Environment International, Vol. 13, pp. 427–436, 1987
Printed in the USA. All rights reserved.

0160-4120/87 $3.00 + .00

VARIABILITY OF THE SORPTION OF Cs, Zn, Sr, Co, Cd, Ce, Ru, Tc AND I AT TRACE CONCENTRATIONS BY A FOREST SOIL ALONG A TRANSECT

W. Schimmack, K. Bunzl, and H. Bachhuber
Gesellschaft für Strahlen- und Umweltforschung München, Institut für Strahlenschutz, D-8042 Neuherberg, Federal Republic of Germany

(Received 31 March 1987; Accepted 10 November 1987)

The variability of the sorption properties (characterized by the distribution coefficient K_d) of a forest soil for Cs, Zn, Sr, Co, Cd, Ce, Ru, Tc, and I were determined along a transect of 150 m in regular intervals of 3 m. Radioactive tracers were used to ensure trace concentrations of these elements. For comparison, for each soil sample the loss on ignition, as a measure of the soil organic matter content, and the pH were also determined. On average, the K_d values increase in the sequence Tc < I < Ru ≈ Co ≈ Zn ≈ Sr < Cd < Ce < Cs; the spatial variability in the sequence I < Zn ≈ Sr ≈ Co ≈ Cd ≈ Ru ≈ Tc < Cs, and I ≈ Ce < Tc. Correlation analysis revealed that, when moving along the transect, the K_d values for some elements changed in a similar, and for others in a dissimilar pattern. In a few cases a correlation between the pH or the loss on ignition and the K_d values was also present. The spatial structure of the data was examined by semivariograms. For the elements Co, Cd, Zn, and Sr, the K_d values showed an almost periodic behaviour along the transect, which is probably due to periodic changes of some soil properties in a forest with regularly spaced trees.

Introduction

The availability of many pollutants (as e.g. radionuclides or toxic heavy metals ions) in the soil for ecological processes depends to a considerable extent on the sorption properties of the soil at the site of interest. If, for example, the soil is able to sorb an added ion strongly, the vertical transport of this ion to the groundwater will be greatly retarded. On the other hand, the ion remains in this case for a long time in the upper soil horizon, from where it can be taken up by plant roots. The extent of this root uptake depends again considerably on the sorption properties of the soil. As a result, detailed information on the sorption properties of representative soils for the various radionuclides and heavy metal ions is needed, if realistic predictions of the behaviour of these pollutants in the environment are to be made.

If the ions are present in the soil in trace quantities only, the extent of sorption is usually characterized by the distribution coefficient K_d defined as

$$K_d\ (\mathrm{cm^3/g}) = \frac{\text{amount of ion sorbed per gram of air dry soil}}{\text{amount of ion per millilitre of solution}}\ . \quad (1)$$

If, for a given ion and a given soil, the K_d value and the hydraulic properties are known, its vertical rate of migration can be estimated (Bolt, 1970; Frissel and Reiniger, 1974; Bachhuber *et al.*, 1982; Schimmack and Bunzl, 1986). At present, distribution coefficients for many radionuclides and heavy metal ions in various soils, also as a function of the depth, are available. However, we have almost no information on the spatial variability of the K_d value in the field. This information is needed, for example, if we want to estimate the minimum number of soil samples that is required to estimate the mean K_d value of a soil with a given error. Also, if we want to describe the migration of a solute in the soil by a stochastic model, the variability of the distribution coefficient has to be known. As shown below, the data can be used also to reveal correlations between the K_d values of the different pollutants and between the K_d value and a given soil property, if its spatial variability is determined as well.

In a previous investigation (Bachhuber *et al.*, 1986), we determined the spatial variability of the K_d value of

---

Correspondence and proofs to: Dr. K. Bunzl, Gesellschaft für Strahlen- und Umweltforschung München, Institut für Strahlenschutz, D-8042 Neuherberg, FRG.

Cs, Zn, Sr, Co, Cd, Ce, Ru, Tc, and I in a cultivated Parabrown earth soil (Alfisol). We showed that in this case the spatial variability depends strongly on the element used, increasing from Cs to Ce by about one order of magnitude. When moving along the transect, the K_d values for several elements changed in a similar way.

To find out whether a similar behaviour is observed for other soils, this paper establishes the spatial variability of the K_d value for these ions along a transect of 150 m in the A_h horizon of a podsol forest soil. This soil exhibits quite different sorption properties than the cultivated Alfisol. To investigate whether the observed distribution pattern of the K_d values can be associated with the variability of certain soil properties, we also determined at each sampling location the pH and, as an estimate of the soil organic matter, the loss on ignition of the soil. The interdependency of the K_d values of an individual ion along the transect (i.e. the spatial structure) was analysed by calculating the corresponding semivariograms.

For the experimental determination of the K_d values at trace concentrations, we used radioactive tracers of all elements. To separate the spatial variability of the K_d value from the variance of a K_d, arising from the experimental error of measurement, this latter quantity was determined for each of the 50 soil samples by separately measuring four replicates (see: Procedures).

Material and Methods

Site

The pine plantation (*pinus silvestris*, circa 50 years of age) from which the soil samples were taken is located in Northern Bavaria, 2.5 km north of the village Altenschwand on an almost plain plateau, 400 m above mean sea level. It receives an average 710 mm of rain per year. The mean annual temperature (1955–1986) is 7.9 °C (2 m above ground). The trees were planted in parallel rows (distance between the rows circa 4–5 m). The undergrowth is dominated by Calluna vulgaris, Vaccinium myrtillus, Vaccinium vitis-idaea, and cetraria islandica.

