

Role of Certain Stream- Sediment Components in Radioion Sorption

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TRANSPORT OF RADIONUCLIDES BY STREAMS

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TRANSPORT OF RADIONUCLIDES BY STREAMS

ROLE OF CERTAIN STREAM-SEDIMENT COMPONENTS IN RADIOION SORPTION

By E. A. JENNE and J. S. WAHLBERG

ABSTRACT

"Natural" and laboratory "dialysis" mass-action selectivity coefficients were determined for the <60-mesh (<0.25 mm) and the 9- to 60-mesh (2-0.25 mm) sediment fractions to evaluate the comparability of these two types of selectivity coefficients and the effectiveness of nonclay components in controlling the distribution of radioions between solid and liquid phases.

Stream water and surficial bed sediment were sampled in Whiteoak Creek, Tenn., from a small stilling basin. This creek carries low-level-radioactive waste waters from Oak Ridge National Laboratory to the Clinch River. Appropriate mass-action selectivity coefficients were calculated following determination of the soluble radioions in the water and the exchangeable radioions on the sediment. Portions of the size-fractionated sediment were air dried and used for 2-day radioion dialysis sorption experiments.

Sorption of strontium-90 was controlled by in situ precipitated carbonates. The solubility of the precipitated carbonates was sufficient in ammonium acetate and ammonium chloride leaches to yield selectivity coefficients which were high for the natural as compared with the dialysis values—9.6 versus 1.2 for the <60-mesh fraction. The carbonate solubility was sufficient to preclude determination of dialysis selectivity coefficients with sodium as the competing cation owing to the compounding effects of calcium plus magnesium. Cobalt-60 sorption was controlled by manganese and iron oxides and yielded high natural selectivity coefficients for the <60-mesh fraction owing to partial dissolution of the oxides in the extracting solution. The dialysis selectivity coefficients were greater for the 9- to 60-mesh fraction, where the oxides were most abundant. Sorption of cesium-137, in contrast to strontium-90 and cobalt-60, was controlled by the clay minerals. The observed higher natural selectivity coefficients for cesium-137, as compared with laboratory selectivity coefficients, are attributed to the slow diffusion of cesium into the interlayer spaces of illite and vermiculite, the dominant layer silicates.

Precipitation of cerium-144 during dialysis precluded determination of laboratory selectivity coefficients. Exchangeable and soluble zirconium-95 and niobium-95 were below detection level.

The results of the study indicate that nonclay minerals control the distribution between the solid and the liquid phases of two out of the three dominant radioions in Whiteoak Creek. Natural and laboratory selectivity coefficients were not comparable in many instances. This is attributed to partial dissolution of fine-grained carbonates and of manganese and iron oxides, and in

part to the largely irreversible nature of cobalt-60 and cesium-137 sorption. The laboratory and the natural selectivity coefficients for cesium-137 agreed within a factor of 2.

INTRODUCTION

Thousands of laboratory radioion distribution coefficients have been determined in recent years as a part of governmental radiological safety programs. These radioion sorption determinations have been made on soils and various types of rocks near sites proposed for nuclear detonations or radioactive-waste disposal. Similar studies have been made on reference clays. The usefulness of these data for predicting radioion sorption by stream sediments is quite limited for several reasons. These data, although extensive, are scattered and remain unsummarized. To be generally useful, the distribution coefficients must be transformed into mass-action selectivity coefficients. This is not generally possible, as the equilibrium aqueous phase concentration of the principal competing cations must be known. This information is very scarce in the distribution-coefficient literature. There is almost a total lack of data on the radioion-sorption properties of the nonclay minerals that occur in stream sediments. The sparse data available indicate that certain of the nonclay minerals, as well as organics, may be rather highly selective cation sorbers (Hechter and others, 1959; Tamura, 1962; Jenne and Wahlberg, 1965). A further limitation of the application of available selectivity-coefficient data is that drying and storage effects—such as desiccation of biota, irreversible dehydration of hydrous oxides, oxidization of reduced metal ions and organics, and precipitation of sparingly soluble salts and trace metals—are to be expected. It is not known whether these changes will alter the mean cation (and anion) selectivity of the earth material enough to seriously affect the usefulness of the laboratory data for field application. In addition, quantitative

clay mineralogy, which is required if the sorption characteristics of a sediment are to be predicted, is neither simple nor easy to obtain. Finally, the similarity of chemical properties of "reference clays" (often incorrectly referred to as "standard clays") to those of clays occurring in stream sediments is questionable.

Dissimilar chemical properties of reference and stream-sediment clays should be expected. The literature indicates that clay minerals in soils and recent sediments are commonly (1) poorly crystallized; (2) mixed-layer rather than discrete mineral species; (3) interlayered with aluminum (and less commonly magnesium, iron, or organics); and (4) physicochemically admixed with organic matter and (or) the oxides of aluminum, silicon, iron, or manganese.

Physicochemical responses in soils and sediments—such as cesium, potassium, ammonium, and phosphate fixation—as well as liming requirements (for soils), are different for poorly crystalline and intergrade layer silicates than for the reference clays.

The clay minerals in stream sediments have been reported as being poorly crystalline (Gorbunova, 1961; Clanton, 1963). The effect of varying degrees of crystallinity of the layer silicates on their chemical properties is known for only relatively few minerals. Ormsby, Shartsis, and Woodside (1962) have shown, for kaolins, that crystallinity decreases with decreasing particle size, whereas surface area and cation exchange capacity increase. Other studies have shown that prolonged grinding (hours) reduces the degree of crystal perfection of clays with concomitant increase in surface area, cation exchange capacity, and phosphate fixation.

Natural 14-A (angstrom) layer silicates, which have properties intermediate between those of typical chlorites and typical vermiculites or montmorillonites and which form as a result of weathering, are common in soil clays and have been reported by numerous investigators during the last 15 years. (See, for example, Weed and Nelson, 1962, and Carstea, 1965.) Rich (1960) concluded that the presence of interlayer hydroxy-aluminum compounds resulted in a marked decrease in the capacity of vermiculitic soil clays to irreversibly sorb ammonium and, presumably, other large fixable cations such as cesium.

Iron and manganese oxide coatings are extensive in sediments, and Sumner (1962) has shown that the iron oxides increase the number of positive exchange sites and have a variable effect on the number of negative sites depending on the pH of the system. The degree of crystallinity, as well as the crystallographic form of iron oxide coatings, has been shown to influence the

anion and cation exchange capacity of earth materials (Sumner, 1963). Because the physicochemical interaction of iron and organic matter in soils having a high iron oxide content sometimes precludes the complete oxidization of organic matter with hydrogen peroxide without prior iron removal, not all of the cobalt-60 associated with organic matter is available for cation exchange. Baas Becking and Moore (1959) concluded that most of the iron in sediments exists in complexes, chiefly with organic matter. Similarly, Berg (1960) noted that, when ferric chloride was hydrolyzed in the presence of clays, iron precipitated on the surface of clay particles until some maximum value (which appeared to vary with the surface area of the clay) was reached, and then it precipitated as discrete particles.

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APPROACH AND OBJECTIVES

The release of low-level-radioactive waste by the Oak Ridge National Laboratory into Whiteoak Creek provided a suitable opportunity to obtain samples with which to make appropriate comparisons between natural and laboratory selectivity coefficients. Whiteoak Creek, a small tributary of the Clinch River, has a mean annual discharge at the sample-collection point of about 9.5 cfs (cubic feet per second). (See fig. 1.)

The objectives of this study were to compare the natural radioion distribution in a stream with that obtained by the conventional laboratory (dialysis) technique of air-drying, storing, and equilibrating portions of the sediment with artificial solutions; and to evaluate the role of nonclay stream-sediment minerals in radioion sorption.

