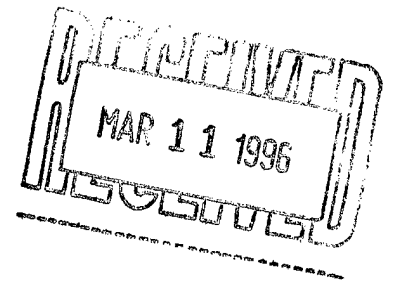


THESIS



Sorption Kinetics of Cs and Sr in Sediments of a
Savannah River Site Reservoir

Submitted by

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MASTER

In partial fulfillment of the requirements

for the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Spring 1996

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COLORADO STATE UNIVERSITY

January 18, 1996

WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR
SUPERVISION BY JOHN STEPHENS ENTITLED SORPTION KINETICS OF CS
AND SR IN SEDIMENTS OF A SAVANNAH RIVER SITE RESERVOIR BE
ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE.

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ABSTRACT

SORPTION KINETICS OF CS AND SR IN SEDIMENTS OF A SAVANNAH RIVER SITE RESERVOIR

Laboratory measurements of the sorption and desorption of ^{134}Cs and ^{85}Sr to sediments were conducted. These sediments were sampled from the profundal zone of Par Pond at the Savannah River Site, Aiken, South Carolina. The isotopes ^{134}Cs and ^{85}Sr were used to trace the sorption properties of the main contaminants found in the reservoir which are ^{137}Cs and ^{90}Sr respectively. The sorption behavior of these two elements was studied using spiked sediment/water slurries of a known mass to volume ratio. The results reveal that Sr undergoes significant reversible sorption while a fraction of Cs irreversibly sorbs to the sediment. The calculated distribution coefficient K_d at equilibrium was $(3\pm 0.6)\times 10^3$ for ^{134}Cs after 60 d and $(1\pm 0.2)\times 10^3$ for ^{85}Sr after 7 d at pH ≈ 6 and slurry ratio of 1:1000 g/ml. The K_d for ^{134}Cs ranged from 2×10^2 to 3×10^4 , depending on pH and conductivity. The ^{85}Sr reached equilibrium in a few days, while ^{134}Cs reached an apparent equilibrium in 1-2 months. The K_d for ^{134}Cs was a function of the slurry ratio, pH, conductivity, and contact time. These factors were inter-related since the sediments released ions to the slurry mixture which decreased the pH and increased the conductivity. A sorption isotherm measured for ^{134}Cs was linear at water concentrations from 60 mBq/ml to 20 Bq/ml. A kinetic model was proposed to describe the basic sorption of ^{134}Cs to Par Pond sediments under homogeneous laboratory conditions.

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Sorption Kinetics of Cs and Sr in Sediments of a Savannah River Site Reservoir

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INTRODUCTION

The Savannah River Site is a U.S. Department of Energy facility that was used for four decades to produce special nuclear materials. Par Pond at the Site was the primary cooling reservoir for P and R reactors (Fig. 1). During the years of site operation, the leakage of fuel rods led to the discharge of fission products into nearby canals and cooling ponds (Carlton 1994). The primary contaminants remaining from this discharge are ^{137}Cs and ^{90}Sr . The vast majority of the contamination in this and other reservoirs of the cooling water system was found to reside in the sediments (Whicker et al. 1990; Whicker et al. 1993).

The Savannah River Site provides opportunities for research on contaminants in environmentally dynamic systems. Qualities of Par Pond sediments that contribute to the dynamic behavior of these contaminants are: low lime content, high organic acids content, relatively low irreversible exchange capacity for the mineral component, highly permeable soils, large area to average depth, resulting in significant resuspension, naturally fluctuating competing cations such as NH_4^+ , Cs^+ , K^+ , Fe^{+3} , Mn^{+2} , etc., and annual stratification in the reservoir. Previous studies conducted on the sediments from the site have reported a reversible ion exchange of ^{137}Cs leading to the mobilization of a fraction (0.5%) of this contaminant during annual stratification of the reservoir (Evans 1983). This was attributed in part to the paucity of clays with interlayer exchange sites which irreversibly bind the

^{137}Cs and also to ammonium ion production during periods of anoxia at the sediment/water interface. However, the chemical and physical parameters needed to understand the sorption kinetics and equilibria in these particular sediments have not been adequately investigated.

The general purpose of this study was to characterize the sorption behavior of ^{137}Cs and ^{90}Sr in the profundal sediments of Par Pond. This research examined the equilibrium of these elements between the water and sediments using the isotopic tracers ^{134}Cs and ^{85}Sr . Of specific interest were: a) equilibrium K_d values; b) sorption rates; c) chemical and physical factors affecting K_d ; and d) capacity of competing ions to displace Cs or Sr from sediment. From such information, predictions about the long-term mobility of ^{137}Cs and ^{90}Sr in Par Pond and similar impoundments can be made for remedial action decisions and intelligent response to any future accidental releases.

MATERIALS AND METHODS

Study Site

Par Pond is a warm monomictic mesotrophic reservoir of 10 km^2 (Table 1). The Par Pond system has been described in detail (Marshall and LeRoy 1971; Marshall and Tilly 1971; Tilly 1975). The Par Pond water column cycles annually, stratifying during summer and depleting the hypolimnion of oxygen. Alberts et al. reported that the water activity concentration of ^{137}Cs cycled, coinciding with the annual stratification period (1979). It was determined that during the summer period some ^{137}Cs is mobilized from the sediments back to the water by ammonium ions released by anaerobic decomposition of organic matter (Evans et al. 1983). Ruhe and Matney (1980) studied the composition of sediment from Par Pond.

Sampling

Sediments were collected from the profundal zone ($\approx 12 \text{ m}$ water depth) of Par Pond using a $15 \times 15 \text{ cm}$ custom ponar dredge in the fall of 1994 when the reservoir was drawn down 6 m. A description of the drawdown and its impacts is provided by Whicker et al. (1993).

The top 1 cm of the readily resuspendable material was scraped off and used for this study. Water was sampled at the surface of the reservoir. The samples were stored in a refrigerator to reduce microbial activity. The sediments were oven dried at 60-70 °C for 12 h and then crushed using pestle and mortar which homogenized the sediment while preserving the integrity of the mineralogy. The impact of the pretreatment on the sediments was assumed negligible. Much longer drying times and higher temperatures have been shown to change the sediment characteristics (Roy et al. 1992). A subsample of the sediments was delivered in a saturated state to the Soils Testing Laboratory, Colorado State University for chemical and physical analysis. Aliquots of the water were also analyzed for soluble ions. The pH of the lake water and of a sediment paste were measured on the day of sampling.

Sediment Clay Mineral Analysis

An x-ray diffraction pattern of the sediment was obtained at the Earth Resources Department, Colorado State University. The soil sample was sonically dispersed in suspension and then transferred to a glass slide with an eye dropper for x-ray analysis. Another sediment aliquot was obtained and the clay fraction was separated in suspension. This fraction was analyzed in greater detail for clay minerals at the Savannah River Ecology Laboratory, Aiken, South Carolina.

Radioactivity Measurements

The purpose of the tracers was to characterize the sorption behavior of the main contaminants in Par Pond. The tracers ^{134}Cs and ^{85}Sr were measured using a NaI well detector and an Auto- γ NaI[†]. These isotopes are high yield gamma emitters, and they can be easily distinguished from the ^{137}Cs and ^{90}Sr already present in the sediments. Each time water samples were counted, a background and a standard reference were counted as part of the quality control program. The background was de-ionized H_2O in the same geometry. The standard reference was a known aliquot of the stock spike solution. This was used to normalize the water sample count rate and to estimate the counting yield. To estimate loss from the system in the batch method, whether sorption to the containment vessel or other loss mechanisms, Par Pond water in a centrifuge tube without sediment was

also spiked with tracer. This was considered the control. Each time a water sample from the experimental tubes was measured, a 5 ml water sample was also pipetted from the control tube and counted.

Radioactive Tracers

The tracers were in chloride form contained in aqueous solution. The specific activities of the tracers were quoted by the respective commercial suppliers. The specific activity of ^{134}Cs was 326 MBq $^{134}\text{Cs}/\text{mg CsCl}$ (43.4 MBq $^{134}\text{Cs}/\mu\text{mol CsCl}$)^{††}, and the specific activity of ^{85}Sr was 463 MBq $^{85}\text{Sr}/\text{mg SrCl}_2$ (40.6 MBq $^{85}\text{Sr}/\mu\text{mol SrCl}_2$)^{†††}. The tracers were in dilute HCl (7.83 MBq $^{134}\text{Cs}/\text{mmol HCl}$ and 3.70 MBq $^{85}\text{Sr}/\text{mmol HCl}$). A simple calculation shows that the CsCl carrier concentration was 2 orders of magnitude higher than the $^{134}\text{CsCl}$ concentration, and the SrCl_2 carrier concentration was 3 orders of magnitude higher than the $^{85}\text{SrCl}_2$ concentration. Furthermore, the HCl concentration was 3-4 orders of magnitude higher than the respective carrier concentrations.

Batch Equilibrium Method

The amount of ^{134}Cs and ^{85}Sr tracer sorbed to the sediment was measured using the batch equilibrium method (Roy et al. 1992). All sorption measurements were at room temperature (20-23° C). A sediment and water slurry occupying a 40 ml volume was mixed in a known sediment mass to water volume ratio in 50 ml centrifuge tubes. After the tracer was added to the slurry, the slurry was mixed using a mechanical rotator consisting of a turntable with tube holders inclined at 30° and rotated @ 30 rpm. After allowing the tracer to partition, the sediment was separated by centrifuging for 15 min @ 4000 rpm and a 5 ml water sample was pipetted for counting.