Soil

The soil present in the forest is classified as podsol (FAO-UNESCO system: Spodosol, suborder orthod), consisting of a black partially decomposed forest litter (O-horizon; 5–0 cm) over a gray layer of sand (E-horizon; 0–8 cm), containing less than 2% of clay. Several physical and chemical properties of the E-horizon are given in Table 1.

Table 1. Chemical and physical properties of the soil.

pH ($CaCl_2$)	3.3
Carbonate as $CaCO_3$	0%
Loss on ignition	7%
Total N	0.1%
Clay	3%
Silt	17%
Sand	80%
CEC (T-value)	125 me/kg
Ca	11 me/kg
K	≤1 me/kg
Mn[a]	1 mg/kg
Fe[a]	360 mg/kg

[a] in EDTA extract.

Sampling

Fifty soil samples were taken within one day (December 19, 1985) along a transect of 150 m in regular intervals of 3 m. The transect was running at a small angle with respect to the direction of the rows of the trees. After removing the O-horizon, about 1 kg soil from the E-horizon was taken.

Radionuclides

To ensure trace concentrations of the ions in the solution phase, carrier-free radionuclides were used for all sorption experiments as far as possible. ^{137}Cs, ^{131}I, and ^{57}Co were obtained from Amersham Buchler, ^{65}Zn, ^{85}Sr, ^{103}Ru, ^{109}Cd, ^{141}Ce, and ^{95m}Tc from New England Nuclear; technetium was applied as TcO_4^-, iodine as NaI, and the remainder as chlorides.

Procedure

The soil sample from each sampling point was air dried, sieved to 2 × 2 mm and carefully mixed. To determine the K_d values by sorption experiments as realistic as possible, we first prepared a separate soil solution for each soil sample by shaking very gently in intervals 10 g soil with 25 ml demineralised water for three days, followed by centrifugation at 4500 rpm, until a clear supernatant solution was obtained. To determine the distribution coefficient, 24.5 ml of this soil solution were mixed with 10 g soil from the same sampling point and 0.5 ml of an aqueous solution containing known amounts of all radionuclides simultaneously. This mixture was agitated at 293 K for 20 days very gently and in intervals in capped polyethylene centrifuge tubes. After that time the suspension was centrifuged at 4500 rpm and the activity of individual radionuclides in the clear supernatant counted separately using a HPGe-detector and a multichannel analyser. From the initial and the final activity of each radionuclide in the solution the amount sorbed of each radionuclide can be obtained and the K_d values calculated with help of Eq. (1).

Detailed preliminary kinetic experiments showed that for most of the radionuclides the sorption is a slow process. However, the period of 20 days used was sufficient for all radionuclides to attain the sorption equilibrium with the soil (Bachhuber *et al.*, 1984). It

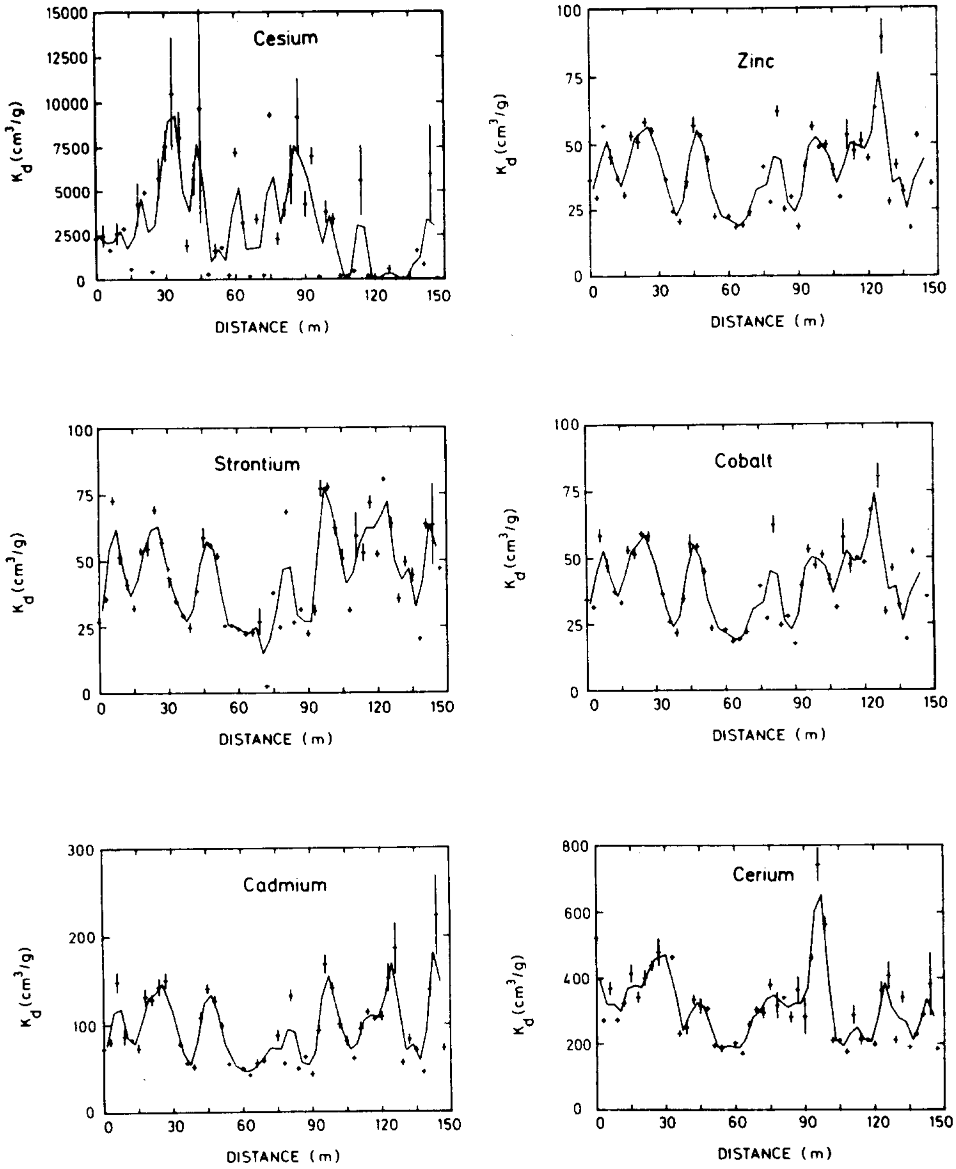

Fig. 1. Distribution coefficients K_d of Cs, Sr, Cd, Zn, Co, and Ce in a forest soil along a transect. The solid line is the running mean of two successive values each.

