

A kinetic approach to describe trace-element distribution between particles and solution in natural aquatic systems

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Abstract—The partitioning of radioactive trace elements between seawater and particulate matter from surface sediments and sediment traps was investigated in laboratory experiments. For the elements Na, Zn, Se, Sr, Cd, Sn, Sb, Cs, Ba, Hg, Th and Pa (group I) constant distribution coefficients (K_d) were found after a few days of equilibration, whereas the elements Be, Mn, Co and Fe (group II) showed an increasing K_d over the whole time of observation of 108 days. The time dependence of K_d is described by an adsorption-desorption equilibrium (group I elements), followed by a lattice transport reaction step (group II elements). The reaction rate constants are compared to Mn oxidation rates and to adsorption rate constants derived from in situ measurements of the U/Th disequilibrium as available from literature.

1.0 INTRODUCTION

DIFFERENT CONCEPTS have been used to model trace element cycling in aquatic systems: Thermodynamic models, which assume complete equilibrium in the multiphase system, have been used to explain trace element removal from the oceans (GOULD, 1967; SCHINDLER, 1975; LI, 1981). For open systems, an equilibrium approach may hold only if the time scales of interest are large compared to any physical, chemical and biological reaction times (IMBODEN and LERMAN, 1978). In this case, the equilibrium is the dynamic balance of two opposite chemical reactions, *e.g.* for first order reactions:



$$K(\text{eq}) = [B]/[A] = k_1/k_{-1} \quad (1b)$$

where

$K(\text{eq})$: thermodynamic equilibrium constant
 k_1, k_{-1} : reaction rate constants.

The boundary conditions (*i.e.* initial conditions, magnitudes of inputs and sinks) will determine whether an equilibrium (or "quasi equilibrium") or a kinetic approach is more appropriate to describe the system.

For example, when using Eqn. (1) to describe scavenging of a dissolved element in the ocean by settling particles, the approach to be taken will depend upon the residence time of the suspended particles compared to the reaction times of adsorption and desorption of the element considered. If the particle residence time is short compared to the adsorption time, no equilibrium condition can be attained, but a steady state will be established for the partitioning between particulate and dissolved form of the element. An analogous situation is encountered when the input into the system is changing with time, *e.g.* in the case of man made pollution or in case of periodical cycles of biological processes. Here a kinetic approach is basically more appropriate to describe the system. Hence the need for knowing reaction rate constants arises.

Unfortunately a kinetic approach is generally much more complex than an equilibrium approach, because it requires the knowledge of the elementary reaction pathways and their rate constants. A rigorous investigation of trace element cycling in natural waters would require that beside trace element speciation, all reactions of the dissolved element with the solid phase and its surface are known. Just a short look at the literature of adsorption chemistry tells us how ambiguous such an attempt would be.

One step toward a kinetic approach is to remain on a macroscopic and therefore phenomenological level by studying the kinetics of adsorption reactions in the field or in the laboratory under defined natural conditions (*e.g.* T , pH, p_e , salinity). It is clear that such investigations will deliver system specific information, but one might encounter difficulties when attempting to generalize the results.

In the present study we investigated the interactions of dissolved trace elements in radioactive form with top layer sediments of different origin and with oceanic particles caught in sediment traps. We attempted to answer the following questions:

a) Can a constant distribution of trace element between solution and solid phase be established within the time scale of particle residence times in natural waters?

b) Can the adsorption kinetics of a trace element be described in terms of simple overall reaction rate constants?

The goal was not to investigate the very fast adsorption rates as observed in many adsorption studies of dissolved elements with pure phases (*e.g.* ATKINSON *et al.*, 1972), but the mostly "diffusion controlled"

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partitioning (*i.e.* diffusion into pore spaces, tunnels, different surface sites, etc.) ranging in time from days to months. The overall sorption reaction can also include isotopic exchange and/or coagulation reactions of radioactively tagged colloids and particles, that are expected to take days for completion. An extensive review on the fast sorption kinetics can be found in the book by ANDERSON and RUBIN (1981). The resulting parameters will form the basis of a numerical kinetic transport model to describe trace element cycling in natural aquatic ecosystems (NYFFELER *et al.*, in preparation).

2.0 EXPERIMENTAL METHODS AND MATERIALS

For the determination of distribution ratios from adsorption or desorption experiments, a modified suspension technique described by DUURSMA and BOSCH (1970) was applied in batch process using radiotracers ^7Be (52 d), ^{22}Na (2.6 y), ^{54}Mn (312 d), ^{59}Fe (45 d), ^{60}Co (5.3 y), ^{65}Zn (244 d), ^{75}Se (120 d), ^{83}Sr (65 d), ^{109}Cd (453 d), ^{113}Sn (115 d), ^{123}Sb (2.8 y), ^{134}Cs (2.1 y), ^{133}Ba (10.5 y), ^{203}Hg (47 d), ^{228}Th (1.9 y) and ^{233}Pa (27 d). All experiments were performed in a dark cold room ($2.0 \pm 0.5^\circ\text{C}$). Seawater ($S = 30\%$, $\text{pH} = 8.1$) was refiltered through a $0.4 \mu\text{m}$ Nucleopore filter before addition of the radioisotopic spikes. Spike additions were kept minimal in order to keep natural conditions, *i.e.* trace element concentrations, salinity and pH the same. For each experiment $10 \mu\text{l}$ of spike were added from an acidic stock solution at $\text{pH} \approx 0.5$ to 99.5 g of seawater in a plastic bottle. The spike aliquot contained 10^{-14} to 10^{-16} moles of each radiotracer (up to twelve) and 10^{-11} to 10^{-13} moles of carrier as indicated by the manufacturer. The solution was then equilibrated by shaking it at 200 rpm in a mechanical shaker for a couple of hours after which it was measured on a Ge(Li) detector coupled to a 4096 multichannel analyzer to determine its total activity. From a stock suspension of sediment materials, 0.5 g seawater containing approximately 10 mg of sediments were added to the spiked water. The pH was measured after a short time of continuous shaking. The mechanical shaker kept the sediment in suspension. At predetermined times, the bottle was removed, and after measuring the pH, its content was filtered through a double Nucleopore filter of $0.4 \mu\text{m}$ pore size and 25 mm diameter. The change in pH during the experiments was less than 0.1 . For each sample, filter, filtrate, filter blank and plastic bottle were gamma-counted.

