

KINETICS AND REVERSIBILITY OF RADIOCAESIUM SOLID/LIQUID PARTITIONING IN SEDIMENTS

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Abstract

The kinetics and reversibility of radiocaesium solid/liquid partitioning in sediments have been reviewed and interpreted in terms of a mechanistic framework. This framework is based on the premise that radiocaesium is almost exclusively and highly-selectively bound to the frayed particle edges of illitic clay minerals in the sediments. Several processes with distinctly different rates can be distinguished in radiocaesium sorption to sediments. 2- and 3-box kinetic models can describe both the overall solid/liquid partitioning in sediments and the reversible (exchangeable) and irreversible (non-exchangeable or "fixed") fractions of radiocaesium in sediments over time scales relevant for natural aquatic systems. The obtained rate parameters indicate that reversible partitioning of radiocaesium dominates over the first few days following a contamination event, whereas irreversible kinetics becomes important over time scales of weeks to months. The slow process, which reduces the exchangeability of sediment-bound radiocaesium over time, is believed to result from a migration of radiocaesium from exchangeable sites on the frayed edges of illite towards less-exchangeable interlayer sites. Long-term extraction of radiocaesium from historically contaminated sediments has given evidence for a reverse (remobilization) process with a half-life of the order of tens of years. These findings suggest that the long-term exchangeability of radiocaesium in sediments may be higher than the few % which is generally assumed.

Introduction: radiocaesium binding in sediments

Freshwater sediments in Europe have generally recorded the Chernobyl accident in April 1986 by a distinct radiocaesium peak. The accident has renewed

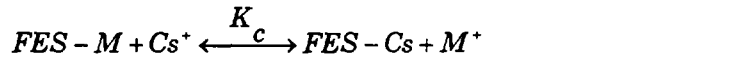
the interest in the mobility of radiocaesium isotopes in the aquatic environment, both from a radioecological and from a sediment-dating point of view. The traditional way to express mobility, e.g. in contaminant/radionuclide transport models, is by means of the solid/liquid distribution coefficient or K_D (L/kg):



$$\text{or } K_D = \frac{[{}^{137}\text{Cs}^+]_{ads}}{[{}^{137}\text{Cs}^+]_{aq}} \quad (2)$$

where $[{}^{137}\text{Cs}^+]_{aq}$ and $[{}^{137}\text{Cs}^+]_{ads}$ represent the activity of radiocaesium in the aqueous (Bq/L) and particulate phase (Bq/kg), respectively. The K_D -model cannot, however, account for differences in binding properties of different sediments, which has resulted in a variability in published K_D -values for radiocaesium of more than 3 orders of magnitude (e.g. Smith, 1993). These large differences hamper the general use of K_D -based sediment transport models.

Studies since the 1960s have shown that Cs is sorbed very selectively by micaceous clay minerals, particularly illite, a process which is believed to be analogous to the fixation of potassium in the clay interlayer structures (e.g. Bolt *et al.*, 1963; Sawhney, 1972). The more recent work by Cremers and co-workers (e.g. Cremers *et al.*, 1988) has enabled a quantitative characterisation of the Cs-selective sorption sites in soils and sediments, which are believed to be located on the frayed edges of illite (the "frayed edge sites" or FES). These authors have shown that the interaction of caesium with sediment and soil particles can be described more mechanistically in terms of an ion exchange process:



The relative affinity of the illite surface for Cs^+ , relative to the competing metal M^+ , can then be expressed in terms of a selectivity coefficient, $K_c^{Cs/M}$:

(4)

$$K_c^{Cs/M} = \frac{\left([Cs_{FES}^+] / [FES] \right) \cdot [M^+]}{\left([M_{FES}^+] / [FES] \right) \cdot [Cs^+]}$$

where $[Cs_{FES}^+]$ and $[M_{FES}^+]$ are the concentrations of caesium and the competing metal M^+ adsorbed on the frayed edge sites (eq/kg), $[Cs^+]$ and $[M^+]$ represent the aqueous concentrations (eq/L), and $[FES]$ is the frayed edge site capacity of the sediment (eq/kg). At the negligible stable caesium concentrations in the natural aquatic environment $[Cs_{FES}^+] / [FES] \rightarrow 0$ and $[M_{FES}^+] / [FES] \rightarrow 1$, hence:

(5)

$$K_c^{Cs/M} = \frac{[M^+] \cdot \left([Cs_{FES}^+] / [FES] \right)}{[Cs^+]}$$

substituting for K_D (L/kg) which, for radiocaesium, can be calculated from its activity in the particulate (Bq/kg) and aqueous (Bq/L) phase:

(6)

$$K_c^{Cs/M} = \frac{[M^+] \cdot K_D}{[FES]}$$

hence, K_D is given by:

(7)

$$K_D = \frac{K_c^{Cs/M} \cdot [FES]}{[M^+]}$$

or

(8)

$$\log[K_D] = \log K_c^{Cs/M} \cdot [FES] - \log[M^+]$$

The major metal ions (M^+) competing with radiocaesium on the frayed edge sites on illitic clays in natural freshwater environments, are generally potassium (K^+ ; in oxic environments, e.g. in unsaturated soils and surface waters) and ammonium (NH_4^+ , under anoxic conditions in sediments).

Fig. 1 shows a compilation of *in-situ* K_D -values from a number of different European sediments (Comans *et al.*, 1998) and reveals a single relationship between the (total, see below) radiocaesium K_D and the pore-water ammonium concentration. This observation is consistent with the above ion-exchange theory in that, among the major ions that compete with caesium for binding sites on illite clays, NH_4^+ outcompetes K^+ in anoxic sediments as it reaches higher concentrations and is about five times more selectively bound than K^+ (De Preter, 1990). Fig. 1 clearly indicates that the data follow a straight line with a slope close to -1.