was also assured that sorption of the radionuclides at the walls of the vials at the conditions of the batch experiments was negligible (K_d value of the vials: < 0.1 cm³/g). The concentrations of the radionuclides in the solution phase were, as calculated from the specifications of the manufacturers (in mol/L): ^{57}Co: (1.2 × 10^{-10}) ^{65}Zn: (5.8 × 10^{-8}) ^{85}Sr: (3.6 × 10^{-8}) ^{95m}Tc: (10^{-11}) ^{103}Ru: (6.2 × 10^{-8}) ^{109}Cd: (5.6 × 10^{-9}) ^{131}I: (1.5 × 10^{-11}) ^{137}Cs: (9.2 × 10^{-9}) ^{141}Ce: (6.9 × 10^{-11}).

Each K_d determination was repeated four times by equilibrating further soil samples from the same sampling point with the corresponding soil solution containing the radionuclides of interest. At the end of each experiment the pH of the equilibrium solution was determined with a glass electrode. (The frequently used method in soil science to determine the pH in a KCl or $CaCl_2$ solution was not applied here, because it will not necessarily yield the same pH as present in the equilibrium solution of a batch-K_d experiment). To determine the loss on ignition, 5 g air-dry soil were placed in a crucible and ignited to constant weight in a furnace (1120 K, 90 min).

Results and Discussion

A preliminary screening of the data revealed that at a few sampling points obvious anomalies were present. These involved not only the distribution coefficients but also the soil pH. At one sampling point, for example, the K_d (in cm³/g) of Ce was 1880 (average of four

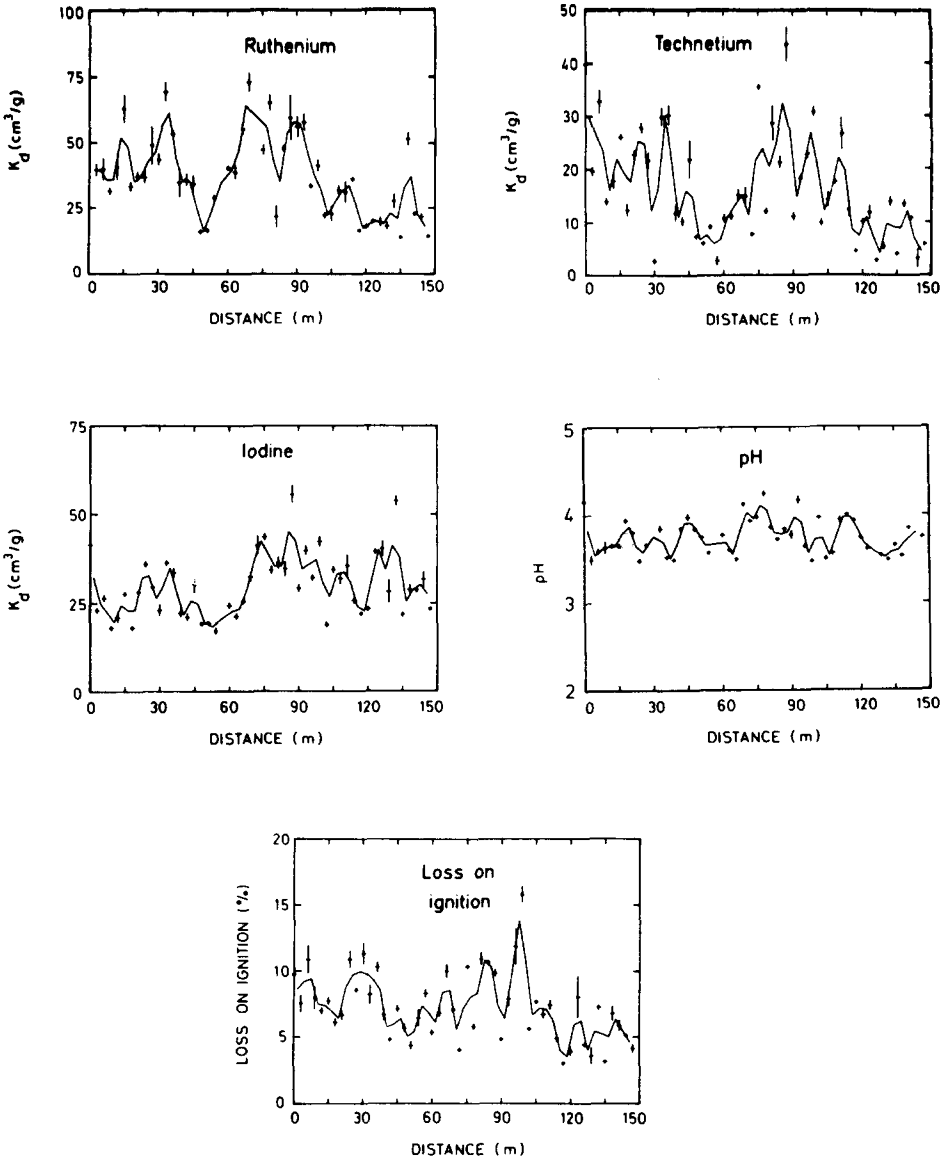

Fig. 2. Distribution coefficients K_d of Ru, Tc, I, the pH and the loss of ignition of the soil sample in a forest soil along a transect. The solid line is the running mean of two successive values each.