EXPERIMENTAL METHODS

In August 1963, about 40 liters of stream water and 3 liters of surface bed sediment were collected from a stilling basin above the Cipolletti weir, 1.1 miles below Oak Ridge National Laboratory and 1.6 miles above the Clinch River. The water sample was obtained by lowering 18-liter plastic bottles into the shallow pool above the weir. The bottles were filled

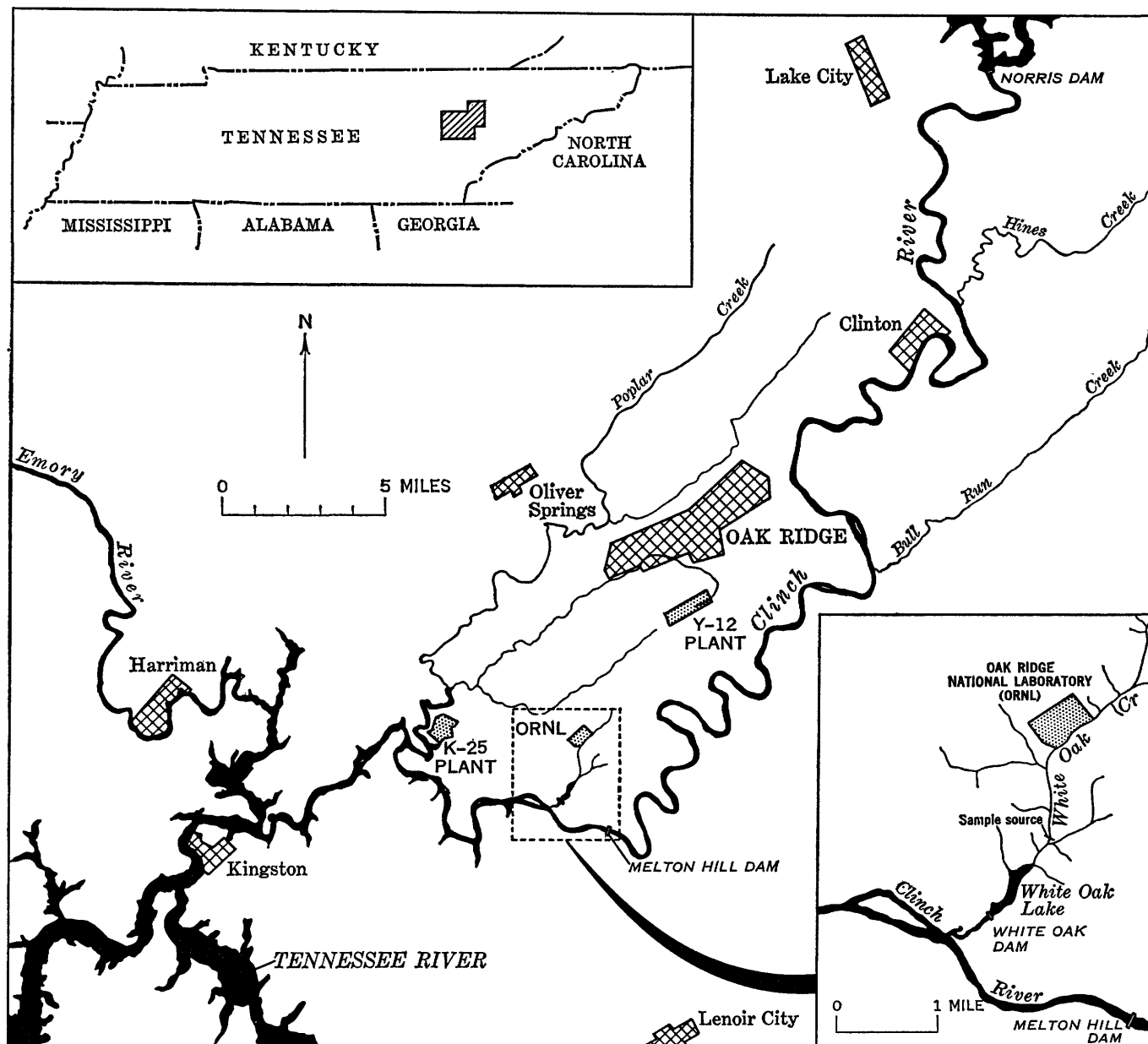


FIGURE 1.—Location of Whiteoak Creek, Tenn. Drawing courtesy of Oak Ridge National Laboratory.

with additional water dipped from the pool. Although the stream water was quite clear at the time of sampling, the turbulence resulting from the sampling procedure caused some of the fine-grained bed sediment to become suspended. The surface bed sediment in the pool was sampled by scraping with a plastic beaker to a depth of approximately one-third inch. The sediment samples were taken to Denver by air and refrigerated. No preservatives were added to either the water or the sediment. The water sample was shipped

by Railway Express. The stream discharge was almost constant at 0.662 cfs for a 6-hour period prior to the time of sample collection.

When the water sample reached the laboratory—10 days after sampling—the water, containing a considerable amount of suspended sediment, and the slurry of surficial stream-bed sediment were combined. The combined material was then equilibrated for about 24 hours, and the solid and liquid phases were quantitatively separated. There was no observable color or

odor change between the time of sampling and the time of sediment separation. The sediment was size fractionated into >9-mesh (>2 mm in diameter), 9- to 60-mesh (2–0.25 mm), and <60-mesh (<0.25 mm) fractions. The >9- and the 9- to 60-mesh fractions were separated by wet sieving, and the <60-mesh fraction was recovered by passing the slurry at a rate of 300 millimeters per minute through a continuous-flow Servall SS-1 superspeed centrifuge at 15,000 revolutions per minute. Approximately equal amounts of the sediment were found in each of the three size fractions. The >9-mesh fraction was not used because of the difficulty in obtaining representative subsamples. The clear centrifugate was acidified (\approx pH 3) to decrease the probability of precipitation, biological growth, and adsorption on polyethylene containers.

Natural selectivity coefficients, $K_{i\bar{x}+j}^{Nat}$,¹ were calculated using the quantities of the radioions extracted from portions of the sized sediment and in the stream water. The exchangeable cations were extracted from the undried 9- to 60-mesh and <60-mesh sediment fractions in a Buchner funnel by leaching with a volume of 2*N* (normal) ammonium acetate (pH 7) such that the total milliequivalents of ammonium exceeded the exchange capacity of the sediment by approximately 40 times. A total contact time of 24 hours between leachate and sediment was maintained. A second leach of similar volume and contact time was conducted with 2*N* ammonium chloride (pH 3).

Ammonium acetate was used as the primary extractant of the exchangeable cations because it is the most commonly used salt for this purpose, and it can be volatilized at reasonably low temperatures, as can ammonium chloride (with fuming nitric acid). Two-liter aliquots of the leachates were concentrated by evaporation to volumes of 10–15 milliliters. This degree of concentration would not have been possible if other commonly used salts, such as potassium chloride or calcium chloride, had been used to displace the exchangeable ions.

An appropriate carrier—that is, a nonradioactive material isotopic with the radioion—was added to separate aliquots of stream water and sediment leachates following the evaporation step. This procedure was repeated for each radioion whose presence was anticipated (Morton, 1961). The aliquots were then evaporated to dryness. Dissolved organic matter as well as the ammonium chloride and ammonium acetate were

destroyed by adding fuming nitric acid and again evaporating to dryness. Chemical separations were made as follows: Cesium by a silicotungstic perchlorate method (Glendenin and Nelson, 1951), strontium by carbonate precipitation followed by a fuming nitric acid separation method (Beaufait and Lukens, 1952), cobalt by an α -nitroso β -naphthol chloroform extraction method (Sandell, 1959), ruthenium by a distillation method (Glendenin, 1951), cerium and rare earths by fluoride precipitation followed by an oxalate precipitation method (Ballou, 1951), zirconium and niobium by oxalate precipitation followed by a phenylarsonic acid extraction procedure (Steinberg, 1951). In the last procedure, oxalate was decomposed by fuming with sulfuric acid instead of boiling with potassium chlorate as in the reference. The amount of each radioion was determined by comparison of its count rate with that of Nuclear Chicago² standards.

Dialysis selectivity coefficients, $K_{i\bar{x}+j}^{Dial}$, for strontium, cesium, cerium, and cobalt were determined for comparison with the natural selectivity coefficients, $K_{i\bar{x}+j}^{Nat}$. Four hundred milligrams of sized and air-dried sediment was transferred into a 2-ounce polyethylene bottle. Twenty milliliters of a solution containing tracer quantities (approximately 10^{-10} *N*) of one of the radiocations and known concentrations of calcium chloride or sodium chloride were also added to the bottle. Twenty milliliters of the identical solution were sealed in a cellulose dialysis casing (by tying knots in the ends) and inserted in the same 2-ounce bottle. The bottle was then placed on a slow-speed shaker and the contents allowed to equilibrate for 2 days. Experiments with reference clays indicate that 95–97 percent as much strontium is sorbed in 2 days as in 4 days. Since Whiteoak Creek sediment contains rock fragments, it may not have approached equilibrium as closely in 2 days as did the reference clays. However, when equilibration times of 4 days or more are used, appreciable biotic growth occurs. In addition, the dissolution of slightly soluble phases becomes an increasing problem with extended equilibration time, as discussed later for carbonates.

Immediately after the equilibration period, the dialysis tube was removed from the bottle and opened, and duplicate 1-milliliter aliquots of solution from inside the dialysis tube were pipetted to counting tubes. This technique avoided the problem of incomplete separation of solid and liquid phases by centrifuging. The relative quantity of a given radioion in the solution inside the dialysis casing was compared with that of an equal-volume aliquot of input solution to determine the

¹ i = i th exchangeable ion, j = j th competing ion, and \bar{x} or \bar{X} =cation exchange site (where the bar over the X signifies that the site is assumed to be of a monovalent nature).