The K_d is defined as the ratio of the dry sediment concentration to the water concentration:

$$K_d = C_{\text{sediment}} / C_{\text{water}} \quad (1)$$

The slurry ratio R is defined here as the ratio of the dry mass of sediment (g) to the volume of water (ml):

$$R = M_{\text{sediment}} / V_{\text{water}}, \quad (2)$$

The amount of tracer absorbed by the sediment from the water is $Q_w(0) - Q_w(t)$, where $Q_w(0)$ is the initial spike activity and $Q_w(t)$ is the water activity at time (t). The K_d was calculated from the normalized ratio of the initial to final water activities (Equation 3). The expression for K_d in Equation 3 neglects physical loss, whether from sorption to the tube wall, or mass loss of water or sediment. The loss of sediment and sorption to the tube wall were considered negligible since the samples were well homogenized and the tubes were of polyethylene type material. Based on counts of water in the control tube, the loss from the water appeared to be less than 5-10%. An equivalent expression in Equation 3 was also used to calculate K_d from the normalized water activity concentrations, where $C_w(0)$ is the initial water activity concentration and $C_w(t)$ is the measured water activity concentration at time (t).

$$K_d(t) = \frac{(Q_w(0) / Q_w(t) - 1) / R}{(C_w(0) / C_w(t) - 1) / R} \quad \text{or} \quad (3)$$

Study of the Sorption Isotherms

Two sorption isotherms were measured using the ^{134}Cs tracer. The first was defined by increasing the slurry ratio and maintaining a constant spike activity. Adjusting the slurry ratio changed the amount of sediment to water available for the partitioning. The second sorption isotherm was defined by changing the amount of the tracer spike for a given slurry ratio. For the first sorption isotherm, a set of six slurries ranging from 1:2 to 1:8000 g/ml were spiked with about 35 kBq ^{134}Cs and equilibrated for 1 d. For the second sorption isotherm, 9 slurries of 1:100 g/ml were spiked with activities ranging from 34 Bq to 280 kBq ^{134}Cs and equilibrated for 1 d. A sorption isotherm for ^{85}Sr was not measured, since sorption of Sr to sediment was found to be more sensitive to HCl than ^{134}Cs , and the HCl concentration was 4 orders in magnitude higher than the SrCl_2 concentration.

The first sorption isotherm was one more empirical method to obtain a range of concentrations of ^{134}Cs for K_d . EPA in 1992 recommended this procedure for each individual soil type (Roy et al. 1992). EPA did not necessarily recommend one particular slurry ratio in the range from 1:4 to 1:10,000 g/ml. Previous studies recognized that lower slurry ratios would correspond better to the actual ratio in the water column (Nyffeler et al. 1984). Still, there was a trade-off between decreasing the slurry ratio, to accurately represent the seston K_d which pertains to the processes of settling and resuspension, and maintaining a sufficient subsample mass.

Another important reason for examining the lower slurry ratios was that the K_d for seston has been recognized as a sensitive parameter affecting Cs availability in the water column. The rate of Cs transport from the water column to sediments is affected by the seston K_d , as well as the rate of settling of the suspended particulates (Nyffeler et al. 1986; Santschi et al. 1986). The seston K_d was the first partitioning point in the general limnological models developed after the Chernobyl accident (Hakanson 1991).

Equilibration

The tracer partitioning between sediment/water was measured as a function of time. Two 1:1000 g/ml slurries were spiked, one with about 4.9 kBq ^{134}Cs and the other with 2.3 kBq ^{85}Sr , and the slurries were placed on the rotator. At selected times after the spike, the slurries were removed from the rotator and the sediment separated from the water by centrifugation. This was done at 1 h, 9 h, and 1, 2, 3, 4, 5, 7, 11, 15, 20, 25, 30, 35, 40, 46, 51, and 62 d for the ^{134}Cs spiked slurry and at 6 h, and 1, 2, 3, 4, 5, and 7 d for the ^{85}Sr spiked slurry. After counting, which required <20 min, the water samples were returned to the slurries and continued to mix on the rotator.

Extraction Method

The amount of tracer displaced from the sediment was measured by extraction. The extraction procedure followed the batch equilibrium process, except that after tracer equilibrium was attained, the water phase was separated by centrifugation and discarded,

and then replaced with a solution of competing cations. The slurry was again mixed, allowing the cations in solution to exchange with the tracer on the sediment. The slurry was again separated by centrifuging, and a second liquid phase sample was taken for measurement.

We spiked 15 slurries of 1:1000 g/ml ratio, 6 with 980 Bq ^{134}Cs and the other 9 with 460 Bq ^{85}Sr . The slurries were rotated for 7 and 3 d, respectively. After centrifuging, the remaining liquid phase was discarded, and a fresh solution containing a 5 mM concentration of the soluble cation was added to the sediment. The solutions chosen for the extraction contained soluble cations which are found naturally in the reservoir (Evans et al. 1983). The solutions chosen for the extraction of ^{134}Cs from the sediments were NH_4NO_3 , KCl , CsCl , HCl , NaCl , and CaCl_2 . The solutions chosen for the extraction of ^{85}Sr from the sediments were HCl , FeCl_3 , SrCl_2 , CaCl_2 , MnCl_2 , MgCl_2 , KCl , NH_4NO_3 , and NaCl . The slurries were rotated for 1 d with the extract solutions.

The relationship between the fraction of ^{134}Cs extracted from the sediment and the extract concentration was measured for KCl and NH_4NO_3 . The extraction procedure used concentrations of 10 μM , 100 μM , 1 mM, and 10 mM of KCl and NH_4NO_3 which spanned the concentrations of these cations found naturally in the reservoir (Evans et al. 1983). The slurries were rotated for 1 day allowing the tracer to equilibrate with the sediment, then rotated 1 d with the extraction solution to allow displacement of the tracer off the sediment. The 1 d extraction was assumed to be adequate time to extract the majority of the available Cs. Other methods which measured available Cs at longer extraction times reported slightly higher yields (by 5-10%; Madruga 1993; DePreter 1990).

The fraction of ^{134}Cs extracted from the sediment was measured as a function of equilibration time. We spiked 5 slurries of 1:100 g/ml ratio with about 4.9 kBq ^{134}Cs tracer, and placed the slurries on the rotator. Slurries were removed from the rotator at 1, 5, 11, 30, and 57 d. After removal from the rotator, the ^{134}Cs tracer was extracted from the sediment using a 1 d extraction at concentration of 100 mM KCl .

RESULTS AND DISCUSSION

Sediment and Water Characterization

The sediments analyzed were low in lime (<1%) and extremely high in organic material (Table 2). The organic matter was 28% of the sediment mass (Ruhe and Matney 1980 measured 9% organic matter in Par Pond sediments). The pH of a sediment paste measured 2.2 at the time of sampling (Ruhe and Matney 1980 measured a pH of 3.4 for a 1:1 paste of Par Pond sediment). The low sediment pH was attributed largely to the organic fraction of the sediment composition which contained organic acids such as fulvic and humic.

Some of the main cations measured in the sediments by an ammonium extraction were Fe, Mn, and K (Ruhe and Matney noted for Par Pond Ca, Mg, Na, and K instead). The cation exchange capacity was 32 meq/100 g, similar to illite clays alone (Sposito 1989; Ruhe and Matney measured 30 meq/100g). The texture estimate of the sediment was 53-45-2% for the clay-silt-sand fractions (Ruhe and Matney 1980 measured 74-22-4%).

The first x-ray diffraction spectrum displayed reflections from kaolinite clay and quartz sand, but not illite (Ruhe and Matney 1980 measured 7% illite). The $\leq 2 \mu\text{m}$ particle size fraction displayed x-ray diffraction peaks corresponding to kaolinite clay, hydroxy-interlayered vermiculite (HIV), gibbsite, and quartz (Ruhe and Matney measured 8% chlorite/vermiculite). The analysis showed kaolinite to be the primary clay mineral, but also consisting of HIV, with lesser amounts of gibbsite and quartz[¶]. There was no detectable amount of illite or expandable 2:1 layered clay types.

The bottom topography and sediment characteristics are spatially complex in Par Pond, which may account for differences between our data and Ruhe and Matney's (1980). This single sample of sediment was obtained in the deepest central region of Par Pond where the finer particulate matter tends to accumulate. The sediment composition could have been considerably different if sampled in another region of Par Pond, for example, the less organic and more sandy sediments near the shoreline of the reservoir. The sediments we sampled contained higher concentrations of ^{137}Cs than sediments at most other regions of Par Pond (3-9 Bq/g Table 2). Sediments sampled from other locations in Par Pond

ranged from 0.1 to over 10 Bq/g but averaged 1.2 Bq/g (Whicker et al. 1993). The extractability of ^{137}Cs from Par Pond sediments was reported by Evans et al. (1983) to be 16%. Current work indicates about 22% of ^{137}Cs to be extractable for a similar sediment type from Par Pond^{XX}.

