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Relative mobility of radioactive trace elements across the sediment-water interface in the MERL model ecosystems of Narragansett Bay

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ABSTRACT

The "mobilities" of radioactive trace elements across the water sediment boundary of a coastal marine ecosystem were investigated. The studies carried out included chemical speciation experiments of the solution and solid phases, as well as verification experiments in controlled model ecosystems ("MERL" tanks). The latter included backdiffusion experiments under oxic and anoxic conditions and experiments with artificially increased sediment resuspension rates. These studies have produced seven general conclusions:

(1) The backdiffusion of Cs, Mn, Co, and Zn radiotracers across the sediment-water interface into oxic waters and of Mn and Co radiotracers into anoxic waters was predicted from laboratory experiments. (2) The removal from the water and the partial immobilization in the sediments of Cs, Zn and Cd tracers, during anoxic conditions, agreed with results from selective leaching experiments of surface sediments with dithionite-citrate solution, a mildly reducing agent which can reprecipitate liberated metals as sulfides. While most nuclides were leached by this solution to the same extent as by hydroxylamine, another reducing agent, Zn, Cd and Cs tracers were not, possibly due to the formation of sulfidic and other phases by the former solution. (3) Radioisotopes of particle-reactive elements (Sn, Fe, Hg and Cr) were shown by sequential extraction and ultrafiltration experiments to be involved in the dynamic cycle of colloid formation and aggregation in the water column and sediments. (4) In order to extend the information on nuclide behavior gained from the radiotracer methodology to stable trace elements, (which are often introduced into coastal water in ionic form) stable metals were added to one tank. Radiotracer behavior in the water column (removal rates and extent of uptake by suspended particles) was quite similar to that of their stable metal counterparts at ambient concentrations (Mn, Cr, Fe, Cd and Zn), added simultaneously to one tank, and to the metal behavior in other tanks operating under similar conditions. (5) The experiments with increased

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resuspension rates without concomitant increased bioturbation rates had, as expected, only small effects on removal rates of the radiotracers. (6) Sediment profiles of the tracers revealed both seasonal and element-specific differences in mobility near the sediment interface. Tracer profiles allowed the calculation of bioturbation (tracer microspheres) and pore water diffusion (^{22}Na) rates, as well as an investigation of the spacial and temporal dynamics of trace element cycling near the sediment-water interface. (7) Se and Cr nuclides which were added in different oxidation states to different tanks, showed that the higher oxidation state forms (Se-VI, Cr-VI) are removed more slowly from the water column than the lower oxidation state forms (Se-IV, Cr-III). Furthermore, speciation experiments have shown that the increase in the colloidal fraction of Se may be used to calculate the characteristic times of Se-reduction to elemental or organically-bound forms.

1. Introduction

Many studies in the past decades have investigated the environmental fate of trace elements (or compounds) in aquatic environments. However, very few studies have taken a holistic approach, that is, simultaneously studying the interrelated physical, chemical, sedimentological and biological factors which control the fate of the elements in question. This approach is feasible and most fruitful in controlled ecosystems (model ecosystems, microcosms or mesocosms). Controlled ecosystems have been successfully used in the past to study the rates and routes of transport and transformation of contaminants in various environmental reservoirs (e.g., water, sediments, biota). The MERL mesocosms of the Marine Ecosystems Research Laboratory in Narragansett, R.I., have established a credible record of replicating most of the critical physical, chemical, sedimentological and biological processes occurring in adjacent Narragansett Bay (see below). They are, therefore, ideally suited as test systems for studying the fate of trace elements under different but controlled environmental conditions. In this paper, we describe experiments testing the applicability of empirical chemical speciation techniques (sequential chemical extraction) for trace elements in the water and sediments as a tool for predicting: (1) their mobility across the sediment-water interface and (2) the potential for release of these trace elements to the water column from contaminated sediments. Of great interest are the mechanisms leading to the release of trace contaminants from sediments under oxic or anoxic conditions, and under more turbulent (i.e. storm) conditions. As our information about transport and transformation rates in controlled ecosystems is mostly gained from radiotracer additions to these systems, it was also important to compare radioactive and stable element pathways in order to better relate them to each other.

Coastal areas are usually the sites of high energy inputs, in physical form as tides or storms, and in chemical form as large supplies of nutrients. Unfortunately, they are often also the sites of heavy hydrocarbon and trace metal pollutant inputs. Large nutrient fluxes can lead to increased primary production rates, which stimulate benthic activity. These, in turn, lead to greater particle fluxes brought about by higher resuspension rates of surface sediments. The increased rates of sediment resuspension

are due in part to the greater erodibility of surface sediments, caused by bioturbational activities of the macrobenthic communities (Rhoads *et al.,* 1978). Therefore, large nutrient fluxes can indirectly increase the resuspension rates of surface sediments; this is in addition to the actions of storms and tides. A critical aspect is the coupled nature of these processes.

Higher organic carbon fluxes can also lead to temporarily anoxic conditions in deeper basins with restricted circulation. The effects of these changing conditions on the cycling of trace elements in coastal waters are not clear. Based on observations in the field and in experimental systems, increased removal rates from the water column (e.g., Santschi *et al.,* 1980a, 1982, 1983a) as well as increased remobilization rates from sediments (e.g., Oviatt *et al.,* 1981b) have been predicted as the primary effects of high sediment resuspension regimes. Anoxic conditions in bottom waters and sediments, too, can lead to either remobilization or increased removal, depending on the trace element (e.g. Emerson *et al.,* 1983; Jacobs and Emerson, 1982).

In order to investigate these interrelated processes, we tested, on an ecosystem level, the potential for release of trace elements from sediments and the mechanisms and rates of their release. The experiments also allowed comparison of the ecosystem results with predictions of tracer mobility based on laboratory extraction and leaching experiments. Our approach consisted of (1) sequential extraction (or leaching) techniques on water, suspended particle and sediment samples to study the chemical forms of the radiotracers: knowing the speciation will assist in predicting the potential for mobilization of radioactive trace elements under different environmental conditions in coastal areas; (2) the comparison of the vertical distribution of radiotracers in the sediments to those of inert plastic particles, and the measurement of radiotracer activities in the pore waters; (3) tracer backdiffusion experiments carried out in the MERL tanks under oxic and anoxic conditions, and with normal and high sediment resuspension rates, the latter generated by increased turbulence of the overlying water; (4) whenever possible, measurements of stable metals at natural or elevated concentrations through spike inputs helped to relate the results of the radioactive species to the behavior of the stable elements. In addition, the degree of equilibration of radioactive and stable trace metals in sediment and pore water reservoirs was investigated. We report here the results of unpublished experiments conducted in 3 MERL tanks during 1982 (tanks MO, MQ and MP), and of some earlier experiments conducted in 1979 (tanks ME, MH and MJ: Adler, 1981; Amdurer, 1983). As some interpretations of the new data rest on earlier observations made in these systems, we refer the reader to earlier publications whenever appropriate.

2. Experimental methods

a. MERL tanks

The MERL tank mesocosms, constructed of fiberglass reinforced polyester with 5 cm of polyurethane foam insulation, are 5.5 m high and 1.8 m in diameter. They

contain 13.2 m^3 of water from adjacent Narragansett Bay and a 30 cm deep layer of relatively undisturbed silty clay sediments also from Narragansett Bay. Seawater is delivered to the mesocosms through diaphragm pumps which are nondestructive to planktonic organisms, giving water in the tanks a 27-day residence time, similar to that of water in the bay itself. Alternatively, the mesocosms may be run as a closed (batch) system. To facilitate mass balance, most radiotracer experiments were run in the batch mode. Previous studies have shown that a batch experiment can continue for at least seven months with no appreciable chemical and biological divergence from flow-through conditions (Pilson *et al.*, 1980b).

The mesocosms are exposed to natural light and temperature variations. The light profile is similar to that of Narragansett Bay (Nixon *et al.*, 1980). The mesocosms' water columns receive sufficient sunlight to support phytoplankton primary production rates and standing crops close to those in the bay. The tanks are deep enough, however, to ensure that the benthos receive ≤1% of surface illumination, keeping the benthic biota heterotrophic (Pilson *et al.*, 1980b, Nixon *et al.*, 1980). Water temperatures in the insulated tanks seldom differ by more than ±2°C from the ambient bay temperature. However, the tank water may be heated or cooled with a heat exchange system, and the tanks may be operated at a constant temperature differential or with a vertical temperature gradient to simulate stratified conditions.

The water columns in the tanks are mixed by plungers which move in a vertical orbit on a 2 hour on, 4 hour off cycle to simulate the tidal currents, turbulence and sediment resuspension rates of Narragansett Bay; the settling of resuspended particles is allowed. The tanks are well mixed by this system within 15 minutes of the start of mixing (Nixon *et al.*, 1980).

There were several critical advances in the experimental design which greatly contributed to the successes of the MERL mesocosms: The ability to: (i) emplace natural sediments in an undisturbed condition; (ii) introduce unaltered plankton with the inflowing water into the tanks; (iii) control wall fouling by rotary brushes; (iv) control temperature; (v) simulate turbulence and tidal action by a rotating plunger which also creates appropriate levels of resuspended sediments; (vi) properly sample all major species, reservoirs, and fluxes; and (vii), carry out long term studies of 2 years or more.

Inter- and intra-tank replicability has been described by Adler *et al.* (1980), Oviatt *et al.* (1980) and Smith *et al.* (1982). It has also been shown that the gross features of the MERL tanks' biological community (abundance, species composition, seasonal cycles of succession), the nutrient fluxes (N, P and Si), sediment respiration (O$_2$ uptake), sediment mixing and bioturbation depth, sediment resuspension rates and thorium removal rates are typical for those observed in the bay (Pilson *et al.*, 1980a,b; Oviatt *et al.*, 1981a; Elmgren *et al.*, 1980, Elmgren and Frithsen, 1982; Santschi *et al.*, 1980a, 1982). A recent review of the pertinent literature on MERL experiments can be found in Santschi (1985).

Table 1. Stable metal additions to tank MP.

Element	Background Conc. (μMol/l)	Spike addition form	μMol/l	Spiked conc. (multiples of background conc.)
Mn	~0.1	$MnCl_2$	1.13	10
Cr	~0.03	$CrCl_3$	0.29	10
Fe	~0.01	$FeCl_3$	1.40	10^2
Cd	~0.01	$CdCl_2$	0.06	10
Zn	~0.10	$ZnCl_2$	0.16	10^0

b. Tracer experiments

Mesocosm operation. A series of radiotracer experiments were conducted in the MERL tank ecosystems in order to study the mechanisms and degree of trace metal removal to, and remobilization from, oxic or anoxic sediments. The water columns of three tanks (MO, MQ and MP) were spiked on April 15, 1982, with an acid-stabilized mixture of gamma-emitting radionuclides in ionic form. These isotopes included $^{113}Sn(IV)$, $^{59}Fe(III)$, $^{54}Mn(II)$, $^{60}Co(II)$, $^{51}Cr(III)$, $^{65}Zn(II)$, $^{22}Na(I)$ and $^{134}Cs(I)$ nuclides, and ^{141}Ce as inert tracer microspheres (plastic particles of 15 μm diameter). In addition, $^{109}Cd(II)$ was added to tank MO and MP, and $^{75}Se(VI)$ and $^{75}Se(IV)$ were added to tanks MO, and MP, respectively, to examine the effect of oxidation state on the behavior of this element.

Tank MP received the stable metal additions listed in Table 1. The potential toxic effects of these additions to organisms were not tested but were inferred to be minimal from the nutrient, O_2, plankton biomass and particle measurements as no significant differences were evident in biological productivity. However, observations by Hunt (pers. communication) who had added similar levels of trace metals to other MERL tanks, indicated possible adverse effects on bacterioplankton.

Tank MQ was stirred before the start of the experiment at more than twice the normal rate to loosen up the surface sediment. Various stirring rates were then tested and a rate of 8 rpm was selected to give a sediment flux rate of ~9 mg cm^{-2} day^{-1} in tank MQ which is close to the summer rates in the bay. This is in comparison to flux rates of 0.2–1 mg cm^{-2} day^{-1} in tanks MO and MP which are typical of winter conditions in Narragansett Bay.

The experiments thus consisted of a radioactive and stable metal spiked tank (MP), a tank with higher ("summer") sediment resuspension rates (MQ), and a control tank (MO). In order to prolong winter conditions, the mesocosm water columns were cooled by heat exchangers as ambient temperatures increased during the spring–summer months.

Samples of water, suspended and settling particles, sediments, plankton, benthic fauna and wall material were collected and gamma-counted on a Ge(Li) detector, coupled to a 4096 channel analyzer and a computer. Activities were all normalized to

the same geometry (using standards of the same nuclide) and decay-corrected to the beginning of the experiment (Amdurer *et al.,* 1982, 1983, Santschi *et al.,* 1982, 1983b). Removal rates of radiotracers from the water to the sediments were followed over 55 days. At this time, the overlying water of tank MO was changed in order to monitor the release of the tracers from the oxic sediments to the overlying water. After 110 days from the initial spike (and 55 days from the water change), 90% of the overlying water was drained and the remaining 10% of the water of tank MO was sealed airtight to cause the system to become anoxic. Concentrations of tracers, nutrients and oxygen were then monitored for another 30 days. Stable metal analysis on unfiltered water samples was carried out using graphite furnace AAS techniques as described in Hunt and Smith (1983) and Santschi *et al.* (1984).

