KINETICS OF TRACE METAL INTERACTIONS WITH LAKE SEDIMENTS

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ABSTRACT

This study evaluates: (1) the use of a radiotracer technique to obtain kinetic data on trace metal interactions with sediments in a freshwater environment, and (2) the importance of kinetic considerations in trace metal partitioning between sediment and water in a lake.

The technique consists of measuring the distribution of a small radiotracer spike between the sediment and the aqueous phase over time. The system is assumed to be at equilibrium prior to spiking. The radiotracer uptake by sediments is first determined, the aqueous phase is then replaced by a non-tracer solution, and finally the tracer release is measured.

Preliminary studies with cadmium and zinc showed: (1) stable solution conditions (no tracer added) with negligible change in trace metal concentrations and master parameters (pH, DOC) over several weeks, (2) precision in replicate analysis and experiments, and (3) confirmation of the technique as demonstrated with a synthetic TiO_2 suspension.

A novel experimental design was devised, consisting of a kinetic model fitting using the "adsorption" kinetic data, followed by confirmation comparing the model data to "desorption" kinetic data. The technique was applied to surficial samples from three lacustrine systems using ^{65}Zn and ^{109}Cd. The kinetics of metal exchange are very similar for all samples for both "adsorption" and "desorption". The general kinetic behaviour was a fast reaction (hours) followed by a slower interaction (weeks).

Three kinetic models were investigated to explain the "adsorption-desorption" data. A two-box model (TBM), describes the system as a reversible solid-liquid first-order reaction. It does not, however, explain the slower exchange well. Two other models include two distinctive kinetic reactions. They differ mostly by the nature of the "desorption" reaction prediction. A "two-box model with a leak" (TBL) considers a fast reversible first-order reaction followed by a slower first-order reaction (leak). A "restricted three-box model" (RTB) considers two independent reactions, both first-order and reversible, but of different rates. The TBL and RTB models can be fitted to the "adsorption" data very well. The "desorption" data is, however, better predicted by the TBL model revealing the slower short-term (hours-days) interactions of trace metals with lake sediments.

Trace metal partitioning determined by short-term (hours-days) interactions gives higher solution concentration than longer-term (weeks-months) "equilibrium" partitioning. Thus short-term prediction of metal partitioning based on long-term "equilibrium" distribution would overestimate the role of natural sediments as metal sinks.

This kinetic approach gives good estimates of the uptake and release of trace metals between sediment and water in lacustrine systems.

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CHAPTER 1

INTRODUCTION

1.1 STATEMENT OF THE PROBLEM:

Man's activities have resulted in the mobilization of many trace metals into the environment. More specifically, fluxes of trace metals to the aquatic environment have drastically increased. This trace metal enrichment in aquatic systems often results in toxicity problems. Consequently, a special effort to understand the speciation, transport and fate of trace metals in aquatic systems is required. Furthermore, a better knowledge of trace metal cycling is necessary in order to make rational decisions concerning the management of trace metals in the global environment.

Dissolved trace metal concentrations in aquatic systems depend on their interactions with suspended matter and bottom sediments. One result is that trace metals are concentrated by solid substrates with respect to their dissolved concentrations, on a phase carrier weight basis. Often the distribution of total trace metals between natural solids and the ambient water is assumed to represent an equilibrium state of the system (e.g. Kramer, 1967). It has been recently suggested, however, that in some situations solute-solid interactions are sufficiently slow or time of contact is short enough to invalidate the assumption of equilibrium (Nyffeler et al. 1984, 1986; Santschi et al. 1986a, b; Wu and Gschwend, 1986; Anderson et al.

1987). Until now, only a few studies have investigated kinetics of trace metal exchange with natural suspended particles or sediments, mostly in marine systems. There is a paucity of information on freshwater systems.

This study provides a better understanding of trace metal cycling in freshwater systems by the description of time-dependent interactions of trace metals with surficial lake sediments through the application of a kinetic technique, and by the confirmation of the need to consider time-dependent relationships in order to adequately predict short-term (weeks or less) trace metal partitioning between sediment and water.

1.2 TRACE METALS IN LAKES:

Trace metals are distributed into three major compartments of a lake. These compartments are: (1) water column, (2) surficial sediments, and (3) deep sediments. Surficial and deep sediments are generally characterized by oxic and anoxic environments, respectively. The oxic overlying water and surficial sediments constitute a zone of particular importance in the overall cycling of trace metals. The thickness of this zone is variable and depends on perturbation events (e.g. resuspension, bioturbation, bio-irrigation). The formation of diagenetic iron and manganese oxyhydroxides generally takes place in this particular area.

The distribution of trace metals between ambient water and surficial sediment reflects, for a large part, the affinity of the metals for the solids in these compartments. The kinetics of trace metal exchange between solid and liquid phases also influence the partitioning of trace metals. In general, the interactions of dissolved trace metals with surficial sediments lead to a net metal enrichment of the solid phase. The active process responsible for the observed distribution of trace metals in sediment suspensions is not well understood. The major difficulty is the complexity of the natural material. In fact, trace metals in sediment suspensions are distributed among different physico-chemical forms which include the following:

(i) hydrated metal ions,
(ii) inorganic complexes,
(iii) organic complexes,
(iv) colloidal species
    - inorganic
    - organic
    - mixed

Trace metals are also found as discrete compounds or sorbed on particulate materials in association with different constituents as governed by different types of interactions. As pointed out in a recent review (Campbell and Tessier, 1987), trace metals are:

(i) adsorbed on particle surfaces,
(ii) present as discrete carbonate minerals or coprecipitated with the major carbonate phases,

(iii) occluded in iron and/or manganese oxyhydroxides, either as discrete nodules or as coatings on particles,

(iv) bound to organic matter, in either living or detrital form,

(v) bound in amorphous authigenic sulfides or in more crystalline forms,

(vi) bound in lattice positions in alumino-silicates, in resistant oxides or in resistant sulfides.

Due to the various forms and associations of trace metals in natural systems, most information regarding the distribution of trace metals comes from measurements through operational methods (e.g. Tessier et al. 1979, Laxen and Harrison, 1981, Muller and Kester, 1990). In order to simplify both conceptual and experimental approaches, sorption processes expected to be active in natural systems have been predominantly studied with model particles in well defined media.

1.3 SORPTION PROCESSES:

The generic term "sorption" defines the various ways that trace metals in solution interact with the surfaces of adjacent solid phases. Sorption processes can be separated into three major classes (Sposito, 1986): (1) absorption, (2) adsorption, and (3) precipitation. A brief definition of each process, listed in Table 1.1, is presented with reference to the trace metal interactions with model metal oxide particles in well

TABLE 1.1 Sorption processes.

Absorption:		
Adsorption:	- Physical:	- electrostatic
		- polarization
	- Chemical:	- metal surface complexation
		- ternary surface complexation
Precipitation:	- Pure phase	
	- Coprecipitation	
	- Surface precipitation	

defined media.

Absorption refers to the penetration of a chemical into a solid phase. This displacement inside the solid must exceed the nanometer depth (operationally defined) beyond the interfacial region (Sposito, 1986). Absorption of trace metals by particulate materials (e.g. penetration in solid pores) is often an intermediate step prior to adsorption or precipitation.

By definition, adsorption is an accumulation of matter at an interface without the development of a three dimensional molecular arrangement (Corey, 1981; Honeyman and Santschi, 1988). As pointed out by Sposito (1986), adsorption can also be considered as the initial step of the precipitation process. Although it is convenient to distinguish between physical and chemical interactions, both types of adsorption result from electrostatic attractions and repulsions between positive nucleus and negative electrons.

Physical adsorption is a long-range interaction also called outer-sphere interaction. Electrostatic physical adsorption refers to formal charge or permanent dipole interactions, whereas the interaction from induced dipoles is defined as polarization. In a polar solvent such as water, electrostatic interactions are energetically predominant. A characteristic of physical adsorption is that adsorbed elements are free to move along the solid-liquid interface. Since most natural particles are negatively charged at environmental pH, physical adsorption is favoured for cations and not for anions.

Chemical adsorption is defined as a short-range or inner-sphere interaction.

Trace metals chemically adsorbed to solids are fixed to their sites of association. The interaction involved in chemical adsorption is stronger than in physical adsorption. Chemical adsorption consists of coordination reactions analogous to aqueous ligand exchange reactions. Two chemical adsorption interactions of trace metals with solids may be described: (1) metal surface complexation, and (2) ternary surface complexation. Chemical adsorption of trace metal ions is represented as a competitive surface complex formation involving one or two surface hydroxyls. This reaction results in a displacement of solid associated hydrogen atoms by dissolved trace metals. Ternary surface complexes describe an interaction at surface sites involving trace metals and ligands. There are two common types of ternary complexes. In type A, the metal is located between the surface and the ligand whereas in type B, the sequence between trace metal and ligand is inverted. Schematic examples of these types of interactions are presented in Table 1.2. In addition, chemical adsorption often leads to the development of formal charges and long-range effects, directly affecting the physical adsorption of other species.

The growth of a solid phase in three dimensions by repetition of its unit cell defines the general process of precipitation. Three mechanisms of precipitation may be described: (1) pure phase precipitation, (2) coprecipitation, and (3) surface precipitation. Pure phase precipitation only occurs when the solubility product of a solid is exceeded. This process is also called homogeneous nucleation. Coprecipitation or heterogeneous nucleation refers to the introduction of foreign elements, molecules or particles in the nucleation reaction. Surface precipitation is defined as the growth of

TABLE 1.2 Chemical adsorption interactions.

Metal surface complexation:

$\text{S-OH} + \text{M}^{Z+} <===> \text{S-OM}^{(Z-1)+} + \text{H}^{+}$

$2\ \text{S-OH} + \text{M}^{Z+} <===> (\text{S-O})_2\text{M}^{(Z-2)+} + 2\ \text{H}^{+}$

Ternary surface complexation:

type a:

$\text{S-OH} + \text{ML} <===> \text{S-OML}^{-} + \text{H}^{+}$

type b:

$\text{S-OH} + \text{LM} <===> \text{S-L-M}^{+} + \text{OH}^{-}$

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a solid solution on the surface of a pre-existent solid phase. The process is depicted as a continuum between adsorption reactions and precipitation. The presence of foreign species in the hydrated surface layer of a solid may cause the new material to grow as a solid solution rather than as a pure solid.

Under natural conditions, all of these sorption processes may potentially occur. Knowledge of system characteristics (e.g. pH, ligands) is required to determine which process controls the concentration of a given trace metal in solution. For example, most metals with a stable oxidation state (e.g. Zn and Cd) are normally undersaturated with respect to known solid phases in oxic, neutral to acidic, fresh-water lakes. Sposito (1986) states, however, that the control of aqueous trace metal concentrations in natural systems by precipitation should not be ignored even if undersaturation in the aqueous phase is observed with respect to pure solid phases. He supports this view by the uncertainty of solubility constants resulting from the unproven assumption of "unit activity" for natural solid phases. Iron and manganese are typical examples of dissolved trace metals controlled by precipitation as both metals form stable precipitates (oxyhydroxides of iron and oxides of manganese), under oxic conditions and over a natural pH range. According to Corey (1981) surface precipitation is, among other sorption processes, quite common. Farley et al.(1985) and Davis et al.(1987) also maintain that solid solutions are likely formed in surface films of a variety of solid substrates. The complex nature of aqueous natural particles suggests that the physical transport of trace metals in and between particles to interaction sites is an important step in the overall time-dependent sorption process.

Nevertheless, adsorption is generally regarded as the predominant sorption process of trace metal-particle interactions.

It has been proposed that trace metal interactions with natural solids are analogous to trace metal adsorption at a pure metal oxide-water interface in a well defined media. There are many similarities between natural solids and pure oxides. For instance, natural solids existing in an oxidized environment are either organic or mineral, and possess mostly oxygen bonds as electron donors (Leckie, 1986). It is also well recognized that organic materials and metal oxyhydroxides are of particular importance for binding trace metals (Jenne, 1968, 1977; Luoma and Davis, 1983). Coating of natural particles by organic matter and metal oxyhydroxides is believed to be responsible for many of the observed interactions.

Our current understanding of trace metal interactions with natural solids is mainly based on the principles of surface complexation; this approach was developed to characterize the trace metal interactions taking place at the oxide-solution interface. Unfortunately, analytical techniques have not been sufficiently developed to directly discriminate, qualitatively and quantitatively, the different types of trace metal interactions with natural heterogeneous solids.

1.4 PARTITIONING OF TRACE METALS:

The prediction of trace metal distribution among environmental phases (i.e. sediment, water, biota) is difficult because trace metals exist in different forms in water, the sediment is made up of a variety of solid components capable of binding trace metals, and different sorption processes may be simultaneously active.

As an attempt to model the tendency of trace metals to move from one environmental phase to another and to develop a national sediment quality criteria, the US Environment Protection Agency is currently considering the equilibrium partitioning approach (Shea, 1988). This approach requires the characterization of each trace metal interaction by a specific equilibrium constant (i.e. intrinsic sorption constant). The equilibrium partitioning model should eventually permit the prediction of the distribution of trace metals between sediment and water in a system under specific conditions.

The common way to describe the overall trace metal distribution between sediment and water is to measure their respective trace metal concentration. The following simplified association-dissociation reaction represents the overall sediment-water exchange of trace metals:

$$Me_w \leftrightarrow Me_s \tag{1.1}$$

where Me_w and Me_s represents a given trace metal in the liquid phase, and associated to the solid, respectively. The operational definition of these two phases is directly dependent on the method of separation applied.

It is also common to quantify the partitioning of a trace metal between sediment and water by a distribution coefficient (Kd). By definition, Kd is expressed as the ratio of the trace metal concentration associated with sediments ($\{Me_s\}$; mole/g) over the trace metal concentration in the ambient water ($[Me_w]$; mole/mL).

$$Kd\ (mL/g) = \frac{\{Me_s\}}{[Me_w]} \tag{1.2}$$

When applied to a batch sediment suspension, Kd is represented better in terms of the following measurable variables:

$$Kd = \frac{[Me_s]}{[Me_w]\ Cp} \tag{1.3}$$

and,

$$Kd = \frac{[Me]_T - [Me_w]}{[Me_w]\ Cp} \tag{1.4}$$

where $[Me_s]$ and $[Me_w]$ denote the trace metal concentration associated with solids and in water, in mole per volume of suspension (mole/mL), respectively. The total number of moles of trace metals per volume of suspension is represented by $[Me]_T$, whereas Cp is the weight of particles per volume of suspension (g/mL).

Kd's represent the trace metal partitioning between sediment and water under specific conditions. Many parameters are known to influence the trace metal distribution in sediment suspensions. For instance, ligands present in the liquid phase, pH of the solution, particle concentration and particle size are all involved in the solid-liquid distribution of metals. Kd values are directly affected by any change in the system conditions.

The surface complexation theory can predict the influence of some parameters on the change (or at least the direction of the change) of trace metal partitioning between solid and water. As an example, the acidity characterizing the adsorbent as well as the affinity of association characterizing the adsorbate are predictable. In addition, ionic strength, complexing ligands, and the competition of solutes for surface sites, can to a certain degree explain the sorption behaviour of trace metals. However, several adsorption conditions have been observed that are not currently accounted for by the surface complexation theory (Honeyman and Santschi, 1988). These conditions are: (1) surface heterogeneity of a pure solid phase, (2) particle concentration, (3) non additivity of multiple-adsorbent systems, and (4) slow sorption kinetics.

The equilibrium partitioning approach considered by the EPA (Shea, 1988) is based on the premise that: (1) a continuous exchange exist between the various solid components and trace metal forms, and (2) trace metal solid-liquid interactions are rapidly reach an equilibrium or steady state. In order to investigate the overall kinetics of trace metal interactions between sediment and water, radioactive trace metals are used. This approach allows one to control the experimental conditions while focusing on the solid-liquid exchange of trace metals. Thus, the addition of radioactive metals to one phase of the sediment suspension (e.g. water) would create an isotopic disequilibrium and initiate the redistribution of radiotracers between the phases. The change of trace metal radioactivity in solution as a function of time, based on the overall continuous trace metal exchange described by Equation 1.1, is expressed as follows:

$$\frac{d[Me_w^*]}{dt} = -\,k_f\,[Me_w^*] + k_r\,\{Me_s^*\} \qquad (1.5)$$

where asterisks denote radioactive species. Substitutions of $\{Me_s^*\}$ by $([Me^*]_T - [Me_w^*])/Cp$ (see Equations 1.2 to 1.4) and k_r/Cp by k'_r (see below) lead to:

$$\frac{d[Me_w^*]}{dt} = -\,k_f\,[Me_w^*] + k_r'\,([Me^*]_T - [Me_w^*]) \qquad (1.6)$$

where k_f and k'_r are the apparent overall first-order rate constants for the forward and reverse reactions, respectively. Units for k_f and k'_r are t^{-1}. Rate constants k_f and k'_r characterize the overall time-dependent exchange of radioactive trace metals in a sediment suspension. These conditional rate constants incorporate many other variables assumed to be constant (e.g. Cp in k'_r), and are specific to the system studied. The mathematical solution of Equation 1.6, when all radioactive trace metals, $[Me^*]_T$, are initially in the liquid phase, is:

$$[Me_w^*](t) = \frac{k_r^{'}\ [Me^*]_T}{k_f + k_r^{'}} + \left[\frac{k_f\ [Me^*]_T}{k_f + k_r^{'}}\ \exp^{-(k_f + k_r^{'})\, t} \right] \tag{1.7}$$

where t is the time.

Characterization of the time-dependent sorption process by k_f and k'_r has been the approach most often considered. For this reason, rate constants for a variety of different systems are available from the literature. Generally, a graph of trace metal radioactivity in solution versus time shows an exponential decrease until a minimum is reached. This time-dependent relationship has been interpreted as a pseudo first-order reversible reaction controlling the exchange process. Rate constants, k_f and k'_r characterize the rate of the overall exchange and define the final distribution of trace metals between solid and liquid.

Reversibility is considered in this work only as the recovery of masses between compartments in a specified time period. More specifically, it relates to the exchange of radiotracers between operationally defined solid and liquid phases.

1.5 TIME DEPENDENT INTERACTIONS:

Time-dependent trace metal interactions with natural solids have been presented in terms of a pseudo first-order reversible reaction without discussing the rate limiting step. There are at least three potential steps in the trace metal solid-solution interactions that can be rate limiting. These steps are: (1) the formation of reactive species in solution, (2) the transport of the species to the site of interaction, and (3) the interaction itself.

Metal species are known to reach an equilibrium or steady state ($t_{½}$ < minute) in the aqueous phase (e.g. Olson and Shuman, 1985). Thus, the rate of formation of reacting dissolved species is not expected to be the rate limiting step of the overall trace metal solid-solution interaction.

Physical displacement of trace metal species to reacting sites may occur via: (1) advection in the bulk solution, (2) film diffusion close to the particle, and (3) intra-inter particle diffusion. Recently, Leach (1989) showed that neither the transport of trace metals by advection nor film diffusion is the rate controlling step under the natural conditions of surface sediment resuspensions. Transport of trace metals inside the particle (intra) or between particles (inter) may, however, be the potential rate limiting step. The importance of intra-inter diffusion is related to physical factors such as: (1) size of particles, (2) porosity and tortuosity of the particles, (3) size and charge of diffusing species, and (4) structural arrangement between particles. Transport of trace metals in or between isolated minerals or a mixture of solid particles has been studied under different conditions (e.g. Jackman and Ng, 1986). Unfortunately, experimentation with surficial sediments under natural conditions is almost non-existent. In most of the studies, the natural sediments were drastically modified or the natural conditions were not appropriately represented.

The third potential rate limiting step is the sorption reaction of trace metal species with solid sites. The accumulation of trace metals by particles in natural systems involves the interaction of dissolved species and solid sites. The heterogeneous nature of sediment particles suggests that a variety of sites are available and a spectrum of affinity is offered for any given trace metal (Buffle et al. 1990). Consequently, a variety of reaction rates is expected between trace metals and sediment particles. In addition, interactions between particles (e.g. particle coagulation; Santschi, 1986, Honeyman et al. 1988) may lead to a redistribution of trace metals by increasing or reducing the number of available or readily accessible sites. Due to the fact that trace metal in solution are defined according to the method of solid-liquid separation, colloids are, to a certain extent, part of the liquid phase. This leads to an observed combined effect of both types of interactions. Interactions of dissolved species with sediment particles (e.g. adsorption) and interactions between particles (e.g. coagulation) are, in practice, difficult to separate.

Since kinetic processes are pathway dependent, it is essential to study the exchange rates of trace metals with sediments under representative conditions. Kinetic studies should be performed under the natural conditions of: (1) temperature, (2) total concentration of trace metals, (3) ionic strength, (4) pH, (5) concentration of solid in suspension representing common resuspension events, and should also include a natural variety of: (6) solids, (7) organic and inorganic ligands, and (8) competitive species. In addition, natural suspensions should not be pretreated by: (9) drying the sediment, (10) adding chemicals to buffer or sterilize the suspension, and (11) removing the smallest particles.

The best way to achieve these requirements is obviously to perform the kinetic studies directly in a natural system. This is not always possible as in-situ studies require infrastructures that are not always accessible. An alternative option is to bring natural sediment and water to the laboratory and use radiotracers to monitor the solute-solid exchange of trace metals as a function of time. Unlike the common addition of total metals, addition of radiotracers does not change the natural trace metal concentrations. This option is a promising avenue by which one may obtain representative kinetic data and develop time dependent relationships for trace metal sediment-water interactions.

1.6 OBJECTIVES:

A limited number of studies have used radiotracers to obtain kinetic data of trace metal exchanges between natural solid and water. Radiotracer techniques have been used mostly for seawater suspensions. Kinetics of radiotracer sediment-water exchanges using a sequential uptake and release technique have never been investigated. The advantages and limits of the radiotracer approach are not well documented.

This work attempts to demonstrate that under controlled experimental conditions, the sequential uptake and release technique using radiotracers offers an excellent approach to study kinetics of trace metal exchanges occurring in freshwater systems.

In addition, this work examines specifically the kinetic behaviour of radioactive trace metals (^{65}Zn and ^{109}Cd) in their interactions with surficial lake sediments. Time-dependent interactions are investigated in order to demonstrate that long-term "equilibrium" distribution coefficients obtained from total trace elements do not appropriately represent short-term (weeks or less) trace metal partitioning between sediment and water.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 STUDY AREA, SAMPLING, AND PREPARATION:

The aquatic systems studied (Harp Lake, Rabbit Bay from Lake of Bays, and St-Nora Lake) are located in southern Ontario in the counties of Muskoka and Haliburton approximately 250 km north of Toronto and 200 km southeast of Sudbury. These cities are the closest centres of industrial activity.

The three lakes are situated within the Canadian Shield (Precambrian). Their waters are characterized by a weak capacity to buffer acidity. Evans et al.(1983) have suggested that atmospheric deposition is the major source of zinc and cadmium to these dimictic lakes.

Sediment and water samples were collected on three occasions. In March 1988 and in March 1989, Harp Lake was the only lake sampled; at this time of the year Harp Lake was ice covered. In 1989, the three lakes were sampled in early summer (June), approximately 2 months after spring melt. Sampling stations are shown in Figure 2.1 for the freshwater lakes investigated.

Similar sampling procedures were used in both winter and summer. In winter, a hole was dug through the ice cover at the sampling stations whereas in the summer, an inflatable boat was used to reach the sampling stations. The natural

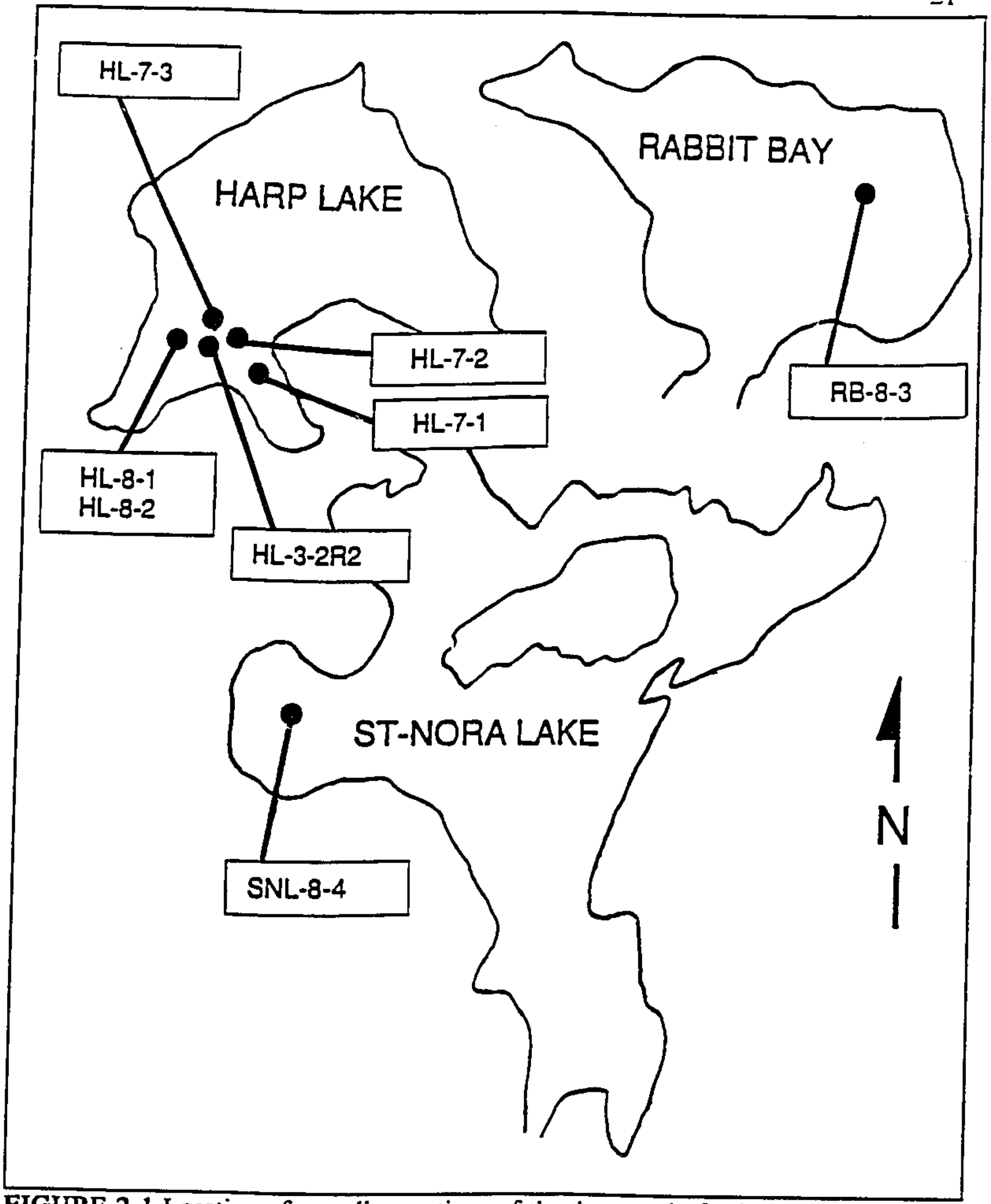

FIGURE 2.1 Location of sampling stations of the three study freshwater lakes.

Harp Lake	(45 23' N, 79 08' W)
Rabbit Bay	(45 15' N, 79 00' W)
St-Nora Lake	(45 10' N, 78 50' W)

sediments and the overlying water were collected using an Ekman grab sampler (20 cm X 20 cm) and a Van-Dorn bottle (3 or 6 litres), respectively. The water, collected within one meter above the sediment, was immediately filtered (in-situ) through a 100 μm nylon membrane and kept in the dark (in opaque plastic bags) at a low temperature (in a cooler with ice or snow). Some filtered water was used to rinse the vessels which were used in the preparation of the concentrated mixture of sediments. The top lake sediments were sampled with a grab sampler from which the overlying water was slowly drained out. A thin oxic layer (i.e. 2 mm) was scrapped from the surface sediments with a plastic spatula and passed through a coarse sieve in order to remove the bigger particles ($>$ 0.5 mm). Filtered natural water previously transferred in a wash bottle was used to dilute the surface sediment and to accelerate the sieving. The finest size fraction of the mixture ($<$ 100 μm) was generally isolated by differential settling and transferred into another bottle. The concentrated sediment mixture ($\approx$ 1 g/L) was used as a sediment source in order to prepare the experimental suspensions. A final dilution was performed, in the laboratory, using the sediment source and the filtered ($<$ 100 μm) natural water. A two litre suspension was prepared for each kinetic experiment.

Between 12 and 24 hours were allowed for each suspension to equilibrate under experimental conditions (i.e. temperature, light, and agitation) before beginning a kinetic experiment. When a longer period of time was allowed prior to commencing the experiment, the suspension was considered "aged". Table 2.1 reports the general sampling and preparation characteristics of the suspensions investigated.

TABLE 2.1 Sampling and preparation of freshwater sediment suspensions.

Suspension	Sampling date	Aquatic system	Sampling depth (m)	pH of the suspension
HL-3-2R1	March '88	Harp Lake	12	6.68
HL-3-2R2	March '88	Harp Lake	12	6.56
HL-7-1	March '89	Harp Lake	3	6.80
HL-7-2	March '89	Harp Lake	10	6.73
HL-7-3	March '89	Harp Lake	15	6.76
HL-8-1	June '89	Harp Lake	16	6.75
HL-8-2	June '89	Harp Lake	16	6.78
RB-8-3	June '89	Rabbit Bay	13	6.70
SNL-8-4	June '89	St-Nora Lake	15	6.70

Suspension	Particle concentration (mg/L)	Maximum particle size (mm)	Experiment duration (d)	Suspension condition
HL-3-2R1	≈ 250	1.0	0.44	Aged
HL-3-2R2	≈ 250	1.0	17	Aged
HL-7-1	70	0.1	14	Fresh
HL-7-2	75	0.1	14	Fresh
HL-7-3	75	0.1	14	Fresh
HL-8-1	55	0.1	12	Fresh
HL-8-2	55	0.1	12	Fresh
RB-8-3	55	0.1	12	Fresh
SNL-8-4	55	0.1	12	Fresh

2.2 CHARACTERIZATION:

2.2.1 LIQUID PHASE:

Three categories of suspensions were investigated: (1) Harp Lake represents suspensions HL-3-2R1, HL-3-2R2, HL-7-1, HL-7-2, HL-7-3, HL-8-1, HL-8-2; (2) St-Nora Lake represents suspension SNL-8-4 and (3) Rabitt Bay represents suspension RB-8-3. Table 2.2 shows the overall aquatic chemistry for each category of the study suspensions. Each value reported in Table 2.2 represents the average of at least three subsamples from a given kinetic experiment. Additional results reported by Tessier et al. (1987) are shown in parentheses.

Readings of pH were obtained from a Dual Channel pH meter (IDG-8800) with a combined pH electrode (Orion model 13-641-817) coupled to a computer. Due to the fact that pH readings of natural water tend to drift over time, pH values are recorded automatically (computer program) until the slope of the change in pH is smaller than .01 pH unit/minute. Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were analyzed with a Dorhmann Carbon Analyzer (DC-80, UV lamp and IR detector). Major anions, $SO_4^{=}$ and Cl^- were analyzed by ion chromatography using a Wescan Ion Analyzer (conductivity detector) and a Vydac 302 IC column (250 mm X 4.6 mm). Zinc was analyzed from acidified samples (0.1% HNO_3) by flameless atomic absorption spectrometry (Perkin Elmer 2380, graphite furnace HGA-400, auto sampler AS-40, deuterium background correction).

TABLE 2.2 Characteristics of the liquid phase for each category of suspensions studied by kinetic experiments. Values in parentheses are from Tessier et al. (1987).

Parameter	Harp Lake[a]	Rabbit Bay	St-Nora
pH	6.56-6.80 (7.0)	6.70 (6.9)	6.70 (6.8)
DOC (mg/L)	3.6-3.9 (7.12)	2.5 (5.55)	2.9 (5.65)
DIC (mg/L)	0.85 (2.66)	0.95 (1.80)	0.70 (1.88)
Ca (mg/L)	----- (2.3-2.5)	----- (2.2-2.4)	----- (2.5-2.6)
Na (mg/L)	----- (0.90-0.99)	----- (1.2-1.3)	----- (1.0)
Mg (mg/L)	----- (0.75-0.80)	----- (0.61-0.63)	----- (0.78-0.85)
K (mg/L)	----- (0.27-0.39)	----- (0.20-0.27)	----- (0.27-0.39)
SO_4 (mg/L)	7.5-7.7 (6.4)	8.0 (6.2)	7.2 (7.4)
Cl (mg/L)	1.4-1.5 -----	3.84 -----	2.76 -----
Zn (μg/L)	3-3.5 (1.5-2.4)	2.3 (1.7-2.5)	----- (1.5-1.8)
Cd (μg/L)	----- (0.015)	----- (0.0076)	----- (0.011)
Fe (mg/L)	----- (25)	----- (29)	----- (13)

[a] samples collected in 1989 exclusively.

Pyrocoated graphite tubes were used with L'vov platforms. Results were determined from a calibration curve, the precision was within 10%, and the accuracy was confirmed by analysis of reference materials (SLR-1 from NRC and 1643b from NBS, after dilution).

2.2.2 SOLID PHASE:

Characterized solid phases were from the sediment sources used to prepare the final suspensions that serve in the kinetic experiments. The liquid was removed after the particles had settled. At this point, the wet solid was oven dried at 110 °C over night, cooled in a desiccator and transferred to a plastic vial. Correction for trace metals in the liquid phase was not necessary. The zinc content of sediments was determined after digestion-dissolution of the solids. The digestion procedure is described thoroughly in Table 2.3. Zinc concentrations were measured by flameless atomic absorption spectrometry, as described above, after the appropriate dilution. Reference sediments were also digested and analyzed along with the natural sediments investigated. Table 2.4 reports the analytical results. It was necessary to correct the results for an incomplete digestion based on a systematic bias (-17% ± 2%) observed in the results of three reference sediments according to their certified values (MESS-1 and BCSS-1 from NRC and 1646 from NBS). An independent analysis by X-ray fluorescence spectrometry of sediment sample HL-M'88 validated the correction (see Table 2.4). Cadmium results were judged to be unreliable because of the low content

TABLE 2.3 Procedure of digestion-dissolution of sediments.

---

a) Weigh precisely, approximately 200 mg of a dry sediment;
b) Transfer the solid to a 50 mL teflon dissolution vessel (Parr model #4745);
c) Add 5 mL of concentrated HF;
d) Seal the dissolution vessel, enclose it in its steel jacket, and place in an oven at 130°C for 48 hours;
e) Remove the steel jacket from the oven and let it cool at room temperature for about 1 hour;
f) Retrieve the teflon dissolution vessel from the steel jacket, wipe the dust from the outside, place on a hot plate at 90°C until the solution is dried;
g) Cover the hot plate with a plastic shield to avoid contamination by falling dust particles;
h) Remove the beaker from the hot plate and let it cool at room temperature;
i) Add 5 mL of concentrated HF and few drops of concentrated HNO_3;
j) Repeat steps (d) to (h);
k) Slowly add 5 mL of H_2O_2 30% to the teflon dissolution vessel;
l) When the reaction is completed, add an additional 5 mL of H_2O_2 and put the teflon dissolution vessel on the hot plate at 90°C;
m) Cover the hot plate with the plastic shield;
n) After approximately one hour, turn off the hot plate and leave the beaker on the hot plate over night;
o) Turn on the hot plate at 90°C and evaporate the solution;
p) Remove the beaker from the hot plate and let it cool at room temperature;
q) Add 5 mL of concentrated HCl;
r) Seal the dissolution vessel, enclose it in its steel jacket, and place in an oven at 130°C for 24 hours;
s) Remove the steel jacket from the oven and let it cool at room temperature for about 1 hour;
t) Retrieve the teflon dissolution vessel from the steel jacket, wipe the dust from the outside, then put it on a hot plate at 90°C until formation of a mush;
u) Cover the hot plate with a plastic shield to avoid contamination by falling dust particles;
v) Transfer the mush to a 25 mL volumetric flask;
w) Fill to 25 mL with 1.25 M HCl.

TABLE 2.4 Characteristics of sediments used to prepare experimental suspensions.

Suspension	[Zn] (µg/g)	[Zn][d] (µg/g)	[Cd][de] (µg/g)
HL-March '88[a]	229[c]	57	1.25
HL-7-1	172		
HL-7-2	188		
HL-7-3	145		
HL-June '89[b]	168		
RB-8-3	181	68	0.94
SNL-8-4	141	105	0.85

a suspensions HL-3-2R1 and HL-3-2R2.
b suspensions HL-8-1 and HL-8-2.
c 234 µg/g from XRF analysis.
d summation of all fractions from sequential extraction (Tessier et al., 1987).
e addition of 0.25 µg/g to compensate for the limit value of < 0.5 µg/g from the residual fraction.

of total cadmium in these sediments, the limited size of the samples, and the relative high concentration of Cd found in the blanks. Table 2.4 is augmented by the analytical results of total Zn and Cd in oxic sediments from the same lakes, reported by Tessier et al. (1987).

The particle size distribution of selected suspensions was also determined. Particles were separated by gravity using a settling technique. Subsamples were taken at predetermined times after the beginning of the settling sequence. Five particle size intervals were calculated from the Stoke's law, assuming the average density of particles to be 2.6 $g.cm^{-3}$. Figure 2.2 shows the particle size distribution of samples HL-7-1, HL-7-2 and HL-7-3.

2.3 RADIOTRACER TECHNIQUE:

Radiotracer techniques are widely used in science and frequently in kinetic experiments (Evans and Muramatsu [Eds.], 1977). By the use of radioactive isotopes, it is possible to follow the exchange of trace metals among different physical states. Such exchange occurs whether or not labelled material is present but can be detected only when one phase (physical state) differs in isotopic composition from the other.

If a radioactive form, Me^*, of a trace metal Me is added to the liquid phase of a suspension where the trace metal concentration in solution, Me_w, is assumed to be at sorptive equilibrium with the trace metals associated to the solid phase, Me_s, then Me_w^* would exchange with Me_s according to the following equation:

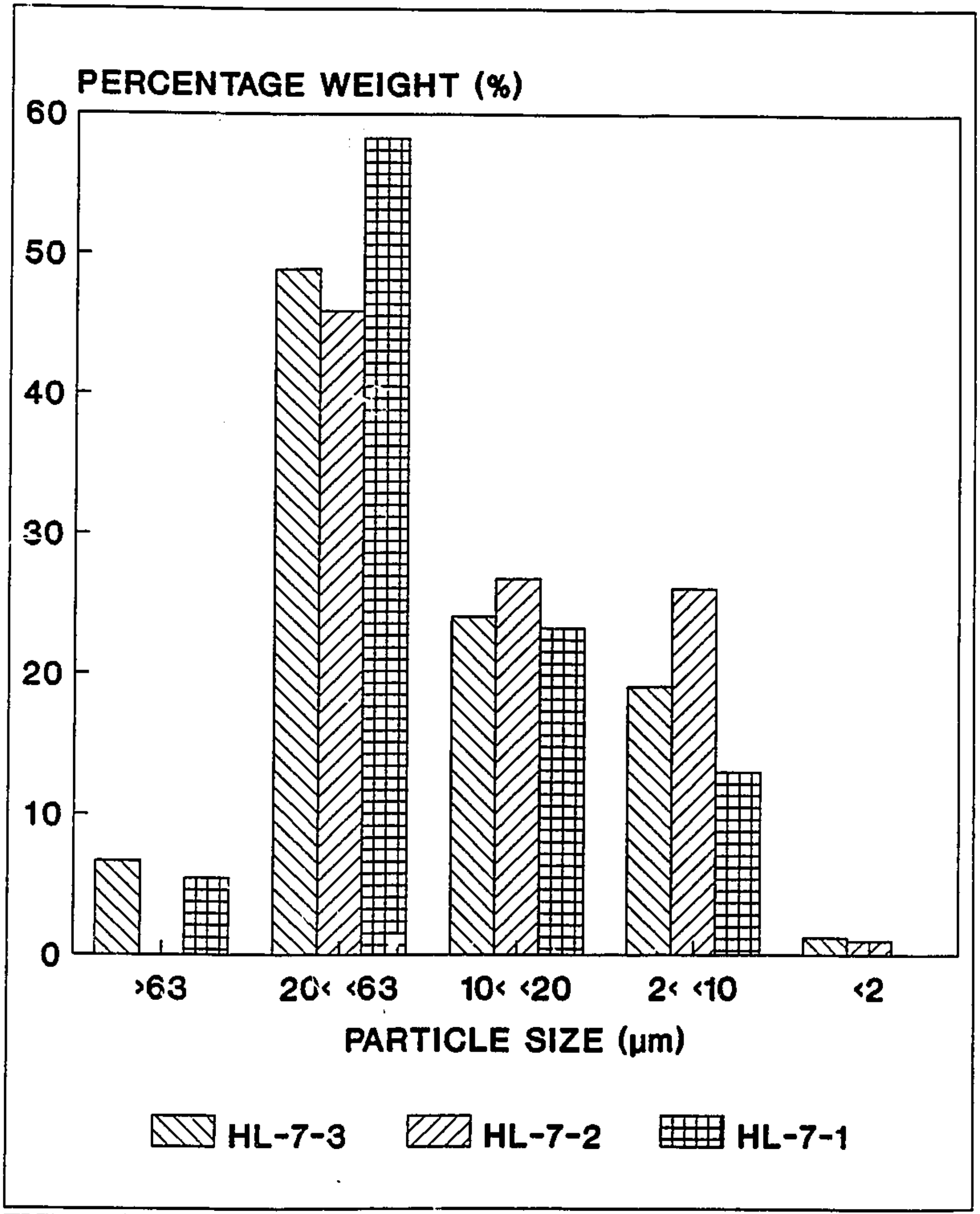

FIGURE 2.2 Particle size distribution of sediment suspensions HL-7-3, HL-7-2 and HL-7-1.

$$Me_w^* + Me_s \rightleftharpoons Me_w + Me_s^* \tag{2.1}$$

The monitoring of Me_w^* over time provides the necessary information to evaluate the rate of trace metal exchange under experimental conditions. The summation of Equation 1.1 and Equation 2.1 leads to:

$$Me_w^* \rightleftharpoons Me_s^* \tag{2.2}$$

The distribution of radioactive species is defined in the following manner:

$$Kd^* = \frac{\{Me_s^*\}}{[Me_w^*]} = \frac{[Me_s^*]}{[Me_w^*]\ Cp} \tag{2.3}$$

At time approaching infinity, Kd^* is expected to approach Kd since radioactive trace metals, Me^*, and non radioactive trace metals, Me; are expected to reach an identical distribution. Therefore, the following equality should be verified:

$$Kd = Kd^* = \frac{[Me_s]}{[Me_w]\ Cp} = \frac{[Me_s^*]}{[Me_w^*]\ Cp} \tag{2.4}$$

In principle, one can determine Kd* values for a variety of elements in a given sediment suspension by using a set of radiotracers. Artificial radioisotopes are particularly convenient because of their quasi non-existence in nature. Artificial radiotracers such as ^{65}Zn and ^{109}Cd are available in solutions of high specific activities. The technique consists of measuring the distribution of a small radiotracer spike between sediment and aqueous phase over time. The tracer radioactivity must be high enough to permit reliable radioactivity counting. The suspensions investigated in this study (Table 2.1) are separated in the following series:

series A: HL-3-2R1; HL-3-2R2
series B: HL-7-1; HL-7-2; HL-7-3
series C: HL-8-1; HL-8-2; RB-8-3; SNL-8-4

Table 2.5 reports the net addition of zinc and cadmium (total elements) to each suspension series based on the average aqueous concentration of Zn (2 μg/L) and Cd (0.01 μg/L) in sediment suspensions (Table 2.2). For series B and C, the final zinc concentrations are practically unchanged whereas final cadmium concentrations have increased by 40%. The change in the total zinc concentration resulting from the addition of radiotracers is more important for series A. The effect of an increase of total element concentrations on rate constants is further discussed in Section 3.2.2.