In separate calibration experiments, geometry factors to convert from filter to bottle or scintillation vial geometries were determined for all radioisotopes. For each experiment, a mass balance was calculated in order to check for losses by adsorption during filtration. Losses could be kept minimal when all glassware and bottles were soaked in seawater for a couple of days before use. Cleaning the filter apparatus with diluted HNO_3 lead to significant adsorption losses for Be, Mn, Co, Zn and Hg. Adsorption on the Nucleopore filters turned out to be negligible. A series of blank experiments (*e.g.* without sediments) were also carried out to check for any precipitation over a period of 119 days. The highest precipitation artifacts were observed for Fe with $<5\%$ of the total activity, Sn and Se with $<3\%$, Be and Co with $<1\%$ after 119 days (the values increased with time). For all other isotopes precipitation was unmeasurably small.

The distribution ratio K_d from adsorption experiments was then calculated using Eqn. (2):

$$K_d = c_s/c_w = (A_s * gf / A_w) * (V/m) \quad (2)$$

where

- c_s : concentration in sediments [mole/kg dry sediments]
 c_w : concentration in seawater [mole/kg]
 A_s : activity of radio-tracer in the sediment [cpm]

- A_w : activity of radio-tracer in the seawater [cpm]
 V : mass of seawater [kg]
 m : mass of the sediment [kg]
 gf : geometry factor (filter to bottle).

The relative errors in K_d are dominated by counting statistics. For the adsorption experiments the relative errors (2σ) are 4% to 10% for all elements with the exception of Na ($2\sigma \approx 80\%$) and Fe for equilibration times larger than 50 days ($2\sigma < 15\%$).

Desorption experiments were carried out using the thin layer technique (DUURSMA and BOSCH, 1970). 10 mg of sediments were shaken for 50 days in 100 g of spiked seawater and then filtered. The filter was then fixed on the bottom of a petri dish and gamma-counted. The sediments were kept wet by adding some droplets of seawater on its top. Afterwards, 6 g of freshly filtered seawater were carefully overlaid on the filter. At set intervals, 4 g of seawater from the petri dish was gamma-counted in a scintillation vial and returned to the petri dish. The distribution ratios were then calculated using Eqn. (3):

$$K_d = c_s/c_w = ((A_s * gf - A_w * rv) / A_w * rv) * (V/m) \quad (3)$$

where

- A_t : total activity [cpm]
 gf : geometry factor (filter to scintillation vial)
 rv : ratio of total solution to aliquot counted.

The relative errors (2σ) of the distribution ratios in case of the desorption experiments are between 15% and 30% for all isotopes except Na ($2\sigma \leq 80\%$).

The particulate matter used in our experiments was top layer sediment from Narragansett Bay, San Clemente Basin, MANOP site H, and sediments and fecal pellets from sediment traps deployed in the North Atlantic. For the adsorption experiments, the suspended particle concentration (cp) was all about 100 mg/l , except that the cp of the sediment trap materials was only 27.5 mg/l . After sampling, the particulate matter was kept wet at low temperature and under oxic conditions. The five sediment types are characterized in Table 1.

From each sediment type a stock solution was prepared with freshly filtered seawater and equilibrated for a week before addition to the spiked solutions. After the gamma-counting, the weight of the particulate matter was determined.

3.0 RESULTS AND DISCUSSION

Adsorption studies with pure phases such as SiO_2 , Al_2O_3 or TiO_2 (KINNIBURGH and JACKSON, 1981 and

Table 1. Characterization of the fine particulate materials used in the sorption experiments.

Sample	NB	SCB	MSH	sp	fp
Depth (m)	9		3700	237	62
C(org) %	2	2	1	6.7	10.1
CaCO ₃ %			0.1	21.7	17.6
Si %		19.9	22.3		
Al %	2.6	2.4	4.5		
Fe %	2.9	3.9			
Mg %	0.8	0.9	1.2		
Ca %	1.35	0.6	1.6		
Mn %	0.04	0.09	3.5		
C_T (mg/l/kg)*	0.49	0.27	2.8		
S (m ² /g)**	12.9	10.0	110		

NB: Narragansett Bay surface sediments

SCB: San Clemente Basin surface sediments,

MSH: MANOP site H surface sediments

sp: N. Atlantic sediment trap materials ($38^\circ 05' \text{N}$, $73^\circ 47' \text{W}$),
 fp: N. Atlantic fecal pellets in sediment trap ($38^\circ 06' \text{N}$, $73^\circ 55' \text{W}$).

*Total exchange capacity, determined by L. Balistrieri (Tritium method).

