Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 177, No. 2 (1994) 381–391

VARIATION OF THE ELEMENTAL COMPOSITION OF PLANTS AND SOILS

I. V. SHTANGEEVA

Institute of Earth Crust, St. Petersburg State University, St. Petersburg (Russia)

(Received July 13, 1993)

INAA with thermal and epithermal irradiation has been applied for determination of 40 chemical elements in soils and different organs of plants. The time and spatial variations of elemental composition of plants and soils are studied.

At present, neutron-activation analysis (NAA) seems to be one of the most promising analytical techniques for solving ecological and biological problems. In recent years NAA has been widely used for determination of trace elements in different biological samples.[1–8] There are relatively few data available in the literature on variations of elemental composition in plants and soils with time. Several authors have studied season variations of contents of trace elements in plants.[9–11] 24-hour variation of K in plants was reported.[12]

Unfortunately, in many publications of trace element analysis a number of parameters of the sampling procedure such as time and date of sample collection, species and organs of plants studied, etc., are not listed or are described only very briefly. Considerable variations should be expected of plants, which are caused mainly by vital functions of plants themselves.

Experimental

For a detailed investigation of element distribution two plants widely spread in Europe and Asia have been chosen: couch grass (Elytrigia repens) and plantain (Plantago major). In addition, the growing soil was also sampled. The sampling of the plants and soils (from the horizons 0–5 cm) was caried ot during some vegetation seasons (from April to November) on different sites both in an industrial city (St. Petersburg) and in sufficiently ecologically clean zones (forests and parks far away from the city).

Samples were collected as carefully as possible to avoid contamination from the environment. At least two plants of every species were sampled at each site. The plants were carefully washed to remove dust and soil particles and dried at room temperature.

Elsevier Sequoia S. A., Lausanne
Akadémiai Kiadó, Budapest

Ashing was not performed, the plants and soils were analyzed in their natural state. Each plant was divided into roots, leaves, seeds and stems below the seeds, and packed in paper bags. The time and weather conditions during sampling were noted. Total number of plants studied was about 500 and the number of soils sampled was more than 80.

The analysis of elemental composition was performed by means of INAA. 4 multielemental standards were used for calculations of element concentrations: Granite (AGV–1), Basalt (BCR–1) and Russsian standards – RZS–3 and SBMT–01 (biological material). Corrections for spectral interferences were introduced in all necessary cases.

The samples and standards were placed in ampoules made of extrapure quartz (the latter having impurities concentrations several orders less than in the samples studied) and were irradiated for 2–3 days in a nuclear reactor at a neutron flux density of 10^{14} n $\cdot$ cm^{-2} $\cdot$ s^{-1}. Thermal and epithermal irradiation were applied. Measurements were carried out several times with two detectors. After 4 and 30 days of cooling the irradiated samples were analyzed by a Ge(Li) detector (volume 21 cm^3, resolution 2.1 keV for 1332 keV) and after 7–10 days of cooling – by hyperpure germanium detector (volume 60 mm^3, resolution 0.35 keV for 122 keV).

Statistical error of determination of elements in plant samples was < 5% for Na, K, Sc, Cr, Fe, Co, Zn, Br, Rb, Ba, La, Sm, Eu, Hf, Au and U; < 10% for Ca, As, Sr, Mo, Ag, Cd, Sb, Cs, Ce, Tb, Yb, Ta, W, Hg and Th; < 15–20% for Ni, Se, Zr, Sn, Nd, Gd, Tm, Lu and Ir. Concentrations of chemical elements in soils are usually higher than those in plants. Therefore, statistical errors of determination of elements in soils in most cases are lower than those in plants (perhaps except for Au).

Results and discussion

The elements investigated, the nuclides induced, the measured γ-energy and detection limits in soils and plants are listed in Table 1. The INAA results for the soils and different organs of plants are presented in Tables 1, 2 and 3.

