

# The Aquatic Chemistry of Rare Earth Elements in Rivers and Estuaries

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**Abstract.** Laboratory experiments were carried out to determine how pH, colloids and salinity control the fractionation of rare earth elements (REEs) in river and estuarine waters. By using natural waters as the reaction media (river water from the Connecticut, Hudson and Mississippi Rivers) geochemical reactions can be studied in isolation from the large temporal and spatial variability inherent in river and estuarine chemistry. Experiments, field studies and chemical models form a consistent picture whereby REE fractionation is controlled by surface/solution reactions. The concentration and fractionation of REEs dissolved in river waters are highly pH dependent. Higher pH results in lower concentrations and more fractionated composition relative to the crustal abundance. With increasing pH the order of REE adsorption onto river particle surfaces is LREEs > MREEs > HREEs. With decreasing pH, REEs are released from surfaces in the same order. Within the dissolved (< 0.22  $\mu\text{m}$ ) pool of river waters, Fe-organic colloids are major carriers of REEs. Filtration through filters and ultrafilters with progressively finer pore sizes results in filtrates which are lower in absolute concentrations and more fractionated. The order of fractionation with respect to shale, HREEs > MREEs > LREEs, is most pronounced in the solution pool, defined here as < 5K and < 50K ultrafiltrates. Colloidal particles have shale-like REE compositions and are highly LREE enriched relative to the REE composition of the dissolved and solution pools. The addition of sea water to river water causes the coagulation of colloidal REEs within the dissolved pool. Fractionation accompanies coagulation with the order of sea water-induced removal being LREEs > MREEs > HREEs. While the large scale removal of dissolved river REEs in estuaries is well established, the release of dissolved REEs off river particles is a less studied process. Laboratory experiments show that there is both release and fractionation of REEs when river particles are leached with seawater. The order of sea water-induced release of dissolved REE(III) (LREEs > MREEs > HREEs) from Connecticut River particles is the same as that associated with lowering the pH and the same as that associated with colloidal particles. River waters, stripped of their colloidal particles by coagulation in estuaries, have highly evolved REE composition. That is, the solution pool of REEs in river waters are strongly HREE-enriched and are fractionated to the same extent as that of Atlantic surface seawater. This strengthens the conclusions of previous studies that the evolved REE composition of sea water is coupled to chemical weathering on the continents and reactions in estuaries. Moreover, the release of dissolved Nd from river particles to sea water may help to reconcile the incompatibility between the long oceanic residence times of Nd (7100 yr) and the inter-ocean variations of the Nd isotopic composition of sea water. Using new data on dissolved and particle phases of the Amazon and Mississippi Rivers, a comparison of field and laboratory experiments highlights key features of REE fractionation in major river systems. The dissolved pool of both rivers is highly fractionated (HREE enriched) with respect to the REE composition of their suspended particles. In addition, the dissolved pool of the Mississippi River has a large negative Ce-anomaly suggesting in-situ oxidation of Ce(III). One intriguing feature is the well developed maximum in the middle REE sector of the shale normalized patterns for the dissolved pool of Amazon River water. This feature might reflect competition between surface adsorption and solution complexation with carbonate and phosphate anions.

**Key words:** Rivers, estuaries, rare earth elements, colloids, Amazon River, Mississippi River, Connecticut River.

## 1. Introduction

The solution and mineral properties of rare earth elements (REEs) make these trace elements excellent probes of low temperature geochemical reactions. Studies of rivers and estuaries have yielded fundamental features of the aquatic geochemistry of REEs (Martin *et al.*, 1976; Goldstein and Jacobsen, 1987, 1988; Sholkovitz and Elderfield, 1988; Elderfield *et al.*, 1990; Sholkovitz, 1992, 1993; Sholkovitz *et al.*, 1992). A major conclusion is that chemical weathering reactions on the continents leads to extensive fractionation between the dissolved REE composition of river waters and that of river suspended particles and continental rocks. Solution and surface chemistry play a major role in establishing the REE composition of freshwater. Both the concentration and the extent of fractionation of dissolved REEs in river waters are dependent on pH and on the presence of colloidal particles. High pH waters have the lowest REE concentrations and the most fractionated composition (heavy REE enriched). A large proportion of the dissolved REE inventory in river waters is associated with colloids which undergo large scale coagulation in estuaries. This process results in highly fractionated (or evolved) solution phases being transported in rivers from the continents to the oceans. Hence, fractionation within REE(III)s and between the oxidation states (III and IV) of Ce must be considered when interpreting low temperature processes such as chemical weathering of rocks, soils and minerals and oceanic geochemical cycles.