**BET surface, determined by B. Trusch.

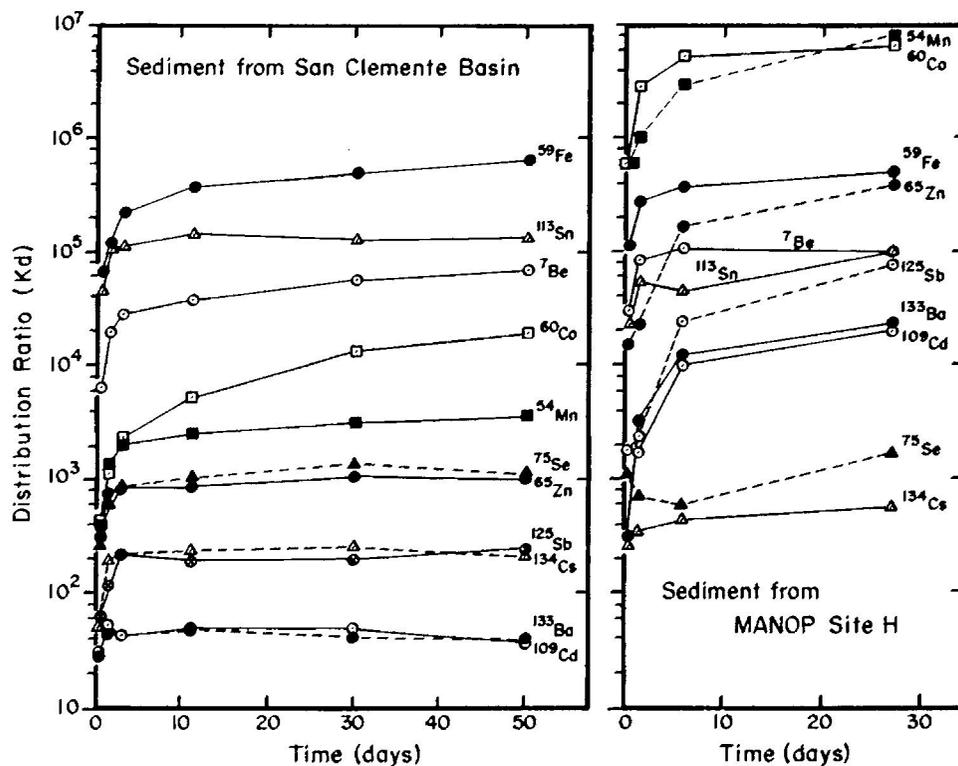


FIG. 2. Adsorption distribution ratios of various radiotracers as a function of time using surface sediments from San Clemente Basin (left) and MANOP site H (right).

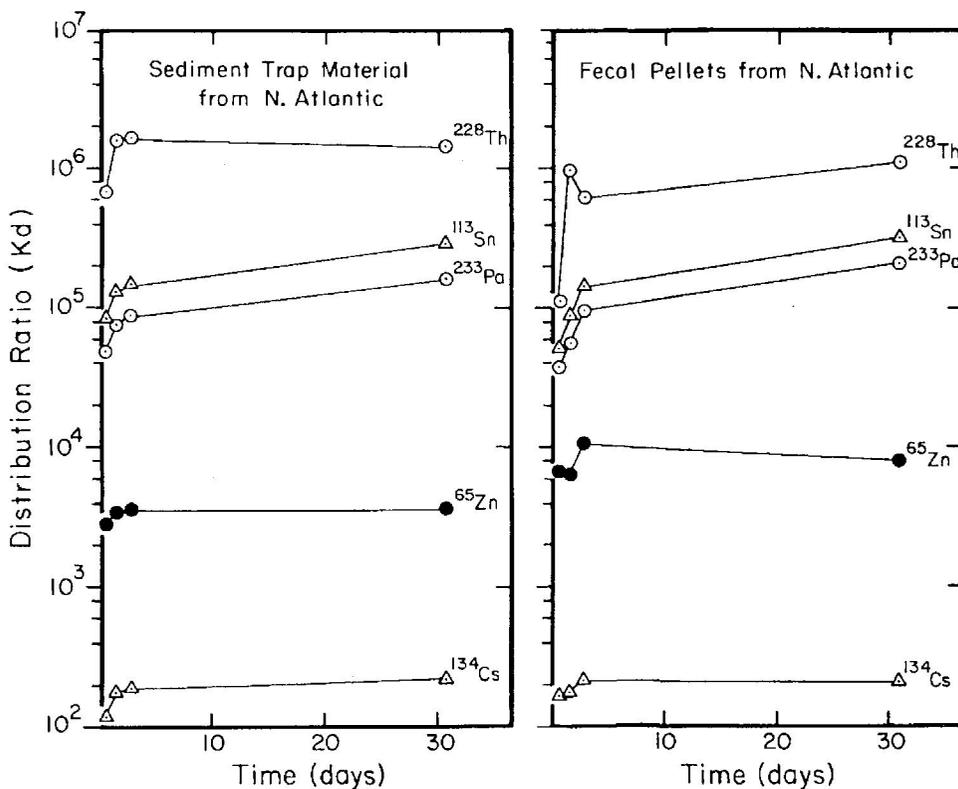


FIG. 3. Adsorption distribution ratios of radiotracers as a function of time using sediment trap materials (left) and fecal pellets (right) from North Atlantic.

