Journal of Radioanalytical and Nuclear Chemistry, Vol. 231, Nos 1–2 (1998) 101–106

Variation of the rare earth element concentrations in the soil, soil extract and in individual plants from the same site

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(Received November 21, 1997)

Samples of various types (spruce needles, blackberry leaves, soils, and soil extracts) have each been taken at 6 places from the same site. In addition, 4 whirls each from 2 spruce trees were sampled. Rare earth elements (REEs) were determined in these samples by neutron activation analysis with a chemical group separation. Variations between places were found to be small with soils and soil extracts, but large with plants. Variations between whirls were small. Plants neither reflected the soil nor the soil extract. Both plant species were dissimilar, but the logarithm of their ratio was a linear function of the atomic number of the REE. A negative Ce anomaly (with respect to soil) was found in both plant species.

Introduction

In previous work[1] we investigated the concentrations of REEs in needles of 6 individual spruce trees from the same site and in the soils in which these trees were growing. Results indicated: (a) small variations between the 6 soils, (b) large variations between the 6 spruce trees, (c) uniform distribution patterns of the REEs in the soils, identical to that in the upper continental crust, (d) nonuniform distribution patterns in the trees and large differences between the trees and the soil.

These results indicate a regular behaviour of the soils and a somewhat irregular behavior of the trees. Different concentrations of trace elements in individual plants from a given site are usually found,[2] and different distribution patterns of the REEs in plants and soil (equivalent to a fractionation between the plant and soil) have been reported before.[3,4] However, different distribution patterns among individual plants of the same species, growing on a uniform soil, were unexpected and show that plants do not take up the various REEs as equal members of a chemically homogeneous series. Such differences have never been reported before.

In order to obtain more information on these effects, the present work reports the following additional investigations:

I. The soil samples referred to above were extracted in order to see if the variations between trees were due to a different extractability at the various places.
II. Leaves of blackberry plants were sampled close to the 6 trees in order to test if they show the same nonuniformity as the trees.
III. Four different whirls of 2 trees were each sampled to test the variability within trees.

Experimental

Sampling area

Site characteristics of the sampling area at Chanéaz (Switzerland) and soil properties are given in Reference 1. On this site 6 places, each with an area of 10 m^2 and containing one spruce tree, were defined; sampling was restricted to these places.

Soil extraction

Aliquots of the 6 soil samples analyzed previously for total REE concentrations were extracted with the Lakanen solution[5] (0.5M acetic acid, 0.5M NH_4-acetate, 0.02M EDTA, pH 4.65) in order to estimate "available" levels. 1 g of soil was shaken twice with 10 ml solution for 1 hour. The 2 extracts were combined and taken to dryness.

In addition, 1 g samples from 3 horizons of a soil profile were extracted twice with 10 ml water. The resulting coloured solutions had a pH of 4.5–4.8, slightly less acid than the soil itself (3.3–3.8).

Plant samples

Needles of age class 5 from Norway spruce trees (*Picea abies*) were collected from 4 whirls (numbers 5, 7, 9 and 11) of 2 previously analyzed trees. Blackberry leaves (*Rubus fruticosus*) were collected at a distance less than 2 m from the 6 trees; 1 sample was subsequently lost during analysis. Plants were collected during the dormant season. Aerosols on plant surfaces were carefully removed prior to the drying of the plant samples.[2]

0236–5731/98/USD 17.00

Elsevier Science B. V., Amsterdam
Akadémiai Kiadó, Budapest

Table 1. REEs extracted with Lakanen solution from the soil from 6 places. Results are given as ng REE extracted from 1 g of dry soil

Place	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
I	1918	3611	1937	484	96	71	172	19
II	1826	3513	1653	428	85	66	137	14
III	1721	3013	1716	442	89	61	149	15
IV	2137	3754	1972	494	99	76	162	17
V	1730	2963	1601	423	87	70	140	14
VI	1940	3693	1906	484	99	78	149	16
Mean:	1879	3425	1798	459	92	70	152	16

Table 2. REEs extracted with water from different horizons of a soil profile. Results are given as ng REE extracted from 1 g of dry soil

Horizon*	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Ah	25	53	33	9	1.7	1.3	4.1	0.3
B	78	160	124	31	6.4	4.7	15.7	1.9
Sw	53	106	92	24	4.6	3.3	13.2	1.7

* These samples were taken at a soil depth of (0–5), (5–20), and (20–50) cm.