In addition to the results of the MO-MP-MQ experiments, some unpublished results from previous experiments are included in this paper. These experiments include tanks ME (Jan. 23–April 9, 1979), MJ (Aug. 11–Nov. 5, 1979) and MH (Aug. 11–Nov. 1, 1979), operated in a batch mode. The additional isotopes used in these tanks were ^{7}Be(II), ^{231}Pa(V), ^{125}Sb(III), ^{74}As(V), ^{48}V(III) and ^{133}Ba(II).

Chemical speciation. The experimental techniques for studying the various chemical forms of the radiotracers are described in more detail in Adler *et al.,* 1980, Amdurer *et al.,* 1982, 1983, and Amdurer, 1983. In short, water samples were chemically fractionated using various columns containing resins (Chelex-100, Amberlite IRA-938, XAD-2) or activated coconut charcoal, after filtering through 0.45 μm Nucleopore filters. In addition, other water samples were sequentially fractionated using Amicon (model 52) stirred ultrafiltration cells with membrane filters with nominal molecular weight cut-offs of 10^5, 10^4 and 10^3 amu to study the colloidal associations of the radiotracers.

An extensive series of leaching experiments was performed on surface sediment (0–3 cm) from tank MJ (summer 1979), collected 9 months after the tank was spiked (i.e. spring 1980; this time period is similar to that which pollutants might have for equilibration in sediment which underwent seasonal changes in redox potential, bioturbational intensity etc.). Stable Mn, Fe, and Zn were measured on some of the leachates using flame AAS techniques in order to compare with corresponding radiotracer results and calculate specific activities. The methods are described in Amdurer (1983); Hunt and Smith (1983), and Santschi *et al.* (1984).

After surveying the literature on leaching procedures (e.g. Gibbs, 1977; Nissenbaum 1972; Tessler *et al.,* 1979) and performing tests of our own (Amdurer, 1983), the following sequential scheme was selected:

(1) Oxic seawater (releases weakly-bound ions),

(2) 1 N Mg Cl$_2$ (releases ions from ion exchange sites),

(3) 1 N hydroxylamine · HCl in 25% acetic acid (dissolves carbonates and leaches Fe and Mn oxides), or in sodium dithionite-sodium citrate at pH 7 with NaHCO₃ buffer (leaves organic compounds intact but may reprecipitate liberated metals as sulfides).

(4) 30% H_2O_2 (oxidizes organics and sulfides, but also leaches some Fe and Mn oxides),

(5) 0.5 N HCl (leaches some sulfides, organics and clays),

(6) 4 N HCl or HNO₃ for "total" elements, and

(7) residual radiotracer activity in sediments.

In some additional experiments, pH 7 buffered sodium dithionite-citrate solution was substituted for hydroxylamine · HCl, and H_2O_2 was sometimes placed before the hydroxylamine · HCl leaching step. A duplicate leach of another sediment sample was done to check the replicability, and parallel (rather than sequential) leaches were carried out using each of the leaching solutions as well as acetic acid and 0.5 N HCl for various time periods (Amdurer, 1983).

Preweighed sediment samples (0.4–1 g of sediment) were placed in polycarbonate centrifuge tubes, 10–20 ml of the appropriate leaching solutions added, and the sample was shaken using a wrist-action shaker (unless otherwise stated, each leach lasted for 1–3 days) (Amdurer, 1983). The sample was then centrifuged and filtered, the supernate removed by pipetting, and the next leaching solution added. Empty centrifuge tubes were also gamma-counted to check for wall adsorption. An average of only 2–3% of Cd, 1–2% of Zn and Be, and ≤1% of all other radiotracers were found on the tube walls.

In an earlier experiment in tank MJ (summer 1979), 10 cores, among them core MJC-390 (12 cm long) were taken by hand during draindown (90 days after the spike). Core MJC-390 was sliced in a glove box under an N_2 atmosphere. Pore water was extracted from each slice by centrifugation and both the solid residue and the pore water were gamma-counted, and analyzed for selected stable trace metals (e.g., Mn). These analyses allowed for the calculation of *in situ* distribution coefficients as a function of depth, and an estimate of the degree of equilibration of radiotracers with the stable metal (Adler, 1981). Various other sediment cores were also taken during earlier experiments to monitor radiotracer penetration into the sediments and sediment inventories of the tracers. Cores MJC270 and MEC180 were taken during experiment MJ (summer 1979) and ME (winter 1979), 47 and 44 days after the initial spike addition, respectively. These cores were immediately sliced into 3 mm sections and gamma-counted. Further details of the procedures and descriptions of these sediment cores can be found in Adler (1981).

Table 2. Chemical speciation* (as %).

Isotope	Tank	Filter (≥0.45μ)	Charcoal	Chelex	Amberlite	Effluent	XM100 (MW ≥ 1E5)	UM10 (1E5 ≥ MW ≥ 1E4)	UM2 (1E4 ≥ MW ≥ 1E3)	Effluent (MW ≤ 1E3)
								Amicon ultrafiltration		
^{59}Fe(III)	MO	65-100	20-1	1-0	10-0	5-0	25-20	1	2	≤1
	MP	65-97	15-1	1-0	7-0	5-0	5	≤1	≤1	≤1
	MJ	15	40-30	5	10	20-0	80	1	1	1
^{113}Sn(IV)	MO	25-30	30-40	10-2	20-2	5-25	5-35	1-20	8-5	40-0
	MP	60-90	20-5	5-1	8-1	5-1	3	1	1	10-5
	MJ	25-50	40-10	20	8	10	50-70	5	10-1	20-2
^{203}Hg(II)	MO	55-20	30-10	5	10-5	5-60	35-20	1-10	3-5	3-50
	MP	60-70	20-10	2	5	5-10	10-20	1	1	3
	MJ	30	60	2-1	10-15	10-0	70	1	20-1	3
^{233}Pa(V)	MJ	10-100	50-0	5-0	20-0	20-0	65-40	5-0	1-0	20-40
^{7}Be(II)	MJ	1-7	90-65	5-0	1-2	5-30	5-10	3	2	90-85
^{51}Cr(III)	MO	30-3	15-65	20-1	5-0	25-70	10-0	1	5-0	40-95
	MP	65-75	15-5	5-1	5-1	5-10	5	≤1	≤1	3
	MJ	35-0	40-25	0	10	15-80	60-40	2-3	5-0	0-40
^{54}Mn(II)	MO	15-10	5	80-85	≤1	≤1	≤1	≤1	1	≤1
	MP	5-30	5	90-65	≤1	≤1	≤1	≤1	≤1	≤1
	MJ	5-20	2	95-80	0	0	2	0	0	95

Table 1. (Continued)

Element	Fraction									
60Co(II)	MO	3	60	35	3	≤1	≤1	≤1-2	3-1	≤1
	MP	1-3	50	45	3	≤1	≤1	≤1	1	≤1
	MJ	1-5	15-20	80-70	0	0	0	2-5	0	95
65Zn(II)	MO	1-2	85-75	13-20	≤1	1-2	≤1	≤1	3-1	95-85
	MP	3-5	75-65	15-30	1	1	≤1	≤1	≤1	95
	MJ	2	40	60	0	0	1	1	5-0	90-98
109Cd(II)	MO	≤1	85	15	≤1	≤1	≤1	1	≤1	99
	MP	≤1	85-70	15-30	≤1	≤1	≤1	1	≤1	99
	MJ	≤1	40	60	0	2-0				
75Se(VI)	MO	1	0-3	1	1	99-96	1	≤1	2-1	98
75Se(IV)	MP	2-10	2-25	1	≤1	95-65	≤1	≤1	≤1	98-90
	MH	3-20	5-65	2	≤1	90-15	10-5	10	15-20	40
74As(V)	MH	1-3	5-15	1	≤1	95-80	≤1	2	20-30	80
48V(III)	MC	0-2	15-20	70-80	≤1	15-0	—	—	—	—
125Sb(III)	ME	≤1	1	1	≤1	98	—	—	—	—
133Ba(II)	MH	≤1-20	3	3	0	95-80	0	1	5	95
134Cs(I)	MO	≤1	0-1	1	1	99	≤1	≤1	≤1	99
	MP	≤1	≤1	≤1	≤1	99	≤1	≤1	≤1	99
	MJ	≤1	≤1	≤1	≤1	99	≤1	≤1	≤1	99

*In most cases, there is a clear time trend in the partitioning into the above-mentioned fractions from day 1 to day 32. (i.e. continuous increase or decrease). We have therefore chosen to report only the partitioning on day 1 (first value) and day 32 (second value). Charcoal adsorbs nonpolar, high molecular weight organic colloids, chelex ionic, inorganic forms of transition metals, Amberlite IRA-938 mostly inorganic colloids, XAD-2 (not shown here) mostly organic colloids. For a further discussion of the different fractions, see text.

3. Results and discussion

a. Chemical forms of radiotracers in the water column and in the sediments: tests of the potential for release and/or remobilization

Chemical speciation. The results of the chemical speciation experiments (Table 2) indicate that, in the water column, elements can be partitioned into several empirically defined fractions, including particulate, ultrafilterable ($\geq 10^5$, 10^4 or 10^3 amu), or extractable by different resins or activated charcoal. The interpretation of these various fractions is facilitated by the differential sorption behavior of the tracers on the various resin and charcoal columns: *Activated charcoal* is known to adsorb nonpolar, high-molecular weight organics and colloids of different kinds; *Chelex-100* adsorbs mostly the inorganic forms of ionic species of transition metals; while *Amberlite IRA-938* resin, which is a basic, macroreticular anion exchange resin with a mean pore size of 7×10^4 Å, is particularly suited for adsorption of mostly inorganic colloids such as colloidal silica or hydrous metal oxides or hydroxides. Occasionally, we also used *XAD-2* resin to adsorb radiotracers from seawater samples acidified to pH 2. This resin consists of inert, 0.3–0.4 mm diameter beads of nonionic macroreticular (porous) copolymer, prepared by polymerization of styrene and acrylic esters. It has been shown to adsorb from seawater $\geq 90\%$ of the terrestrial and marine humic matter occurring in the colloidal size class (e.g. Stuermer and Harvey, 1977). In general, the nonpolar resin XAD-2 is highly selective for aromatic compounds, particularly in polar solvents such as water, but it is a very poor adsorbent for polar organic compounds such as phenols, carbohydrates, proteins and amino acids (Ram and Morris, 1982). Riley and Taylor (1968) reported that these resins adsorb no inorganic cations or anions, while Mackay (1982) found that they may adsorb very small amounts of some cations. We used both XAD and Amberlite resins in series after the water passed a 0.45 μ nucleopore filter and charcoal and chelex columns in order to identify the nonfilterable ($< 0.45 \mu$) colloids.

The combined use of Amberlite IRA-938 (ambient pH) and XAD-2 (pH 2) resins offers a means to differentiate between them. Because of their surface charge characteristics at different pH, we realize, however, that often hydrous oxides are covered by organic films composed of humic and fulvic acids, and the distinction can become blurred. A reversal of the sequence charcoal-chelex revealed that uncharged species extracted by charcoal can also be retained by chelex resin (Amdurer *et al.*, 1983). In addition, the ultrafiltration results should be considered as order-of-magnitude only, since it has been shown that ultrafilters do not always separate molecules of known sizes correctly (for a review, see Amdurer, 1983; Amdurer *et al.*, 1983).

In accordance with Amdurer *et al.* (1983), we interpret the fraction retained by charcoal as indicative of an inorganic or organic colloidal fraction. Table 2 does not include the results of the XAD-2 extractions, which showed that only Hg(II) isotopes
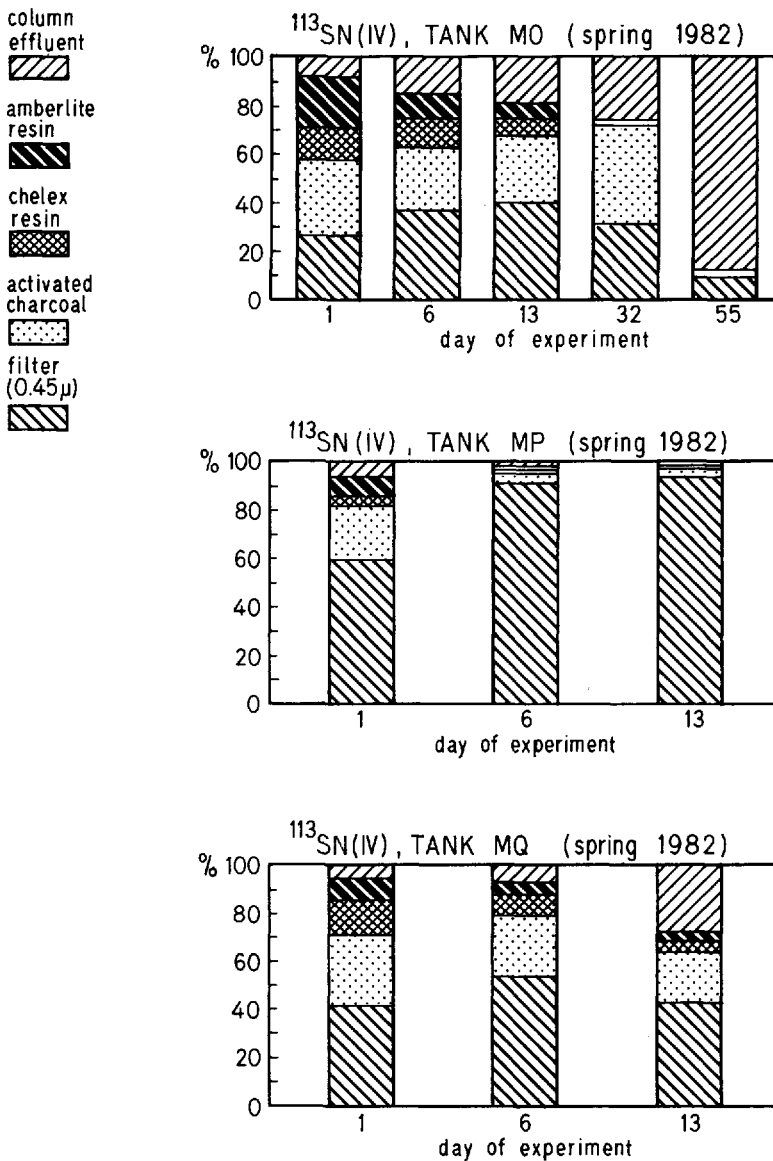
Figure 1. (a) Chemical speciation of ^{113}Sn which shows the typical partitioning for a "particle-reactive" element, in tanks MO, MP, MQ (spring), (b) ME (winter) and MJ (summer). Amberlite resin was used only on days 0, 1, 3, 11 in tank MJ, and not at all in tank ME; (c) chemical speciation of ^{75}Se(IV) in tank MP and of ^{75}SE(VI) in tank MO.