The observations and conclusions outlined above come from field studies of a variety of rivers and estuaries around the world. These rivers drain different geological terrain and exhibit large ranges in their water discharge, concentration of suspended and colloidal particles and chemical composition. Therefore, it is difficult to decipher how any one of the important variables (e.g., pH, colloids, salinity) affects the fractionation of REEs. Many of the processes described above require confirmation through more comprehensive study. The quantitative role of colloids is a prime example as the direct measurement of river colloids have not been reported. A better understanding of reactions in aquatic systems can come from a combination of field and laboratory studies. Experiments designed to determine how pH, salinity and colloids control the fractionation of REEs in river and estuarine waters are reported in this paper. By using natural waters as the reaction media, in this case the river water from the Connecticut, Hudson and Mississippi Rivers, reactions can be studied in isolation from the large temporal and spatial variability inherent in river water composition. Observations from experiments, field studies and chemical models are forming a consistent picture of the aquatic geochemistry of REEs.

## 2. Analytical, Filtration and Sampling Methods

REE concentrations of filtrates, colloids and suspended particles were measured by isotope dilution (ID) mass spectrometry using either thermal ionization (TIMS) (Greaves *et al.*, 1989; Sholkovitz and Schneider, 1991; Piepgras and Jacobsen, 1992; Schneider and Palmieri, 1994) or inductively coupled plasma (ICP-MS) methods (Schneider and Palmieri, 1994). For both methods water samples (50 to 2000 g) were spiked with enriched isotopes, and the REEs were preconcentrated by iron hydroxide precipitation. The REEs were then collected as a single group by ion exchange. Prior to all TIMS analysis the REEs were further separated into three groups. With respect to ICP-MS measurements, some samples had this three group separation while other samples were run using a single solution containing all the REEs. The precisions, based on replicates, of all REE concentrations by TIMS ranged between 0.5 and 2%. ICP-MS precisions were 4–6%. No La data are reported for the ICP-MS measurements as a signal from Ba-138 was usually present as a large isobaric interference.

Total Fe concentration was measured by the ferrozine method following the reduction of Fe(III) to Fe(II) with hydroxylamine hydrochloride (Stookey, 1970). Color (a proxy for organic matter) is reported as the absorbance of filtered samples at 280 nm relative to distilled water. These two parameters were measured on many but not all of the samples. The concentration of dissolved organic carbon (DOC) was measured on only one (20 July 1992) set of Connecticut River ultrafiltrates and retentates using the high temperature combustion method of Martin and McCorkle (1993).

Several types of filtration methods were used. To separate dissolved from particulate phases, Millipore Durapore membrane filters (nominal pore diameters 0.22  $\mu\text{m}$ ) were employed using either disc membranes (47 mm diameter) or Millipak cartridges (Sholkovitz, 1991). The separation and collection of colloids employed both disc- and ultrafiltration. Small pore-sized (0.025  $\mu\text{m}$ ) disc filters were used, and filtration was by nitrogen pressure (Sholkovitz, 1992). With disc filtration only the filtrates were collected and analyzed. Colloidal particles and ultrafiltrates were collected using tangential flow ultrafilters (Ultrasette model from the Filtron Technology Corporation) with nominal cut-offs of 5,000 and 50,000 molecular weight. Both the colloid-bearing retentate and the ultrafiltrate (solution form) were collected using a peristaltic pump to recirculate a prefiltered sample over the ultrafilter. Two to four liters of 0.22  $\mu\text{m}$  prefiltered river water was passed over the ultrafilter until the retentate was reduced to about 100 ml.