In this study, a radiotracer technique was used to evaluate the exchange rate of trace metals between the solid and liquid phases in freshwater sediment

TABLE 2.5 Change in total concentration of trace metals from addition of radiotracers.

Series	Reported specific activity (μCi/μg)	Amount net added per litre of suspension (μCi/L)	Addition of total trace metal (μg/L)	factor of increase[a] (%)
Zinc				
Series A	9.49	20	2.1	105
Series B	890	10	0.012	0.6
Series C	890	10	0.012	0.6
Cadmium				
Series B	1100	4	0.004	40
Series C	1100	4	0.004	40

[a] compared to 2 μg/L of Zn and 0.01 μg/L of Cd (see text).

suspensions. The general approach is briefly outlined:

- 1- a sediment suspension is prepared, generally ≈ 70 mg/L;
- 2- radiotracers (^{65}Zn and ^{109}Cd) are added in their aqueous forms;
- 3- the suspension is continuously agitated at constant temperature in a cold room;
- 4- the suspension is subsampled at designated time intervals during the experiment;
- 5- for each subsample taken, the liquid phase is immediately separated from the rest of the suspension by centrifugation;
- 6- the radioactivity of a specific volume of the liquid phase is counted.

This approach produces "adsorption" kinetic data of radiotracer exchange. The decrease of radioactivity in the liquid phase reflects the uptake of radiotracers by the solid phase.

In certain experiments, a few additional steps complete this procedure:

- 7- about 6 days after the beginning of the experiment the agitation is stopped and the suspended particles are allowed to settle over night (≈ 15 hours);
- 8- about 4/5 of the overlying water is removed and replaced by an equivalent volume of freshwater without radiotracers.

These steps initiate the release of radiotracers by the solid phase. This approach is needed to properly assess forward and reverse rate coefficients. Steps 4, 5 and 6 from the first part of the technique are repeated in the second part of the technique in order to get "desorption" kinetic data of radiotracer exchange. Figure 2.3 shows the sequential steps required to obtain "adsorption and desorption" kinetic data with the radiotracer technique.

All subsamples are analyzed for activity by gamma spectroscopy using either a germanium (Li) coaxial detector interfaced to a Canberra Series 40 multichannel analyzer or a sodium iodide (Tl) scintillation detector (CompuGamma Counter, model 1282). The data are expressed relative to the total radioactivity initially added to the suspension liquid phase. The counts are not corrected for geometry effects or radioactive decay since: (1) a unique counting technique is used for all the subsamples of a given experiment, and (2) the counting is performed over a short period of time relative to the half-live of each radiotracer. The technique is particularly appropriate to determine rate constants of exchange characterized by half-lives in the order of hours to days.

2.4 EXPERIMENTAL CONSIDERATIONS:

2.4.1 NATURAL CONDITIONS:

In order to maximize the stability of the natural suspensions in

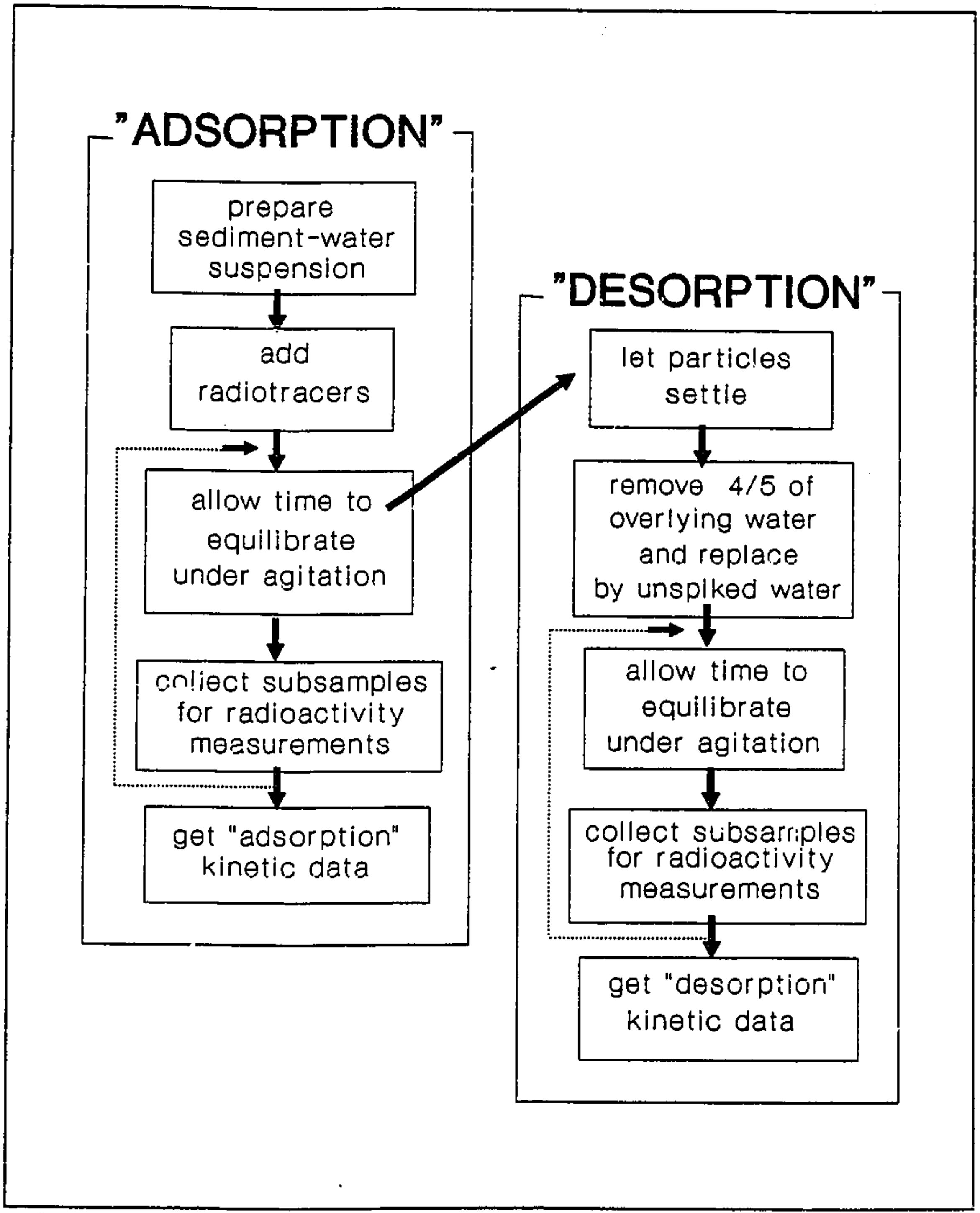

FIGURE 2.3 Sequential steps involved in obtaining "adsorption" and "desorption" kinetic data with the radiotracer technique.

laboratoryexperiments, the following criteria were considered:

(1) the stations sampled are deep enough to ensure that no light reaches them.

Table 2.1 shows that all the samples but one are taken from a minimum depth of 10 meters. Sample HL-7-1 is the only exception, the sampling at that station was done in March after 3-4 months of darkness were provided by the ice cover. In order to reproduce natural conditions, all the samples were kept in the dark in either a cooler, a refrigerator or a cold room. In all experiments, suspensions were exposed to light only when diluting or subsampling. With the exception of one suspension, all the others were kept in the dark for about 99% of the time every day. Due to an intensive subsampling sequence, suspension HL-3-2R1 was exposed to light more frequently.

(2) the water temperature at sampling stations is as low as possible but above the freezing point.

Water temperature of stations sampled in winter was approximately 4°C. Water samples collected in summer were at a slightly higher temperature. In both cases, great care was taken to avoid changing the original temperature of samples. Table 2.6 reports the experimental temperature range. The lower limit (3°C) corresponds to stations sampled in winter whereas the upper limit (8.5°C) reflects stations sampled in summer. When considered individually, the variation of temperature within a single experiment does not exceed ± 1°C, with very few exceptions; each temperature value is precise at ± 0.5 °C. Figure 2.4 shows the

TABLE 2.6 Experimental conditions of kinetic experiments.

Suspension	Temperature °C	Separation technique	Agitation	Experimental step(s)
HL-3-2R1	3-5	filtration	frequent	adsorption
HL-3-2R2	3-5	filtration	periodic	adsorption
HL-7-1	7-8	centrifugation	continue	adsorption/desorption
HL-7-2	7-8	centrifugation	continue	adsorption/desorption
HL-7-3	7-8	centrifugation	continue	adsorption/desorption
HL-8-1	7.5-8.5	centrifugation	continue	adsorption
HL-8-2	7.5-8.5	centrifugation	continue	adsorption/desorption
RB-8-3	7.5-8.5	centrifugation	continue	adsorption/desorption
SNL-8-4	7.5-8.5	centrifugation	continue	adsorption/desorption

Suspension	Dilution factor	Radiotracer(s)	Suspension condition	Counting technique
HL-3-2R1	none	Zn-65	natural	Ge(Li)
HL-3-2R2	none	Zn-65	natural	Ge(Li)
HL-7-1	0.1425	Zn-65/Cd-109	natural	NaI(Tl)
HL-7-2	0.2134	Zn-65/Cd-109	natural	NaI(Tl)
HL-7-3	0.1591	Zn-65/Cd-109	natural	NaI(Tl)
HL-8-1	none	Zn-65/Cd-109	natural	NaI(Tl)
HL-8-2	0.2590	Zn-65/Cd-109	natural	NaI(Tl)
RB-8-3	0.1447	Zn-65/Cd-109	natural	NaI(Tl)
SNL-8-4	0.1027	Zn-65/Cd-109	natural	NaI(Tl)

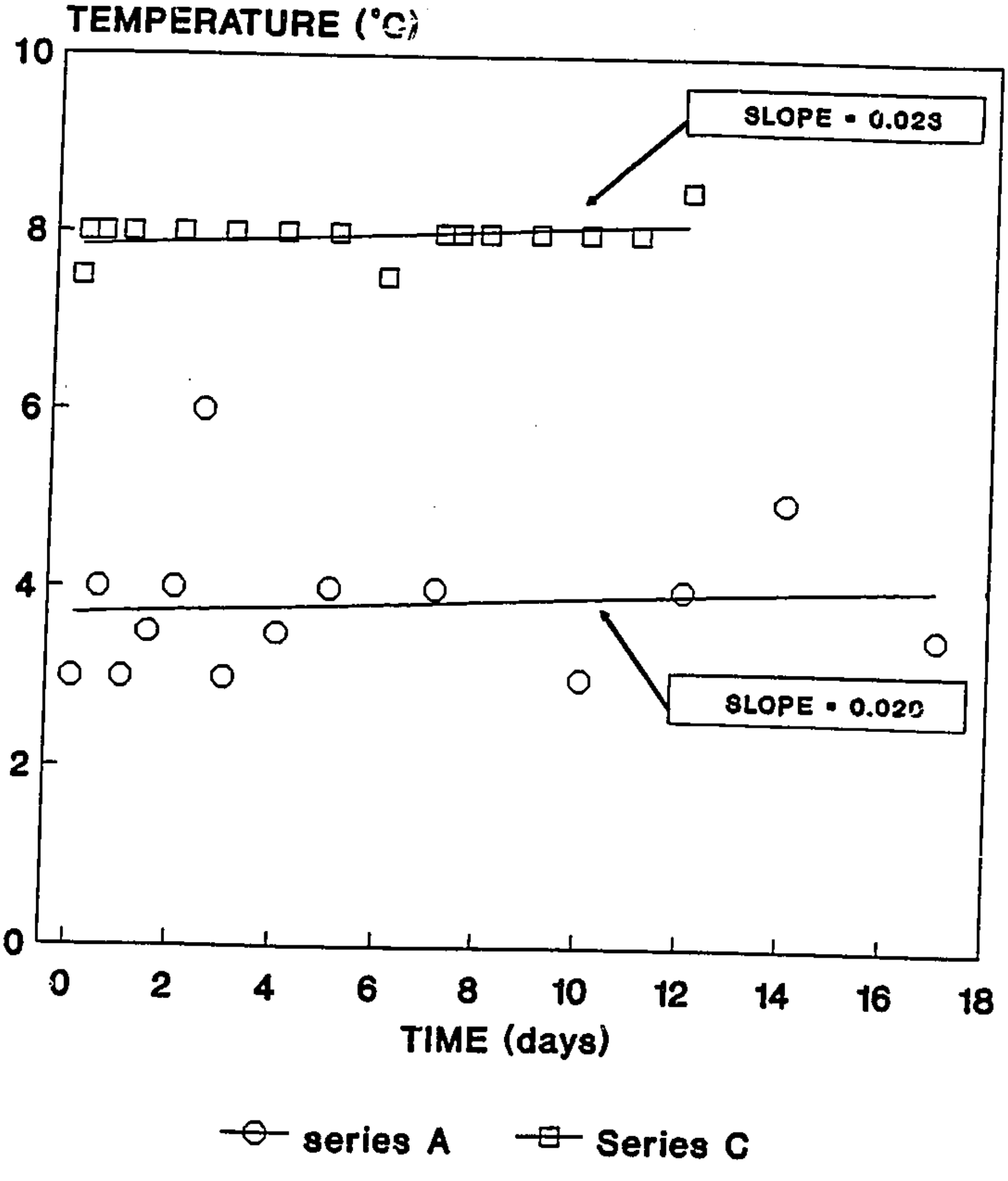

FIGURE 2.4 Temperature variation in two series of kinetic experiments.
series A: HL-3-2R1; HL-3-2R2
series C: HL-8-1; HL-8-2; RB-8-3; SNL-8-4

temperature range of two of the three series of experiments. For clarity, series B is not shown; but essentially it expresses similar variations of temperature over the length of the experimentation. The experimental temperature was representative of natural conditions at sampling time. Low temperatures and no light slow down the biological activity that may in turn alter the natural conditions (e.g. oxic versus anoxic conditions).

(3) only the oxic layer of surficial sediment is collected in order to avoid further oxidation.

A careful sampling procedure is required to make sure that only the thin oxic layer of surficial sediment is collected. Tessier et al.(1987) have recently reported sediment porewater profiles of many dissolved trace metals for the three lakes investigated in this study. These results suggest that the thickness of the oxic layer, where the concentration of trace metals in the porewater is very similar to the concentration in the overlying water, is approximately 1 cm.

(4) the optimum range of particle sizes subject to a resuspension experiment is considered.

In certain experiments, the largest particle diameter is in the range of 1 mm, but in most experiments particles are smaller than 0.1 mm. Small particles are obviously the focus of consideration as they are easily resuspended and certainly the most active in terms of surface reactions. The fraction < 63 μm has been recommended by many authors (e.g. Förstner and Salomons, 1980; de Groot et al., 1982). The maximum particle size in most of the following experiments is close to the suggested limit (Table 2.1, Figure 2.2).

2.4.2 LABORATORY CONDITIONS:

Certain factors must be accounted for in order to simultaneously reproduce specific conditions representative of the natural environment, and make the experimentation feasible. These factors include: (1) solid concentration of the suspension, (2) agitation of the suspension, and (3) separation of solid and liquid phases.

(1) Solid concentration of the suspension:

Experiments performed in the laboratory are designed to represent resuspension events. In such an event, the particle concentration in water may be highly variable. Assuming that about 99% (weight) of the surficial sediment is water, one obtains a particle concentration in the order of 10 g of dried solid per litre of suspension. On the other hand, suspended particle concentrations in the water column of a lake are generally in the order 1 mg/L. This range covers four orders of magnitude.

The selection of the particle concentration is based on the specific sorption behaviour of Zn and Cd. For particles smaller than 100 μm, at a particle concentration of approximately 70 mg/L, the removal of trace metals from the solution is always within the range of 30% to 80% for the study suspensions. An adequate distribution of trace metals in sediment suspensions also reduces the contamination of one phase by another during the separation process.

(2) Agitation of the suspension:

The type and strength of agitation applied to the natural suspensions in the laboratory must be specified. The two extreme situations which may exist are: (1) without agitation, and (2) under very strong agitation keeping the suspension completely homogeneous. In order to simulate a resuspension event, static systems cannot be considered. The best simulation would occur under conditions where sediments are periodically resuspended.

Two agitation options are considered. In the first, the suspension is hand shaken at the same frequency that subsamples are taken. Each agitation lasts only a few minutes, just enough to homogenize the mixture. The second option provides a continuous gentle agitation to the mixtures by a roller mill. Prior to the subsampling, the suspension is hand shaking in a similar manner to the first method. Figure 2.5 shows the apparatus designed to keep the sediment suspensions under gentle agitation. Bottles are allowed to rotate on their side at a frequency of 5.3 revolutions per minute for a 2 litre bottle (diameter = 120 mm); and at a frequency of 7.1 revolutions per minute for a 1 litre bottle (diameter = 90 mm). This method of gentle agitation does not, however, keep the suspension homogeneous; the heaviest particles are

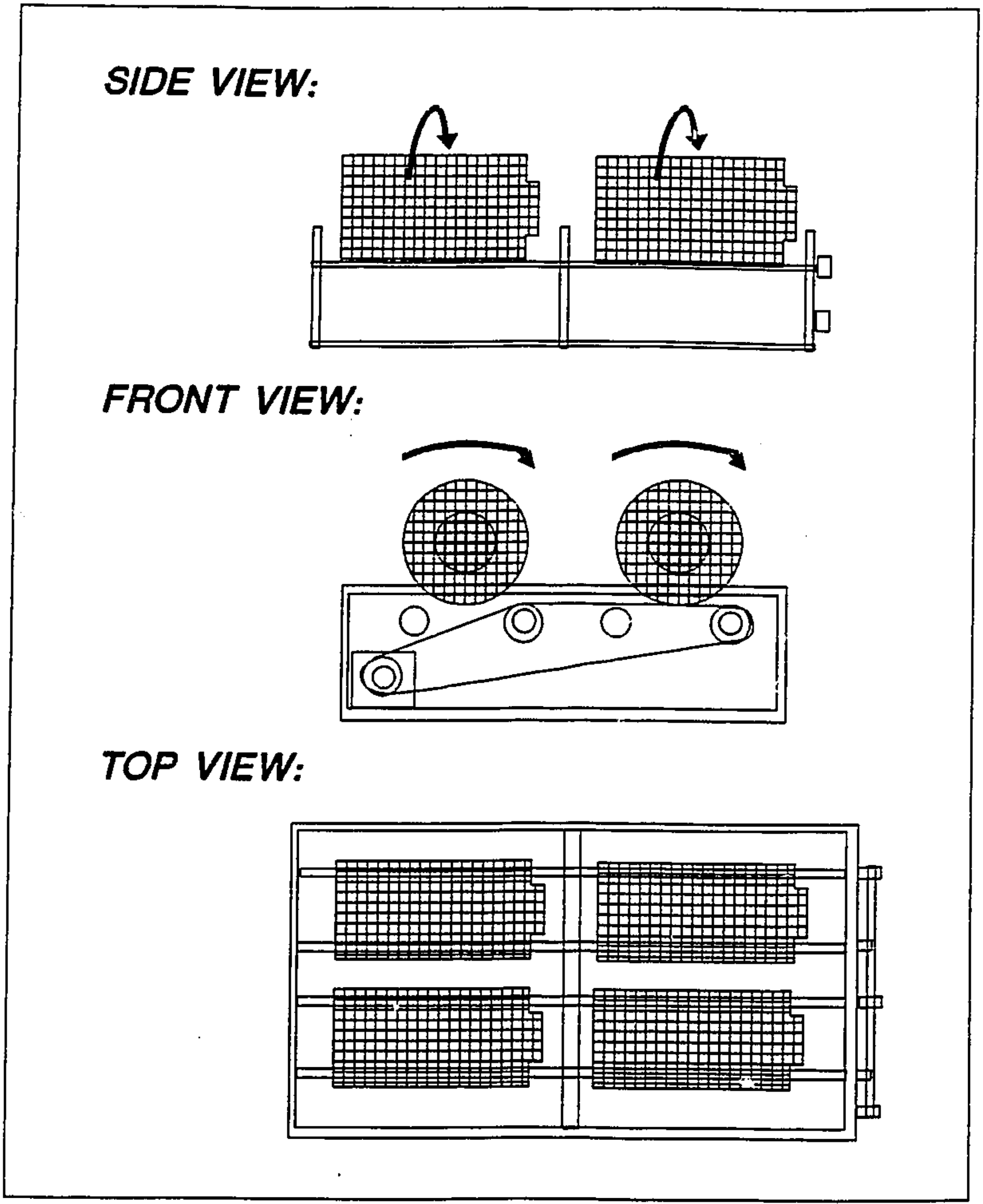

FIGURE 2.5 Side, front and top view of the roller mill used to keep particles in suspension.

concentrated in the bottom portion of the bottle. Nevertheless, this method is believed to reproduce the natural movement of particles better than a vigorous agitation.

Under periodic hand shaking agitation, the diffusive film surrounding particles is expected to be significant. By increasing the frequency of agitation, the average thickness of the surface film is reduced leading to a faster rate of radiotracer exchange. Short-term trace metal-sediment exchanges are presented in Figure 2.6 for two frequencies of hand shaking agitation. Results show a difference in the rate of zinc transfer, suggesting that the transfer is controlled by transport of metals across the film. If the transport of metals is the limiting step in the exchange, then trace metal interactions with solid sites are expected to be fast. This is consistent with the fast adsorption reactions reported between trace metals and metal oxides (Yasunaga and Ikeda, 1986). Another potential explanation of the difference of trace metal transfer rates between solid and liquid phases may be the change in particle sizes caused by agitation. This possibility is further discussed in section 2.5.

(3) separation of solid and liquid phases:

There are many methods that isolate the liquid phase from a suspension. Among them, centrifugation and filtration separation techniques were investigated. In each method, 5 mL (filtrate or supernatant) were collected for counting and trace metal analysis and another 10 to 15 mL were used for other measurements (e.g. pH, DOC). As this study predominantly used the centrifugation technique, only it is thoroughly described.

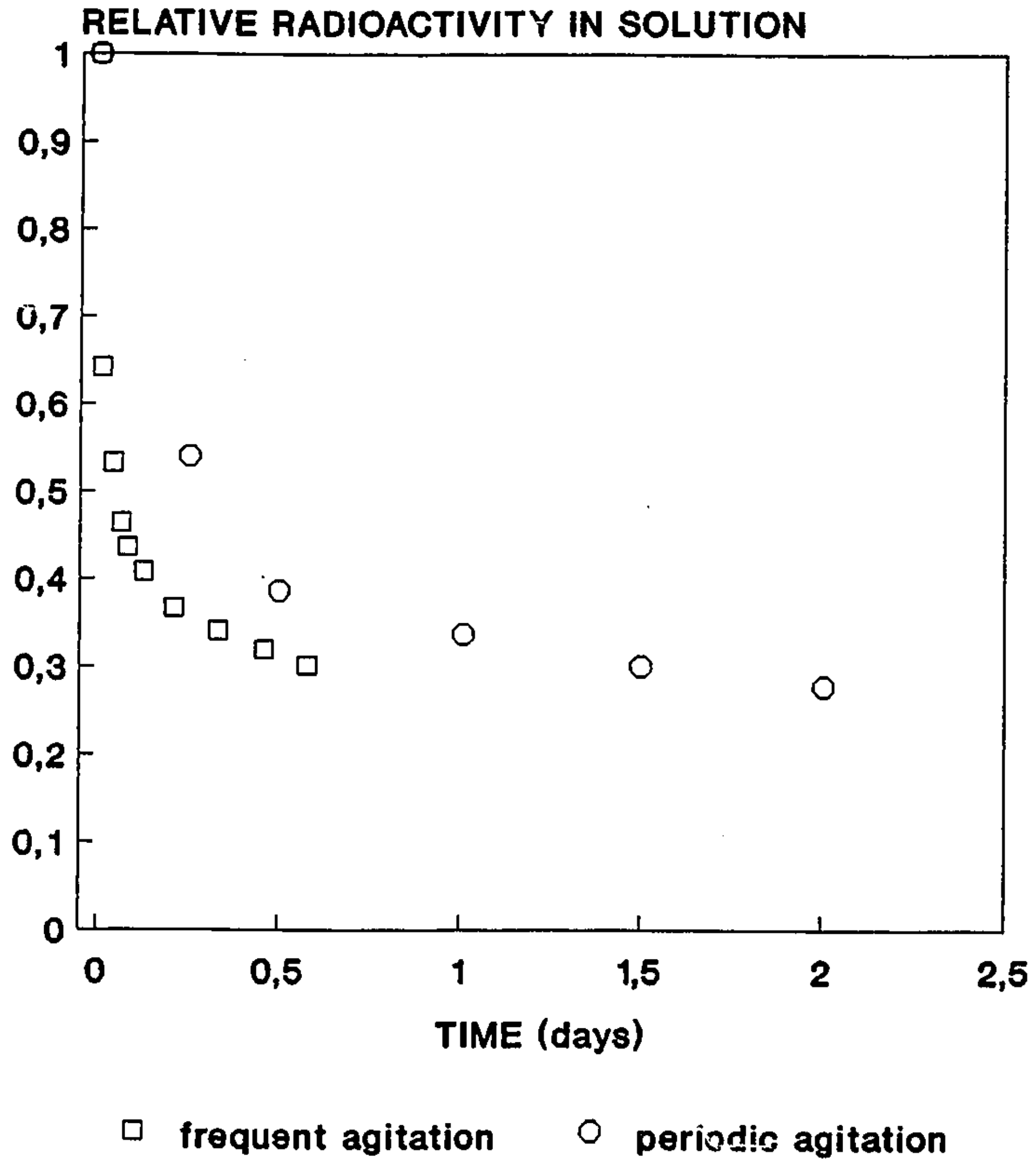

FIGURE 2.6 Effect of the frequency of hand shaking agitation on the general "adsorption" kinetic data of dissolved ^{65}Zn with a surficial sediment.

A centrifugation technique is applied to separate the liquid phase from the surface sediment particles. The centrifuge machine used is a SORVALL model RC2-R and a rotor (SS-34) with a capacity of eight centrifuge tubes. The apparatus possesses a temperature control set in the range of 2-8°C. The centrifugation sequence is presented in Table 2.7. The complete centrifugation procedure is described as follows:

(1) each centrifuge tube receives a subsample of the suspension investigated;
(2) a cap with a small hole in the middle is fitted to each tube;
(3) centrifuge tubes are weight balanced and placed in opposite positions in the rotor;
(4) the centrifugation sequence is then started (Table 2.7);
(5) when the rotor is immobilized, 5 mL of supernatant are collected by suction in a teflon vial;
(6) each centrifuge tube is removed and 10-15 mL of supernatant are decanted into a plastic vial.

The pretreatment of centrifuge tubes and plastic vials is described in detail in section 2.4.3.

Step (5) is crucial and demands additional explanation. As shown in Figure 2.7 a small tube is inserted in the centrifuge tube at a given depth defined by the guide cap. Vacuum is applied to transfer the undisturbed supernatant in the teflon vial. Between each transfer, the tubing line is sequentially washed; first with HNO_3 (10%),

TABLE 2.7 Sequence of steps in centrifugation.

1- The speed is first set to 5 000 RPM;

2- When the rotor reaches 5 000 RPM, the speed is increased to 10 000 RPM;

3- When the rotor reaches 10 000 RPM, the speed is increased to 12 500 RPM;

4- When the rotor reaches 12 500 RPM, the speed is increased to 15 000 RPM;

5- The timer is set at 20 minutes;

6- When the time is elapsed, the rotor is forced to stop by auto-breaks;

7- It takes about 10 minutes to immobilize the rotor.

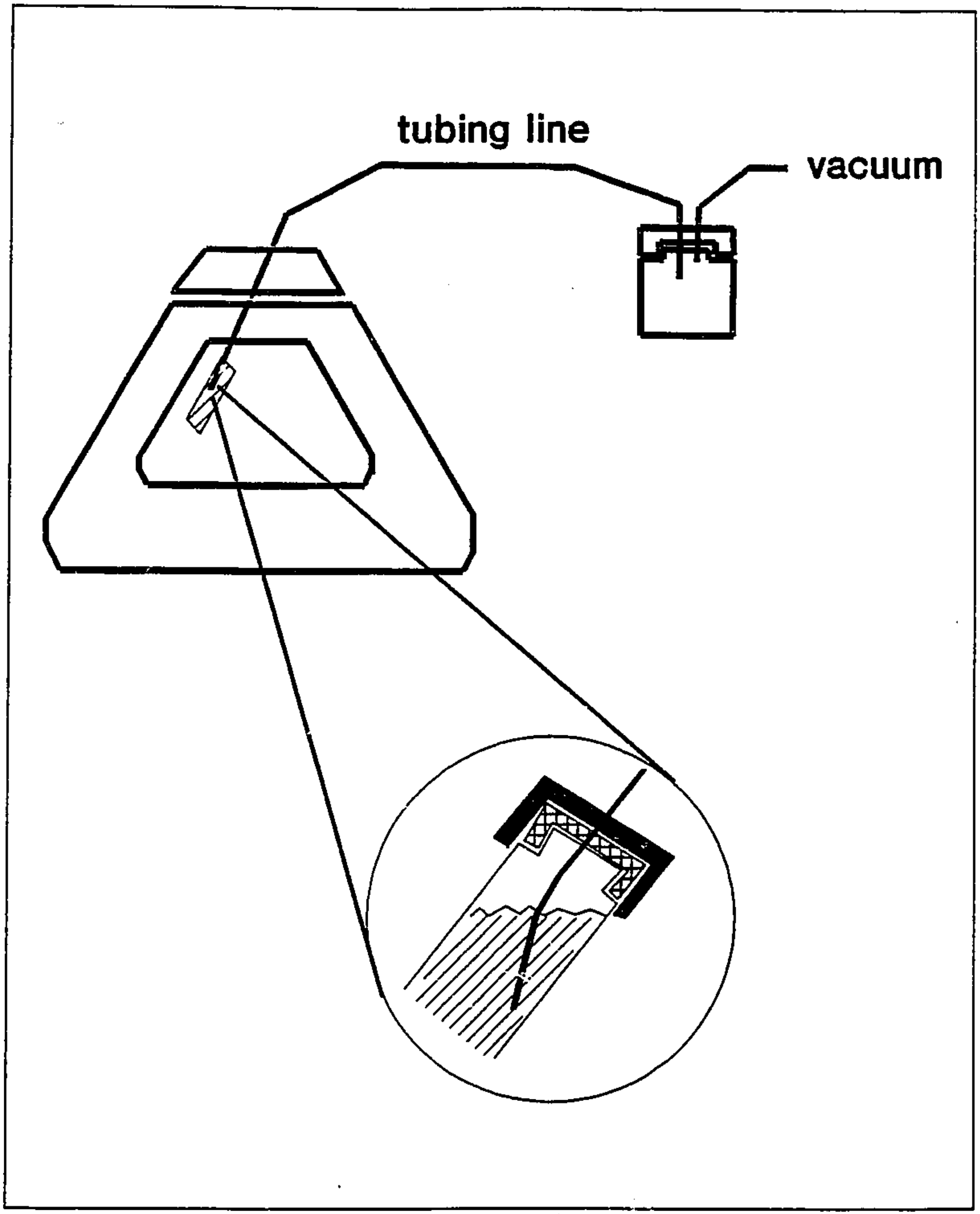

FIGURE 2.7 Set up for centrifugation and transfer of supernatant.

then with H_2O (milli-Q water), and finally with a synthetic freshwater solution. The synthetic solution is characterized by an ionic strength representative of the natural freshwater systems studied and has no trace metal added (see Table 2.10).

Filtration and centrifugation are never combined in a single experiment. It is convenient, however, to compare the degree of separation obtained by these two techniques. In a specific test, the efficiency of separation between centrifugation at 27 000 X g and filtration through 0.2 μm membrane pore size was compared. Results suggest a slightly higher degree of separation by filtration compared to centrifugation. The details of this test are presented and discussed in the next section.

2.4.3 GAIN AND LOSS OF TRACE METALS:

Specific tests on the gain and loss of trace metals were performed to discriminate between separation techniques and to assess the storage and transfer procedures. The overall procedure was also tested; results are presented in section 2.6.

The gain and loss of trace metals in laboratory procedures depends on a variety of factors including: contaminant dust, the type and concentration of trace metals, the characteristics of the solution, and the vessels used. Gain of trace metals refers to contamination which normally originates from air dust and/or from a contaminated vessel. Loss of trace metals is mainly related to surface adsorption onto the wall of the vessel. Among others, Seiler (1986) and Chang et al. (1987) have reported gain (contamination) and loss of trace metals, respectively. In order to reduce the potential error from these sources, great care is required when working with low concentration of trace metals. For instance, all containers (bottles, centrifuge tubes and vials) receiving neutral or acidified solutions, or sediment suspensions, are made of teflon FEP (fluorinated ethylene-propylene) or PFA (perfluoroalkoxy). The plasticware is pretreated in the following manner:

(1) washed with soap and hot tap water;
(2) rinsed with tap water;
(3) rinsed with milli-Q water (Millipore system)
(4) soaked in 10 % v/v HNO_3 for at least 24 hours;
(5) rinsed with Milli-Q water (Millipore System);
(6) rinsed with synthetic freshwater without trace metals added.

The last step in this pretreatment is performed in order to reduce the net loss of trace metals by adsorption to the wall of the vessel. The synthetic solution is exclusively made of major ions which are expected to compete with trace metals for sites on the wall of the vessel.

Small materials (e.g. small vials, pipet tips) are pretreated in a large container and either dried in a clean area (a plexiglass box, with filtered air and positive pressure), or rinsed before used with a portion of sample. Steps (3) to (5) are applied to pretreat the filtration membranes, which are dried in a clean area.

In the first series of tests, centrifugation and filtration were investigated.

Solutions at pH 6.0, 6.75 and 7.5, containing 2 μg/L Zn and 2 μg/L Cd (total element) and traces of radioactive metals (^{65}Zn, ^{109}Cd), at freshwater ionic strength, are used to compare separation techniques (centrifugation and filtration) on: (1) loss of trace metals by adsorption to the wall of the vessel, and (2) the contamination of total elements. Concentrations and radioactivities reported in Figures 2.8 and 2.9 are relative to the test solutions prior to centrifugation or filtration. The precisions (σ) of the values reported in Figures 2.8 and 2.9 are 10% and 5%, respectively. Results suggest a notable contamination of total zinc and a net loss of radioactive cadmium when filtration is applied.

The degree of separation provided by the two techniques was also investigated. Separation techniques were tested using a synthetic sediment suspension at equilibrium with radioactive Zn and Cd. Four replicates of: (1) centrifugation, (2) filtration, and (3) filtration immediately (less than 5 minutes) after the addition of high concentrations of zinc and cadmium ($\approx$ 1 mg/L). Such a massive addition of metals prevents a net loss of radioactive trace metals by adsorption on the wall of the filtration apparatus. The degree of separation and the imprecision of the separation techniques on total and radioactive metals are reported in Table 2.8. The degree of separation is represented by the percentage of trace metals found in solution after the separation step and is relative to the average value obtained from the results of the three techniques. The imprecision is represented by the maximum deviation from the average value among replicates. Comparison of the degree of separation was done by considering the radioactive species only; this option eliminates the error from

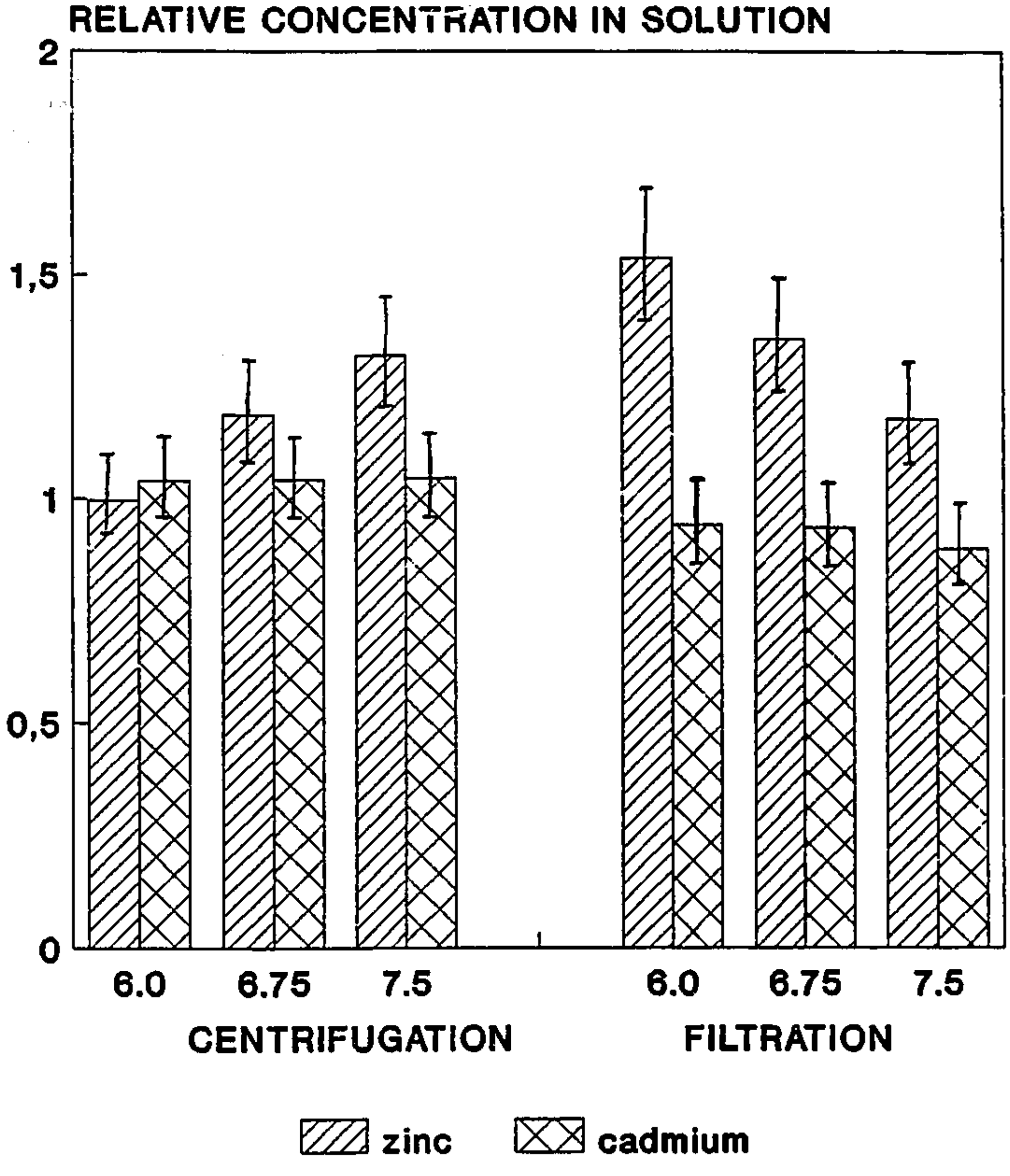

FIGURE 2.8 Fraction of total metal (Zn and Cd) recovered after centrifugation or filtration treatments of synthetic solutions at different pH (6.0, 6.75 and 7.5). The error bars represent 1 σ.

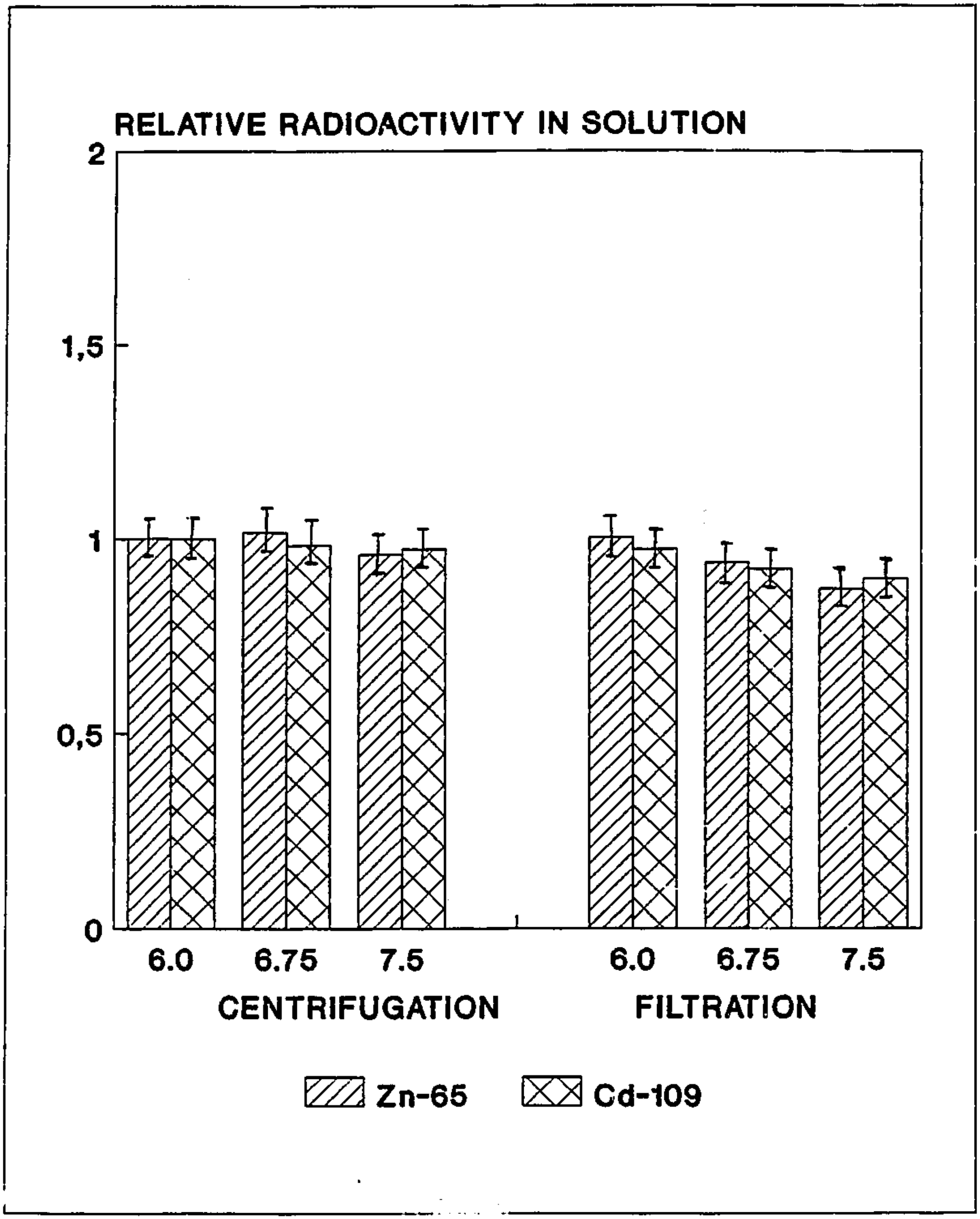

FIGURE 2.9 Fraction of total radio[illegible] [illegible]Zn and ^{109}Cd) recovered after centrifugation or filtration treatments [illegible] [illegible]tic solutions at different pH (6.0, 6.75 and 7.5). The error bars represent 1 σ.