Figure 1. (Continued)
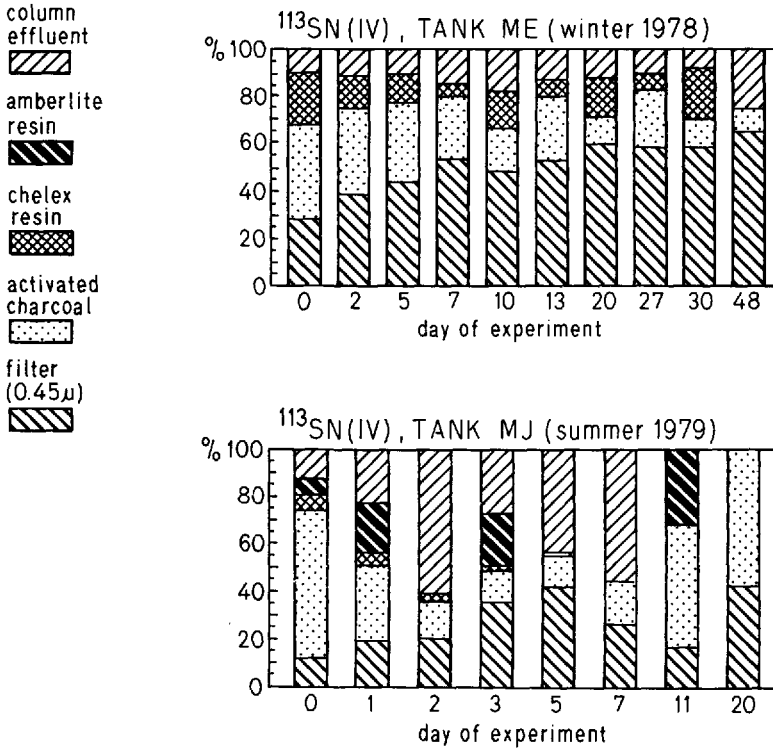
(30–50% of the soluble fraction) and Se(IV) (30% of the soluble fraction) were significantly retained by this resin (Amdurer *et al.*, 1983). Since these isotopes were also retained by charcoal by about the same amount, but were not significantly adsorbed by Amberlite IRA-938 resin, this suggests an organic nature of these Se colloids. We also do not show here the results from tank MQ, as they were very similar to those from tank MO. However, we included data from previous experiments for comparison purposes [i.e., tanks ME and MH for ^{74}As(V), ^{48}V(III) ^{125}Sb(III), ^{133}Ba(II) and ^{7}Be(II) (Amdurer *et al.*, 1983)].

Based on the results presented in Table 2, we can make the following qualified generalizations: The alkaline (e.g. Na$^+$, Cs$^+$) and alkaline earth ions (e.g. Ba^{+2}) in the effluent fraction from filtration as well as Mn(II), Co(II), Zn(II) and Cd(II) in chelex fractions, predominantly appear in cationic (or in neutral, labile, complexed) forms, the charcoal fraction of Co, Zn, and Cd may represent neutral complexes, while the major species of Se(VI), Cr(VI) and Sb(III) are nonadsorbing, negatively or neutrally charged species. Significant fractions (i.e. >50%) of Fe, Sn, Hg, Pa and Cr isotopes are attached to particulate ($\geq$0.45 μm) and colloidal matter ($\leq$0.45 μm). In the $\leq$0.45 μm fraction about 60% of Hg(II) and 30–60% of Se(IV) (increasing in time) are observed
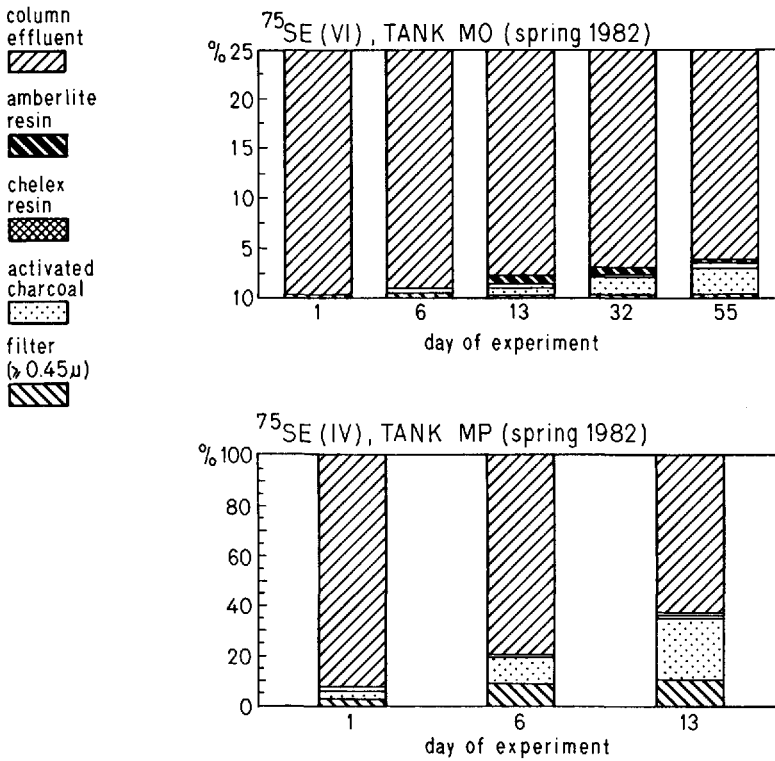
Figure 1. (Continued)

as high and low molecular weight organic colloidal forms, 2–20% of Se(VI), As(V) and Zn(II) in both low molecular weight and high molecular forms (40–60% found in charcoal fraction) and 10–70% of Sn(IV), Pa(V) and Fe(III) as high molecular weight inorganic forms (probably bound to iron or manganese oxyhydroxides). The distinction between organic and inorganic colloids was made by assuming that XAD-2 resin adsorbs mostly organic colloids (which are hydrophobic at pH 2), while Amberlite IRA-938 resin adsorbs mostly inorganic colloids. The total of these two fractions should correspond approximately to the charcoal fraction. The molecular weight distribution is assumed to be represented by the ultrafiltration fractions.

The colloidal fraction of Sn, Hg and Fe nuclides (charcoal, amberlite resin, and ultrafiltered colloids) often decreased in time in the first weeks of the experiment (see Fig. 1) while the particulate fraction increased (Amdurer *et al.*, 1983) suggesting transfer from the colloid to the particulate pool. When first introduced to the water column, radiotracers might rapidly attach to the colloidal oxidation products of the reduced forms of iron, possibly associated with organic matter. Over a time scale of days to weeks, the colloids containing these radiotracers have been shown to be scavenged onto larger particles (Amdurer *et al.*, 1983; Nyffeler *et al.*, 1984, 1986).

Table 3a. Percentage in each sequentially leached fraction, with the normal sequence of extractions (Experiment A). The residual fraction is found by difference to 100% from Σ (1)–(5).

Experiment A:

Isotope	Exchangeable by		(3) Reducible by 1N Hydroxylamine·HCl	(4) Oxidizable by 30% H_2O_2	(5) Acid extractable by 0.5 N HCl	Σ(1)–(5)
	(1) Seawater	(2) 1N $MgCl_2$				
^{59}Fe	≤1	≤1	95	5	≤1	100
^{113}Sn	≤1	≤1	20	5	30	55
^{233}Pa	≤1	≤1	10	15	5	30
^{7}Be	5	≤1	92	3	≤1	99
^{51}Cr	≤1	≤1	100	≤1	≤1	100
^{54}Mn	25-30	10-30	45	3	≤1	100
^{60}Co	5	5	45	40	5	100
^{203}Hg	≤1	≤1	60	35	5	100
^{65}Zn	1	2	95	5	≤1	100
^{109}Cd	3	5	92	≤1	≤1	100
^{134}Cs	10	2	70	10	2-8	94-100

Table 3b. Percentage in each sequentially leached fraction with order of leach (3) and (4) reversed (Experiment B) and using a different reducing agent for fraction (3) (Experiment C). Fractions (1) and (2) are the same as in Experiment A.

| | Experiment B: | | | Experiment C: | | | |
| | (3) Oxidizable by 30% H_2O_2 | (4) Reducible by 1N Hydroxylamine HCl | $\Sigma(1)-(5)$ | (3) Na-Dithonite-citrate | (4) Oxidizable by 30% H_2O_2 | (5) Acid extractable by 0.5 N HCl | $\Sigma(1)-(5)$ |
Isotope							
^{59}Fe	5	90	95	85	10	3	98
^{113}Sn	≤1	50	80	10	5	30	45
^{233}Pa	≤1	5	10	≤1	20	10	30
^{7}Be	5	85	100	55	40	5	95-100
^{51}Cr	70	30	100	90	10	≤1	100
^{54}Mn	40	5	100	40	3	≤1	100
^{60}Co	90	10	100	45	40	10	100
^{203}Hg	80	10	90	70	20	8	100
^{65}Zn	90	5	100	10	80	10	100
^{109}Cd	30	50	85	10	70	10	90
^{134}Cs	10	35	65	5	20	15	50

After 3–4 weeks into the experiment, the colloidal fractions of the particle-reactive isotopes often started to increase again, coinciding with a temperature increase in tank MO but not in tank MJ (see Fig. 1). This observation could indicate that particle disintegration is a considerably slower process than the settling of suspended and resuspended particles in the water column of this system (0.1–10 days for summer and winter seasons, respectively). These observations support our "colloid hypothesis" to explain the relatively slow radionuclide scavenging by particles (Nyffeler *et al.*, 1984, 1986, Li *et al.* 1984, and Santschi *et al.*, 1986).

Se(VI) in tank MO was removed more slowly than Se(IV) in tank MP. This difference in removal rates can be attributed to the difference in oxidative states. It is well known that Se(IV) sorbs readily to Fe oxyhydroxides, while the thermodynamically stable form of Se, Se(VI), is only weakly adsorbed to particulate matter (National Research Council, 1976). Further evidence can be found in the results of our chemical speciation experiments, which showed a significantly greater fraction of Se(IV) associated with particles of colloidal and noncolloidal nature than did Se(VI) (Table 2). The reduced forms of Se, SeO_3^{2-} and elemental (Se°) or organically bound forms (e.g. Se amino acids or peptides) have been identified in "regenerative" environments (i.e. environments where organic carbon is degraded rather than synthesized, Cutter and Bruland, 1984, Takayanagi and Wong, 1985).

We can calculate the time-scale for the reductive uptake, if we interpret the slow but steady increase of Se in the charcoal (or XAD extractable) fraction (which is also ultrafiltrable) in the experiments in tanks MO, MP and MH (Table 2, Fig. 1 and Amdurer, 1983) as a slow reductive uptake of Se (IV or VI) into the plankton biomass of the MERL tanks, followed by the relatively fast release as "dissolved" organically-bound or elemental Se (characteristic time of ≤5 days), then:

$$C = Co(1 - e^{-\lambda \Delta t})$$

with C = Charcoal fraction of 2.6% for Se(VI) and 15.8% for Se(IV), after $\Delta t = 55$ days for Se(VI) and 13 days for Se(IV), respectively, see Figure 1c.

Co = Charcoal fraction after $\Delta t = \infty$ days is assumed to be 100%.

λ = first order rate constant for reductive uptake of Se (= $1/\tau$)

Residence times (τ) of 54–76 days and ~2×10^3 days for the reductive uptake of SeO_3^{2-}, and SeO_4^{2-}, respectively, can be estimated for coastal marine environments. This is in accordance with results from Cutter and Bruland (1984).

b. *Association of tracers with sediments and suspended particles*

Although chemical leaching techniques for sediments have recently been criticized as giving biased results through uncontrolled reactions (e.g. Rendell *et al.*, 1980; Etcheber *et al.*, 1983; Jouanneau *et al.*, 1983; Sigg *et al.*, 1984), the results of our leaching experiments of the surface sediments did nonetheless give some nonambiguous results (Table 3). They indicate, for example, that a small but significant

fraction of Mn (30%), Co (5%), Cs (10%), Be (1–5%) and Cd (3%) isotopes are leachable by seawater alone, and are thus readily exchangeable. These fractions are of similar magnitude to those found in an experiment on the release of tracers from sediment trap material (see below). The (subsequent) 1 N $MgCl_2$ leach also released about the same amount as seawater alone. The dominant fraction for most isotopes is the reducible fraction, indicating that a large fraction of the radiotracers was associated with Fe and Mn oxide phases (Fe, Cd, Zn, Cr, Cs isotopes). The oxidizable fraction, representing mostly organic and sulfidic phases (for Co, Mn and Hg isotopes) and the residual fraction (for Sn and Pa isotopes) made up the major part of the remaining categories.