The ion sorption properties of the clay mineral fraction for the sediments from Par Pond helps to explain the relatively high mobility of ^{137}Cs (Evans et al. 1983). For a long time, researchers have known that clays bind Cs strongly (Francis and Brinkley 1976). Therefore, clays play a major role in determining the availability of Cs in soils. Previous work revealed that Par Pond clays contained a deficient amount of 2:1 layered clay types which have a higher interlattice site exchange capacity (Evans et al. 1983). In the sediments we studied, even the 2:1 HIV has much less irreversible binding capacity than HIV's true 2:1 analogs^Y. The layers in HIV are connected by an incomplete Al-hydroxy interlayer. This gibbsite-like interlayer sheet has a net positive charge which tends to block the migration of cations into the interlattice spaces and prevents the potential collapse and expansion of the interlayers. The results in this study could have been different if the sediment clays had contained illite. Illite is also a 2:1 fixed layered clay, interlayered by fixed K or even Cs. Illite contains considerably more of a potential for Cs to irreversibly fix and collapse interlayers than a 1:1 clay type such as kaolinite.

Recent advancements in soils science motivated by the Chernobyl accident have led to methods of quantifying the frayed-edge sites, for which Cs would selectively seek in soils from Europe containing illite (Cremers et al. 1988). This was done by masking the readily-exchangable sites with a AgTU complexor. The resulting sorption isotherm at concentrations which saturated the remaining exchange sites yielded an estimate for the frayed-edge site capacity (Cremers and Pleysier 1973; Cremers et al. 1988).

These researchers proposed an ion selectivity coefficient K_C which predicted K_d given assumptions of agricultural conditions in which ^{137}Cs was carrier-free and the frayed-edge sites had an occupancy of Cs and K relative to the frayed-edge site capacity. Thus, the Cs K_d was predicted given a natural concentration of K^+ . The definition of K_C

was expanded in the 1990's to include multiple competing cations which are naturally present by employing a weighted relative selectivity (DePreter 1990; Madruga 1993).

Recent studies reported the method using the AgTU complexor as a better predictor than extractions for Cs mobility, uptake, and effects due to liming (Wauters et al. 1994; Vidal et al. 1995). Wauters et al. (1995) reported for illite clay a decrease in the extractability of Cs after liming, yet no significant increase in K_d . On the other hand, Madruga (1993) reported an overall increase in K_d for Cs and a decrease in the extractability after liming. Madruga (1993) concluded, without speculation as to the mechanism, that strongly hydrated cations such as Ca^{+2} , Mg^{+2} , and Na^+ increase the potential for the Cs to fixate, while the poorly hydrated cations such as K^+ and NH_4^+ promote sorption reversibility.

Sorption Isotherms

The first sorption isotherm was calculated from the measured ^{134}Cs water activity concentration as a function of the slurry ratio. The K_d at each point on this sorption isotherm decreased as the slurry ratio increased (Fig. 2). The drop in K_d was colinear with an increasing conductivity and decreasing pH. As the slurry ratio increased, more ions naturally contained in the sediments were released into the water phase, thus decreasing the pH and increasing the conductivity (Fig. 3). The conductivity is proportional to total dissolved solids and hence can be a general indicator of the amount of ions dissolved in solution. However, the conductivity includes H^+ in solution. The linear relationship between the pH and R suggested that the amount of H^+ released from the sediment was proportional to the amount of sediment in the slurry (Fig. 3).

The second sorption isotherm was defined for ^{134}Cs by increasing the amount of tracer spike for a given slurry ratio. The slurry ratio was arbitrarily chosen as 1:100 g/ml and corresponds to the third point in Fig. 2. This sorption isotherm was linear at low activity concentrations ($<20 \text{ Bq/ml}$) where the calculated K_d was $(2 \pm 0.4) \times 10^3$. The calculated sediment activity concentration plotted as a function of the measured water

activity concentration approximated linearity for the first 5 points (Fig. 4). This result confirmed that the exchange capacity of the sediment was not exceeded over this range of sediment concentrations. At higher concentrations, the K_d decreased and was associated with a drop in pH. The change in pH was attributed mainly to the HCl contained in the tracer spike. The H^+ was buffered less as the amount of HCl approached the exchange capacity of the sediment. A simple calculation shows that the pH decreased as the amount of HCl in the spike approached the exchange capacity of 400 mg of sediment (130 μ eq).

A previous study measured a sorption isotherm for ^{137}Cs and found the relationship to be non-linear (Kirikopoulos et al. 1994). Kirikopoulos et al. (1994) reported the sediment concentration to be proportional to the square root of the water concentration. In comparison, their sediment sample was organically rich (>5%). A direct comparison with our results is impossible without knowing the differences in mineralogy. Furthermore, Kirikopoulos et al. (1994) did not report data on the sediment/water slurry chemistry or the clay type.

These researchers used CsNO_3 as the carrier for the ^{137}Cs tracer, and perhaps their method was better since the spike did not contain HCl. The range of concentrations they measured for the sorption isotherm was 3-4 orders of magnitude above the concentration plotted as the fifth point in Fig. 4 at pH of 4.8. This point in Fig. 4 was estimated by a conversion to be 100 ppb of stable Cs. The sediment concentrations of stable Cs for the sorption isotherm measured by Kirikopoulos et al. (1994) ranged from 500 to 10^5 ppm. The specific activity of our ^{134}Cs tracer was 4 orders in magnitude higher than the specific activity of ^{137}Cs reported at 15 m depth in Par Pond during thermal stratification (13 kBq ^{137}Cs /mg Cs by Evans et al. 1983). Therefore, Cremer and Pleysier's (1988) assumption of carrier-free ^{137}Cs for agricultural conditions to predict K_d from K_c may need to be reapplied for the specific activity of ^{137}Cs in Par Pond.

Sorption Rate

The time the tracer was allowed to sorb to the sediment in the sorption isotherm

experiments was arbitrarily chosen at 1 d. This was further investigated by measuring the rate of tracer sorption to the sediments. To measure the net sorption rate, the slurry water activity concentration was measured as a function of time of post-spiking for a slurry ratio of 1:1000 g/ml (at pH 6.2). The change in water activity concentration showed that the sediment initially sorbed 90% of the ^{134}Cs activity from the water in <1 d (Fig. 5). The ^{134}Cs continued to sorb to the sediments at a slower rate over the next 10 d. Gradually over 1-2 months, the system approached an apparent equilibrium. The multi-component nature of the sorption curve suggested that there was more to the conceptual model for Cs than a simple two-compartment interchange. Also, the curve illustrated that the sorption isotherms measured after 1 d of tracer sorption represented the portions of Cs which rapidly sorb.

We proposed a conceptual model consisting of an irreversible exchange between two compartments (Fig. 5). The first compartment q_1 represented both the water and readily exchangeable sites, partitioned by a readily exchangeable K_d . The second compartment q_2 represented the irreversible exchange sites of a finite capacity C . The rate of sorption k was assumed to decrease toward zero as q_2 approached C . The analytical solution to the rate equation for $W(t)$ the water compartment as a function of time for this particular conceptual model was similar to the logistic function (Appendix A; Equation 4).

$$W(t) = (1-C) / (1 - C \exp(-k(1-C)t)) / (1 + K_d R), \quad (4)$$

The non-linear least squares fit to the data of the analytical function using the commercial software HiQ converged on values of $C=0.65$, $K_d=8600$, and $k=0.39/\text{d}$ ~~YYY~~ (Appendix A). This model assumed no loss from the system, and hence C was slightly over estimated in the model fit.

The ^{85}Sr water activity concentration reached equilibrium in ≤ 2 d (Fig. 6). This sorption curve was consistent with the conceptual model of a two-compartment reversible interchange. The conceptual model had one compartment for water and the other compartment for sediment with exchange rate constants k_1 and k_2 (Fig. 6). The amount in the water compartment $W(t)$ was expressed as an analytical function of time (Equation 5;

Whicker and Schultz 1982).

$$W(t) = k_1(1 - \exp(-(k_1 + k_2)t)) / (k_1 + k_2) + \exp(-(k_1 + k_2)t) \quad (5)$$

A least squares fit of this function to the data returned values of $k_1 = 4.28$ /d and $k_2 = 4.31$ /d (Appendix B). Conceptually, if the sorption of ^{85}Sr was fast and reversible, K_d may be an accurate representation of Sr sorption to sediments.

Previous work on two different salt-water sediments, one sampled from Narragansett Bay and the other from San Clemente Basin, demonstrated that ^{134}Cs and ^{85}Sr sorb rapidly and approach an equilibrium in the first few days (Nyffeler et al. 1984). However, the study found that for sediments sampled from MANOP site H, the ^{134}Cs continued to sorb further to the sediment at a slower rate over 30 days (0.016 /d Table 3 Nyffeler et al. 1984). These researchers reported the empirical nature of the results and that any number of sorption processes could combine to control sorption of the tracer to the sediment. These researchers did not report the mineralogy of the sediments. Instead, they reported percent composition of common elements (Nyffeler et al. 1984). These researchers reported two sorption kinetic conceptual models depending on the tracer and the sediments. The first was a two-compartment interchange between sediment and water, and the second had a third compartment as a sink representing the irreversible exchange sites.