The intercept $K_c^{\text{Cs}/\text{NH}_4}[\text{FES}]$ can be independently measured when the FES are "isolated" by blocking all other exchange sites in sediments with AgTU (Cremers *et al.*, 1988; De Preter, 1990). Using this procedure, Wauters (1994) has measured $K_c^{\text{Cs}/\text{NH}_4}[\text{FES}]$ for the sediments in Fig. 1. Based on these values, Fig. 1 includes the theoretical relationship between K_D and $[\text{NH}_4^+]$ for the lowest (Ketelmeer) and highest (Esthwaite) $K_c^{\text{Cs}/\text{NH}_4}[\text{FES}]$ value. The interpretation of the radiocaesium K_D s in Fig. 1 clearly shows that ^{137}Cs in the aquatic environment obeys ion-exchange theory. The ion-exchange model then allows the solid-liquid distribution coefficient (K_D) of this radionuclide in sediment transport models to be predicted from environmental variables (i.e. the quantity of FES in the sediments and the pore-water NH_4^+ concentration), rather than to be erroneously treated as a constant.

Modelling kinetics and reversibility of radiocaesium partitioning

Another important feature of radiocaesium partitioning in sediments is its apparently irreversible behaviour. It has generally been observed that K_D increases and the exchangeability of radiocaesium bound to aquatic particles decreases, with increasing contact time between the radionuclide and the particles (e.g. Konoplev *et al.*, 1996). This observation has been interpreted as a slow migration of radiocaesium from the frayed edge sites towards the deeper interlayer spaces between the illite layers, from where it cannot easily be released (Evans *et al.*, 1983; Comans *et al.*, 1991). It is, therefore, important to obtain rate parameters for this process in order to enable prediction of the long-term availability of radiocaesium to the aqueous phase, and thus for uptake in the aquatic food chain and/or for further transport.

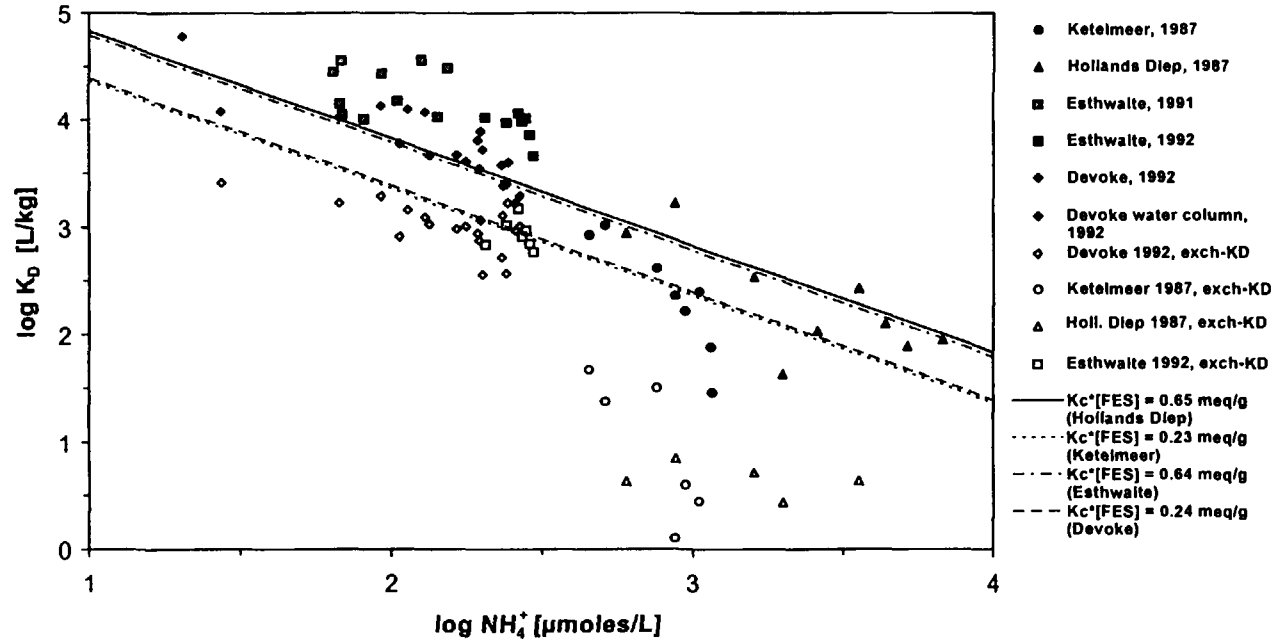


Figure 1. Total (closed symbols), exchangeable (open symbols), and predicted (lines) in-situ K_D -values for different w-European lake sediments (Comans et al., 1998).

Laboratory sorption measurements of up to 1 month reaction time have shown that the overall kinetics of the sorption process of radiocaesium on illite cannot be described by a single rate, but involves at least a fast and a slower process (Comans *et al.*, 1991). Fig. 2 illustrates that radiocaesium adsorption/desorption on sediments from the lakes Ketelmeer and Hollands Diep in the Netherlands, at different total-Cs concentrations, shows the same features (Comans, 1998). Multiple-process kinetic models are, therefore, needed to obtain reliable rate parameters for the interaction of radiocaesium with natural sediments.