Table 3. REE concentrations (ng/g d.w.) in leaves of blackberry plants from 5 places. The sample from place II was lost during analysis

Place	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Ce-anomaly*
I	362	237	116	17.5	3.15	2.48	4.00	0.464	0.44
III	244	128	112	22.8	4.63	3.54	4.24	0.500	0.31
IV	270	158	114	21.9	4.52	3.29	3.94	0.507	0.37
V	565	276	288	55.7	11.43	7.87	9.05	1.146	0.28
VI	237	126	75	16.1	3.59	2.59	3.83	0.509	0.37
Mean:	336	185	141	26.8	5.46	3.95	5.01	0.625	0.34

* The Ce anomaly is expressed relative to the soil at each place. It is expressed as CR1(Ce)/CR1(Ce*), where CR1 = plant/soil. CR1(Ce) is the value actually found. CR1(Ce*) is the value expected from interpolation between La and Nd; it is given by $(CR1(La)^2 \times CR1(Nd))^{1/3}$.

Table 4. REE concentrations (ng/g d.w.) in needles of age class 5 from different whirls of 2 Norway spruce trees

Place	Whirl	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
IV	5	73.7	63.4	58.9	15.6	3.60	3.80	9.81	1.15
	7	73.8	63.5	54.4	15.0	3.46	3.89	9.03	1.08
	9	71.9	61.6	57.8	14.6	3.26	3.73	9.30	1.18
	11	73.1	62.4	62.0	15.4	3.37	3.68	9.06	1.15
Mean:		73.1	62.7	58.3	15.1	3.42	3.77	9.30	1.14
VI	5	98.3	70.5	73.3	19.2	4.35	4.65	8.95	1.11
	7	89.4	63.4	61.8	16.7	3.82	3.85	7.80	0.95
	9	90.0	65.0	63.7	17.2	3.93	4.06	8.56	1.07
	11	99.4	70.5	73.4	19.4	4.33	4.51	8.69	1.13
Mean:		94.3	67.3	68.0	18.1	4.11	4.26	8.50	1.06

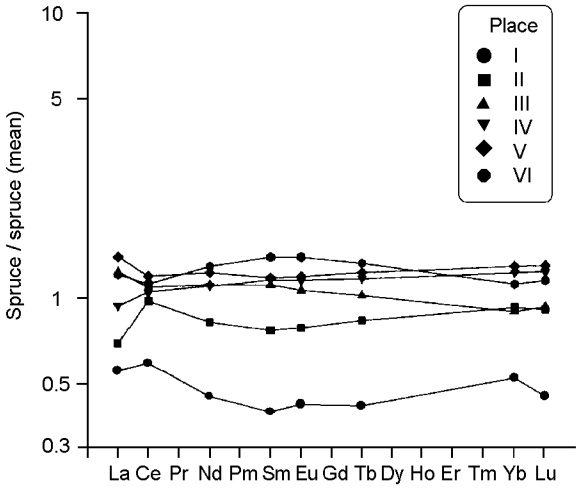

Fig. 1. Normalized values for REE concentrations in needles of 6 individual spruce trees. The numerical values and the system mean, which is used for normalization, are given in Table 2 of Ref. 1. ANOVA results for this system are given here in Table 5

Table 5. Analysis of variance (ANOVA) of REE concentrations in soils, soil extracts, and plants

System*	*k*	*N*	Variability (CV), %	
			Between groups	Within groups
A soil	6	48	3.7	2.7
B soil extracts	6	48	7.7	4.2
C spruces	6	48	29.7	9.4
D blackberries	5	40	49.4	15.3
E whirls	8	64	4.6	2.4

* System designation is A: soils (total concentrations), B: soil extracts with Lakanen solution, C: individual spruce trees (needles), D: blackberries (leaves), each at *k* places. System E is 4 whirls each from 2 spruce trees (needles).