² Nuclear Chicago Corp., 333 East Howard Ave., Des Plaines, Ill.

fraction of radioion sorbed by the sediment. The quantity of added radioion was sufficiently greater than that already on the sediment so that the contribution of the latter could safely be ignored. Both calcium plus magnesium and sodium were used as competing cations.

Sodium and potassium were determined on a flame photometer, and calcium plus magnesium was determined by versene titration (Rainwater and Thatcher, 1960). Cation exchange capacities were determined with 1N cesium chloride spiked with cesium-137 (Beetern and others, 1962) using two 4-hour and one overnight equilibration periods. After removing the free salt with ethanol, the oven-dry sample weight and the count rate of the cesium-137 sorbed by the sample were obtained. Comparison of the count rates (counts per minute per milliequivalent) of 1 milliequivalent of the 1N cesium chloride solution with the count rate of the sample made possible the calculation of the cation exchange capacity of the sample.

The layer-silicate clay minerals were disaggregated and concentrated in a $<2\mu$ (micron) fraction. Five-gram portions of the $<60\mu$ and the 9- to 60-mesh fractions were suspended in distilled water and disaggregated in a Waring Blendor. After blending for 1 minute, the suspension was poured onto a 44μ screen and washed with distilled water. The sediment remaining on the screen was again blended with distilled water for 1 minute and then sized. This cycle was repeated until the filtrate was almost clear. The $<44\mu$ material was separated at 20μ by decantation, and the $20\text{--}44\mu$ material alternatively blended and sized until the decantate was almost clear. The $<20\mu$ material was fractionated at 2μ without further blending.

CALCULATIONS

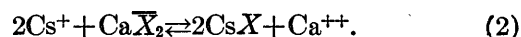
The distribution coefficient, K_d , is a common means of expressing the exchange sorption of a cation. If f_s represents the fraction of radiocation which is adsorbed by the sediment and $1-f_s$ represents the fraction remaining in solution, then

$$K_d = \frac{f_s V}{(1-f_s) M} \quad (1)$$

where V is the solution volume, in milliliters, and M is mass of the sediment, in grams. It is apparent that the absolute amount of a radioion in either solid or liquid phase need not be known to calculate the K_d . One needs to know only the relative count rate for a particular radioion sorbed on M grams of sediment and that for V milliliters of equilibrium solution (or alternatively, the count rate for V milliliters of both the

original and the equilibrium solutions). The distribution coefficient then has units of milliliters per gram.

The relationship between K_d and $K_{i\bar{x}+j}$, the mass-action selectivity coefficient, is quite simple. Consider the reaction describing the equilibrium exchange of Cs^+ (cesium) in solution for exchangeable Ca^{++} (calcium):



Solving for $K_{i\bar{x}+j}$ yields

$$K_{\text{Ca}\bar{x}+\text{Cs}} = \frac{(\text{Cs}\bar{X})^2 (\text{Ca}^{++})}{(\text{Cs}^+)^2 (\text{Ca}\bar{X}_2)} \quad (3)$$

From equation 1 it is apparent that

$K_{d_{\text{Cs}}} = (\text{fraction sorbed/fraction unsorbed}) (V/M) = (\text{Cs}\bar{X})/(\text{Cs}^+)$; thus, equation 3 may be rewritten as

$$K_{\text{Ca}\bar{x}+\text{Cs}} = (K_{d_{\text{Cs}}})^2 \frac{(\text{Ca}^{++})}{(\text{Ca}\bar{X}_2)} \quad (4)$$

where (Cs^+) and (Ca^{++}) represent solution concentrations, in milliequivalents per milliliter, and terms $(\text{Cs}\bar{X})$ and $(\text{Ca}\bar{X}_2)$ represent the quantity of exchangeable cations, in milliequivalents per gram.

The selectivity-coefficient equations in this paper are all written as in equation 3, where the radiocation is uniformly taken to be the j th competing cation. Hence, the greater the $K_{i\bar{x}+j}$ value, the greater is the selectivity of the sediment for the radiocation relative to the selectivity of the sediment for the competing cation(s).

Equation 4 is applicable in the presence of one, two, or several competing cations. Therefore, to calculate $K_{i\bar{x}+j}$ from a particular K_{d_j} , only the concentration of the competing cation of specific interest on the exchanger (sediment) and in the liquid phase (stream water) need be known.

Ion exchange reactions of reference clay minerals are rapid for the most part—that is, of the order of minutes (Kennedy and Brown, 1966)—and they are reversible. However, in dealing with earth materials in general and stream sediments in particular, extended times are often required to reach an apparent equilibrium because of (1) slow diffusion rates into the interstices of rock fragments and cemented secondary aggregates due to (a) extreme tortuosity, (b) double-layer salt sieving (Kemper, 1960), and (c) edge collapse (pinching of particle edges) of expansible layer silicates of high-charge density (Walker, 1959, 1963); and (2) secondary reactions such as (a) fixation due to collapse of an expanded or partially expanded layer silicate mineral to a spacing of approximately 10 Å, (b) pre-

cipitation — for example, $\text{Co}^{++} + 2\text{OH}^- \rightleftharpoons \text{Co}(\text{OH})_2$ — and (c) isomorphous substitution of the type $\text{Sr}_x^{++} + \text{CaCO}_3 \rightleftharpoons (\text{Ca}_{1-x}, \text{Sr}_x)\text{CO}_3 + \text{Ca}_x^{++}$.

Some of the secondary reactions noted above are not readily reversible; hence, an apparent, rather than true, equilibrium is obtained. Most of the values of K_{i+j} reported in the literature for earth materials exhibit a dependence on the concentration of the competing cation(s) as a result of secondary reactions of the types noted.

Another reason why K_{i+j} values reported in the literature show the influence of the concentration of the competing cations is the use of concentrations rather than activities. To obtain thermodynamically valid K_{i+j} values, which by definition are invariant with competing cation activities, ion activities rather than ion concentrations must be used. Activities can readily be calculated for salts in the aqueous phase (however, the accuracy decreases markedly for solutions whose ionic strength is greater than 0.1N). Currently there are major uncertainties in assigning values for the activities of solid-phase (exchangeable) cations.

The use of the term “mass-action equilibrium constant” is generally reserved for those reactions where (1) activities of the reacting ions can be unambiguously calculated or determined, (2) reversibility of the exchange reaction is demonstrated or can reasonably be expected to occur, and (3) secondary reactions of the types noted above are unlikely to occur. Under these conditions, selectivity coefficients and mass-action equilibrium constants are equivalent.

RESULTS

MINERALOGY

Grain thin sections made from the 9- to 60-mesh fraction were examined through a petrographic microscope, and the composition was estimated: quartz, 40–50 percent; chert, 10–15 percent; and rock fragments, 30–35 percent. Mica, chlorite, and feldspar grains were very rare.

Several X-ray diffraction patterns were obtained for randomly oriented powder specimens. Representative patterns are shown in figure 2. The powder patterns indicate the dominance of quartz, and the presence of