It was found that concentrations of the absolute majority of elements studied in plants are lower than those in soil. A considerable number of elements are rather unevenly distributed in different organs of couch grass and plantain. For example, roots are enriched in many chemical elements in comparison with other organs. On the other hand, seeds and stems below the seeds are depleted in some elements as compared with roots and leaves. In many cases, stems and seeds are characterized by low variations in concentrations of these elements too. Thus, plants obviously possess certain defence mechanisms which prevent excessive heavy metals from penetrating generative and especially reproductive organs.

Table 1
INAA of chemical elements in soils, ppm

Element	Induced nuclide	Gamma-energy, keV	Detection limit in plants	Detection limit in soils	Mean ± S.D.
Na%	^{24}Na	1368.5	0.0002t	0.01e	1.3 ± 0.5
K%	^{42}K	1524.7	0.02t	1.0e	1.9 ± 0.6
Ca%	^{47}Ca	1297.1	0.1t	0.1e	2.8 ± 0.9
Sc	^{46}Sc	889.3	0.004t	0.03t	4.1 ± 1.7
Cr	^{51}Cr	320.1	0.1e	1.3e	5.7 ± 1.9
Fe%	^{54}Mn	834.8	0.003t	0.09e	1.2 ± 0.4
	^{59}Fe	1099.2	0.009t	0.02e	
Ni	^{58}Co	810.8	0.3t	1.8e	8.7 ± 3.0
Co	^{60}Co	1332.5	0.01t	0.07e	3.7 ± 1.3
Zn	^{65}Zn	1115.5	0.3t	1.2t	48.2 ± 15.6
As	^{76}As	559.1	0.05t	0.9e	5.1 ± 1.8
Se	^{75}Se	121.1*	0.02e	0.2e	0.8 ± 0.3
Br	^{82}Br	619.1	0.3e, t	0.9e	6.0 ± 2.0
Rb	^{86}Rb	1076.6	1.3e	4.7e	96.5 ± 34.9
Sr	^{85}Sr	514.0	5.0t	35.0e	155 ± 63
Zr	^{95}Zr	756.7	1.7t	9.7e	267 ± 86
Mo	^{99}Mo	140.5*	0.04t	0.3e	1.0 ± 0.3
Ag	^{110m}Ag	657.8	0.01t	0.05e	0.38 ± 0.18
Cd	^{115}Cd	336.2	0.,003t	0.5e	3.7 ± 3.6
Sn	^{115m}In	336.3	0.2t	0.3t	3.3 ± 0.9
Sb	^{124}Sb	1691.0	0.01e	0.04e	0.71 ± 0.68
Cs	^{134}Cs	795.8	0.03e, t	0.1e, t	1.7 ± 0.5
Ba	^{131}Ba	123.8*	2.9t	8e	571 ± 230
		496.3	4t	25e	
La	^{140}La	1596.5	0.02t	0.4e	23.2 ± 11.8
Ce	^{141}Ce	145.4*	0.4t	1.4t	32.1 ± 12.7
		145.4	3.0t	1.7t	
Nd	^{147}Nd	91.1*	0.1t	2.0t	14.9 ± 13.4
		531.0	0.6t	4.7e	
Sm	^{153}Sm	103.2*	0.003t	0.01e	3.3 ± 1.9
		103.2	0.005t	0.02e	
Eu	^{152}Eu	1408.0	0.005t	0.009t	0.84 ± 0.36
	^{154}Eu	1274.5	0.008t	0.1e, t	
Gd	^{153}Gd	97.4*	0.2e	0.6e	2.5 ± 1.2
Tb	DyK1	46.0*	0.003e	0.02e	0.44 ± 0.21
	^{160}Tb	879.3	0.007t	0.06e	
Tm	YbK1	52.4	0.001t	0.01e	0.009 ± 0.003
Yb	^{169}Yb	63.1*	0.004t	0.06e	1.5 ± 0.6
	^{175}Yb	396.3	0.8e	0.7t	
Lu	^{177}Lu	208.4	0.004t	0.03e	0.10 ± 0.05
Hf	^{181}Hf	482.2	0.02t	0.3e	5.4 ± 2.2
Ta	^{182}Ta	1221.4	0.006t	0.03e	0.55 ± 0.24

Table 1 (cont.)