The number *n* of elements per group is 8 in all systems (La, Ce, Nd, Sm, Eu, Tb, Yb, Lu), and the total number of observations *N* is $n \cdot k$.

Analysis

Analysis of the REEs was done by neutron activation analysis with a chemical group separation. Methods, precision and accuracy were as given in Reference 1. Water extracts were analyzed by ICP-MS.[6]

Results

Concentrations

Analytical results for Norway spruce needles (age class 5) and for the soils are given in Reference 1. Results for soil extracts are given here in Tables 1 and 2, for blackberry leaves in Table 3, and for the different whirls of spruce trees in Table 4. The numbering of the 6 places in these tables is the same as in Reference 1. Means are arithmetic.

Variation between places

Soils, soil extracts, spruce needles and blackberry leaves (called systems) each show some variation of their REE concentrations between places. This is due (1) to the variation of all REEs as a uniform entity between places and (2) to the deviation of the individual REEs from the general behavior of all REEs. One way analysis of variance (ANOVA)[7] was used to separate these 2 contributions. Input values for ANOVA were the different places as the independent variable (or groups) and the normalized REE concentrations as the dependent variable. Normalization of every REE was conducted using its mean value in the system considered; means are given in the respective tables. As an example, Fig. 1 shows the input values for the system "spruce needles". Both the variation of the REEs as an entity (the variation between groups) and the deviations of the individual REEs (the variation within groups) are clearly visible. Results of ANOVA for all systems are given in Table 5.

Variation between whirls

Variations between whirls were evaluated by ANOVA in the same way as those between places, but using the whirl number as the independent variable. Both trees were treated separately. As their results were similar, only pooled results are given in Table 5.

Discussion

Variability of the various systems

Table 5 shows that the variability of the soil (both between and within groups) is very small and close to the analytical precision, pointing to a large uniformity of the soil at the investigated site. In contrast to this a large variability is found with plants, both with spruce and with blackberry. In plants, the variation between groups is connected to the uptake of the REEs as an entity; the large variability found is in agreement with the great variation usually shown by the concentration of trace elements in individual plants of the same species, even when growing on the same site.[2] With plants, the variability within groups is smaller than between groups, but still substantial, showing that the uptake of individual REEs into the plant is not exactly equal, despite their similar chemical properties.

As the small variability of the soil cannot explain the large variability of the plants, it was suspected that the soil at the different places might differ in the extractability of the REEs and thus cause the variation

found between plants. The variation in the soil extracts is indeed somewhat larger than that in the soils, but still much smaller than in plants, thus eliminating extractability as the major source for the variation in plants.

We finally tested the possibility that the plants themselves are not homogeneous by analyzing different whirls from 2 spruce trees. The results, however, show that this is not the case. The variability both between and within groups are very small in this system. As different whirls are equivalent to different transportation lengths between the roots and the needles, and to different microclimatic conditions for the needles, the results indicate that these factors do not entail a separation between the individual REEs.

Whereas the similarity of the chemical properties of REEs leads to the expectation of similar plant uptake behaviour, this does not apply to Ce. In contrast to all other REEs, which in soil solution are trivalent, Ce can occur also as Ce^{4+}, whose uptake by plants will be smaller than that of the trivalent REEs. The ANOVA was therefore repeated by excluding the Ce values. Results for most systems are very similar to those with Ce included. With blackberry, however, the variation within groups becomes considerably smaller; it drops from 15 to 11%, showing that in this case Ce adds considerably to the variation between the individual REEs. But even after exclusion of Ce the variability in plants remains much larger than that in the soils or the soil extracts.