Table 2. Comparison of the distribution ratios for different sediments after 30 days of equilibrium

	NB†	SCB	MSH	sp	fp	*K ₁ ⁺
Be-7	4.5E+04	5.7E+04	1.0E+05	-	-	2.0E-06
Na-22	~1E+00	~8E-01	2.4E+00	-	-	4.0E-15
Mn-54	5.5E+04	3.3E+03	7.8E+06	-	-	2.0E-11
Fe-59	6.9E+05	5.1E+05	4.5E+05	-	-	5.0E-03
Co-60	2.4E+04	1.4E+04	6.5E+06	-	-	7.9E-10
Zn-65	1.2E+03	1.1E+03	1.4E+05	3.6E+03	9.4E+03	6.3E-10
Se-75	1.8E+02	1.2E+02	8.5E+02	-	-	-
Sr-85	1.8E+00	-	-	-	-	5.0E-14
Cd-109	8.5E+01	4.7E+01	9.5E+01	-	-	1.6E-10
Sn-113	1.9E+05	1.4E+05	1.0E+05	3.0E+05	3.1E+05	-
Sb-125	2.9E+02	2.2E+02	2.1E+04	-	-	-
Ba-133	2.5E+01	4.4E+01	2.0E+04	5.1E+01	5.0E+01	3.2E-14
Cs-134	1.4E+02	2.4E+02	4.0E+02	2.2E+02	2.1E+02	-
Hg-203	1.7E+05	-	-	-	-	1.6E-03
Th-228	-	-	-	1.5E+06	-	-
Pa-233	-	-	-	1.5E+05	2.0E+05	-

† See the footnote in Table 1.

* K₁ first hydrolysis constant (Baes and Mesmer, 1981)

This is not surprising, since both sediments have quite similar sediment surface properties (total exchange capacity, specific surface area, see Table 1) and chemical parameters. A comparison of K_d values for the top layer sediments of San Clemente Basin to those of the settling particles and the fecal pellets from North Atlantic shows a good agreement within a factor of two, with exception of the biophilic element Zn that is slightly (3–9 times) more concentrated in the sediment trap samples, probably due to high organic carbon contents in the trap materials.

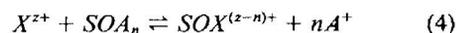
For the sediments from MANOP site H the K_d values are significantly higher for most of the elements. From the surface parameters one expects the K_d values to be five to ten times higher than for Narragansett Bay sediments. But there is obviously only a qualitative positive correlation of K_d to the surface parameters (total exchange capacity, specific surface area): The elements that correlate to Mn, e.g. Co, Zn, Ba and Sb (LI, 1982), show a 100 fold enhancement of the K_d values (Ba even 10^3), whereas Fe, Sn, Na and Cs show almost no change in the distribution ratios. And in fact the observed distribution ratios for MANOP site H sediments agree quite well with the values observed for delta-MnO₂: K_d (Mn) = $5 \cdot 10^7$, K_d (Co) = $2 \cdot 10^6$ and K_d (Zn) = $8 \cdot 10^5$ published by TAKEMATSU (1979).

If the adsorption of the cations on the particles takes place through the formation of a surface complex between cations and the oxygen of the hydrous oxide surface of the particles, then $\log(K_d)$ and the corresponding $\log(*K_1)$ (first hydrolysis constant of cation) should be linearly correlated (SCHINDLER, 1975b; DUGGER *et al.*, 1964). For Narragansett Bay and San Clemente Basin sediments (both low in Mn content, Table 1), the correlation between $\log(K_d)$ and $\log(*K_1)$ is high for Fe, Hg, Be, Zn, Cd, Ba, Sr and Na (Fig. 4). However, the offset of Mn and Co from the correlation line indicates that these elements are deposited on particles through autocatalytic oxidation processes (LI *et al.*, 1984). For the MANOP site H-sediments which have very high Mn contents (Table 1), Ba, Cd, and Zn along with Mn and Co are also offset from the correlation line. In this case, the adsorption of Ba,

Cd and Zn is probably enhanced by the cation exchange between Ba, Cd and Zn on one hand and the lattice-Mn and -Co in MnO₂ coatings on the other. As suggested by LI (1981), the high K_d for Cs (compared to other alkali elements) is not due to the formation of a surface complex between Cs⁺ and the oxygen of hydrous oxide surfaces but rather due to the electrostatic attraction between Cs⁺ and negatively charged particle surfaces. Alternatively, Cs adsorption is also enhanced by cation exchange of Cs⁺ with K⁺ in channel or interlayer positions of clay minerals. This also explains why partitioning of Cs is almost independent of solution pH in the range between 4 to 10 (SIBLEY *et al.*, 1982).

3.3 Approach to sorption kinetics

The sorption of the group I element X by the hydrous oxide surface can be visualized by the following reaction:



and the change of the concentration of X^{z+} with time

$$\begin{aligned} d[X]/dt &= -k_1^*[X]*[SOA_n] + k_{-1}^*([A]^n)*[SOX] \\ &= -k_1^*[X]*cp*\{SOA_n\} \\ &\quad + k_{-1}^*([A]^n)*([X_0] - [X]) \end{aligned}$$

$$d[X]/dt = -k_1*[X] + k_1*([X_0] - [X]) \quad (5)$$

where

- k_1 : the forward rate constant $k_1 = k_1^*cp*\{SOA_n\}$ in day⁻¹
- k_{-1} : the backward rate constant $k_{-1} = k_{-1}^*[A]^n$ in day⁻¹
- []: concentration of species in solution [cpm/l]
- { }: concentration of species in solids [cpm/kg]
- cp: concentration of suspended solids in solution [kg/l]
- S: counterion to O of solid oxide (metal or metalloid e.g. Al, Si, Mn, Fe)
- A: H⁺ or major cation in seawater (e.g. Mg²⁺, Na⁺...)