Jannasch et al. linearization

A very useful approach to identify the number of distinct processes that contribute to the observed overall kinetics and, hence, need to be considered in the development of a suitable kinetic model to evaluate the data, has been presented by Jannasch *et al.* (1988). These authors derived a linearized equation for kinetic sorption controlled by a number of separate processes. Their analysis assumes that only one process controls overall sorption at any time and that each process can be described by a first order reversible reaction:

$$-\ln \left[\frac{[M_d] - [M_d]_e}{[M_t] - [M_d]_e} \right] = (r_f^i + r_b^i) \cdot t \quad (9)$$

where:

- [M_d] = aqueous metal concentration
- [M_d]_e = aqueous metal concentration at equilibrium
- [M_t] = total metal concentration
- r_fⁱ = forwards rate constant for ith first order process
- r_bⁱ = backwards rate constant for ith first order process

Plotting the left hand side of equation (9) versus time, using arbitrary approximations of [M_d]_e, allows the distinct first order processes to be identified. Of course, the slopes and intercepts of the linearizations change for different choices of [M_d]_e, but the number of distinct processes and the time scales over which they dominate remain the same.

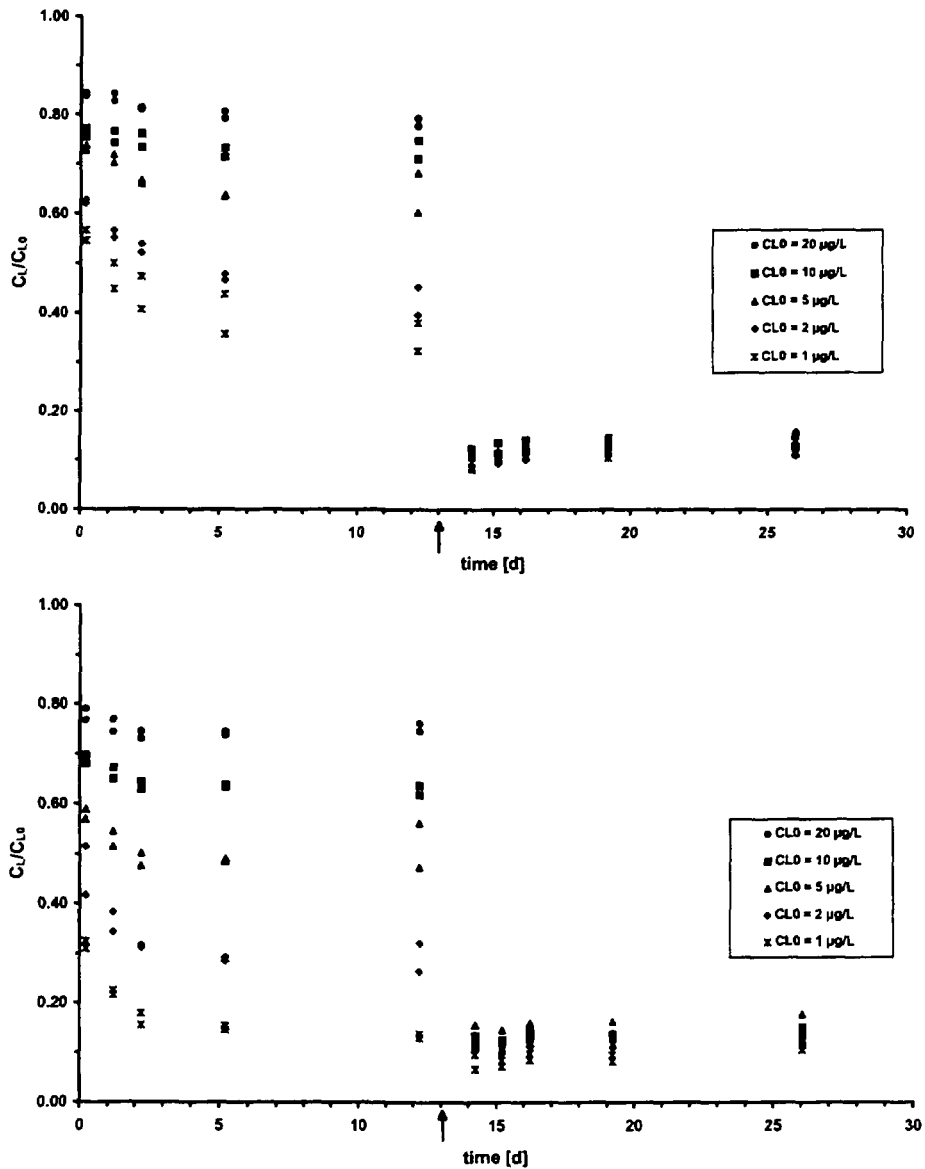


Figure 2. Kinetics of radiocaesium adsorption and desorption on sediments from (top) Ketelmeer and (bottom) Hollands Diep (Comans, 1998). C_{L0} = concentration of Cs in solution at $t = 0$; C_L = concentration of Cs in solution at time t (i.e. C_L/C_{L0} = fraction of total Cs in solution). The arrow indicates the start of desorption.

Fig. 3 shows the linearization applied to the Cs sorption data for the Ketelmeer and Hollands Diep sediments (Comans, 1998). The data show an apparently instantaneous reaction and two other distinct processes. As noted by Jannasch *et al.* (1988), the sampling schedule affects the number of processes revealed by the linearization procedure. In particular, the initial reaction may, with the appropriate experimental technique and sampling schedule, be subdivided into processes operating on minute or sub-minute time scales. The purpose here, however, is to model Cs sorption kinetics on the longer time scales which are more relevant for natural systems.