Element	Induced nuclide	Gamma-energy, keV	Detection limit in plants	Detection limit in soils	Mean ± S.D.
W	^{187}W	685.7	0.002t	0.25e	3.2 ± 1.3
Ir**	^{192}Ir	468.1	0.3t	0.1t	2.0 ± 0.8
Au	^{198}Au	411.8	0.001t	0.003e	0.010 ± 0.006
Hg	^{197}Hg	77.4*	0.02t	0.05e	2.0 ± 0.8
	TlKl	72.9*	0.008t	0.3e	
Th	^{233}Pa	311.8	0.01t	0.09e	6.8 ± 3.1
U	^{239}Np	106.1*	0.02t, e	0.05e	1.7 ± 0.8

t – thermal irradiation.
e – epithermal irradiation.
*Isotope was measured on a hyperpure germanium detector.
**Concentrations expressed as ppb (ng/g).

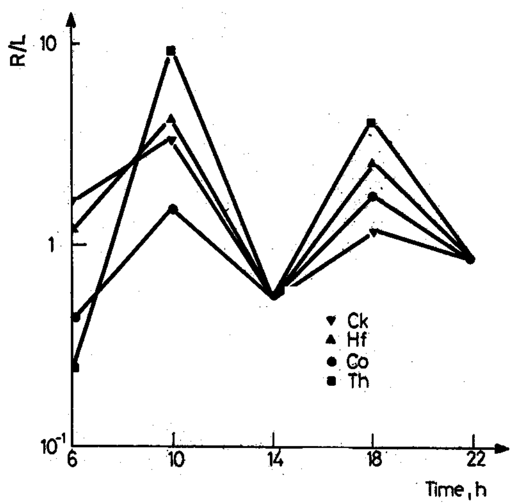

Fig. 1. Variation of the ratio of concentrations of chemical elements in roots (R) to those in leaves (L) for couch grass, sampled on May 1, 1987

Concentrations of chemical elements in plants and soil vary, especially in time. In our work short and long term variations of the elemental composition of plants and soils are studied. Samples of couch grass, plantain as well as their growing soil were collected for a certain period every four hours. Variations of the concentration ratios of elements in roots and in leaves for couch grass sampled on May 1, 1987, are shown in