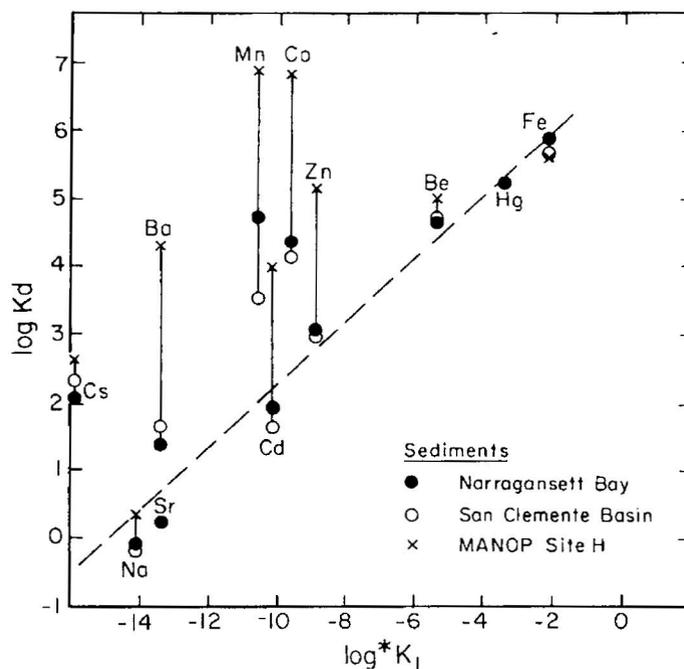


FIG. 4. A plot of the first hydrolysis constants vs. adsorption distribution ratios of cationic radiotracers after 30 days of equilibration using different surface sediments.

n : the average number of A released per X adsorbed

$[X_0]$: initial concentration of element X .

In this approach (Eqn. 4) it is implicitly assumed that the process of sorption includes isotopic exchange and coagulation reactions of radioactively tagged colloids on the particle surface.

The solution of Eqn. (5) is:

$$\frac{[X]}{[X_0]} = \frac{k_{-1}}{(k_1 + k_{-1})} + (1 - \frac{k_{-1}}{(k_1 + k_{-1})}) \cdot \exp[-(k_1 + k_{-1}) \cdot t]. \quad (6)$$

By definition, the distribution ratio is

$$K_d(t) = \frac{\{SOX\}}{[X]} = \frac{([X_0] - [X])/cp}{[X]} \quad (7)$$

and at steady state ($t \rightarrow \infty$):

$$K_d(\infty) = (k_1/cp)/k_{-1}. \quad (8)$$

Therefore, from Eqns. (6) to (8), the reaction rate constants k_1 and k_{-1} can be obtained by curve fitting of the observed $K_d(t)$ values. We have to remember that the rate constants are system specific: they are functions of the pH, the speciation of the dissolved species and the type of site, the total exchange capacity, the concentration of the particles, sorption mechanisms (e.g., adsorption as shown in Eqn. 4, isotopic exchange, coagulation reactions of radioactively tagged colloids on the particles surface, etc.) and the salinity. In our experiments, it can safely be assumed that $\{SOA_n\}$ and $[A]$ are constant ($[X] \ll \{SOA_n\}$, $[A]$). Therefore, k_1 depends on the particle concentration cp only. As different particle concentrations were used in the ex-

periments the reaction rate constants k_1 should be divided by cp for comparison.

In Figs. 5a to 5d some examples of fits of the time function are plotted together with the experimental $K_d(t)$ data for different sediments. In Table 3 all reaction rate constants are summarized, except for the elements Na and Sr, whose distribution does not change after the first equilibration time of approximately 0.5 days.

First note in Table 3 that the adsorption rate constant $k_1^* = k_1/cp$ ($1 \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$) varies over several orders of magnitude for the different elements. The following sequence is found:

$$\begin{aligned} \text{Th} \geq \text{Pa} \approx \text{Hg} \approx \text{Sn} > \text{Ag} > \text{Zn} > \text{Cs} \approx \text{Se} \\ \approx \text{Sb} > \text{Cd} > \text{Ba} > (\text{Sr} \approx \text{Na}) \\ 1.5 \times 10^5 \dots 2 \times 10^4 \dots 6 \times 10^3 \dots \\ 600 \dots 150 \dots 85 \dots 25 \dots (1). \end{aligned}$$

On the other hand the desorption rate constant k_{-1} (day^{-1}) of the different elements varies only over one order of magnitude and shows the following sequence:

$$\begin{aligned} \text{Th} \approx \text{Sn} \approx \text{Hg} \leq \text{Pa} \approx \text{Zn} \leq \text{Sb} \leq \text{Cs} \approx \text{Se} \\ \approx \text{Cd} \approx \text{Ba} (\approx \text{Sr} \approx \text{Na}) \\ 0.1 \dots 0.2 \dots 0.35 \dots 0.5 \dots 0.7 \dots 1.0-2.0. \end{aligned}$$

The small variation of k_{-1} would allow to correlate k_1^* to the first hydrolysis constant $*K_1$ in case of cations (or to $1/*K_1$ in case of oxyanions) and opens the possibility to estimate adsorption rate constants for elements not measured. The small range of k_{-1} may suggest that the radiotracers first adsorb onto colloids,