These results were checked by reversing the sequence of extraction, or by substituting Na-dithionite-citrate for hydroxylamine · HCl (see Table 3b), or by extracting sediments with each of the leaching solutions alone (rather than sequentially). It was found that H_2O_2 mobilizes most of the ^{54}Mn-tracers but very little tracer-^{59}Fe. This suggests a method of separating Fe and Mn oxide phases. Furthermore, the dithionite-citrate leach was as effective a reducing agent as hydroxylamine · HCl for most isotopes except Hg, Zn, Cd, Be and Cs. The latter isotopes might have been immobilized by the formation of sulfur-containing species formed by the disproportionation of dithionite (Tessler *et al.*, 1979). The 5–50% of the ^{134}Cs found in the residual fraction is not fully understood, but might represent Cs^+ which can exchange only with K^+ but not with H^+ in intrastitial sites of clay minerals. Sn, Hg, Pa and Cr nuclides were totally leachable only with 4 N HCl or HNO_3. The basic results remained, however, the same. The results reported in Table 3 thus indicate a considerable potential for release under changing physicochemical conditions.

Radioactive trace elements never fully equilibrated, however, with their stable counterparts in the sediments. A comparison of radioactive and stable element concentrations in each leach indicated that the ratio of the two was closest to that in the water for Zn followed by Mn, and furthest apart for Fe. (Amdurer *et al.*, 1983). While the radiotracers equilibrated fairly quickly with their stable elements in the water column (see later section), they needed, however, much longer time scales in the sediment reservoirs. As a consequence, radiotracers in the sediments are "transient tracers" not only from a physical point of view (bioturbation) but also from a chemical standpoint (isotopic exchange).

We also carried out some ancillary experiments to characterize the speciation of radiotracers attached to falling and suspended particles. To this end, we used either statistical analysis, or some simple leaching or size separation techniques. During plankton blooms, the tracer activities on particles ≥ 10 μm (28% organic carbon, mainly diatoms), which were separated by reverse flow concentration (Hinga *et al.*, 1979), were compared with those in the ≤ 10 μm fraction (only 8% organic carbon, consisting mostly of inorganic sediment particles, and some bacterio-plankton) during a very large diatom bloom in experiment ME (Amdurer, 1983). At the peak of the

bloom, at chlorophyll *a* concentration of up to 70 μg/l, 50–70% of the total particulate activity of Hg, Fe, Cr, Sn, Ba, Mn, Co, Zn, As and Sb were associated with these chain-forming diatoms. When the minimum estimated half-removal times for these elements via settling of planktonic material were compared to the actual half-removal times, it appeared that during conditions of extreme blooms removal by phytoplankton might account for $\geq$ 50% of the removal rate of Ba, Zn, Hg, Fe, Cr and Sn. In addition, during bloom conditions (tank ME, Feb. 1979; tank MH, summer 1979), a strong correlation could be observed between the particulate fraction of some nuclides (^{133}Ba and ^{74}As and possibly ^{65}Zn, but not of any other tracer) and chlorophyll *a* and thus with primary productivity, as these two measures are related (Oviatt *et al.*, 1984) ($r \geq 0.95$ ($P < 0.001$) for the first two isotopes, $r \geq 0.55$ ($P < 0.05$) for ^{65}Zn). However, since during most of the year chlorophyll *a* concentrations are between 1–2 orders of magnitude lower than during these extreme bloom conditions, transport of all radiotracers (except ^{138}Ba, ^{74}As and ^{65}Zn) via phytoplankton incorporation and settling under "normal" conditions accounts only for a small percentage of the observed removal rate (i.e. considerably less than 10%). Furthermore, radiotracer incorporation into zooplankton, as well as transfer to sediments via fecal pellets, has been shown to be insignificant during winter, spring and summer conditions (Adler, 1981; Amdurer, 1983; Santschi *et al.*, 1983a). The reason for this is that the removal rates by the coupled process of sediment resuspension and sediment mixing (Santschi *et al.*, 1980b, 1984, Nyffeler *et al.*, 1986) is much more efficient and therefore faster in these coastal marine environments.

In a separate experiment, we investigated what fraction of the radiotracers associated with falling particles caught in sediment traps was released to seawater within 1–2 days. This was accomplished by returning sediment traps, from which the overlying water was exchanged with fresh (unspiked) seawater, to the water column in a closed position in tank MJ (summer 1979, temperature 22°C). These experiments revealed that significant fractions of some tracers can be released to the water from falling particles. This may be caused to some extent by ion exchange from inorganic particles, but probably mainly by cell lysis or bacterial degradation of plankton. Significant amounts of tracers (15–22% of ^{65}Zn, 7–15% of ^{54}Mn, 9–12% of ^{60}Co, 1.5% of ^{59}Fe and 0.4% of ^{203}Hg per day) were released (this assumes that over the experimental time scale of 28–42 hours, tracers were released at a constant rate). These results indicate that the most labile isotopes associated with suspended particles are those of Zn, Mn and Co. The release rates of Mn and Co from sediment trap material are similar to those of plankton debris observed by Collier and Edmond (1984).

From these sequential and individual leaching experiments we would predict that exchangeable and reducible fractions of isotopes would be able to diffuse out of the surface sediments into the overlying water column under oxic and anoxic conditions, respectively. If anoxia were to proceed to the degree of sulfate reduction, then we

would expect the retention in the sediments of those elements which form sulfidic phases (e.g., Fe, Cd, Hg and Zn).

c. Radiotracer mobility in surface sediments

A comparison of the profiles showing penetration of the tracers into the sediments (Fig. 2) reveals quite different shapes for the different elements. Mid-depth maxima are common and indicate random biological mixing events of pore water and of particles in biological conduits (e.g., burrows and worm tubes). Similar transient peaks have been observed by others for different tracers or chemical species (e.g. Grundmanis and Murray, 1977; Robbins *et al.*, 1979). We can identify particle pathways by the movements of tracer microspheres, and those of pore waters by the movement of ^{22}Na. Since many of the profile shapes reflect the effects of macrobenthic organisms, exact replication in the measured profiles among different sediment cores cannot be expected. However, there are significant seasonal differences above this "noise" between cores. One typical example each from about 10 down-core profiles for the winter (ME) and summer (MJ) experiments is shown in Figure 2. Sediments from both experiments were exposed to the spiked seawater for approximately the same length of time (i.e. ~44–47 days). Moreover, both cores had close to 100% inventory for all the particle-reactive tracers.

The differences between these cores are both seasonal and element specific. The seasonal differences can be exemplified by the tracers which associate with particles to at least a moderate degree. "Tracer microspheres" of 15 μm size track particle mixing events and, when the profiles are fit to a transport model, they yield particle mixing rates. These tracer microspheres clearly penetrate to greater depths in the summer months, indicating higher rates of particle mixing by benthic macrofauna than in winter.

Some isotopes exhibit profiles identical to those of the microspheres (i.e. Sn, Hg, Cr, Pa and Be) while others appear smoother (i.e. Fe, Mn, Co, Zn, Ba, Sb, Na, Cs and Cd). In addition, the subsurface peaks in particle-associated tracers are less defined in the summer, reflecting the homogenizing effects of a greater number of mixing events within the same time span.

Radiotracers not only help to identify, but also to quantify the processes responsible for trace element mobility. Particle mobility can be quantified by the profiles of the tracer microspheres, while pore water mobility can be evaluated from the profiles of ^{22}Na. A comparison of a particular tracer profile with that of either of these end-member profiles will reveal additional localized chemical mobility. A quantitative treatment of all cores during summer or winter experiments, using a numerical removal and mixing model with equilibrium assumptions, produced the following bioturbation (particle mixing) rate constants (D_B) (Adler, 1981):

Average D_B values for the tracer microspheres (15 μm diameter) were $1.1 \pm 0.36 \times 10^{-7}\,\text{cm}^2\,\text{sec}^{-1}$ in winter and $4.0 \pm 0.8 \times 10^{-7}\,\text{cm}^2\,\text{sec}^{-1}$ in summer. The values for the
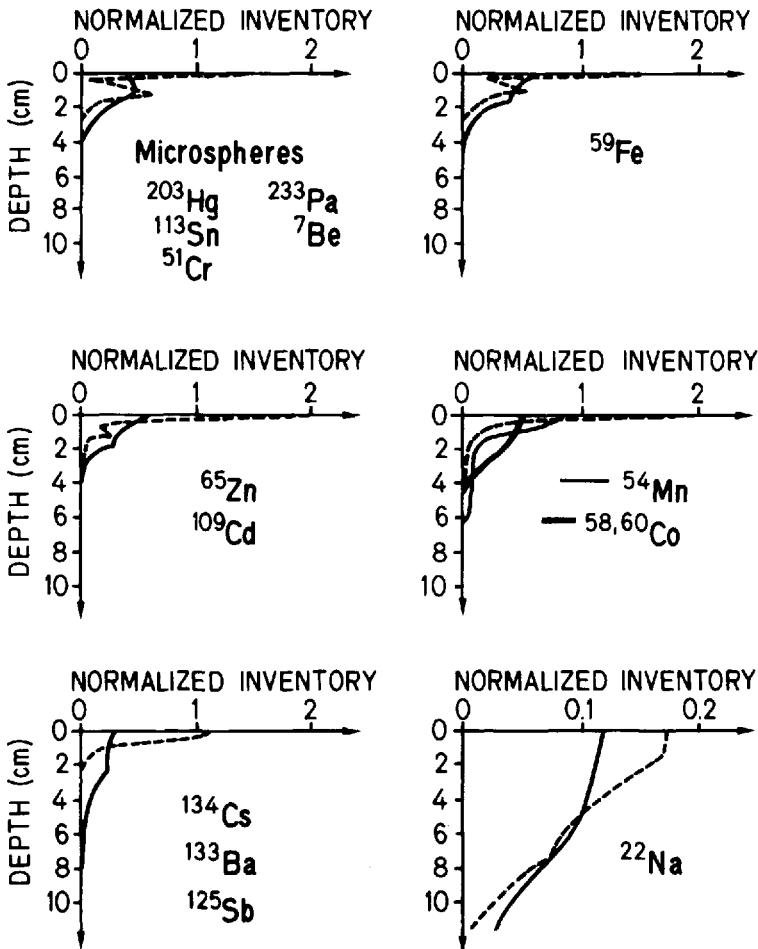
Figure 2. Radiotracer penetration into surface sediments from experiments in tank ME and MJ, taken 47 and 44 days, respectively, after addition of the spike.

winter are somewhat higher than those reported by Santschi *et al.* (1983a), but those for the summer months are similar and also consistent with values obtained by other groups for similar coastal areas (e.g., Aller *et al.*, 1976, 1980; Cochran and Aller, 1979; Benninger *et al.*, 1979).

^{22}Na, as a water tracer, shows the smallest difference of all tracers between winter

and summer seasons. Even though, on the average, ^{22}Na penetrated more quickly and to greater depths in the summer than in the winter, this is not seen so clearly in the otherwise typical profiles depicted in Figure 2. Despite the relatively similar penetration depths of ^{22}Na between summer and winter, the profiles are different in the upper 6 cm. The summer profile exhibits approximately constant concentrations above that depth, possibly indicating pore water irrigation while the winter profile still shows a gradient in the upper part of the profile suggesting a more constant diffusion coefficient throughout the profile.

The penetration of ^{22}Na into the sediments can be modeled by analogy to a one-dimensional case of diffusion from a large reservoir into a semi-infinite reservoir (Crank, 1975). Alternatively, transport can be described using a two-layer submodel (Adler, 1981) for the sediments (each with separate diffusion coefficients D_1, D_2), and an experimentally determined distribution coefficient (K_D) for ^{22}Na of 0.18 ± 0.05 cm^3 g^{-1} (Adler, 1981). This K_D value is in accordance with that determined by Li and Gregory (1974).

The effective diffusion coefficients, D_e (D_e = molecular diffusion coefficient, corrected for tortuosity of sediments), for ^{22}Na in the two profiles displayed in Figure 2 are very similar when a one-layer model is used (i.e. $D_e \sim 1 \times 10^{-5}$ cm^2 sec^{-1}) and slightly higher across the upper 6 cm in the summer core (i.e. $D_e \sim 2.6 \times 10^{-5}$ cm^2 sec^{-1} vs 7.5×10^{-6} cm^2 sec^{-1}) when a two-layer model is assumed. Average one-layer model values of D_e for ^{22}Na in 8–9 cores were in winter $(8.6 \pm 2.9) \, 10^{-6}$ cm^2 sec^{-1} ($n = 9$) and in summer $(2.1 \pm 0.4) \, 10^{-5}$ cm^{-2} sec^{-1} ($n = 8$), over the upper 10 cm. If a two-layer model is assumed to reproduce the summer results, the average value for D_e was $(6.8 \pm 3.2) \, 10^{-5}$ cm^{-2} sec^{-1} above 5.5 cm and $(8.0 \pm 1.5) \, 10^{-6}$ cm^2 sec^{-1} below 5.5 cm. These values can be compared to the calculated pore water diffusion coefficients, D_e, for Na$^+$ (corrected for porosity and tortuosity) of 3.6×10^{-6} cm^2 sec^{-1} at 4°C and 7.5×10^{-6} cm^2 sec^{-1} at 25°C. The experimentally measured values indicate a significant enhancement of pore water diffusion in the upper layers in summer and in winter (by bioturbation and biological irrigation), but a negligible enhancement below approximately 5 cm depth.