Comparison between soil extracts and the soil

The Lakanen solution (Table 1) extracts about 15% of the REEs present in the soil. This large quantity must be due to the pH and the complexing nature of the extractant. The extracted REEs probably originate from soil components such as Fe-Mn-oxihydroxides. Water alone (Table 2) extracts much smaller quantities, typically less than 1% of the REEs present. With both extractants, however, the extracted percentage depends in the same manner on the REE considered, being a maximum for the medium REEs (Eu, Tb) and a minimum for the end members of the series (La, Lu). The same behavior has been found for a range of acidic ground waters and was attributed to complexation, to solid-liquid exchange reactions and to the dissolution of surface coating on soil components.[8]

Comparison between plants and the soil or the soil extracts

Figure 2 gives the direct comparison between the mean concentration of the 2 plant species and the soil (CR1) or the soil extract (CR2). As these distribution patterns are not straight horizontal lines but very irregular curves, it is evident that both plants do not reflect the composition of the soil in which they grow nor the soil extract. This is equivalent to a fractionation between individual REEs in plants with respect to the soil or the soil extract. It is easily recognized from Fig. 2 that this fractionation can reach quite large values. Although there are some claims of no fractionation in the literature,[9,10] most workers have reached conclusions similar to those here.[3,4]

It may further be seen from Fig. 2 that the concentration of Ce in both plants is less than expected from its neighbour elements, both in comparison with the soil and the soil extract. This effect is called a negative Ce anomaly and is usually defined with respect to the soil only. Its mean value is 0.41 for spruce and 0.34 for blackberry, indicating that only 41% and 34% respectively, of the expected Ce concentrations are actually found. Individual blackberry plants show a considerable variation in their Ce anomaly (Table 3), and this is responsible for the large contribution of Ce to the variation within groups revealed by the ANOVA analysis in this system. Since the negative Ce anomaly is due to the presence of Ce^{4+} in the soil solution, it may be concluded that the various places differ in the ratio of available Ce^{4+} to Ce^{3+}, although the soil seems quite homogeneous. It is further remarkable that the 2 plant species, growing in the same place, have a different Ce anomaly, which therefore seems to be, at least partially, plant specific.

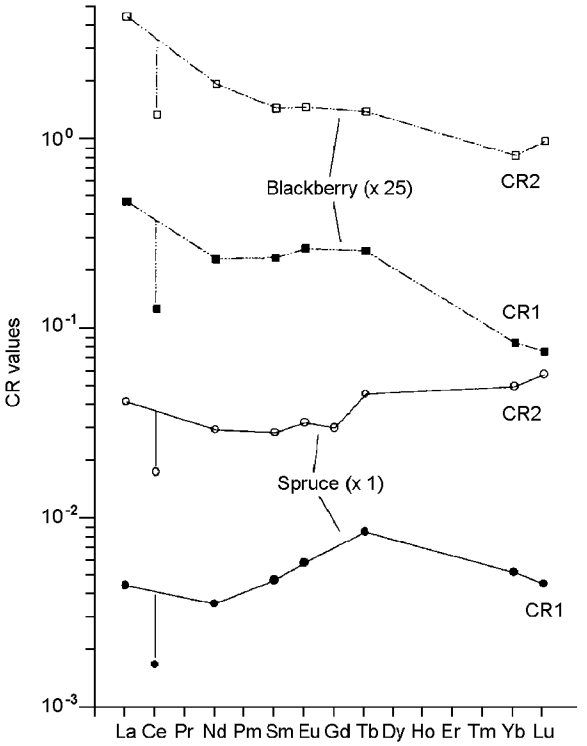

Fig. 2. Comparison between plants and the soil or the soil extracts. Values are normalized REE concentrations of blackberry leaves (squares) and of spruce needles (circles). Normalization is either to the soil (filled symbols, CR1) or to the Lakanen soil extract (open symbols, CR2). Site means were used throughout