TABLE 2.8 Degree of separation[a] and imprecision resulting from the application of different techniques to isolate dissolved (total or radioactive) metals from a synthetic sediment suspension.

Technique applied	65-Zn (% error)[b]	109-Cd (% error)	Total Zn (% error)	Total Cd (% error)
Centrifugation	104.4 (2.9)	104.5 (2.7)	78.9 (8.3)	108.9 (3.5)
Filtration	96.1 (3.0)	97.3 (2.1)	121.1 (11.3)	91.1 (5.1)
Addition[c] and filtration	99.6 (8.9)	98.2 (2.4)	-----	-----

[a] percentage of trace metals found in solution after the separation step relative to the average value obtained from the results of the three techniques

[b] maximum deviation from the mean value of replicates

[c] addition of an excess of metals immediately before filtration

contamination. Results from filtration and filtration immediately after the addition of an excess of metals should be the same if: (1) loss of trace metals by adsorption is negligible (regular filtration) and (2) desorption of trace metals from particles is negligible. The lapse of time between the addition of an excess of metals and the filtration of the suspension is only a few minutes.

The average degree of separation from the two filtration techniques was compared with the degree of separation from centrifugation. Filtration techniques are more efficient to isolate trace metals in the liquid phase from the rest of the suspension. The same trend is observed for total cadmium; the error is, however, slightly increased. Total zinc shows the opposite phenomenon. Contamination of zinc in the filtration procedure may explain this observation (see Figure 2.8).

Centrifugation was the separation technique selected as it provides: (1) a good degree of separation, (2) a negligible loss by adsorption, and (3) an advantageous reduction of zinc contamination, when compared with filtration.

In the second series of tests, the storage of trace metals in different types of vessels was studied. The major difficulty with the storage of solutions at neutral pH and low trace metal concentrations results from the potential loss of metals by adsorption. Teflon centrifuge tubes and teflon bottles were tested with three standard solutions of radioactive and total zinc and cadmium (2 μg/L) at pH 6.0, 6.75 and 7.5. Storage times of these solutions in centrifuge tubes were 1h, 3h, 6h, and 24h, and 3d, 7d, 16d, and 20d in bottles for each series. Each result reported in Table 2.9 expresses the mean value (in percentage) of all storage times relative to the initial

TABLE 2.9 Effects of method of storage on total and radioactive metals (Zn and Cd) from synthetic solutions of different pH, in centrifuge tubes and bottles. Each result expresses the mean value, in percentage, of all storage times relative to the initial solution in the series before storage. Standard deviation (σ) from the mean value of each series is reported in parentheses.

	pH of the synthetic solution		
CENTRIFUGE TUBES	pH=6.00	pH=6.75	pH=7.50
Cadmium:			
total	101.6	100.6	97.8
	(5.6)	(2.2)	(3.5)
radioactive	101.2	98.0	100.9
	(3.6)	(6.6)	(3.8)
Zinc:			
total	103.5	101.8	94.7
	(2.2)	(2.4)	(4.1)
radioactive	103.1	95.4	101.5
	(4.2)	(7.4)	(4.1)
BOTTLES			
Cadmium:			
total	100.7	102.5	96.8
	(5.6)	(1.3)	(4.6)
radioactive	101.5	98.8	99.7
	(3.3)	(4.3)	(3.5)
Zinc:			
total	102.1	96.5	101.4
	(5.5)	(2.6)	(15.1)
radioactive	102.9	98.2	98.9
	(4.6)	(3.8)	(5.1)

radioactivity in solution before storage. The standard deviation (σ) of the mean value from each series is always within 8% of the initial value, with the exception of total zinc in a teflon bottle at a pH of 7.5. In most cases the standard deviation was only 2% to 4% which means that a variation of less than ± 0.1 μg/L of total metal was observed. One should notice that the error reported includes transfer as well as analysis. In addition, no systematic trend with pH was observed.

2.5 STABILITY OF SEDIMENT SUSPENSIONS:

There are at least two approaches to evaluate the stability of sediment suspensions in the laboratory. First, aqueous parameters of sediment suspensions were analyzed and compared with in-situ values (reported by Tessier et al.(1987)) for the same lakes where a porewater-overlying water sampling technique was used. The second approach consists in monitoring the solution conditions of sediment suspensions using master parameters such as pH, DOC, DIC, and total Zn, over the length of various kinetic experiments. Total zinc analyses were performed on the first $\approx$ 5 mL of supernatant collected after the transfer of 2.00 mL for counting. Another part of the supernatant ($\approx$ 15 mL) was used for pH, DOC, and DIC analyses.

The change in the particle size distribution resulting from the agitation of sediment suspensions was investigated. Two equivalent sediment suspensions were prepared and kept under the same conditions for 12 days except one exception was agitated continuously and the other suspension was not stirred. The technique used to determine the particle size distribution is described in section 2.2.

The experimental method using radiotracers may be adequately applied only when the stability of sediment suspensions is confirmed.

2.6 PRECISION:

The precision of the radiotracer technique was evaluated from the relative % deviation of the kinetic experimental data. This assessment was used to determine if a net change of radioactivity in the liquid phase of a suspension is significant. Kinetic experiments of suspensions HL-3-2R2 and HL-8-1 were used to evaluate the precision of the kinetic data.

The precision of kinetic experiments was also evaluated by performing parallel experiments of two equivalent sediment suspensions. "Adsorption" kinetic experimental data of suspensions HL-8-1, HL-8-2 were used for this purpose.

2.7 KINETIC EXPERIMENTS:

2.7.1 SYNTHETIC SUSPENSION:

The "adsorption" and "desorption" sequence of the radiotracer technique was applied to a suspension of rutile (TiO_2) at equilibrium with a synthetic freshwater solution. The system was manipulated as follows in order to obtain similar concentrations in the synthetic TiO_2 and natural systems. The sorptive equilibrium of the synthetic suspension was obtained by mixing the solid and the synthetic freshwater; after one equilibration day, the solution was separated from the suspension and replaced by a fresh portion of synthetic freshwater. This treatment was repeated over a period of 4 days in order to equilibrate the solid with the specific aqueous trace metal concentrations of the synthetic freshwater. Table 2.10 reports the characteristics of the suspension.

2.7.2 SEDIMENT SUSPENSIONS:

Different sampling strategies were considered in order to assess the kinetic variability of solid-liquid trace metal interactions of sediment suspensions. This approach allows the comparison of trace metal exchange kinetics among:

(1) stations from the same lake sampled at different depths. Suspensions HL-7-1, HL-7-2 and HL-7-3 represent three stations, from Harp Lake, sampled at 3 m., 12 m., and 15 m., respectively.

(2) different lakes sampled at a similar depth at the same time of the year. Suspensions HL-8-2, RB-8-3 and SNL-8-4 are from Harp Lake, Rabbit Bay and St-Nora Lake, respectively. All the lakes were sampled in June 1989 at a depth around 10-12 m.

(3) the same lake at different times of the year. Harp Lake was sampled in March 1988 (HL-3-2R2), March 1989 (HL-7-2) and June 1989 (HL-8-2).

All kinetic experiments were started within 48 hours after sampling with the exception of suspension, HL-3-2R2, which was started after 7 days. In the transitional period, suspensions were kept under controlled experimental conditions.

TABLE 2.10 Characteristics of the synthetic suspension made of rutile (TiO_2) and synthetic freshwater.

- Suspension volume: 2 L
- Particle concentration: 100 mg/L
- Particle size distribution:

>63 µm	0 %
$20< <63$ µm	74.3 %
$10< <20$ µm	15.8 %
$3< <10$ µm	9.4 %
< 3 µm	0.4 %

- pH of the synthetic solution: 6.5
- Majors ions added to the synthetic solution to obtain an ionic strength representative of freshwater systems:

  Ca: 1.6 mg/L
  Na: 0.34 mg/L
  Mg: 0.97 mg/L
  K: 0.20 mg/L
  SO_4: 7.7 mg/L
  Cl: 0.7 mg/L

- Trace metal concentrations:

  Cd: 2 µg/L
  Zn: 2 µg/L

- Percentage of increase in total cadmium after addition of ^{109}Cd:

  2 %

CHAPTER 3

RESULTS

3.1 EXPERIMENTAL TECHNIQUES:

In the previous chapter, the experimental considerations of sampling, conservation of natural samples, and the radiotracer technique were presented. These considerations - which attempt to reproduce, as closely as possible, the natural conditions while facilitating the experimental work in the laboratory - are summarized as follows:

- deep sampling stations exempt of light:
- low water temperature;
- oxic layer of the surficial sediment;
- range of particle sizes excluding large particles ($> 100\ \mu m$);
- continuous and gentle agitation of sediment suspensions representing resuspension events;
- solid concentration of sediment suspensions in the range of 55-75 mg/L;
- separation of the liquid phase from the suspension by centrifugation.

In addition to being representative of a natural environment, the laboratory experimental conditions must provide a controlled chemical environment. In fact, the constancy of master parameters included in pseudo rate constants is essential in order to satisfactory apply the radiotracer technique.

Suspension stability was investigated by monitoring a variety of parameters from subsamples collected in kinetic experiments. For instance, pH readings of suspension HL-7-2 taken over the length of the experimentation are plotted in Figure 3.1. Results of total dissolved zinc analyses from subsamples of suspension RB-8-3 are shown in Figure 3.2. In a similar way, but at a lower frequency of subsampling, Figure 3.3 reports DOC values for suspension HL-8-1 and Figure 3.4 reports DIC values for suspension SNL-8-4. Parameters such as pH, total trace metal concentration, DOC, or DIC are expected to be constant with time. A certain experimental variability is always present resulting from: (1) subsampling, (2) separation, (3) transfer, and (4) analysis. Statistical two-tailed student t tests show that pH, DOC and DIC measurements are independent of time, over a period of 12 days, at a level of significance of 95%. The same test performed on total zinc in solution as a function of time rejects the hypothesis of zero slope suggesting a significant decrease in dissolved zinc over the 12 days of experimentation; the does not reject the hypothesis over the first 6 days ("adsorption step").

The stability of the solid phase was also investigated. Two suspensions kept in the laboratory under identical conditions of temperature and lighting but subject to different agitations show only minor changes in their particle size distributions (Figure 3.5). The estimation of the total surface area for each suspension after 12 days of experimentation, assuming spherical particles of identical density, shows to a slight

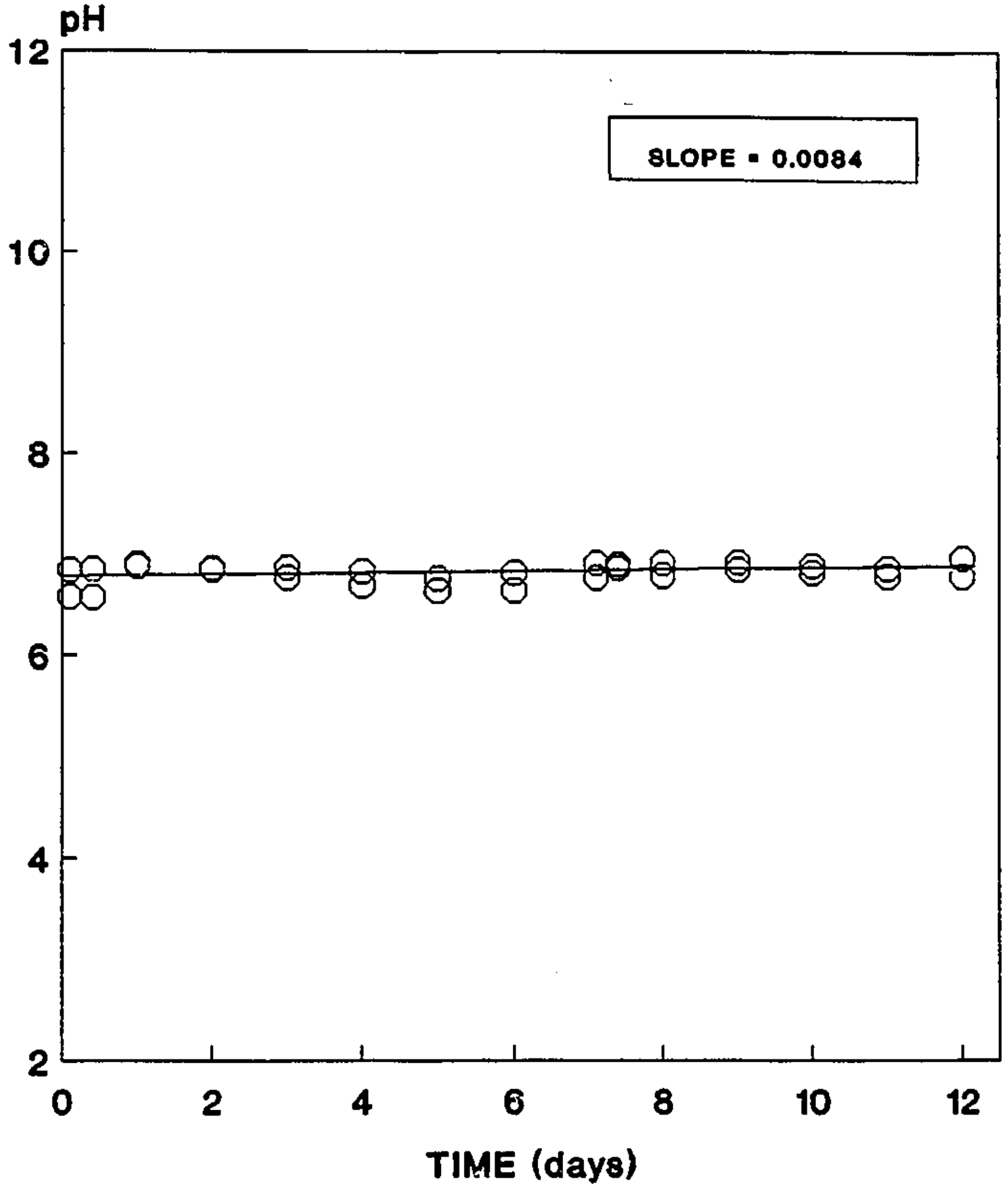

FIGURE 3.1 Variation of pH versus time for sediment suspension HL-7-2. The line represents the linear regression.

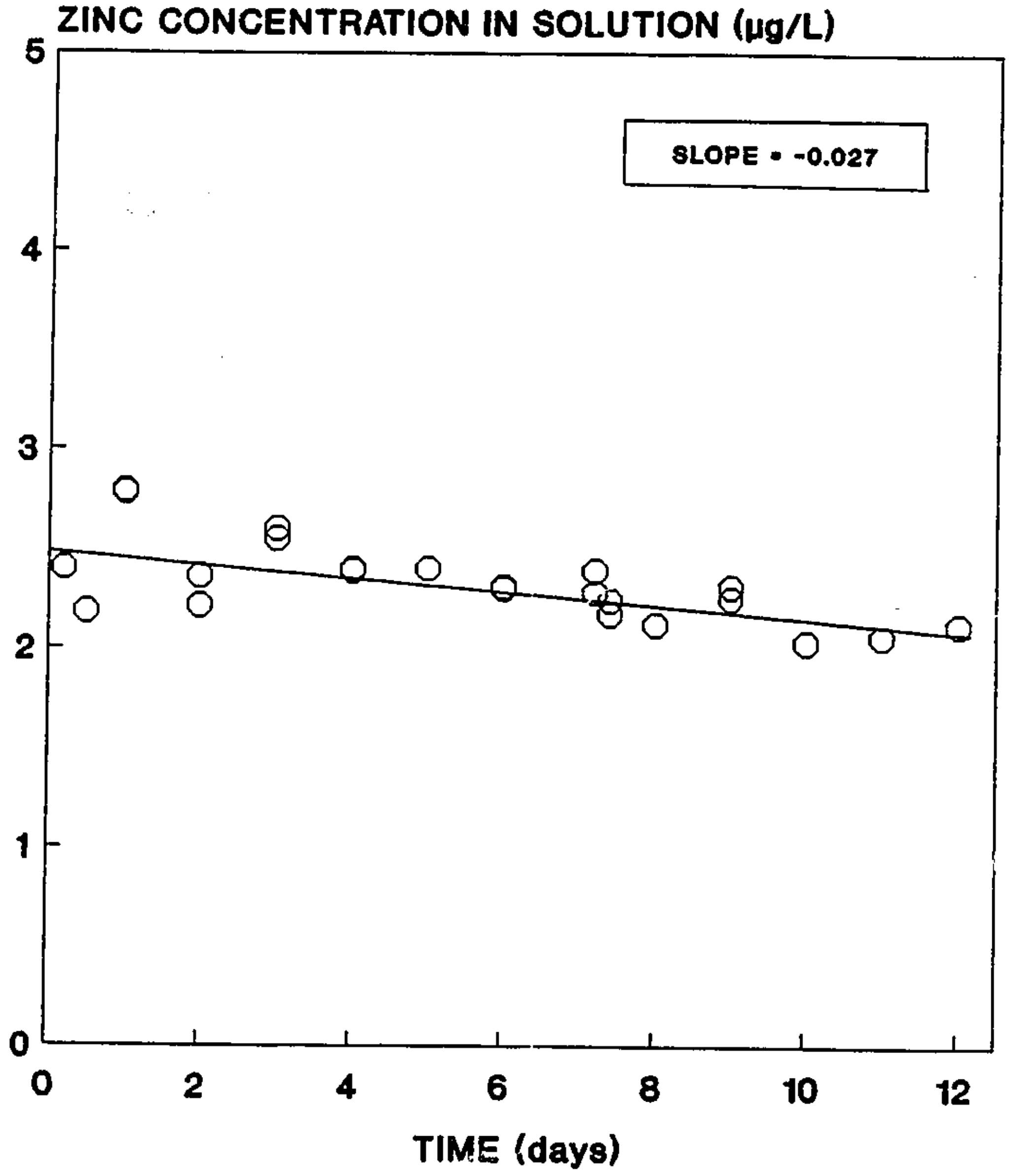

FIGURE 3.2 Variation of total zinc versus time for sediment suspension HL-8-2. The line represents the linear regression.

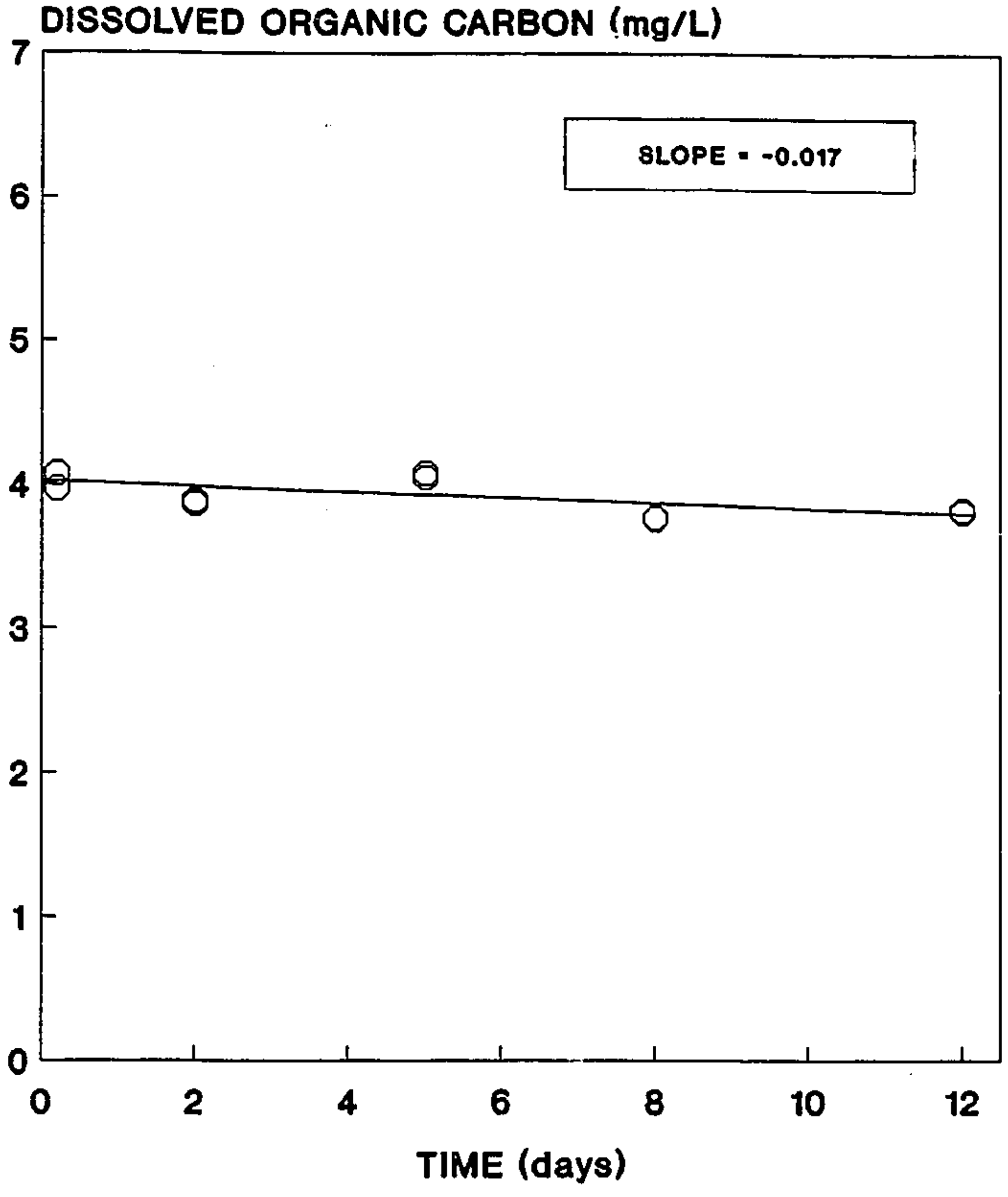

FIGURE 3.3 Variation of dissolved organic carbon (DOC) versus time for sediment suspension HL-8-1. The line represents the linear regression.

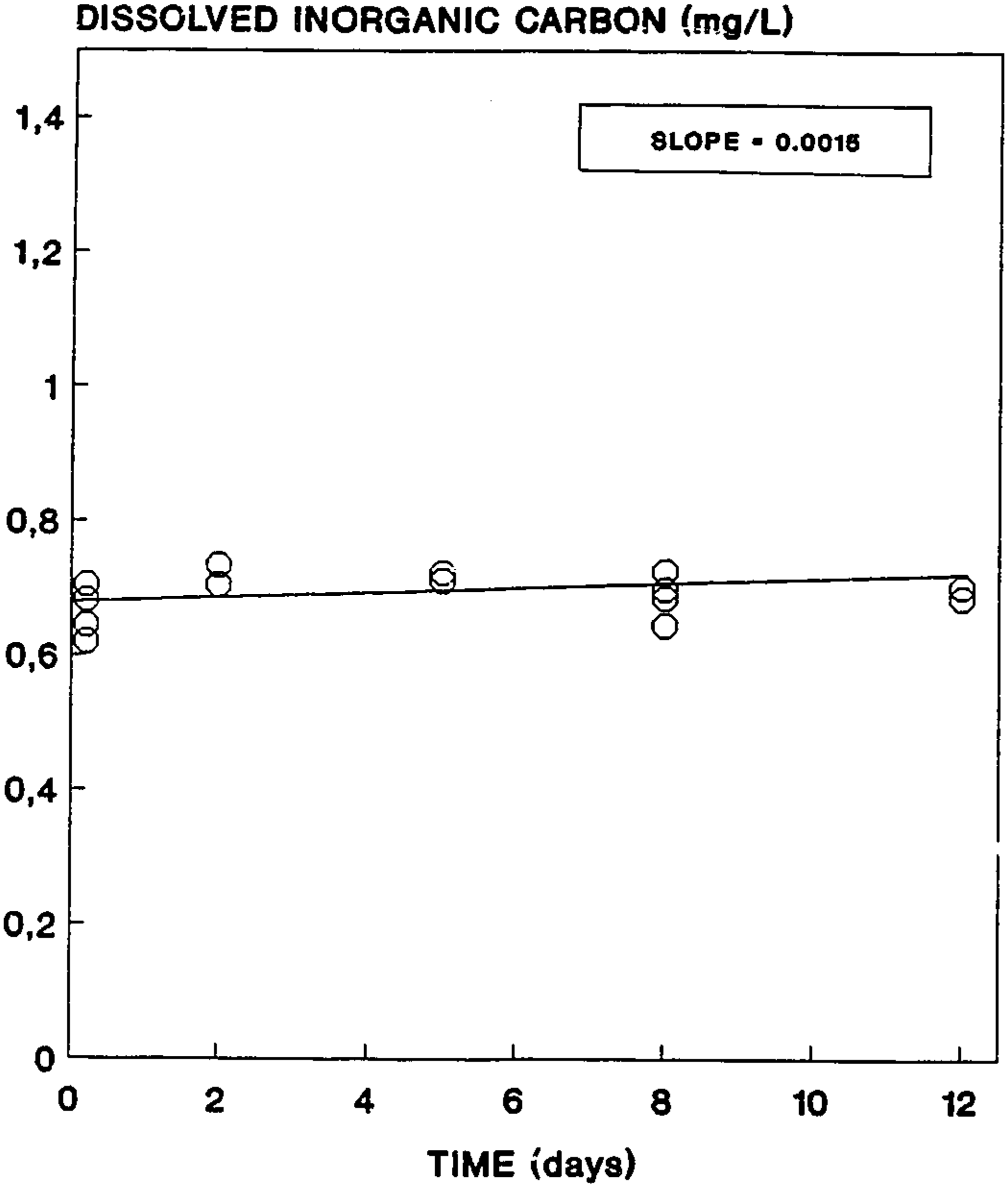

FIGURE 3.4 Variation of dissolved inorganic carbon (DIC) versus time for sediment suspension SNL-8-4. The line represents the linear regression.

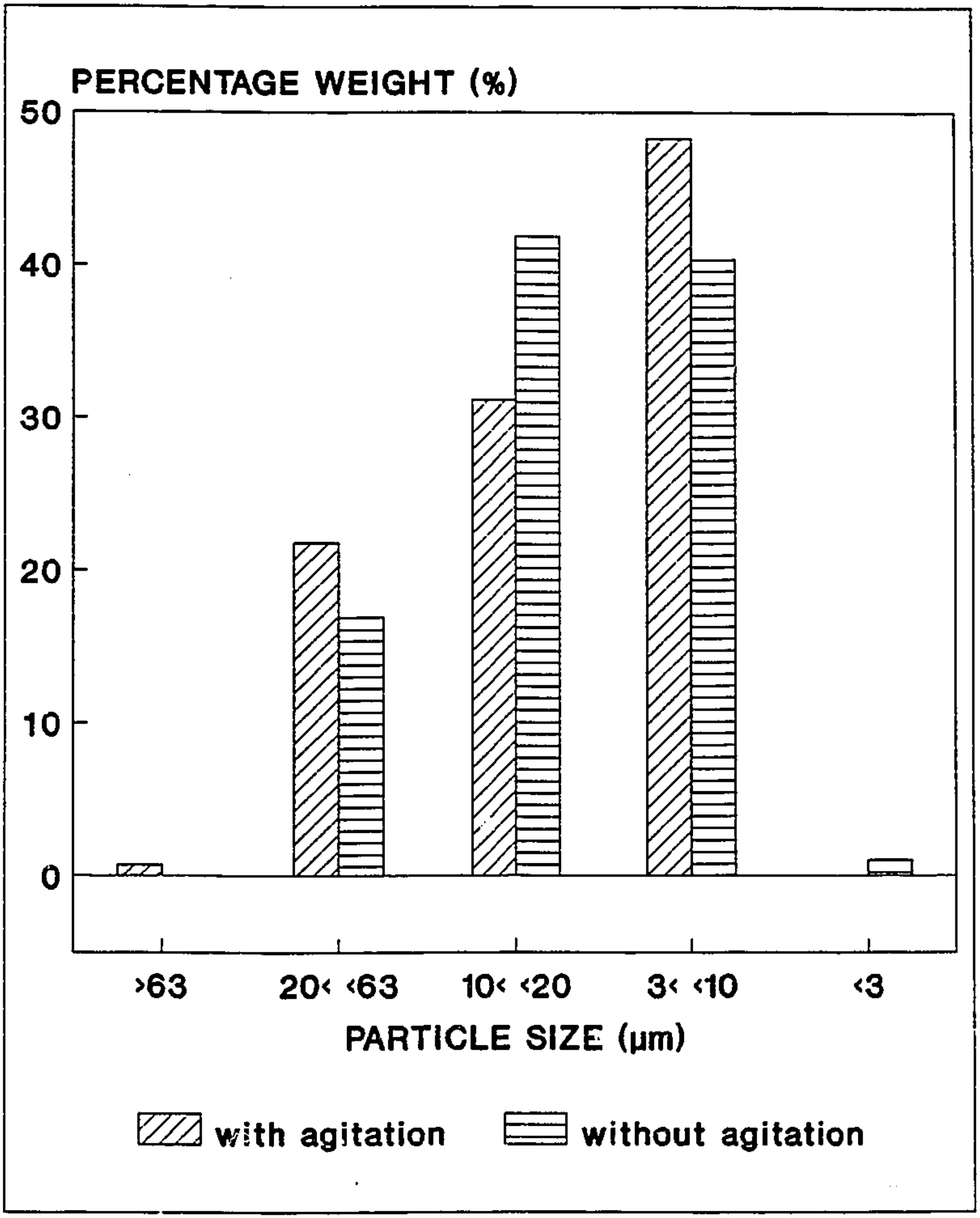

FIGURE 3.5 Particle size distribution of two initially identical sediment suspensions from Harp Lake kept in the laboratory under controlled conditions for 12 days, with and without agitation.

increase (less than 4%) in suspension surface area resulting from agitation.

The activity of trace metal radiotracers in solution was expected to change as the experimentation time progresses until a constant distribution of total elements was reached. In order to evaluate when a change of radioactivity in solution is significant, the precision of the technique was first estimated. Kinetic experimental data of suspension HL-8-1 for Zn and Cd were used to calculate the relative % deviation of trace metal radioactivity in solution. Figure 3.6 shows the relative % deviation of trace metal radioactivity in solution for each step of the subsampling sequence, over the length of the kinetic experiment. A maximum of only 1.4% of the relative deviation of trace metal radioactivity in solution is observed. Both metals illustrate excellent precision (average relative deviation (Zn) = 0.50%, σ = 0.30%; average relative deviation (Cd) = 0.47%, σ = 0.40%).

Another aspect to consider is the precision in replicate kinetic experiments. Kinetic experimental data of two suspensions (HL-8-1 and HL-8-2) of an original mixture from Harp Lake were compared over a period of six days following the addition of Zn and Cd radiotracers. Figure 3.7 reports, for Zn and Cd, the relative % deviation of experimental data of the two suspensions investigated, at each step of the subsampling sequence. Results show precision between duplicate kinetic experiments since the relative deviation of radioactivity in solution is only 0.57% (σ = 0.24%) and 0.46% (σ = 0.31%) for zinc and cadmium, respectively.

The imprecision of experimental data in replicate analysis and replicate experiments is estimated at 1.4% and less than 1%, respectively. Therefore, a

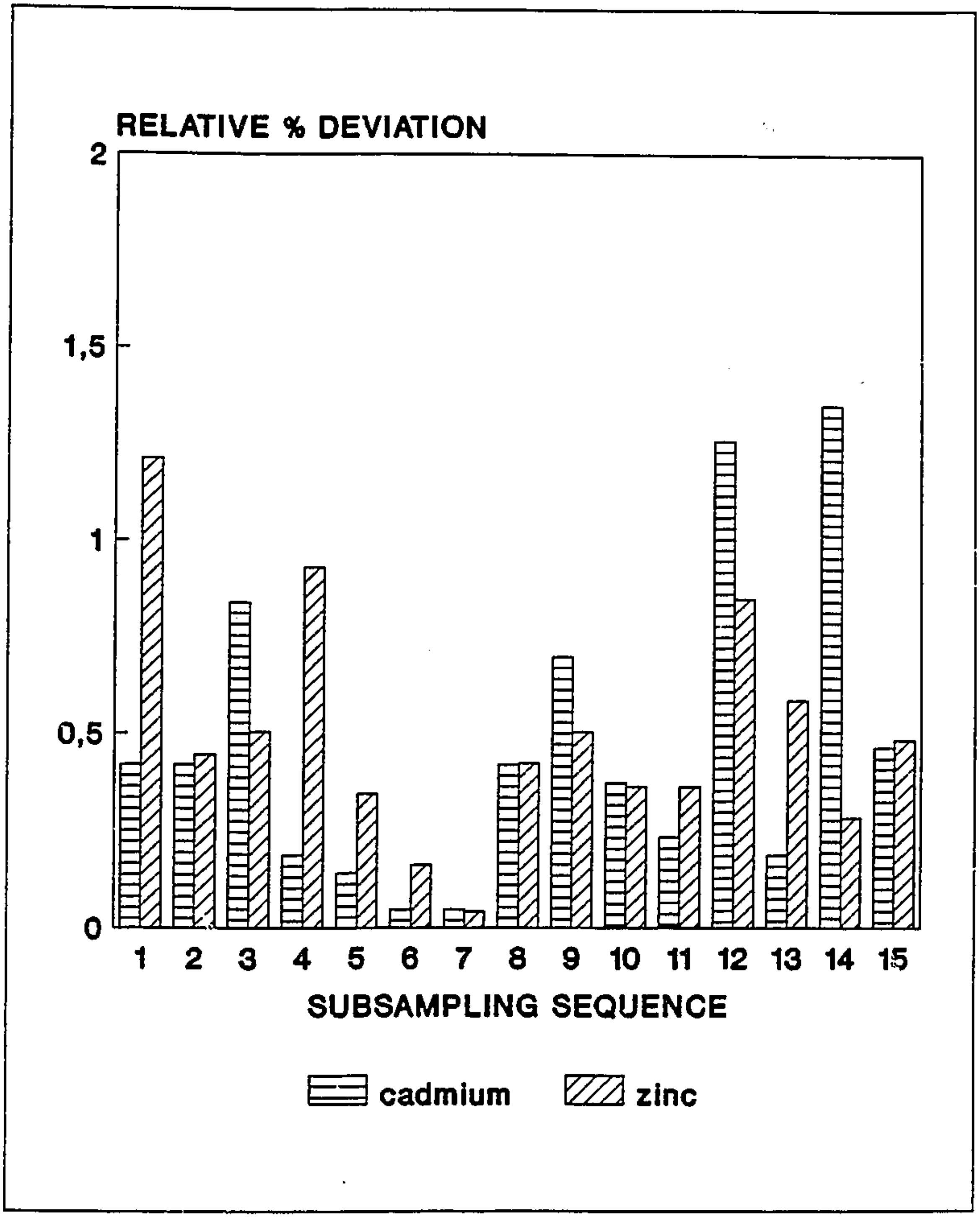

FIGURE 3.6 Relative % deviation of the experimental data for sediment suspension HL-8-1 (Zn and Cd) as a function of the sequence of subsamples collected over 12 days.

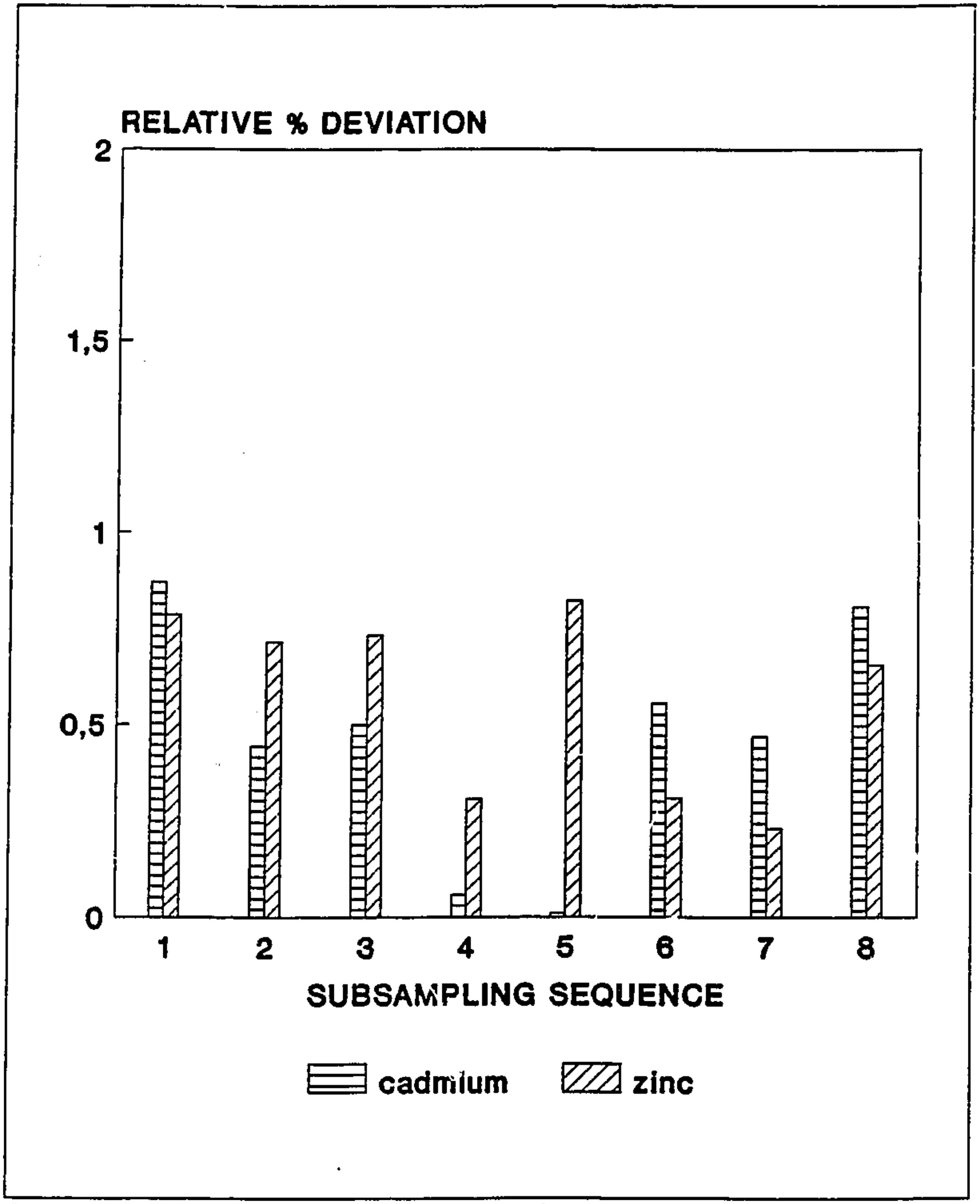

FIGURE 3.7 Relative % deviation of the experimental data for duplicate parallel experiments HL-8-1 and HL-8-2 (Zn and Cd) as a function of the sequence of subsamples collected over 6 days.

significant trend in kinetic data would have to exceed the variability associated with the overall experimental data.

The capability of the experimental approach to preserve the natural conditions of surficial sediments was investigated by comparison of differences between data from this work and data from other studies. Three lakes were considered from which analytical results of selected parameters (Table 2.2) are compared between samples from kinetic experiments and samples from an in-situ sampling and separation technique (Tessier et al., 1987). Generally, the comparison of the overall aquatic chemistry, reported in Table 2.2, between the two studies shows no significant differences considering the precision of the reported values. A certain variation in the natural system is, however, expected from one year to another or from one station to another. In fact, slightly lower pH values of sediment suspensions (0.1-0.4 pH unit) were observed. The small change in pH is sufficient to explain the slight increase of zinc concentration in solution compared to values reported by Tessier et al. (1987); this is based on the adsorption-edge profile generally observed for suspensions of isolated solids or natural sediments. DOC and DIC measurements are, however, systematically different by a factor of about two. Recently, MacDonald and Metcalfe (1991) reported a DOC value of 2.6 mg/L for St-Nora Lake which suggests that analytical results from this work are accurate.

The trace metal content of sediments was also compared. Table 2.4 reports, for the same lakes, there is a systematic lower load of zinc associated with the sediments studied by Tessier et al. (1987) as compared to sediments investigated in the kinetic experiments. According to Dillon and Evans (1982) a wide range of trace metal content of sediments from different stations of the same lake is common. The preparation of sediment suspensions, which includes the elimination of large particles known as weak carriers of trace metals on a weight basis, supports an enrichment of trace metals by the sediments studied in this work.

3.2 KINETIC EXPERIMENTS:

3.2.1 SYNTHETIC SUSPENSION:

The radiotracer technique was first applied to a 2 litre suspension of rutile (TiO_2) characterized by a particle size distribution similar to the natural sediment suspensions investigated. The complete characterization of the synthetic suspension is reported in Table 2.10. Experimental conditions include: temperature 7-8 °C, continuous agitation on a roller mill (Figure 2.5), and separation by centrifugation (Figure 2.7). Kinetic "adsorption" and "desorption" data are obtained by performing the required steps from the radiotracer technique (Figure 2.3).