Figure 3 shows the ratio of the normalized tracer profiles from both cores depicted in Figure 2 compared to the normalized microsphere profiles. This shows the relative mobility of the various tracers compared to the microspheres. A ratio of 1 indicates that tracer mobility is equal to particle mobility. For the particle-reactive isotopes (Sn, Hg, Cr, Pa, Be) there is no significant deviation from a ratio of 1 throughout both profiles indicating no chemical mobility. However, there is a significant maximum of that ratio in core MEC180 at 0.5 cm depth for Na, Ba, Sb, Cs, Mn, Co, Zn, Fe isotopes, possibly due to recent irrigation events of pore waters at that depth. There is also a relative depletion in both cores between 1–2 cm for these isotopes, and a strong positive deviation from a ratio of 1 below 2 cm due to the greater mobility of these tracers compared to the tracer microspheres, which showed a subsurface maximum in
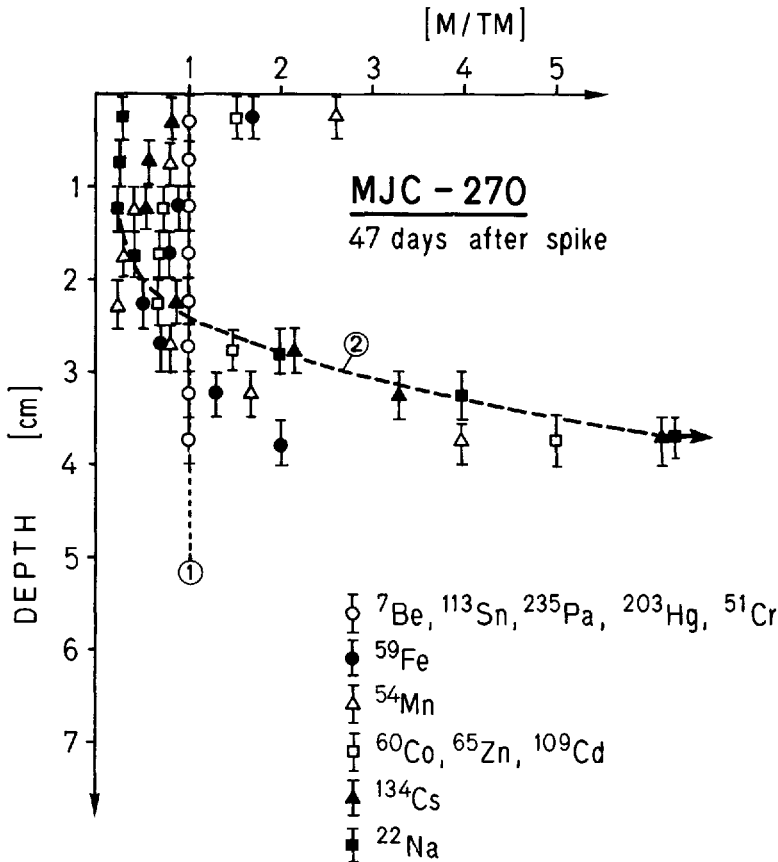
Figure 3. Ratios (R_x) of normalized inventories of radiotracer (M) to that of radioactive plastic "tracer microsphere" particles of 15 μm diameter (TM). The normalized inventory (in cm^{-1}) is the concentration at each depth $(M_x$, in cpm/cm^3 total volume) divided by the total inventory $(\Sigma M$, in cpm/cm$^2)$ of the tracer in that core. Therefore, $R_x = (M_x/\Sigma M)/(TMx/\Sigma TM) = (M_x/TM_x) \cdot$ const. Tracers are expected to follow curve 1, i.e. exhibit a constant ratio of 1, if they behave the same as the tracer microspheres in the sediments. Soluble tracers would show a relative concentration profile more like that of ^{22}Na (curve 2). The shape of the latter curve is determined by the uneven penetration of the tracer microspheres (see Fig. 2) into surface sediments.

these cores. The redox sensitive tracers Fe and Mn show a strong enrichment at the sediment-water interface, along with Co, Zn and Cd nuclides, suggesting remobilization of these elements from greater depths and precipitation in the aerobic sediments near the sediment-water interface. Below 3 cm depth, the isotopes of Na, Cs, Mn, Co, Zn and Cd show high mobility (i.e. strong deviation from a normalized activity ratio of 1). From this analysis, we would predict a release from the sediments into fresh (unspiked) seawater of Na (not shown), Cs, Mn, Co, Zn and Cd.
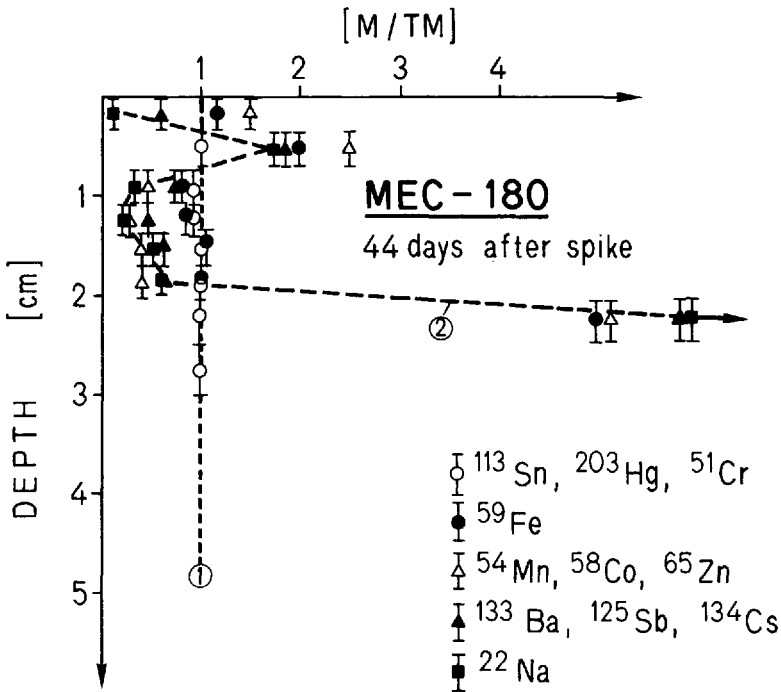
Figure 3. (Continued)

The analysis of the pore waters in core MJC390, collected 90 days after the initial spike addition to the water column, reveals some additional evidence for chemical mobility and the degree of equilibration with the stable elements. The following results can be seen from Figure 4: ^{54}Mn was almost completely equilibrated with stable Mn in the top 2 cm of pore waters as the ^{54}Mn/Mn ratios are about the same as in the overlying water. This similarity is due to the great mobility of Mn across the sediment-water interface. This is expressed also in the low value of the activity ratio on particles vs solution (K_D) of this isotope in the sediments (Fig. 4d). The K_D values of Cs, Fe and Mn isotopes decrease with depth (Figs. 4b, 4c and 4d), possibly as a consequence of slow sorption kinetics (Nyffeler *et al.*, 1986), and show a subsurface maximum at 6.5 cm depth. This coincides with a peak in the activities of tracer microspheres and particle-reactive isotopes in these sediments (not shown here), which indicates transport of particles to this layer from the sediment surface. Mn and Fe nuclides (as well as Co, Cd, Zn and Cs nuclides) also showed a strong enrichment at the sediment-water interface, despite the surface depletion of tracer microspheres and of all particle-reactive isotopes. Again, this suggests that these tracers are rapidly remobilized in the surface sediments and reprecipitated at the sediment surface probably because of reductive dissolution of the Mn oxide carrier at depth in the
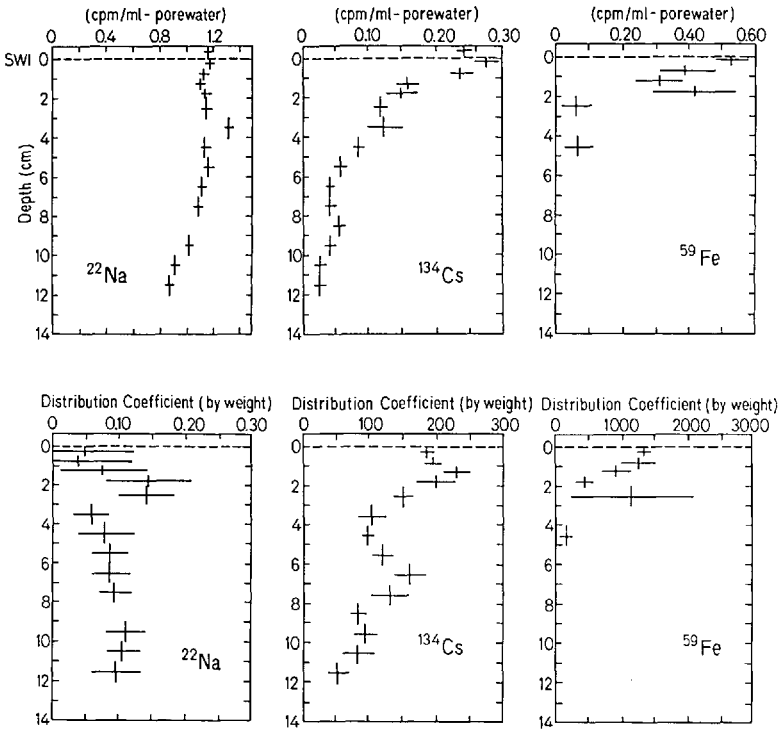
Figure 4. Radiotracer penetration in the pore waters of core MJC-390, (collected 90 days after the spike) is compared to the sediment K_D (i.e., the ratio of pore water activity to the activity in solids) for (a) ^{22}Na, (b) ^{59}Fe, (c) ^{134}Cs, (d) ^{54}Mn. In (e) the stable Mn profile is compared to the specific activity of ^{54}Mn/Mn in the pore waters.

sediments and its subsequent oxidation at the sediment-water interface and in the water column.

d. Radiotracer release from contaminated sediments under oxic and anoxic conditions

Figure 5 shows the results of the backdiffusion experiment in tank MO (summer 1982) for Cs, Mn, Co, Zn and Sn isotopes. This figure also shows predicted curves from the numerical transport model of Nyffeler *et al.* (1986), using typical parameters for spring conditions (Table 4). The modelling of the removal curves is based on parameters measured either during the same or during previous experiments at similar temperatures and seasons. The model curves have used as inputs the observed time-variable particle concentrations (Cp) and particle fluxes (F) of that particular experiment (Fig. 6). The benthic mixing rates (R) are related to the bioturbation rates (D_B) as $R = (1 - \emptyset)\rho D_B/z$, with $\emptyset$ = porosity, ρ = density, z = box thickness (Santschi *et al.,* 1980b). The values of R chosen in the model runs thus have no other physical
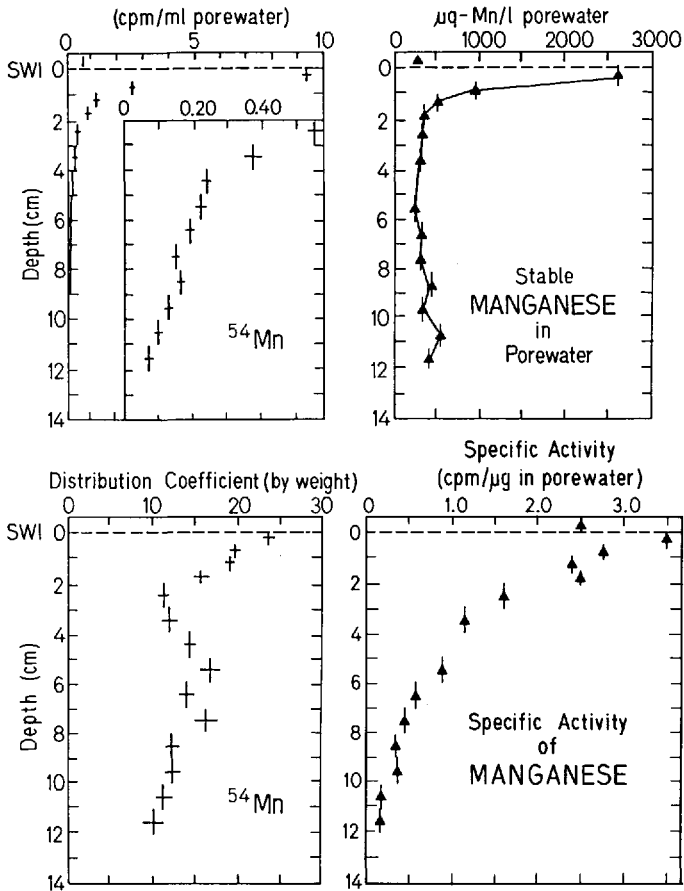
Figure 4. (Continued)