replicates), while those at the five preceding as well as the succeeding points were all between 200 and 300. At the same point the K_d of Cd was 730 (average of four replicates), while those at the five preceding and succeeding points were between 50 and 150. Similar extremely high values at this point were observed for the K_d values of most of the other elements, as well as of the pH which exceeded the values of the neighbouring points by about 4 pH-units. Evaluation of the frequency distribution of all data (see below) also showed clearly that this point has to be considered as an extreme (or outlier). Altogether three outliers were discovered. The data collected at these points are not considered in the following graphs (Fig. 1), the permutation tests, calculation of the means, nor in the semivariograms because they would distort these quantities unrealistically. No points were deleted when nonparametric quantities were used (median, confidence limits of median, relative decile deviation, Spearman correlation coefficient, U-test by Mann and Whitney, Siegel–Tukey test), because these are practically not affected by the presence of a few outliers.

A conclusive explanation for the occurrence of the above outliers cannot be given. However, it seems likely that they arise from local changes in the soil composition as a result of earlier forestry or the activity of animals.

Significance of the spatial variability

In Figs. 1 and 2 the distribution coefficients ob-

Table 2. Averages (median, mean) and variability (95% confidence limit of median, relative decile deviation RDD [see Eq. (2), range and frequency distribution] of distribution coefficients (in cm^3/g) of nine radionuclides, the pH and the loss on ignition of the soil solution from 50 sampling points in the E-horizon of a forest soil.

Radionuclide	Median	95% confidence limit of median	Mean	Relative decile deviation (%)	Range	Frequency distribution
^{137}Cs	2300	610–3800	3100	160	9.5–10500	—[a]
^{65}Zn	41	32–50	41	52	18–89 (1150)[e]	log-normal[d]
^{85}Sr	44	32–53	44	52	2.5–80	normal
^{57}Co	40	33–50	41	54	17–80 (740)[e]	normal[d]
^{109}Cd	87	73–110	97	59	42–222 (730)[e]	log-normal[d]
^{139}Ce	310	270–340	316	47	170–740 (1880)[e]	log-normal[c]
^{103}Ru	36	31–41	37	67	14–73 (400)[e]	normal[d]
^{95m}Tc	14	11–18	16	93	2.7–43	normal
^{131}I	29	26–33	30	38	17–56 (83)[e]	normal[b]
pH	3.7	3.6 - 3.8	3.7	9	3.5 - 4.2 (7.6)[e]	normal[d]
Loss on ignition (%)	7.0	6.1 - 7.9	7.3	49	3.0 - 16	log-normal

[a] Neither a normal nor a log-normal distribution was observed at the 5% level of significance.

[b] If one outlier is not considered.

[c] If two outliers are not considered.

[d] If three outliers are not considered.

[e] If all outliers are considered.

served for Cs, Zn, Sr, Co, Cd, Ce, Ru, Tc, and I along the transect are shown. All K_d values given there are means of four replicate measurements. The resulting experimental error is plotted for each mean as ± 1 standard deviation. To investigate whether these values of the standard deviation change significantly along the transect, the Cochran test (Sachs, 1976) was used. As a result we found that at the 5% level of significance the standard deviations of the K_d values of each element did not change significantly along the transect, if the few outliers mentioned above were omitted. For the K_d values of Cs, however, this was not the case. This is due to the fact that for the very high K_d values observed for this element at several points along the transect the experimental error is much higher than at places with low K_d values. The spatial variability of the K_d values is essentially associated with the spatial variability of those soil properties which affect the sorption of the radionuclides. As mentioned, we determined for this reason also the spatial variability of two important soil properties, the pH of the soil solution and the loss on ignition (as a measure of the soil organic matter content). The observed values of these quantities along the transect are also shown in Fig. 2.

To detect whether trends, minima or maxima of the K_d values or the pH and the loss on ignition are present, we also plotted in Figs. 1 and 2 the running means of two successive values as solid lines. Even though these curves seem to indicate that in several cases (e.g. cesium) regions with higher and lower K_d values are present, this does not necessarily mean that these maxima and minima are also statistically significant. Therefore, to investigate whether or not the K_d values vary along the transect in a random way, we applied a recently developed permutation test (Grundler *et al.*, 1983). With this test the probability α that the observed sequence of K_d values along the transect is a random sequence can be calculated. The values obtained for α showed: the K_d values along the transect do not follow a random sequence for Sr, Ce, Ru ($\alpha < 0.001$), Co ($\alpha < 0.01$), Zn, Cd, Tc and the loss on ignition ($\alpha < 0.05$). On the other hand, for the K_d values of Cs and I, as well as for the pH, α is larger than 0.05, indicating a random arrangement of these values along the transect.