Sorption rates similar to ours were reported for soils sampled from Europe containing illite clays and 5-20% organic material (Madruga 1993). These researchers found that the majority of Cs rapidly sorbed to the sediment in <1 d, and then a portion of Cs sorbed further at a slower rate over the next 10 d, approaching an apparent equilibrium. Madruga proposed a similar sorption kinetic conceptual model except with interchange between q_1 and q_2 (Madruga 1993). Madruga's sorption kinetic model could also be an adequate description of our results yielding sorption rate parameters on the order of $K_d = 9600$, $k_1 = 0.14$ /d, and $k_2 = 0.09$ /d (Appendix C).

More complicated sorption kinetic models are possible to fit to our data with one compartment for water, and compartments for each type of sediment composition fraction or exchange sites and with any combination of interchange. A proper choice of which

sorption kinetic conceptual model to choose is ambiguous. This illustrated that the sorption kinetic conceptual model was chosen apriori before considering additional data other than the water activity concentration as a function of time.

A number of sediment sorption models for Cs have been proposed by many researchers. Some models described the processes of diffusion and advection through the saturated pore space with an analytical function for sorption measurements of cores taken from the lakebed (Kirikopoulos et al. 1994; Ijuin 1973; Antonopoulos-Domis et al. 1995). Other models reported simple interchange between sediment and water and were similar to the models mentioned before in this paper (Nyfeller et al. 1984). A couple of models formulated first order rate equations, describing a kinetics layered approximation and employing the sorption rates or the K_d in conjunction with processes of diffusion, settling, and resuspension to predict the tracer removal from the water column (Nyfeller et al. 1986; Santschi 1986; Adler 1982). Some models were simplifications of the contributing processes and compartments, yet maintained a good prediction for their experiments (Monte et al. 1991; Monte 1993; Monte 1995; Hesslein 1980; Hakonson 1972). Overall, some models have the advantage of formulation, others simplification. All of these models incorporated assumptions and processes of sorption to the sediments whether implicitly or explicitly.

Extractions

The solutions extracting the largest percentages of ^{134}Cs from the sediment were solutions containing NH_4^+ or K^+ (Table 3). The solutions containing Na^+ or Ca^{+2} extracted the smallest percentage of ^{134}Cs from the sediment. The highest fraction of ^{85}Sr extracted from the sediment was 98-100% using chloride solutions of H^+ , Fe^{+3} , and Sr^{+2} which confirmed that Sr appeared to sorb to the sediment in the first few days in a totally reversible reaction (Table 3). Madruga (1993) reported that the sorption of Sr was completely reversible for sediments from Europe. Other solutions containing soluble divalent cations, such as Ca^{+2} , Mn^{+2} , and Mg^{+2} , displaced 85-95% of the ^{85}Sr from the sediment. The solution containing Na^+ extracted the smallest percentage of ^{85}Sr from the

sediment.

An earlier study of the extractability of ^{137}Cs from sediment from Par Pond ranked the percent extractability as $\text{NH}_4^+ > \text{H}^+ > \text{Cs}^+ = \text{K}^+ > \text{Ca}^{+2} > \text{Na}^+ = \text{Mg}^{+2} > \text{Mn}^{+2} = \text{Fe}^{+2}$ (Evans et al. 1983). These workers found that 16% of the ^{137}Cs was extracted from the sediments of Par Pond by saturating with 100 mM NH_4^+ solution and using a slurry ratio $R=1:50$ g/ml (Evans et al. 1988). Among individual clay minerals, they found by extraction that ^{137}Cs was displaced from illite by cations in the order of $\text{NH}_4^+ > \text{K}^+ = \text{Cs}^+ > \text{H}^+ > \text{Na}^+ > \text{Ca}^{+2} > \text{Mg}^{+2}$ (Evans et al. 1983). This result was similar to ours using the whole sediment sample except for an arbitrary choice in the equality signs of $\text{NH}_4^+ \approx \text{K}^+ > \text{Cs}^+ \approx \text{H}^+ > \text{Na}^+ \approx \text{Ca}^{+2}$ (Table 3).

The results of Evans et al. (1983) were explained by assuming that 3 types of exchange sites exist on the sediment particles: readily exchangeable sites, frayed-edge sites which allow for only ions of similar size and charge to displace Cs, and sites along the interlattice layers which fix Cs irreversibly (Evans et al. 1983; Madruga 1993; Wauters 1994). Evans et al. noted that the clay type from Par Pond was of a mineral composition which had relatively fewer interlattice exchange sites. Their sediment type contained detectable amounts of illite clays (7% of clay fraction). Our sediment clay fraction containing HIV might have had less of an interlattice exchange site capacity than the true 2:1 analogs.

The extractions in our work were carried out using concentrations which would saturate the sediments. In some sense, this method was a measure of the fraction of the tracer reversibly bound as defined by the type of sediment exchange sites the cations in the solution might seek. Traditionally, reversibility has been measured by placing contaminated sediments in fresh water to determine if $K_{\text{desorb}} \approx K_{\text{adsorb}}$ (Fukui 1990). However, this method was rate limited, since there was a time dependent interchange between the sediment and water.

Other methods such as sequential extraction or the "infinte-sink" address the rate

limitation of sorption interchange (DePreter 1990; Madruga 1993). The infinite-sink method consists of an absorbent of large exchange capacity and a huge affinity for Cs that is placed in a permeable membrane in the slurry. The absorbent granulates appear to the Cs^+ displaced from the sediment as a sink of infinite capacity. These researchers found, using soils from Europe containing illite and 5-20% organic matter, that the infinite sink method yielded slightly higher Cs^+ extractions. Therefore, this method was possibly a better measure of the total reversibly bound Cs. Also, they found that extractions carried out for time longer than 1 d could yield slightly higher extractable Cs by 5-10%.

The fraction of ^{134}Cs extracted from the sediment was measured as functions of NH_4NO_3 and KCl concentrations (Fig. 7). At concentrations <1 mM, the fraction of ^{134}Cs extracted from the sediment using the ammonium solution was 2-3 times higher than by the K^+ solution. The fractions of ^{134}Cs extracted from the sediment were 40% using either the NH_4^+ or K^+ solutions when the solution concentrations were 10 mM. The 10 mM concentration apparently saturated the exchange sites on the sediment. A simple calculation would show that the moles of NH_4^+ or K^+ was 1-2 orders of magnitude higher than the exchange capacity of the sediment.

The study conducted by Evans et al. (1983) measured the percent of ^{137}Cs released from the sediment as a function of solution concentration for NH_4^+ only. At 100 mM NH_4^+ , 20% of the ^{137}Cs was extracted. They measured the percent extracted for <100 μM NH_4^+ by incubating the sediment/water slurry for 24 h and measuring the NH_4^+ generated by anaerobic activity. At concentrations of NH_4^+ corresponding to that which is found naturally in the lake (40 μM), they found only 1% of the ^{137}Cs was released. These researchers implied that NH_4^+ displaced the Cs off the sediment, nevertheless, this was an inference of causality based on a correlation.

Other work by Madruga (1993) noted findings similar to ours in which extract solutions containing NH_4^+ or K^+ displaced similar fractions of Cs off the sediment when using saturation concentrations (1 M). At lower concentrations (1 mM), solutions containing NH_4^+ displaced 3-4 times more Cs than solutions of K^+ . This was explained conceptually by the formulation of the ion selectivity coefficient K_C proposed by Cremers and Pleysier (1988). This formulation described the relative competitiveness between Cs^+ and other cations at concentrations that would be found naturally in the field, and also incorporated competition when one competing cation is in the presence of the other by weighting the cation concentrations (Madruga 1993; Vidal 1995).

The fraction of ^{134}Cs extracted from the sediment with 100 mM KCl was measured as a function of tracer equilibration time. The extracted fraction decreased from 70 to 45% in the first 10 d equilibration and appeared to remain constant for longer equilibration times (Fig. 8). This result corresponded to the same time frame of the slower sorption component of the measured water activity concentration curve (Fig. 5). Evans et al. (1983) found that the percent of ^{134}Cs extracted from the sediment decreased from 65 to 55% in the first day of tracer equilibration, then continued to decrease to 25% over 200 days.

These researchers implied that given enough time, the Cs^+ would seek the irreversible exchange sites such that sorbed Cs could no longer be displaced by a competing species. Although they did not necessarily demonstrate the different types of exchange sites, they did describe their results by acknowledging that Cs^+ preferentially seeks the frayed-edge sites (Cremers 1988; DePreter 1990; Madruga 1993). Also, they noted that conceptually these frayed-edge sites could undergo weathering, either increasing the number, or increasing the amount of Cs irreversibly bound by collapsing a frayed-edge site around a sorbed Cs so that it could no longer be displaced by a competing species.

CONCLUSIONS

The sorption behavior of ^{134}Cs and ^{85}Sr to the sediments of Par Pond was characterized

by the following:

- Sr sorbed rapidly in a totally reversible reaction to the sediment in 2-3 days.
- About 90% of the Cs sorbed in <1 day; the remainder sorbed to the sediment at a slower rate.
- An isotherm for Cs was linear, i.e. a constant K_d , over several orders of magnitude in concentration: 50 mBq/ml to 20 Bq/ml, pH 4.6 to 4.8, 1 d tracer sorption, $R=1:100$ g/ml, $K_d=(2\pm0.4)\times10^3$.
- A second isotherm revealed that increasing the sediment to water slurry ratio can lower the K_d by releasing competing cations, whether dominated by the acids released or by other cations contained in the sediments.
- The main cations competing to displace Sr from the sediments were H^+ , Fe^{+3} , and other divalent cations. The main cations competing to displace Cs from the sediments were NH_4^+ and K^+ . The competition of Na^+ was low for displacing Cs and Sr from the sediment, and the competition of a divalent cation (Ca^{+2}) was low for Cs.
- The K_d measured in the batch-type method was found to be affected by the amount of the spike which contained tracer, carrier, and H^+ at much higher concentrations. Also, the measured K_d was affected by the slurry ratio and the tracer equilibrium time.