Samples of surface water from the Connecticut River were collected off a floating dock at Middletown, CT. Sampling over a period of one year was needed to carry out the experiments described in the next section. Surface water from the Hudson River was also collected from a floating dock at Castleton on Hudson, NY on 23 October 1992. The Mississippi River was sampled during a high discharge period at Vicksburg, MS on August 20, 1993 from a US Corp. of Engineers

boat. Surface waters were collected from the center of the river by dipping cleaned bottles. After filtering through Millipak cartridge ( $0.22\ \mu\text{m}$ ) filters within two hours of collection, the filtrates were acidified. At Woods Hole the retained particles were resuspended and decanted from the Millipak filter, dried and totally dissolved by fusion with lithium metaborate (Sholkovitz, 1990). A diluted aliquot was spiked with REEs and analyzed by TIMS. Samples from the head of the Amazon River estuary were collected in August 1989 using Millipak filtration. No samples were obtained from the river proper but rather the Amazon sample discussed in this paper has a salinity of 0.30. The dissolved REE data from the estuary are reported in Sholkovitz (1993). Suspended particles of the Amazon River and Connecticut River waters were also fused prior to analyses by TIMS.

### 3. Results and Discussion

Different types of experiments are presented in each of the following subsections. The format of each subsection will be one of combining experimental protocol with the presentation and interpretation of the results. Subsections will cover the effects of pH, salinity and colloids. A final section will integrate the experimental results into a more broad geochemical context.

By design, the experiments have used natural river waters rather than pure oxides, specific organic compounds and artificial water. While this approach means that the chemical properties of both the particulate and solution phases are largely unknown and complex, it better simulates reactions in natural waters. The Connecticut River was chosen as the main source of river water for experiments because it drains a large region of the northeast United States and Canada and is the largest river within a short drive of Woods Hole. Experiments could be started within four hours of collecting samples. The Hudson River and, to a smaller degree, the Mississippi River were also used in experiments.

#### 3.1. DEFINITION OF TERMS

Discussions will center around four forms or pools of REEs (and other elements) based on the filtration protocols. *Suspended particles* are those retained by a  $0.22\ \mu\text{m}$  filter. The *dissolved* form consists of REEs in the  $0.22\ \mu\text{m}$  filtrate. The dissolved form, in turn, will be divided further into the *colloidal* form and the *solution* form. Colloids are those particles within the  $0.22\ \mu\text{m}$  filtrate which are retained by  $0.025\ \mu\text{m}$  disc filters or 5K and 50K ultrafilters. Ultrafiltration yields two types of samples, retentates defined as colloids and ultrafiltrates defined as the solution form. When referring to published data, the type of filtration employed will be noted. The use of different types of filters and filters with different nominal pore-sizes makes it difficult to confidently compare and cross-interpret studies of natural water chemistry. There are other problems inherent in filtration such as self adsorption of trace elements by the filter system and the aggregation and diaggre-

gation of colloids during ultrafiltration. One artifact observed in our ultrafiltration study will be addressed.

The rare earth element series will be referred to as light, middle and heavy REEs (LREEs, MREEs and HREEs). This division is arbitrary and is based on the separations used in the author's preconcentration methods (LREEs = La and Ce; MREEs = Nd, Sm, Eu and Gd; HREEs = Dy, Er, Yb and Lu. One exception is for Nd which will be referred to as a LREE. The shale REE concentrations used for normalization purposes is that of the shale composite as reported in Sholkovitz (1989). It should be emphasized that shale acts as a reference against which to compare REE compositions of samples. Since different shales for normalization result in quite different REE patterns (Sholkovitz, 1990), it is important to use the same shale values in interpreting data. The Ce anomaly is defined in terms of shale normalized compositions as follows:  $Ce\ Anom. = 3(Ce)_n / (2(La)_n + (Nd)_n)$  where  $n$  refers to the shale normalized ratios. A value of 1 means that Ce is not fractionated relative to the crustal composition. A depletion of Ce relative to its REE(III) neighbors yields values less than 1, so called negative Ce anomalies. Positive anomalies have values greater than 1.