significance than to parameterize particle mixing as a constant exchange of particles between boxes. R is dependent on the thickness of the boxes (z), while D_B decreases with depth when R is constant. Values of D_B were assumed to be similar to those in earlier experiments (Santschi *et al.*, 1982, 1983b; Adler, 1981) at similar temperature conditions. The kinetic constants for adsorption, k_1 and k_{-1}, are assumed to be similar to those given in Nyffeler *et al.* (1984) for Narragansett Bay sediments. The adopted values were, however, further adjusted in the model so that (1) $K_D(t)$ in the water column fit the measured values of K_D for sediment trap particles, and (2) the concentration in the water column (C), normalized to the initial concentration (C_o), i.e. C/C_o fit the observed removal curve. Furthermore, the kinetic constants (and thus the K_D values in the sediments) for the different tracers were chosen in such a way that for Mn, Fe, and Cs, the resulting distribution coefficients K_D in the sediment-pore
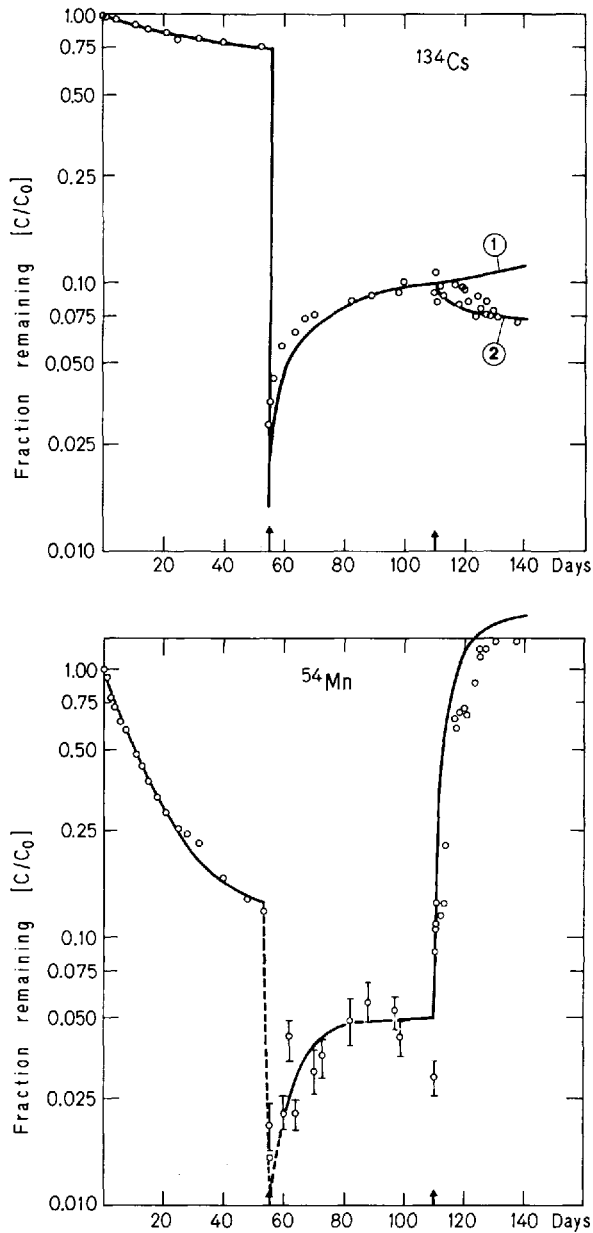
Figure 5. Removal from the water column of tank MO and backdiffusion of radionuclides from oxic and anoxic sediments is shown for (a) ^{134}Cs, (b) ^{54}Mn, (c) ^{60}Co and ^{65}Zn (^{109}Cd is not shown, but behaved like ^{65}Zn), (d) ^{113}Sn. The arrows indicate the beginning of the backdiffusion experiments into oxic and anoxic water, respectively. Curve 1 shows backdiffusion under oxic conditions, curve 2 under anoxic conditions. Dashed lines show modeled removal and backdiffusion curves. Curve 1 and 2 were calculated using different parameters listed in Table 4. For discussion, see text.
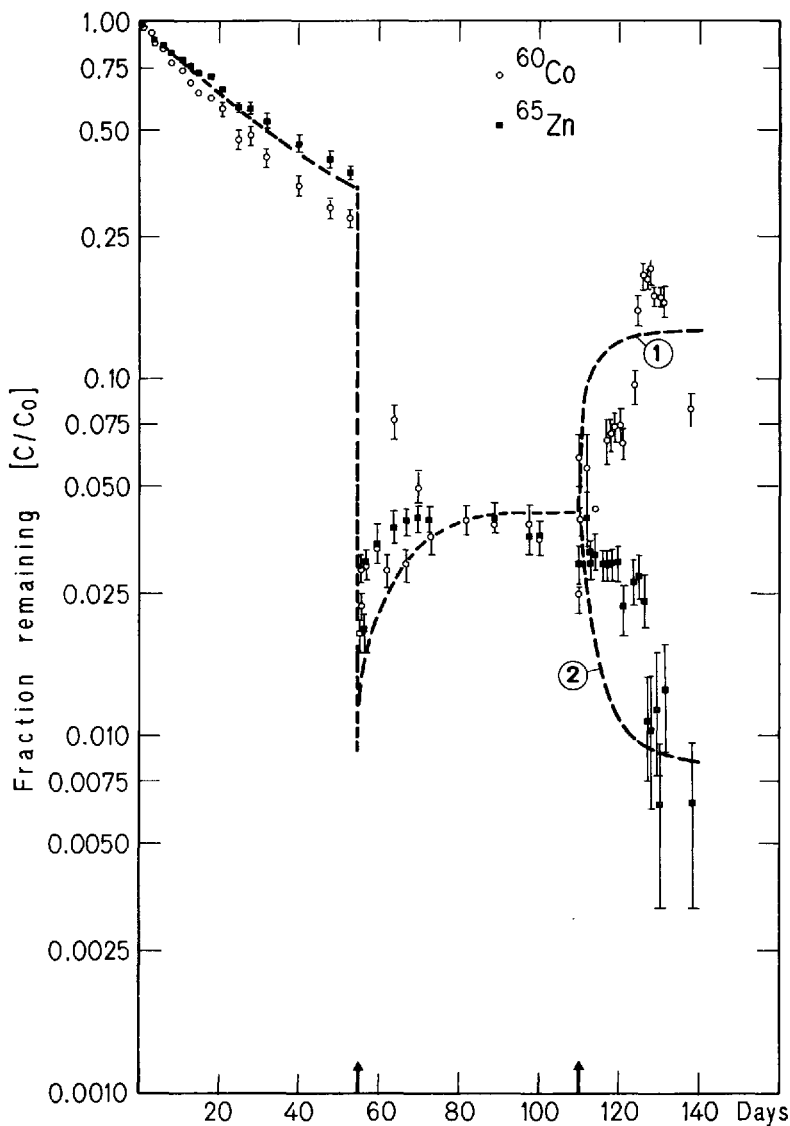
Figure 5. (Continued)

water system matched the measured values. For the other tracers, the values were adjusted within the range given by previous experiments. The values of the different parameters used for the different model runs are given in Table 4. Further details of the model and of the importance of using a kinetic rather than an equilibrium approach for tracer equilibration in multi-reservoir ecosystem experiments can be found in Nyffeler *et al.* (1986).
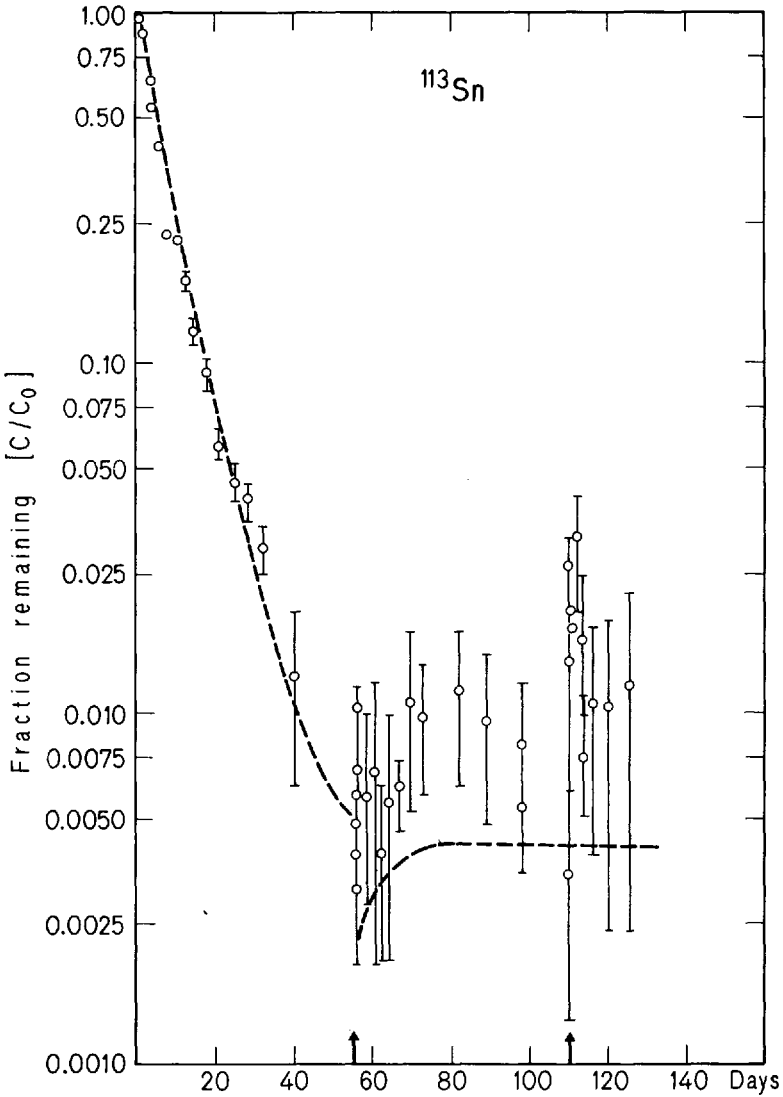
Figure 5. (Continued)

These model simulations cannot be taken, however, as proof that we have parameterized the removal and backdiffusion processes exactly, but rather suggest that the basic features of the tracer movements through the system can be reproduced by the transport model used and thus that the proposed mechanisms such as the particle and water exchange processes across the sediment-water interface are reasonable and self-consistent.

As expected for oxic conditions, only the more soluble tracers such as Cs, Mn, Co,

Table 4. List for model parameters* used in Figure 4.

			Sorption constants†					
					Sediments			
		Model	Water		Oxic		Anoxic	
	Depth	run						
Isotope	(cm)	no.	k_1	k_{-1}	k_1	k_{-1}	k_1	k_{-1}
[134]Cs		1	130	1	180	1	180	1
		2	130	1	—		360	1
[54]Mn	0	1	2×10^4	0.1	1×10^5	1	7.5×10^3	1
	0.1	1	—	—	5×10^3	1	2.5×10^1	1
	0.2	1	—	—	2.5×10^1	1	2.5×10^1	1
[65]Zn, [60]Co		1	1×10^3	0.2	5×10^3	1	2.5×10^3	1
		2	1×10^3	0.2	—		1.5×10^4	1
[113]Sn		1	1×10^5	0.4	1×10^5	0.4	1×10^5	0.4

*The model and its parameters are described in detail in Nyffeler *et al.* (1985). The parameters, which were left constant for all isotopes, are typically: particulate matter concentration $= 2 \times 10^{-6}$ g cm^{-3}, particle flux $= 1 \times 10^{-3}$ g cm^{-2} d^{-1}, particulate bioturbation rate const. $= 1 \times 10^{-7}$ cm^2 s^{-1}, biodiffusion coefficient $= 1 \times 10^{-4}$ cm^2 s^{-1}, stagnant film thickness = 0.1 cm.

†k_1 (cm^3 g^{-1} d^{-1}) and k_{-1} (d^{-1}) are the constants for the reaction $M^* + S \; \underset{\overline{k}_{-1}}{\overset{k_1}{\rightleftharpoons}} \; M^*S$ with $M^* = $ tracer ion, $S = $ particle surface, $K_D^\circ = k_1 < K_{-1}$.

Zn and Cd reversibly desorbed from the (contaminated) oxic sediments into the unspiked seawater, whereas the particle-reactive tracers (Sn, Fe, Cr, and Hg) did not show any backdiffusion. Also, Se and Sb nuclides (not shown here) were not released significantly to the overlying water column. These results were expected from the previous discussion on chemical speciation and leaching results.

Under anoxic conditions, only Mn and Co nuclides were further released into the unspiked seawater, whereas Cd (not shown here), Zn and Cs concentrations decreased significantly during the subsequent 30 days of the anoxic experiment, probably indicating rapid formation of sulfides in the anoxic sediments for Zn and Cd. The factor of two increase in effective K_D of [134]Cs in the anoxic sediments, needed to model the decrease of [134]Cs in the water after anoxic conditions set in, is similar to the K_D increase from oxic to anoxic Black Sea sediments observed by Duursma and Gross (1971), for [134]Cs. This increase is, however, not understood, as Cs-sulfides and polysulfides are soluble in seawater. No noticeable releases were observed under anoxic conditions for Fe, Se, Hg and Sn nuclides.

In summary, the predicted mobilities of the various tracers, based both on chemical speciation/leaching experiments and on examination for spiked sediments, are as follows:

— High mobility exists for Mn, Co, Zn, Ba, Cs, Sb and Cd nuclides in sediments and across the interface, under oxic conditions (under anoxic conditions for Mn and Co only);
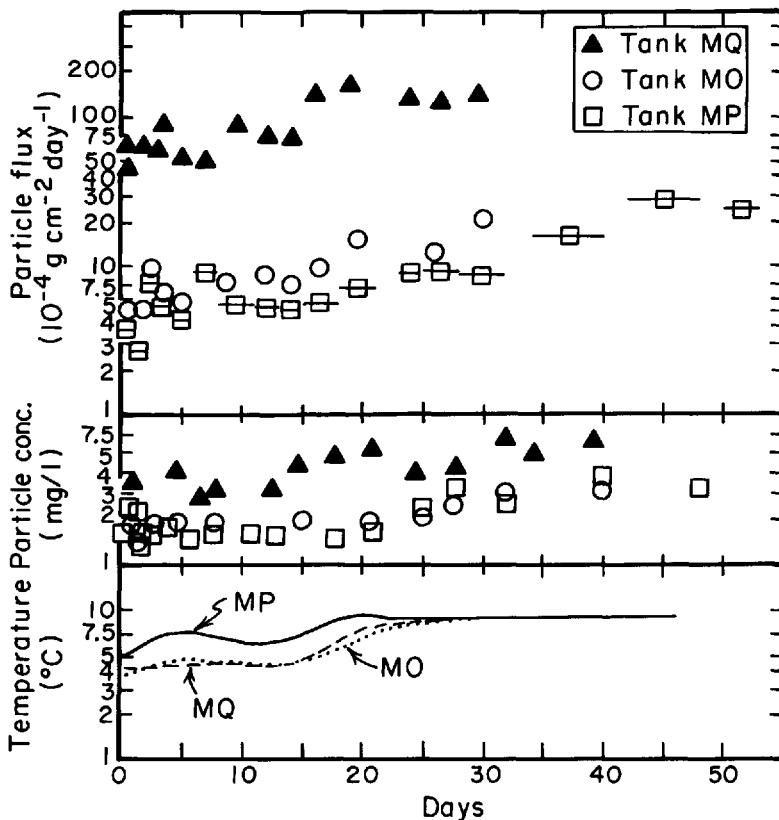
Figure 6. Ancillary data to the experiments in tanks MO, MQ and MP: temperature, particle concentration and particle flux as a function of time.