Table 2
Trace element mean concentrations ± SD in couch grass, ppm

Element	Roots	Leaves	Seeds	Stems below the seeds
Na%	0.14 ± 0.14	0.06 ± 0.02	0.075 ± 0.021	0.032 ± 0.017
K%	1.2 ± 0.5	3.0 ± 1.2	1.7 ± 0.7	2.0 ± 1.2
Ca%	0.61 ± 0.32	0.71 ± 0.20	0.7 ± 0.2	0.55 ± 0.30
Sc	0.33 ± 0.14	0.14 ± 0.07	0.13 ± 0.05	0.11 ± 0.04
Cr	8.9 ± 2.9	3.3 ± 1.2	2.7 ± 0.8	2.2 ± 0.5
Fe	2530 ± 2500	762 ± 280	436 ± 141	363 ± 150
Ni	1.4 ± 0.6	0.9 ± 0.3	1.0 ± 0.4	
Co	1.5 ± 1.2	0.8 ± 1.8	1.1 ± 0.4	0.7 ± 0.3
Zn	115 ± 100	53 ± 22	68 ± 28	40 ± 13
As	2.5 ± 1.8	1.0 ± 0.4	0.57 ± 0.26	0.89 ± 0.32
Se	0.2 ± 0.1	0.1 ± 0.1	0.06 ± 0.05	0.03 ± 0.02
Br	7.2 ± 3.0	8.0 ± 5.9	2.9 ± 0.8	4.7 ± 2.1
Rb	21.7 ± 7.3	24.6 ± 8.9	25.7 ± 11.8	23.8 ± 7.9
Sr	126 ± 208	71.8 ± 20.0	100 ± 19	71.3 ± 30.6
Zr	32.1 ± 29.2	25.0 ± 20.7	42.8 ± 8.7	25.9 ± 12.5
Mo	0.56 ± 0.26	0.37 ± 0.12	0.24 ± 0.12	0.31 ± 0.16
Ag	0.50 ± 0.18	0.28 ± 0.08	0.24 ± 0.09	0.21 ± 0.10
Cd	2.33 ± 1.46	1.41 ± 0.76	1.36 ± 0.44	1.05 ± 0.34
Sb	0.71 ± 0.33	0.43 ± 0.18	0.42 ± 0.20	0.38 ± 0.14
Cs	0.26 ± 0.11	0.11 ± 0.06	0.13 ± 0.05	0.18 ± 0.08
Ba	93.5 ± 47.2	81.2 ± 21.0	50.8 ± 19.3	51.0 ± 23.0
La	3.1 ± 1.1	0.87 ± 0.30	0.56 ± 0.24	0.36 ± 0.09
Ce	2.5 ± 1.0	1.1 ± 0.5	1.4 ± 0.5	3.3 ± 11.6
Nd	12.4 ± 6.0	7.5 ± 3.2	6.3 ± 2.4	4.8 ± 1.3
Sm	0.97 ± 0.52	0.21 ± 0.08	0.08 ± 0.02	0.06 ± 0.02
Eu	0.15 ± 0.07	0.12 ± 0.03	0.11 ± 0.04	0.14 ± 0.05
Tb	0.08 ± 0.03	0.05 ± 0.02	0.05 ± 0.02	0.05 ± 0.02
Yb	0.15 ± 0.12	0.10 ± 0.08	0.07 ± 0.02	0.07 ± 0.04
Lu	0.06 ± 0.03	0.04 ± 0.01	0.03 ± 0.01	
Hf	0.42 ± 0.13	0.29 ± 0.11	0.19 ± 0.06	0.11 ± 0.04
Ta	0.09 ± 0.03	0.05 ± 0.02	0.04 ± 0.02	0.03 ± 0.01
W	0.17 ± 0.15	0.09 ± 0.02	0.08 ± 0.06	0.03 ± 0.02
Ir*	6.0 ± 3.9	4.0 ± 2.3	3.8 ± 1.1	
Au	0.14 ± 0.13	0.07 ± 0.08	0.02 ± 0.01	0.04 ± 0.02
Hg	0.54 ± 0.61	0.14 ± 0.40	0.17 ± 0.22	
Th	0.33 ± 0.14	0.15 ± 0.13	0.13 ± 0.03	0.09 ± 0.03
U	0.51 ± 0.25	0.13 ± 0.05	0.19 ± 0.10	0.08 ± 0.03

*Concentrations expressed as ppb (ng/g).