Descriptive statistics

The central tendencies of the K_d values for the various elements, the pH and the loss on ignition are given in Table 2. Application of the chi-square goodness-of-fit test at the 0.05 level revealed that the frequency distribution of the K_d values (Table 2, last column) was in some cases normal (strontium, cobalt, ruthenium, technetium, iodine), log-normal (zinc, cadmium, cer), or neither normal nor log-normal (cesium). For the loss on ignition, the frequency distribution was log-normal, for the solution-pH normal. For this reason the central tendencies of the K_d values, the pH and the loss on ignition were characterised not only by the mean but also by the median and its 95% confidence limits. By far the highest median K_d value was observed for cesium (2300 cm^3/g), while those for the other elements were substantially lower (29–310 cm^3/g). If the median K_d values are arranged for increasing values, the following sequence is obtained:

$$\mathrm{Tc} < \mathrm{I} < \mathrm{Ru} \approx \mathrm{Co} \approx \mathrm{Zn} \approx \mathrm{Sr} < \mathrm{Cd} < \mathrm{Ce} < \mathrm{Cs},$$

where the decision, whether the median K_d values of two elements differ significantly, was made by application of the U-test by Mann and Whitney at the 5% level of significance (Sachs, 1976). High K_d values of Cs and Ce as compared to I of Tc have also been observed previously (Bunzl *et al.*, 1984; Bachhuber *et al.*, 1986) for several cultivated soils. However, in the latter case the K_d values of Zn, Co, and Cd, though also in between Cs and Tc, were much higher than observed now for the forest soil. Heavy metal ions, like Zn, Co, and Cd are preferentially sorbed by the soil organic matter, especially if the pH is high. Therefore, the comparatively low K_d values of these ions observed now for the forest soil are probably the result of the low pH of this soil (3.7), as compared to the pH of cultivated soils, which are in general above 6.

To characterise the variability of a quantity the coefficient of variation of data is used frequently. However, this quantity is affected considerably by the presence of outlying observations. Because we observed such outliers in several cases (see above and Table 2), we rather calculated as a measure of dispersion the relative decile deviation RDD, defined as

$$\mathrm{RDD}\ (\%) = \frac{0.5\ (D_9 - D_1)}{\text{median}} \cdot 100, \qquad (2)$$

where D_1 and D_9 are the first and the ninth of the deciles, which divide the frequency distribution in 10 equal portions by area (Sachs, 1976). The RDD thus takes 40% of the values to the right and 40% of the values to the left of the median into consideration. In this way the effect of outliers is avoided but 80% of the observations are taken into account. [If the frequency distribution is normal, the coefficient of variation CV can be estimated from the RDD as CV = 0.78 · RDD (Sachs, 1976).] The RDD of the K_d values, as obtained for each radionuclide, is given also in Table 2. On the basis of these values we can see that the spatial variability of the K_d values depends on the radionuclide and increases from an RDD of 38% to 160%. To find out, for which radionuclides these differences were also statistically significant, we applied the (nonparametric) Siegel–Tukey test (Sachs, 1976) at the 5% level (two tailed), and obtained the following sequence for the RDD of the K_d values:

$$\mathrm{I} < \mathrm{Zn} \approx \mathrm{Sr} \approx \mathrm{Co} \approx \mathrm{Cd} \approx \mathrm{Ru} \approx \mathrm{Tc} < \mathrm{Cs}.$$

Ce cannot be included in this sequence, because its RDD, though similar to that of I and Zn, is significantly smaller than that of Tc. The RDD of the pH of the samples along the transect is comparatively small (9.1%); the RDD of the loss on ignition is 49% (see Table 2).

As mentioned, the presence of a spatial variability of the K_d value of an ion is obviously due to the presence of the spatial variabilities of those soil properties, which affect the sorption of this ion. Because, in general, different soil components (with different spatial variabilities) will be responsible for the sorption of different ions, the above sequence of the elements, arranged for increasing RDD values, will be different for different soils and sites. However, even if for two soils the spatial variability of the soil properties would be the same, the RDD for different ions would be different, because different ions will, with respect to the sorption, respond with different sensitivity to a given change of a soil property (as e.g. the pH). The sequence of the K_d values as well as the sequence of their spatial variability is thus a characteristic property of a given site.

Correlations

The distribution coefficients determined for the elements at each of the 50 sampling points can be used to find out whether significant correlations are present. Because, as mentioned before, normal frequency distributions of the K_d values were not always observed, the (nonparametric) Spearman correlation coefficient was calculated for this purpose in each case. The resulting significance levels for these correlations between K_d values of the various elements are summarised in Table 3. Several significant correlations exist between the K_d values of the nine elements investigated. If the observed correlation is significantly positive, one can conclude that the K_d values for the two elements change in a similar pattern as one moves along the transect. Significant correlations of this type were found especially between Zn, Sr, Co, Cd, and Ce.

Alternatively, if a negative correlation is observed (− sign in Table 3), we can expect that the K_d values of the two elements change in a dissimilar pattern along the transect. As significant correlation of this type was present between Ru and Sr, Co, Zn, Cd.

Observed associations between the K_d values and the pH of the soil solution as well as the loss on ignition (as a measure of the soil organic matter) of each soil sample are also given in Table 3. A significant correlation between the pH and the K_d values of several elements is evident (Cs, Zn, Co, Cd, Ce, Tc); a significant correlation between the loss on ignition and the K_d was present for Cs, Ru, Tc, and I.

Table 3. Correlations between the distribution coefficients of several radionuclides in a forest soil (podsol) (E-horizon). Data evaluation of the 50 sampling points with the Spearman correlation coefficient. Levels of signicance (two tailed): ***= 0.001; ** = 0.01; * = 0.05; ns = not significant; (−) = negative association.