### 3.2. WHOLE RIVER pH TITRATION

The objective of "whole river pH titration" experiments was to determine the effect of pH on the concentration and fractionation of dissolved REEs in the river water. The inclusion of suspended particles in the acid- and base-titrated river water results in a pH-controlled sorption between surface and dissolved forms.

Unfiltered river water from the Connecticut River was collected in a 20 liter carboy on 14 January 1992. Immediately after collection two liter aliquots were transferred to eight 2-liter polyethylene bottles which were pre-loaded with varying amounts of ultrapure HCl. This procedure resulted in a pH range of 7.0 (the initial river water) to 1.6. After a reaction period of 10 h, the samples were filtered in parallel through both 0.22 and 0.025  $\mu\text{m}$  pore-sized filters. The 0.025  $\mu\text{m}$  filtration will have removed a large portion of REE-containing colloids within the dissolved ( $< 0.22\ \mu\text{m}$ ) pool (Sholkovitz, 1992). A similar experiment was carried out with Hudson River water collected on 23 October 1992. The main difference was that the addition of acid to unfiltered aliquots took place after a storage period of 8 h and only 0.22  $\mu\text{m}$  filtration was carried out. The pH was also raised by adding pure ammonia solution. The pH of the Hudson River samples (initial pH = 7.0) ranged from 3.1 to 9.5. pH was measured using a Ross-type electrode and certified buffer salts with pHs of 4.01 and 7.40.

Both experiments show two main features. First the concentrations of dissolved REEs increase with decreasing pH, and second the release of REEs off river particles is not uniform across the series but rather exhibits a significant amount of fractionation. The greatest increase in dissolved REE concentrations occurs between pH of 6 and 5 for the Connecticut River and between pH of 7 and 6 for

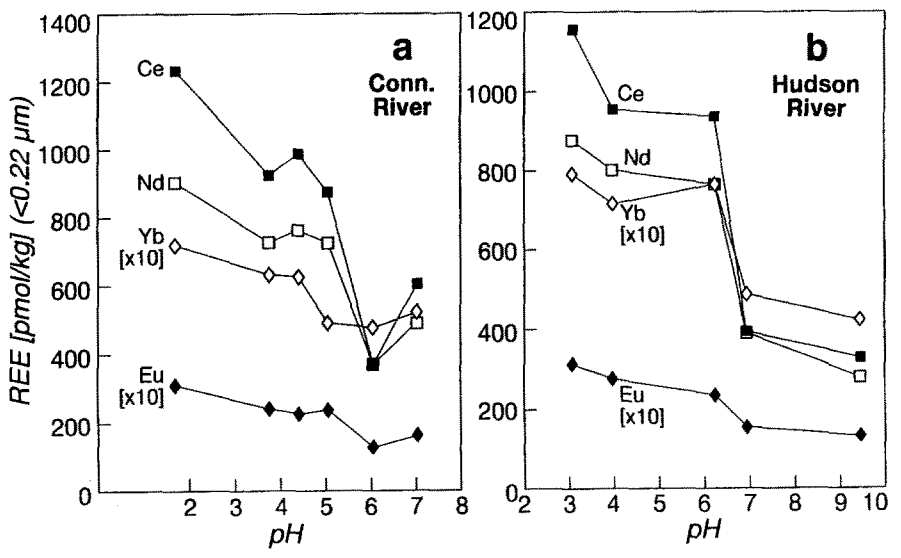


Fig. 1. Whole river titration experiment results for the Connecticut River (A) and Hudson River (B): the concentrations of dissolved (<math><0.22 \mu\text{m}</math>) Nd, Ce, Eu and Yb plotted against pH of the river water.