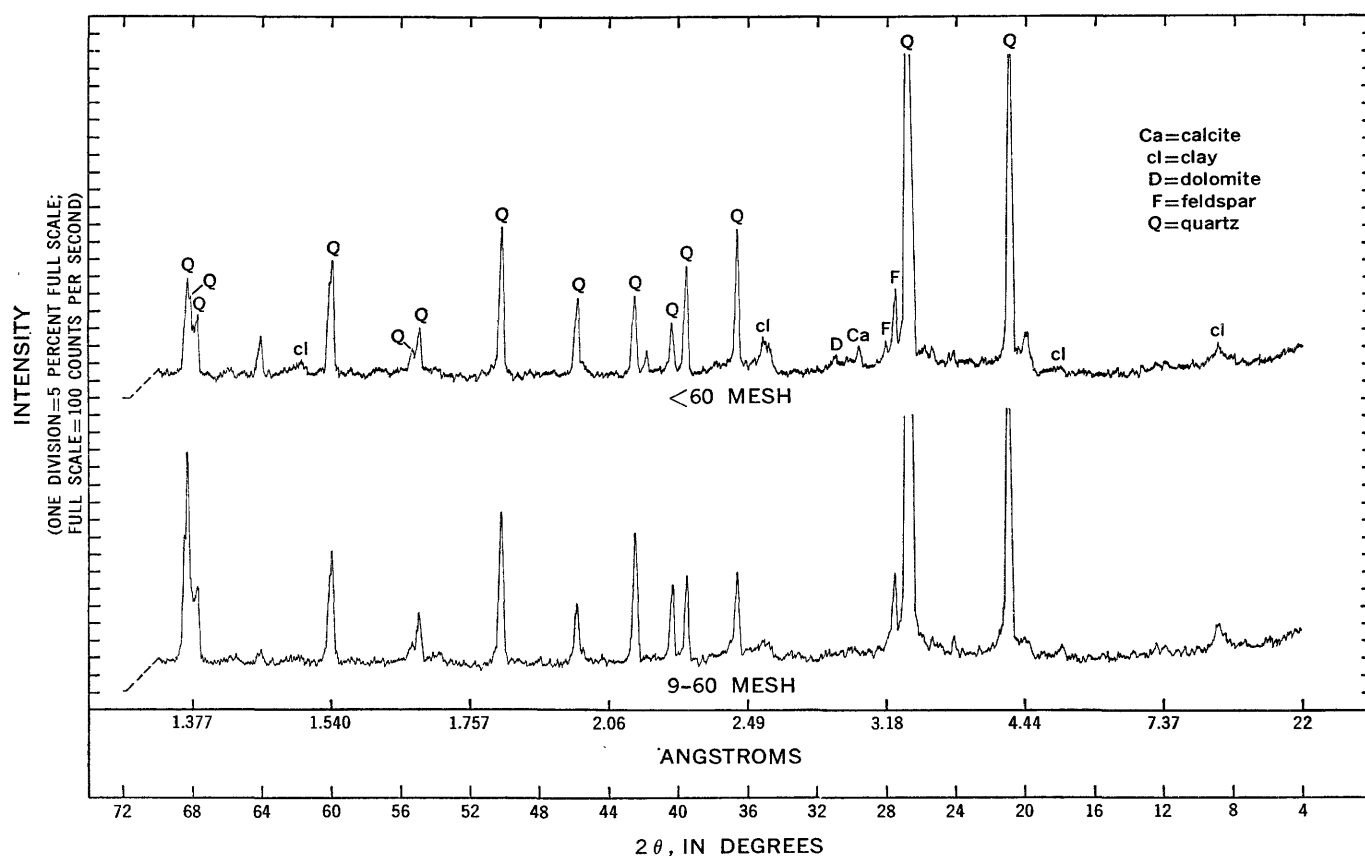


FIGURE 2.—X-ray diffraction powder patterns of sized Whiteoak Creek sediment [ground to –100 mesh; Cu $K\alpha$ radiation].

clay at 10.10 Å, 4.98 Å, 2.56 Å, and 1.50 Å, and some feldspar at 3.24 Å. One weak calcite and two very weak dolomite reflections were found in the diffraction patterns of the <60-mesh fraction. These reflections were not apparent in all the powder patterns. The maximum intensity of the calcite (3.02 Å) and dolomite (1.78 Å and 2.89 Å) reflections was 7 and 5 percent above background, respectively. Neither calcite nor dolomite reflections could be identified in the 9- to 60-mesh fraction. The calcite and dolomite reflections disappeared entirely upon treatment of the sample with ammonium acetate and ammonium chloride. No iron oxides were identified in the powder patterns, although total iron, calculated as Fe_2O_3 , was 3.6 and 6.1 weight percent in the <60- and the 9- to 60-mesh fractions, respectively.

The Waring Blender was very effective in breaking down the shale fragments, and it facilitated the concentration of the clays in the <2 μ fraction, as shown by the absence of layer-silicate reflections in the X-ray powder patterns of the >44 μ or 20–44 μ separates of both the <60- and 9- to 60-mesh fractions (patterns not shown). In fact, only a minor amount of clay was found in the parallel-oriented slides made from the 2–20 μ separates (fig. 3), indicating that the clay had been successfully concentrated in the <2 μ fraction. The size distribution resulting from the Waring Blender disaggregation process was 28.4, 21.0, 36.0, and 11.1 weight percent for the >44 μ , 20–44 μ , 2–20 μ , and <2 μ separates of the <60-mesh fraction, respectively. The size distribution for the 9- to 60-mesh fraction was 62.3, 11.8, 18.6, and 6.3 weight percent for the <44 μ , 20–44 μ , 2–20 μ , and <2 μ separates, respectively. Sample loss in the fractionating process amounted to 3.5 and 0.9 weight percent for the <60- and the 9- to 60-mesh fractions, respectively.

Roughly equivalent intensities of illite (10 Å) and vermiculite (14 Å) reflections were obtained upon magnesium saturation and glyceration of the <2 μ separate of the <60-mesh fraction (fig. 3). As was expected, there was less vermiculite in the <2 μ separate from the 9- to 60-mesh fraction than from the <60-mesh fraction. The high diffraction intensity in the region between the 10-Å and 14-Å peaks indicated that random mixed-layered illite-vermiculite was also present in addition to their occurrence as separate minerals.

Potassium saturation and air drying resulted in considerable enhancement of the 10-Å illite peak and a concomitant decrease in the 14-Å vermiculite peak. There did not appear to be any decrease in intensity in the 12-Å to 13-Å region as might have been expected,

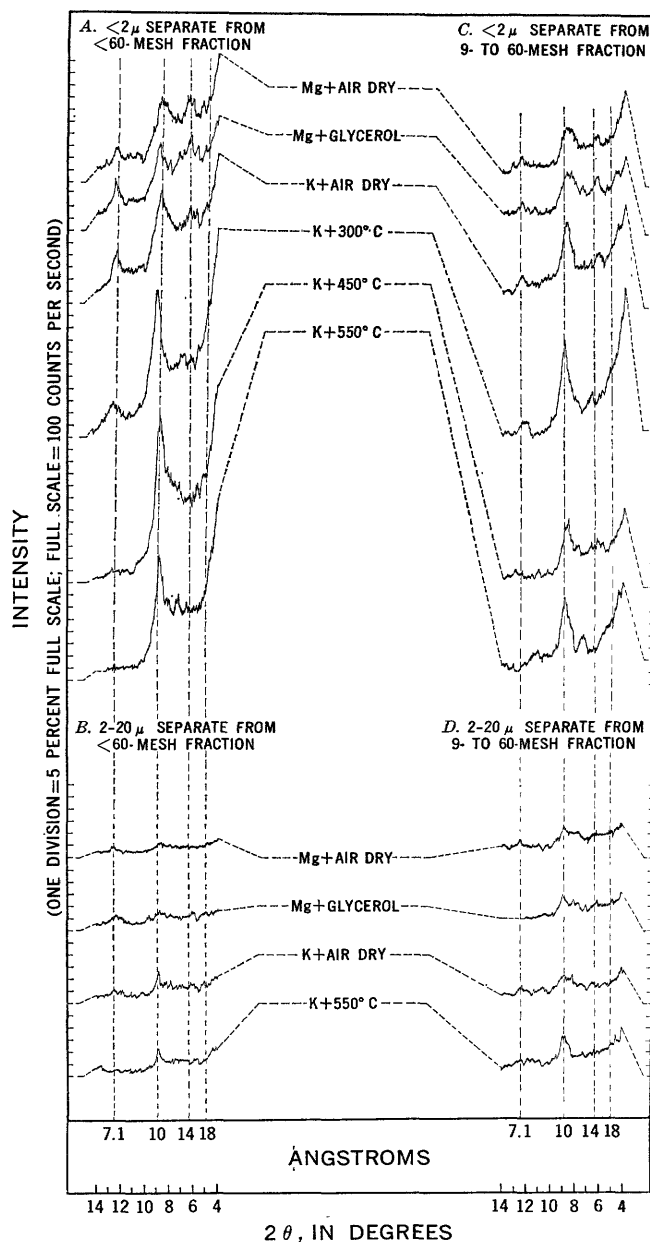


FIGURE 3.—X-ray diffraction patterns of parallel-oriented specimens of Whiteoak Creek sediment. [The <60- and 9- to 60-mesh fractions were separated by wet sieving. The <2 μ and 2–20 μ separates were obtained by physical disaggregation of the sized sediment in a Waring Blender. $\text{Cu K}\alpha$ radiation.]

because of collapse of part of the vermiculite to 10 Å. The 10-Å peak was sharpened by heating the sample to 300° Celsius (centigrade) because further dehydration and collapse of the vermiculite component occurred.

The absence of discrete montmorillonite was indicated by the failure of a 17-Å to 18-Å reflection to occur upon glyceration. However, in the <2 μ separate of the <60-mesh fraction, glycerol solvation caused a

small reduction in the intensity of the 14-A reflection relative to that of the 10-A reflection. This would indicate that something in excess of 10 percent of the layers yielding the 14-A reflection were irregularly interstratified montmorillonite.