The radioactivity of ^{109}Cd in solution relative to the total radioactivity added to the liquid phase of the synthetic suspension as a function of time is shown in Figure 3.8 . Three data points from the "adsorption" part of kinetic data include a minor correction (< 10%). The occasional erratic variations of both ^{65}Zn and ^{109}Cd, at the same subsampling times, in the "adsorption" kinetic experiment were probably due to

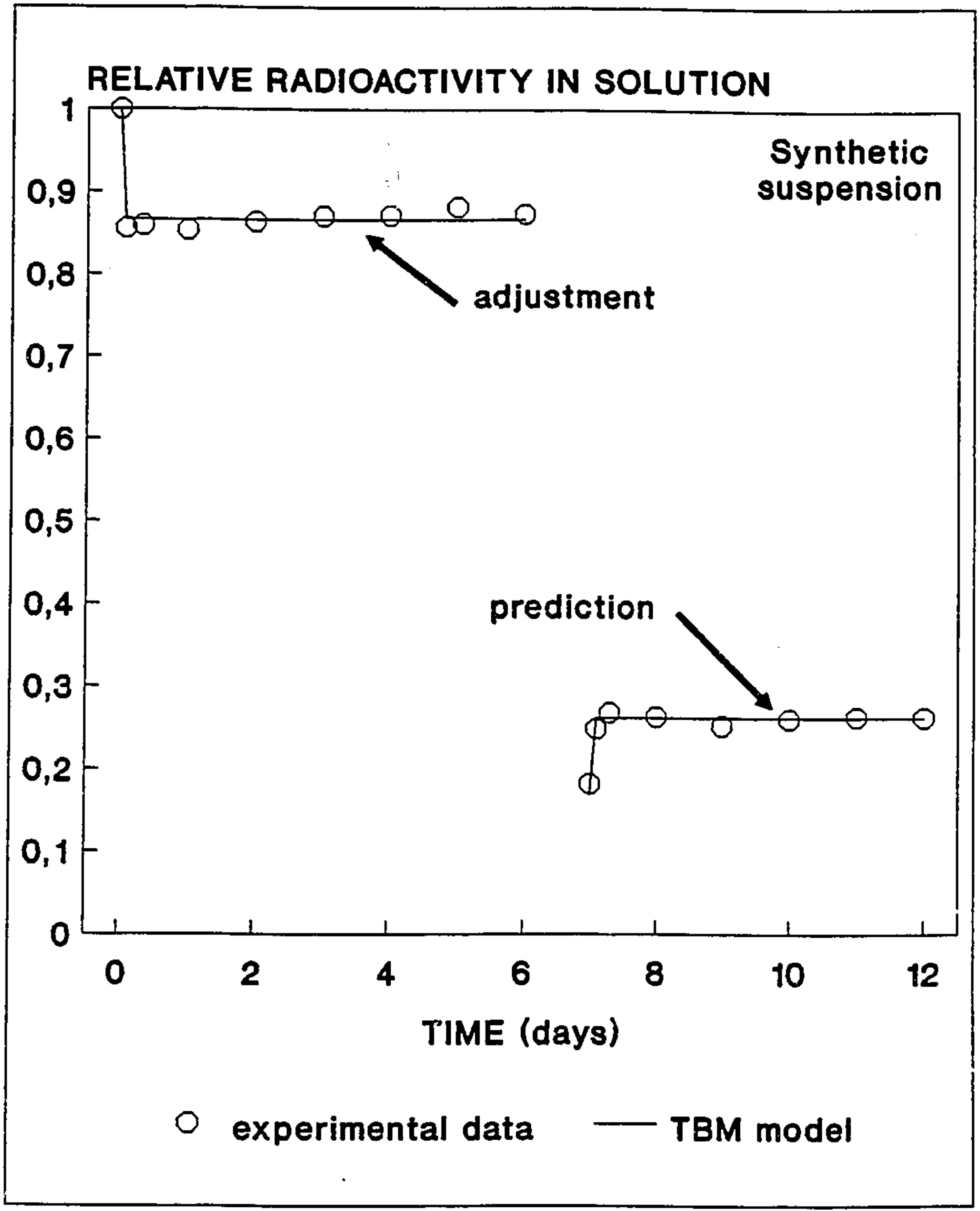

FIGURE 3.8 "Adsorption-desorption" experimental data of cadmium exchange in a TiO_2 suspension. TBM model is adjusted to the "adsorption" experimental data and is used to predict the "desorption" experimental data.

difficulties in the separation step. Under the prevailing experimental conditions, ^{65}Zn was not statistically removed from the solution (t test; level of significance 95%) justifying such a correction. To initiate the "desorption" step, particles were allowed to settle overnight. Then, 79 percent of the overlying water was replaced by an equivalent amount of synthetic freshwater with the same concentrations of metals but without radiotracers, 7 days after the beginning of the "adsorption" experiment.

The two-compartment model (TBM) was adjusted to the ^{109}Cd "adsorption" kinetic data. The relative radioactivity of ^{109}Cd in the liquid phase as a function of time, is represented in Equation 3.1 by $[Me^*_w](t)$.

$$[Me_w^*](t) = \frac{k_r' \, [Me_w^*]_i}{k_f + k_r'} + \left[\frac{[Me_w^*]_i \, k_f}{k_f + k_r'} \exp^{-(k_f + k_r')\, t} \right] \tag{3.1}$$

This equation is adapted from Equation 1.7 since, at the beginning of the experiment, the trace metal radioactivity is present exclusively in the liquid phase. The TBM model optimisation program is reported in Appendix B (B1a). The following forward and backward rate constants are obtained: $k_f = 18.8\ d^{-1}$, $k'_r = 119.5\ d^{-1}$. The TBM "desorption" profile was then predicted using the overall rate constants obtained from the "adsorption" step and the following equation:

$$[Me_w^*](t) = \frac{[Me_w^*]_i\, k_r^{'} + [Me_s^*]_i\, k_r^{'}}{k_f + k_r^{'}} + \left[\frac{[Me_w^*]_i\, k_f - [Me_s^*]_i\, k_r^{'}}{k_f + k_r^{'}} \exp^{-(k_f + k_r^{'})t} \right] \tag{3.2}$$

Equation 3.2 is the mathematical solution of Equation 1.5 (after substitution of $\{Me^*_s\}$ by $[Me^*_s]/Cp$, and k_r/Cp by k^*_r) when the trace metal radioactivity is initially distributed between the two compartments (Jacquez, 1985). The initial relative radioactivity of ^{109}Cd in the liquid phase is represented by $[Me^*_w]_i$ whereas $[Me^*_s]_i$ represents the initial relative radioactivity of ^{109}Cd associated to the solid phase. The simulation computer program is reported in Appendix B (B1b).

The fitting of the "adsorption" kinetic data by the TBM model and the prediction of the "desorption" profile are in very good agreement with the experimental data (Figure 3.8). The high rate constants obtained reflect the nearly instantaneous reaction of trace metal exchange between the two phases. Consequently, the radiotracer technique is appropriate to study both uptake and release sorption kinetics of solid-liquid trace metal exchange. Cadmium contamination from the addition of the radiotracer is limited at 2 percent and has no significant effect on kinetic data.

3.2.2 SEDIMENT SUSPENSIONS:

When applied to natural sediment suspensions, the two-compartment (box) model (TBM) does not always accurately describe the "adsorption" kinetic data. As suggested by Nyffeler et al.(1984), trace metals are believed to participate in a two step sequential reaction with the solid phase. Serial reversible reactions are represented by Equation 3.3.

$$Me_w^* \rightleftharpoons Me_{s1}^* \rightleftharpoons Me_{s2}^* \qquad (3.3)$$

where subscripts w, s1 and s2 refer to the aqueous phase and the solid phase (site 1 and site 2), respectively. This model introduces two additional parameters to be optimised when compared with the two-compartment (box) model (TBM). In order to reduce the complexity of the model, Nyffeler et al.(1984) suggested to ignore the backward reaction involving the second type of solid sites (s2) for short term (weeks or less) interactions. Accordingly, Equation 3.3 becomes:

$$Me_w^* \underset{k_{r1}^{'}}{\overset{k_{f1}}{\rightleftharpoons}} Me_{s1}^* \xrightarrow{k_{f2}^{'}} Me_{s2}^* \qquad (3.4)$$

and describes a two-compartment (box) model with a leak (TBL). In this model, the leak signifies that trace metals involved in the rearrangement reaction (site 1 to site 2) are not returning to solution (very slow reversible reaction).

The following mathematical development considers the serial reactions represented by Equation 3.4. Assuming first-order reactions relative to the radiotracer activity, the time-dependent change of trace metal radioactivity, Me*, in each compartment is represented as follows:

$$\frac{d[Me^{*}_{w}]}{dt} = - k_{f1}\ [Me^{*}_{w}] + k_{r1}\ \{Me^{*}_{s1}\} \tag{3.5(a)}$$

$$\frac{d[Me^{*}_{s1}]}{dt} = k_{f1}\ [Me^{*}_{w}] - k_{r1}\ \{Me^{*}_{s1}\} - k_{f2}\ \{Me^{*}_{s1}\} \tag{3.5(b)}$$

$$\frac{d[Me^{*}_{s2}]}{dt} = k_{f2}\ \{Me^{*}_{s1}\} \tag{3.5(c)}$$

or,

$$\frac{d[Me^{*}_{w}]}{dt} = - k_{f1}\ [Me^{*}_{w}] + \frac{k_{r1}}{Cp}\ [Me^{*}_{s1}] \tag{3.6(a)}$$

$$\frac{d[Me^{*}_{s1}]}{dt} = k_{f1}\ [Me^{*}_{w}] - \frac{k_{r1}}{Cp}\ [Me^{*}_{s1}] - \frac{k_{f2}}{Cp}\ [Me^{*}_{s1}] \tag{3.6(b)}$$

$$\frac{d[Me^{*}_{s2}]}{dt} = \frac{k_{f2}}{Cp}\,[Me^{*}_{s1}] \qquad (3.6(c))$$

or,

$$\frac{d[Me^{*}_{w}]}{dt} = -\,k_{f1}\,[Me^{*}_{w}] + k'_{r1}\,[Me^{*}_{s1}] \qquad (3.7(a))$$

$$\frac{d[Me^{*}_{s1}]}{dt} = k_{f1}\,[Me^{*}_{w}] - k'_{r1}\,[Me^{*}_{s1}] - k'_{f2}\,[Me^{*}_{s1}] \qquad (3.7(b))$$

$$\frac{d[Me^{*}_{s2}]}{dt} = k'_{f2}\,[Me^{*}_{s1}] \qquad (3.7(c))$$

where $[Me^{*}_{w}]$, $[Me^{*}_{s1}]$ and $[Me^{*}_{s2}]$ denote the relative radioactivity of a given trace metal per volume of suspension (radioactivity/L) in the liquid phase, associated with the first type of solid sites, and associated with the second type of solid sites, respectively. The rate constants characterize the radiotracer exchange under prevailing experimental conditions: it is assumed that rate constants incorporate parameters considered constant through kinetic experiments. Rate constants represent first-order trace metal reactions from the solution to the first type of solid sites (k_{f1}), from the first type of sites to the solution (k'_{r1}), and from the first type of solid sites to the second type of solid sites (k'_{f2})(see Equation 3.4). Units for k_{f1}, k'_{r1} and k'_{f2} are t^{-1}.

The general solution of Equations 3.7 (in reference to the concentration of Me^* in solution) is taken from Jacquez (1985) and has the following form:

$$[Me_w^*](t) = \left[\frac{[Me_w^*]_i \; Y2 - [Me_{s1}^*]_i \; k_{r1}' + [Me_w^*]_i \; k_{f1}}{Y2 - Y1} \right] \exp^{Y1\,t} +$$

$$\left[\frac{[Me_{s1}^*]_i \; k_{r1}' - [Me_w^*]_i \; Y1 + [Me_w^*]_i \; k_{f1}}{Y2 - Y1} \right] \exp^{Y2\,t} \qquad (3.8)$$

where,

$$Y1 = -\frac{k_{f1} + k_{r1}' + k_{f2}'}{2} - \sqrt{\frac{(k_{f1} + k_{r1}' + k_{f2}')^2 - 4\,(k_{r1}' + k_{f2}')}{2}}$$

and,

$$Y2 = -\frac{k_{f1} + k_{r1}' + k_{f2}'}{2} + \sqrt{\frac{(k_{f1} + k_{r1}' + k_{f2}')^2 - 4\,(k_{r1}' + k_{f2}')}{2}}$$

To apply this equation, the initial trace metal radioactivity in the liquid phase, $[Me_w^*]_i$, and the trace metal radioactivity associated with the first type of solid sites, $[Me_{s1}^*]_i$, at t=0 are required.

The TBL model is adjusted to the "adsorption" experimental data by optimisation of the three rate constants (k_{f1}, k'_{r1}, k'_{r2}). The mathematical approach maximizes the fitting of the model to the kinetic experimental data by the minimisation of the absolute weighed difference (WDIFF) between experimental and predicted values. The following equation is used to calculate the WDIFF value corresponding to a given set of rate constants:

$$WDIFF = \sum_{i=1}^{n} \frac{|act(i) - simul(i)|}{act(i)} \tag{3.9}$$

where "act(i)" represents the experimental relative radioactivity and "simul(i)" the simulated relative radioactivity, for the "i"th out of a series of "n" experimental data points. The TBL model optimisation computer program is reported in Appendix B (B2a).

Sediment suspensions were studied according to the experimental approach described in section 2.7.2. First, the kinetic variability of different stations from the same lake, sampled at different depths, was investigated. Figures 3.9 a,b,c show the kinetic experimental data for zinc and cadmium and their corresponding profiles simulated by the TBL model for three stations of Harp Lake sampled at 3 meters, 12 meters and 15 meters, respectively. Next, the spatial variability of kinetic results obtained from different freshwater lakes was assessed. Figures 3.10 a,b,c show the

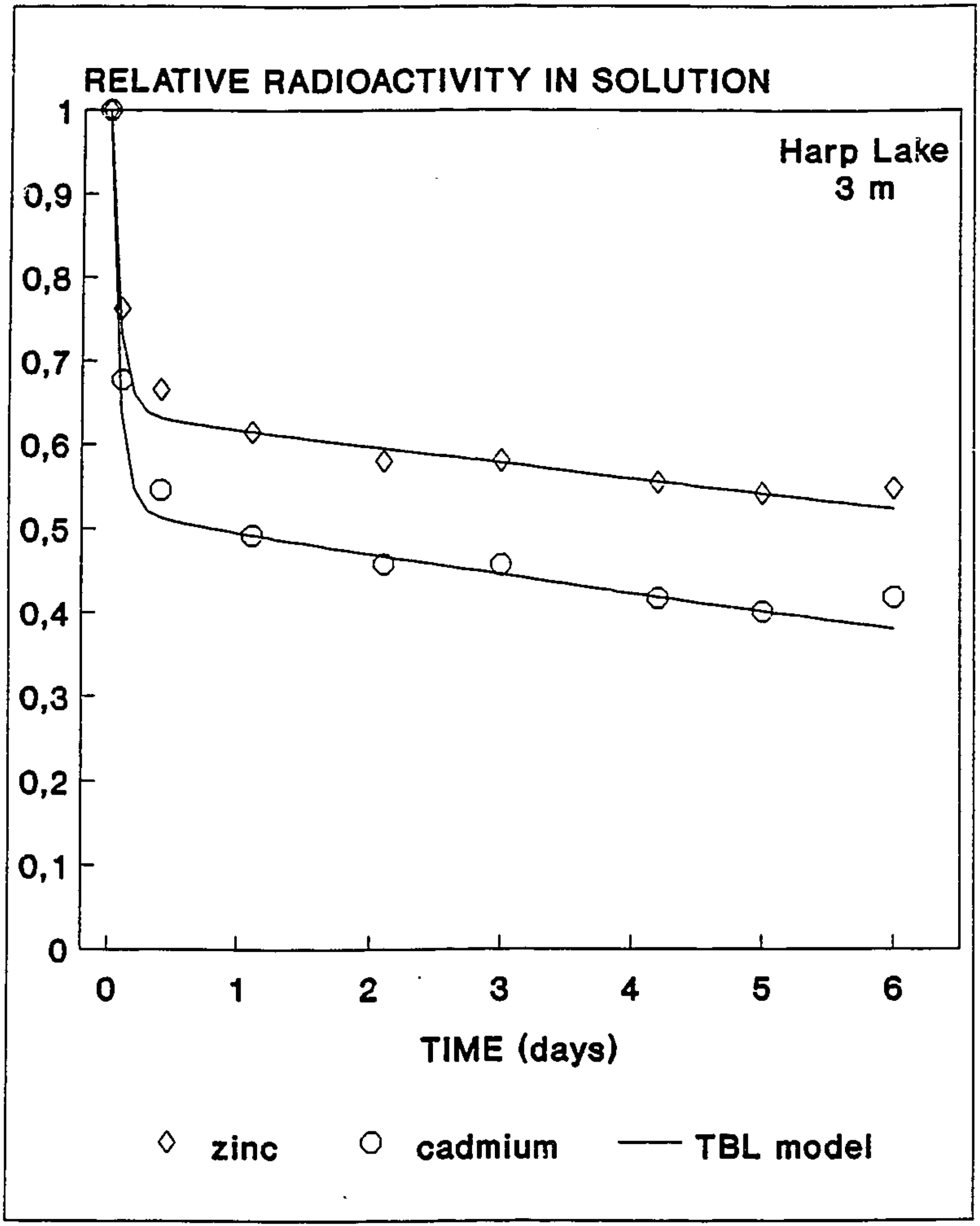

FIGURE 3.9 (a) "Adsorption" profiles of ^{65}Zn and ^{109}Cd kinetic exchange for sediment suspension HL-7-1. TBL model (solid line) is adjusted to the experimental data (symbols).

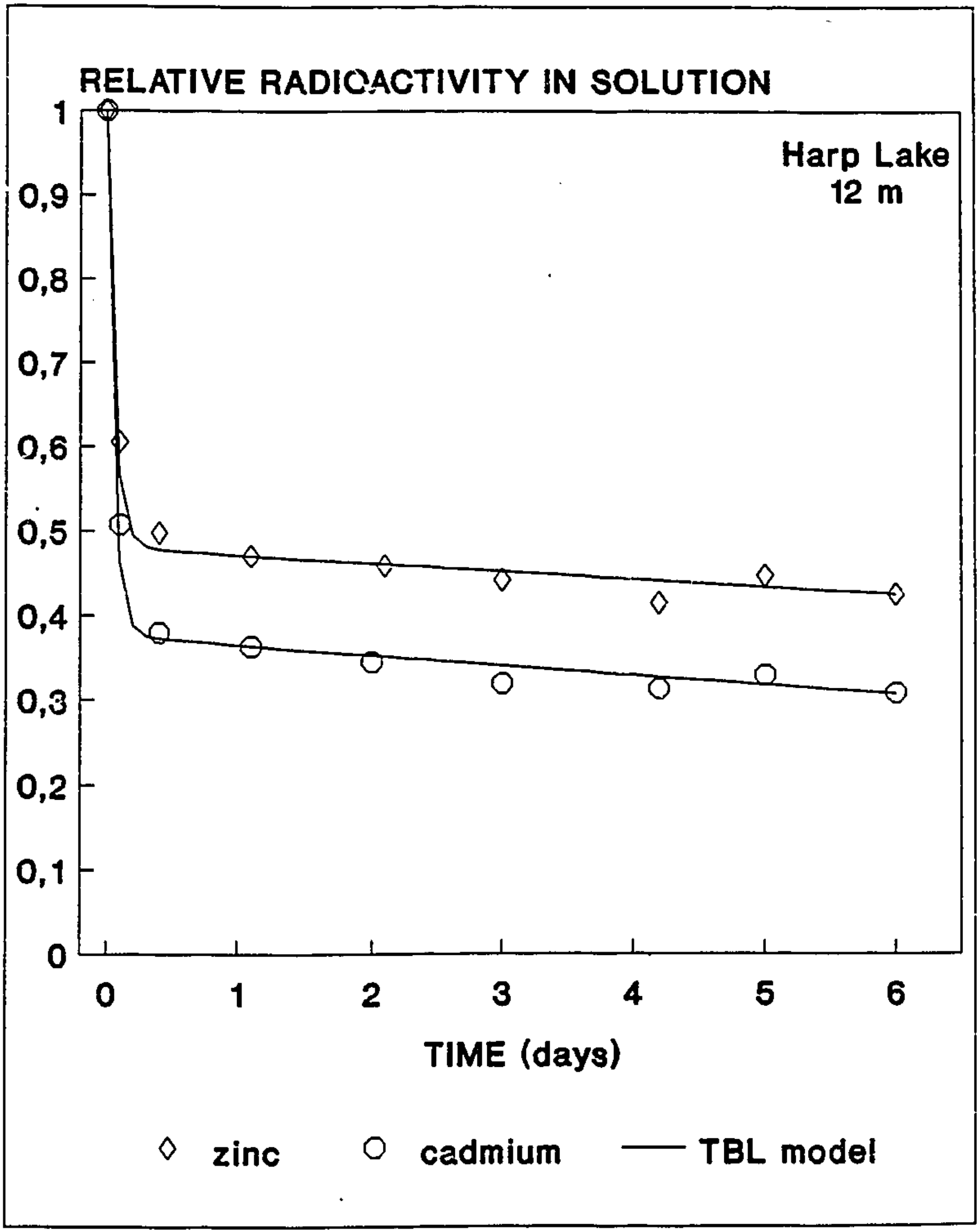

FIGURE 3.9 (b) "Adsorption" profiles of ^{65}Zn and ^{109}Cd kinetic exchange for sediment suspension HL-7-2. TBL model (solid line) is adjusted to the experimental data (symbols).

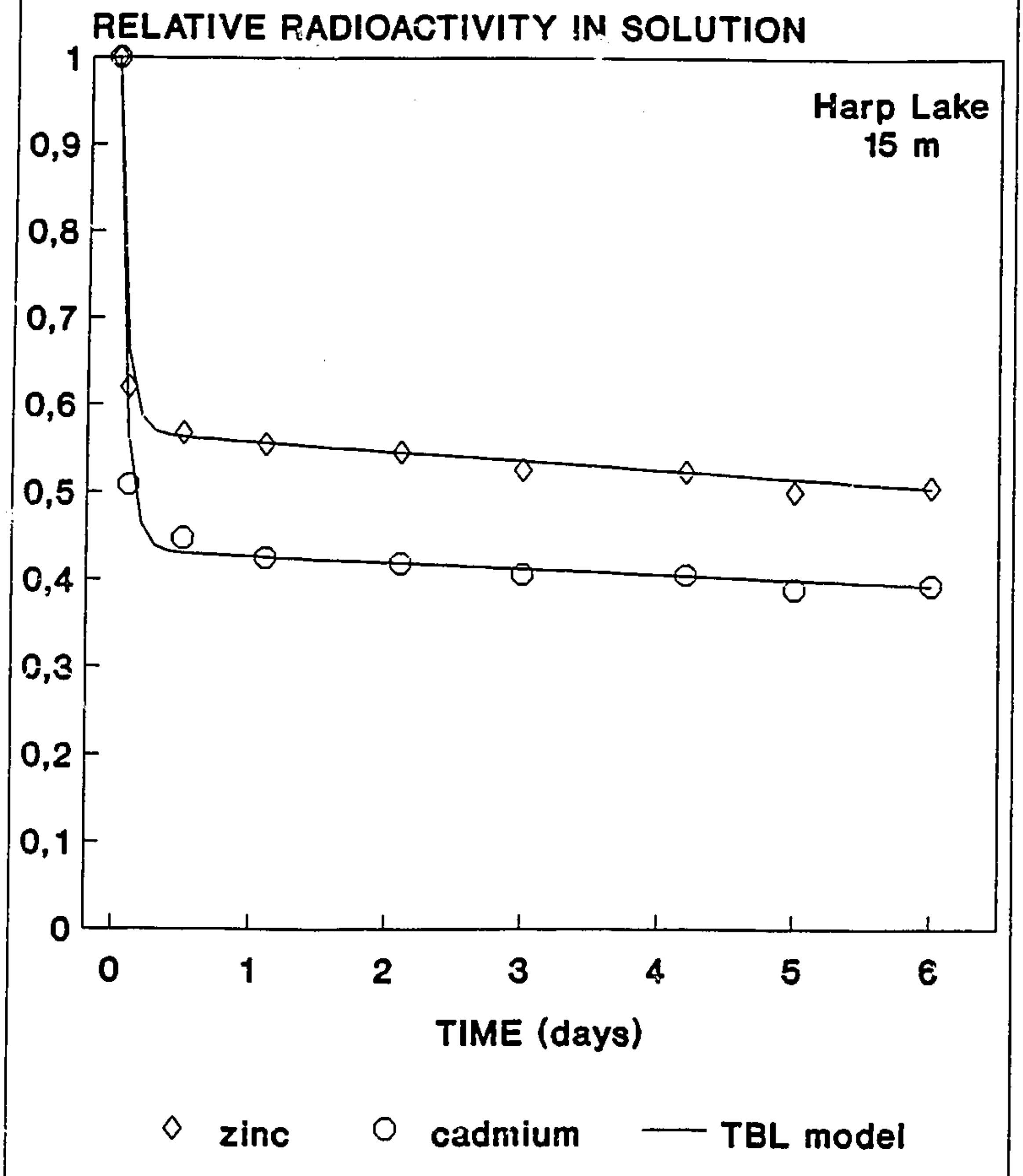

FIGURE 3.9 (c) "Adsorption" profiles of ^{65}Zn and ^{109}Cd kinetic exchange for sediment suspension HL-7-3. TBL model (solid line) is adjusted to the experimental data (symbols).

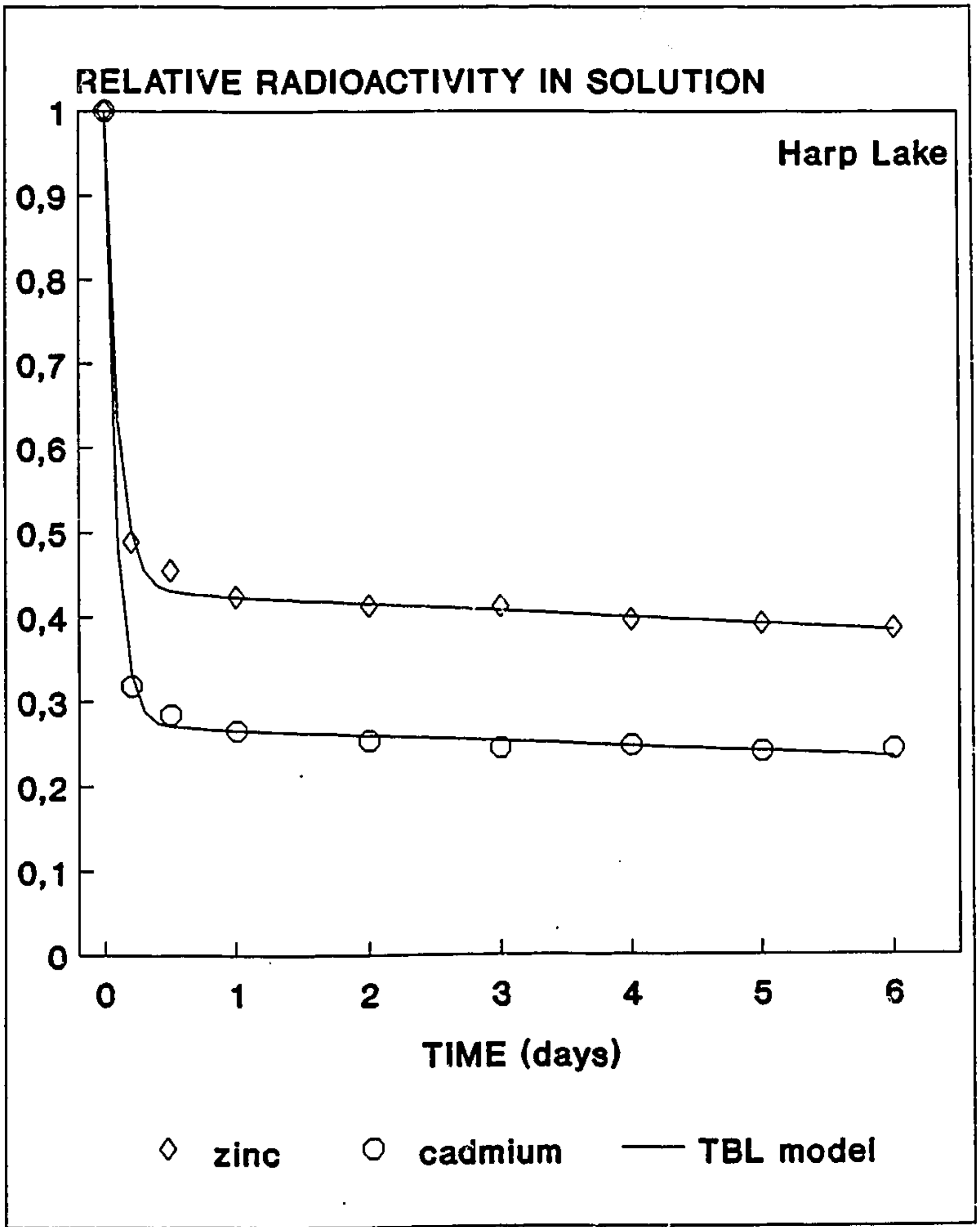

FIGURE 3.10 (a) "Adsorption" profiles of ^{65}Zn and ^{109}Cd kinetic exchange for sediment suspension HL-8-2. TBL model (solid line) is adjusted to the experimental data (symbols).

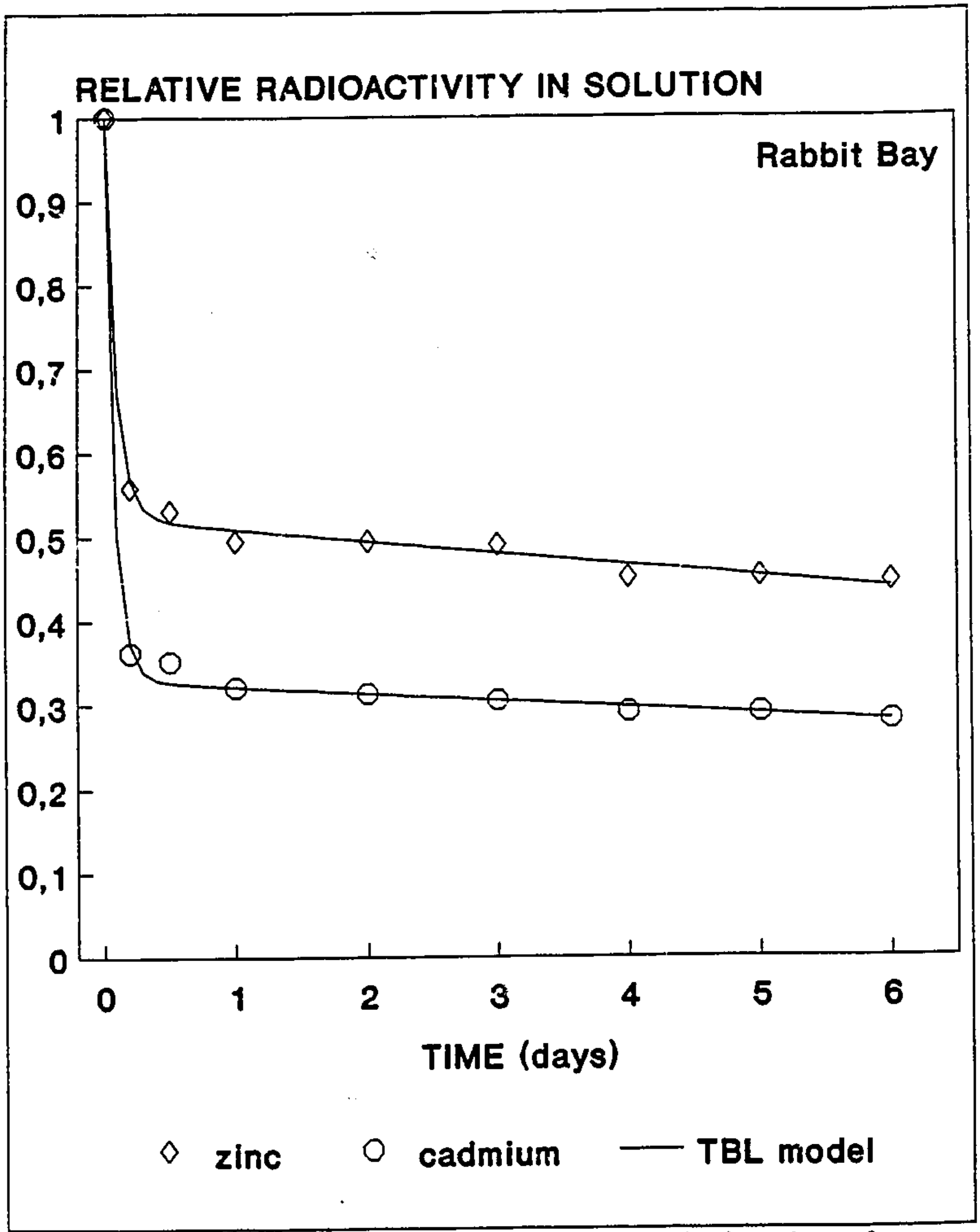

FIGURE 3.10 (b) "Adsorption" profiles of ^{65}Zn and ^{109}Cd kinetic exchange for sediment suspension RB-8-3. TBL model (solid line) is adjusted to the experimental data (symbols).

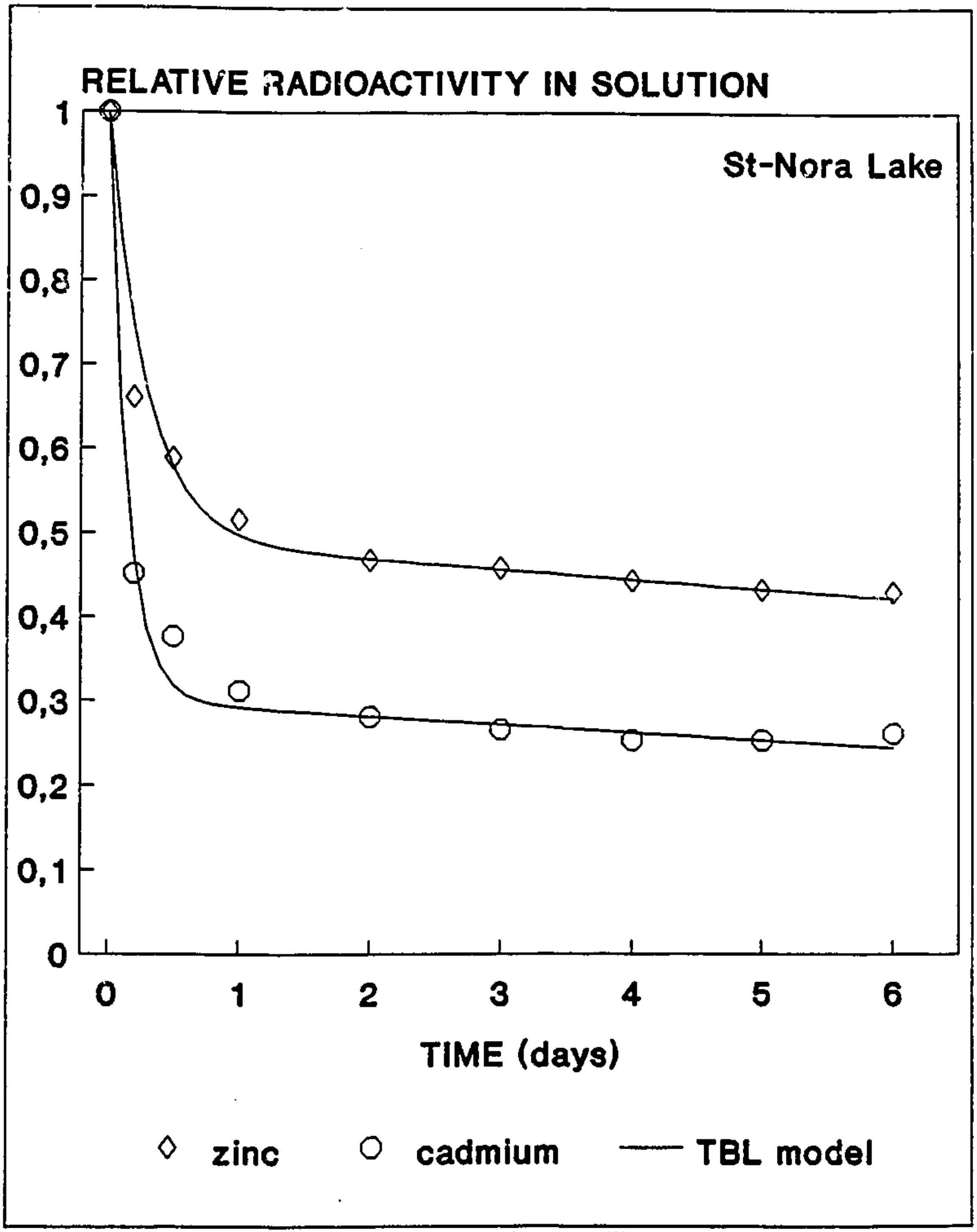

FIGURE 3.10 (c) "Adsorption" profiles of ^{65}Zn and ^{109}Cd kinetic exchange for sediment suspension SNL-8-4. TBL model (solid line) is adjusted to the experimental data (symbols).

kinetic experimental data for zinc and cadmium and their corresponding profiles simulated by the TBL model for Harp Lake, Rabbit Bay and St-Nora Lake, respectively. Finally, the temporal variability of kinetic results was obtained after sampling the same lake on different occasions (seasons) through the year. Figures 3.11 a,b,c show the kinetic experimental data for zinc and cadmium and their corresponding profiles simulated by the two compartment (box) model with a serial leak (TBL) for three natural suspensions from Harp Lake sampled in March 1988 (HL-3-2R2), March 1989 (HL-7-2) and June 1989 (HL-8-1).

In these figures, only the average radioactivities in solution are presented. The complete data are reported in Appendix A. Zinc and cadmium "Adsorption" profiles were obtained by the TBL model simulation computer program (Appendix B (B2b)) using optimised rate constants (k_{f1}, k'_{r1}, k'_{f2}) Table 3.1.

In some suspensions, the addition of radiotracers leads to a significant increase of total trace metal concentrations (Table 2.5). A net addition of metals in the liquid phase is expected to affect the rate of radiotracer exchange at the beginning of the experiment. The effect of an increase of total trace metal concentrations on the rate of trace metal exchange results in an overestimation of the forward rate constant (kf1). The bias in the experimental data (the first few data points) does not exceed, however, the experimental variability of the data under prevailing conditions. A new trace metal sorptive equilibrium in sediment suspensions is expected from the increase of total trace metal concentrations.

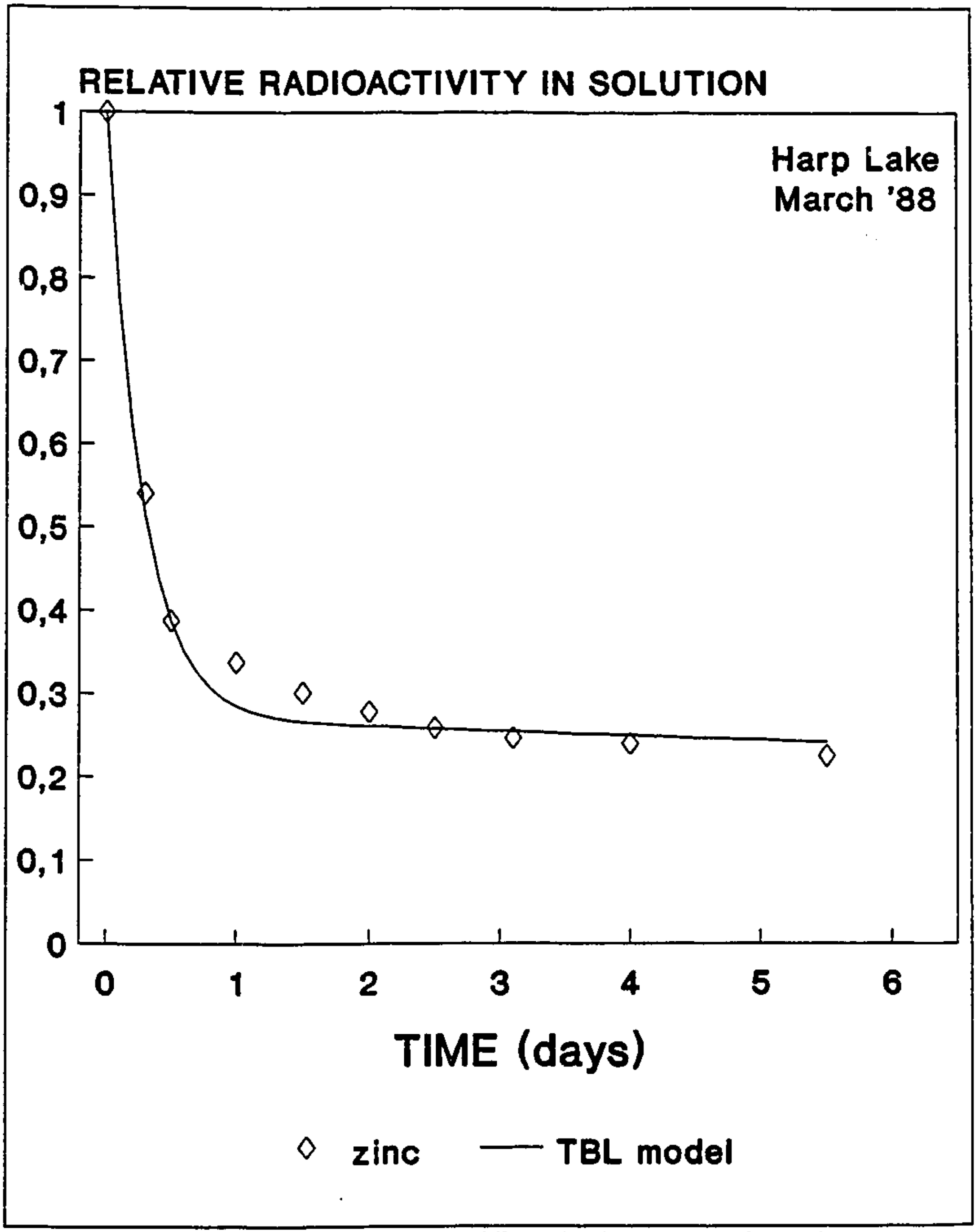

FIGURE 3.11 (a) "Adsorption" profile of ^{65}Zn kinetic exchange for sediment suspension HL-3-2R2. TBL model (solid line) is adjusted to the experimental data (symbols).