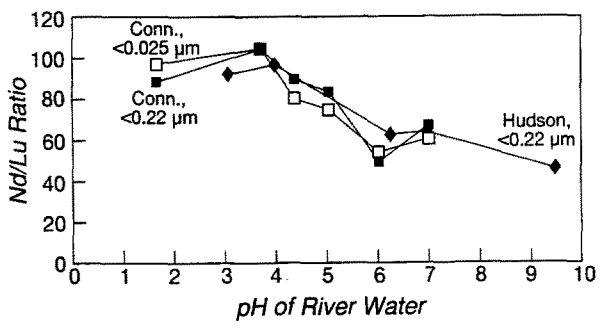


Fig. 2. Whole river titration experiment results for the Connecticut River and Hudson River: the Nd/Lu ratio of filtered river water as a function of pH. Nd/Lu represents a light to heavy REE ratio.

the Hudson River (Figure 1). Nd, for example, increases by almost a factor of two over these pH ranges in both rivers. The only other pH-sorption experiment is that of Koepenkastrup and DeCarlo (1992) who used amorphous  $\text{FeOOH}$  in a high ionic strength (0.7 M) solution of  $\text{NaNO}_3$ . They reported that the adsorption of La, Eu and Yb increased most markedly in going from pH 5.5 to 7.5.

Fractionation due to pH variation is illustrated in two ways. Figure 2 shows that there is a gradual two-fold increase in the Nd/Lu ratio as the pH decreases from 9.5 to 1.7. (Nd is the lightest trivalent-only REE measured by ICP-MS). Hence, there is preferential release of the LREE over the HREE at lower pHs. There is good continuity in the Nd/Lu-pH relationship between the two rivers and between 0.22 and  $0.025 \mu\text{m}$  filtrates from the Connecticut River. Figure 3 further demonstrates

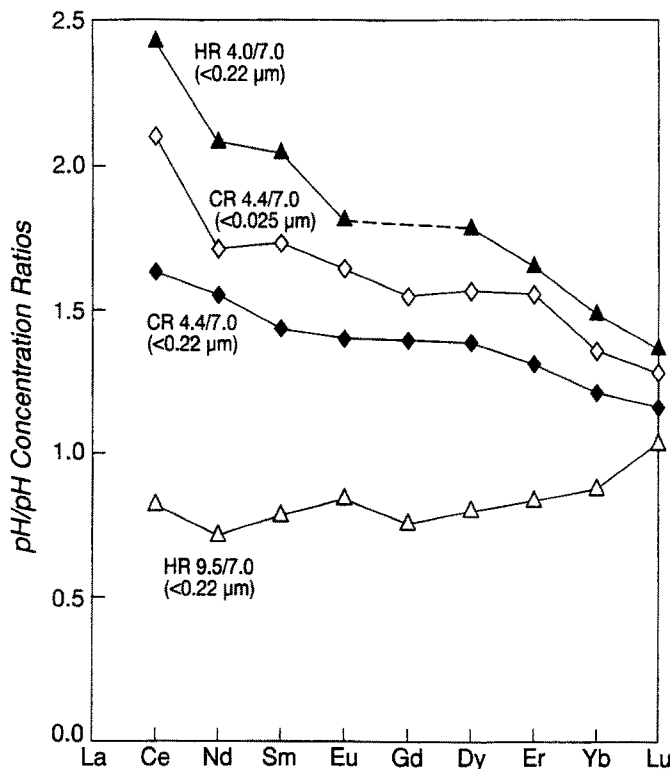


Fig. 3. Whole river titration experiment results for the Connecticut River and Hudson River: the dissolved REE concentrations of acidified and basefied river waters are normalized to the dissolved REE concentrations of the river waters at ambient pH (7) water. These pH/pH = 7 plots indicate the order of fractionation when lowering or raising pHs.

that there is a progressive increase in the extent of release in going from the heaviest (Lu) to the lightest (Nd) REE(III) as the initial pH of the two rivers is lowered. That is, the order of release upon lowering the pH is LREEs > MREEs > HREEs. For example, the pH 4.4/pH 7.0 ratios of Nd and Lu are 1.54 and 1.14 respectively for the 0.22  $\mu\text{m}$  filtrates of the Connecticut River. For the Hudson River these ratios are 2.08 and 1.35. On raising the pH of the Hudson River water from 7.0 to 9.5 there is a decrease in REE concentrations due to adsorption onto particles and the fractionation upon removal of REE(III) at higher pHs has the order LREEs > MREEs > HREEs. For example, the pH 9.5/pH 7.0 ratio gradually increases from a value of 0.71 for Nd to a value of 1.01 for Lu, indicating that there is no removal of the heaviest REE(III) and a 29% removal of a LREE(III).