A small amount of kaolinite in the $<2\mu$ separates was indicated by a 7-A peak, which was unaffected by cation saturation, glyceration, or heating to temperatures of up to 350°C for 1 hour. The 7-A reflection completely disappeared after the sample was heated at 550°C for 1 hour. A small amount of halloysite was indicated by a broad peak, or sometimes by a plateau, from about 7.1 Å to 7.9 Å, with a tendency for discrete peaks in the 7.4 Å–7.9 Å region. The intensity of the variable peaks in the latter region was not perceptibly influenced by free iron oxide removal, whereas the intensity of the 7-A peak was increased. The increased intensity of the 7-A peak was ascribed to removal of iron oxide coatings; this removal allowed more complete orientation of the kaolinite platelets parallel to the plane of the glass slide. The halloysite occurred predominantly in the $<2\mu$ fraction.

The absence of discrete chlorite was indicated by (1) no decrease in intensity of the 14-A reflection upon heating the sample at 550°C, as compared to 350°C, for 1 hour; (2) the broad 14-A reflection in most patterns, often ranging from 12.6 Å to 14.2 Å; and (3) complete loss of the 7-A reflection at 550°C.

The 2–20 μ separates showed a small amount of illite and a trace of kaolinite. The intensity of the illite reflection was enhanced by the heat treatments. The 7-A kaolinite reflection was eliminated by heating the sample to 550°C.

No indication of hydroxy interlayers was found from either X-ray-diffraction or cation-exchange-capacity measurements made before and after free iron oxide removal.

SOLUBLE AND EXTRACTABLE (EXCHANGEABLE) CATIONS

Studies of the Clinch River downstream from the mouth of Whiteoak Creek (Morton, 1961) have shown that, as of 1958, the relative abundance of radioisotopes in the surface bed sediments of the Clinch River—and, hence, presumably of Whiteoak Creek—was cesium-137 > cerium-144 > cobalt-60 > rare earths plus yttrium-90 > strontium-90. However, according to Morton (1962), cesium-137, cobalt-60, strontium-90, and ruthenium-106 were considered to be of primary importance with regard to health safety on the basis of their low maximum permissible concentrations in drinking

water, relatively high abundance, and long half lives (cesium-137=30 yr, cobalt-60=5.24 yr, strontium-90=28 yr, ruthenium-106=371 days). Our analyses for cesium-137, cerium-144, cobalt-60, rare earths, strontium-90, ruthenium-106, and zirconium-95 plus niobium-95 revealed the presence of cesium-137, strontium-90, cobalt-60, and rare earths in both the stream water and leachates. Ruthenium-106 was found only in the stream water. If present, cerium-144 and zirconium-95 plus niobium-95 were below our detection levels.

Soluble calcium plus magnesium was slightly more than twice the value for soluble sodium in the stream water (table 1). As K_{Na+Ca} for clays is of the order of 3–9 (Wahlberg and others, 1965), it could be predicted that most of the cation exchange sites of the clays present in the stream sediment would be saturated with calcium plus magnesium.

The extractable cations (exchangeable plus those dissolved from carbonates) were found to be predominantly calcium plus magnesium (table 1) as anticipated. The sum of the extracted cations is greater than the cation exchange capacity by a factor of about 4 for the <60 -mesh fraction, whereas the two values are equivalent for the 9- to 60-mesh fraction (table 1).

The excess of extractable calcium plus magnesium over the cation exchange capacity for both size fractions indicates that some solid phase containing calcium and magnesium was dissolved. The discrepancy is greater for the <60 -mesh fraction than for the 9- to 60-mesh fraction. Several lines of evidence indicate that in situ precipitated carbonates were the source of the dissolved calcium plus magnesium.

TABLE 1.—Major soluble cations in the stream water, major extractable (exchangeable) stable cations, and cation exchange capacities of the sized Whiteoak Creek sediment

Extractant	Sodium	Potassium	Calcium plus magnesium	Cation exchange capacity
Stream water † (me/ml)				
.....	12×10^{-4}	0.69×10^{-4}	27×10^{-4}
<60 mesh (me/g)				
NH ₄ C ₂ H ₃ O ₂	2.5×10^{-4}	2.2×10^{-4}	0.16
NH ₄ Cl.....	$.42 \times 10^{-4}$	$.31 \times 10^{-4}$.068
.....	0.11
9–60 mesh (me/g)				
NH ₄ C ₂ H ₃ O ₂	1.9×10^{-4}	1.4×10^{-4}	0.081
NH ₄ Cl.....	$.37 \times 10^{-4}$	$.18 \times 10^{-4}$.008
.....	0.083

† The conductance of the stream water (after centrifugation) was 1.0×10^5 μ mhos/cm at 25°C. The pH of the water (before centrifugation) was 7.14.

Field observation (R. J. Pickering, oral commun., 1965) indicates that carbonates are presently precipitating in Whiteoak Creek. This is in accordance with the greater amount of calcium plus magnesium extracted from the <60-mesh than the 9- to 60-mesh fraction by the ammonium acetate and ammonium chloride leaches. A marked decrease in the calcium plus magnesium in the ammonium chloride extract of both fractions as compared with the ammonium acetate extract (pH 3 versus pH 7) may indicate that the carbonates present were largely removed during the course of the ammonium acetate extraction. Serial 1*N* ammonium acetate pH 5 extractions (Jackson, 1956) of portions of the ammonium acetate plus ammonium chloride leached sediment yielded a small additional amount of calcium plus magnesium from both fractions in the first two 30-minute extractions, but none was detected in subsequent extractions.

STRONTIUM

Strontium desorbed from the 9- to 60-mesh fraction with ammonium acetate gave a $K_{Ca\bar{x}+Sr}^{Nat}$ value of 1.9 compared with 1.1 for the dialysis experiment. However, the $K_{Ca\bar{x}+Sr}^{Nat}$ values for the <60-mesh fraction were eight times that of the laboratory value. The larger values of $K_{Ca\bar{x}+Sr}^{Nat}$ than $K_{Ca\bar{x}+Sr}^{Dial}$ are attributed to dissolution of $(Ca, Sr^{90})CO_3$ by the ammonium acetate (and ammonium chloride) leach yielding strontium-90 in addition to the strontium-90 that was exchangeable.

The dialysis experiment yielded $K_{Ca\bar{x}+Sr}^{Dial}$ values (table 2) for both size fractions that are essentially identical with those obtained for sorption of strontium by reference clay minerals (Wahlberg and others, 1965). This would not have occurred if the concentration of calcium in the starting solution had been used in the calculation, since appreciable calcium plus magnesium dissolved from the sediment in the course of the 2-day equilibrium period. The use of strontium-85 for the dialysis experiments was also fortunate because of the release of strontium-90 by the dissolving carbonates. Whether strontium-85 and strontium-90 were in exchange equilibrium or not is immaterial, since a cation at the trace level ($<10^{-8}N$) competes with the dominant competing cation, not with other cations present in trace concentrations.

Examination of grain thin sections from air-dried unextracted sediment failed to reveal any discrete carbonate particles in either size fraction. However, detrital carbonates may exist as cement in some of the numerous rock fragments. The results of Clanton (1963)

TABLE 2.—*Distribution and selectivity coefficients for strontium-90 sorption by Whiteoak Creek sediment*

[Strontium-85 was used in the dialysis sorption studies; strontium-90 concentration in the stream water was found to be 1,200 pc/l (picocuries per liter)]

Extractant	Natural		Dialysis
	K_{dSr}	$K_{i\bar{x}+i}^{\dagger}$	$K_{i\bar{x}+i}^{\dagger}$
<60 mesh			
$NH_4C_2H_3O_2$ -----	405	9.6	1.2
$NH_4C_2H_3O_2 + NH_4Cl^*$ -----	527	12.5	-----
9-60 mesh			
$NH_4C_2H_3O_2$ -----	57	1.9	1.1
$NH_4C_2H_3O_2 + NH_4Cl^*$ -----	67	2.2	-----

$\dagger K_{i\bar{x}+i}^{\dagger}$ for the reaction $\frac{1}{2}(Ca\bar{X}_2 + Mg\bar{X}_2) + Sr^{++} \rightleftharpoons Sr\bar{X}_2 + \frac{1}{2}(Ca^{++} + Mg^{++})$.
*The total strontium-90 from both ammonium acetate and ammonium chloride extracts was used in this $K_{i\bar{x}+i}^{Nat}$ and K_d calculation.

indicate that significant exchange of strontium-90 in solution for the calcium plus magnesium of well-crystallized carbonates is not likely to occur within a day or two. He demonstrated that sorption of strontium-90 by detrital calcite plus dolomite was very slow. The average strontium-90 sorption (in what was initially distilled water spiked with strontium-90) only increased from 52.8 percent after 1 hour to 55.4 percent after 7 days. Hence, the nature of the carbonate present in a stream sediment may be much more significant than the quantity of the phase present, as it affects the rate of the reaction $CaCO_3 + Sr^{++} \rightleftharpoons SrCO_3 + Ca^{++}$.