The Jannasch *et al.* linearization implicitly assumes a linear K_D relationship between dissolved and sorbed concentrations. Earlier kinetic models, such as that of Nyffeler *et al.* (1984), also adopt that assumption. However, the data for Ketelmeer and Hollands Diep sediments in Fig. 2 cover a range of initial Cs concentrations for which sorption isotherms are non-linear. This non-linearity implies that K_D -models cannot be used to model sorption kinetics over the whole concentration range. Kinetic models that include non-linear isotherm equations have been used successfully to describe metal mobilities in soil systems (e.g. Amacher *et al.*, 1986; Amacher *et al.*, 1988 and references therein). It should be noted that isotherm non-linearity does not invalidate the above conclusion that a number of distinct processes are active. Fig. 3 clearly shows that the individual processes operate within similar time frames over a wide concentration range.

In view of the similarities between the kinetic sorption behaviour of caesium on illite (Comans & Hockley, 1992) and natural sediments (Comans, 1998; Fig. 2-3), the 2- and 3-box models of Comans & Hockley (1992) have been used to model and obtain rate parameters for the sediment data in Fig. 2 (Comans, 1998).

2- and 3-box models for caesium sorption

The four and five parameter (2- and 3-box) kinetic models of Comans & Hockley (1992) have been fitted to the sediment data of Ketelmeer and Hollands Diep (Comans, 1998). No three parameter model could adequately describe these data. The differential equations defining the models were solved using a finite difference method and parameter fitting was done with a non-linear least squares regression package.

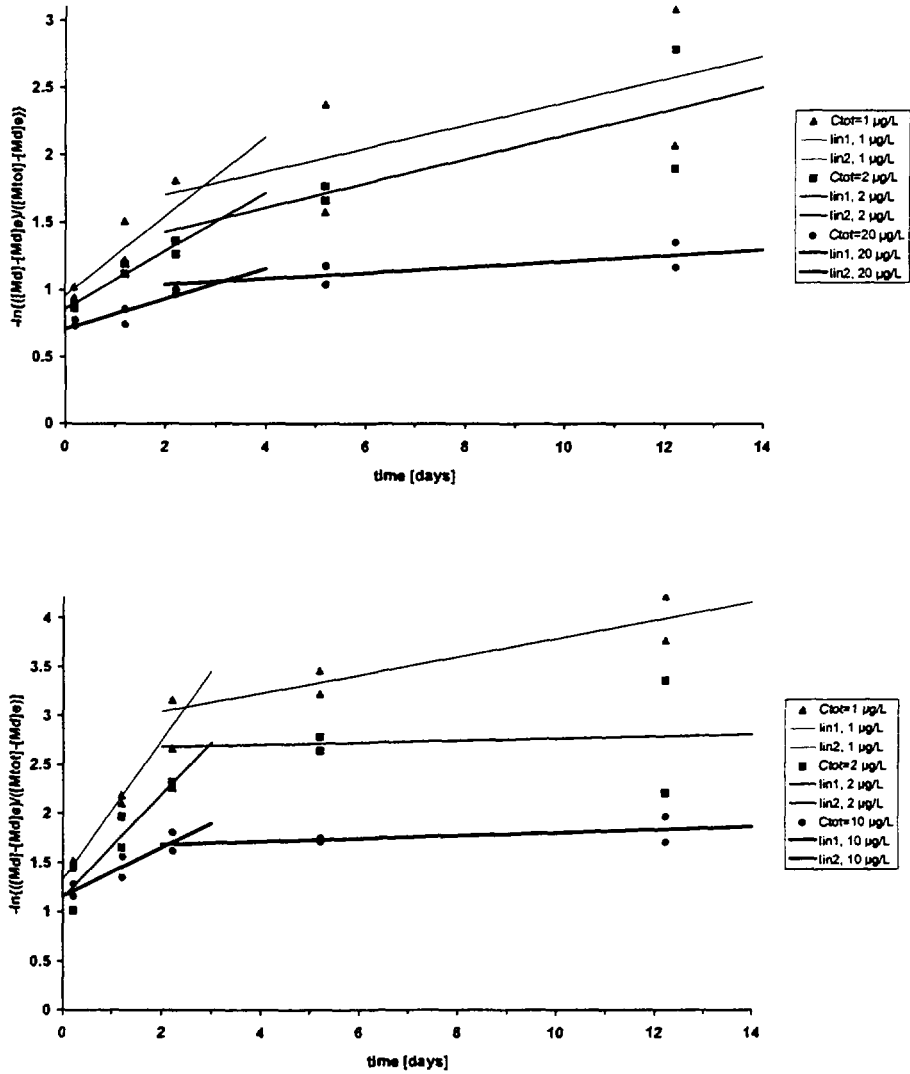


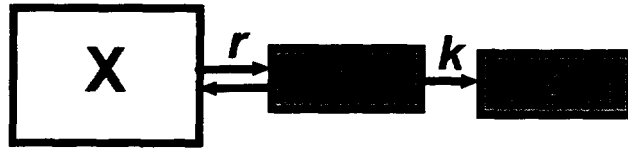
Figure 3. Kinetic data of Cs adsorption on (top) Ketelmeer and (bottom) Hollands Diep sediments linearized according to the method of Jannasch et al. (1988); (Comans, 1998).

The first "two-box" model includes a reversible Freundlich reaction followed by an irreversible first order process. The equations defining this model are shown in Fig. 4. There are four independent parameters: the Freundlich parameters, K and n , the reversible rate constant, r , and the irreversible rate constant, k . Initial estimates for the Freundlich parameters were obtained from independent isotherm fits of the data after approximately 2 weeks of adsorption. Fitting the kinetic data by eye provided the initial estimates for r and k .