Table 3
Trace element mean concentrations ± SD in plantain, ppm

Element	Roots	Leaves	Seeds	Stems below the seeds
Na%	0.098 ± 0.029	0.050 ± 0.009	0.031 ± 0.004	0.021 ± 0.002
K%	2.1 ± 0.7	3.4 ± 1.4	1.6 ± 0.3	1.8 ± 0.8
Ca%	0.71 ± 0.34	1.84 ± 0.63	0.74 ± 0.56	0.55 ± 0.21
Sc	0.33 ± 0.13	0.19 ± 0.04	0.13 ± 0.06	0.08 ± 0.03
Cr	3.5 ± 1.4	2.2 ± 1.1	1.8 ± 0.8	1.4 ± 1.0
Fe	921 ± 223	586 ± 230	421 ± 178	303 ± 80
Ni	0.81 ± 0.30	0.91 ± 0.51	1.3 ± 0.5	2.6 ± 0.5
Co	0.77 ± 0.35	0.35 ± 0.10	0.74 ± 0.70	0.45 ± 0.02
Zn	68 ± 136	60 ± 50	39 ± 13	30 ± 24
As	1.8 ± 1.2	0.75 ± 0.38	0.51 ± 0.04	0.31 ± 0.05
Se	0.29 ± 0.20	0.2 ± 0.1	0.22 ± 0.15	0.06 ± 0.04
Br	3.4 ± 1.4	5.4 ± 1.7	1.8 ± 1.0	1.6 ± 0.4
Rb	19.7 ± 6.6	20.3 ± 6.8	21.1 ± 10.4	15.2 ± 5.5
Sr	73.6 ± 40.5	106 ± 50	60.3 ± 26.4	60.4 ± 20.0
Zr	23.4 ± 8.2	15.0 ± 6.9	25.0 ± 5.5	21.4 ± 12.1
Mo	0.36 ± 0.11	0.32 ± 0.12	0.22 ± 0.04	0.17 ± 0.06
Ag	0.4 ± 0.1	0.25 ± 0.11	0.18 ± 0.08	0.12 ± 0.05
Cd	1.7 ± 1.7	1.5 ± 0.5	0.96 ± 0.39	0.89 ± 0.54
Sb	0.51 ± 0.16	0.43 ± 0.15	0.33 ± 0.22	0.18 ± 0.05
Cs	0.18 ± 0.10	0.12 ± 0.04	0.12 ± 0.04	0.11 ± 0.04
Ba	92.6 ± 25.0	87.8 ± 34.0	41.7 ± 15.0	44.7 ± 11.1
La	1.8 ± 1.7	0.78 ± 0.23	0.03 ± 0.74	0.38 ± 0.11
Ce	2.0 ± 0.8	2.0 ± 1.7	4.7 ± 1.8	4.4 ± 1.3
Nd	7.4 ± 4.0	6.8 ± 4.6	3.9 ± 1.5	2.4 ± 0.2
Sm	0.38 ± 0.12	0.21 ± 0.15	0.14 ± 0.06	0.04 ± 0.02
Eu	0.12 ± 0.07	0.13 ± 0.07	0.07 ± 0.04	0.06 ± 0.02
Tb	0.06 ± 0.04	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
Yb	0.07 ± 0.05	0.07 ± 0.03	0.08 ± 0.03	0.06 ± 0.02
Lu	0.04 ± 0.02	0.04 ± 0.02	0.05 ± 0.04	
Hf	0.37 ± 0.23	0.23 ± 0.16	0.29 ± 0.07	0.07 ± 0.03
Ta	0.05 ± 0.02	0.03 ± 0.01	0.03 ± 0.01	0.04 ± 0.01
W	0.05 ± 0.02	0.08 ± 0.07	0.08 ± 0.03	0.03 ± 0.01
Ir*	2.9 ± 1.7	4.0 ± 4.1	4.1 ± 2.0	
Au	0.04 ± 0.06	0.03 ± 0.01	0.020 ± 0.005	0.04 ± 0.02
Hg	0.56 ± 0.51	0.16 ± 0.05	0.15 ± 0.05	
Th	0.33 ± 0.16	0.27 ± 0.24	0.22 ± 0.05	0.11 ± 0.04
U	0.21 ± 0.05	0.34 ± 0.06	0.33 ± 0.03	0.05 ± 0.01

*Concentrations expressed as ppb (ng/g).

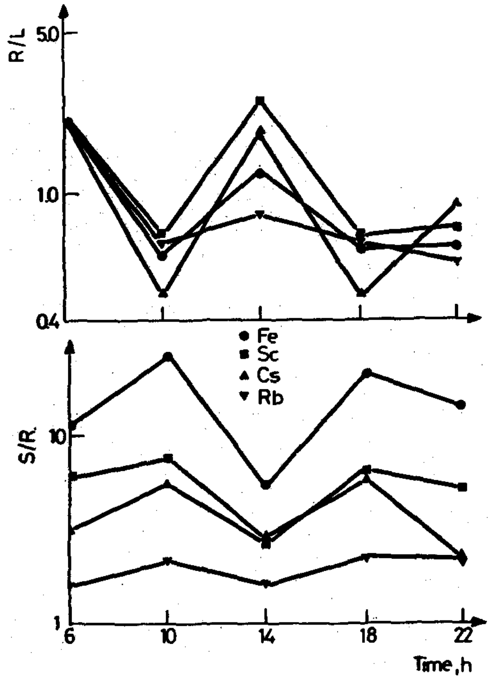

Fig. 2. Variation of the ratio of R/L and S/R for plantain, sampled on May 1, 1987

Fig. 1. Figure 2 shows the dynamics of concentration ratios of chemical elements in roots to those in leaves for plantain sampled on May 1, 1987.