FOOTNOTES

† Packard Auto-Gamma Model 5550.

†† Amersham Life Science, 2636 S. Clearbrook Drive, Alington Heights, IL 60005. (800) 323-9750.

††† DuPont NES, Medical Products Dept., Relmington, DE 19898. (800) 551-2121.

¥ Seaman, John. Private correspondence. October 1, 1995. seaman@srel.edu, Savannah River Ecology Lab, University of Georgia, Aiken, SC.

¥¥ Hinton, Tom; Malek, Mira. Private correspondence of yet to be published results. December 8, 1995. Fax:(803) 557-7324, (803) 557-7454, Par Pond Radioecology Lab, Savannah River Ecology Lab, University of Georgia, Aiken, SC.

¥¥¥ National Instruments, HiQ for Macintosh Version 2.1, 6504 Bridge Point Parkway, Austin, TX 78730-5039, (512) 794-0100, 1994.

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TABLE 1
Limnological properties of Par Pond.

Area (km ²)	10
Mean Depth (m)	6.2
Maximum Depth (m)	17
Maximum Temperature (°C)	31
Minimum Temperature (°C)	8
Depth of Thermocline (m)	6-8
Conductivity (μS/cm)	56
HCO ₃ ⁻ (mg/L)	22.7
Na ⁺	4.5
K ⁺ (mg/L)	1.4
Mg ⁺² (mg/L)	0.3
pH	5.8*

*on the day of sampling

TABLE 2
Sediment characterization.

Lime Estimate	Low (<1%)			
Organic Matter	28%			
Texture Estimate	Sandy Clay Loamy			
Cation Exchange Capacity (meq/100g)	32			
Particle Density (g/cm ³)	2.5			
Porosity	0.6			
pH of paste	2.2*			
¹³⁷ Cs Activity Concentration (Bq/g)	3-9			
NH ₄ HCO ₃ Extraction (ppm):				
Fe	Mn	K	Zn	Cu
252	191	70	7.1	5.7

*pH of paste on the day of sampling

Table 3
Fraction of tracer extracted from sediment, 5 mM extract, 1 d extraction, and R=1:1000 g/ml.

¹³⁴ Cs		⁸⁵ Sr	
<u>Extract</u>	<u>% Extracted</u>	<u>Extract</u>	<u>% Extracted</u>
NH ₄ NO ₃	41	HCl	100
KCl	37	FeCl ₃	99
CsCl	22	SrCl ₂	98
HCl	21	CaCl ₂	94
NaCl	6	MnCl ₂	91
CaCl ₂	4	MgCl ₂	85
*7 d tracer equilibrium		KCl	67
		NH ₄ NO ₃	45
		NaCl	23
		*3 d tracer equilibrium	

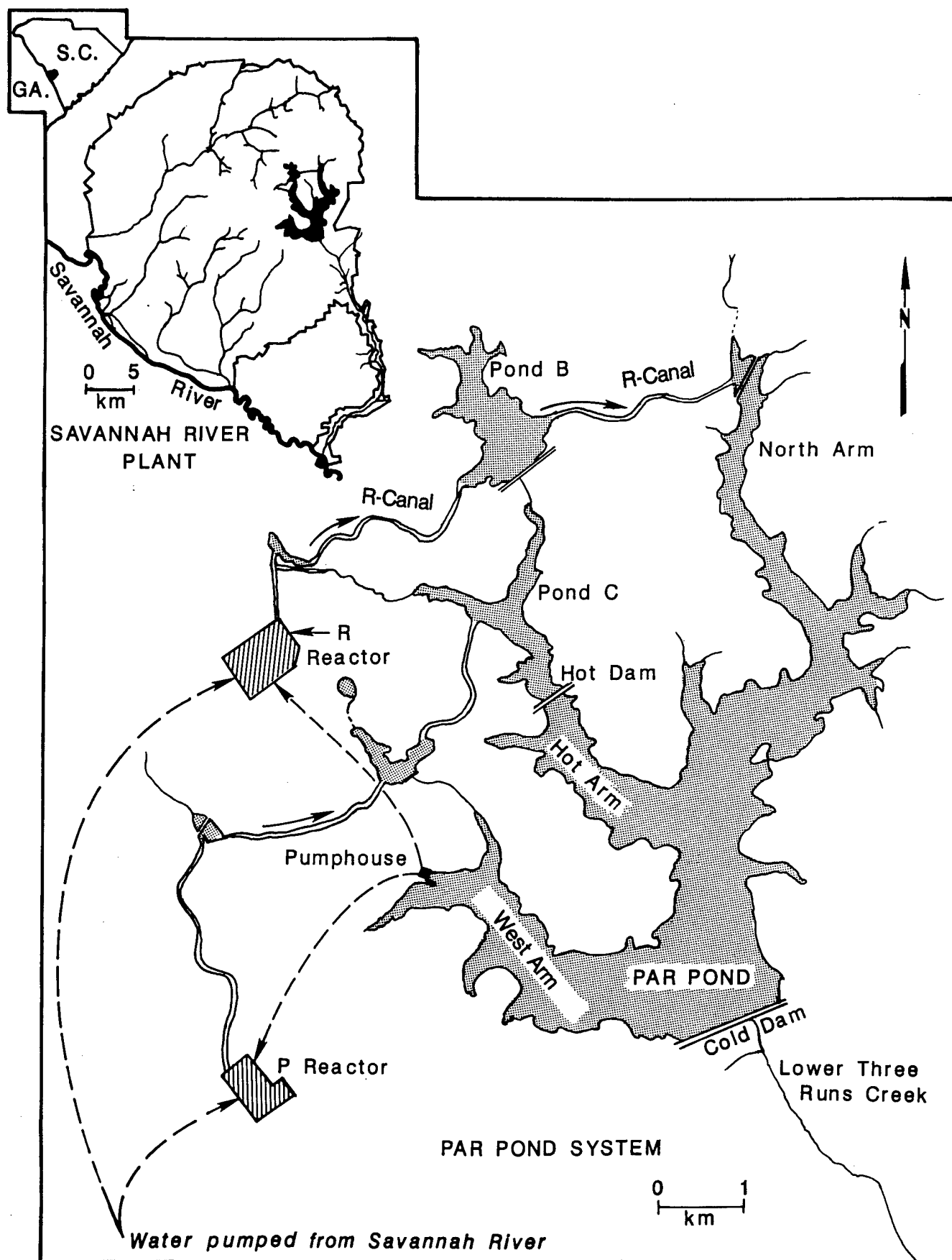


Fig. 1. Map of the cooling water system for R and P reactors, including Ponds B and C, Par Pond and connecting canals.

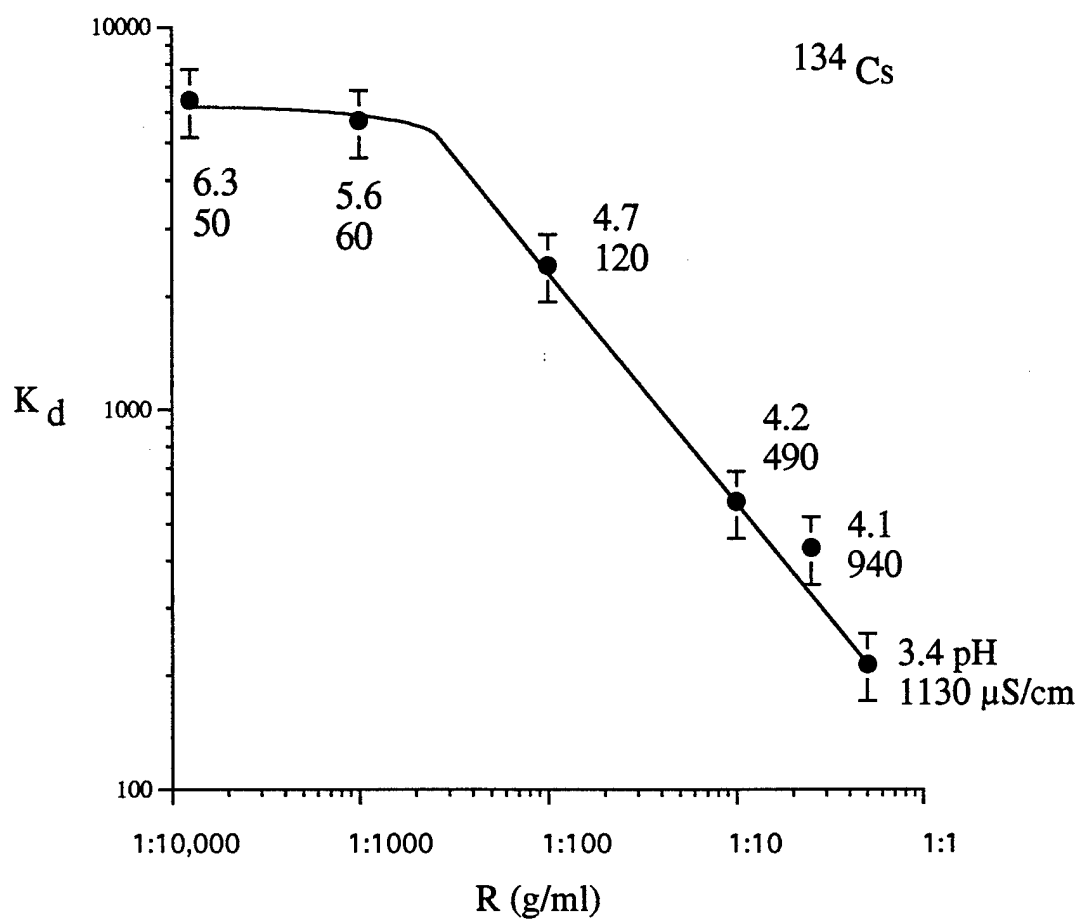


Fig. 2 . K_d as a function of the slurry ratio (R) for ^{134}Cs . The pH and conductivity values for the solution are also shown.