Ratios of strontium-90 to calcium plus magnesium in the extracts are presented in table 3. The similarity of values for a given size fraction calculated for the two leaches indicates a relatively constant content of strontium-90 in the calcium plus magnesium phase dissolved. That it is a carbonate phase which is being dissolved is indicated by the disappearance of the calcite and dolomite reflections in the X-ray patterns following the ammonium acetate plus ammonium chloride leaches. That this carbonate phase is an in situ precipitate is indicated by the rapid rate at which it dissolves.

TABLE 3.—*Ratio of strontium-90 to calcium plus magnesium in ammonium acetate and ammonium chloride extracts of Whiteoak Creek sediment*

[(pc Sr⁹⁰/g)/(me Ca+Mg/g)]

Extractant	Size fraction	
	<60 mesh	9-60 mesh
$NH_4C_2H_3O_2$ -----	5, 500	900
NH_4Cl -----	2, 200	1, 400

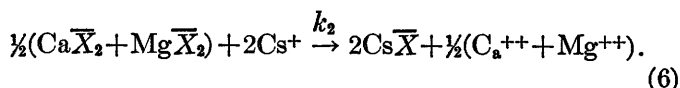
CESIUM

The predominantly irreversible³ nature of cesium sorption by Whiteoak Creek sediment is indicated by the data in table 4, which show that only a small portion of the cesium-137 present was removed by the two 24-hour extractions. It is noteworthy that the percentage of cesium-137 extracted by ammonium acetate and ammonium chloride from the 9- to 60-mesh fraction was appreciably less than from the <60-mesh fraction. This difference is ascribed to the higher illite content of the coarser size fraction (fig. 3, A and C). However, the absolute amount of cesium-137 extracted from the two size fractions was not sufficiently different, when compared with the concentration in the stream water, to yield markedly different $K_{Ca\bar{x}+Cs}^{Nat}$ values.

TABLE 4.—Percentage of total radioactivity removed from Whiteoak Creek sediment by ammonium acetate plus ammonium chloride extractions

Size fraction	Beta count	Gamma count	
		Cs ¹³⁷	Co ⁶⁰
<60 mesh-----	32	17	12
9-60 mesh-----	14	4	<1

Both size fractions sorbed equivalent quantities of cesium in the dialysis experiment. The $K_{Ca\bar{x}+Cs}^{Dial}$ values are of the same order of magnitude, although higher than those determined from the cesium-137 content of the leachate and stream water ($K_{Ca\bar{x}+Cs}^{Nat}$). Since the combined ammonium acetate plus ammonium chloride extraction time was equivalent to the sorption time in the dialysis experiment (48 hr), k_2 must be greater than k_1 , where k_1 and k_2 are the rate constants for reactions 5 and 6, respectively:



Thus, perhaps a dialysis equilibrium time of 1 day might have resulted in a $K_{Ca\bar{x}+Cs}^{Dial}$ value identical with that obtained after the 48-hour desorption period.

The Conasauga Shale is one of the principal formations in the area drained by Whiteoak Creek, which presumably accounts for the illitic nature of the sediment. Reference samples of illite commonly continue

to sorb additional quantities of cesium for several days, at a decreasing rate. Thus, after only a 2-day equilibrium period, the rate of cesium uptake in dialysis experiments may still have been fairly rapid. Thus, in comparing these data with other literature values, variable time factors must be taken into account.

Release of cesium from interlayer sorption sites of illite is essentially a diffusion process, so that one might expect that considerably more cesium would have been removed from the sediment if the extraction time had been prolonged. This is indicated in table 5, where it is shown that 20-30 percent of the total cesium-137 extracted was removed in the second 24-hour extraction period. This is in accordance with findings of various investigators that the displacement of a readily exchangeable portion of the total potassium is followed by a slow release of interlayer potassium (or cesium) from micas and illites, as indicated by the amount of potassium extracted or by increased cation exchange capacity values. (See, for example, Schnepfe, 1960; Mortland and Lawton, 1961.)

TABLE 5.—Distribution and selectivity coefficients for cesium-137 sorption by Whiteoak Creek sediment

[Cesium-137 concentration in the stream water was found to be 670 pc/l]

Extractant	Natural		Dialysis
	K_{dCs}	$K_{i\bar{x}+j}^{\dagger}$	$K_{i\bar{x}+j}^{\dagger}$
>60 mesh			
NH ₄ C ₂ H ₃ O ₂ -----	814	16, 000	56, 000
NH ₄ C ₂ H ₃ O ₂ + NH ₄ Cl*-----	1, 030	25, 000	-----
9-60 mesh			
NH ₄ C ₂ H ₃ O ₂ -----	642	13, 000	57, 000
NH ₄ C ₂ H ₃ O ₂ + NH ₄ Cl*-----	786	20, 000	-----

[†] $K_{i\bar{x}+j}^{\dagger}$ for the reaction $\frac{1}{2}(Ca\bar{X}_2 + Mg\bar{X}_2) + 2Cs^+ \rightleftharpoons 2Cs\bar{X} + \frac{1}{2}(Ca^{++} + Mg^{++})$.

*The total cesium-137 from both ammonium acetate and ammonium chloride extracts was used in this $K_{i\bar{x}+j}^{Nat}$ and K_d calculation.

Previous laboratory studies (Wahlberg and Fishman, 1962) on several reference layer-silicate minerals yielded $K_{Ca\bar{x}+Cs}^{Dial}$ values ranging from 2.8×10^3 (kaolinite) to 4×10^7 (illite)⁴ for tracer-level ($\approx 10^{-10}N$) cesium in the presence of 0.003N calcium chloride. The same authors found $K_{Ca\bar{x}+Cs}$ values of $2-4.4 \times 10^4$ and $0.9-1.2 \times 10^4$ for American Petroleum Institute montmorillonites No. 11 and 21 respectively. This range in $K_{Ca\bar{x}+Cs}$ values ($0.9-4.4 \times 10^4$) for montmorillonite encompasses the range found for the stream sediment ($2.0-2.9 \times 10^4$)

³ Where irreversible sorption is understood to pertain to that portion of the element not desorbed within the time interval of the experiment.

⁴ J. S. Wahlberg, unpub. data.

and is similar to the range obtained by dialysis ($5.6\text{--}5.7 \times 10^4$) in this study.

The question arises as to why the sediment, which X-ray diffraction shows to be principally illite and vermiculite, behaves chemically toward cesium like montmorillonite, yielding $K_{\text{Ca}\bar{x}+\text{Cs}}$ values of the order of 10^4 instead of 10^7 . One possibility is that coatings of organic matter, iron, manganese, and possibly aluminum and silicon on the primary particles present a diffusion barrier; thus, the equilibration time used in these experiments may simply have been inadequate. Rock fragments have been found to require up to twice as much time as reference clays to reach equilibrium in ion exchange reactions.⁵ In view of the considerable portion of rock fragments present in this stream sediment, inadequate equilibration time seems certain to be a contributing factor to the discrepancy. Further credence is given to this possibility by the significant amount of cesium-137 removed in the second 24-hour extraction (ammonium chloride) of the undried sediment (table 5).

COBALT

Some type of an essentially nonreversible mechanism is indicated for the sorption of cobalt-60 by Whiteoak Creek sediment. Table 4 illustrates that ammonium acetate plus ammonium chloride extractions removed practically none of the cobalt-60 from the 9- to 60-mesh fraction. In fact, so little cobalt-60 was displaced from this fraction that the K_d and $K_{\text{Ca}\bar{x}+\text{Co}}$ values can be considered as indicative only. Clinch River status reports have suggested that sorption of cobalt-60 from solution was due primarily to organics (Morton, 1961, 1962). However, manganese and iron oxides have recently been established as the primary scavenging agents in Whiteoak Creek sediment (Jenne and Wahlberg, 1965), organic matter being of secondary importance. Analysis of the ammonium acetate and ammonium chloride extracts for manganese and iron revealed that considerable manganese, but very little iron, had been dissolved. Thus, a large portion of the cobalt-60 extracted is presumed to have been released by dissolution of manganese oxides.

The results obtained show that $K_{\text{Ca}\bar{x}+\text{Co}}^{\text{Nat}}$ from the <60-mesh fraction was 7.5 times greater than the comparable value determined by the dialysis technique (table 6), in spite of the fact that only 12 percent of the total cobalt-60 content of the <60-mesh fraction was removed (table 4).