The following conclusions can be drawn from these figures.

(1) A regular redistribution of chemical elements between roots and leaves occurs during the day.

(2) Plantain and couch grass sampled at the same place and at the same time behave differently.

(3) For each species studied and for most of the elements studied the R/L ratio observed at a particular time remains constant. For example, for plantain sampled at 6.00 the ratio $R/L = 2.43$. For couch grass sampled at 14.00 the ratio $R/L = 0.66$, and for the couch grass ampled at 22.00 the ratio $R/L = 1.27$.

Variations of the ratio of concentrations of chemical elements in soil to those in roots for plantain are shown in Fig. 2. It appears that the higher the S/R value, the lower the R/L ratio and vice versa. In addition, the lowest S/R ratios for every sampling day are observed at 14.00. Thus, it may be supposed that the redistribution of chemical elements between soil and different organs of plants is caused mostly by changes of the Sun's activity.

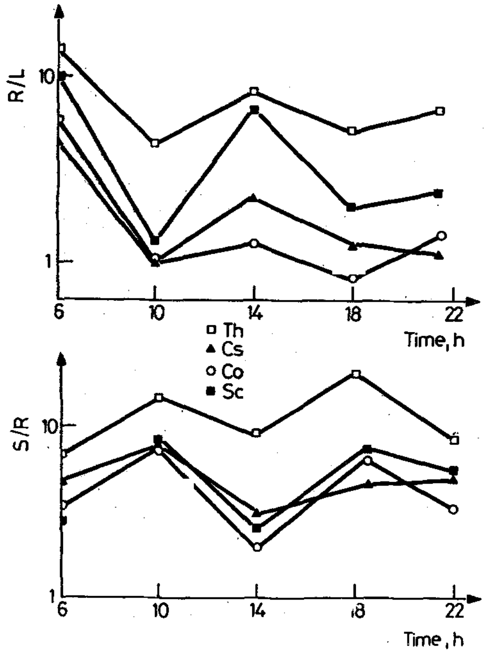

Fig. 3. Variation of the ratios of *R/L* and *S/R* for couch grass, sampled on May 24, 1987