The two-box model fits to the data are shown in Fig. 5. The parameter values are listed in Table I. The model provides an adequate description of the data, but tends to overpredict radiocaesium sorption during the first 24 to 48 hours, particularly at low total-Cs concentrations. As was needed for Cs sorption on illite (Comans & Hockley, 1992), an additional (fast) reaction may be considered to allow for a better overall prediction of the data points. The apparently irreversible reaction in the model, which predicts readsorption during the desorption phase (period between 13-26 days in Fig. 5), is not reflected in the data points, as was the case for Cs sorption on illite (Comans & Hockley, 1992). Possibly, some ammonium was produced by the breakdown of organic matter in the sediments at the later times during the experiments (sediments were not spiked with bacteriocides). Competition by ammonium for frayed edge sites could have prevented the readsorption of radiocaesium that was noticed in the experiments with illite.

The second model, shown in Fig. 4, provides the additional reaction by splitting the initial process of the two-box model into an equilibrium reaction and a parallel reversible reaction. Both these reactions tend towards the same Freundlich equilibrium. This model can be conceptualized as dividing a single set of Freundlich sorption sites into a portion which is rapidly accessible and a portion which is kinetically controlled. The Freundlich processes are followed in series by a third, irreversible process. In addition to the four independent parameters of the first model, the three-box model includes f , the fraction of the Freundlich sorption sites reaching equilibrium instantaneously.

Fig. 5 includes the three-box model fitted to the data. The rate parameters obtained on the basis of this model are included in Table I. The fit is slightly better, particularly for the first 48 hours, than that of the two-box model. Again, readsorption is predicted for the desorption period, albeit slightly less than the extent predicted by the two-box model. However, one might argue

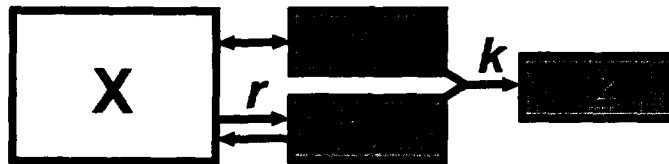


$$\frac{d[\gamma]}{dt} = r(K[X]^n - [\gamma]) - k[\gamma]$$

$$\frac{d[z]}{dt} = k[\gamma]$$

Mass Balance:

$$[X] + ([\gamma] + [z])C_p = [X]_0 + ([\gamma]_0 + [z]_0)C_p$$



$$[\gamma_1] = fK[X]^n$$

$$\frac{d[\gamma_2]}{dt} = r((1-f)K[X]^n - [\gamma_2]) - k[\gamma_2]$$

$$\frac{d[z]}{dt} = k([\gamma_1] + [\gamma_2])$$

Mass Balance:

$$[X] + ([\gamma_1] + [\gamma_2] + [z])C_p = [X]_0 + ([\gamma_1]_0 + [\gamma_2]_0 + [z]_0)C_p$$

Figure 4. Schematic representation and equations defining the 2-box (top) and 3-box (bottom) kinetic models (Comans & Hockley, 1992). "X" represents metal in the dissolved state. The shaded boxes represent sorbed metal. The subscript "0" denotes concentrations at time zero.