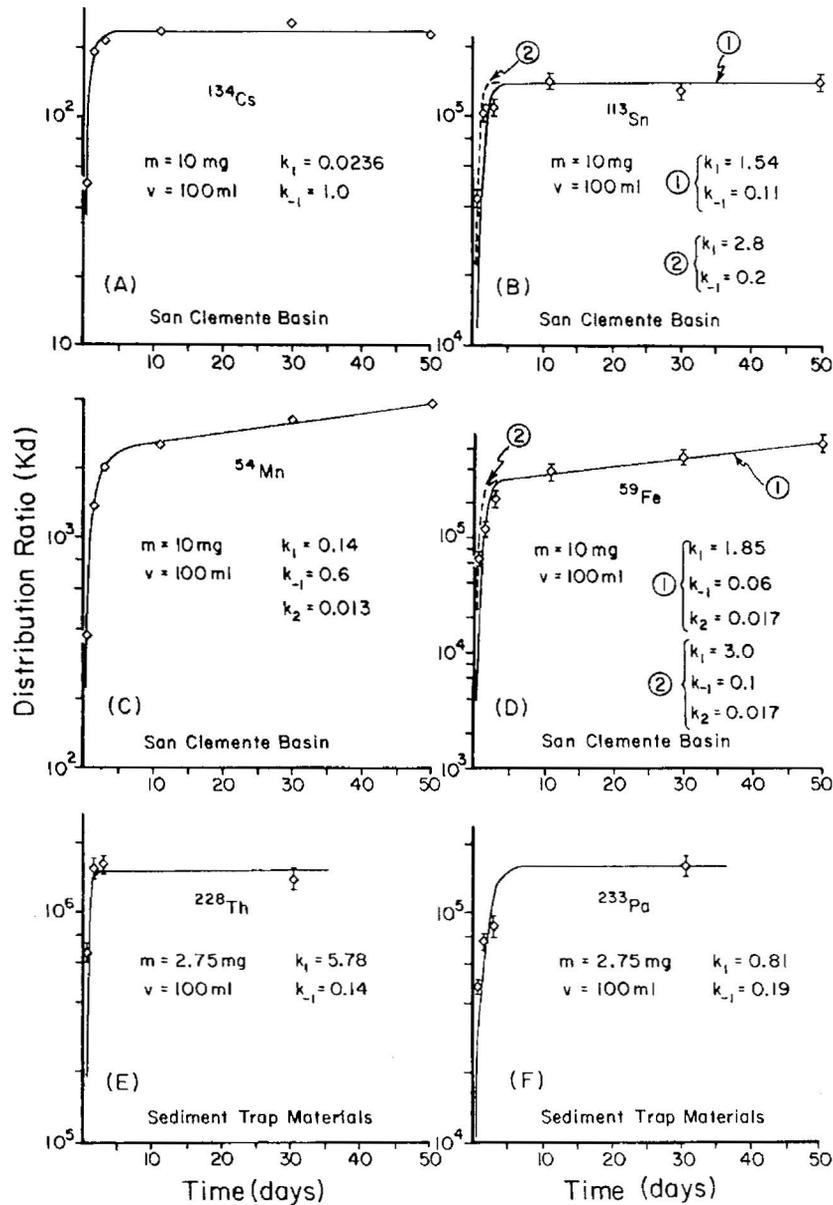


FIG. 5. The model fits (solid and dotted lines) of adsorption distribution ratios as a function of time, adjusting parameters, k_1 , k_{-1} and k_2 [d^{-1}].

then colloids coagulate on larger particles, and the desorption step only represents the disaggregation of colloids from larger particles. Further investigations are needed.

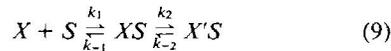
All experimental data of the group I elements could be fitted reasonably well with this simple approach of using first order reactions. However, as we did not create a dense set of data in the first time period of the experiments during which the K_d values change most significantly, the analysis is not very sensitive to the reaction mechanism: As all data points were used with equal weight for curve fitting, the first order reaction rate constant k_1^* expresses a mean adsorption rate over a time scale of a day that could be composed

of a cascade of many adsorption steps of the dissolved species with different types of sites on the surface running simultaneously. The data for Sn in Fig. 5b, for instance, indicate that the adsorption of Sn is initially faster and slows successively down to reach the equilibrium. As it has been mentioned before, other interpretations of the observed slow adsorption include exchange reactions with Mg^{2+} for example, which covers natural particles in seawater to a large extent (SCHINDLER, 1975), or diffusion-controlled adsorption to sites in pore spaces or lightly covered by organic or oxide coatings. Irrespective of interpretation, our data are confirmed by field experiments, as we will show later.