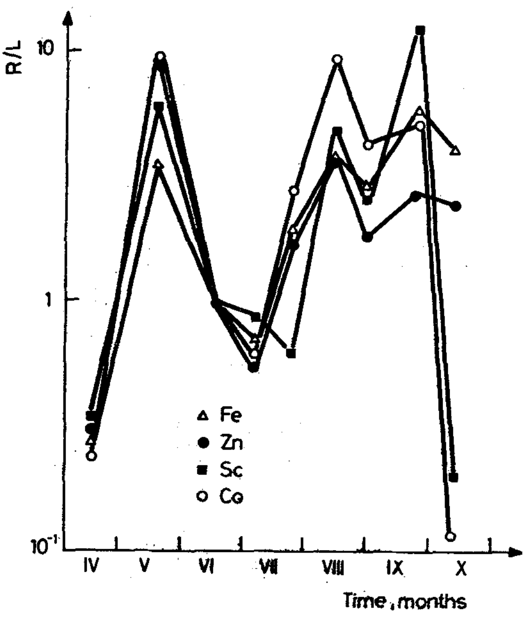

Fig. 4. Variation of the ratio of *R/L* for couch grass, sampled during 1988

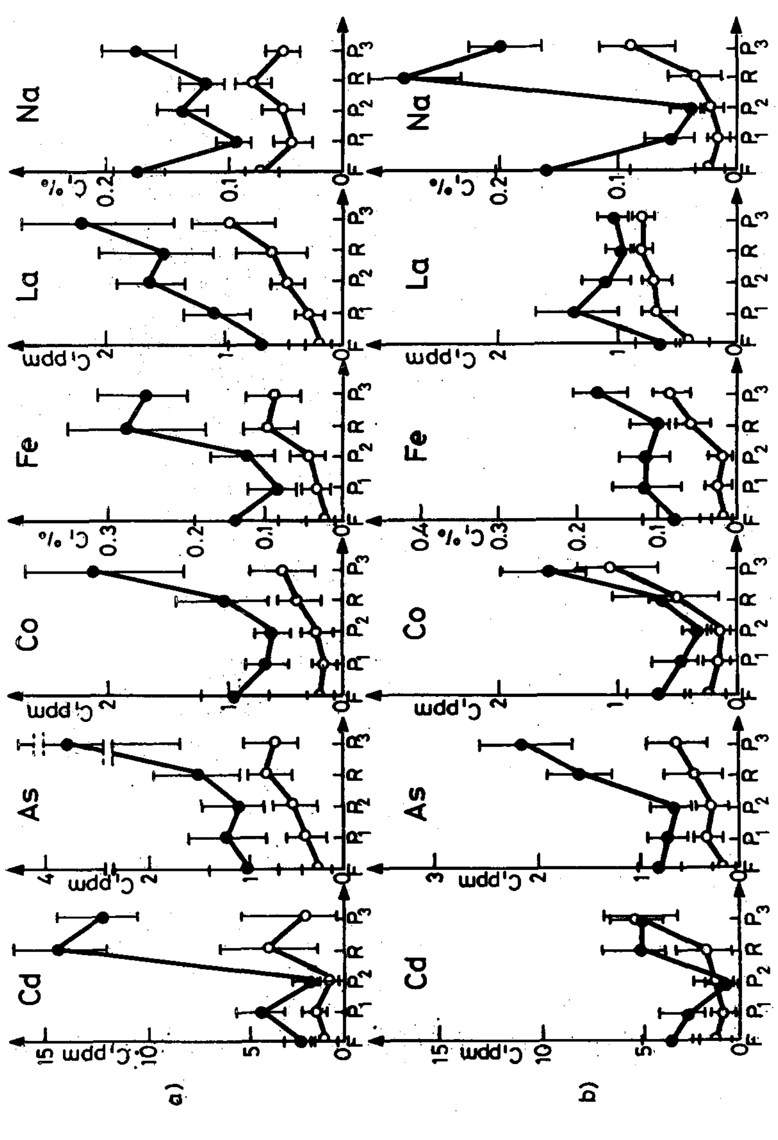

Fig. 5. Distribution of mean concentrations of chemical elements in samples of couch grass (a) and plantain (b), collected in forest (F), parks of Pushkin (P1) and Pavlovsk (P2), near the roads (R) and industrial enterprises (P3)

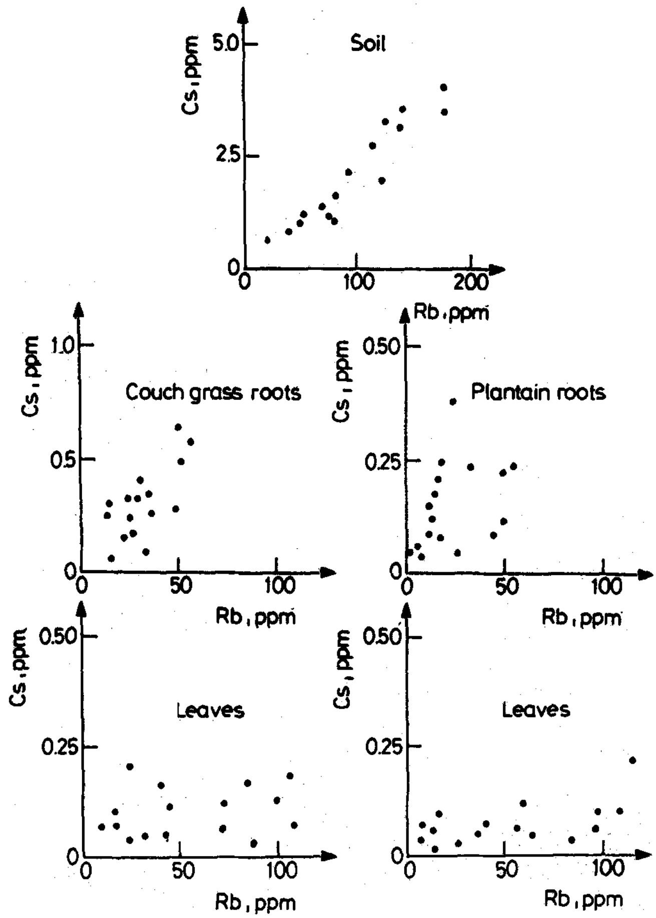

Fig. 6. Distribution of Rb and Cs in different samples. *R* – roots, *L* – leaves

