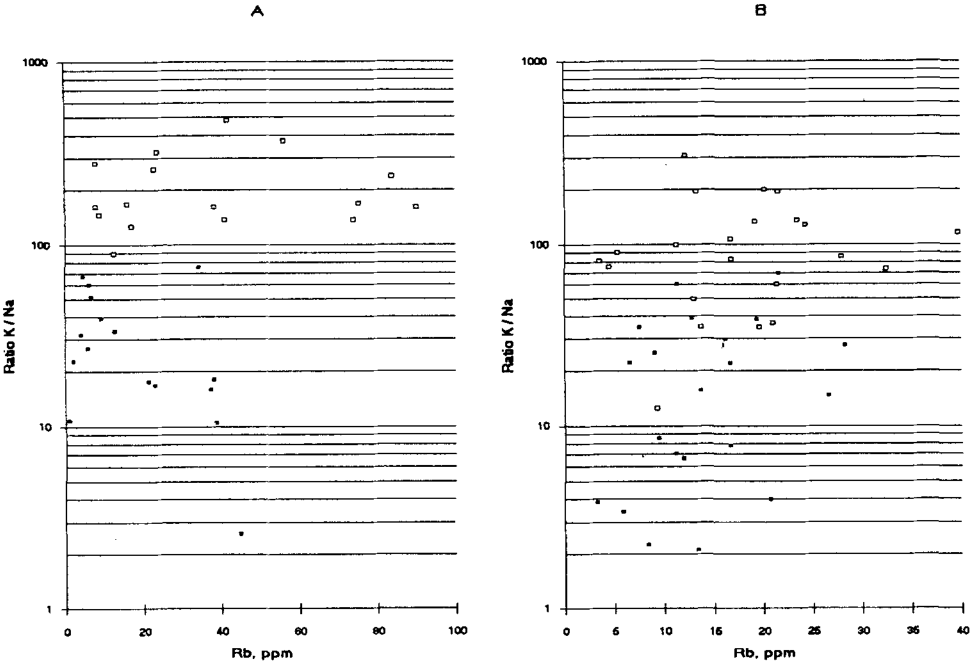

Figure 4 Relationship between rubidium concentration and ratio of potassium and sodium (K/Na) for roots (■) and leaves (□) of plantain. A. background, B. city.

and the presence of contaminants may stimulate additional protective mechanisms in plants, and the relationships between elements become more close.

Finally, the behaviour of rare earth elements in different natural processes have not yet been studied sufficiently (Liu and Jervis, 1992; Summerton, 1992), even though REE (specifically, europium) have a prime interest for the interpretation of some ecological phenomena owing to their ability to change valency depending on environmental conditions, such as pH and redox (German *et al.*, 1991).

One method of presentation is shown in Figure 6, where REE concentrations in the samples are normalized to that of a reference material (in this case, chondritic meteorites, Henderson, 1984). Values for urban and background samples of soil and roots and leaves of plantain are shown and are similar for couch grass. It is evident that urban leaves are enriched with all REE compared with those from background samples, and urban roots are enriched only with heavy REE. Moreover, a clear positive europium anomaly in urban roots and leaves was found, whereas this was not found in urban and background soils, nor in plants from the background sites. It was also found that pH values of urban and background soils were different (on average, 6 for unpolluted sites and 7 for city). Karasawa *et al.* (1994), showed that increase of pH values of soil from 4 to 7 promotes significant increase in ammonium uptake by rice cells. The variations in soil pH probably led to a change in europium mobility and thus to increased europium accumulation in plant tissues, even though