Radionuclide	Cs	Zn	Sr	Co	Cd	Ce	Ru	Tc	I
Cs	/	ns	ns	ns	ns	*	**	**	ns
Zn	ns	/	***	***	***	***	*(−)	ns	ns
Sr	ns	***	/	***	***	*	***(−)	ns	ns
Co	ns	***	***	/	***	ns	**(−)	ns	ns
Cd	ns	***	***	***	/	***	*(−)	ns	ns
Ce	*	***	*	ns	***	/	**	**	***
Ru	**	*(−)	***(−)	**(−)	*(−)	**	/	**	**
Tc	**	ns	ns	ns	ns	**	**	/	**
I	ns	ns	ns	ns	ns	***	**	**	/
pH	**	*	ns	**	*	*	ns	*	ns
Loss on ignition	*	ns	ns	ns	ns	ns	**	***	**

Semivariograms

It is conceivable that soil samples taken close to each other may exhibit soil properties (and thus K_d values for a given element) which are more similar than those from samples further apart. An appropriate measure of spatial variation of individual observations is the semivariogram $\gamma(h)$, (see e.g. Burgess and Webster, 1980a, 1980b; Webster and Burgess, 1980; Zirschky, 1985; McBratney and Webster, 1986; Davidoff *et al.*, 1986). In the present case, where distribution coefficients were determined at equal distances in the field $\gamma(h)$ can be estimated from:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} (Kd_i - Kd_{i+h})^2 \qquad (3)$$

where h is the separation distance, $N(h)$ the number of pairs of observations at lag h, and Kd the distribution coefficient.

By definition, $\gamma(h)$ should start at the origin, because $\gamma(0) = 0$. When a certain distance (denoted at range) exists beyond which the samples are independent, the semivariogram levels off and approaches a maximum value (approximately the sample variance) called the sill. In practice, however, the limiting value of $\gamma(h)$ at lag zero will not be zero. The resulting value $\gamma(0)$, called the nugget variance is the result of measurement errors and variation over distances much smaller than the closest sampling interval.

The resulting semivariograms, as calculated from the distribution coefficients of the various elements along the transect, are shown in Figs. 3 and 4. For comparison, the semivariograms of the pH and the loss on ignition are included. Also shown in these figures is the sample variance (dotted lines). The following results can be obtained.

1. For the elements Cd, Co, and Zn an almost periodic structure of the semivariance is present, with maximum values at about 4, 12, and 19 lags and mimimum values at 0, 8, 16, and 23 lags. This repetitive structure is the result of successive maxima and minima of the K_d values of these elements along the transect (see Fig. 1). The distance between successive maxima (or minima) of the K_d values is circa 24 m, corresponding to a lag of $24/3 = 8$. Thus, whenever the distance between sampling points along the transect is circa 8, 16, or 24 lags (24, 48, or 72 m), the K_d values of the above elements ar rather similar (small semivariance), while they are comparatively different (large semivariance), if the distance is about 4, 12, or 20 lags (12, 36, or 60 m).
2. For the elements Ce and Sr the semivariograms are similar to those of Cd, Co, and Zn, even though the periodic structure is not so conspicuous. For Ce the three maxima are still visible. In the case of Sr, however, the two maxima at 12 and 19 lags are not well resolved.
3. The semivariograms of Tc and the loss on ignition increase with increasing distance up to about 16 lags and then decrease again. Values of the K_d of Tc and of the loss on ignition from samples along the transect thus exhibit the largest differences if they are about $16 \times 3 = 48$ m apart.
4. For Ru the semivariograms increase with increasing distances and reaches the maximum (sill) after about 10 and 5 lags, respectively. Therefore, K_d values from samples which are closer to each other than this range will be more similar than from more widely spaced samples.
5. For I, Cs and the pH, the semivariograms show a rather flat shape, where the sill is reached at short lag distances. Thus, the spatial structure of these quantities, if present at all, seems to be small.