A regular redistribution of elements between roots and leaves and between roots and soil was also observed for different days of sampling. Variations of the *R*/*L* and *S*/*L* ratio for couch grass sampled on the May 24, 1987, are presented in Fig. 3. Although the time of sampling remained the same, there are some differences between Fig. 1 and Fig. 3 observed due to the change of weather conditions, the Sun's activity and certain reduction of physiological activity of the plants.

In our work the observations for long period variations of concentrations of chemical elements in plants and soils were carried out for two years on the same site. Variations of elemental composition, especially in roots, were more expressed for the warm and dry 1988, than for the cool and rainy 1987. The dynamics of *R/L* ratio for couch grass sampled during 1988 is shown in Fig. 4.

Variations of elemental composition of plants sampled on different sites were studied too. The distribution of mean concentrations of elements in plantain and couch grass sampled in a forest, in suburban parks of Pushkin and Pavlovsk and in the vicinity of motor roads and industrial enterprises are represented in Fig. 5.

The following conclusions can be drawn from this figure. First, it is clear that concentrations of chemical elements in plants sampled near the roads and factories are higher than those in the relatively ecologically clean zones. And secondly, the concentrations of the majority of elements in the roots are higher than those in the leaves. It is typical both for toxic trace elements like Cd, As, etc., and for many other elements.

Figure 6 illustrates the distribution of Rb and Cs in the samples of soils, roots and leaves of plantain and couch grass. One may notice a strong correlation between Rb and Cs in soil. Sufficiently strong correlation between Rb and Cs in roots of plantain and couch grass is obvious, too. However, in leaves of plants the correlation between Cs and Rb is absent. Thus, it may be supposed that chemical elements in roots and leaves of plants play different roles.

Conclusions

INAA has been used to determine the distribution of forty chemical elements in soil and different organs of couch grass and plantain. The variations of elemental composition were studied. In the system soil-roots-generative organs-reproductive organs a regular redistribution of separate elements takes place, mostly due to photosynthetic and reproductive processes.

References

1. R. W. JENKINS, H. J. GRUBBS, R. H. NEWMAN, R. T. BASS, J. S. BRENISER, D. C. JONES, T. G. WILLIAMSON, D. A. DANEHOWER, R. C. LONG, J. Radioanal. Nucl. Chem., 113 (1987) 477.
2. J. CAPLAN, E. LOBERSLI, R. NAEUMANN, E. STEINNES, J. Radioanal. Nucl. Chem., 114 (1987) 13.
3. I. L. SZIKLAI, M. ÖRDÖGH, E. MOLNÁR, E. SZABÓ, J. Radioanal. Nucl. Chem., 122 (1988) 233.
4. S. BAJO, A. WYTTENBACH, L. TOBLER, H. CONRADIN, J. Radioanal. Nucl. Chem., 134 (1989) 181.
5. L. TRAN VAN, D. K. TEHERANI, J. Radioanal. Nucl. Chem., 135 (1989) 443.
6. F. D. BUSHE, J. Geoch. Exp., 32 (1989) 199.
7. C. E. DUNN, G. E. M. HALL, E. HOFFMAN, J. Geoch. Exp., 32 (1989) 211.
8. M. Z. IQBAL, M. A. QADIR, J. Radioanal. Nucl. Chem., 145 (1990) 189.
9. B. MAKERT, Anal. Chem., 333 (1989) 11.
10. J. D. STEDNICK, W. C. RIESE, J. Geoch. Exp., 27 (1987) 53.
11. N. H. BRUNDIN, J. I. EK, O. C. SELENUS, J. Geoch. Exp., 27 (1987) 157.
12. J. H. WILLS, Biol. Plant., 29 (1987) 221.