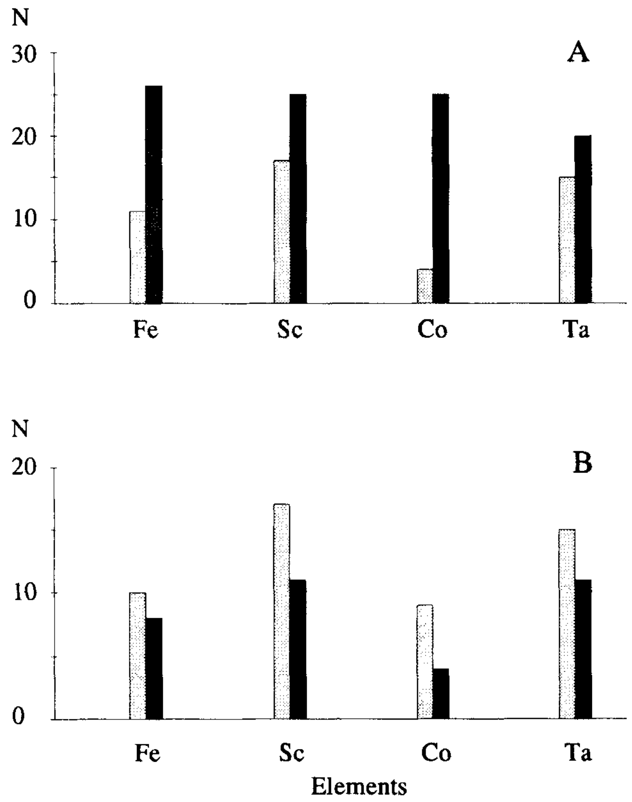

Figure 5 Number (N) of statistically significant correlation relationships ($P < 0.05$) between some individual elements (Fe, Sc, Co, Ta) and all other elements studied in plants (a) and soils (b). Light-coloured rectangles – background samples, dark-coloured rectangles – urban samples.

the small variation in pH in soils did not cause a difference in the europium content of the soils.

CONCLUSIONS

It may be concluded from this study that

1. Chemical element concentrations in plants are not constant. The variations in their element composition under stable conditions have a cyclic nature due to the rhythm of different biochemical processes. Contamination of the environment by some chemicals also leads to variation in the element concentrations of plant tissues. Plants appear to be more sensitive to changes in environmental status than are soils.
2. It is reasonably safe to suggest that all elements are important to the normal function of plants, and that their relationships must be reasonably constant for normal plant function.

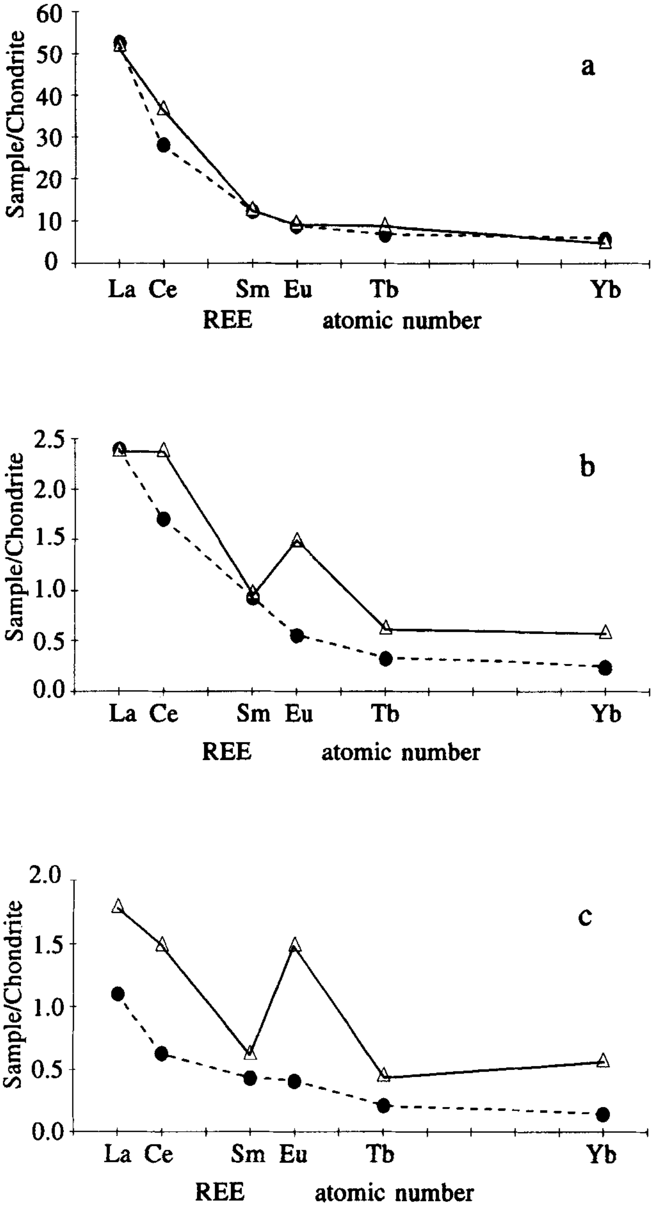

Figure 6 Chondrite normalized REE data for soils (a), roots (b) and leaves (c) of plantain from city (solid line) and background (dashed line) sites.

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