A comparison of the REE composition of the 0.22  $\mu\text{m}$  and 0.025  $\mu\text{m}$  Connecticut River filtrates at pHs of 4.4 and 7.0 shows that the smaller pore-sized filtrate is lower in absolute REE concentrations and also fractionated relative to the 0.22  $\mu\text{m}$  filtrate (Figure 4). The 0.025  $\mu\text{m}$  filtrate is HREE-enriched relative to the 0.22  $\mu\text{m}$  filtrate as the order of removal due to filtration through a finer filter is LREEs > MREEs

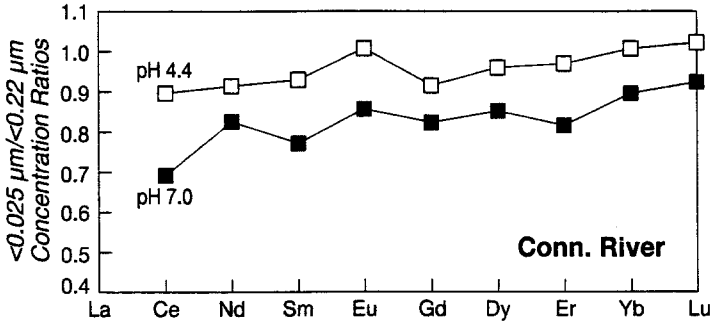


Fig. 4. Whole river titration experiment results for the Connecticut River: the REE concentrations of the  $< 0.025 \mu\text{m}$  filtrate are normalized against the REE concentrations of the  $< 0.22 \mu\text{m}$  filtrate for experiments run at pH 4.4 and 7.0.

$>$  HREEs. This confirms a previous observation for the same river that colloidal particles (defined here as  $0.22$  to  $0.025 \mu\text{m}$ ) are LREE enriched (Sholkovitz, 1992). The extent of removal of  $0.22 \mu\text{m}$  filtered REEs by the  $0.025 \mu\text{m}$  filter is smaller at pH 4.4 than at pH 7.0. This suggests that the higher pH water has a larger proportion of colloidal REEs and that lowering the pH either releases REEs from colloidal particles or converts colloidal particles to the solution phase.

In summary, the “whole river pH titration” experiments show that (1) dissolved REE concentrations are inversely proportional to pH; (2) lowering the river water pH causes the dissolved form to be preferentially enriched in LREEs while raising the pH preferentially removes the LREEs; (3) shale normalized compositions are more HREE-enriched at higher pHs (data not shown here); and (4) colloidal REEs are more abundant at higher pHs. These features are consistent with field observations (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990). However, the field data show much greater increases in concentrations as functions of decreasing pH. For example, in the carbonate rivers of England, dissolved ( $< 0.45 \mu\text{m}$ ) Nd concentrations increase by a factor of 4 as the pH decreases from 7.0 to 6.0 (Elderfield *et al.*, 1990). Goldstein and Jacobsen (1988) report an Nd increase of about 20 fold between pH 8 and 6. While the direction of fractionation with respect to pH is similar in both the field and experimental data, the extent of fractionation in the field studies usually exceeds that observed in the laboratory. Goldstein and Jacobsen (1988) reported that the Nd/Lu ratio of  $0.45 \mu\text{m}$  filtrates of river water ranged from 258 to 23 over a pH range of 6.0 to 7.9. In our experiments this ratio varied from 104 to 44 (Figure 2). The larger concentration range and extent of fractionation in the field data might reflect the fact that field samples come from a large variety of rivers and geological terrain. It might also reflect different time scales of reactions as the laboratory experiments are carried out only for periods of less than one day.



### 3.3. EFFECTS OF SALINITY

Two different types of experiments were run.