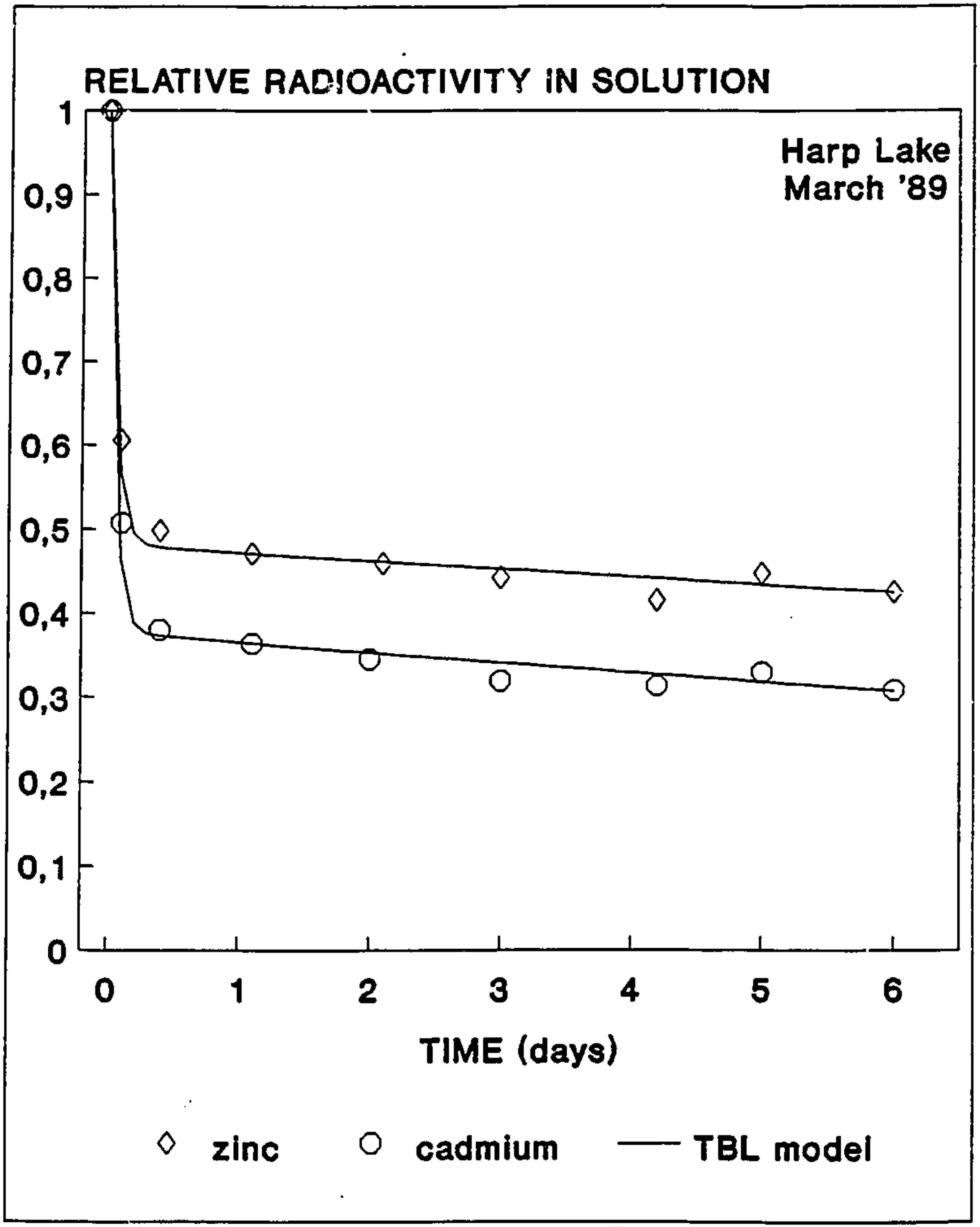

FIGURE 3.11 (b) "Adsorption" profiles of ^{65}Zn and ^{109}Cd kinetic exchange for sediment suspension HL-7-2. TBL model (solid line) is adjusted to the experimental data (symbols).

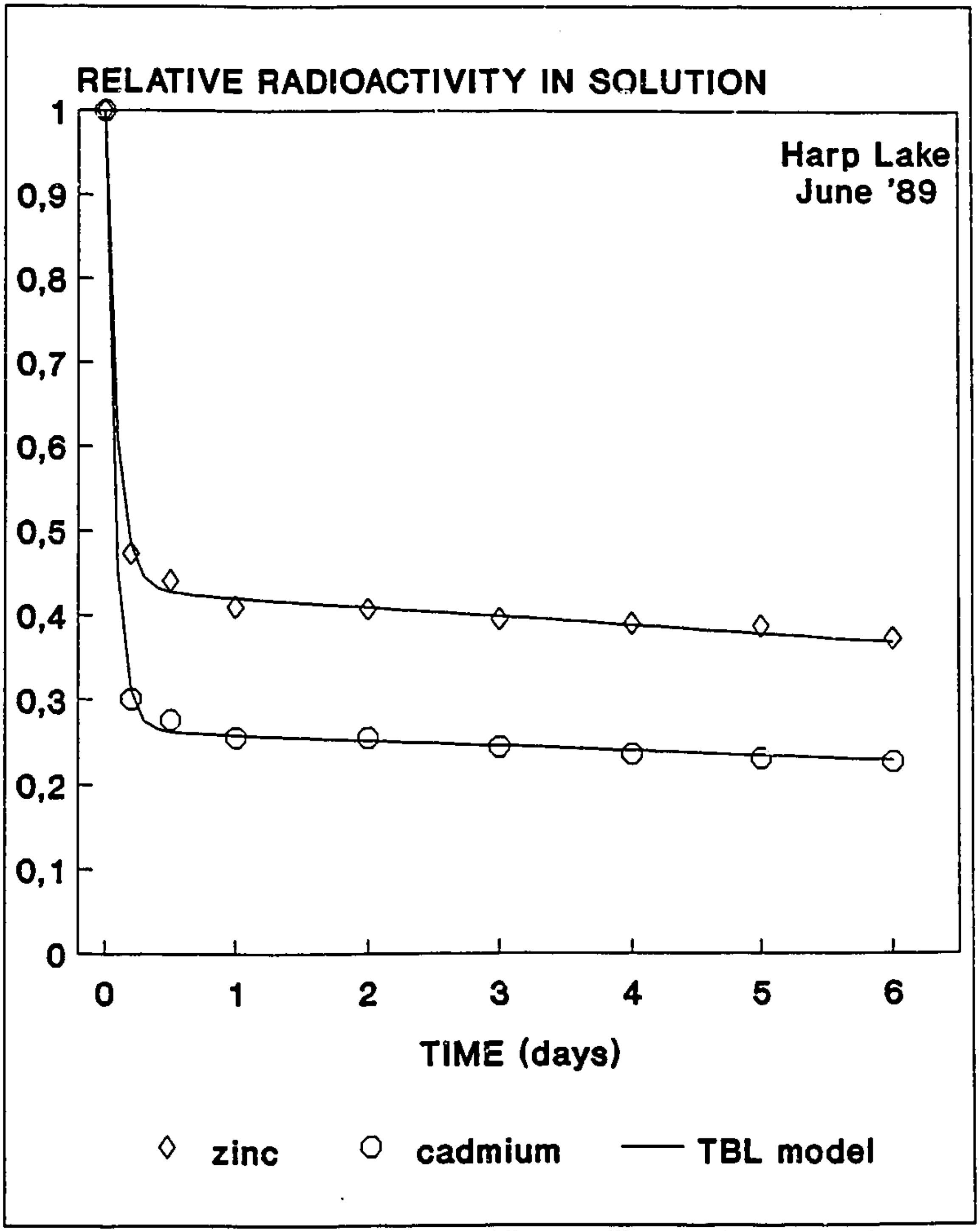

FIGURE 3.11 (c) "Adsorption" profiles of ^{65}Zn and ^{109}Cd kinetic exchange for sediment suspension HL-8-1. TBL model (solid line) is adjusted to the experimental data (symbols).

TABLE 3.1 Optimised overall rate constants resulting from the adjustment of the TBL model to the "adsorption" kinetic data of sediment suspensions grouped by sampling strategy. Rate constants (k_{f1}, k'_{r1}, k'_{f2}) are defined in Equations 3.7.

sediment suspension	Zn k_{f1} (d^{-1})	 k'_{r1} (d^{-1})	 k'_{f2} (d^{-1})	Cd k_{f1} (d^{-1})	 k'_{r1} (d^{-1})	 k'_{f2} (d^{-1})
strategy : different stations, same lake						
HL-7-1 (3 m)	4.80	8.40	0.052	6.65	7.15	0.102
HL-7-2 (12 m)	9.25	8.55	0.043	12.15	7.30	0.091
HL-7-3 (15 m)	6.55	8.60	0.035	8.15	6.20	0.038
strategy : different lakes						
HL-8-2 (Harp Lake)	5.90	4.45	0.046	9.00	3.30	0.094
RB-8-3 (Rabbit Bay)	5.50	6.00	0.056	9.05	4.40	0.082
SNL-8-4 (St-Nora Lake)	1.75	1.65	0.054	4.85	2.00	0.122
strategy : different seasons, same lake						
HL-3-2R2 (March '88)	2.66	0.92	0.084	-----	-----	-----
HL-7-2 (March '89)	9.25	8.55	0.043	12.15	7.30	0.091
HL-8-1 (June '89)	6.65	5.00	0.062	9.95	3.50	0.101

CHAPTER 4

DISCUSSION

4.1 ADVANTAGES AND LIMITATIONS OF TECHNIQUE:

The experimental approach applied in this study to obtain trace metal exchange rates of sediment suspensions offers numerous advantages. Specifically, the natural conditions of temperature, light, and agitation of resuspended sediments are accounted for in the sampling and the conservation of natural samples. Most importantly, the use of radiotracers allows experimental work at natural levels of trace metal concentrations.

The stability of a variety of parameters suggests that experimental conditions are controlled well. When significant, only small variations of total trace metal concentrations in solution were observed during the investigation of gain-loss of trace metals or kinetic experimentations. No significant changes were observed for both radioactive Zn and Cd (Figure 2.9). The reliability of the technique was also supported by the precision of the experimental data in replicate analysis (Figure 3.6) and the precision of experimental data in replicate kinetic experiments (Figure 3.7).

A novel experimental design consisting of an "adsorption-desorption" sequence was applied to surface sediment suspensions. This laboratory approach permits the investigation of the rate of both forward and reverse trace metal interactions with natural solids. An example of the overall technique, characterizing a fully reversible fast exchange, was depicted in Figure 3.8 for cadmium with a synthetic TiO_2 suspension.

In spite of these advantages, the experimental approach and the radiotracer technique have certain limits. For instance, the application of the technique is appropriate for only a restricted range of trace metal exchange rates: extremely fast and very slow processes cannot be investigated with precision by this technique. The limits of the technique are the result of: (1) the time required to collect the first subsample, and (2) the imprecision of the technique to discern small differences of radioactivity in solution.

The time between the beginning of the kinetic experiment and the first subsampling is critical. At best, the first subsample was taken only 2 hours (0.08 d) after the addition of radiotracers to the suspension liquid phase. Thus, the lack of information in the earliest stage of the trace metal radiotracer exchange limits its kinetic description to rate constants characterized by a half-life in the order of few hours or more. Values reported in Table 3.1 represent minimum rate constants. In most cases, however, the fast reactions have not reached an equilibrium state before the first subsample is taken; the relative radioactivity in solution shows a continuous fast decrease among the first few experimental data points (see Figures 3.9 - 3.13). The rate constants reported in Table 3.1 adequately characterize the kinetics of trace metal interactions with lake sediments. The kinetic exchange of ^{109}Cd with a synthetic TiO_2 suspension (Figure 3.8) shows that relatively fast solid-liquid trace metal interactions ($t_{1/2}$ ≤ hours) are obtainable by the technique.

The second restriction concerns the limit of the technique to detect small differences in trace metal radioactivity in solution. The TBL model, represented by Equations 3.7, is used to verify the presence of a slow trace metal solid-liquid exchange. Any significant change in radioactivity in solution must exceed the experimental imprecision of the data, which is estimated to be approximately ± 0.02 unit of relative radioactivity in solution (Figures 3.6 and 3.7). This variability is the result of experimental error from: (1) the preparation of the sample for counting (i.e. separation of the liquid from the suspension and transfer of a specific volume for counting), and (2) the counting step itself (i.e. time allowed for counting); the former being the main source of error. At least 4-5 days of trace metal exchange characterize the slow process, in the adsorption step, the variation of radioactivity in solution should be at least 0.008 unit of relative radioactivity per day over 5 days in order to reveal a significant change. The contribution of the rearrangement reaction in the overall radiotracer exchange process, is described in the TBL model, by the magnitude of the rate constant k'_{f2} and the concentration of radioactive metals associated to the first type of solid sites (Equation 3.7(c)).

$$\frac{d[Me^{*}_{s2}]}{dt} = k'_{f2}\,[Me^{*}_{s1}] \tag{4.1}$$

If one accepts that the first exchange has much faster rates than the rearrangement reaction and reaches a steady state (k_{f1} $[Me^*_w]$ = k'_{r1} $[Me^*_{s1}]$ > > k'_{f2} $[Me^*_{s1}]$) then, one may approximate the change of radioactivity associated with the first type of solid sites by the change of radioactivity in solution, and express $[Me^*_{s1}]$ in terms of rate constants only. The following equation is obtained:

$$\frac{d[Me^*_w]}{dt} \approx - k'_{f2} \ [Me^*_{s1}] \approx - k'_{f2} \frac{k_{f1} \ [Me^*_T]}{(k_{f1} + k'_{r1})} \tag{4.2}$$

This equation is used to calculate, for each sediment suspension, the maximum rate of radioactive trace metal exchange in solution resulting from the slow exchange process. The rate of trace metal exchange obtained by Equation 4.2 is maximal as the highest possible value of $[Me^*_{s1}]$ is considered in the calculation. Using rate constants reported in Table 3.1, the maximum rate (relative radioactivity/day) of each sediment suspension is calculated and reported in Table 4.1. In all the suspensions investigated, a minimum change of 0.008 units of relative radioactivity in solution per day over at least 5 days is always exceeded which supports the presence of a slow process.

The imprecision of the experimental data also has important implications concerning the overall methodological approach. In fact, when most of the trace metal radioactivity is found in solution or associated with the solid, estimations of rate constants and trace metal partitioning may become very imprecise. Experimental imprecision results from two factors: (1) small counting error, under the best

TABLE 4.1 Maximum rates characterizing the rearrangement reaction of zinc and cadmium in sediment suspensions as defined in the TBL model. Maximum rates are calculated using rate constants reported in Table 3.1.

Suspension	Zinc[a]	Cadmium[a]
HL-7-1	0.019	0.049
HL-7-2	0.022	0.057
HL-7-3	0.015	0.022
HL-8-2	0.026	0.069
RB-8-3	0.027	0.055
SNL-8-4	0.028	0.086
HL-3-2R2	0.062	-----
HL-8-1	0.035	0.075

a maximum rates are expressed in relative radioactivity in solution per day.

conditions, is difficult to avoid, and (2) contamination during separation of phases is most significant for the lesser phase. In order to avoid such situations, the suspension particle concentration has to be carefully selected. For example, a suspension with a particle concentration of 100 mg/L leads to distribution coefficients of trace metals (Equation 1.4) ranging between log Kd = 2.3 and log Kd = 5.7 when 2% and 98% of the total radioactivity is removed from the solution, respectively. Ideally, the combination of distribution coefficient/particle concentration should lead to an almost even distribution of trace metals between the two phases. An appropriate selection of particle concentration minimises the errors in the separation step and allows the investigation of the slow reactions. These conditions also permit the experimentation of the "desorption" step. For a suspension of 100 mg/L, log Kd values of approximately 4 give an adequate distribution of trace metals between solid and liquid.

Many studies have investigated multiple radiotracers in a single suspension with reported Kd values ranging over four orders of magnitude (e.g. Santschi et al.,1984; Nyffeler et al., 1984). This situation makes the interpretation of results difficult for elements such as Fe (up to 98 % removal from the solution) or Cs (only 2 % of its concentration is removed from the solution of a 100 mg/L suspension). A much higher degree of precision from the separation technique and from the detection method is then required. Balistrieri and Murray (1984) have shown that 3 different particle concentrations (1 mg/L, 10 mg/L and 100 mg/L) are needed to obtain precise values of the distribution of 13 common trace metals in marine sediment suspensions. Thus, it is clear that for a given suspension the radiotracer technique is applicable to only a limited selection of trace metals. The choice of trace metals is restricted by the particle concentration of the suspension.

The use of radiotracers also has some drawbacks such as: (1) only a limited number of radioactive trace metals with a half-life in the order of days or more are available, and (2) there is a lack of radioactive solutions characterized by very high specific activities causing either significant increases of total element concentrations or difficulties in getting acceptable counting statistics.

Kinetic results are more likely to be affected by experimental conditions, which emphasizes the need for large similarity between the experimental and natural conditions. Experimental conditions should reflect - as closely as possible - the natural environment. This requirement has been met through the experimental design of this study. Some existing processes occurring at the natural sediment-water interface are, however, difficult to duplicate in laboratory. These include: (1) the addition of newly settled particles, (2) the gradual elimination of particles excluded from natural resuspension events, and (3) the natural fluxes of elements or compounds to and from the water at the sediment-water interface.

4.2 INTERPRETATION OF KINETIC RESULTS:

4.2.1 INVESTIGATED SUSPENSIONS:

The solid-liquid exchange of cadmium in a synthetic TiO_2 suspension was characterized by fast, quasi-instantaneous interactions. Such a fast cadmium exchange is consistent with fast reactions of inorganic ions at oxide surfaces reported by numerous authors (e.g. Leckie et al. 1980, Chang et al. 1987, Theis et al. 1988, Hachiya et al. 1984, Hayes and Leckie 1986). Some authors have occasionally observed a second slow reaction following the initial fast removal of trace metals from the solution. The explanation of the slow reaction, even in simplified systems, is still unclear. Possible interpretations include: (1) physical mass transfer of metals into the solid, (2) chemical reaction(s), or (3) a combination of both processes. Transformation of the solid phase is occasionally reported (e.g. crystallisation of amorphous material).

The description of cadmium-TiO_2 kinetic data requires only the consideration of fast interactions (Figure 3.8). It is possible, however, that the exchange involves a slow reaction, but the small fraction of cadmium associated to the solid, and the variability of the experimental data may hide the slow reaction.

The situation is different for sediment suspensions where a slow reaction is observed for all the suspensions (Table 4.1). Thus, the description of kinetic experimental data requires the inclusion consideration of a slow reaction in the trace metal interactions with lake sediments.

It was also observed from the "adsorption" data reported in Figures 3.9 to 3.11, that cadmium is systematically removed from the solution to a greater extent than zinc. This contrasts with the common trend observed between distribution coefficients of metals with oxides and constants of hydrolysis for the same metals (Stumm and Morgan, 1981). The stronger affinity of cadmium for the sediment by comparison with zinc is, however, supported by (1) Kd values (total elements) for the suspensions investigated in this work (section 4.4) and for other systems (e.g. Mouvet and Bourg, 1983), (2) the same relative reactivity of these metals with humic substances (Gamble, 1986), and (3) higher affinity of dissolved trace metal for a solid at lower densities of adsorption (Benjamin and Leckie, 1981).

The results of the three experimental strategies applied to sediment suspensions are discussed on the basis of the optimised rate constants and the sensitivity of the model (see below). Rate constants k_{f1}, k'_{r1} and k'_{r2} reported in Table 3.1 characterize the best fit of the experimental data by the TBL model for each sediment suspension. A sensitivity estimate of the TBL model is made by arbitrary reducing the optimisation criteria (WDIFF; Equation 3.9) by 10% relative to the best fit. For some sediment suspensions, k_{f1} and k'_{r1} values vary by more then 30% and rate constant k'_{r2} varies by about 20% under this sensitivity test. These ranges of rate constants are used to compare kinetics of trace metal interactions among the sediment suspensions.

First, rate constants characterizing the exchange of radioactive zinc and cadmium with different stations of a given lake (Figures 3.9 (a),(b),(c)) are not significatively different (Table 3.1). The similarity of rate constants among these suspensions is supported by their quasi-common chemical (Table 2.2) and physical (Figure 2.2) characteristics.

Secondly, all natural freshwater lakes studied show very similar kinetic behaviour (e.g. Figures 3.10 (a),(b)). Kinetic experimental data of St-Nora Lake

(Figure 3.10 (c)) are described by slightly smaller rate constants for both metals, which suggests a slower exchange . Since rate constants are assumed to be (pseudo) first-order, the half-life of each interaction can be calculated from the following relation:

$$t_{1/2} = \frac{\ln 2}{k} \tag{4.3}$$

where $t_{½}$ represents the half-life of a the reaction and k, its rate constant. Kinetics of trace metal interactions with natural freshwater sediments are described by an initial fast exchange with a half-life in the range of 1 to 10 hours, followed by a slower reaction with a half-life in the range of 0.8 to 2.1 weeks.

Finally, rate constants of three Harp Lake suspensions sampled at different times of the year are compared. Kinetic experimental data of two suspensions. sampled in March and June, 1989, respectively, are described by very similar rate constants (Figures 3.11 (a),(b)). Rate constants of the suspension sampled in March 1988 are smaller, particularly the fast reversible exchange. This does not necessarily imply slower exchange kinetics as suspension HL-3-2R2 (March 1988; Figure 3.11 (c)) was investigated using a slightly different radiotracer technique in terms of the agitation, separation of the liquid phase from the rest of the suspension, and experimental temperature (see Table 2.6). Lower rate constants of suspension HL-3-2R2 may be explain by direct effects of experimental conditions. These are: (1)

the temperature effect (rate constants decrease by lowering the temperature) as observed by Salim and Cooksey (1980), and (2) the agitation effect (rate constants decrease under periodic compared to continuous agitation) as shown by the kinetic experimental data reported in Figure 2.6.

Rate constants of replicate suspensions, HL-8-1 and HL-8-2, are also compared. Both suspensions are essentially identical with the exception that the "adsorption" data of suspension HL-8-1 covers 12 days, whereas suspension HL-8-2 is limited to 6 days. The difference in rate constants for Zn and Cd is not significant between these two experiments based on the model sensitivity. Thus, it is possible to get a very good estimation of rate constants with only 6 days of experimentation. In other words, one can predict precisely the "adsorption" kinetic data over at least 12 days from the rate constants obtained after an experiment of only 6 days. This option is profitable when the sequence "adsorption-desorption" is performed.

In summary, freshwater sediments of three different lakes, sampled at different stations (depth) or at different times of the year, exhibit similar reaction dynamics for zinc and cadmium. For the first time, a general kinetic behaviour, consisting of a fast reaction (hours) followed by a slower step (weeks) is displayed.

4.2.2 COMPARISON WITH OTHER KINETIC STUDIES:

4.2.2.1 Characteristics of a variety of kinetic studies:

The two-compartment model with a serial leak (TBL) is chosen to describe the kinetic data of trace metal exchange with sediments because: (1) rate constants are available for a variety of kinetic studies reported in the literature , and (2) TBM model, a simplified version of TBL model, is also widely used. Tables 4.2 (Zn) and 4.3 (Cd) present rate constants and other characteristics of a variety of sediment suspensions.

Brief descriptions of studies reported in Tables 4.2 and 4.3, are presented below. Nyffeler et al.(1984), did laboratory studies with more than one dozen trace metals including ^{65}Zn and ^{109}Cd, using a variety of marine substrates. Surface sediments from Narragansett Bay (N.B.), St-Clemente Basin (S.C.B.) and MANOP site H (MANOP-H1) were investigated for both Zn and Cd, whereas sediment materials (SET-PAR) and faecal pellets (FEC-PEL) collected by sediment traps in North Atlantic were investigated for Zn only. Their batch suspensions were prepared by the addition of concentrated sediment materials to spiked seawater (30‰ salinity). Mixtures were kept in the dark and in suspension using a mechanical shaker. Particle concentration, pH, temperature, and their rate constants are reported in Tables 4.2 and 4.3.

TABLE 4.2 Suspension characteristics of a variety of kinetic studies using ^{65}Zn. Rate constants (k_{f1}, k'_{r1}, k'_{r2}) are obtained from the adjustment of the TBL model to the kinetic experimental data.

#	Suspension	pH	Cp (mg/L)	T (°C)	k_{f1} (1/d)	k'_{r1} (1/d)	k'_{r2} (1/d)	PMe^*_w (%)	Ref.
1	N.B.	8.1	100	2	0.039	0.320	0.000	89.14	(1)
2	S.C.B.	8.1	100	2	0.066	0.600	0.000	90.09	(1)
3	MANOP-H1	8.1	100	2	1.000	0.070	0.040	6.54	(1)
4	SET-PART	8.1	27.5	2	0.198	2.000	0.000	90.99	(1)
5	FEC-PEL	8.1	27.5	2	0.259	1.000	0.000	79.46	(1)
6	MANOP-HS	8	75	4	0.800	0.014	0.014	1.72	(2)
7	MANOP-HN	8	75	4	3.550	0.005	0.006	0.15	(2)
8	MANOP-H2	7.8	1	20	0.014	0.108	0.000	88.52	(3)
9	MANOP-R1	7.8	10	2	0.066	7.700	0.000	99.15	(4)
10	MANOP-R2	7.8	880	2	18.150	19.000	0.010	51.14	(4)
11	P.S.	7.9	1	2	0.070	1.900	0.160	96.45	(5)
12	L302S-1^a	6.5	100	nr	8.000	1.000	-----	11.11	(6)
13	L302S-2^a	4.8	100	nr	0.130	1.000	-----	88.50	(6)
14	L-114-1^a	6.5	100	20	3.800	0.500	-----	11.63	(7)
15	L-114-2^a	4.3	100	20	0.180	1.000	-----	84.75	(7)
16	HL-3-2R2	6.6	≈ 250	4	2.66	0.92	0.084	21.30	(8)
17	HL-7-1	6.8	70	7	4.80	8.40	0.052	63.64	(8)
18	HL-7-2	6.7	75	7	9.25	8.55	0.043	48.03	(8)
19	HL-7-3	6.8	75	7	6.55	8.60	0.035	56.77	(8)
20	HL-8-1	6.8	55	8	6.65	5.00	0.062	42.92	(8)
21	HL-8-2	6.8	55	8	5.90	4.45	0.046	43.00	(8)
22	RB-8-3	6.7	55	8	5.50	6.00	0.056	52.17	(8)
23	SNL-8-4	6.7	55	8	1.75	1.65	0.054	48.53	(8)

(1) Nyffeler et al. 1984
(2) Santschi et al. 1984
(3) Balistrieri and Murray 1984
(4) Li et al. 1984
(5) Jannash et al. 1988
(6) Nyffeler et al. 1986
(7) Santschi et al. 1986a
(8) This work

C_p = particle concentration
PMe^*_w = percentage of metals in solution (see Equation 4.6)
nr = not reported
a = rate constants (k_{f1}, k'_{r1}) are obtained from the adjustment of the TBM model to the kinetic experimental data.

TABLE 4.3 Suspension characteristics of a variety of kinetic studies using ^{109}Cd. Rate constants (k_{r1}, k'_{r1}, k'_{r2}) are obtained from the adjustment of the TBL model to the kinetic experimental data.

#	Suspension	pH	Cp (mg/L)	T (°C)	k_{r1} (1/d)	k'_{r1} (1/d)	k'_{r2} (1/d)	PMe^{*}_{w} (%)	Ref.
1	N.B.	8.1	100	2	0.009	1.000	0.000	99.16	(1)
2	S.C.B.	8.1	100	2	0.005	1.000	0.000	99.53	(1)
3	MANOP-H1	8.1	100	2	0.290	0.300	0.040	50.85	(1)
8	MANOP-H2	7.8	100	20	0.435	1.580	0.005	78.41	(3)
9	MANOP-R1	7.8	10	2	9.100	36.400	0.000	80.00	(4)
10	MANOP-R2	7.8	880	2	28.160	74.400	0.000	72.54	(4)
17	HL-7-1	6.8	70	7	6.65	7.15	0.102	51.79	(8)
18	HL-7-2	6.7	75	7	12.15	7.30	0.091	37.55	(8)
19	HL-7-3	6.8	75	7	8.15	6.20	0.038	43.22	(8)
20	HL-8-1	6.8	55	8	9.95	3.50	0.101	26.03	(8)
21	HL-8-2	6.8	55	8	9.00	3.30	0.094	26.82	(8)
22	RB-8-3	6.7	55	8	9.05	4.40	0.082	32.72	(8)
23	SNL-8-4	6.7	55	8	4.85	2.00	0.122	29.20	(8)

(1) Nyffeler et al. 1984
(3) Balistrieri and Murray 1984
(4) Li et al. 1984
(8) This work

C_p = particle concentration
PMe^{*}_{w} = percentage of metals in solution (see Equation 4.6)

Santschi et al. (1984) investigated pulverised surface sediments (MANOP-HS) and ferro-manganese nodules (MANOP-HN) from MANOP site H, in order to determine the kinetics of nine radiotracers, including ^{65}Zn, in laboratory experiments. Their suspensions of particles in seawater at concentrations between 50 and 100 mg/L were equilibrated at 4°C in an automatic shaker. Partition coefficients were determined after filtration and γ-counting of solid and liquid fractions. Only a few values of log Kd versus time were reported for their kinetic experiments. The following procedure is used to calculate the relative radioactivity of a trace metal in solution from a reported value of log Kd. The total radioactivity of the suspension is first set at 1, and Equation 1.4, adapted for radiotracers, becomes:

$$Kd = \frac{1 - [Me_w^*]}{[Me_w^*]\ Cp} \tag{4.4}$$

after rearrangement, one obtains:

$$[Me_w^*] = \frac{1}{(\ Kd\ Cp + 1\ )} \tag{4.5}$$

where $[Me^*_w]$ is the relative radioactivity in solution, Kd and Cp represent the coefficient of distribution and the concentration of particle in mL/g and g/mL, respectively. Equation 4.5 permits one to obtain the relationship between experimental $[Me^*_w]$ and time if Cp and the relationship between log Kd and time are known. Rate constants optimised with the TBL model, are reported in Tables 4.2 and 4.3 for zinc and cadmium, respectively.

Balistrieri and Murray (1984) also investigated the interaction of trace metals with natural interfacial sediments from MANOP site H (MANOP-H2). Along with 11 other radiotracers, ^{65}Zn and ^{109}Cd were equilibrated in Teflon centrifuge tubes at room temperature for more than 45 days. Their experimental results - reported as the percent of trace metals adsorbed by solids as a function of time - were transformed to relative radioactivity in solution versus time. Rate constants were obtained according to the TBL model. Tables 4.2 and 4.3 report rate constants for zinc and cadmium, respectively.

Li et al. (1984) studied the change of the partition coefficient, Kd, as a function of time for up to 13 radioactive trace metals including zinc and cadmium. Suspensions of fine particles from MANOP site R (red clays) and New York coastal water, were prepared and allowed to equilibrate for more than one week as a pretreatment. A concentrated suspension (880 mg/L ; MANOP-R1) and a dilute suspension (10 mg/L : MANOP-R2) were investigated. Radiotracers were added to the suspensions agitated by a wrist shaker in a dark cold room. "Adsorption" experiments were performed by subsampling the mixtures over 20 days. Subsamples were filtered through 0.4 μm pore size membrane, and activities of the two fractions were γ-counted. Their experimental data were transformed to relative radioactivity in solution versus time, using Equation 4.5. Optimised rate constants for zinc and cadmium are listed in Tables 4.2 and 4.3, respectively.

Jannash et al. (1988) reported sorption kinetics of four radiotracers with natural particles from Puget Sound (P.S.) seawater. Their general experimental method is very similar to the method reported by Nyffeler et al. (1984). The following differences are, however, noted: (1) the particle concentration was only 1.0 mg/L, (2) radiotracers were added to suspensions rather than the particles being added to a radioactive spiked solution of seawater, (3) magnetic stirrers were used to keep suspensions homogeneous, and (4) more data were obtained at the early stage of their experiments. The reported rate constants (Table 4.2) describe the kinetic experimental profile of ^{65}Zn according to the TBL model.

Nyffeler et al. (1986) estimated the uptake rates of selected radiotracers, including ^{65}Zn, by the sediments of Lake 302S from ELA (Experimental Lakes Area), in Northwestern Ontario. Kinetics of two sediment suspensions (pH = 6.5 (L302S-1); pH = 4.8 (L302S-2)), with a particle concentration of 100 mg/L, were investigated in laboratory batch experiments. The two-compartment (box) model (TBM) was adjusted by the authors to their experimental data (not reported in their study); forward and backward rate constants are reported in Table 4.2.

Santschi et al. (1986a) reported kinetic parameters for the sorption of ^{65}Zn with sediments of Lake 114 from ELA at pH = 6.5 (L-114-1) and pH = 4.3 (L-114-2) determined in laboratory batch experiments at 20°C. They adjusted the TBM model to their kinetic experimental data. Their optimised rate constants are reported in Table 4.2.

Tables 4.2 and 4.3 report the overall results of 8 suspensions for Zn and 7 suspensions for Cd, investigated in this work, in addition to the 15 suspensions for zinc and 6 suspensions for cadmium from the above cited studies.

4.2.2.2 Maximum rates:

An objective comparison of the kinetic behaviour of trace metal among a variety of sediment suspensions is difficult due to differences of experimental conditions and suspension characteristics (e.g. temperature, agitation, particle concentration; concentration of dissolved trace metals, pH, ionic strength, etc). The application of a common kinetic model to describe kinetic experimental data simplifies the comparison task, although this approach requires certain conditions. For instance, pseudo rate constants - resulting from the interpretation of the kinetic experimental data in terms of the TBL model, as reported in Tables 4.2 and 4.3 - can only be compared when all experimental parameters and conditions are identical. Unfortunately, this important requirement is not met.

Instead of comparing conditional pseudo rate constants among a variety of kinetic studies, it is more appropriate to directly compare maximum rates of trace metal exchange obtained under controlled conditions. The maximum rate is defined, according to the TBL model, as the rate when k_{f1} $[Me^{*}_{w}]$ is equal k'_{r1} $[Me^{*}_{s1}]$ for the first time after the addition of the radiotracer. It represents the fastest rate, in relative radioactivity per day (r.r./d), of the continuous trace metal exchange between solid and liquid at steady state. The following equation is used to calculate maximum rates of metals in the kinetic experiment:

$$MAXIMUM \quad RATE = k_{r1}^{'} \, [Me_{s1}^{*}] = k_{f1} \, [Me_{w}^{*}] = \frac{k_{f1} \, PMe_{w}^{*}}{100} \tag{4.6}$$

where PMe$^*_w$ represents the percent of Me* in solution at sorptive equilibrium with the first type of solid sites. Due to the fact that the maximum rate is reached at the early stage of the trace metal exchange, PMe$^*_w$ can be expressed in terms of the fast reversible reaction only. One can use Equation 4.5 to calculate PMe$^*_w$ if Kd and Cp are known, or directly use rate constant values (Table 4.2 and 4.3) in the following equation:

$$PMe_{w}^{*} = 100 \, [Me_{w}^{*}] = \frac{100}{(k_{f1} \, / \, k_{r1}^{'}) + 1} \tag{4.7}$$

From the values reported in Tables 4.2 and 4.3, only 3 out of the 21 suspensions investigated by other authors are characterized by PMe$^*_w$ values are in the range of 20% to 80%. For the majority of these suspensions, less than 20% of total trace metals are found in one of the two phases. Important errors in the determination of Me$^*_w$ values, and consequently in rate constants are easily introduced.

Maximum rates (Zn and Cd) of a variety of seawater and freshwater suspensions are reported in Figures 4.1 and 4.2 . Suspension numbers on these figures correspond to suspensions described in Tables 4.2 and 4.3. In general, zinc and cadmium maximum rates are similar in a given sediment suspension. Maximum rates may, however, be very different among suspensions. The range of maximum rates covers up to three orders of magnitude presumably resulting from the influence of many parameters. For instance, the effect of some intrinsic characteristics of seawater suspensions (e.g. higher ionic strength and pH) may result in lower maximum rates of trace metal exchange in comparison with freshwater systems as suggested in Figures 4.1 and 4.2. The large surface area expected in fine clay suspensions (9) and (10) may explain the high maximum rate calculated. In fact, surface area seems to play an important role in kinetics of trace metal interactions with sediments. Freshwater suspensions described in Figure 4.1 include a first group (19 and up) where the range of particle size is limited to particle sizes smaller or equal to 100 μm, and a second group (12 to 16) characterized by an unaltered particle size distribution (i.e. including large particles). The first group (large surface area) shows higher maximum rates of zinc exchange. These observations suggest that the rates of trace metal exchange with sediments are proportional to the surface area provided by the suspension. This view is consistent with the results of Honeyman and Santschi (1988) showing a strong and positive function between the rate of solid-liquid trace metal interactions and solid concentration. Suspension surface area has been excluded from rate equations because this parameter was assumed to be constant and incorporated in the overall rate constants.

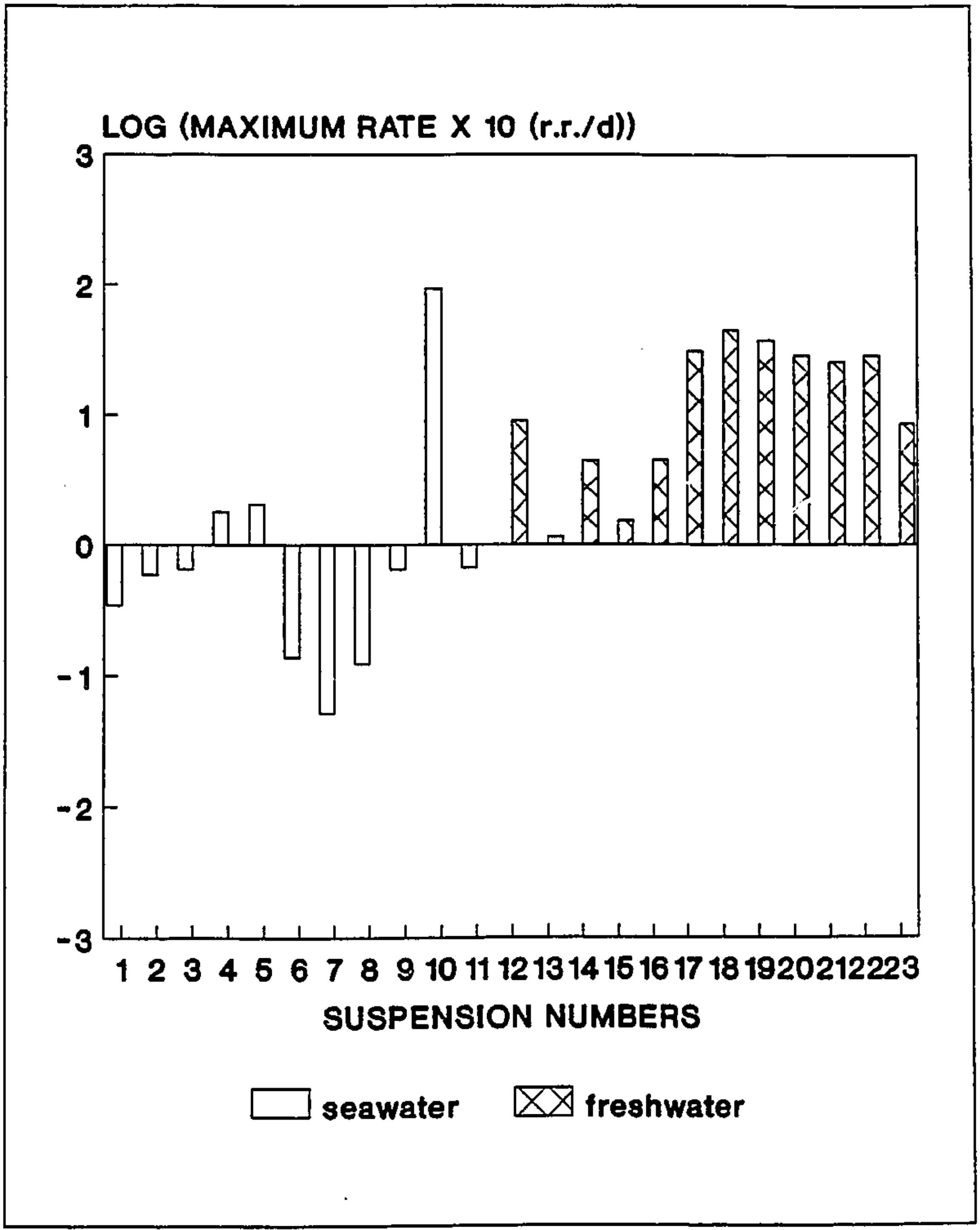

FIGURE 4.1 Maximum rates (X 10; log scale) characterizing the overall ^{65}Zn solid-liquid exchange of a variety of seawater or freshwater suspensions. Suspension numbers are defined in Table 4.2.

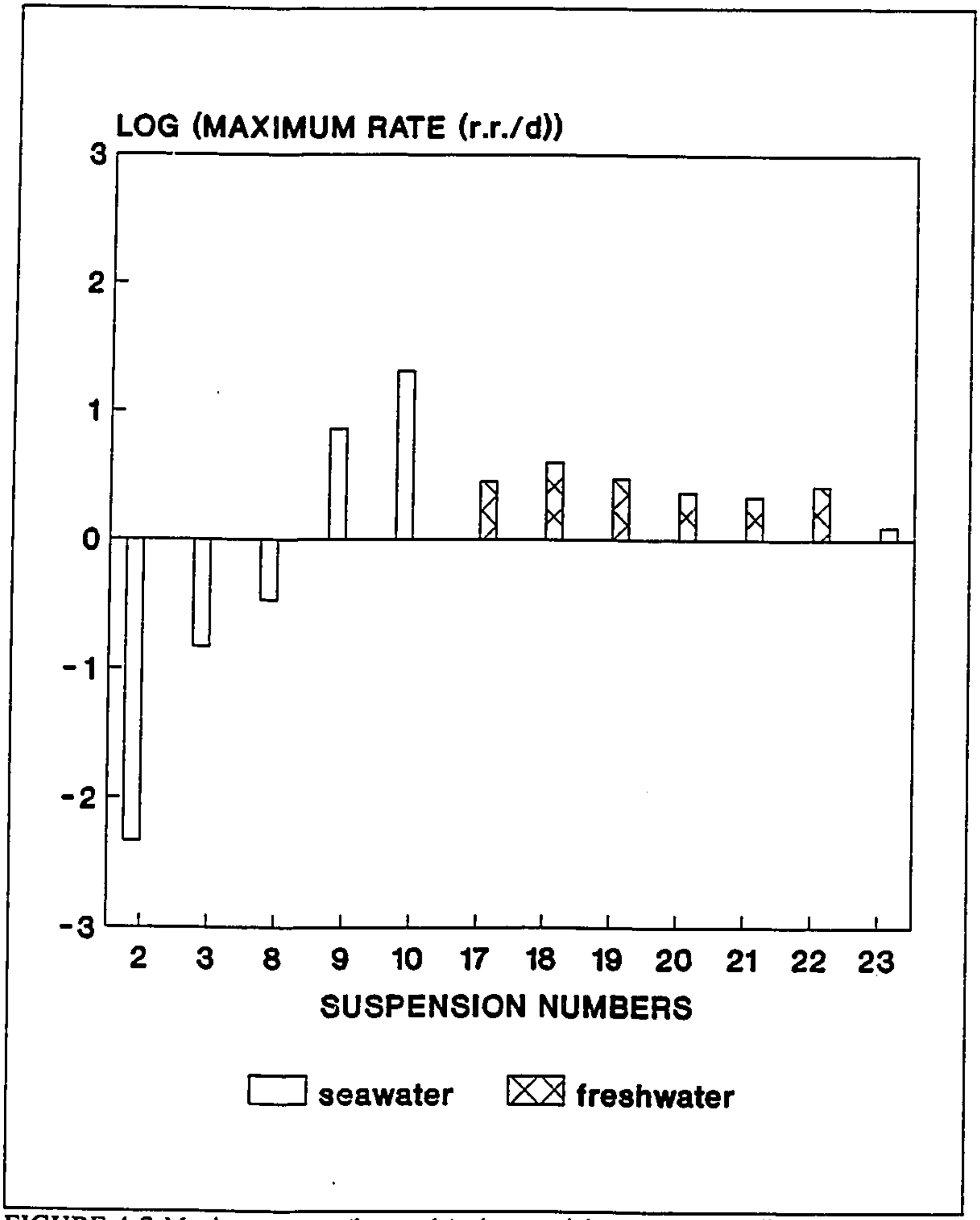

FIGURE 4.2 Maximum rates (log scale) characterizing the overall ^{109}Cd solid-liquid exchange of a variety of seawater or freshwater suspensions. Suspension numbers are defined in Table 4.3.