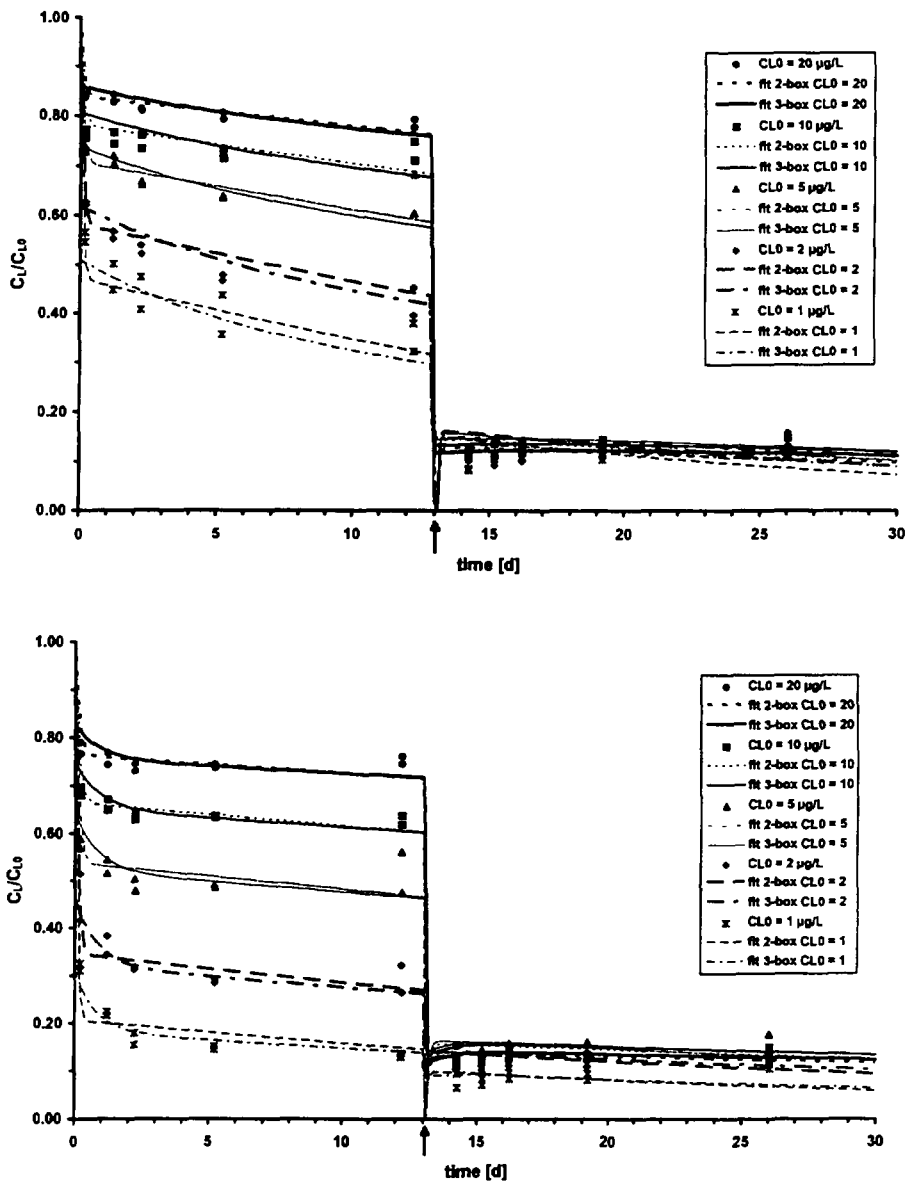


Figure 5. 2- and 3-box model predictions of Cs sorption on (top) Ketelmeer and (bottom) Hollands Diep sediments (Comans, 1998). C_0 = concentration of Cs in solution at $t = 0$; C_t = concentration of Cs in solution at time t (i.e. C_t/C_0 = fraction of total Cs in solution). The arrow indicates the start of desorption.

whether the addition of a fifth fitting parameter in the model is statistically justified in this case.

The obtained rate parameters shown in Table I are very similar, for both models, to those obtained for Ca-saturated illite by Comans & Hockley (1992). The sorption experiments with Ketelmeer and Hollands Diep sediments (Figs. 2, 3 and 5; Comans, 1998) were also carried out in a Ca-environment. If we use the three-box model for the best fit to the early data points, the fast reversible process (r) has a half life of a few (1-4) days. The slower, irreversible, process (k) has a half life of approximately 20-50 days.

The above models should not be used to predict Cs-sorption reversibility over time frames of more than a few months. Observations that radiocaesium, which has been in contact with contaminated sediments for many years, can still be mobilized by enhanced ammonium concentrations (Evans *et al.*, 1983; Comans *et al.*, 1989) give evidence for a backwards reaction. This reaction, which is interpreted as a remobilization of radiocaesium from edge-interlayer sites on illite, is apparently too slow to be observed in laboratory experiments of many weeks. Therefore, extraction of radiocaesium from historically contaminated sediments have been used to obtain a first estimate of this slow remobilization rate.

Table I. Parameter values of the 2-box and 3-box kinetic models obtained after fitting the sorption data of Cs on sediments from Ketelmeer and Hollands Diep (Comans, 1998).

	Ketelmeer	Hollands Diep
K* (2-box)	7.82± 0.404	15.34± 0.64
n*	0.5076± 0.0256	0.4160± 0.0185
r (d⁻¹)	8.55300± 2.2470	5.8090± 0.9480
k (d⁻¹)	0.04037± 0.00711	0.01736± 0.00448
RSS	8.92E-02	8.84E-02
K* (3-box)	10.25± 4.22	16.36± 1.00
n*	0.4976± 0.0256	0.4071± 0.0172
f	0.669± 0.2552	0.6757± 0.0695
r (d⁻¹)	0.1558± 0.2495	0.9964± 0.6226
k (d⁻¹)	0.02543± 0.01969	0.01314± 0.00511
RSS	8.69E-02	6.93E-02

*Freundlich const. using µg/L and µg/g for aqueous and sorbed concs., resp.

Exchangeability and slow remobilization of radiocaesium in sediments

Exchangeability of sediment-bound radiocaesium

The exchangeability of sediment-bound radiocaesium has been investigated by Comans *et al.* (1998) by extracting sediments with 0.1 M NH_4 -acetate. These extractions have been performed on all sediments shown in Fig. 1. Sediment samples from different depths were extracted three times sequentially, each step for 24 hours, with 0.1 M NH_4 -acetate at a liquid/solid ratio of 10 L/kg. Further details on the extraction procedure and radiocaesium measurements are given in Comans *et al.* (1998).

The exchangeable amounts of ^{137}Cs are given in Table II. The amount of ^{137}Cs that can be released by the three sequential NH_4 -extractions from the more mineral sediments of Hollands Diep, Ketelmeer and Esthwaite is very low; on average 2, 3, and 7%, respectively. The more organic-rich sediments of Devoke show a much higher exchangeability of 16%. The values for the three mineral sediments are low when compared, for instance, with those of Evans *et al.* (1983), who have measured ^{137}Cs exchangeabilities (also in 0.1 M NH_4^+) of 10-20% in the sediments of the Par Pond reservoir, 15-20 years after contamination. These authors attribute their relatively high exchangeabilities to the high kaolinite content of the Par Pond sediments. Western European sediments generally contain illite as the major clay mineral, which likely causes the strong fixation of radiocaesium that has been observed in the Hollands Diep, Ketelmeer and Esthwaite sediments. Devoke apparently behaves more like the Par Pond sediments in that similar amounts of ^{137}Cs are exchangeable.

If we accept that radiocaesium in all four of the above sediments is bound solely to frayed edge sites on illitic clays in the sediments, the up to one order of magnitude differences between the exchangeable fractions of radiocaesium in these sediments are unexpected. The differences are clearly not related to the different contact times of radiocaesium with the sediments, as the lowest values are found for the sediments sampled only 1.5 years after the Chernobyl accident (Hollands Diep and Ketelmeer).

Table II. Total and exchangeable radiocaesium in the different sediment cores (Comans et al., 1998).