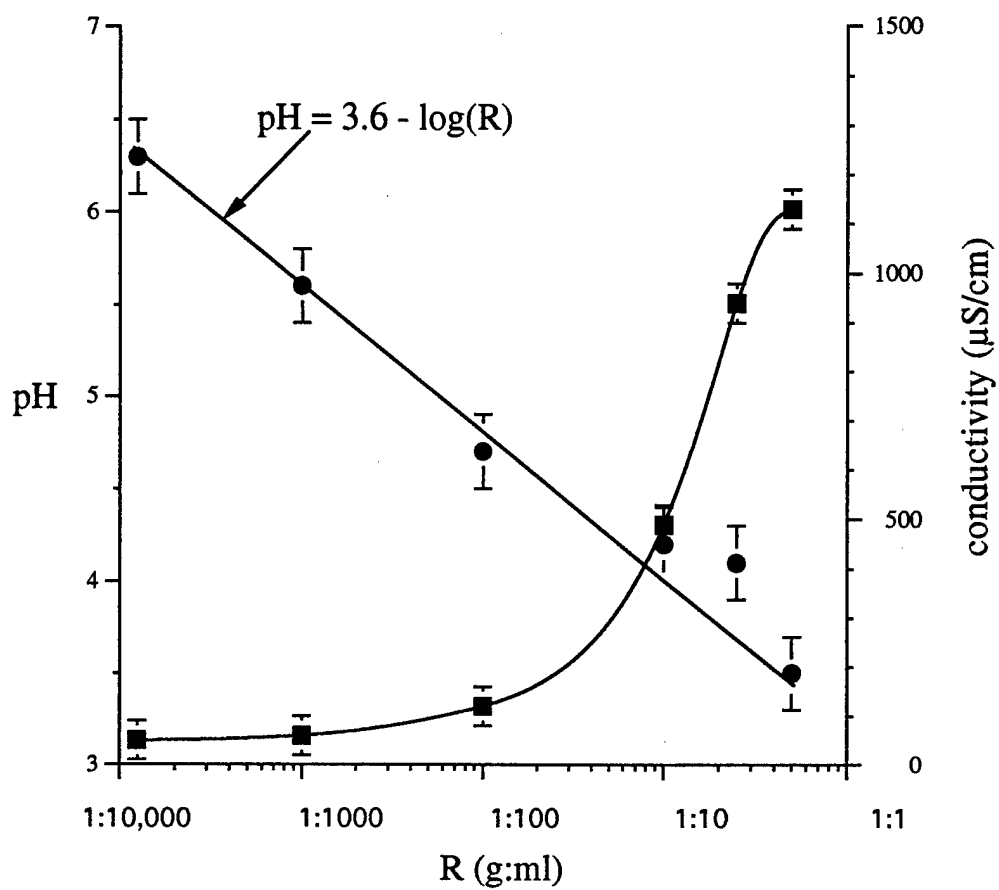


Fig. 3 . The pH and conductivity as a function of the sediment/water slurry ratio.

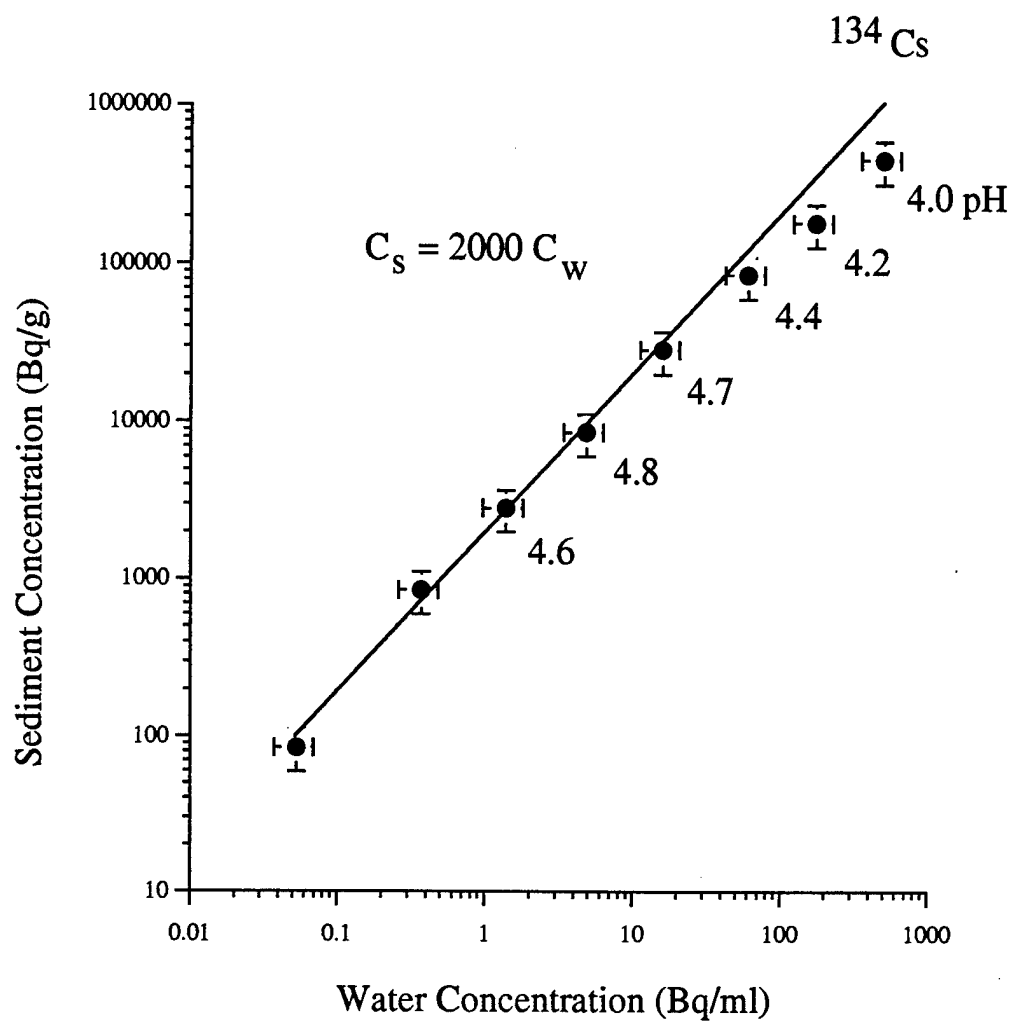


Fig. 4 . Calculated sediment concentration as a function of water concentration for ^{134}Cs where $R=1:100$ g/ml and pH ranged from 4.0 to 4.8.

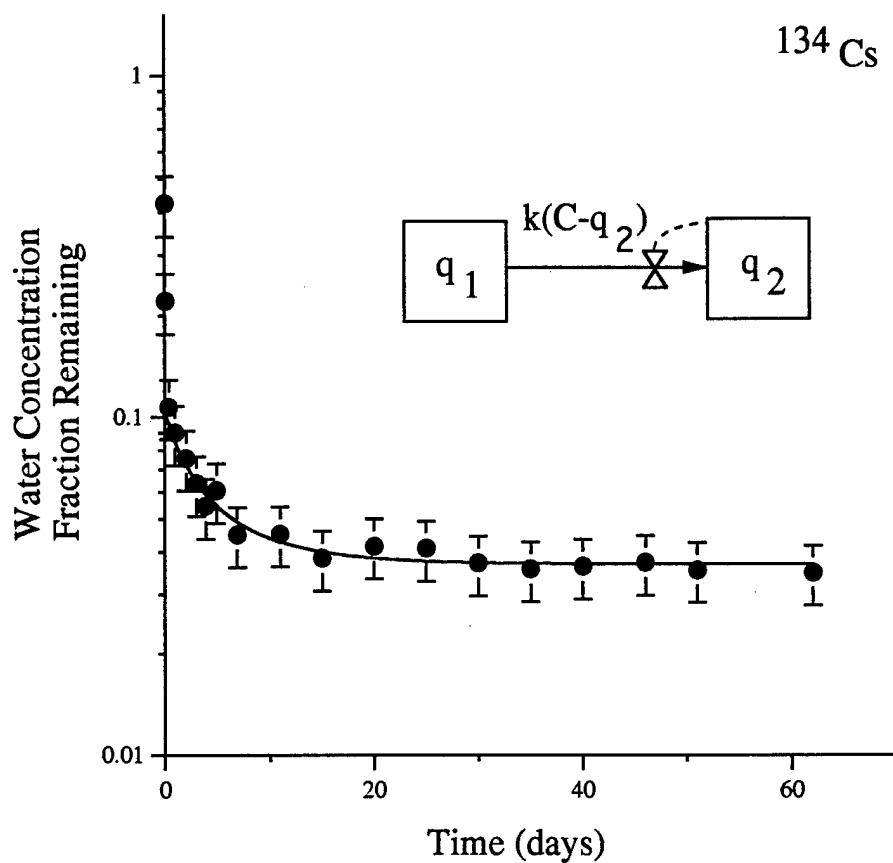


Fig. 5 . The fraction of the water concentration remaining measured as a function of time for ^{134}Cs using $R=1:1000$ g/ml and $\text{pH}\approx 6$.