In summary, seawater suspensions generally show lower maximum rates compared to freshwater suspensions; at least two parameters (pH and ionic strength) are different between the two types of suspensions. The investigation of maximum rate also suggests that trace metal kinetics are proportional to the surface area of sediment suspensions.

4.2.2.3 Linear free energy relationship:

Another way to compare the kinetic behaviour of trace metals among a variety of suspensions is to consider linear free energy relationship (LFER). This approach consists of verifying the existence of a direct relationship between trace metal exchange kinetics and the quality of sites provided by the solids. It is first assumed that natural sediments are made of sites characterized by a range of interaction energies. This is supported by experimental studies where a decrease of affinity, Kd, at high densities of trace metal bound sites on solids, has been observed for: (1) isolated oxides (Benjamin and Leckie, 1981), (2) seawater sediments (Balistrieri and Murray, 1984), and (3) freshwater sediments (Lebeuf, 1985). The general explanation of the observed trend resides in the saturation of high energy sites at high adsorption density followed by trace metal reactions with less energetic sites. Consequently, sediments characterized by high Kd values (strong affinity for a metal) possess high energy sites for the metal. A relation between sorption rate constants and "equilibrium" sorption coefficients, Kd, is expected; when such a relationship is linear, it is usually referred to as a linear free energy relationship (LFER)(Hoffmann, 1981). Recently, Brusseau and Rao (1989) have reported a LFER for the sorption of organic solutes by soils and sediments.

To assess LFER of trace metal interactions in sediment suspensions, sorption rate constants and "equilibrium" sorption coefficients need to be redefined. Nyffeler et al. (1984) suggested a general bimolecular forward reaction to describe trace metal interactions. Then, the sorption rate constant, k_{f1}, can be expressed by:

$$k_{f1} = k'_{f1}\ [FS_{s1}] = k'_{f1}\ Cp\ \{FS_{s1}\} \tag{4.8}$$

where $[FS_{s1}]$ and $\{FS_{s1}\}$ represent the concentration of free (first type of solid) sites, per litre of suspension and per gram of dry sediments, respectively. The sorption rate constant k'_{f1} has units of $L.site^{-1}.d^{-1}$ and Cp represents the solid concentration (mg/L) of the suspension. Nyffeler et al. (1984) also assumed a constant ratio of sites per gram of sediments, independent of the particle concentration or the type of the suspension. By using radiotracers to estimate kinetic parameters, $\{FS_{s1}\}$ is considered constant and the sorption rate constant is expressed as follows:

$$k1 = \frac{k_{f1}}{Cp} = k'_{f1}\ \{FS_{s1}\} \tag{4.9}$$

where k1 has units of $L.g^{-1}.d^{-1}$. Therefore, sorption rate constants, k1, can be used to compare systems of different particle concentrations. "Equilibrium" sorption coefficients, represented by distribution coefficients, Kd, are expressed by the ratio of k_{f1} over $k'_{r1}.Cp$. Values of k_{f1}, k'_{r1}, and Cp are obtained from Tables 4.2 and 4.3. Calculated values of log k1 and log Kd for zinc and cadmium from a variety of suspensions are reported in Table 4.4. The log-relationship between rate constant, k1, and "equilibrium" sorption coefficient, Kd, is plotted for zinc and cadmium in Figures 4.3 and 4.4, respectively. In these figures, the delimited area represents the results from this work and the solid line has a slope of one. Sorption rate constants are generally more or less one order of magnitude of the regression values predicted by Kd for both zinc and cadmium. In practice, this means that Kd values can introduce as much as 900% error in the prediction of sorption rate constants.

Jannash et al. (1988), and Honeyman and Santschi (1988) have recently pointed out that a single value, close to one, can represent the reverse rate constant, k'_{r1}, for a wide range of trace metals from a variety of suspensions. Regression lines between log k1 and log Kd exhibit slope values close to unity (Zn: 0.97; Cd: 1.14). The coefficient of determination between log k1 and log Kd for zinc ($r^2 = 0.23$), does not, however, support a linear free energy relationship.

The lack of correlation between log k1 and log Kd is probably due to invalid assumptions. For example, parameters such as pH, or T° are expected to have an effect on kinetics or trace metal distribution and are not equivalent for the suspensions.

TABLE 4.4 Calculated values of log kl and log Kd for zinc and cadmium from a variety of suspensions investigated by radiotracer experiments. Values of k_{f1}, k'_{r1} and Cp are from Tables 4.2 and 4.3.

		-------- zinc -------		---- cadmium ----	
#	Suspension	log kl[a]	log Kd[b]	log kl[a]	log Kd[b]
1	N.B.	2.591	3.086	1.929	1.929
2	S.C.B.	2.820	3.041	1.672	1.672
3	MANOP-H1	4.000	5.155	3.462	3.985
4	SET-PART	3.857	3.556	-----	-----
5	FEC-PEL	3.973	3.973	-----	-----
6	MANOP-HS	4.028	5.882	-----	-----
7	MANOP-HN	4.675	6.959	-----	-----
8	MANOP-H2	4.146	5.113	3.638	3.440
9	MANOP-R1	3.820	2.933	5.959	4.398
10	MANOP-R2	4.314	3.036	4.505	2.634
11	P.S.	4.845	4.566	-----	-----
12	L302S-1	4.903	4.903	-----	-----
13	L302S-2	3.114	3.114	-----	-----
14	L-114-1	4.580	4.881	-----	-----
15	L-114-2	3.255	3.255	-----	-----
16	HL-3-2R2	3.922	4.065	-----	-----
17	HL-7-1	4.836	3.912	4.896	4.124
18	HL-7-2	5.091	4.159	5.149	4.346
19	HL-7-3	4.941	4.007	4.967	4.243
20	HL-8-1	5.082	4.383	5.214	4.713
21	HL-8-2	5.030	4.382	5.170	4.696
22	RB-8-3	5.000	4.222	5.163	4.573
23	SNL-8-4	4.503	4.285	4.897	4.644

[a] $kl = k_{f1}/Cp$

[b] $Kd = k_{f1}/k'_{r1}.Cp$

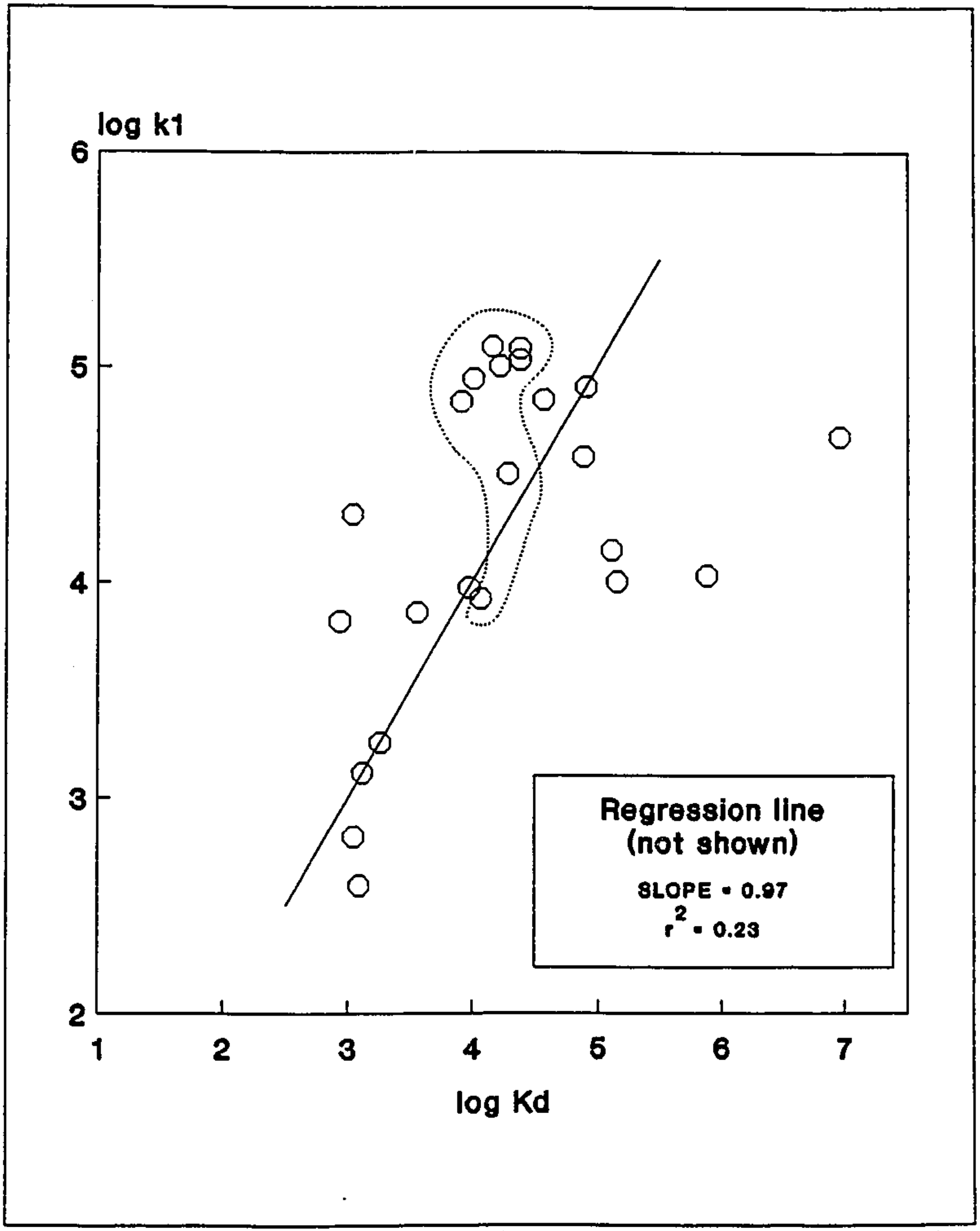

FIGURE 4.3 Log - log relationship for Zn between k1 (sorption rate constant) and Kd (equilibrium sorption coefficient). The delimited area represents results from this study. The solid line has a slope of one.

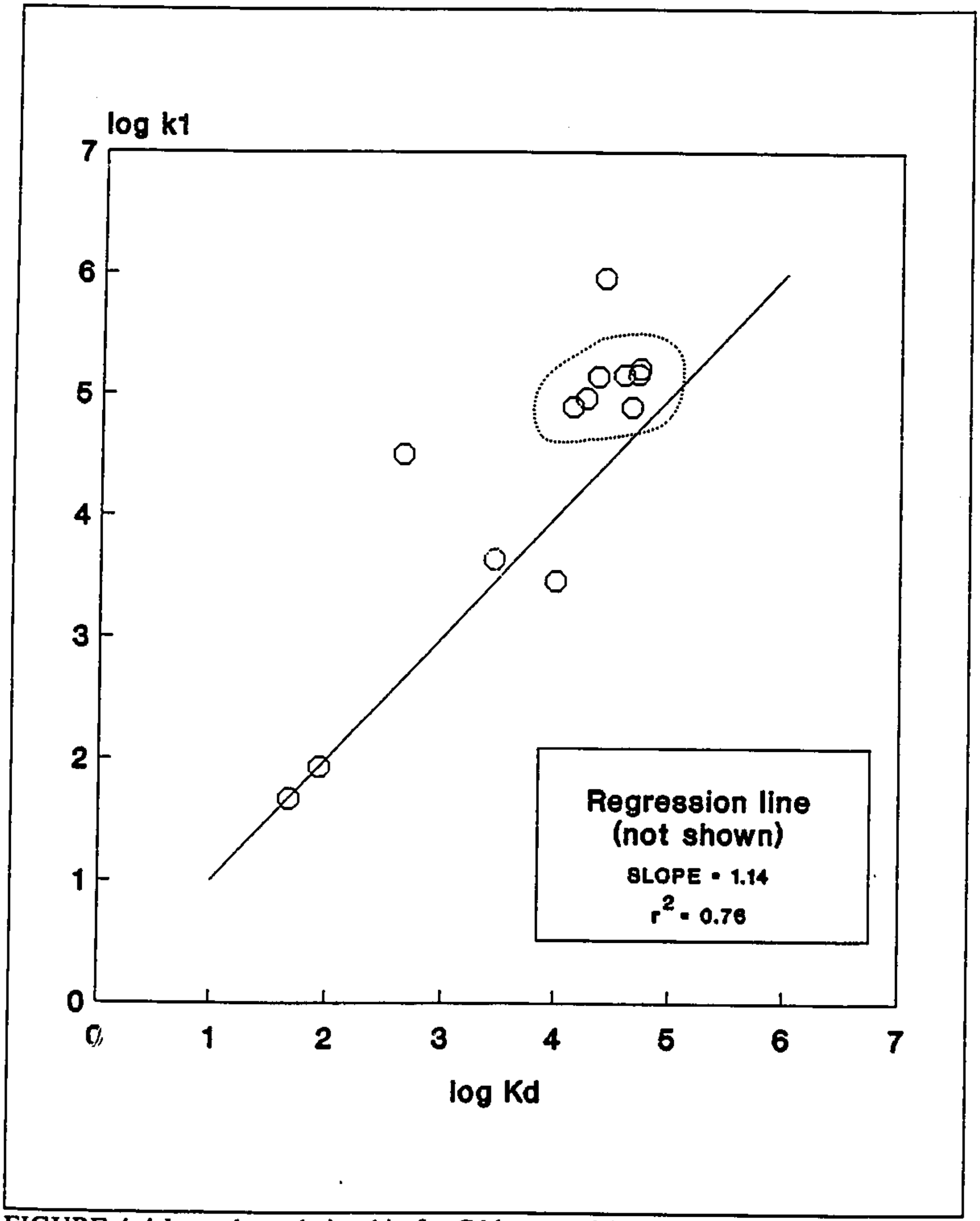

FIGURE 4.4 Log - log relationship for Cd between k1 (sorption rate constant) and Kd (equilibrium sorption coefficient). The delimited area represents results from this study. The solid line has a slope of one.

Briefly, the linear free energy relationship between sorption rate constants (k1) and their respective equilibrium sorption coefficients (Kd) is not supported well by Zn and Cd data in freshwater sediment suspensions. This contrasts with the general conclusion reported by Jannash et al. (1988) and Honeyman and Santschi (1988), and suggests that LFER (log k1 versus log Kd) must be interpreted with caution.

4.3 RESTRICTED THREE-COMPARTMENT MODEL:

The TBL model relies on a simple mechanism of trace metal sorption kinetics. It is a chemical model which consists of two sequential trace metal reactions between sediment and water. The first reaction is a fast reversible first-order surface reaction and the second reaction, which immediately follows the first, is a slow first-order rearrangement reaction where the reverse reaction is negligible over a period of a few weeks.

There are other kinetic models that are able to describe the kinetic experimental data in terms of reactions with sediments. For instance, the following three-compartment model considers two independent reactions (or types of solid sites), both first-order and reversible, but of different rates. One can restrict the model by assuming that the first type of solid sites reaches an instantaneous equilibrium distribution with dissolved trace metals whereas the second type of solid sites is involved in a slow reaction. This restricted three-compartment (box) model (RTB) is used to describe the kinetic experimental data. The RTB model is represented by:

$$\begin{tikzcd} Me^*_w \arrow[r, shift left, "k_f"] \arrow[d, leftrightarrow, "K"'] & Me^*_{s2} \arrow[l, shift left, "k_r"] \\ Me^*_{s1} & \end{tikzcd} \qquad (4.10)$$

where Me^*_w represents the radioactivity of a given trace metal in solution while Me^*_{s1} and Me^*_{s2} stand for the radioactivity of the same trace metal associated to the first type of solid sites and the second type of solid sites, respectively. $[Me^*_w]$ and $\{Me^*_{s1}\}$ are associated by the following relation:

$$[Me^*_{s1}] = K\,[Me^*_w] \qquad (4.11)$$

where K characterizes the equilibrium distribution of radioactive trace metals between the two compartments. Trace metal radiotracers in the liquid phase and associated with the second type of solid sites are related by a first-order reaction characterized by k_f (forward), and k_r (reverse) rate constants. The time-dependent change of radiotracers in these compartments is described as follows:

$$\frac{d[Me^*_w]}{dt} = -\,k_f\,[Me^*_w] + k_r\,\{Me^*_{s2}\} \qquad (4.12(a))$$

$$\frac{d[Me^{*}_{s2}]}{dt} = k_f\,[Me^{*}_{w}] - k_r\,[Me^{*}_{s2}] \qquad (4.12(b))$$

or,

$$\frac{d[Me^{*}_{w}]}{dt} = -\,k_f\,[Me^{*}_{w}] + \frac{k_r}{Cp}\,[Me^{*}_{s2}] \qquad (4.13(a))$$

$$\frac{d[Me^{*}_{s2}]}{dt} = k_f\,[Me^{*}_{w}] - \frac{k_r}{Cp}\,[Me^{*}_{s2}] \qquad (4.13(b))$$

and finally,

$$\frac{d[Me^{*}_{w}]}{dt} = -\,k_f\,[Me^{*}_{w}] + k_r'\,[Me^{*}_{s2}] \qquad (4.14(a))$$

$$\frac{d[Me^{*}_{s2}]}{dt} = k_f\,[Me^{*}_{w}] - k_r'\,[Me^{*}_{s2}] \qquad (4.14(b))$$

$[Me^{*}_{w}]$ and $[Me^{*}_{s2}]$ represent the relative radioactivity of trace metals per volume of suspensions (relative radioactivity/L) in the liquid phase and associated to the second type of solid sites, respectively. The overall rate constants, k_f and k'_r, are expressed in time^{-1}.

The distribution of the total radioactivity among the three compartments is expressed in the following equation:

$$1 = [Me_{s1}^{*}]_i + [Me_{s2}^{*}]_i + [Me_{w}^{*}]_i \tag{4.15}$$

The general solution of Equations 4.14, in reference to the concentration of Me^{*} in solution, has the following form:

$$[Me_{w}^{*}](t) = \frac{1}{1 + K}\left[[Me_{w}^{*}]_i - ([Me_{s2}^{*}]_i - CTE2)\exp^{-CTE1\,t} - CTE2\right] \tag{4.16}$$

where,

$$CTE1 = \frac{k_f}{1 + K} + k_r^{'}$$

and,

$$CTE2 = \frac{k_f\,[Me_{w}^{*}]_i}{k_f + k_r^{'} + K\,k_r^{'}}$$

To apply Equation 4.16, it is necessary to know the initial relative radioactivity of at least one out of the three compartments defined in the RTB model. Due to the fact that radioactive trace metals are added to the suspension liquid phase at beginning of a kinetic experiment, Equation 4.16 can be further simplified.

The RTB model is adjusted to the "adsorption" experimental data of each sediment suspension by optimising K, k_f and k'_r. The mathematical adjustment is based on the minimization of the difference between experimental and predicted values as previously described by Equation 3.9. The RTB optimisation computer program is reported in Appendix B (B3a). Optimised parameters are summarized in Table 4.5 for all of the investigated sediment suspensions. Each "adsorption" profile is simulated by the RTB simulation computer program (Appendix B (B3b)) using the optimised values of K, k_f and k_r. Figures 4.5 a,b,c show zinc results for suspensions HL-7-1, HL-8-2 and RB-8-3, respectively, and Figures 4.6 a,b,c show cadmium results for suspensions HL-7-2, RB-8-3 and SNL-8-4, respectively. In these figures, only average experimental values, at each subsampling time, are represented. The complete data are reported in Appendix A. Generally, the RTB model offers a very good description of the "adsorption" experimental data.

TABLE 4.5 Optimised parameters resulting from the adjustment of the RTB model to the "adsorption" experimental data of sediment suspensions.

Suspension	Zn			Cd		
	K	k_f (d^{-1})	k'_r (d^{-1})	K	k_f (d^{-1})	k'_r (d^{-1})
HL-3-2R2	1.17	0.80	0.32	-----	-----	-----
HL-7-1	0.30	0.40	0.78	0.43	0.68	0.70
HL-7-2	0.37	0.73	1.10	0.89	1.03	0.81
HL-7-3	0.72	0.07	0.20	0.98	0.64	1.15
HL-8-1	1.27	0.70	0.013	0.44	0.12	0.025
HL-8-2	0.98	0.64	1.05	2.23	0.67	0.74
RB-8-3	0.69	0.45	0.87	1.56	0.74	0.80
SNL-8-4	0.51	0.71	0.79	0.89	1.53	0.79

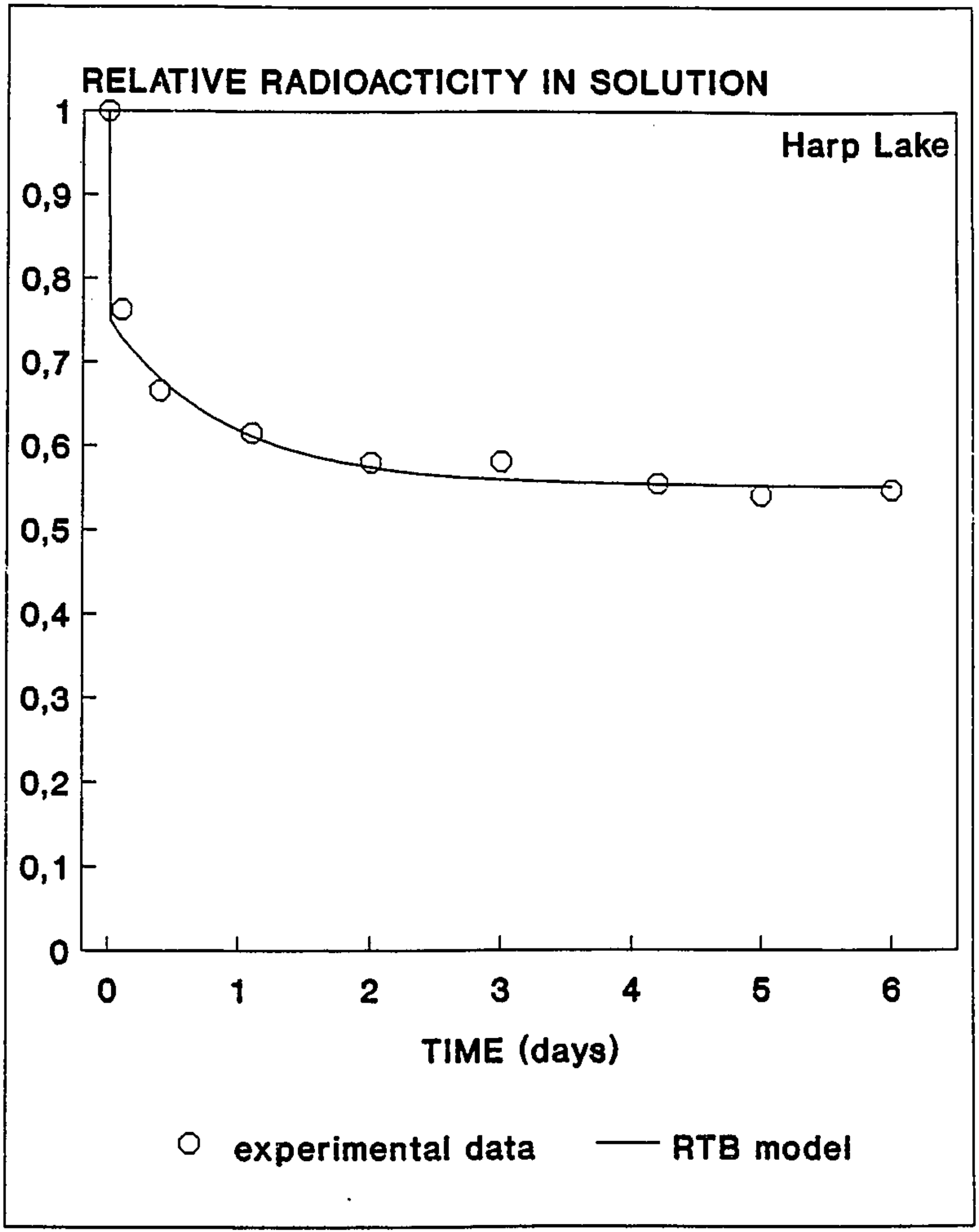

FIGURE 4.5 (a) "Adsorption" profile of ^{65}Zn kinetic exchange for sediment suspension HL-7-1. RTB model (solid line) is adjusted to the experimental data (symbols).

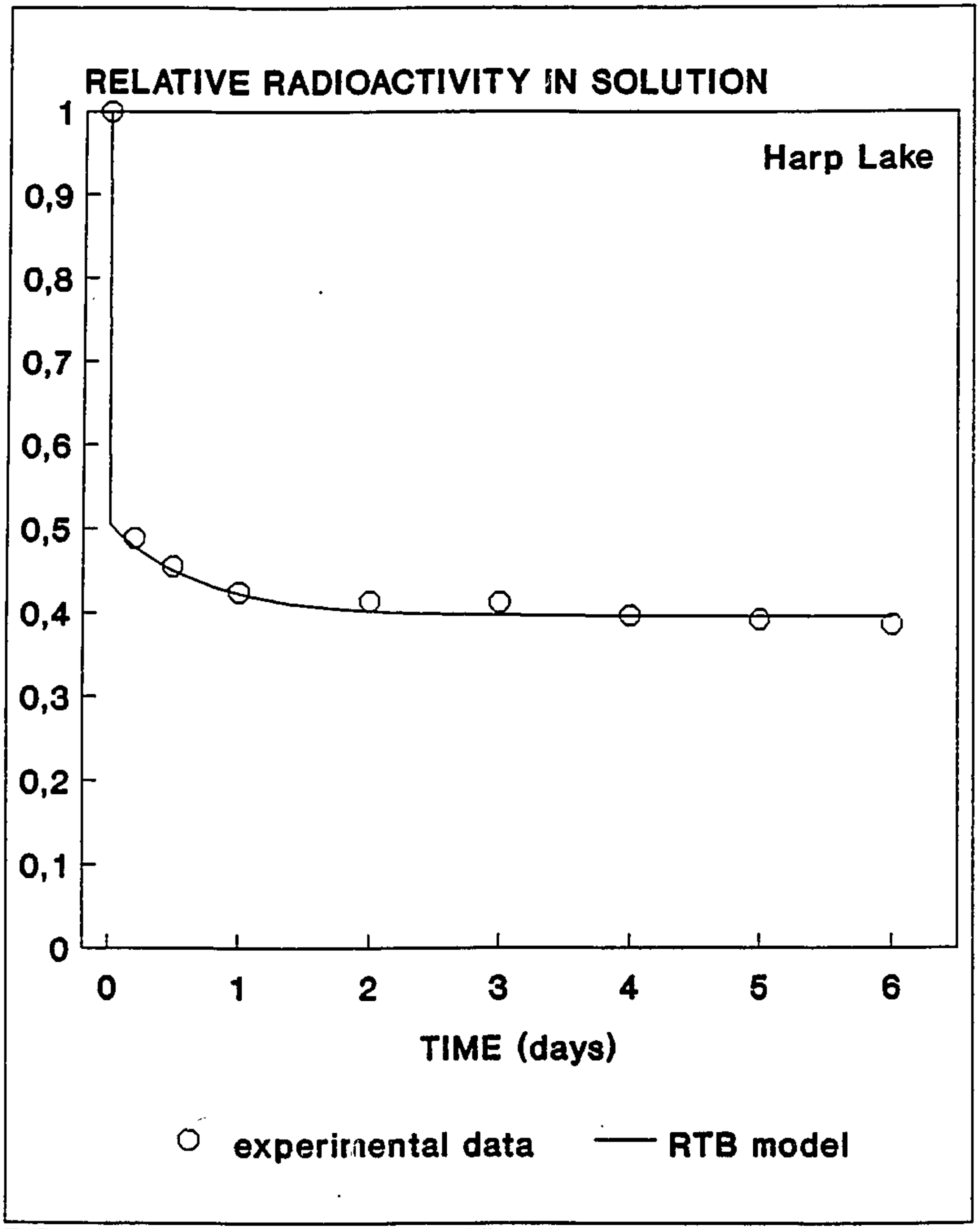

FIGURE 4.5 (b) "Adsorption" profile of ^{65}Zn kinetic exchange for sediment suspension HL-8-2. RTB model (solid line) is adjusted to the experimental data (symbols).

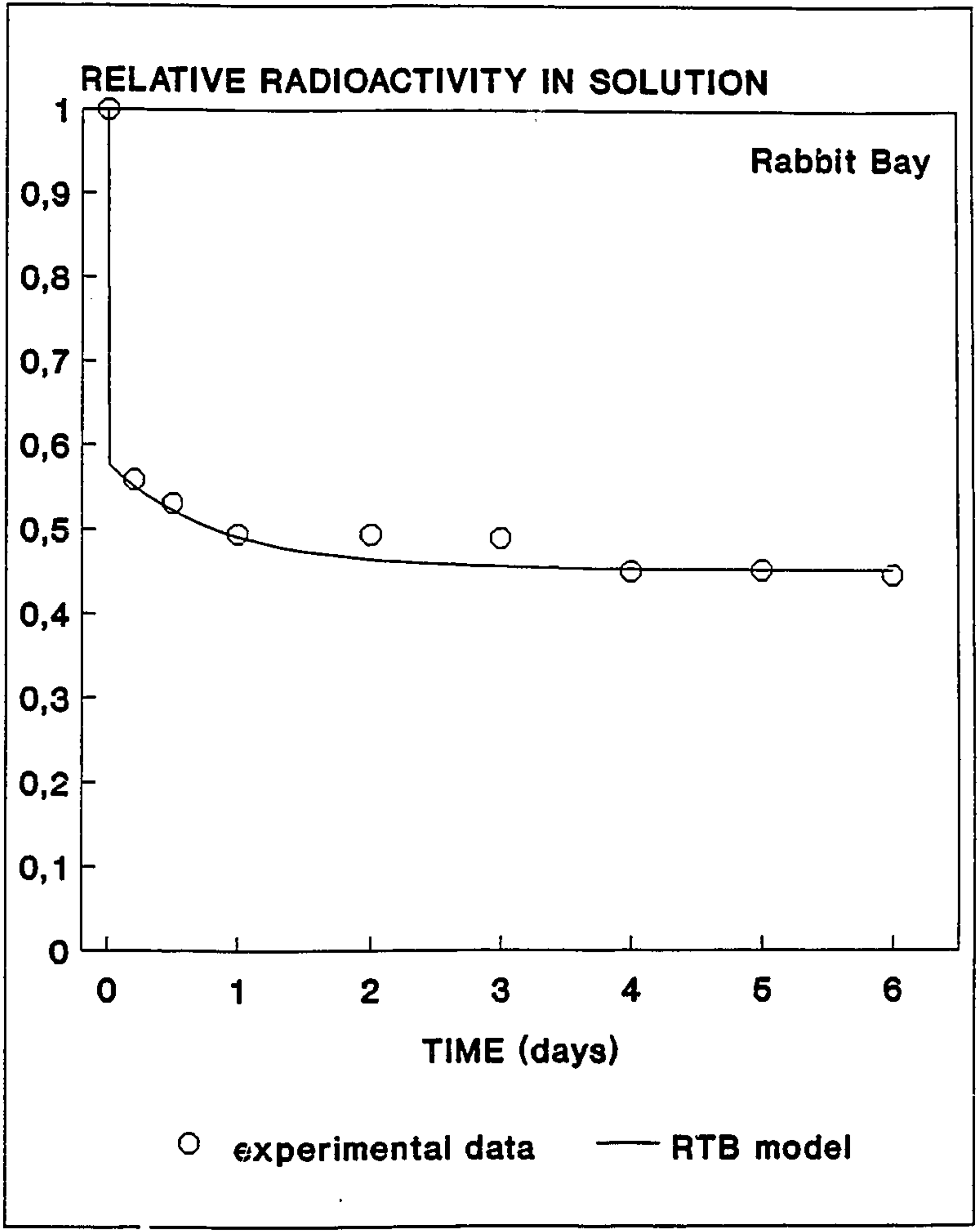

FIGURE 4.5 (c) "Adsorption" profile of ^{65}Zn kinetic exchange for sediment suspension RB-8-3. RTB model (solid line) is adjusted to the experimental data (symbols).

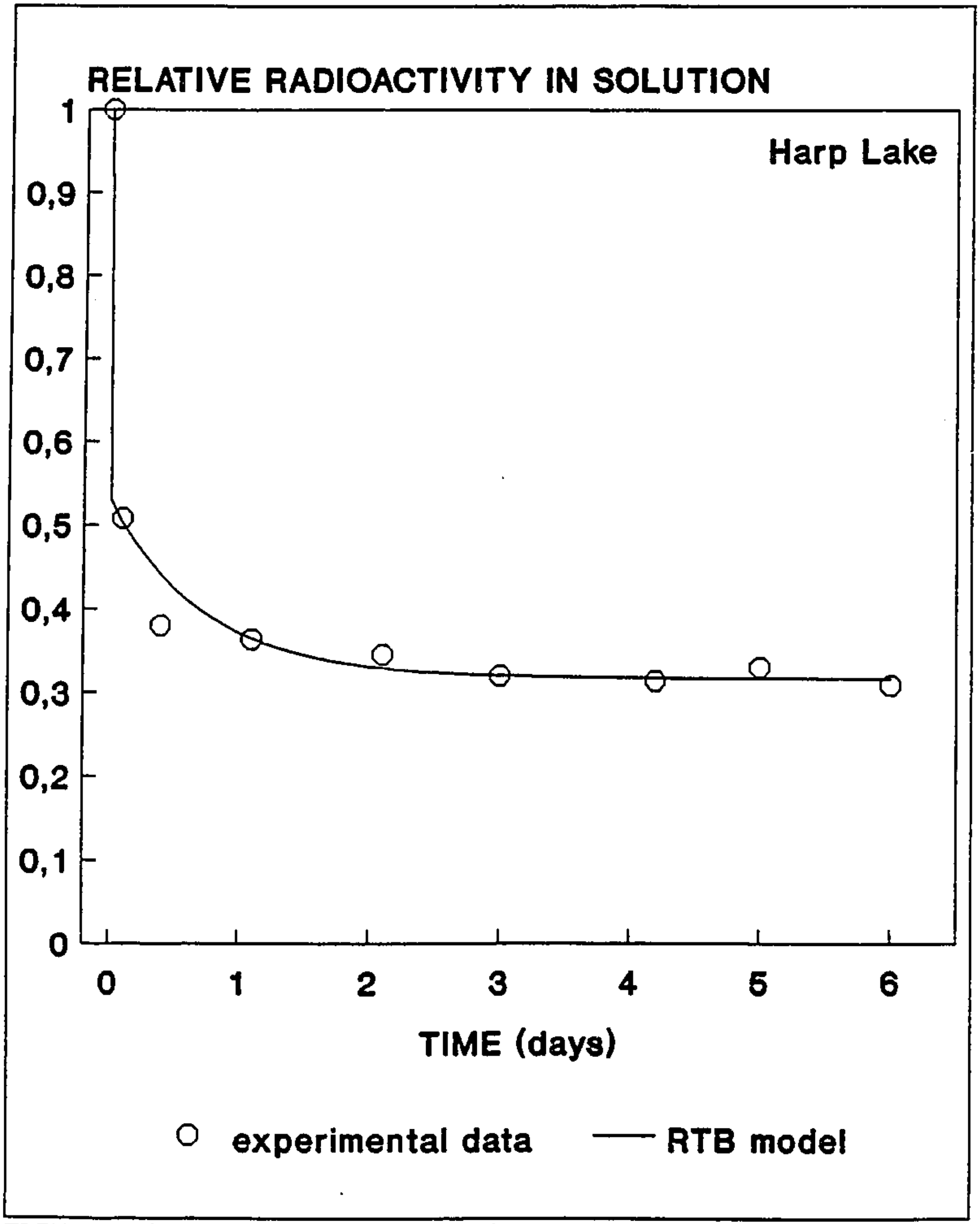

FIGURE 4.6 (a) "Adsorption" profile of ^{109}Cd kinetic exchange for sediment suspension HL-7-2. RTB model (solid line) is adjusted to the experimental data (symbols).

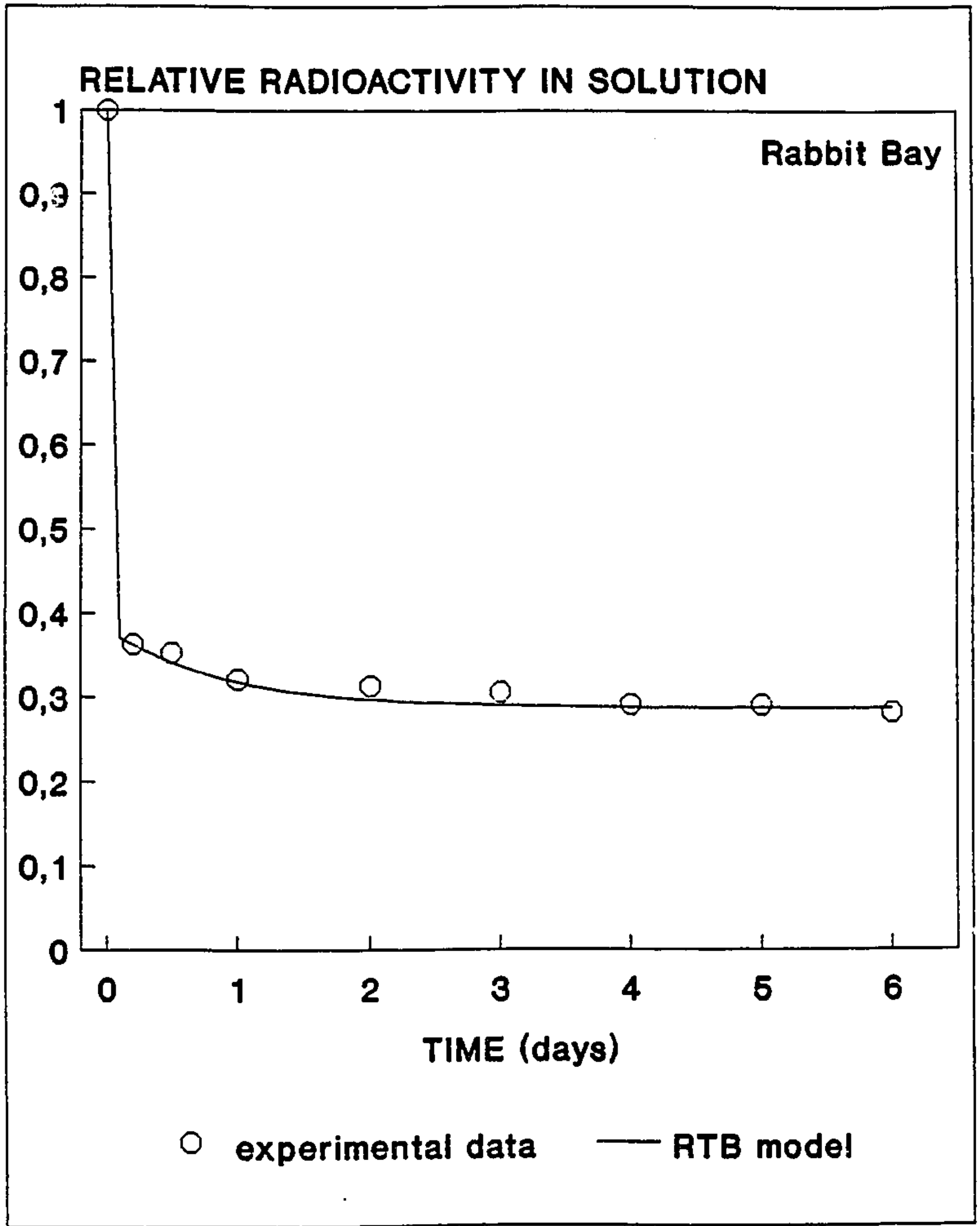

FIGURE 4.6 (b) "Adsorption" profile of ^{109}Cd kinetic exchange for sediment suspension RB-8-3. RTB model (solid line) is adjusted to the experimental data (symbols).