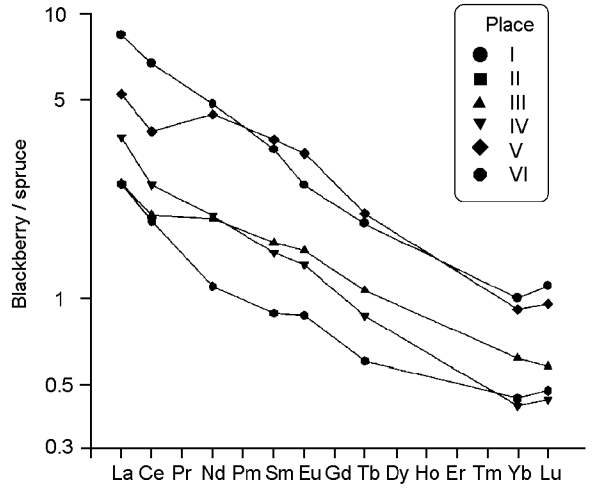

Fig. 3. The ratio of individual blackberry plants to individual spruce trees at the various places. The blackberry sample from place II was lost during analysis

Comparison between the 2 plant species

Figure 3 gives the direct comparison between individual spruce trees and blackberry plants growing in the same places. It is seen that the places have widely separated lines (the range is about a factor of 4), showing that this concentration ratio varies considerably between places. This leads to the conclusion that concentrations in individual plants are not mainly determined by some specific property of the places, but must have other causes.

The distribution patterns in Fig. 3 all show a decrease from the lightest to the heaviest REE about a factor of 6. This is equivalent to a substantial fractionation of light and heavy REEs between the 2 plant species. Since all places roughly show the same pattern, this fractionation seems to be linked to the plants, i.e., to be species specific. The patterns are surprisingly smooth and can indeed be approximated by a linear function of Z, the atomic number of the REE. The average residual standard deviation of the points in a linear regression (a separate one for each place) is only a factor of 1.16, which indicates a rather regular dependence of the individual REEs on their atomic number. This dependence suggests that some chemical property, such as complexation, is responsible for the observed difference between species. Similar differences were also found between pooled samples of other plant species from the present site,[11] and it has been suggested that they are due to complexation of the REEs in the rhizosphere of these plants.

The element showing the largest deviation from a straight line in Fig. 3, especially at places IV, V, and VI, is Ce. This is due to a different Ce anomaly of both plants at these places. The Ce anomalies of blackberry and spruce at all places show no significant correlation ($n=5$, $r=0.845$, $p>0.05$) which might be due to slightly different Eh-pH-conditions in the respective rhizospheres at a given place.

Conclusions

The present work has shown that REE concentrations in plants differ from those of the soil (both total and extractable concentrations) in several aspects.

Plant concentrations are smaller than soil concentrations, i.e., the CR1 and CR2 values (Fig. 1) are much less than 1. In this aspect REEs do not deviate from other trivalent cations.

REE in plants have distribution patterns very different from the soil. This shows that total as well as extractable soil concentrations are very poor analogues of the actual uptake of the REEs. The fact, however, that the 2 plant species have nonidentical distribution patterns suggests that the plant itself is involved in the process of generating distribution patterns different from the soil.

Variability between individual plants (of the same species) is much greater than that of the respective soils. Variability between groups, which concerns the REEs as an entity, is in agreement with the findings for other trace elements. Variability within groups, however, shows that the individual REEs do not behave in exactly the same way in individual plants, notwithstanding their similar chemical properties. It could be shown that a different transportation length in the plant does not contribute to this variability, but its causes remain unclear. However, the assumption of a complexation of REEs in the rhizosphere of the plants, which can vary between places and be different for different plant species, even when growing on the same soil, might be a possible explanation for the varying uptake, especially in view of the observation that the ratio of the 2 plant species is a smooth function of the atomic number of the REEs.

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We thank J. BUCHER and W. ZIMMERMANN (Swiss Institute for Forest, Snow and Landscape Research) for their help with plant collection and the soil profile, M. BURGER and A. JAKOB (AC Laboratory Spiez, Switzerland) for the help with the ICP-MS measurements of the water extracts, and J. CASTA (Austrian Research Center Seibersdorf) for his help with the neutron irradiations.

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