The objective of the first type of experiment was to follow the removal and fractionation of dissolved REEs due to salt-induced coagulation of colloidal REEs from river water. Mixing experiments, modeled after those in Sholkovitz (1976), were performed. Filtered ( $0.22\ \mu\text{m}$ ) Connecticut River water was mixed for 24 h with REE-free filtered seawater. The REEs were first removed from the seawater end member (Sargasso Seawater with salinity of 35) by co-precipitation with iron hydroxides. The REE concentrations in the filtered mixtures were measured by ICP-MS.

A desorption experiment was carried out to determine the extent to which REEs are released from particles upon contact with seawater. Filtered seawater (not REE-free) was passed over suspended particles collected from the Connecticut and Mississippi Rivers. The river particles were collected in Millipore Millipak-20 cartridge filters with a  $0.22\ \mu\text{m}$  pore size (Sholkovitz, 1991). These particle-loaded cartridges served as the reaction vessels. That is, two liters of Millipak  $0.22\ \mu\text{m}$  filtered Buzzards Bay water (salinity of 32) was recirculated through the cartridges with a peristaltic pump for 8 h. A second leach of the same particle-loaded cartridges was carried out with a new two-liter aliquot of filtered seawater. A control experiment was run in which prefiltered Buzzards Bay seawater was recirculated through a Millipak cartridge in order to determine if the cartridge filter itself altered the REE composition of the leaching seawater. All cartridges were precleaned by flushing them with 1N HCl and purified water. The leaching experiments took place about one week after collection during which time the river particles were stored wet in the Millipak cartridges at room temperatures. The REE compositions of the leachates (samples and controls) and the original seawater were measured by TIMS.

The mixing experiment results for the Connecticut River are shown in Figure 5 in which the river water normalized concentrations of Nd, Er and Yb are plotted against the salinity of the mixtures. The percentage removals of each REE at the salinity of 15.0 are presented in Table I and are calculated relative to REE concentrations predicted by dilution only (conservative mixture of river and REE-free seawater end-members). Yb removal is 28%, while Er and Nd have 50% and 70% removal respectively. Hence, the extent of removal from river water follows the order LREEs > MREEs > HREEs.

Table I compares the percentage removal of dissolved REEs observed in estuaries and measured in the laboratory. Like Fe, the coagulation of colloidal REEs in the low salinity regime of estuaries appears to be a universal feature (Goldstein and Jacobsen, 1988; Sholkovitz and Elderfield, 1988; Sholkovitz, 1993). A previous study of the Connecticut River water showed that colloids ( $0.025\text{--}0.22\ \mu\text{m}$  size range) are LREE-enriched (Sholkovitz, 1992). This feature will be reconfirmed in the next section. Hence, one would predict the fractionation of the type observed in