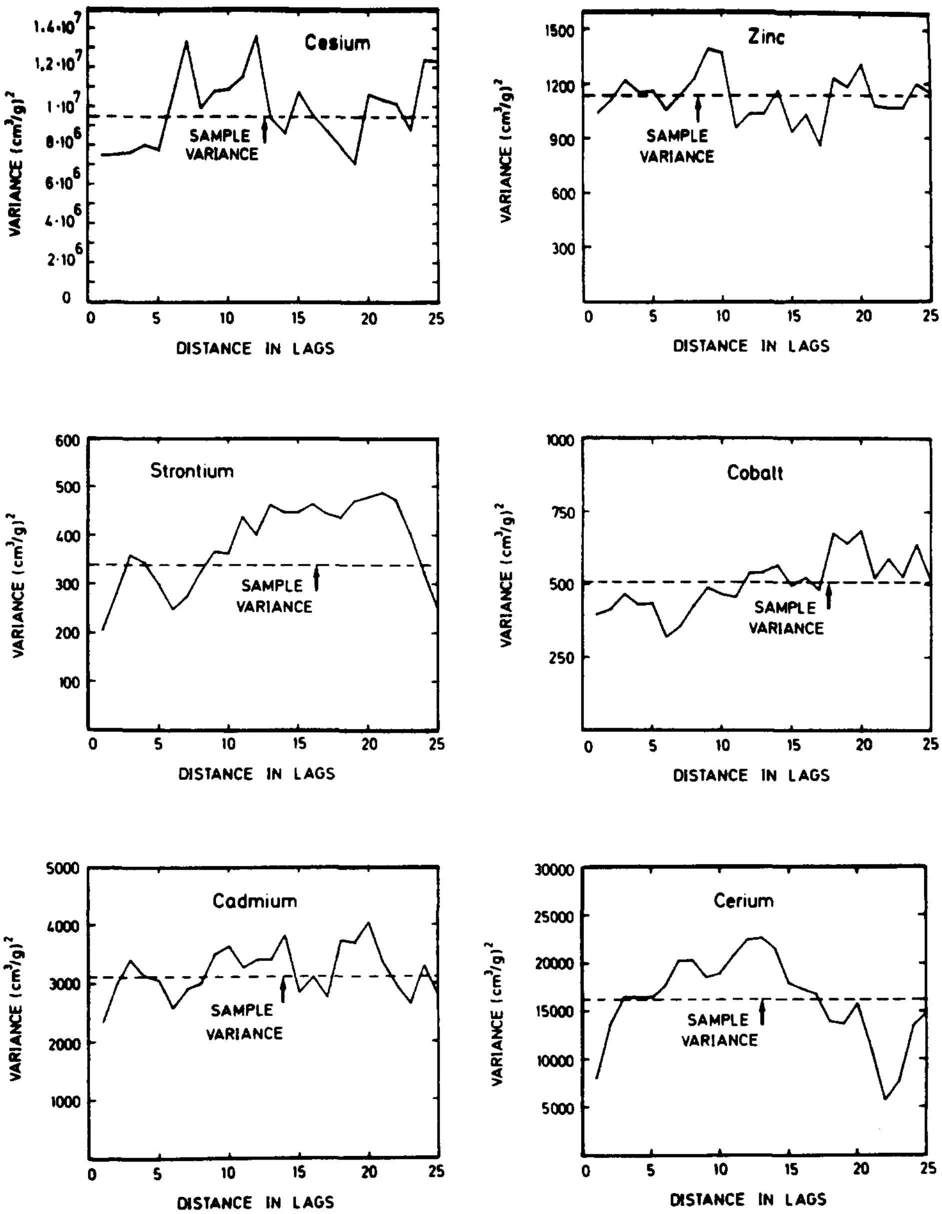

Fig. 3. Semivariograms of the distribution coefficients K_d of Cs, Sr, Cd, Zn, Co, and Ce in a forest soil. One lag corresponds to 3 m.

This is in accordance with the result of the permutation test (see above) which also indicated that the data for these quantities along the transect vary essentially in a random way.

For a complete structural analysis, including an autocorrelation analysis, stationarity of the data means and variances is required. The presence of locally changing drifts of the K_d values, as evident from Figs. 1 and 2 and the permutation tests, shows that these assumptions are violated. However, the methods available for removing these drifts require that the nugget variance is small (Webster and Burgess, 1980). Because this is not the case for our data (Figs. 3 and 4), a more detailed structural analysis was not performed.

The conclusions from the semivariograms may be compared with those obtained from calculating the correlation coefficients between the K_d values (see above). In principle, we should expect that if a highly significant correlation is observed between the K_d values of two elements along the transect, the shapes of their semivariograms are similar. In the present case this is observed for the K_d values of Cd, Co, Zn, Ce, and Sr. The correlations between the K_d values of these elements are highly significant and the spatial structure as obtained from the semivariograms are also similar. The highly significant positive association observed between K_d values of Tc and the loss on ignition is also in agreement with the similar spatial structure of these two quantities. The significant negative association observed between Ru and Sr, Co, Zn, and