Table 3. Reaction rate constants derived from adsorption experiments

	Narragansett Bay			San Clement Basin			MANOP site H		
	k^*_1	k_{-1}	k_2	k^*_1	k_{-1}	k_2	k^*_1	k_{-1}	k_2
Be-7	4000	0.10	0.006	9500	0.30	0.020	4.2E+04	1.0	0.035
Mn-54	1600	0.035	0.018	1400	0.60	0.013	4.0E+04	0.018	0.048
Fe-59	1.5E+04	0.023	0.006	2.5E+04	0.080	0.017	3.5E+04	0.10	0.013
Co-60	500	0.013	0.010	1000	0.25	0.070	5.0E+04	0.011	0.013
Zn-65	390	0.32	0.0	660	0.60	0.0	1.0E+04	0.070	0.040
Se-75	180	1.0	0.0	480	0.40	0.0	850	1.0	0.040
Cd-109	85	1.0	0.0	47	1.0	0.0	2900	0.30	0.040
Sn-113	2.0E+04	0.10	0.0	1.5E+04	0.11	0.0	2.1E+04	0.20	0.0
Sb-125	150	0.50	0.0	110	0.50	0.0	4300	0.20	0.065
Ba-133	25	1.0	0.0	89	2.0	0.0	1900	0.095	0.008
Cs-134	140	1.0	0.0	240	1.0	0.0	600	1.5	0.016
Hg-203	3.5E+04	0.20	0.0	-	-	-	-	-	-
	settling particles			fecal pellets					
	k^*_1	k_{-1}	k_2	k^*_1	k_{-1}	k_2			
Zn-65	7200	2.0	0.0	9400	1.0	0.0			
Sn-113	9.1E+04	0.29	0.0	3.8E+04	0.12	0.0			
Cs-134	220	1.0	0.0	320	1.5	0.0			
Th-228	2.1E+05	0.14	0.0	4.4E+04	0.044	0.0			
Pb-210	5.1E+04	0.34	0.0	3.1E+04	0.16	0.0			

For the elements of group II the postulated reaction mechanism consists of a sorption reaction of the type expressed in Eqn. (4) followed by a reaction of the cation X on the surface sites, *i.e.*



with

k_1, k_{-1}, k_2, k_{-2} : rate constants

S : surface sites, $S = \{SOA_n\} = \text{const.}$

Hereby, the rate constants k^*_1 and k_{-1} are expected to be in the order of magnitude of those of group I elements, *e.g.* k_{-1} around 0.1 day^{-1} and k^*_1 as estimated from the correlation of k^*_1 with $*K_1$. As it can be seen from the experiments (*e.g.* Fig. 1), no overall equilibrium is reached within the time of observation. This indicates that k_{-2} has to be much smaller than 0.006 day^{-1} and cannot be obtained by our experiments. Therefore, the approach for group II elements had to be restricted to following reaction type:



where

X : concentration of cation in solution

Y : concentration of cation on surface sites

Z : concentration of cation in crystal lattice.

The appropriate differential equations are:

$$dX/dt = -k_1 * X + k_{-1} * Y \quad (11a)$$

$$dY/dt = k_1 * X - (k_{-1} + k_2) * Y \quad (11b)$$

$$dZ/dt = k_2 * Y \quad (11c)$$

The boundary conditions for $t = 0$ are $X = X_0$, $Y = 0$ and $Z = 0$ for adsorption experiments. The solution of Equation (11) is then given by Eqn. (12):

$$Z = X_0 * [1 - 1/(1/R_1 - 1/R_2)] * [(1/R_1) * \exp(R_1 * t) - (1/R_2) * \exp(R_2 * t)] \quad (12a)$$

$$Y = -X_0 * [1 / \{(k_{-2}) * (1/R_1 - 1/R_2)\}] * [\exp(R_1 * t) - \exp(R_2 * t)] \quad (12b)$$

$$X = X_0 - Y - Z \quad (12c)$$

where

$$R_1 = [-b + \sqrt{b*b - 4g}] / 2, R_2 = [-b - \sqrt{b*b - 4g}] / 2$$

$$b = k_1 + k_{-1} + k_2, g = k_1 * k_2.$$

The distribution ratio is by definition:

$$K_d(t) = [(Y + Z) / cp] / X \quad (13)$$

From the observed $K_d(t)$ values the reaction rate constants for Be, Mn, Fe and Co can now be obtained as follows: k_2 is determined from the increase of K_d at experimental equilibration times larger than 15 days. k_1 and k_{-1} are obtained by curve fitting of the initial $K_d(t)$ values. The resulting rate constants are summarized in Table 3. It is seen that the range of k_2 is quite small and k_2 lies between 0.006 and 0.07 day^{-1} . In case of Mn the reaction times of the constant reaction step, $\tau_r = \ln(2) / k_2$, is approximately 50 days for sediments from Narragansett Bay and from San Clemente Basin, and 15 days for sediments from MANOP site H that have a significant higher concentration in total Mn. For Fe the reaction times (τ_r) are slightly higher and lie between 40 and 115 days.

As has been already mentioned in the introduction, the goal of this study was to find an approach to describe sorption kinetics for applications in studies of trace element removal from the water column, flux studies at the sediment water interface and within the sediments. The given approach of assuming a reaction mechanism which involves the two types of connected reaction steps allows a reasonable representation of the observed partitioning kinetics. However, it is not possible to separate between adsorption and possible effects of isotopic exchange on particle surface or coagulation reactions of radioactively tagged colloids on the larger particles.

It is interesting to notice that the reaction times for the consecutive reaction of Mn determined in this study ($50 > \tau_r > 15$ days) are very close to the reaction times of Mn oxidation in natural waters of $\tau_r \approx 35$

days found by SUNG and MORGAN (1981). This coincidence indicates that we probably observe Mn oxidation on the surface of the particles in our experiments.

Another indication of the relevance of the K_d measurements in the laboratory comes from a direct comparison with a controlled ecosystem study (AMDURER, 1983). If the comparison is made for the K_d values after 5 days of equilibration (*i.e.* the average residence time of the suspended particles in the MERL tanks during the winter experiments), then the agreement for the elements Mn, Fe, Co, Zn, Sn, Cs and Hg is better than $\pm 25\%$.