Sediment	Depth	total ¹³⁷Cs	exchange- able ¹³⁷Cs	exchange- able ¹³⁷Cs [fraction of the total]
	[cm]	[Bq/kg]	[Bq/kg]	
Hollands Diep	0.5	249.15	0.85	0.003
	1.5	269.79	0.69	0.003
	3.5	83.05	0.55	0.007
	6.5	5.00	0.50	0.100
	9.5	17.90	-	-
	16.5	46.31	0.51	0.011
	24.5	47.96	1.36	0.028
	31.5	21.31	5.01	0.235
	40.4	21.70	-	-
				<i>average* ± s.d.: 0.022 ± 0.038</i>
Ketelmeer	1	115.46	10.06	0.087
	3	124.73	4.33	0.035
	5.5	224.23	5.33	0.024
	8.5	59.07	0.27	0.005
	11.5	37.466	0.76	0.020
	18.5	64.41	0.61	0.009
	25.5	51.79	14.89	0.288
	31.5	9.44	2.94	0.312
				<i>average* ± s.d.: 0.030 ± 0.030</i>
Esthwaite	0.5	214.80	13.60	0.063
	2.5	330.73	22.12	0.067
	4.5	545.61	32.31	0.059
	6.5	474.14	38.44	0.081
	8.5	353.43	24.93	0.071
	10.5	345.36	18.06	0.052
	12.5	325.69	21.99	0.068
	14.5	266.41	20.31	0.076
	16.5	164.03	15.03	0.092
	18.5	42.73	9.329	0.218
	20.5	21.59	4.791	0.222
				<i>average* ± s.d.: 0.070 ± 0.012</i>

Table II cont.

Sediment	Depth	total ¹³⁷ Cs	exchange- able ¹³⁷ Cs	exchange- able ¹³⁷ Cs [fraction of the total]
	[cm]	[Bq/kg]	[Bq/kg]	
Devoke	0.5	1813	343.78	0.190
	1.5	1860	401.78	0.216
	2.5	2142	345.69	0.161
	3.5	2598	375.72	0.145
	4.5	3096	363.83	0.118
	5.5	2579	270.93	0.105
	6.5	1524	208.66	0.137
	7.5	1023	237.20	0.232
	8.5	848	174.72	0.206
	9.5	727	181.78	0.250
	10.5	644	140.63	0.218
	11.5	653	44.73	0.068
	12.5	719	108.70	0.151
	13.5	685	94.97	0.139
	14.5	588	81.80	0.139
	15.5	392	58.42	0.149
	16.5	244	103.70	<i>0.426</i>
	17.5	146	81.32	<i>0.558</i>
18.5	130	68.18	<i>0.523</i>	
19.5	106	56.20	<i>0.531</i>	
				<i>average* ± s.d.: 0.164 ± 0.050</i>

*average and s.d. values exclude the (unexplained) high exchangeabilities in the bottom sections of each core (indicated in italics)

“Exchangeable” K_D -values for radiocaesium in the sediments, calculated from the exchangeable rather than total amount of ¹³⁷Cs in the sediments, are included in Fig. 1. We would expect “exchangeable” K_D s to correspond better with values predicted on the basis of (short-term) laboratory measurements of K_C^{Cs/NH_4} [FES] than the total K_D s. Although this may be the case for the Devoke sediments, total and exchangeable K_D -values for Esthwaite correspond about equally with the predictions, whereas the “exchangeable” K_D s for Hollands Diep and Ketelmeer deviate much more from the predicted values than the total K_D s. These observations strongly suggest that short-term exchangeability measurements of radiocaesium, especially in the more mineral sediments, underestimate the amount of the radionuclide that is actually taking

part in ion-exchange with the pore waters and, hence, is available for remobilization by high concentrations of ammonium.

Slow (reverse) migration of radiocaesium from clay-mineral interlayers into solution

In the kinetic models discussed above, a reverse process of radiocaesium remobilization from interlayer sites was not considered. The equilibration times of up to 4-weeks were too short for the reverse process to become apparent. Nevertheless, the fact that radiocaesium in sediments is still exchangeable to a certain extent after more than 20 years of contact with sediments (Evans *et al.*, 1983), indicates that such a reverse process must exist.

Because of its relevance for the long-term availability of sediment-bound radiocaesium, the long-term release of particle-bound radiocaesium has been studied in more detail (Comans *et al.*, 1998). The primary objective of this part of the study was to estimate the existence and magnitude of a slow remobilization (reverse rate) of radiocaesium from clay mineral interlayers during contact with a high concentration of competing ions. After the three sequential 0.1 M NH₄-acetate extractions, the sediments were resuspended for a fourth time in a fresh 0.1 M NH₄-acetate solution and have been allowed to equilibrate for more than one year (400-842 days). After this period, the additional amount of extracted radiocaesium was measured.

Table III shows the average fraction of exchangeable-¹³⁷Cs in sediments after 3 sequential 24-hr NH₄-extractions and the additional fraction mobilized after the 4th, long-term (400-842 days) extraction. Assuming (1) that all (rapidly) "exchangeable" radiocaesium had been removed by the three prior extractions, and (2) a first order remobilization process, we can roughly calculate the reverse rate constant that describes the slow remobilization of ¹³⁷Cs from the sediments. Table III indicates that the half-life of this reaction, which is interpreted as the slow release of radiocaesium from the interlayer sites, is of the order of 30-100 y⁻¹. These findings suggest that radiocaesium on interlayer sites, which is generally referred to as being "fixed", is not truly immobilized but can, at least partly, be very slowly remobilized.

Table III. Average fraction of exchangeable- ^{137}Cs in sediments after 3 sequential 24-hr NH_4 -extractions and the additional fraction mobilized after a 4th 400/560-d extraction. A reverse rate constant and half-life for the slow remobilisation of ^{137}Cs from the sediments has been calculated on the basis of the 4th extraction, assuming a first order process (Comans *et al.*, 1998).