TABLE 6.—Distribution and selectivity coefficients for cobalt-60 sorption by Whiteoak Creek sediment

[Cobalt-60 concentration in the stream water was found to be 47 pc/l]

Extractant	Natural		Dialysis
	$K_{d\text{Co}}$	$K_{i\bar{x}+i}^{\dagger}$	$K_{i\bar{x}+i}^{\dagger}$
<60 mesh			
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ -----	1,400	33	4.3
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 + \text{NH}_4\text{Cl}^*$ -----	2,400	57	-----
9-60 mesh			
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ -----	$\dagger 13$	$\dagger 0.4$	17
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 + \text{NH}_4\text{Cl}^*$ -----	$\dagger 13$	$\dagger .4$	-----

[†] $K_{i\bar{x}+i}$ for the reaction $\frac{1}{2}(\text{Ca}\bar{x}_2 + \text{Mg}\bar{x}_2) + \text{Co}^{++} \rightleftharpoons \text{Co}\bar{x}_2 + \frac{1}{2}(\text{Ca}^{++} + \text{Mg}^{++})$.

*The total cobalt-60 from both ammonium acetate and ammonium chloride extracts was used in this $K_{i\bar{x}+i}$ and K_d calculation.

[†]Quantity determined was extremely close to detection level; hence, values are only approximate.

Cobalt sorption by reference clays in the presence of dilute concentrations (0.1–0.001N) of calcium or sodium is of similar magnitude to that of strontium (data not presented). Cobalt sorption equivalent to that of strontium was also indicated by Sorathesn, Bruscia, Tamura, and Struxness (1960) for distilled-water systems and by Graham and Killion (1962) for 0.013M (molar) calcium chloride systems. In the presence of organics (peat), the cobalt selectivity is much enhanced relative to strontium (Graham and Killion, 1962). Because little cobalt-60 was found in the organic fraction of this stream sediment (Jenne and Wahlberg, 1965), the $K_{\text{Ca}\bar{x}+\text{Co}}^{\text{Dial}}$ value of 4.3 (<60-mesh fraction) indicates scavenging of the cobalt-60 from the solutions by manganese and iron oxides, in addition to sorption on exchange sites of the silicate minerals. The greater laboratory sorption by the coarse, as compared with the fine, sediment fraction reflects the greater amount of manganese and iron oxides present in this fraction. In contrast, the $K_{\text{Ca}\bar{x}+\text{Co}}^{\text{Nat}}$ value is higher in the <60-mesh fraction because the ammonium acetate plus ammonium chloride extractants dissolved a greater portion of the fine-grained manganese and iron oxides.

RARE EARTHS

Dialysis sorption experiments yielded highly erratic results ranging from 63 to >99 percent uptake of tracer-level cerium-144 (originally trivalent) in competition with 10^{-3} – 10^{-1} N calcium chloride. The extent of cerium sorption was not obviously related to competing cation concentrations. The count rates of different aliquots of the original input solutions were also noted to be erratic. Three separate series of aliquots were

⁵ E. A. Jenne, and V. C. Kennedy, unpub. data.

taken from the original input solutions after these solutions had been stored for several days. Aliquots were taken with a minimum of disturbance, after vigorous shaking, and after acidification of the solutions. This sequence of aliquots yielded increasing count rates, indicating that precipitation or radiocolloid formation had occurred. Thus, the laboratory sorption data were invalidated and are therefore not presented here.

If precipitation occurred in the cerium dialysis experiments (average pH of 7.6 with extremes of 7.3 and 7.8), as it apparently did, then a similar process might be expected to occur in Whiteoak Creek. If rare earths were present in the sediment as precipitates which were insoluble in the ammonium acetate plus ammonium chloride leachates, the low $K_{Ca^{++}+Ce}^{Nat}$ values shown in table 7 would be explained. The higher concentration of rare earths in the solution phase, relative to the exchangeable phase, may be due to organic complexing agents in the stream. In fact, the fraction of the rare earths present which was removed by the ammonium acetate leach may have been combined with organics and, thus, may have escaped inorganic precipitation in the stream.

The selectivity constant approach does not appear to be applicable for cerium except in acid waters. Bensen (1960) noted that the uptake of cerium was essentially 100 percent at pH above 5 for a calcareous soil regardless of the initial valence of the cerium. Similar results were obtained with yttrium. The reversibility of the uptake was not reported for either element.

RUTHENIUM

From the presence of 230 picocuries of ruthenium-106 per liter in the water and the absence of ruthenium-106 from the leachates, one would conclude that ruthenium is

TABLE 7.—Natural distribution and selectivity coefficients for rare-earth sorption by Whiteoak Creek sediment

[Rare-earth (R.E.) concentration in the stream water was found to be 44 pc/l as cerium-144; rare-earth concentration in the ammonium chloride extracts was below detection]

Extractant	$K_{R.E.}$	$K_{i\bar{x}+j\bar{y}}$ †
<60 mesh		
NH ₄ C ₂ H ₃ O ₂ *-----	180	0.5
Do-----	140	.3
9-60 mesh		
NH ₄ C ₂ H ₃ O ₂ *-----	89	0.3
Do-----	73	.2

† $K_{i\bar{x}+j\bar{y}}$ for the reaction $3(Ca\bar{X}_2 + Mg\bar{X}_2) + 2(R.E.)^{++} \rightleftharpoons 2(R.E.)\bar{X}_3 + 3(Ca^{++} + Mg^{++})$.
* Concentrations found were extremely close to detection levels; hence, values are only approximate.

either irreversibly sorbed or not sorbed at all. Failure of the sediment to sorb ruthenium was indicated by an insufficient amount present in the sediment to be identified in the gamma spectrums. Other investigators (Bensen, 1960; Friend and Porcella, 1962; Story and Gloyna, 1963) also indicated that ionic uncomplexed ruthenium is only slightly sorbed by earth materials. As information on the valence state of ruthenium (which varies from 0 to +8) in Whiteoak Creek was not available at the time of the present study, the laboratory determination of distribution coefficients on the sediment was somewhat pointless.

In contrast to the findings in the present study, Pickering, Carrigan, Tamura, Abee, Beverage, and Andrew (1966) reported the presence of 16 curies of ruthenium-106 in Clinch River bed sediments as of July 1, 1962. Lomenick and Gardiner (1965) reported $1,038 \pm 88$ curies of ruthenium-106 in the bed of White Oak Lake as of December 1962. The latter authors noted that the ruthenium-106 is concentrated in a small area of the upper lake bed which roughly coincides with inlets of two surface streams which drain the intermediate-level-radioactive liquid-waste seepage-pit area. They stated that most of the ruthenium-106 is retained in the upper few inches of soil whereas a portion of the ruthenium migrates underground. Pickering, Carrigan, Tamura, Abee, Beverage, and Andrew (1966) suggested that the ruthenium-106 in the Clinch River bed sediment is in the form of nitrosyl ruthenium hydroxide, $RuNO(OH)_3(H_2O)_2$. Both ion exchange and physical sorption would be involved in the retention of this rather large ion by sediments.

DISCUSSION

It is believed that the soluble and exchangeable radioions were essentially in equilibrium at the time of separation of the sediment and aqueous phases for several reasons. First, about 40 days had elapsed since the last rain of sufficient magnitude to cause significant sediment movement. Hence, the sediment in the stilling basin would have been in the process of equilibrating with the low-level waste from the Oak Ridge National Laboratory for this period of time. Second, the time of travel of the creek water from the Oak Ridge National Laboratory to the stilling basin, a distance of 1.1 miles, was approximately 2½ hours at the discharge rate which prevailed (W. M. McMaster, written commun., 1966). In conjunction with the shallow nature of the creek and the coarse-textured highly permeable stream bed, this time and distance of travel is adequate to smooth out any short-time fluctuations in radioisotope dis-

charge from the laboratory. Thus, changes in the radioisotope concentration in the stilling basin in response to releases from the laboratory would occur slowly over a period of many hours. Third, upon receipt of the water in the U.S. Geological Survey's Denver laboratory about 10 days after collection, the slurry of surficial bed sediment was mixed with the water and allowed to equilibrate further for 24 hours before separation. Since the permeability of the polyethylene bottles to oxygen and carbon dioxide is appreciable, and because there was no detectable change in the odor of the water as a result of transport, there is reason to believe that the biological population of the water would not have changed sufficiently during transit to have affected the radioion distribution.

The data presented indicate strongly that ammonium acetate "extractable" strontium, cobalt, and cesium are not identical with the quantity of these ions that is "exchangeable"—that is, sorbed reversibly onto electrostatic exchange sites. This situation results from the dissolution of significant amounts of solid phases containing strontium and also cobalt, and from the diffusion-controlled release of cesium from the micaceous minerals. Thus, the amount of these radioions extracted is partly dependent on the duration of the extraction and the solid to solution ratio utilized. However, this does not invalidate equation 3 because the strontium in the in situ precipitated carbonate, the cobalt in the hydrous manganese and iron oxides, and the interlayer cesium in illite are in equilibrium with the stream water. However, the accuracy of the resultant selectivity coefficients is adversely affected because the optimum extraction time is unknown.