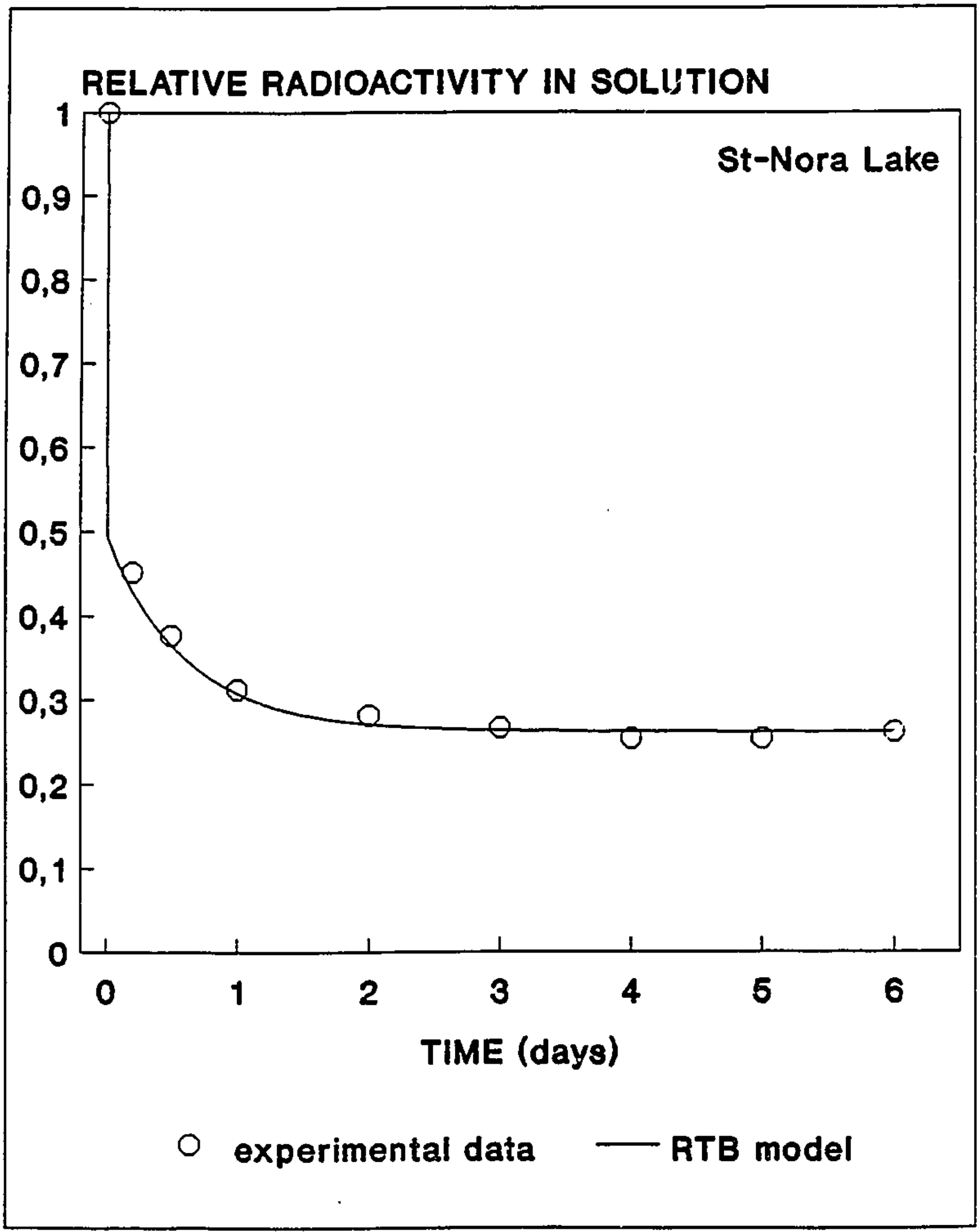

FIGURE 4.6 (c) "Adsorption" profile of ^{109}Cd kinetic exchange for sediment suspension SNL-8-4. RTB model (solid line) is adjusted to the experimental data (symbols).

4.4 OVERALL COMPARISON:

Three models have been applied to describe the kinetic experimental data of sediment suspensions. Among these models, the two- compartment model (TBM) requires the optimisation of two parameters to fit the kinetic experimental data whereas the two-box model with a serial leak (TBL) and the restricted three-box model (RTB) necessitates the optimisation of three parameters. The success of each model to describe the experimental data is estimated by the magnitude of the average weighed difference (AWD) between simulated values and experimental "adsorption" values. By definition, the average weighed difference is the sum of the differences between predicted and experimental values normalized by the number of experimental values. Table 4.6 reports AWD values for zinc and cadmium calculated for each model and suspension.

In general, the three models provide an acceptable representation of the "adsorption" experimental data. It is clear, however, from the mean values (x) reported in Table 4.6, that the average weighed difference (AWD) between "adsorption" experimental data and the simulated values for both metals, is more than two times higher for the TBM than the other models. Due to its poor fit of the "adsorption" experimental data, the TBM model is excluded from the following comparison.

Both RTB and TBL models fit the "adsorption" experimental data equally well (Table 4.6). In order to discriminate between these models, the "desorption" step

TABLE 4.6 Average weighed difference (AWD) between "adsorption" experimental data and simulated values (Zn and Cd) by the TBM, TBL and RTB models.

Suspension	ZINC			CADMIUM		
	TBM	TBL	RTB	TBM	TBL	RTB
HL-3-2R2*	0.1082	0.0487	0.0480	------	------	-------
HL-7-1	0.0447	0.0167	0.0150	0.0697	0.0259	0.0295
HL-7-2	0.0396	0.0206	0.0272	0.0526	0.0232	0.0341
HL-7-3	0.0318	0.0076	0.0157	0.0302	0.0107	0.0180
HL-8-1	0.0753	0.0143	0.0203	0.0768	0.0137	0.0219
HL-8-2	0.0342	0.0102	0.0136	0.0342	0.0181	0.0139
RB-8-3	0.0442	0.0153	0.0184	0.0482	0.0126	0.0208
SLN-8-4	0.0430	0.0222	0.0127	0.0640	0.0412	0.0170
mean	0.0447	0.0153	0.0176	0.0537	0.0208	0.0222
std. dev.	0.0144	0.0052	0.0050	0.0176	0.0106	0.0072

* not include in the statistical calculation

(second step in the experimental procedure) must be considered. The RTB model is characterized by a slow reaction that reaches a steady state over a short period of time (days) whereas the TBL model is characterized by a slow reaction where its reverse reaction is too slow to reach a steady state over the same period of time. This distinction allows a specific investigation of the slow kinetics of trace metal interactions with sediments. As a result, the relative radioactivity in solution after the beginning of the "desorption" step is expected to be lower for the TBL model than for the RTB model. Each "desorption" profile is predicted using optimised rate constants and partition coefficient (RTB model) obtained from the adjustment of "adsorption" kinetic data. Kinetic experimental data, adjusted "adsorption" kinetic profiles, and predicted "desorption" kinetic profiles are presented in Figures 4.7 a,b,c,d and e, for a selection of suspensions.

Predicted "desorption" values are compared with experimental "desorption" data and average weighed differences (AWD) are reported in Table 4.7. Results show that predicted "desorption" values are always better for zinc than for cadmium. Furthermore, AWD values for both metals, are lower for the TBL model than for the RTB model. On the basis of goodness-of-fit (AWD values), the TBL model describes the overall kinetic experimental data better than the RTB model. Profiles predicted by the RTB model are generally higher than experimental values which support the hypothesis that trace metal exchange does not reach a steady state over a short period of time (days). The trend expressed by the "desorption" experimental data, however, is better described by the RTB model. This observation is supported by the presence

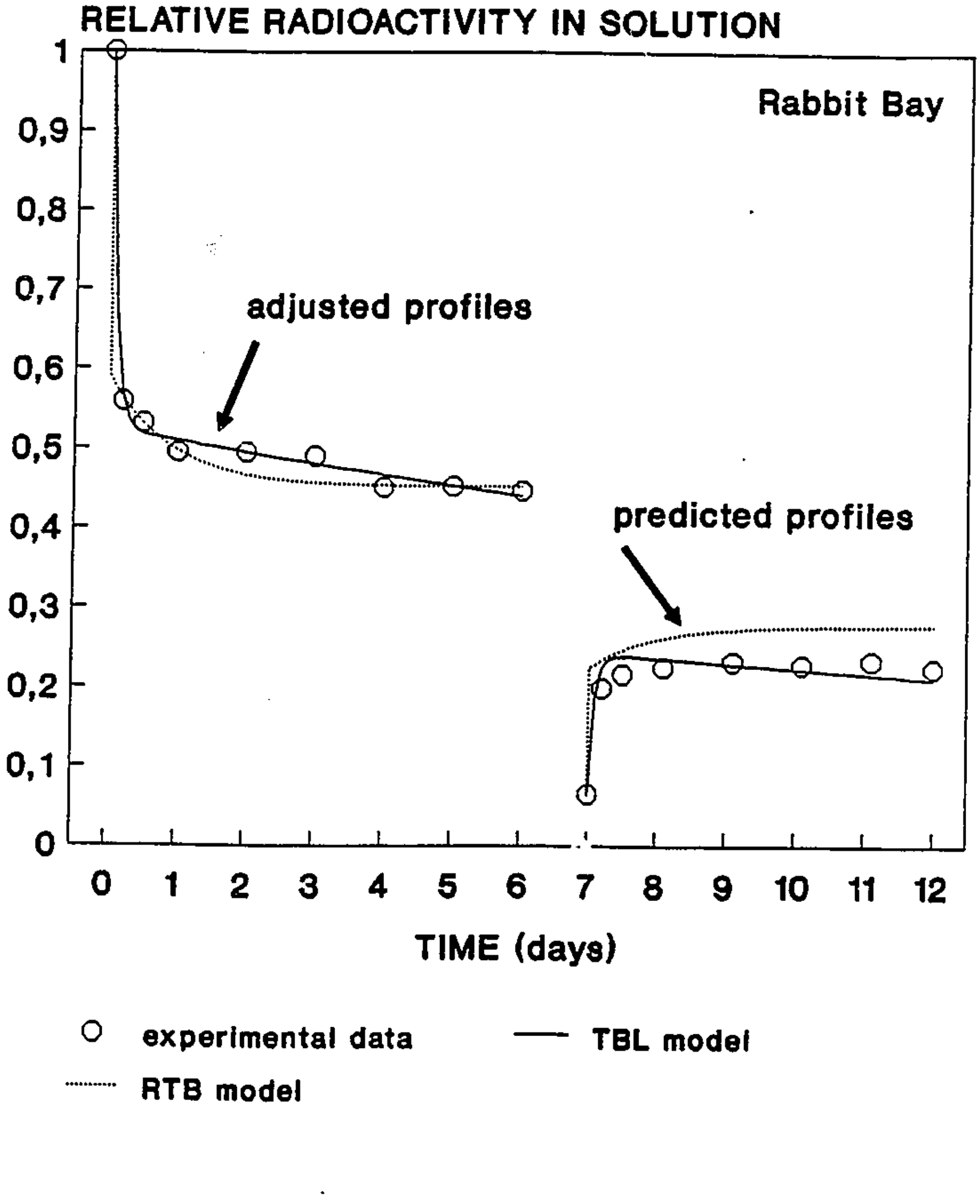

FIGURE 4.7 (a) Comparison between TBL and RTB models. "Adsorption" experimental data (time ≤ 6 days) of ^{65}Zn kinetic exchange for sediment suspension RB-8-3 are adjusted and "desorption" profiles (time ≥ 7 days) are predicted.

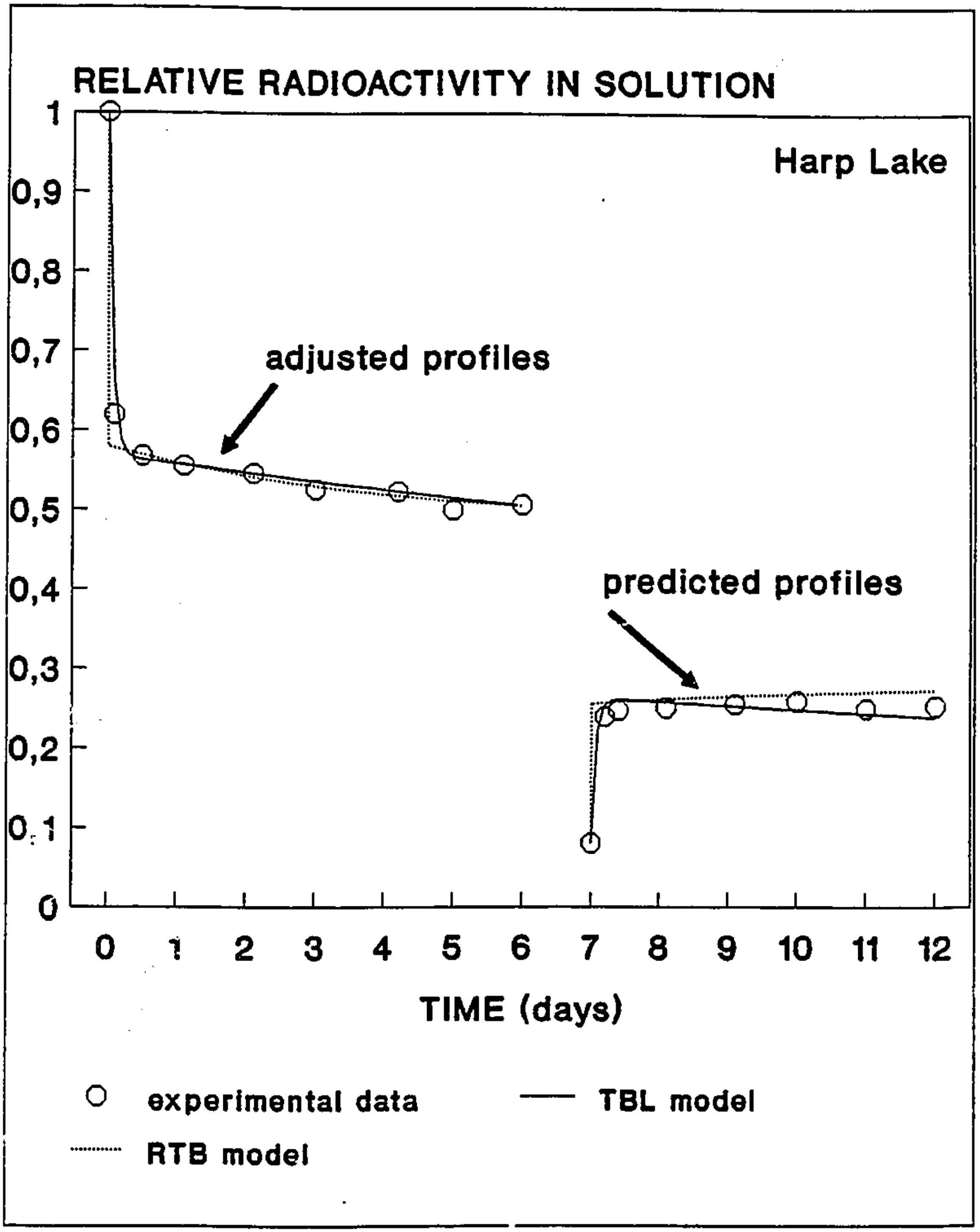

FIGURE 4.7 (b) Comparison between TBL and RTB models. "Adsorption" experimental data (time ≤ 6 days) of ^{65}Zn kinetic exchange for sediment suspension HL-7-3 are adjusted and "desorption" profiles (time ≥ 7 days) are predicted

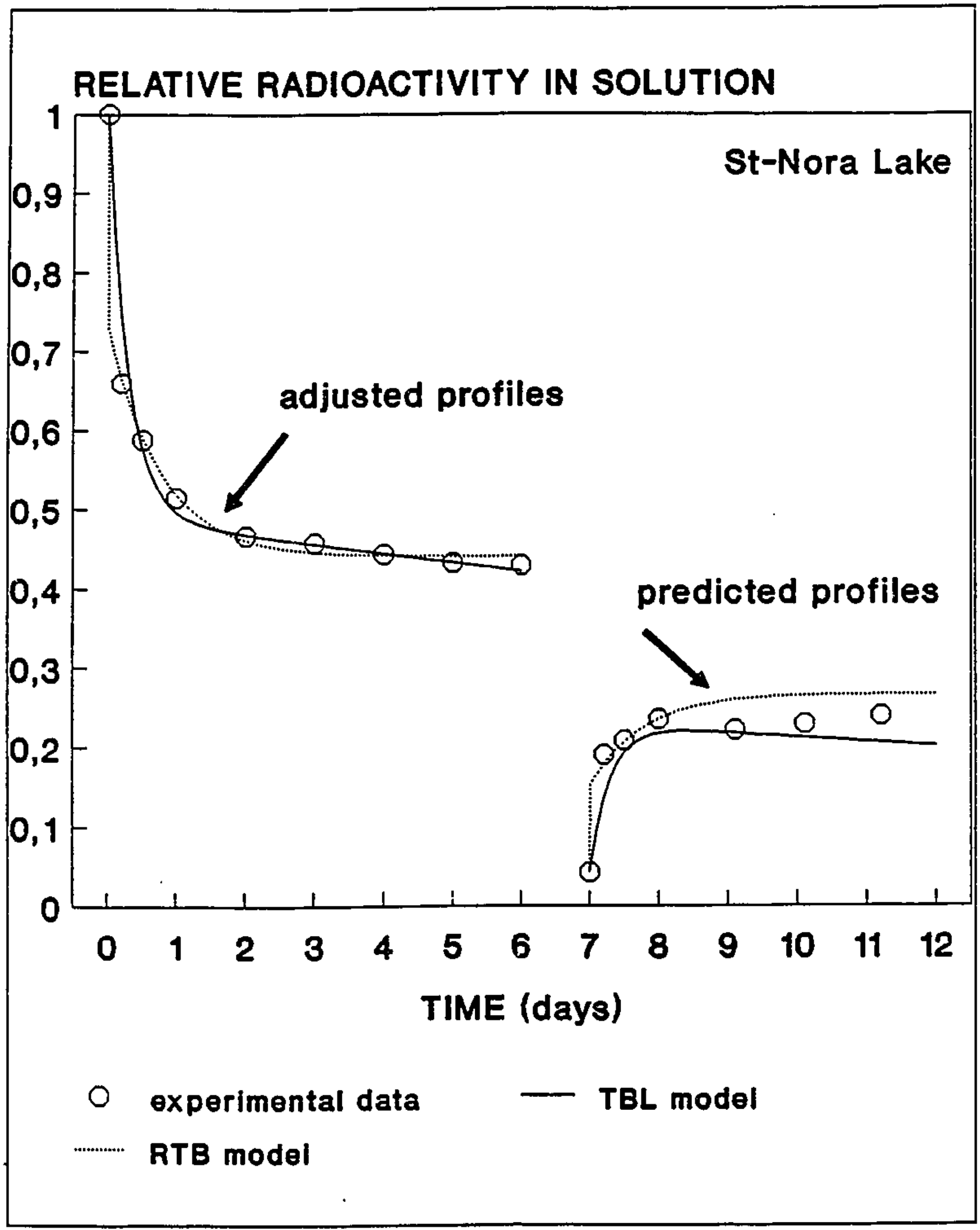

FIGURE 4.7 (c) Comparison between TBL and RTB models. "Adsorption" experimental data (time ≤ 6 days) of ^{65}Zn kinetic exchange for sediment suspension SNL-8-4 are adjusted and "desorption" profiles (time ≥ 7 days) are predicted.

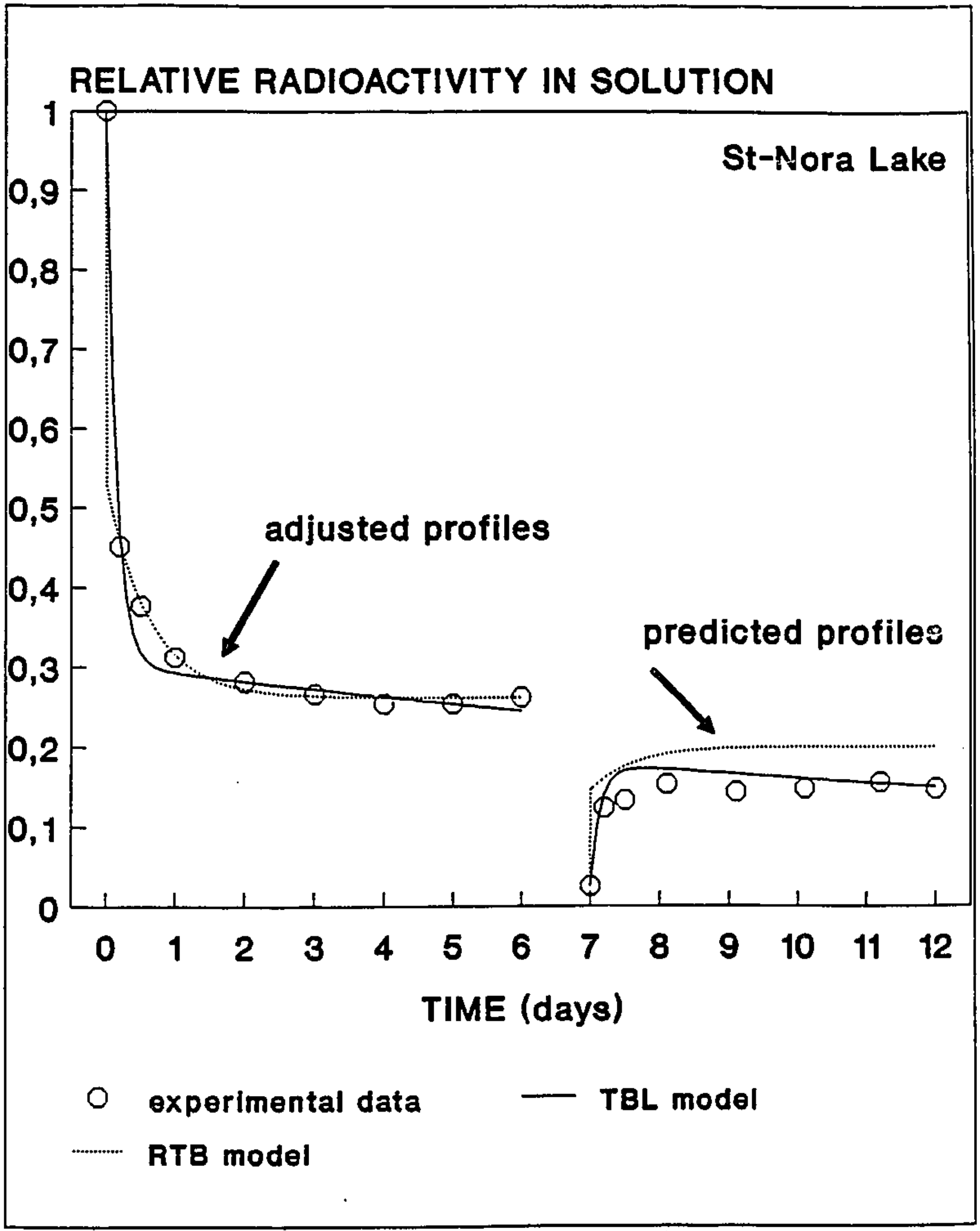

FIGURE 4.7 (d) Comparison between TBL and RTB models. "Adsorption" experimental data (time ≤ 6 days) of ^{109}Cd kinetic exchange for sediment suspension SNL-8-4 are adjusted and "desorption" profiles (time ≥ 7 days) are predicted.

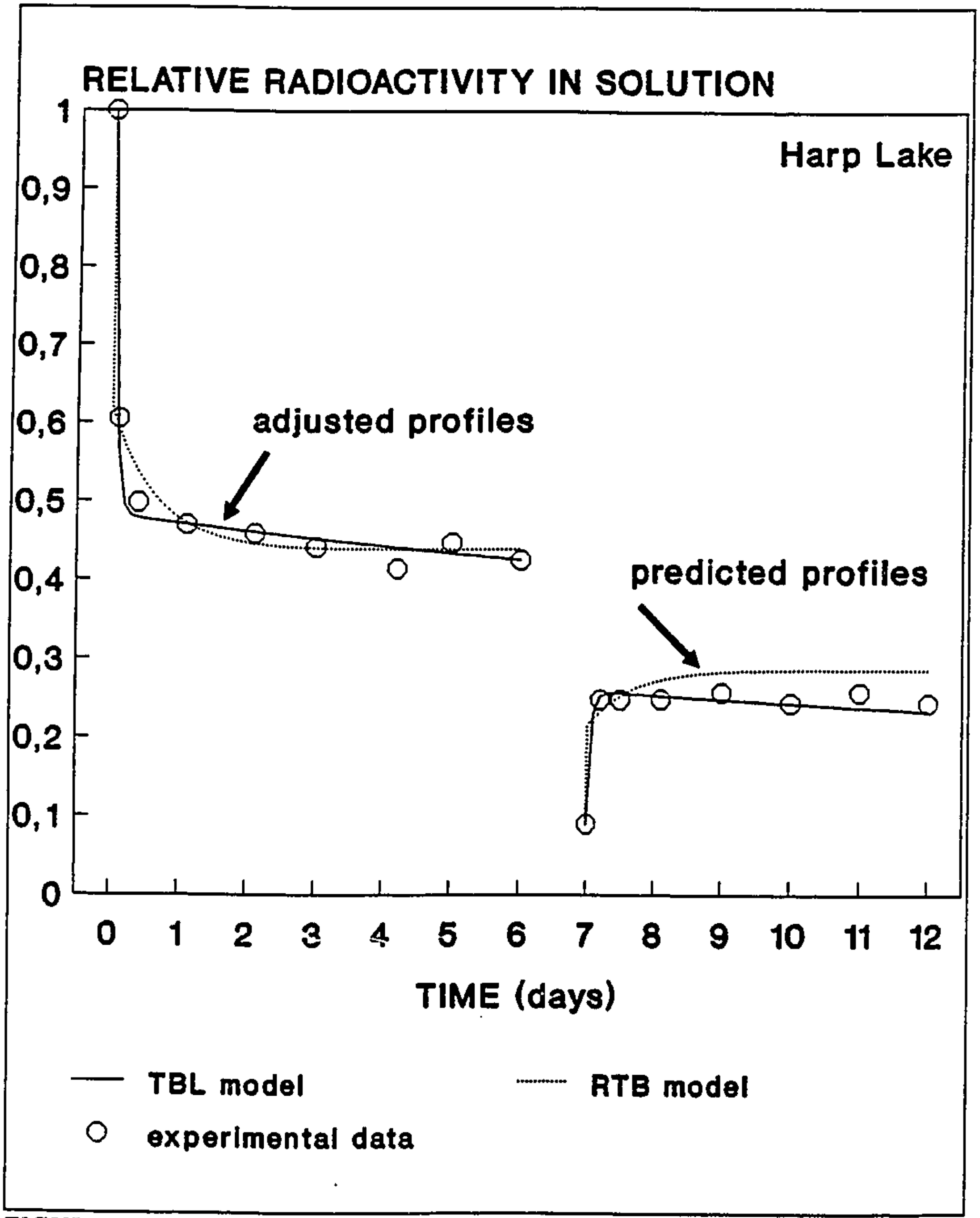

FIGURE 4.7 (e) Comparison between TBL and RTB models. "Adsorption" experimental data (time ≤ 6 days) of ^{109}Cd kinetic exchange for sediment suspension HL-7-2 are adjusted and "desorption" profiles (time ≥ 7 days) are predicted.

TABLE 4.7 Average weighed difference (AWD) between "desorption" experimental data and simulated values (Zn and Cd) by the TBL and RTB models.

Suspension	------------ ZINC	------------	-------- CADMIUM	--------
	TBL	RTB	TBL	RTB
HL-7-1	0.0882	0.1397	0.1157	0.2415
HL-7-2	0.0308	0.1084	0.0553	0.1436
HL-7-3	0.0351	0.0587	0.1193	0.2197
HL-8-2	0.0673	0.1819	0.2083	0.3410
RB-8-3	0.0693	0.1858	0.2166	0.3418
SNL-8-4	0.1053	0.0898	0.0984	0.3060
mean	0.066	0.127	0.136	0.266
std. dev.	0.029	0.051	0.064	0.078

of a plateau in the "desorption" experimental data (RTB model) instead of a continuous loss of trace metals as predicted by TBL model.

In summary, the TBL and RTB models, in spite of their successful adjustments of the "adsorption" experimental data, cannot perfectly predict the "desorption" experimental data. On a statistical basis (Table 4.7) and in my own opinion, the TBL model is mechanistically more realistic since it involves a slow reaction that does not reach a steady state over a short period of time (days) which may represent the slow transport (intra/inter diffusion) of trace metal inside the solid phase.

4.5 DISTRIBUTION COEFFICIENTS:

The models investigated describe time-dependent trace metal interactions based on isotopic tracer exchanges. The exchange of trace metal radiotracers with sediments, after a short time of contact, leads to a characteristic trace metal distribution. At time approaching infinity, the distribution of radiotracers and the distribution of total metals are expected to be identical. There is, however, a range of time (i.e. between short time of contact and time approaching infinity) where the distribution of trace metals is uncertain. The degree of error in the prediction of Kd in this time interval depends on the difference of trace metal distribution between radiotracers (short period of time) and total metals (infinite time).

On one hand, the radiotracer distribution coefficient, Kd_r, is calculated in terms of radiotracer experiment parameters by the following relationship:

$$Kd_r\ (mL/g) = \frac{(1 - RRS)}{RRS}\ \frac{10^6}{Cp} \tag{4.16}$$

where RRS represents the relative radioactivity of tracer in solution at the end of the "adsorption" experiment (i.e. between 6 and 17 days after the beginning of the kinetic experiment). Cp is the particle concentration, in mg/L, of the suspension.

On the other hand, the total element distribution coefficient, Kd_T, is calculated from the concentration of total elements in the liquid phase, $[Me_w]$, in μg/L, and associated to the solid phase $\{Me_s\}$, in μg/g, using the following equation:

$$Kd_T\ (mL/g) = \frac{\{Me_s\}}{[Me_w]} \tag{4.17}$$

Table 4.8 reports log Kd_r and log Kd_T values of sediment suspensions for the three lakes studied. St-Nora Lake and Rabbit Bay are represented by suspensions SNL-8-4 and RB-8-3, respectively. Harp Lake is represented by two suspensions (HL-3-2R2 and HL-7-2) reflecting two distinctive particle concentrations. Kd_T values of sediment suspensions are available for zinc only. Fortunately, Tessier et al. (1987)

TABLE 4.8 Distribution coefficients of sediment suspensions calculated from radiotracer experiments (Kd_r) and total element analysis (Kd_T).

Metal	Suspension	RRS^a	Cp (mg/L)	log Kd_r (mL/g)	$\{Me_s\}$ (µg/g)	$[Me_w]$ (µg/L)	log Kd_T (mL/g)
Zn	(RB-8-3)	0.45	55	4.35	181	2.2	4.92
Zn	(RB-8-3)	0.45	55	4.35	68^b	1.7	4.60
Zn	(SNL-8-4)	0.43	55	4.38	141	2.7^d	4.72
Zn	(SNL-8-4)	0.43	55	4.38	105^b	2.1	4.70
Zn	(HL-3-2R2)	0.19	250	4.26	232	3.2	4.86
Zn	(HL-3-2R2)	0.19	250	4.26	57^b	2.0	4.45
Zn	(HL-7-2)	0.42	75	4.27	188	3.2	4.77
Zn	(HL-7-2)	0.42	75	4.27	57^b	2.0	4.45
Cd	(HL-7-2)	0.31	75	4.44	1.25^{bc}	0.015	4.92
Cd	(SNL-8-4)	0.43	55	4.38	0.85^{bc}	0.0076	5.05
Cd	(RB-8-3)	0.28	55	4.66	0.94^{bc}	0.011	4.93

a relative radioactivity of trace metals in solution at the end of the "adsorption" experiment (see text)

b summation of all fractions from sequential extraction (Tessier et al. 1987)

c addition of 0.25 µg/g of Cd to compensate for the limit value of <0.5 µg/g from the residual fraction

d estimated value according to the trend between trace metals in solution reported by Tessier et al. 1987, and our analytical results of trace metals in solution for Harp Lake and Rabbit Bay (see Table 2.2) reported concentrations of zinc and cadmium in solution and associated with sediments for the same lakes (Table 2.4). Their analytical results are used to calculate Kd_T values for each lake. Figure 4.8 shows the relationship between distribution coefficients from radiotracer experiments and from total trace metal analysis of sediment suspensions. The straight line expresses the equivalence between the two distribution coefficients. It is clear in this figure that Kd_T values, from both Tessier et al. (1987) and this work, are systematically greater than Kd_r values.

This observation supports the trend previously reported by different authors for other types of suspensions. For instance, Li et al. (1984) reported an average difference of 2 orders of magnitude between Kd_T and Kd_r for as many as 13 trace metals including Zn and Cd in seawater suspensions of red clays. Their Kd_T values are calculated from the elemental concentration ratio of oceanic pelagic clays and average seawater. Balistrieri and Murray (1984) also reported radiotracer distribution coefficients and partition coefficients of total elements - for a variety of trace metals, including Zn and Cd - in sediment suspensions from MANOP site H and from San Clemente Basin. They expressed the radiotracer distribution coefficients in terms of binding constants which are converted in Kd_r values using the total number of exchangeable surface sites, for the two sediments, reported by Nyffeler et al. (1984). Their partition coefficients of total elements are calculated using trace metal concentrations in sediments corrected for the contribution of trace metals from the crustal rock, and transformed in terms of Kd_T using a combination of: (1) their own data (Table 1), (2) the data from Li (1982) (Table 1), and (3) the data from Nyffeler

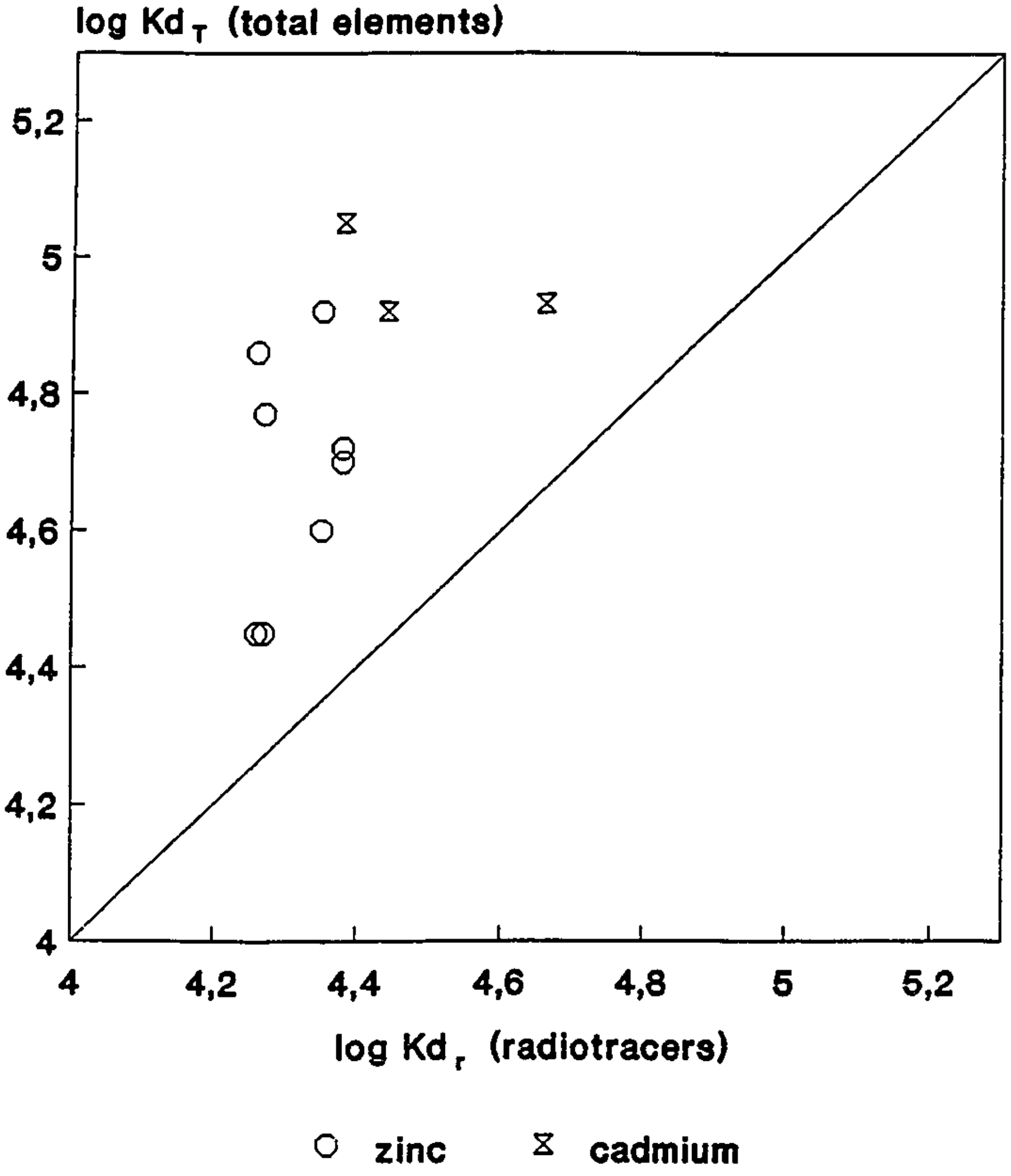

FIGURE 4.8 Relationship between distribution coefficients of sediment suspensions calculated from radiotracer experiments (log Kd_r) and total element analysis (log Kd_T).

et al. (1984) (Table 1). Resulting differences between Kd_r and Kd_T are systematically about one order of magnitude for suspensions from MANOP site H and two orders of magnitude for suspensions from San Clemente Basin, both supporting the same trend (i.e. $Kd_T > Kd_r$). Li et al. (1984) suggested that the difference between Kd_r and Kd_T is the result of: (1) a continuous particle coating by freshly precipitated oxides providing additional adsorption sites for the trace metals, and (2) a "colloid sorption" dominant process. In a recent review on radionuclide sorption reactions, Santschi et al. (1986b) argued that coagulation of radioactively tagged colloids onto larger, filterable particles explains most experimental observations better.

4.6 OVERALL TIME-DEPENDENT PROCESSES:

There is a large body of literature on dissolved trace metal interactions with isolated solid phases. Generally, the kinetic behaviour of trace metals in simplified suspensions is characterized by fast surface reactions that are commonly understood by surface complexation (adsorption) models. These extremely fast surface reactions occur in matter of seconds or less (e.g. Hachiya et al. 1984). Similar fast metal-solid interactions are observed in natural sediment suspensions. Fast reactions in these complex systems possess a half-life ($t_{1/2}$) in the order of hours.

Surface reactions of trace metals with sediments are often followed by a slower trace metal exchange process. The exact process is not yet elucidated; as a matter of fact, a variety of possibilities exists. The slow time-dependent reaction may be the result of: (1) an inter-intraparticle transport of trace metals, (2) a slow reaction with a specific type of solid sites (e.g. RTB model), (3) a surface rearrangement reaction (e.g. TBL model), or (4) a structural rearrangement reaction. This last option describes the transformation of the solid phase by processes such as crystallization of amorphous material or coagulation-dispersion of colloids. The half-life ($t_{1/2}$) of the slow process is in the range of days to weeks or longer.

The slow exchange explains only a limited part of the overall exchange of radiotracers with freshwater sediments. According to the RTB model, the instantaneous reaction describes an average of 70% of the distribution of radioactive trace metals in sediment suspensions, after a short time of contact (e.g. one week).

Fast trace metal solid-liquid interactions are generally observed in simplified suspensions where an isolated mineral constitutes the solid phase. Results of cadmium in a TiO_2 suspension obtained in this study support this view. When sediment suspensions are considered, the overall exchange shows an additional slow reaction as supported by the good adjustment of the "adsorption" kinetic data by the TBL and RTB models.

It is possible to predict the trace metal exchange in sediment suspensions over a period of several days by either RTB or TBL models. It seems more appropriate, however, to use Kd_T values to predict long-term (weeks-months) "equilibrium" partitioning of trace metal with sediments. There is, nevertheless, a range of time where the predictions of the trace metal partitioning are very inaccurate. As a first approximation, the difference between Kd_t and Kd_T will give the importance of the slow kinetics in the overall process of exchange of trace metals with sediments. In the strict sense, Kd_T should not be used to predict the distribution of trace metals between solid and liquid after a short time of contact (weeks or less). This supports the necessity of considering time-dependent interactions of dissolved trace metals with natural sediments.

4.7 APPLICATIONS:

Most of the predictive models are based on the assumption that contaminant-sediment interactions are fast. This view is common for both inorganic and organic substances. As a result, the solid-liquid partitioning of these substances is generally described by equilibrium distribution coefficients calculated from total elements. The EPA approach to predict the solid-liquid partitioning of trace metals focuses on the application of distribution coefficients as well (Shean, 1988).

There are environmental conditions where the partitioning of trace metals among natural compartments very likely reaches an equilibrium or steady-state. For example, sediment and porewater, in contact for a long period of time, are expected to lead to an "equilibrium" distribution of trace metals. Many natural environments, however, are much more dynamic and do not necessarily reach an "equilibrium" partitioning of trace metals. As a matter of fact, natural processes are frequently characterized by solid-solution time of contact shorter than a few weeks. Particle settling in the water column, resuspension of surficial sediments, water column mixing (turnover) or spring melt are examples of events of limited duration. Under these variable conditions. the solid-liquid partitioning of trace metals is in transition toward an equilibrium state. In addition to these natural processes, one can include sediment dredging, industrial discharges or chemical spills. These aquatic perturbations by humans create new environmental conditions which directly affect the behaviour of trace metals.

In order to adequately predict natural and man-made impacts in aquatic systems, time-dependent interactions of trace metals need to be systematically investigated. The "adsorption-desorption" experiments reported in this work show that trace metal interactions with surficial sediments have both fast and slow reaction steps. The slow sediment-water trace metal exchange is a predominant consideration in models focusing on the restoration of natural systems. For instance, the prediction of the release of trace metals by sediments after a "desorption" event would be overestimated by an equilibrium partitioning approach, leaving behind sediments more contaminated than expected. In addition, a net difference of trace metal distribution coefficients between short-term exchange (Kd_r; radiotracers) and long-term "equilibrium" partitioning (Kd_T; total elements) is observed in freshwater sediment suspensions. The error introduced in the prediction of dissolved trace metals, using Kd_T, reaches 19% for cadmium and up to 27% for zinc, after 6 to 14 days of radiotracer exchange in freshwater suspensions.

To summarize, the differences between Kd_τ and Kd_τ, and the evidence of slow trace metal-sediment interactions limit considerably the application of Kd_τ as a predictive tool and consequently require a kinetic characterization of the trace metal exchange with freshwater sediments.

CHAPTER 5

CONCLUSIONS

This study shows that the kinetic partitioning of trace metals between the sediment and aqueous phases is mandatory to adequately describe short-term natural events of approximately a few weeks or less, in freshwater systems.

Three major conclusions are made: (1) the radiotracer technique developed in this work is a reliable method to investigate the kinetics of trace metal interactions with lake sediments under natural conditions; (2) short-term trace metal-sediment kinetics show a fast reversible exchange followed by a slower reaction; and (3) without a valid kinetic model, Zn and Cd partitioning may be significantly overestimated as being retained by the sediment.

The radiotracer technique is shown to be precise in replicate analysis and experiments. The technique permits the determination of "adsorption" and "desorption" kinetics with little chemical alteration of the overall system, and avoids drastic changes of the system chemistry by addition of excess reactants (i.e. trace metals). The kinetics is ascertained when a "desorption" (release) study of radiotracer is determined after the "adsorption" (uptake) of the radiotracer. The amount of total labile metal in the liquid and solid phases must be similar in amount for proper assessment.