Sediment	exch. ^{137}Cs after 3x 24-hr extraction [fraction of the total]	additional exch. ^{137}Cs after 400- 842-d extraction* [fraction of the total]	reverse rate constant [y^{-1}]	$t_{1/2}$ [y]
Hollands Diep	0.022 ± 0.038	0.0089 ± 0.0050	0.0082	85
Ketelmeer	0.030 ± 0.030	0.0095 ± 0.0030	0.0087	79
Esthwaite	0.070 ± 0.012	0.0156 ± 0.0053	0.0068	102
Devoke	0.164 ± 0.050	0.0380 ± 0.0355	0.0220	31

*equilibration time 4th extraction = 400 days for Hollands Diep & Ketelmeer; 560 days for Devoke; 842 days for Esthwaite.

Comparison of rate parameters with other estimates

Slow uptake rates

As was mentioned above, the slow uptake of radiocaesium by illite, and sediments containing illite, is interpreted as a migration towards interlayer sites on this clay mineral. This process has been recognized for many years to cause the so-called "potassium fixation" in (agricultural) soils. De Haan *et al.* (1965) have studied the kinetics of that process by following the ^{40}K -uptake from solution by illite clay over a period of 16 months. The removal of the radiotracer from solution was interpreted as isotopic exchange with interlayer-potassium, i.e. as a slow diffusion of ^{40}K into the illite lattice. Re-evaluated in terms of a first order uptake process, their data indicate a rate constant for the interlayer migration of the order of 10^{-3} d^{-1} . This value is very similar to the values found by Comans & Hockley (1992) for Cs-sorption on illite in a K-dominated environment, which lends support to the hypothesis of a similar binding mechanism for Cs and K. The slow Cs-uptake rate was found to be approximately an order of magnitude faster for a Ca-illite, which is supported by the values

found for the illite-containing sediments of Ketelmeer and Hollands Diep in a Ca-solution (Table I). Comans & Hockley (1992) have shown that the slow interlayer migration of caesium proceeds faster when the edges of illite are expanded by reaction with calcium, relative to the collapsed structure of a K-saturated illite.

Evans *et al.* (1983) have studied the "fixation" of ^{134}Cs by freshwater sediments over a period of 180 days. The increasingly incomplete extractability of radio-caesium, using 0.1 M NH_4 , with Cs-sediment contact time was interpreted as a slow movement of radiocaesium to clay interlayer sites in the sediment. If the Evans *et al.* (1983) data are interpreted in terms of a first order process, a rate of 10^{-2} - 10^{-3} d^{-1} is obtained, which is again of the same order as the values found for illite (Comans & Hockley, 1992) and for Hollands Diep and Ketelmeer sediments (Table I).

Finally, Nyffeler *et al.* (1984) have modelled radiocaesium uptake by marine sediments, using a multi-reaction model with an irreversible process similar to that in the 2- and 3-box models of Fig. 4. These authors have also obtained a similar rate of 10^{-2} d^{-1} .

Reverse (remobilization) rates

Smith & Comans (1996) have developed a transport model that includes radio-caesium sorption kinetics to simulate radiocaesium in each of three phases in the sediment profiles of Ketelmeer and Hollands Diep: aqueous, exchangeably-bound and slowly reversible (often termed "fixed"). The model gave evidence for a reverse reaction from less-exchangeable to exchangeable sites with a half-life of order 10 years, which is close to the independent estimates by the long-term extractions in Table III.

Using the exchangeability measurements of Evans *et al.* (1983), 85% fixed/15% exchangeable (after 180 days contact of ^{134}Cs with the sediment), and a forward rate constant of half-life 100 days, a reverse rate of half-life 2 years is estimated. The same estimate can be made from the short-term exchangeability measurements of Comans *et al.*, (1998) shown in Table II (84-98% fixed/2-15% exchangeable). It is reasonable to assume that the long-term extractions discussed above have led to an upper estimate of the remobilization rate, as a new equilibrium between NH_4 and remobilized Cs may have been reached during the single long-term extraction step. Given the limited available data, the

remobilization half-life of sediment-bound radiocaesium may, therefore, be expected to be of the order of a few years to a few tens of years.

Conclusions

The kinetics and reversibility of radiocaesium solid/liquid partitioning in sediments have been reviewed and interpreted in terms of a mechanistic framework. This framework is based on the premise that radiocaesium is almost exclusively and highly-selectively bound to the frayed particle edges of illitic clay minerals.

Several processes with distinctly different rates can be distinguished in radiocaesium sorption. 2- and 3-box models can describe both the overall partitioning in sediments and the reversible (exchangeable) and irreversible (non-exchangeable/"fixed") fractions of radiocaesium over time scales relevant for natural aquatic systems. The models are consistent with knowledge of radiocaesium sorption mechanisms in sediments. The obtained rate parameters indicate that reversible partitioning of radiocaesium dominates over the first few days following a contamination event, whereas irreversible kinetics becomes important over time scales of weeks to months. The slow process, which reduces the exchangeability of sediment-bound radiocaesium over time, is believed to result from a migration of radiocaesium from exchangeable sites on the frayed edges of illite clays towards less-exchangeable interlayer sites. This hypothesis is supported by comparison of model results with previous findings.

Observations that radiocaesium, which has been in contact with contaminated sediments for many years, can still be mobilized have given evidence for a backwards reaction. This reaction is interpreted as a remobilization of radiocaesium from interlayer sites on illite, and is apparently too slow to be observed in laboratory experiments of many weeks. Long-term extraction of radiocaesium from historically contaminated sediments has confirmed the existence of a reverse reaction and has provided a first estimate of the half-life of this slow remobilization rate of the order of tens of years. These findings suggest that the long-term exchangeability of radiocaesium in sediments may be higher than the few % which is generally assumed.

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