Carbonates present a twofold problem. First, ammonium acetate, even at pH 7, dissolves an appreciable quantity of fine-grained carbonates (Hanna and Reed, 1948; Bower and others, 1952); hence, where strontium is a component of stream carbonates, either through coprecipitation or by isomorphous substitution for calcium or magnesium in detrital carbonates, the amount of exchangeable strontium as well as calcium plus magnesium will be overestimated. Secondly, during the equilibration of strontium with the sediment in the dialysis technique, carbonates also dissolve when the solution is undersaturated with respect to calcium carbonate (as would commonly be the situation), yielding additional strontium to the solution but, more importantly, depressing strontium sorption by increasing the concentration of competitive divalent cations (calcium plus magnesium). Thus, calcium plus magnesium is not constant, but increases during the

equilibration period. Strontium sorption in the presence of sodium as the competing ion (data not presented) revealed that in the <60-mesh fraction the calcium plus magnesium concentration increased from 0 to $2-5 \times 10^{-3}N$. Here, the strontium-90 that came into solution caused no problem, as the dialysis experiments were carried out with strontium-85. Also, the amount of strontium dissolved was insignificant in comparison with the calcium plus magnesium concentration. That is, the sorption of a cation present at the trace level is controlled by the selectivity of the exchanger for it and the dominant cation(s) on the exchange complex, not by other trace elements. This situation is illustrated for cesium in the report of Wahlberg and Fishman (1962).

The large amount of fixed, relative to exchangeable, cobalt-60 led to a companion study (Jenne and Wahlberg, 1965) where an attempt was made to identify the agent(s) in the sediment responsible for scavenging of cobalt-60. Metal oxide reduction treatments (Jackson, 1956) with interspersed organic-matter oxidization revealed that most of the cobalt-60 was in the reducible metal oxide fraction. It was concluded that 95 percent of the cobalt-60 was distributed between these two scavenging agents, and that much more was in the manganese than in the iron oxide fraction, even though the sediment contains 30 times more iron than manganese.

The sorption and desorption of strontium, cesium, and cobalt were shown to be significantly time dependent. Thus, the rates at which these reactions occur may be of equal or greater significance than the ion exchange capacity, as regards the retention of radioions.

FUTURE STUDIES

Many problems are inherent in the accurate prediction of field uptake of radioions on the basis of laboratory sorption measurements. The time dependency of many sorption and other concomitant reactions is the source of several problems.

Ideally, a complete in situ separation of the stream water and sediment should be made immediately after sampling, followed by size separation of the sediment, displacement of the exchangeable ions, and determination of the major cations. Ammonium chloride appears to be the most suitable extractant, as carbonates and manganese oxides are believed to be less soluble in ammonium chloride than in ammonium acetate. The use of a nonvolatile salt is precluded by the need to concentrate the extract.

The ammonium chloride used to displace exchangeable cations should be adjusted to a pH such that, after leaching through the sample, the leachate pH is identical with that of the stream water. Alternatively, the extractant pH could be adjusted to the pH of the stream water. However, the former is preferable because the higher salt concentration of extractant displaces hydrogen ions from the exchange sites, increasing the solution-phase activity of hydrogen so that it can attack carbonates. Thus, to maintain the pH of the extractant in contact with the sample at the pH of the stream water, it may be necessary to start with the ammonium chloride solution at a slightly higher pH than that of the stream water.

Portions of extracted and unextracted sediment could then be dried immediately. The clarified stream water and ammonium chloride extracts should be acidified to pH 2-3 to reduce biotic growth, container sorption, and precipitation, especially where waters may be supersaturated with respect to calcium carbonate. The stream water would be clarified by filtration through a 0.05μ filter. If significant amounts of suspended sediment were present, the water could first be passed through a continuous flow centrifuge to reduce filtration time.

The next steps would entail the transfer of appropriate aliquots of the sediment-free stream water to plastic bottles, addition of known amounts of appropriate carriers to duplicate aliquots, and capping of the bottles for return to the laboratory for concentration, radiochemical separations, and quantitative radioactivity assay.

It would be necessary to treat the various aliquots of stream water so as to insure the same oxidation state for both the carriers and radioions. Errors in the estimation of the concentration of a given element in the stream water, due to container sorption or radio-colloid formation, would be essentially eliminated by the above procedures, inasmuch as the addition of a known amount of a carrier allows the percentage recovery of a given element to be determined. Changes in the quantity of radioions in the liquid and solid phases due to changes in redox potential, temperature, and biota during transport could thus be avoided. The determined radioion distribution would be very nearly that which actually existed in the stream at the time of sampling.

It would be desirable to extract a portion of the sediment with sodium chloride or some other highly soluble salt in which organics, manganese oxides, and carbonates would be less soluble than in ammonium chloride. The difference in the calcium, magnesium, manganese, and iron concentrations in this extract and in the ammonium

chloride extract would indicate the extent to which minor phases were being dissolved in the ammonium chloride extract. However, the use of a nonvolatile salt is precluded for determining the amount of trace-level radioisotopes because extract volumes of the order of liters must be concentrated to volumes of the order of milliliters.

In any future studies of this type, it would be essential to determine the rates of the sorption-desorption reactions. The leachate might well be collected in several sequential portions so that the fraction of each radioion removed could be determined as a function of leaching time. Sorption-desorption curves of the type illustrated in figure 4 may be expected for any radioion where a portion of the sorption is irreversible (that is, within the time interval of the experiment). In addition to furnishing a best estimate of the amount of exchangeable ion, the time curves indicate the degree of permanence with which the radiocation has been fixed and permit an estimate of the time required for the nonexchangeable portion to be extracted. If a leaching solution were used which was similar in composition to the stream water, except for the absence of the radiocation, the time required for the radiocation content of the sediment to drop to background, when and if its source to the stream were cut off, could be estimated.

A mobile field laboratory would be essential for such a study in view of the amount of work which should be performed on site.

CONCLUSIONS

In situ precipitated carbonates controlled the sorption of strontium-90, the hydrous oxides of manganese and

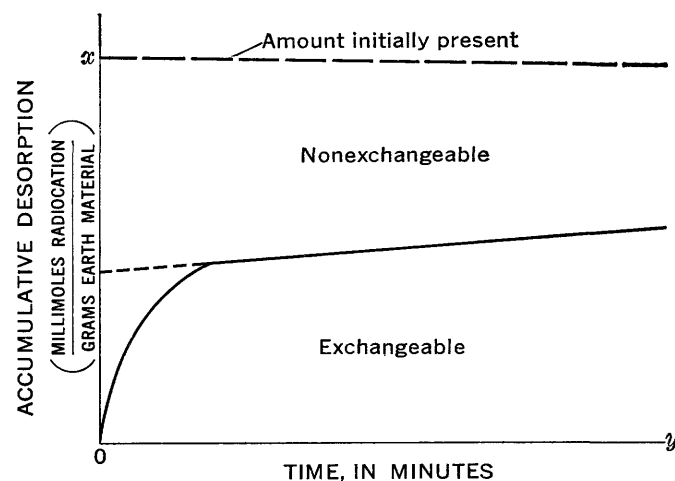


FIGURE 4.—Graph showing generalized curve for the desorption of a radiocation from multiple-phase earth-material specimen.

iron controlled the sorption of cobalt-60, and illite controlled the sorption of cesium-137 in Whiteoak Creek (Oak Ridge, Tenn.) sediment. Rare earths precipitated at the neutral pH of the stream water, whereas ionic, uncomplexed ruthenium was sorbed only very slightly by the sediment.

Agreement between "natural" and "laboratory" selectivity coefficients (nonequilibrium mass-action constants) for the <60- and the 9- to 60-mesh fractions of the sediment was only fair. High values for the natural selectivity coefficients for strontium-90 and cobalt-60 are attributed to the dissolution of fine-grained carbonate and hydrous manganese and iron oxides, respectively, in the ammonium acetate and ammonium chloride leachates. High laboratory selectivity coefficients for cobalt-60 in the 9- to 60-mesh fraction is believed to be due to the greater quantities of the hydrous oxides in this size fraction. The larger cesium-137 laboratory selectivity coefficient (by a factor of 2) is believed to be due to more rapid rates of cesium-137 sorption than desorption by illite, the dominant clay mineral in the sediment. Much less cobalt-60 was desorbed from the 9- to 60-mesh than from the <60-mesh fraction of the sediment owing to the lesser amount of hydrous oxides of manganese and iron present in the coarser fraction. Much less cesium-137 was desorbed from the coarser fraction owing to the slower diffusion of cesium-137 out of the larger illite particles.

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