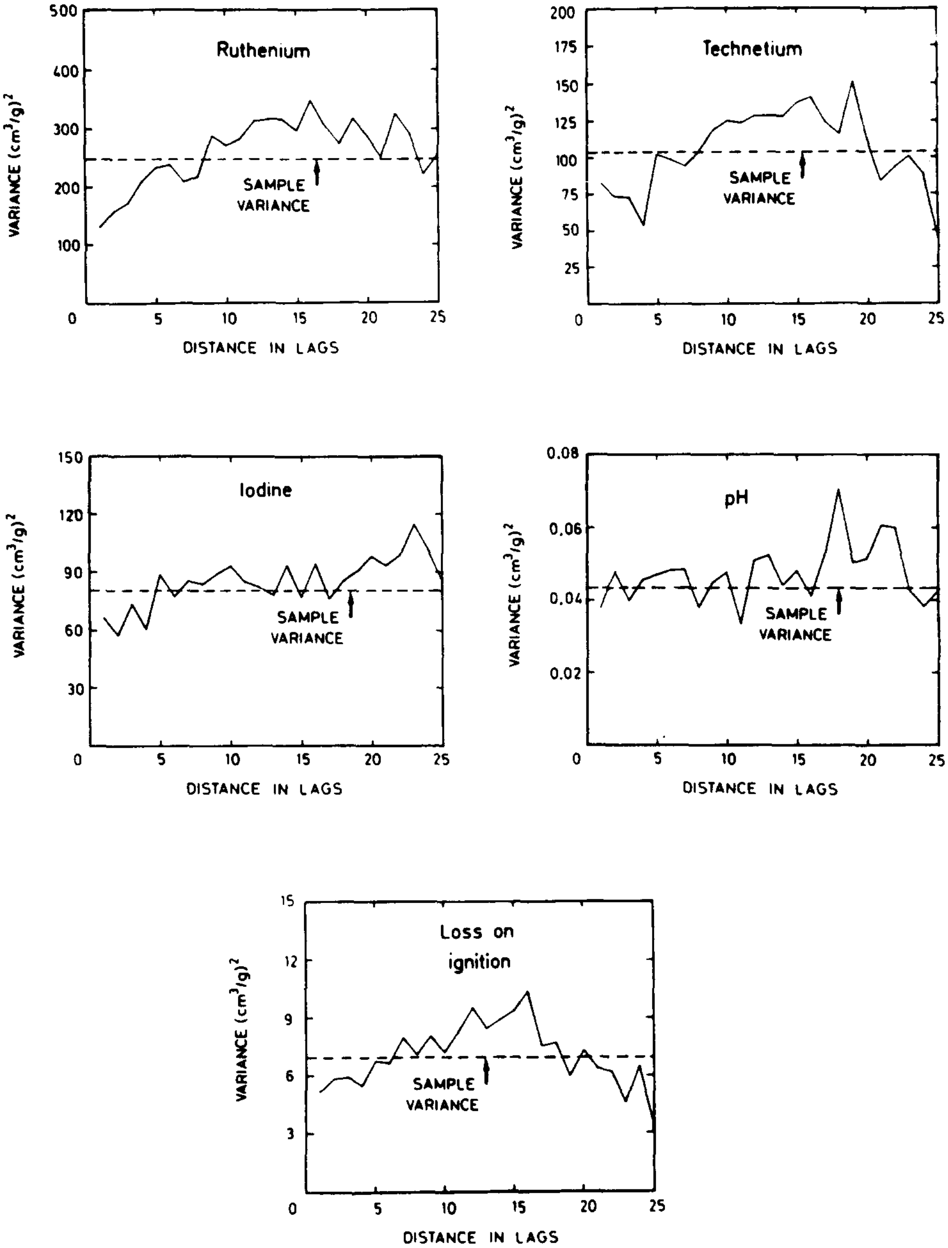

Fig. 4. Semivariograms of the distribution coefficients K_d of Ru, Tc, I, the pH and the loss of ignition in a forest soil. One lag corresponds to 3 m.

Cd corresponds also with the quite different spatial structure of Ru when compared with these other elements. On the other hand, the significant positive association observed between the K_d values of I and Ce or the pH and the K_d values of Co is not immediately evident from their semivariograms.

The almost periodic behaviour of the distribution coefficients of Co, Cd, Zn, Sr, and to some extent also for Ce along the transect can only be attributed to a periodic change of those soil properties which are responsible for the sorption of these elements. In a forest it is very probable that many soil properties are not spatially homogeneously distributed but depend on the distance from a tree, e.g. as a result of falling needles or leaves which are converted to soil organic matter. In the present case the trees were planted in parallel rows, where the distance between the rows was about 4–5 m, the distance between the trees along the rows varied between 2–4 m. The transect did not run parallel to the rows but rather at a small angle with respect to it. In this way the sample points approached the rows of the trees periodically. This might explain the periodicity of the K_d values observed for some elements, even though the exact distances between the transect and all neighbouring trees were not determined.

Acknowledgement — The valuable technical assistance of M. Haimerl, W. Schultz, and W. Schneider is gratefully acknowledged.

References

Bachhuber, H., Bunzl, K., Dietl, F., Schimmack, W., and Schultz, W. (1984) Sorption and Ausbreitung von Radionukliden in zwei Ackerböden der Bundesrepublik Deutschland, GSF-Bericht S-1071, Gesellschaft für Strahlen- und Umweltforschung München, Neuherberg, FRG.

Bachhuber, H., Bunzl, K., and Schimmack, W. (1986) Spatial variability of the distribution coefficients of ^{137}Cs, ^{65}Zn, ^{85}Sr, ^{57}Co, ^{109}Cd, ^{103}Ru, ^{95m}Tc and ^{131}I in a cultivated soil, *Nucl. Technol.* **72,** 359–371.

Bachhuber, H., Bunzl, K., Schimmack, W., and Gans, I. (1982) The migration of ^{137}Cs and ^{90}Sr in multilayered soils: Results from batch, column and fallout investigations, *Nucl. Technol.* **59,** 291–302.

Bolt, G. H. (1979) *Soil Chemistry, B. Physico-Chemical Models.* Elsevier, Amsterdam, Holland.

Bunzl, K., Bachhuber, H., and Schimmack, W. (1984) Distribution coefficients of ^{137}Cs, ^{85}Sr, ^{141}Ce, ^{103}Ru, ^{131}I and ^{95m}Tc in the various horizons of cultivated soils in Germany, *Proc. Int. Symp. on Recent Investigations in the Zone of Aeration* P. Udluft, B. Merkel, and K. H. Prösel, eds., pp. 567–573. Technical University Munich, Dept. of Hydrogeology and Hydrochemistry. FRG.

Burgess, T. M. and Webster, R. (1980a) Optimal Interpolation and isarithmic mapping of soil properties, 1. The semi-variogram and punctual Kriging, *J. Soil Sci.* **31,** 315–331.

Burgess, T. M. and Webster, R. (1980b) Optimal interpolation and isarithmic mapping of soil properties, 2. Block Kriging, *J. Soil Sci.* **31,** 333–341.

Davidoff, B., Lewis, J. W., and Selim, H. M. (1986) Variability of soil temperature with depth along a transect, *Soil Sci.* **142,** 114–123.

Frissel, M. J. and Reiniger, P. (1974) *Simulation of Accumulation and Leaching in Soils.* Centre of Agricultural Publishing and Documentation, Wageningen, Holland.

Grundler, W., Keilmann, V., Putterlik, V., Santo, L., Strube, D., and Zimmermann, I. (1983) Nonthermal resonant effects of 42 GHz microwaves on the growth of yeast cultures, in *Coherent Excitations in Biological Systems,* H. Fröhlich and F., Kremer, eds., pp. 21–28. Springer Verlag, Berlin, FRG.

McBratney, A. B. and Webster, R. (1986) Choosing functions for semi-variograms of soil properties and fitting them to sampling estimates, *J Soil Sci.* **37,** 617–639.

Sachs, L. (1976) *Angewandte Statistik.* Springer Verlag, Berlin, FRG.

Schimmack, W. and Bunzl, K. (1986) Migration of solutes in a cultivated soil: Effect of ploughing, *Geoderma* **38,** 155–163.

Webster, R. and Burgess, T. M. (1980) Optimal interpolation and isarithmic mapping of soil properties, 3. Changing drift and universal Kriging, *J. Soil. Sci.* **31,** 505–524.

Zirschky, J. (1985) Geostatics for environmental monitoring and survey design, *Environ. Int.* **11,** 515–524.