Natural sediments in three different lakes, in different environments and at different times, exhibit similar reaction dynamics for Zn and Cd. This generalization permits for the first time an investigation of the overall kinetic model. Of three models chosen, a fast reversible first-order reaction coupled with a slow first-order reaction fit the "adsorption" and the "desorption" kinetic data best. The results show that steady state is not reach in short-term trace metal interactions with lake sediments. When "adsorption" kinetic data are inadequate to differentiate between goodness-of-fit of the various models, then "desorption" kinetic data are required. Thus both uptake followed by release studies are imperative to define the kinetics without ambiguity. This research has generated a general time-dependent function for the partitioning of reactive Cd and Zn between sediment and water. It is proposed that this function should be applicable to other lacustrine environments with the same general chemistry and heterogeneous sediments.

Distribution coefficients calculated from total element analysis estimates (Kd_T) are significantly lower than distribution coefficients determined using radiotracers (Kd_r). As a result, short-term uptake of trace metal by sediments, as estimated by Kd_T is overestimated by 19% for Cd and up to 27% for Zn. This systematic bias of non-kinetic considerations can affect toxicity estimates and trace metal cycling predictions.

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APPENDICES

APPENDIX A. RESULTS OF KINETIC EXPERIMENTS.

Experiments HL-3-2R1, HL-3-2R2

HL-3-2R1 (ZINC)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.25	0.668	0.616	0.642
0.58	0.587	0.551	0.569
0.98	0.568	0.497	0.533
1.55	0.480	0.448	0.464
2.00	0.441	0.431	0.436
3.08	0.406	0.411	0.409
5.12	0.379	0.355	0.367
8.03	0.348	0.334	0.341
11.03	0.325	0.315	0.320
13.90	0.307	0.296	0.302

HL-3-2R2 (ZINC)

TIME[c]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.25	0.577	0.503	0.540
0.50	0.397	0.376	0.387
1.01	0.353	0.321	0.337
1.50	0.306	0.295	0.301
2.01	0.277	0.278	0.278
2.50	0.265	0.251	0.258
3.01	0.257	0.234	0.246
4.01	0.237	0.241	0.239
5.49	0.223	0.226	0.225
7.00	0.236	0.258	0.247
10.07	0.208	0.216	0.212
12.01	0.201	0.229	0.215
14.12	0.195	0.192	0.194
17.07	0.190	0.190	0.190

a hour
b relative radioactivity in solution
c day

Experiments HL-7-1, HL-7-2.

HL-7-1 (ZINC)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.08	0.757	0.767	0.762
0.40	0.675	0.657	0.666
1.12	0.611	0.620	0.615
2.08	0.549	0.611	0.580
3.04	0.579	0.583	0.581
4.21	0.557	0.552	0.555
5.01	0.543	0.539	0.541
6.00	0.543	0.553	0.548
7.02[c]	--------	--------	--------
7.18	0.221	0.203	0.212
7.49	0.225	0.211	0.218
8.06	0.231	0.230	0.231
9.05	0.235	0.237	0.236
10.00	0.242	0.244	0.243
11.00	0.250	0.222	0.236
12.01	0.250	0.245	0.248

HL-7-1 (CADMIUM)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.08	0.679	0.676	0.677
0.43	0.551	0.542	0.546
1.12	0.469	0.515	0.492
2.08	0.442	0.474	0.458
3.04	0.462	0.452	0.457
4.21	0.419	0.415	0.417
5.01	0.395	0.407	0.401
6.00	0.419	0.417	0.418
7.02[c]	--------	--------	--------
7.18	0.184	0.173	0.179
7.49	0.185	0.173	0.179
8.06	0.189	0.189	0.189
9.05	0.210	0.196	0.203
10.00	0.203	0.189	0.196
11.00	0.207	0.193	0.200
12.01	0.214	0.206	0.210

HL-7-2 (ZINC)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.08	0.603	0.607	0.605
0.44	0.492	0.503	0.498
1.12	0.463	0.477	0.470
2.08	0.466	0.451	0.459
3.04	0.439	0.444	0.442
4.21	0.414	0.415	0.415
5.01	0.446	0.449	0.448
6.00	0.417	0.434	0.425
7.02[c]	--------	--------	--------
7.18	0.247	0.250	0.248
7.49	0.252	0.245	0.248
8.06	0.245	0.252	0.248
9.05	0.253	0.261	0.257
10.00	0.235	0.252	0.244
11.00	0.255	0.261	0.258
12.01	0.251	0.237	0.244

HL-7-2 (CADMIUM)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.08	0.505	0.510	0.508
0.43	0.389	0.371	0.380
1.12	0.357	0.371	0.364
2.08	0.349	0.341	0.345
3.04	0.297	0.342	0.320
4.21	0.314	0.313	0.314
5.01	0.325	0.334	0.330
6.00	0.309	0.309	0.309
7.02[c]	--------	--------	--------
7.18	0.196	0.199	0.197
7.49	0.200	0.189	0.195
8.06	0.197	0.195	0.196
9.05	0.204	0.208	0.206
10.00	0.191	0.185	0.188
11.00	0.203	0.211	0.207
12.01	0.204	0.184	0.194

a day
b relative radioactivity in solution
c beginning of the "desorption" step

Experiment HL-7-3.

HL-7-3 (ZINC)				HL-7-3 (CADMIUM)			
TIME[a]	A[b]	B[b]	AVERAGE[b]	TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000	0.00	1.000	-----	1.000
0.14	0.611	0.628	0.619	0.14	0.501	0.516	0.508
0.48	0.569	0.565	0.567	0.48	0.444	0.450	0.447
1.12	0.557	0.554	0.555	1.12	0.428	0.423	0.425
2.08	0.542	0.549	0.546	2.08	0.414	0.424	0.419
3.04	0.523	0.528	0.525	3.04	0.403	0.409	0.406
4.21	0.527	0.520	0.523	4.21	0.410	0.401	0.405
5.01	0.500	0.500	0.500	5.01	0.380	0.398	0.389
6.00	0.521	0.491	0.506	6.00	0.400	0.387	0.394
7.02[c]	--------	--------	--------	7.02[c]	--------	--------	--------
7.18	0.237	0.242	0.239	7.18	0.193	0.204	0.198
7.49	0.239	0.256	0.248	7.49	0.190	0.211	0.200
8.06	0.256	0.245	0.251	8.06	0.226	0.202	0.214
9.05	0.253	0.256	0.255	9.05	0.211	0.214	0.212
10.00	0.256	0.262	0.259	10.00	0.216	0.225	0.220
11.00	0.248	0.251	0.249	11.00	0.212	0.216	0.214
12.01	0.255	0.250	0.253	12.01	0.217	0.222	0.220

a day
b relative radioactivity in solution
c beginning of the "desorption" step

Experiments HL-8-1, HL-8-2.

HL-8-1 (ZINC)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.22	0.485	0.460	0.473
0.48	0.436	0.445	0.441
1.03	0.405	0.415	0.410
1.98	0.417	0.397	0.407
3.02	0.399	0.391	0.395
4.00	0.391	0.388	0.390
5.03	0.387	0.386	0.387
6.02	0.368	0.377	0.372
7.22	0.372	0.362	0.367
7.47	0.354	0.346	0.350
8.05	0.353	0.360	0.356
9.07	0.348	0.330	0.339
10.10	0.335	0.323	0.329
11.15	0.330	0.324	0.327
12.02	0.312	0.302	0.307

HL-8-1 (CADMIUM)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.22	0.305	0.296	0.301
0.48	0.271	0.281	0.276
1.03	0.247	0.265	0.256
1.98	0.257	0.253	0.255
3.02	0.246	0.243	0.244
4.00	0.236	0.235	0.236
5.03	0.230	0.231	0.231
6.02	0.222	0.231	0.227
7.22	0.227	0.212	0.219
7.47	0.216	0.208	0.212
8.05	0.218	0.213	0.215
9.07	0.227	0.199	0.213
10.10	0.210	0.205	0.208
11.15	0.213	0.183	0.198
12.02	0.191	0.181	0.186

HL-8-2 (ZINC)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.22	0.488	0.489	0.488
0.48	0.464	0.446	0.455
1.03	0.428	0.421	0.424
1.98	0.420	0.406	0.413
3.02	0.414	0.409	0.411
4.00	0.386	0.406	0.396
5.03	0.395	0.388	0.391
6.02	0.386	0.385	0.385
6.99[c]	--------	--------	--------
7.22	0.226	0.232	0.229
7.47	0.236	0.227	0.232
8.05	0.228	0.236	0.232
9.07	0.237	0.236	0.236
10.10	0.235	0.228	0.231
11.15	0.224	0.231	0.227
12.02	0.220	0.220	0.220

HL-8-2 (CADMIUM)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.22	0.310	0.327	0.318
0.48	0.291	0.279	0.285
1.03	0.272	0.260	0.266
1.98	0.251	0.257	0.254
3.02	0.246	0.242	0.244
4.00	0.242	0.252	0.247
5.03	0.237	0.243	0.240
6.02	0.247	0.238	0.243
6.99[c]	--------	--------	--------
7.22	0.152	0.143	0.148
7.47	0.147	0.144	0.146
8.05	0.145	0.152	0.149
9.07	0.159	0.146	0.152
10.10	0.136	0.147	0.141
11.15	0.139	0.133	0.136
12.02	0.136	0.136	0.136

a day
b relative radioactivity in solution
c beginning of the "desorption" step

Experiments RB-8-3, SNL-8-4.

RB-8-3 (ZINC)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.22	0.547	0.570	0.559
0.48	0.532	0.530	0.531
1.03	0.480	0.510	0.495
1.98	0.499	0.489	0.494
3.02	0.495	0.485	0.490
4.00	0.452	0.450	0.451
5.03	0.443	0.462	0.452
6.02	0.443	0.450	0.446
7.00[c]	--------	--------	--------
7.22	0.202	0.195	0.199
7.47	0.218	0.214	0.216
8.05	0.215	0.234	0.224
9.07	0.238	0.226	0.232
10.10	0.230	0.225	0.228
11.15	0.231	0.235	0.233
12.02	0.228	0.219	0.224

RB-8-3 (CADMIUM)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.22	0.358	0.367	0.363
0.48	0.345	0.361	0.353
1.03	0.317	0.325	0.321
1.98	0.314	0.313	0.313
3.02	0.303	0.307	0.305
4.00	0.291	0.291	0.291
5.03	0.284	0.297	0.290
6.02	0.281	0.282	0.281
7.00[c]	--------	--------	--------
7.22	0.141	0.142	0.142
7.47	0.151	0.154	0.152
8.05	0.135	0.169	0.152
9.07	0.167	0.161	0.164
10.10	0.161	0.161	0.161
11.15	0.158	0.168	0.163
12.02	0.155	0.144	0.150

SNL-8-4 (ZINC)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.22	0.659	0.661	0.660
0.48	0.581	0.595	0.588
1.03	0.500	0.531	0.515
1.98	0.466	0.469	0.468
3.02	0.453	0.463	0.458
4.00	0.438	0.449	0.443
5.03	0.431	0.435	0.433
6.02	0.433	0.425	0.429
7.02[c]	--------	--------	--------
7.22	0.199	0.182	0.191
7.47	0.215	0.201	0.208
8.05	0.237	0.232	0.234
9.07	0.220	0.221	0.221
10.10	0.234	0.223	0.229
11.15	0.236	0.241	0.239
12.02	0.215	0.219	0.217

SNL-8-4 (CADMIUM)

TIME[a]	A[b]	B[b]	AVERAGE[b]
0.00	1.000	-----	1.000
0.22	0.445	0.458	0.452
0.48	0.372	0.381	0.377
1.03	0.310	0.315	0.312
1.98	0.278	0.285	0.281
3.02	0.254	0.279	0.266
4.00	0.247	0.260	0.254
5.03	0.249	0.258	0.254
6.02	0.260	0.263	0.261
7.02[c]	--------	--------	--------
7.22	0.129	0.119	0.124
7.47	0.132	0.134	0.133
8.05	0.157	0.148	0.153
9.07	0.136	0.151	0.143
10.10	0.151	0.144	0.147
11.15	0.159	0.152	0.155
12.02	0.144	0.150	0.147

a day
b relative radioactivity in solution
c beginning of the "desorption" step

APPENDIX B - QUICK BASIC CODES FOR MODELS.

B1a. Model TBM: optimisation.

```
* TBM (TWO-BOX MODEL)
* OPTIMISATION PROGRAM
* RADIOTRACER ADDED IN SOLUTION
```

```
* LIST OF VARIABLES
'    FILE$=input file
'    OUT$=output file
'    kf=forward rate constant (d-1)
'    k'r=backward rate constant (d-1)
'    T=time(d)
'    T(n)=nth value of time
'    TMAX=time of the last experimental data
'    [Me*w](t)=radioactivity of Me in solution at time t
'    [Me*s](t)=radioactivity of Me associated with the solid at time t
'    ACT(n)=nth experimental radioactivity of Me in solution
'    SIMUL(n)=nth simulated radioactivity of Me in solution
'    SUMDIFF=sum of the weighed differences between experimental and
'    simulated values
'    DIFF(n)=nth smallest sum of the weighed differences
'    kfS=initial value of kf
'    kfF=final value of kf
'    kfINC=increment of kf
'    k'rS=initial value of k'r
'    k'rF=final value of k'r
'    k'rINC=increment of k'r
'    NSTEPkf=number of steps for kf
'    NSTEPk'r=number of steps for k'r
'    STEPTOT=total number of steps
'    NUMSTEP=number of the current step
'    OPTkf(n)=nth optimised value for kf
'    OPTk'r(n)=nth optimised value for k'r
* PARAMETERS AND FILES
     DIM T(100), ACT(100), SIMUL(100), DIFF(4)
     INPUT " INPUT  FILE:"; FILE$
     INPUT " OUTPUT FILE:"; OUT$
     OPEN FILE$ FOR INPUT AS #1
     OPEN OUT$ FOR OUTPUT AS #2
     PRINT #2, "INPUT  FILE:"; FILE$
```

```
     PRINT #2, "OUTPUT FILE:"; OUT$
 * DATA FROM FILE
     DO UNTIL EOF(1)
     N = N + 1
     INPUT #1, T(N), ACT(N)
     TMAX = T(N)
     LOOP
 * LIMITS AND INCREMENTS
     PRINT " RATE CONSTANT kf"
     INPUT " INITIAL VALUE OF kf ", kfS
     INPUT " FINAL  VALUE OF  kf ", kfF
     INPUT " INCREMENT OF kf     ", kfINC
     PRINT " RATE CONSTANT k'r"
     INPUT "INITIAL VALUE OF k'r ", k'rS
     INPUT "FINAL  VALUE OF  k'r ", k'rF
     INPUT "INCREMENT OF k'r     ", k'rINC
     PRINT #2, "INITIAL VALUE OF kf ", kfS
     PRINT #2, "FINAL  VALUE OF  kf ", kfF
     PRINT #2, "INCREMENT OF kf     ", kfINC
     PRINT #2, "INITIAL VALUE OF k'r ", k'rS
     PRINT #2, "FINAL  VALUE OF  k'r ", k'rF
     PRINT #2, "INCREMENT OF k'r     ", k'rINC
     IF kfINC > .0000001 THEN GOTO 5
     NSTPkf = 1
     GOTO 10
5    NSTPkf = INT(((kfF - kfS) / kfINC) + 1.1)
10   IF k'rINC > .0000001 THEN GOTO 15
     NSTPk'r = 1
     GOTO 20
15   NSTPk'r = INT(((k'rF - k'rS) / k'rINC) + 1.1)
     STEPTOT = NSTPkf * NSTPk'r
20   FOR I = 1 TO 4
     DIFF(I) = 100
     NEXT I
* SIMULATION
     NUMSTEP = 0
     FOR Nkf = 0 TO (NSTPkf - 1)
     FOR Nk'r = 0 TO (NSTPk'r - 1)
     NUMSTEP = NUMSTEP + 1
     kf = kfS + kfINC * Nkf
     k'r = k'rS + k'rINC * Nk'r
     PRINT "LOOP NUMBER:", NUMSTEP
     PRINT "OUT OF     :", STEPTOT
```

```
     PRINT "k_f:", k_f
     PRINT "k'_r:", k'_r
     FOR M = 1 TO N
     T(M) = INT(T(M) * 100 + .1) / 100
     T = T(M)
* MODEL
     CTE1 = k'_r + k_f
     CTE2 = k_f / CTE1
     [Me*_w](t) = CTE2 * EXP(-CTE1 * T) + 1 - CTE2
     [Me*_s](t) = 1 - [Me*_w](t)
     SIMUL(M) = [Me*_w](t)
     NEXT M
* DIFFERENCE BETWEEN EXPERIMENTAL AND SIMULATED VALUES
     SUMDIFF = 0
     M = M - 1
     FOR I = 1 TO M
     SUMDIFF = SUMDIFF + (ABS(ACT(I) - SIMUL(I)) / ACT(I))
     NEXT I
* THE THREE BEST SETS OF CONSTANTS
     FOR I = 1 TO 3
     IF SUMDIFF < DIFF(I) THEN
     FOR J = I TO 3
     DIFF(I + 1) = DIFF(I)
     OPTk_f(I + 1) = OPTk_f(I)
     OPTk'_r(I + 1) = OPTk'_r(I)
     NEXT J
     DIFF(I) = SUMDIFF
     OPTk_f(I) = k_f
     OPTk'_r(I) = k'_r
     GOTO 50
     END IF
     NEXT I
50   NEXT Nk'_r
     NEXT Nk_f
* REPORT THE OPTIMISED CONSTANTS
     PRINT #2, "*********** REPORT **********"
     PRINT #2, "---------------------------------------"
     FOR I = 1 TO 3
     PRINT #2, " RATE CONSTANT          k_f :"; OPTk_f(I)
     PRINT #2, " RATE CONSTANT         k'_r :"; OPTk'_r(I)
     PRINT #2, " SUM OF WEIGHED DIFFERENCES :"; DIFF(I)
     PRINT #2, "---------------------------------------"
     NEXT I
```

```
CLOSE 1
CLOSE 2
END
```

B1b. Model TBM: simulation.

```
* TBM (TWO-BOX MODEL)
* SIMULATION PROGRAM
* RADIOTRACER INITIALLY IN SOLUTION AND ASSOCIATED WITH THE
 SOLID
```

```
* LIST OF VARIABLES
'    kf=forward rate constant (d-1)
'    k'r=backward rate constant (d-1)
'    [Me*w]i=initial radioactivity of Me in solution
'    [Me*s]i=initial radioactivity of Me associated with the solid
'    NVDS=number of simulated values per day
'    NDS=number of simulated days
'    ND=number of time increments
'    T=time(d)
'    [Me*w](t)=radioactivity of Me in solution at time t
'    [Me*s](t)=radioactivity of Me associated with the solid at time t
'    OUT$=output file
* PARAMETERS AND FILE
    INPUT "OUTPUT FILE:"; OUT$
    OPEN OUT$ FOR OUTPUT AS #1
    INPUT "VALUE OF kf:"; kf
    INPUT "VALUE OF k'r:"; k'r
    INPUT "INITIAL VALUE FOR [Me*w]i:"; [Me*w]i
    INPUT "INITIAL VALUE FOR [Me*s]i:"; [Me*s]i
    INPUT "NUMBER OF VALUES PER DAY:"; NVDS
    INPUT "NUMBER OF DAYS:"; NDS
* SIMULATION
    ND = NVDS * NDS
    FOR I = 0 TO ND
    T = I * NDS / ND
    T = INT(T * 1000 + .1) / 1000
* MODEL
    CTE1 = k'r ÷ kf
    CTE2 = ([Me*w]i * kf - [Me*s]i * k'r) / CTE1
    [Me*w](t) = CTE2 * EXP(-CTE1 * T) +[Me*w]i - CTE2
    [Me*s](t) =[Me*w]i + [Me*s]i - [Me*w](t)
```

```
* REPORT
    PRINT #1, T, [Me*w](t), [Me*s](t)
    NEXT I
    CLOSE #1
    END
```

B2a. Model TBL: optimisation.

```
* TBL (TWO-BOX MODEL WITH A SERIAL LEAK)
* OPTIMISATION PROGRAM
* RADIOTRACER ADDED IN SOLUTION
```

```
* LIST OF VARIABLES
'    FILE$=input file
'    OUT$=output file
'    kf1=forward rate constant; solution -> first type of solid sites; (d-1)
'    k'r1=backward rate constant; solution -> first type of solid sites; (d-1)
'    k'f2=forward rate constant; first type of solid sites -> second solid sites; (d-1)
'    T=time(d)
'    T(n)=nth value of time
'    TMAX=time of the last experimental data
'    [Me*w](t)=radioactivity of Me in solution at time t
'    [Me*s1](t)=radioactivity of Me associated with the first type of solid sites
'    at time t
'    [Me*s2](t)=radioactivity of Me associated with the second type of solid sites
'    at time t
'    SIMUL(n)=nth simulated radioactivity in solution
'    SUMDIFF=sum of the weighed differences between experimental and simulated
'    values
'    DIFF(n)=nth smallest sum of the weighed differences
'    kf1S=initial value of kf1
'    kf1F=final value of kf1
'    kf1INC=increment of kf1
'    k'r1S=initial value of k'r1
'    k'r1F=final value of k'r1
'    k'r1INC=increment of k'r1
'    k'f2S=initial value of k'f2
'    k'f2F=final value of k'f2
'    k'f2INC=increment of k'f2
'    NSTPkf1=number of steps for kf1
'    NSTPk'r1=number of steps for k'r1
'    NSTPk'f2=number of steps for k'f2
```

```
'   STEPTOT=total number of steps
'   NUMSTEP=number of the current step
'   OPTkf1(n)=nth optimised value for kf1
'   OPTk'r1(n)=nth optimised value for k'r1
'   OPTk'f2(n)=nth optimised value for k'f2
* PARAMETERS AND FILES
    DIM T(100), ACT(100), SIMUL(100), DIFF(4)
    INPUT " INPUT  FILE:"; FILE$
    INPUT " OUTPUT FILE:"; OUT$
    OPEN FILE$ FOR INPUT AS #1
    OPEN OUT$ FOR OUTPUT AS #2
    PRINT #2, "INPUT  FILE:"; FILE$
    PRINT #2, "OUTPUT FILE:"; OUT$
* DATA FROM FILE
    DO UNTIL EOF(1)
    N = N + 1
    INPUT #1, T(N), ACT(N)
    TMAX = T(N)
    LOOP
* LIMITS AND INCREMENTS
    PRINT " RATE CONSTANT kf1"
    INPUT " INITIAL VALUE OF kf1 ", kf1S
    INPUT " FINAL  VALUE OF  kf1 ", kf1F
    INPUT " INCREMENT OF kf1     ", kf1INC
    PRINT " RATE CONSTANT k'r1"
    INPUT " INITIAL VALUE OF k'r1 ", k'r1S
    INPUT " FINAL  VALUE OF  k'r1 ", k'r1F
    INPUT " INCREMENT OF k'r1     ", k'r1INC
    PRINT " RATE CONSTANT k'f2"
    INPUT " INITIAL VALUE OF k'f2 ", k'f2S
    INPUT " FINAL VALUE  OF  k'f2 ", k'f2F
    INPUT " INCREMENT OF k'f2     ", k'f2INC
    PRINT #2, "INITIAL VALUE OF kf1 ", kf1S
    PRINT #2, "FINAL  VALUE OF  kf1 ", kf1F
    PRINT #2, "INCREMENT OF kf1     ", kf1INC
    PRINT #2, "INITIAL VALUE OF k'r1 ", k'r1S
    PRINT #2, "FINAL  VALUE OF  k'r1 ", k'r1F
    PRINT #2, "INCREMENT OF k'r1     ", k'r1INC
    PRINT #2, "INITIAL VALUE OF k'f2 ", k'f2S
    PRINT #2, "FINAL  VALUE OF  k'f2 ", k'f2F
    PRINT #2, "INCREMENT OF k'f2     ", k'f2INC
    IF kf1INC > .0000001 THEN GOTO 5
    NSTPkf1 = 1
```

```
     GOTO 10
5    NSTPKf1 = INT(((kf1F - kf1S) / kf1INC) + 1.1)
10   IF k'r1INC > .0000001 THEN GOTO 15
     NSTPk'r1 = 1
     GOTO 20
15   NSTPk'r1 = INT(((k'r1F - k'r1S) / k'r1INC) + 1.1)
20   IF k'f2INC > .0000001 THEN GOTO 25
     NSTPk'f2 = 1
     GOTO 30
25   NSTPk'f2 = INT(((k'f2F - k'f2S) / k'f2INC) + 1.1)
     STEPTOT = NSTPkf1 * NSTPk'r1 * NSTPk'f2
* SIMULATION
30   FOR I = 1 TO 4
     DIFF(I) = 100
     NEXT I
     NUMSTEP = 0
     FOR Nkf1 = 0 TO (NSTPkf1 - 1)
     FOR Nk'r1 = 0 TO (NSTPk'r1 - 1)
     FOR Nk'f2 = 0 TO (NSTPk'f2 - 1)
     NUMSTEP = NUMSTEP + 1
     kf1 = kf1S + kf1INC * Nkf1
     k'r1 = k'r1S + k'r1INC * Nk'r1
     k'f2 = k'f2S + k'f2INC * Nk'f2
     PRINT "LOOP NUMBER:", NUMSTEP
     PRINT "OUT OF     :", STEPTOT
     PRINT "kf1:", kf1
     PRINT "k'r1:", k'r1
     PRINT "k'f2:", k'f2
     FOR M = 1 TO N
     T(M) = INT(T(M) * 100 + .1) / 100
     T = T(M)
* MODEL
     CTE1 = kf1 + k'r1 + k'f2
     CTE2 = k'r1 * k'f2
     Y1 = -CTE1 / 2 - (SQR((CTE1 * CTE1) - (4 * CTE2)) / 2)
     Y2 = -CTE1 / 2 + (SQR((CTE1 * CTE1) - (4 * CTE2)) / 2)
     [Me*w](t)A = (( Y2 + kf1) / (Y2 - Y1)) * EXP(Y1 * T)
     [Me*w](t)B = (( Y1 - kf1) / (Y2 - Y1)) * EXP(Y2 * T)
     [Me*w](t) = [Me*w](t)A + [Me*w](t)B
     [Me*s1](t)A = [Me*w](t)A * (Y1 + kf1) / k'r1
     [Me*s1](t)B = [Me*w](t)B * (Y2 + kf1) / k'r1
     [Me*s1](t) = [Me*s1](t)A + [Me*s1](t)B
     [Me*s2](t) = 1 - [Me*w](t) - [Me*s1](t)
```

```
      SIMUL(M) = [Me*w](t)
      NEXT M
  * DIFFERENCE BETWEEN EXPERIMENTAL AND SIMULATED VALUES
      SUMDIFF = 0
      M = M - 1
      FOR I = 1 TO M
      SUMDIFF = SUMDIFF + (ABS(ACT(I) - SIMUL(I)) / ACT(I))
      NEXT I
  * THE THREE BEST SETS OF CONSTANTS
      FOR I = 1 TO 3
      IF SUMDIFF < DIFF(I) THEN
      FOR J = I TO 3
      DIFF(I + 1) = DIFF(I)
      OPTkf1(I + 1) = OPTkf1(I)
      OPTk'r1(I + 1) = OPTk'r1(I)
      OPTk'r2(I + 1) = OPTk'r2(I)
      NEXT J
      DIFF(I) = SUMDIFF
      OPTkf1(I) = kf1
      OPTk'r1(I) = k'r1
      OPTk'r2(I) = k'r2
      GOTO 50
      END IF
      NEXT I
50    NEXT Nk'r2
      NEXT Nk'r1
      NEXT Nkf1
* REPORT THE OPTIMISED CONSTANTS
      PRINT #2, "*********** REPORT **********"
      PRINT #2, "-----------------------------------"
      FOR I = 1 TO 3
      PRINT #2, " RATE CONSTANT        kf1 :"; OPTkf1(I)
      PRINT #2, " RATE CONSTANT       k'r1 :"; OPTk'r1(I)
      PRINT #2, " RATE CONSTANT       k'r2 :"; OPTk'r2(I)
      PRINT #2, " SUM OF WEIGHED DIFFERENCES :"; DIFF(I)
      PRINT #2, "-----------------------------------"
      NEXT I
      CLOSE 1
      CLOSE 2
      END
```

B2b. Model TBL: simulation.

```
* TBL (TWO BOX MODEL WITH A SERIAL LEAK)
* SIMULATION PROGRAM
* RADIOTRACER INITIALLY IN SOLUTION AND ASSOCIATED WITH THE TWO
  TYPES OF SOLID SITES

* LIST OF VARIABLES
'    k_f1=forward rate constant; solution -> first type of solid sites (d^-1)
'    k'_r1=backward rate constant; solution -> first type of solid sites (d^-1)
'    k'_f2=forward rate constant; first type of solid sites -> second type of solid sites
'    ;(d^-1)
'    [Me*_w]_i=initial radioactivity of Me in solution
'    [Me*_s1]_i=initial radioactivity of Me associated with the first type of solid sites
'    [Me*_s2]_i=initial radioactivity of Me associated with the second type of solid sites
'    NVDS=number of simulated values per day
'    NDS=number of simulated days
'    ND=number of time increments
'    T=time(d)
'    [Me*_w](t)=radioactivity of Me in solution at time t
'    [Me*_s1](t)=radioactivity of Me associated with the first type of solid sites
'    at time t
'    [Me*_s2](t)=radioactivity of Me associated with the second type of solid sites
'    at time t
'    OUT$=output file
* PARAMETERS AND FILE
     INPUT "OUTPUT FILE:"; OUT$
     OPEN OUT$ FOR OUTPUT AS #1
     INPUT "VALUE OF k_f1:"; k_f1
     INPUT "VALUE OF k'_r1:"; k'_r1
     INPUT "VALUE OF k'_f2:"; k'_f2
     INPUT "INITIAL VALUE FOR [Me*_w]_i:"; [Me*_w]_i
     INPUT "INITIAL VALUE FOR [Me*_s1]_i:"; [Me*_s1]_i
     INPUT "INITIAL VALUE FOR [Me*_s2]_i:"; [Me*_s2]_i
     INPUT "NUMBER OF VALUES PER DAY:"; NVDS
     INPUT "NUMBER OF DAYS:"; NDS
* SIMULATION
     ND = NVDS * NDS
     FOR I = 0 TO ND
     T = I * NDS / ND
     T = INT(T * 1000 + .1) / 1000
* MODEL
     CTE1 = k_f1 + k'_r1 + k'_f2
```

```
    CTE2 = $k'_{r1}$ * $k'_{r2}$
    Y1 = -CTE1 / 2 - (SQR((CTE1 * CTE1) - (4 * CTE2)) / 2)
    Y2 = -CTE1 / 2 + (SQR((CTE1 * CTE1) - (4 * CTE2)) / 2)
    $[Me^*_w](t)A$ = ((($[Me^*_w]_i$ * Y2 - $[Me^*_{s1}]_i$ * $k'_{r1}$ + $[Me^*_w]_i$
    * $k_{f1}$) / (Y2 - Y1)) * EXP(Y1 * T)
    $[Me^*_w](t)B$ = ((($[Me^*_{s1}]_i$ * $k'_{r1}$ - $[Me^*_w]_i$ * Y1 - $[Me^*_w]_i$
    * $k_{f1}$) / (Y2 - Y1)) * EXP(Y2 * T)
    $[Me^*_w](t)$ = $[Me^*_w](t)A$ + $[Me^*_w](t)B$
    $[Me^*_{s1}](t)A$ = $[Me^*_w](t)A$ * (Y1 + $k_{f1}$) / $k'_{r1}$
    $[Me^*_{s1}](t)B$ = $[Me^*_w](t)B$ * (Y2 + $k_{f1}$) / $k'_{r1}$
    $[Me^*_{s1}](t)$ = $[Me^*_{s1}](t)A$ + $[Me^*_{s1}](t)B$
    $[Me^*_{s2}](t)$ = $[Me^*_w]_i$ + $[Me^*_{s1}]_i$ + $[Me^*_{s2}]_i$ - $[Me^*_w](t)$ - $[Me^*_{s1}](t)$
* REPORT
    PRINT #1, T, $[Me^*_w](t)$, $[Me^*_{s1}](t)$, $[Me^*_{s2}](t)$
    NEXT I
    CLOSE #1
    END
```

B3a. Model RTB: optimisation.

```
* RTB (RESTRICTED THREE-BOX MODEL; TWO PARALLEL SOLID SITES)
(INSTANTANEOUS EXCHANGE WITH THE FIRST TYPE OF SOLID SITES
AND SLOW EXCHANGE WITH THE SECOND TYPE OF SOLID SITES)
* OPTIMISATION PROGRAM
* RADIOTRACER ADDED IN SOLUTION
```

```
* LIST OF VARIABLES
'    FILE$=input file
'    OUT$=output file
'    IN=initial radioactivity in solution after reaction with the first type of solid sites
'    K=distribution of trace metals between the solution and the first type of solid sites
'    $k_f$=forward rate constant; solution -> second type of solid sites; ($d^{-1}$)
'    $k'_r$=backward rate constant; second type of solid sites; ($d^{-1}$)
'    T=time(d)
'    TIME(n)=nth value of time
'    TMAX=time of the last experimental data
'    ACT(n)=nth experimental radioactivity in solution
'    $[Me^*_w](t)$=radioactivity of Me in solution at time t
'    $[Me^*_{s1}](t)$=radioactivity of Me associated with the first type of solid sites
'    at time t
'    $[Me^*_{s2}](t)$=radioactivity of Me associated with the second type of solid sites
'    at time t
'    SIMUL(n)=nth simulated radioactivity in solution
```

```
'    SUMDIFF=sum of the weighed differences between experimental and
'    simulated values
'    DIFF(n)=nth smallest sum of the weighed differences
'    INS=initial value of IN
'    INF=final value of IN
'    ININC=increment of IN
'    kfS=initial value of kf
'    kfF=final value of kf
'    kfINC=increment of kf
'    k'rS=initial value of k'r
'    k'rF=final value of k'r
'    k'rINC=increment of k'r
'    NSTPIN=number of steps for IN
'    NSTPkf=number of steps for kf
'    NSTPk'r=number of steps for k'r
'    STEPTOT=total number of steps
'    NUMSTEP=number of the current step
'    OPTIN(n)=nth optimised value for IN
'    OPTkf(n)=nth optimised value for kf
'    OPTk'r(n)=nth optimised value for k'r
* PARAMETERS AND FILES
     DIM TIME(100), ACT(100), SIMUL(100), DIFF(4)
     INPUT " INPUT  FILE:"; FILE$
     INPUT " OUTPUT FILE:"; OUT$
     OPEN FILE$ FOR INPUT AS #1
     OPEN OUT$ FOR OUTPUT AS #2
     PRINT #2, "INPUT  FILE:"; FILE$
     PRINT #2, "OUTPUT FILE:"; OUT$
* DATA FROM FILE
     DO UNTIL EOF(1)
     N = N + 1
     INPUT #1, TIME(N), ACT(N)
     TMAX = TIME(N)
     LOOP
* LIMITS AND INCREMENTS
     PRINT " INITIAL ACT.   IN"
     INPUT " INITIAL VALUE OF IN ", INS
     INPUT " FINAL  VALUE OF  IN ", INF
     INPUT " INCREMENT OF IN     ", ININC
     PRINT " RATE CONSTANT kf"
     INPUT " INITIAL VALUE OF kf ", kfS
     INPUT " FINAL  VALUE OF  kf ", kfF
     INPUT " INCREMENT OF kf     ", kfINC
```

```
     PRINT " RATE CONSTANT k'_r"
     INPUT " INITIAL VALUE OF k'_r ", k'_rS
     INPUT " FINAL VALUE  OF  k'_r ", k'_rF
     INPUT " INCREMENT OF k'_r      ", k'_rINC
     PRINT #2, "INITIAL VALUE OF IN ", INS
     PRINT #2, "FINAL  VALUE OF  IN ", INF
     PRINT #2, "INCREMENT OF IN     ", ININC
     PRINT #2, "INITIAL VALUE OF k_f ", k_fS
     PRINT #2, "FINAL  VALUE OF  k_f ", k_fF
     PRINT #2, "INCREMENT OF k_f     ", k_fINC
     PRINT #2, "INITIAL VALUE OF k'_r ", k'_rS
     PRINT #2, "FINAL  VALUE OF  k'_r ", k'_rF
     PRINT #2, "INCREMENT OF k'_r     ", k'_rINC
     IF ININC > .0000001 THEN GOTO 5
     NSTPIN = 1
     GOTO 10
5    NSTPIN = INT(((INF - INS) / ININC) + 1.1)
10   IF k_fINC > .0000001 THEN GOTO 15
     NSTPk_f = 1
     GOTO 20
15   NSTPk_f = INT(((k_fF - k_fS) / k_fINC) + 1.1)
20   IF k'_rINC > .0000001 THEN GOTO 25
     NSTPk'_r = 1
     GOTO 30
25   NSTPk'_r = INT(((k'_rF - k'_rS) / k'_rINC) + 1.1)
     STEPTOT = NSTPIN * NSTPk_f * NSTPk'_r
30   FOR I = 1 TO 4
     DIFF(I) = 100
     NEXT I
* SIMULATION
     NUMSTEP = 0
     FOR NIN = 0 TO (NSTPIN - 1)
     FOR Nk_f = 0 TO (NSTPk_f - 1)
     FOR Nk'_r = 0 TO (NSTPk'_r - 1)
     NUMSTEP = NUMSTEP + 1
     IN = INS + ININC * NIN
     k_f = k_fS + k_fINC * Nk_f
     k'_r = k'_rS + k'_rINC * Nk'_r
     PRINT "LOOP NUMBER:", NUMSTEP
     PRINT "OUT OF     :", STEPTOT
     PRINT "IN:", IN
     PRINT "k_f:", k_f
     PRINT "k'_r:", k'_r
```

```
        FOR M = 1 TO N
        TIME(M) = INT(TIME(M) * 100 + .1) / 100
        T = TIME(M)
 * MODEL
        K = (1 - IN) / IN
        CTE1 = k_f / (1 + K) + k'_r
        CTE2 = k_f / ( k_f + k'_r + K * k'_r)
        [Me*_s2](t) = CTE2 - CTE2 * EXP(-CTE1 * T)
        [Me*_w](t) = (1 - [Me*_s2](t)) / (1 + K)
        [Me*_s1](t) = [Me*_w](t) * K
        SIMUL(M) = [Me*_w](t)
        NEXT M
 * DIFFERENCE BETWEEN EXPERIMENTAL AND SIMULATED VALUES
        SUMDIFF = 0
        M = M - 1
        FOR I = 1 TO M
        SUMDIFF = SUMDIFF + (ABS(ACT(I) - SIMUL(I)) / ACT(I))
        NEXT I
 * THE THREE BEST SETS OF CONSTANTS
        FOR I = 1 TO 3
        IF SUMDIFF < DIFF(I) THEN
        FOR J = I TO 3
        DIFF(I + 1) = DIFF(I)
        OPTIN(I + 1) = OPTIN(I)
        OPTk_f(I + 1) = OPTk_f(I)
        OPTk'_r(I + 1) = OPTk'_r(I)
        NEXT J
        DIFF(I) = SUMDIFF
        OPTIN(I) = IN
        OPTk_f(I) = k_f
        OPTk'_r(I) = k'_r
        GOTO 50
        END IF
        NEXT I
50      NEXT Nk'_r
        NEXT Nk_f
        NEXT NIN
 * REPORT THE OPTIMISED CONSTANTS
        PRINT #2, "*********** REPORT **********"
        PRINT #2, "--------------------------------------"
        FOR I = 1 TO 3
        PRINT #2, " INIT. RADIO. SOLN.    IN :"; OPTIN(I)
        PRINT #2, " RATE CONSTANT         k_f :"; OPTk_f(I)
```

```
    PRINT #2, " RATE CONSTANT        k'_r :"; OPTk'_r(I)
    PRINT #2, " SUM OF DIFFERENCE         :"; DIFF(I)
    PRINT #2, "-------------------------------------"
    NEXT I
    CLOSE 1
    CLOSE 2
    END
```

B3b. Model RTB: simulation.

```
--------------------------------------------------------------------------
* RTB (RESTRICTED THREE-BOX MODEL; TWO PARALLEL SOLID SITES)
(INSTANTANEOUS EXCHANGE WITH THE FIRST TYPE OF SOLID SITES
AND SLOW EXCHANGE WITH THE SECOND TYPE OF SOLID SITES)
* SIMULATION PROGRAM
* RADIOTRACER INITIALLY IN SOLUTION AND ASSOCIATED WITH THE TWO
* TYPES OF SOLID SITES
--------------------------------------------------------------------------
* LIST OF VARIABLES
'    IN=initial radioactivity in solution after reaction with the first type of solid sites
'    K=distribution of trace metals between the solution and the first type of solid sites
'    k_f=forward rate constant; solution -> second type of solid sites; (d^-1)
'    k'_r=backward rate constant; solution -> second type of solid sites; (d^-1)
'    [Me*_w]_i=initial radioactivity of Me in solution
'    [Me*_s1]_i=initial radioactivity of Me associated with the first type of solid sites
'    [Me*_s2]_i=initial radioactivity of Me associated with the second type of solid sites
'    NDS=number of simulated days
'    T=time(d)
'    [Me*_w](t)=radioactivity of Me in solution at time t
'    [Me*_s1](t)=radioactivity of Me associated with the first type of solid sites
'    at time t
'    [Me*_s2](t)=radioactivity of Me associated with the second type of solid sites
'    at time t
'    OUT$=output file
* PARAMETERS AND FILE
    INPUT "FILE NAME FOR OUTPUT    : ", OUT$
    INPUT "NUMBER OF DAYS          : ", NDS
    INPUT "INIT. ACT. IN SOLUTION : ", IN
    INPUT "RATE CONSTANT       k_f : ", k_f
    INPUT "RATE CONSTANT       k'_r : ", k'_r
    INPUT "[Me*_w]_i "; [Me*_w]_i
    INPUT "[Me*_s2]_i "; [Me*_s2]_i
    OPEN OUT$ FOR OUTPUT AS #1
```

```
* SIMULATION
    K = (1 - IN) / IN
    FOR i = 0 TO NDS STEP .1
    T = i
* MODEL
    CTE1 =  $k_f$ / (1 + K) + $k'_r$
    CTE2 = $k_f$ * $[Me^*_w]_i$ / ( $k_f$ + $k'_r$ + K * $k'_r$)
    $[Me^*_{s2}]$(t) = $[Me^*_{s2}]_i$ * EXP(-CTE1 * T) - CTE2 * EXP(-CTE1 * T) + CTE2
    $[Me^*_w]$(t) = ($[Me^*_w]_i$ - $[Me^*_{s2}]$(t)) / (1 + K)
    $[Me^*_{s1}]$(t) = $[Me^*_w]$(t) * K
    T = INT(T * 100 + .5) / 100
* REPORT
    PRINT #1, T, $[Me^*_w]$(t), $[Me^*_{s1}]$(t), $[Me^*_{s2}]$(t)
    NEXT i
    CLOSE #1
    END
```