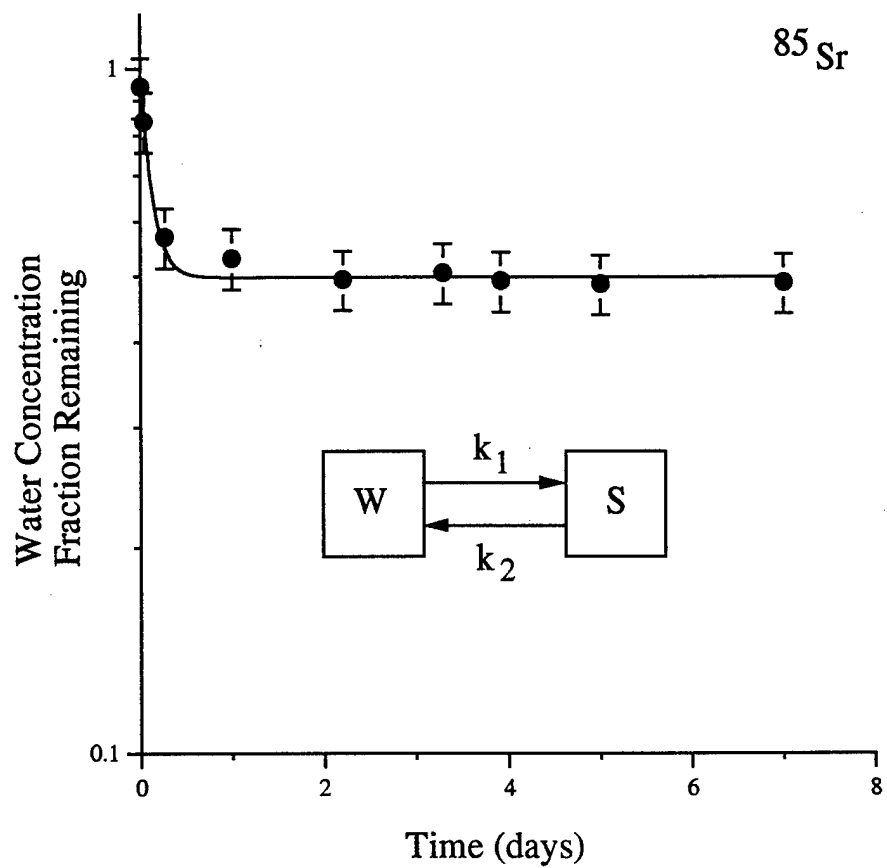


Fig. 6 . The fraction of the water concentration remaining measured as a function of time for ^{85}Sr and the calculated K_d using $R=1:1000$ g/ml.

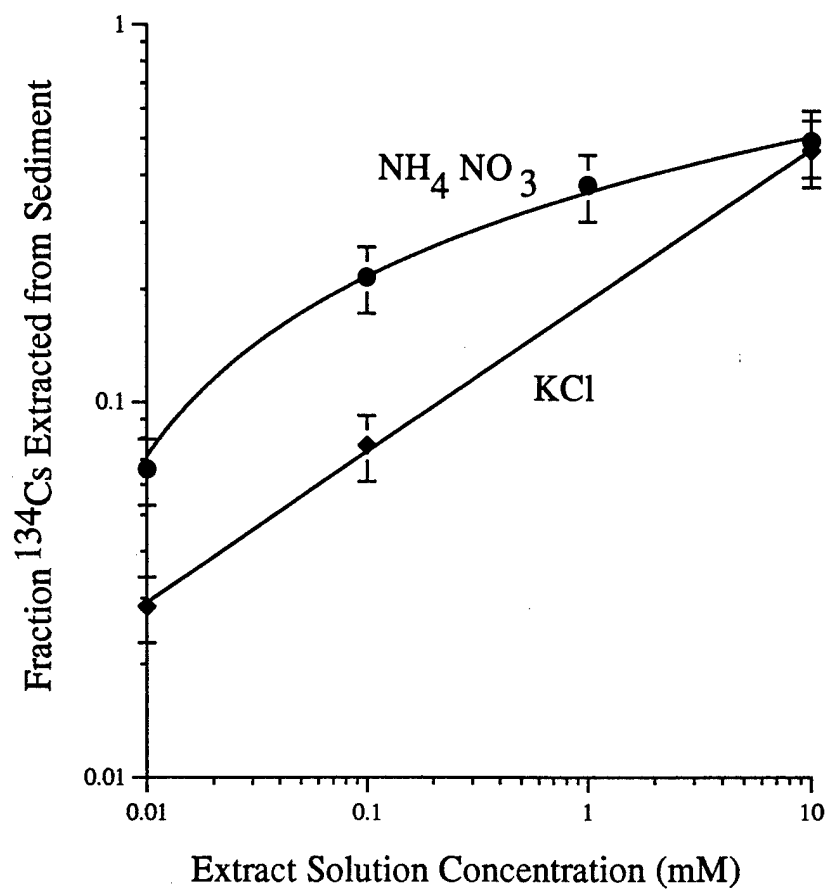


Fig. 7 . Fraction of extracted ^{134}Cs from the resuspendable material after replacing the decant with KCl and NH_4NO_3 , 1 d tracer equilibration, and $R=1:1000$ g/ml.

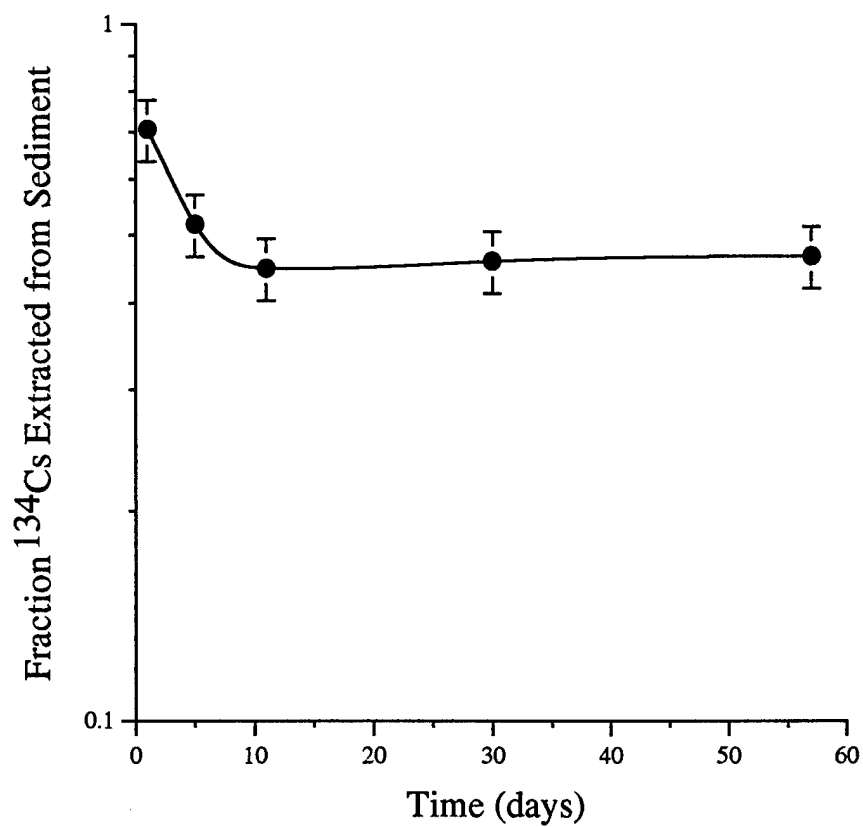


Fig. 8 . Fraction of ^{134}Cs extracted from sediment measured as a function of the tracer equilibration time using $R=1:100$ g/ml, 1 d extraction, and 100 mM KCl extract.

Appendix A

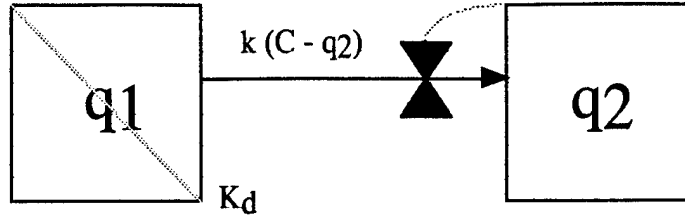


Fig. a1. A second conceptual model for sorption of ^{134}Cs as a function of time.

The conceptual model represents the sorption to irreversible exchange sites with rate constant k and where,

q_1 is the water W and the readily exchangeable sites S_1 such that

$$q_1 = W + S_1, \text{ and} \quad (\text{a1})$$

q_2 the irreversible exchange sites with finite capacity C .