— The particle-reactive isotopes (Sn, Hg, Pa, Be, Cr) behave chemically immobile within the sediment over that time scale.

Scavenging of Zn and Cs isotopes in sulfidic or other phases under anoxic conditions was indicated by the much lower percentage in the Na-dithionite-citrate leach solution as compared to that in the hydroxylamine · HCl leach. The strong redox cycling within sediments of the ^{59}Fe-nuclide could have been predicted from its high concentrations in pore waters.

e. Release of radiotracers under simulated high resuspension regimes and particle flux dependency of tracer removal rates

It has been suggested that intermittent high resuspension rates, caused by storms and tides, may release trace elements which have been stored in the pore waters of surface sediments to the overlying water column (e.g. Duursma and Gross, 1971,
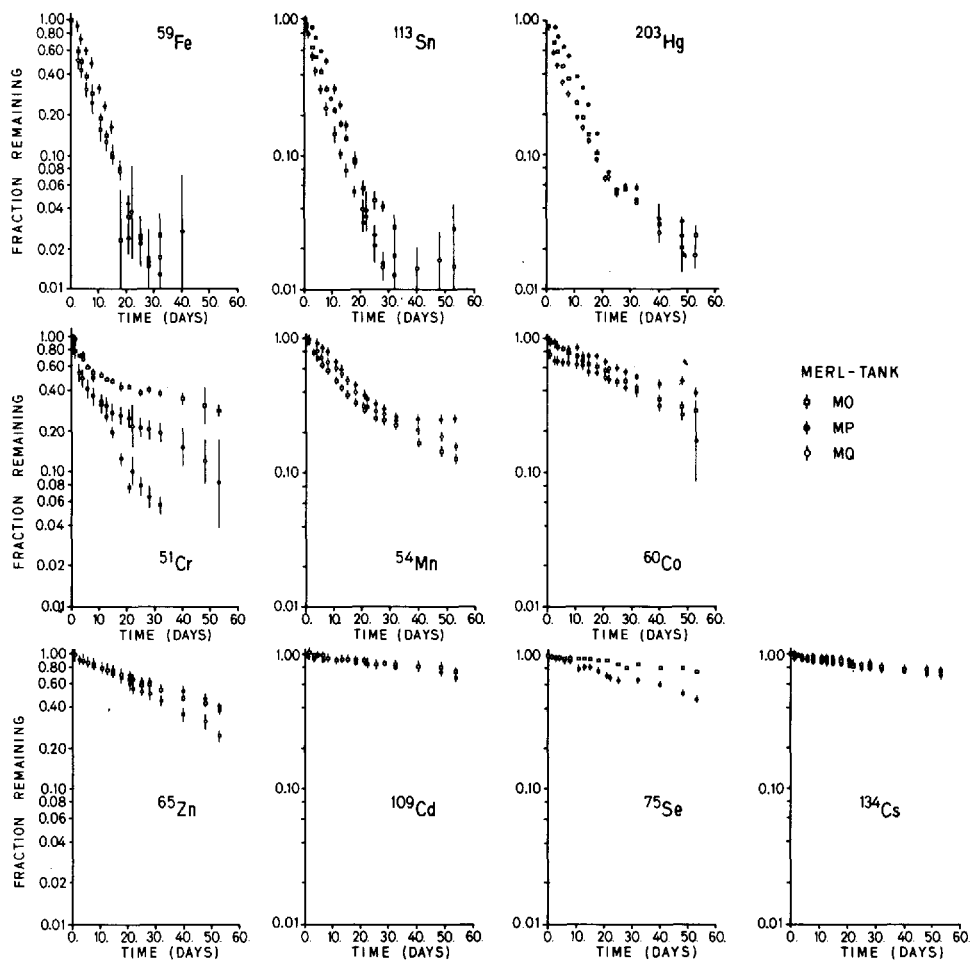
Figure 7. Removal of radiotracers from the water column of MERL tank experiments MO, MQ and MP is shown as the fraction remaining (C/C₀) vs time. Error bars indicate 2 standard deviations. In case none are indicated, they are equal or smaller than the symbol size.

Oviatt *et al.*, 1981b). Consequently, tracers added to such a system would not be removed as efficiently from the water column. We tested this contention in mesocosm experiments with varying resuspension rates (which caused variable particle fluxes), but which also had relatively low rates of particle bioturbation as a consequence of lower temperatures. In the past, we have found removal rates of particle-reactive tracers to be proportional to the particle flux (Santschi *et al.*, 1980a, 1982). However, resuspended sediments are an efficient conveyor belt for particle-reactive substances only if combined with higher rates of benthic mixing (Santschi *et al.*, 1980b).

Particle concentrations and fluxes in tanks MO, MQ and MP as well as temperature

data, are shown in Figure 6; radiotracer removal from the water column of these experiments is shown in Figure 7. The average particle fluxes in the first 30 days of the 3 experiments were: MP (0.6 mg cm^{-2} day^{-1}) $\leq$ MO (1.0 mg cm^{-2} day^{-1}) $\leq$ MQ (10 mg cm^{-2} day^{-1}). When we compare the relative removal rates of the different tracers in these experiments, we find that in general tracers are removed at slightly faster rates in tanks with higher particle fluxes. The removal rates are different at the 0.05 significance level (or better) for all isotopes except for ^{59}Fe (tanks MO and MQ), ^{65}Zn, ^{109}Cd, ^{134}Cs (tanks MO and MP). Additional exceptions to this dependence of the tracer removal rate on the particle flux are exhibited by Mn(II) and Cr(III) nuclides. Seasonal differences in removal rates of the different tracers are however, much larger than the different removal rates here, confirming the contention of Nyffeler *et al.* (1986), that the activity of the benthic macrofauna controls tracer removal rates only if sediment resuspension is coupled to benthic particle mixing and filter feeding.

The reason for the smaller increase of removal rates than expected from the higher particle flux is most likely related to the lower benthic particle mixing rates during the cold season (Adler, 1981, Santschi *et al.*, 1982, 1983b) which only puts a thin layer of sediments in intimate contact with the water. As a consequence, resuspending higher amounts of sediments only cycles more of the same particles through the water column without diluting them much with particles from the underlying surface sediments. This is confirmed by our modelling results and by the low resuspension rates of surface sediments in control tanks as these are often coupled to benthic mixing rates (Rhoads *et al.*, 1978; Santschi *et al.*, 1980, 1982, 1983b).

The removal of ^{113}Sn (as an example of a particle-reactive tracer) in tank MO could be well simulated using our measured parameters (see Fig. 5d). Further information on the modelling of this isotope in tanks MO and MQ can be found in Nyffeler *et al.* (1986). With regard to the anomalous behavior of ^{54}Mn and ^{51}Cr we can only hypothesize. The high resuspension rates in tank MQ seem to have negatively affected the oxidation and adsorption rates of Mn(II), thus slowing down the removal of ^{54}Mn(II) in that tank as compared to the control tank MO. This may have been due to the increased contact time between mildly reducing surface sediments, which were exposed because of the higher sediment resuspension rate, and the oxic water column. For further discussions of the effects of resuspended sediments and benthic mixing on tracer removal the reader is referred to Nyffeler *et al.* (1986).

^{54}Mn as well as ^{51}Cr(III) showed some anomalous behavior also in tank MP. In tanks MO and MQ the removal rates of ^{51}Cr(III) decreased after the first few days, coinciding with a significant increase in the "effluent" fraction in the chemical speciation system. This was shown to represent the oxidation of Cr(III) to Cr(VI) by Amdurer (1983). Similar behavior of ^{51}Cr(III) was not observed in tank MP: instead, ^{51}Cr(III) was removed at a constant rate throughout the experiment, while ^{54}Mn(II) was removed more slowly than in the other tanks possibly indicating slower oxidation rates for both isotopes. The removal rates of both of these isotopes are controlled by the

amounts which are taken up by particles in their transit through the tank water. As the oxidation rates of both [51]Cr(III) and [54]Mn(II) (which are controlling the particle-associations of both of these isotopes, but in an opposite way) are mediated by bacteria on similar time scales as particles are resuspended (Emerson *et al.,* 1979, 1982; Cranston and Murray, 1978; Santschi *et al.,* 1980c), those unexpected features indicate that the trace metal additions to tank MP (see Table 1) could have had some detrimental effects on the microflora in this tank.

Support for this contention comes from preliminary results by Hunt (pers. communication) in tanks with similarly elevated trace metal concentrations of Cr, Cd and Cu. His results indicate that bacterioplankton growth can be significantly depressed by trace metal additions at or above the levels used in our experiments. Alternatively, the small but significant differences between trace element removal rates in the three different tanks could have been influenced by the different temperatures during the first 20 days of the experiment (Fig. 6). However, neither the Mn flux (Hunt, 1983), nor the particle flux (F_p) (Santschi *et al.,* 1983a) which are both strong functions of temperature above 10°C, would be expected to show a significant increase in F_p for a change in temperature of 1–2.5°C below 10°C.

Since, however, the K_D of suspended particles of both radioactive and stable Mn(II) and Cr(III) decreased while the temperature increased with time (Fig. 9), it is possible that we are seeing here a similar phenomenon as that described by Santschi *et al.* (1980c). They observed strong DOC complexation of radiotracers during spring conditions while the temperature was steadily increasing from 4°C to 15°C. Organic complexes of trace metals can interfere in the sorption process of trace metals.

f. *Radioisotopes as tracers of stable element behavior*

We have performed experiments in tank MP to test the assumption that radioactive isotopes behave similarly to their stable counterparts with respect to the processes controlling their cycling in the water column. Even though the tracers were not necessarily added to the MERL tanks in the same chemical form as they are released to natural water bodies by chemical and sewage treatment plants, the advantage of our approach is the known chemical speciation of our trace metals initially present in the controlled ecosystems. This greatly simplifies the interpretation of any change in experimentally defined chemical speciation as was observed here. Furthermore, many trace metals are indeed released into an estuary in ionic form either as acid waste from industrial sources (e.g. Förstner and Wittmann, 1979), or as acidic, wet precipitation or by rivers. They can also be found in seawater in ionic form, for example, allowing their preconcentration as ionic species on chelex resin.

Due to contamination problems with Fe and Zn analysis, we rejected these data and only report here the results from the Mn, Cr and Cd analysis. Figure 8 shows that, after subtracting the appropriate background concentration of stable metals (taken from
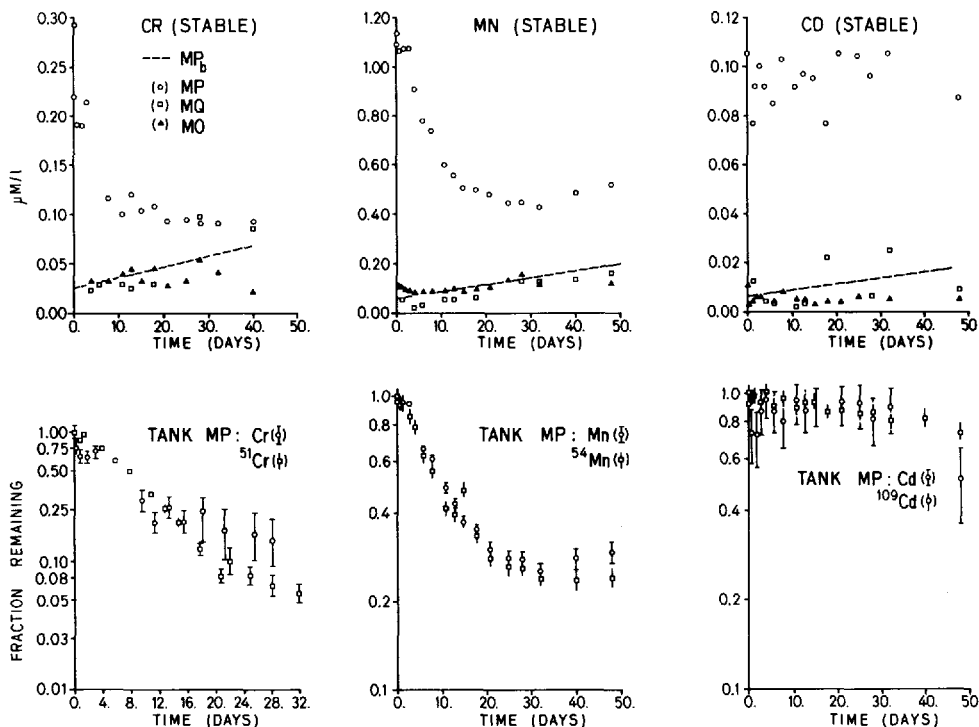
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Figure 8. (a) The removal of radioactive and stable trace metals (Mn(III), Cd(II) and Cr(III)), from the water of MERL tank MP is shown as the concentration or as the fraction remaining (C/C_0) vs time. The fraction of stable trace metals added to the tank was calculated as the measured concentration minus the background concentration, taken as that in the control tanks MO and MQ. The broken line indicates the background concentration which had to be assumed to calculate excess metal concentrations in tank MP.