SANTSCHI *et al.* (1979) obtained the removal rate constant of ^{234}Th from the water column by settling particles in range of $0.07\text{--}0.48\text{ day}^{-1}$ in Narragansett Bay. If one assumes k_1^* for ^{234}Th in Narragansett Bay is similar to those of Fe and Sn ($1.5\text{ to }2 \times 10^4$, see Table 3), then with the cp in the range of $3\text{--}10\text{ mg/l}$ in Narragansett Bay, $k_1 (=k_1^* \cdot cp)$ should be in the range of $0.05\text{--}0.21\text{ day}^{-1}$, in agreement with the field data.

From the ^{230}Th profiles in the Atlantic Ocean, BACON and ANDERSON (1982) and NOZAKI *et al.* (1981) estimated k_1 for ^{230}Th in the range of $0.2\text{--}1.5\text{ yr}^{-1}$ and k_{-1} $1.3\text{--}6.3\text{ yr}^{-1}$. Using our k_1^* value for ^{230}Th in Table 3 and cp of $10\text{ mg}/10^3\text{ l}$ in deep Atlantic Ocean, we obtained $k_1 (=k_1^* \cdot cp)$ in the range of $0.77\text{--}1.5\text{ yr}^{-1}$, again in good agreement with the estimates by BACON and ANDERSON (1982) and NOZAKI *et al.* (1981). However, k_{-1} 's are different. BACON and ANDERSON (1982) find k_{-1} one tenth of the value presented here. There is no ready explanation yet.

Finally, ANDERSON *et al.* (1983) obtained the *in situ* $K_d(\text{Th})/K_d(\text{Pa})$ ratio of about 10 for sediment trap materials in a deep Pacific station. This value is exactly what we found in our adsorption experiments using the sediment trap materials collected in the North Atlantic, even though the absolute K_d values for Th and Pa in the field (ANDERSON *et al.*, 1983) are 10 to 20 times higher than our results (see Table 2).

We conclude then, that a surprisingly good agreement exists between kinetic constants derived from laboratory and field systems. The time constants for the equilibration of a dissolved element with particles are in the order of 1 to 10 days. They are thus of the same magnitude as that of the particle residence times of many natural waters. Typical settling velocities of natural suspended particles range from $0.1\text{ to }10\text{ m day}^{-1}$ (*e.g.*, BACON *et al.*, 1982; SANTSCHI *et al.*, 1979), resulting in particle residence times of a few days in shallow systems. In natural environments where particles do not reside long enough in water to fully equilibrate with trace metal, the transport of trace element by particles can become limited by the kinetics of partitioning.

4.0 SUMMARY

The time dependence of partitioning of radioactive trace elements between seawater and freshly collected

particulate matter from top layer sediments and sediment traps was determined using a suspension technique in batch process. In order not to change natural conditions, spike additions were kept minimal. The particle concentrations were between $27.5\text{ to }135\text{ mg/l}$. The experiments were carried out at 2°C and in the dark. At predetermined times, the solutions were filtered and the distribution ratios K_d determined. For the elements Na, Zn, Se, Sr, Ag, Cd, Sn, Sb, Cs, Ba, Hg, Th and Pa (group I) a constant distribution was found after a few days of equilibration, whereas the elements Be, Mn, Co and Fe (group II) showed an increasing distribution over the whole time of observation (108 days).

For the group I elements the time dependence of partitioning is described by an equilibrium adsorption-desorption reaction [$X + S(\text{ite}) \rightleftharpoons XS$]. The reaction rate constants $k_1 = k_1^*[S] = k_1^*cp\{S\}$ and k_{-1} were obtained by curve fitting of $K_d(t)$. As in our experiments $\{S\}$ is almost constant, k_1 depends primarily on cp . For comparison the adsorption rate constants are presented as $k_1^* = k_1/cp$ and they varied over several orders of magnitude ($1\text{ to }1.5 \times 10^5\text{ l} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$). By contrast, the obtained desorption rate constants k_{-1} varied only over one order of magnitude ($0.1\text{ to }2\text{ d}^{-1}$). The equilibrium distribution ratios of the cations Hg, Be, Zn, Cd, Ba, Sr and Na are highly correlated with the corresponding first hydrolysis constant $*K_1$, as expected from the adsorption model of surface complex formation of cations with the oxygen of hydrous oxide surfaces (SCHINDLER, 1975).

For the description of the time dependence of the group II elements a consequent first order lattice reaction was postulated for the sorbed tracer in addition to the sorption equilibrium: $X + S \rightleftharpoons XS \rightarrow X'S$. Again, the reaction rate constants were obtained by curve fitting of $K_d(t)$. For Mn the range of the lattice reaction rate constant was found to be $.013 \leq k_2 \leq .048\text{ day}^{-1}$, and compares to a rate of Mn oxidation of $.02\text{ day}^{-1}$ found by SUNG (1981). From our experiments, it is not possible to separate adsorption reactions from effects of isotopic exchange on particle surfaces or coagulation reactions of radioactively tagged colloidal matter onto particle surfaces. Our sorption kinetics described in these experiments comprise therefore all those possibilities.

The K_d values determined in laboratory experiments could be compared to those determined in the controlled ecosystem study (AMDURER, 1983) for equilibration times of 5 days (mean particle residence time). An agreement within 25% was found for the elements Mn, Fe, Co, Zn, Sn, Cs and Hg. The adsorption rate constant for Th measured in our laboratory experiments are in good agreement to the rates determined by *in situ* measurements of the U/Th disequilibrium (NOZAKI *et al.*, 1981, BACON and ANDERSON, 1982, SANTSCHI *et al.*, 1979).

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