The rate equations is:

$$dq_1/dt = -kq_1 (C - q_2) \quad (\text{a2})$$

The initial conditions were $q_1(0) = q_0$ and $q_2(0) = 0$. The initial condition was assumed normalized to the initial spike amount.

$$q_0 = 1 \quad (\text{a3})$$

We assumed no loss from the system.

$$q_0 = q_1 + q_2 \quad (\text{a4})$$

Substitute (a4) into (a2) for q_2 .

$$dq_1/dt = -kq_1 (C - q_0 + q_1) \quad (\text{a5})$$

This was the same form as the logistic function shown in (a6) to (a8) (Grossman 1986 p.630).

$$P' = P (\beta - \delta P) \quad (\text{a6})$$

$$\beta = k (q_0 - C) \quad (\text{a7})$$

$$\delta = k \quad (\text{a8})$$

The solution to (a5) was therefore (Grossman 1986):

$$q_1(t) = (q_0 - C) / (1 - C \exp(-k(q_0 - C)t) / q_0) \quad (a9)$$

Substitute q_0 in (a3) into (a9).

$$q_1(t) = (1 - C) / (1 - C \exp(-k(1 - C)t)) \quad (a10)$$

Now q_1 can be expressed as a function of W using K_d defined as

$$K_d = S_1 / WR, \quad (a11)$$

where R is the slurry ratio. First substitute S_1 from (a11) into (a1).

$$q_1 = W (1 + K_d R) \quad (a12)$$

Now substitute (a12) into (a10).

$$W(t) = (1 - C) / (1 - C \exp(-k(1 - C)t)) / (1 + K_d R) \quad (a13)$$

The data was fit to the analytical function (a13) using the default non-linear least squares fit algorithm in HiQ, the Marquardt-Levenberg (National Instruments 1994; Fig. 5). R was held constant at 0.001, and the initial estimates were $C=0.3$, $k=0.0006/d$, and $K_d=7000$. All weights equaled 1. The curve fit converged on values of $C=0.64589$, $k=0.38946/d$, and $K_d=8622.6$.

References for Appendix A

National Instruments, HiQ for Macintosh Version 2.1, 6504 Bridge Point Parkway, Austin, TX 78730-5039, (512) 794-0100, 1994.

Grossman, Stanley I. Multivariable Calculus, Linear Algebra, and Differential Equations. 2nd Ed. Harcourt Brace Jovanovich, Publ. 1986.

Appendix B

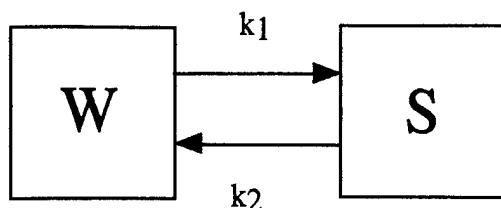


Fig. b1. The conceptual model for a 2 compartment interchange between water and sediment.

The conceptual model represented the interchange of sorption between the water W and the sediment S. The rate equations were:

$$dW/dt = -k_1W + k_2S \quad (a1)$$

$$dS/dt = -k_2S + k_1W \quad (a2)$$

The initial conditions were assumed as $W(0)=W_0$ and $S(0)=0$. The analytical solution to (a1) and for the initial conditions was (Whicker and Schultz 1982 p.86):

$$W(t) = k_1W_0(1-\exp(-(k_1+k_2)t))/(k_1+k_2) + W_0 \exp(-(k_1+k_2)t) \quad (a3)$$

We assumed the initial condition was normalized to the spike amount.

$$W_0=1 \quad (a4)$$

Substituting (a4) into (a3).

$$W(t) = k_1(1-\exp(-(k_1+k_2)t))/(k_1+k_2) + \exp(-(k_1+k_2)t) \quad (a5)$$

The data was fit to the analytical function (a5) using the default non-linear least squares fit algorithm in HiQ, the Marquardt-Levenberg (National Instruments 1994; Fig. 6). The initial estimates were $k_1=k_2=5$ /d. All weights equaled 1. The fit converged on values of $k_1=4.2798$ /d and $k_2=4.3094$ /d.

References for Appendix B

National Instruments, HiQ for Macintosh Version 2.1, 6504 Bridge Point Parkway, Austin, TX 78730-5039, (512) 794-0100, 1994.

Whicker, F.Ward; Schultz, Vincent. Radioecology: Nuclear Energy and the Environment. Volumes 1 and 2. Boca Raton, Florida: CRC Press; 1982.

Appendix C

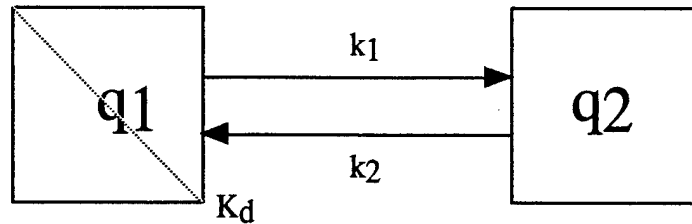


Fig. c1. A second conceptual model for sorption of ¹³⁴Cs as a function of time.

The conceptual model represents the further sorption interchange to a second type of exchange sites with rate constants k_1 and k_2 where,

q_1 is the water W and the readily exchangeable sites S_1 such that

$$q_1 = W + S_1, \text{ and} \quad (\text{a1})$$

q_2 the irreversible exchange sites with finite capacity C (Madruga 1993).

The rate equations are:

$$dq_1/dt = -k_1 q_1 + k_2 q_2 \quad (\text{a2})$$

$$dq_2/dt = -k_2 q_2 + k_1 q_1 \quad (\text{a3})$$

The initial conditions were $q_1(0) = q_0$ and $q_2(0) = 0$. The analytical solution to (a2) for the initial conditions was therefore (Whicker and Schultz 1982 p.86):

$$q_1(t) = \frac{k_1 q_0 (1 - \exp(-(k_1 + k_2)t))}{(k_1 + k_2)} + q_0 \exp(-(k_1 + k_2)t) \quad (\text{a4})$$

We assumed the initial condition was normalized to the spike amount.

$$q_0 = 1 \quad (\text{a5})$$

Substitute q_0 in (a5) into (a4).

$$q_1(t) = \frac{k_1 (1 - \exp(-(k_1 + k_2)t))}{(k_1 + k_2)} + \exp(-(k_1 + k_2)t) \quad (\text{a6})$$

Now q_1 can be expressed as a function of W using K_d defined as

$$K_d = S_1 / WR, \quad (\text{a7})$$

where R is the slurry ratio. First substitute S_1 from (a7) into (a1).

$$q_1 = W (1 + K_d R) \quad (\text{a8})$$

Now substitute (a8) into (a6).

$$W(t) = [k_1(1 - \exp(-(k_1 + k_2)t)) / (k_1 + k_2) + \exp(-(k_1 + k_2)t)] / (1 + K_d R) \quad (a9)$$

The data was fit to the analytical function (a9) using the default non-linear least squares fit algorithm in HiQ, the Marquardt-Levenberg (National Instruments 1994; Fig. c2).

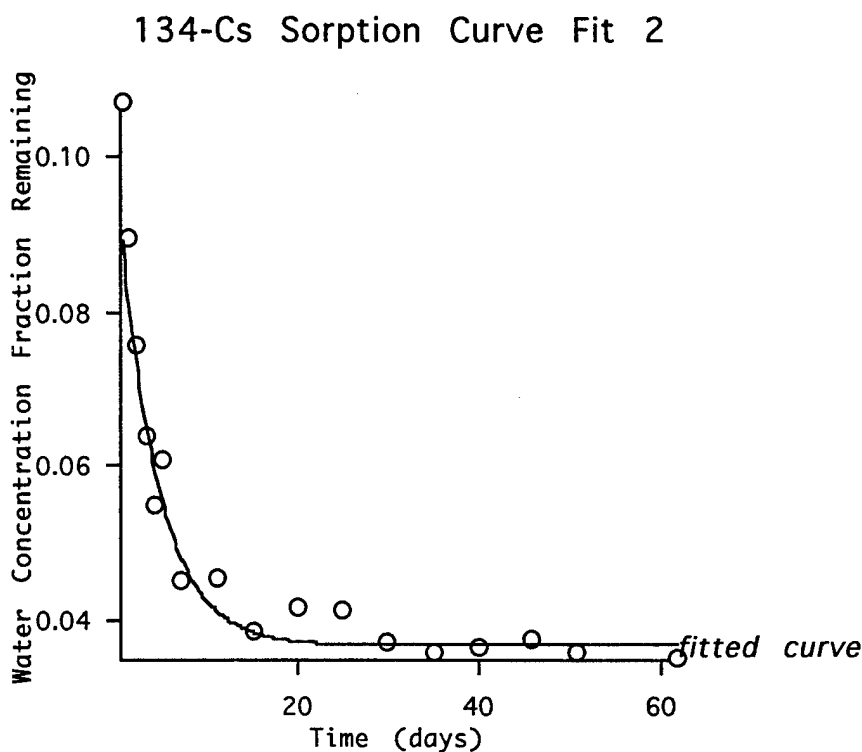


Fig. c2. The least squares curve fit to the water concentration of 134-Cs as a function of time and for the conceptual model in Fig. c1.

R was held constant at 0.001, and the initial estimates were $k_1=0.2$ /d, $k_2=0.01$ /d, and $K_d=5000$.

All weights equaled 1. The curve fit converged on values of $k_1=0.14355$ /d, $k_2=0.0905$ /d, and $K_d=9618.9$.

References for Appendix C

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