measurements in tanks MO and MQ), the relative concentrations of the stable and radioactive metal ions Mn(II), Cr(III) and Cd(II) in the water of tank MP, normalized to the initial concentration, decrease at similar rates (within the errors of the measurements). However, the errors, usually due to the uncertainty in the appropriate background correction, are relatively large. Therefore, one cannot prove perfect agreement. We do have another way to compare radiotracer with stable metal behavior which is in their degree of association with suspended particles, expressed as their K_D-value (ratio of particulate activity to solution activity). Figure 9 shows, that K_D-values of the radioisotopes adsorbed to suspended particles are also similar to those of the stable elements in the same tanks or in tanks with similar conditions of particle concentration and resuspension rate (e.g. tanks MA, ME, MF, Adler, 1981; Amdurer, 1983). K_D values are similar also in tank MQ which had intentionally higher resuspension rates. This demonstrates that radioisotopes are indeed tracing the
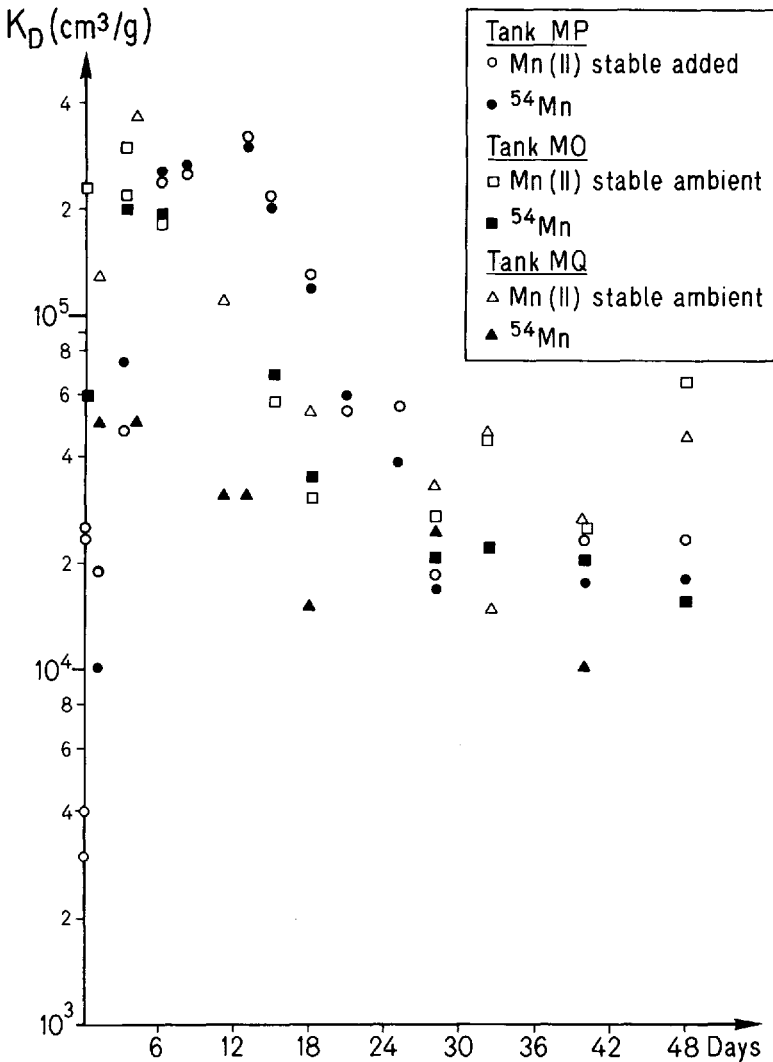
Figure 9. K_D values for the radioactive and stable trace metals (a) Mn, (b) Cr and (c) Cd, on suspended particles, in the tanks MO, MQ, MP, and tank MJ (for [109]Cd only). Uncertainties in K_D values are greater for the stable metals ($\leq$10–50%) than for the radioisotopes (3–10%) due to blank corrections.

removal behavior of stable elements in controlled ecosystem experiments to a remarkable degree. These observations are also in line with those of Amdurer *et al.* (1982), which showed that radioactive and stable Mn behaved similarly in the water column of a MERL tank at natural concentrations, one month after the spike addition. These similarities between radioactive and stable species indicate that our observations on
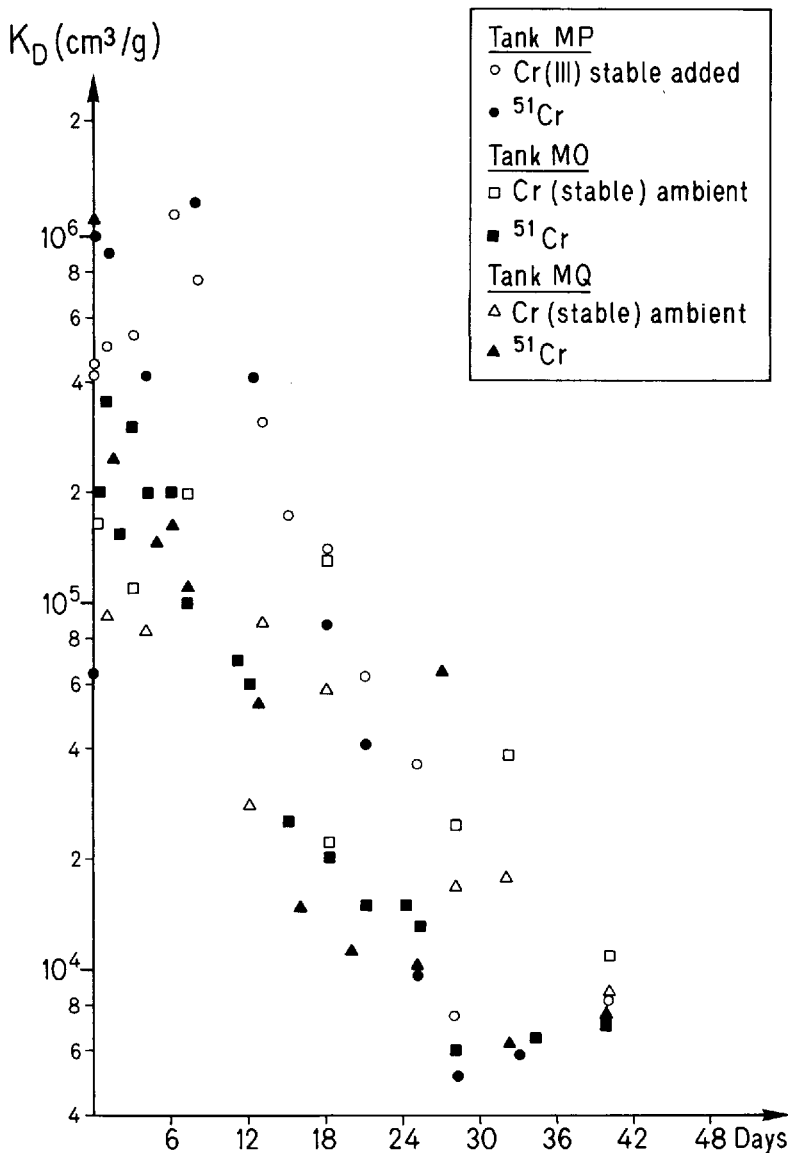
Figure 9. (Continued)

radioactive metal ions in the water of the MERL tank ecosystems are likely to be applicable to the behavior of stable ions in the environment. Our results also confirm our earlier contention that radionuclides trace the cycling of stable trace elements in these controlled ecosystems, and do not simply mark some exotic isotopic ion exchange process on particles unrelated to the behavior of the stable species.
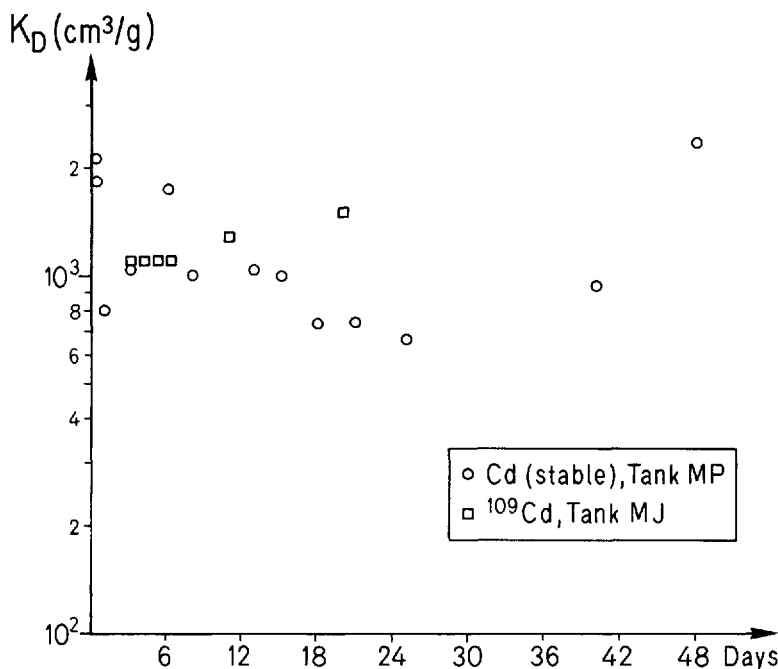
Figure 9. (Continued)

4. Conclusions

(1) Sequential extraction experiments of water samples through filters (0.45 μm) and ultrafilters (10^5, 10^4, 10^3 amu), charcoal, Chelex, Amberlite IRA-938 and XAD-2 resins, show that the particle-reactive isotopes (i.e. Sn, Fe, Cr, Hg, Pa and Be) are significantly associated with colloidal-sized particles of organic (for Hg) and inorganic origin (for the other isotopes).

(2) Sequential leaching experiments of sediments with seawater, 1 N $MgCl_2$, 1 N hydroxylamine · HCl, 30% H_2O_2 and 0.5 N HCl revealed that large fractions of Mn(II) (30%), but also significant fractions of Be, Cd, Zn and Co (5%), can be released by seawater alone. Subsequent leaching with 1 N $MgCl_2$ released about the same amount. *In situ* incubation of sediment trap material revealed that 10–20% of the Mn, Co, Zn and Cd can be released in one day into unspiked seawater. These nuclides remain labile in the sediments and are therefore potentially mobile. The remaining fraction of most nuclides (Fe, Be, Cr, Hg and Cs) was found associated with Mn and Fe oxides (reducible fraction) or with organics (oxidizable fraction). Exceptions to this are Sn, Hg, Cr and Pa nuclides, which could only be mobilized with strong acids (4 N HCl or HNO_3).

(3) Se and Cr nuclides, which were added in different oxidation states to two tanks, showed a faster removal rate when in the lower, more particle-reactive oxidation state.

Furthermore, changes in chemical speciation with time allowed an estimate of the reduction rate of Se. The increase in the colloidal fraction of Se, if interpreted as the production of organic forms of Se, indicates characteristic time scales of 65 and 2000 days for Se(IV) and Se(VI) reduction, respectively.

(4) A comparison of the tracer profiles to those of the tracer microspheres in sediment cores taken ~45 days after the initial spike (tank MJ and ME) revealed that Fe and Mn (as well as Cd, Zn and Co) show strong redox cycling in the surface sediments leading to significant enrichments near the sediment-water interface, especially in the summer. Furthermore, these isotopes, and also the isotopes of Sb, Cs and Na, show high mobility in the deeper sections of these cores. Bioturbation rates, calculated from modelling of 10 cores each in winter and summer experiments, averaged 4×10^{-7} cm^2 sec^{-1} in the summer, and 1×10^{-7} cm^2 sec^{-1} in the winter. Pore water diffusion coefficients calculated from ^{22}Na penetration into the top 5 cm of surface sediments were higher than molecular diffusion throughout the year, by a factor of 2 to 9.

(5) Under oxic conditions, more soluble tracers such as Cs, Mn, Co, Cd and Zn were significantly released into unspiked seawater from contaminated sediments in a whole ecosystem experiment. Under anoxic conditions, only Mn and Co were significantly released, whereas Cd, Zn and Cs were further immobilized, probably due to sulfide formation. The observed behavior could be well modeled using a numerical kinetic transport model and measured kinetic and transport parameters. While the mobility under oxic conditions would have been predicted correctly from the sequential leaching experiments, the immobilization of Zn, Cd nuclides would have only been predicted from the lower percentage leached by sodium dithionite-citrate than by hydroxylamine · HCl, as the dithionite disproportionation can lead to sulfide formation. The slight decrease of ^{134}Cs$^+$ concentrations in the overlying water under anoxic conditions was not expected a priori but agrees with the dithionite-citrate leaching results and with earlier observations by Duursma and Gross (1971).

(6) High resuspension regimes during winter–spring conditions (tank MQ), when particle mixing rates from benthic organisms in surface sediments were still low, increased the removal rates of many radioactive trace elements by a significant but small degree. The behavior of ^{54}Mn(II) in tank MQ, however, was different. Its removal was slowed down by the increase in sediment resuspension rates, possibly because of more intimate contact between oxic water and mildly reducing sediments. The chemical speciation tests in the water column of tank MQ revealed no significant difference compared to the control tanks.

(7) The relative concentrations (normalized to the initial value) and K_D values of radioactive and stable Mn, Cd and Cr in tank MP, tracked each other for every added element within the errors of the measurements. This was true for situations where radioactive or stable metals were added together as well as when compared separately. These results demonstrate that our observations on radiotracer behavior in the MERL

tank ecosystems are indicative of those of stable metals and that radionuclides do indeed trace the cycling of their stable element counterparts in these systems.

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