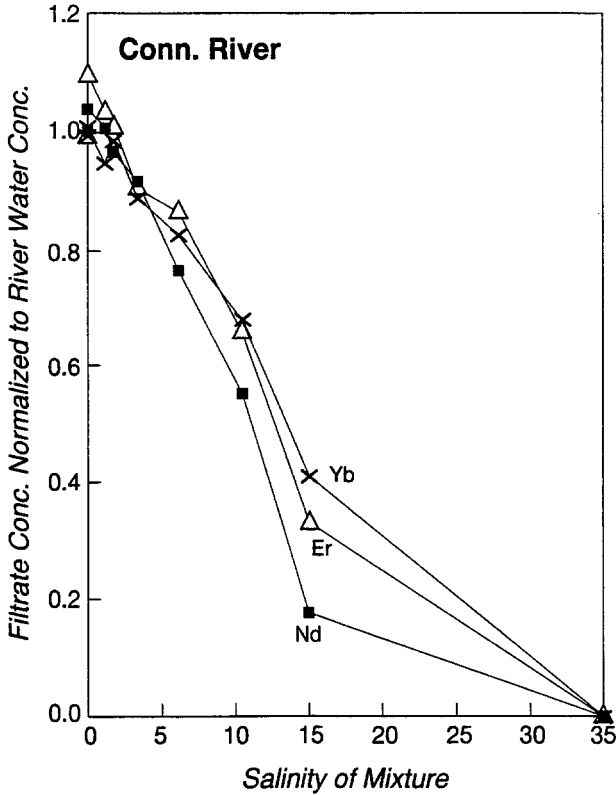


Fig. 5. Results from Connecticut River water and seawater mixing experiments: REE-free and filtered ( $< 0.22 \mu\text{m}$ ) seawater was mixed for 24 h with filtered ( $< 0.22 \mu\text{m}$ ) river water. The resulting  $< 0.22 \mu\text{m}$  filtrate concentrations of Nd, Er and Yb are plotted against salinity. The concentrations of the salinity mixtures have been normalized to their respective river water concentrations in order to equally scale each distribution on the  $y$ -axis.

the mixing experiments (order of coagulation being LREEs  $>$  MREEs  $>$  HREEs) would accompany the coagulation of river colloids. However, field data show a greater extent of removal for all the REEs and smaller degree of fractionation than do laboratory data. In the Amazon River estuary, for example, the percentage removal of dissolved REEs ( $< 0.22 \mu\text{m}$ ) ranges from 95% for La to 86% for Lu. Differences between the laboratory and field results probably reflect the presence in estuaries of large concentrations of suspended particles with surface reactive sites and longer reactions times.

The desorption experiment shows that there is release of dissolved REE(III)s when river particles are leached with seawater. Large scale fractionation accompanies the release as illustrated by normalizing the REE concentrations of the seawater circulated over the particles to the REE composition of the starting seawater (Figure 6). The control experiment, in contrast, shows only a small ( $< 5\%$ ) decrease in REE concentrations and no fractionation. The Connecticut River experiments

TABLE I. Percent removal of dissolved REEs in estuaries.

	Lab. Experiments*		Field Results					
	Conn. S = 15	Hudson S = 13.3	Amaz. <sup>1</sup>	Gir. <sup>2</sup>	Wh. <sup>3</sup>	Susq. <sup>4</sup>	Del. <sup>5</sup>	Mul. <sup>5</sup>
La	–	–	95	90	73	–	–	74
Ce	74	35	97	85	60	85	95	74
Nd	70	34	95	75	60	80	80	73
Sm	63	27	94	85	54	75	78	70
Eu	59	39	94	75	39	75	–	69
Gd	66	36	92	80	–	80	60	70
Dy	50	26	91	–	53	70	80	60
Er	50	15	88	–	39	60	56	67
Yb	28	15	87	50	43	60	51	–
Lu	< 20	9	86	55	42	60	–	56

<sup>1</sup>Sholkovitz, 1993; <sup>2</sup>Martin *et al.*, 1976;

<sup>3</sup>Goldstein and Jacobsen, 1988; <sup>4</sup>Sholkovitz and Elderfield, 1988;

<sup>5</sup>Elderfield *et al.*, 1990; \*this study

Amaz = Amazon, Gir. = Gironde, Wh. = Great Whale

Susq. = Susquehanna, Del. = Delaware, Mul. = Mullica

show that the release increases systematically from Lu to La. Specifically, the three heaviest REEs (Er, Yb and Lu) in the first leachate all increase in concentration by a factor of 2.3–2.8; a middle REE, Eu increases by a factor of 6.5; and La, the lightest REE increases by a factor of 7.8. A second leach of the same sample of particles with fresh seawater shows a similar form of fractionation. The absolute increase in REE concentration and the extent of fractionation (e.g., gradient between La and Lu) is much less in the second leachate (Figure 6a). The salt-induced release has the order LREEs > MREEs > HREEs, the same order of fractionation that is observed when lowering the pH (Figure 3). Ce shows only a slightly smaller extent of release than its trivalent neighbors.

The results of the desorption experiment with Mississippi River particles are intriguing. Leaching with seawater leads to a systematic increase in the extent of release from Lu to Eu (Figure 6b). In fact, fractionation from the Lu to Eu is identical to that observed with Connecticut River particles (Figure 7). However, between Eu and La, there is a two-fold decrease in the extent to which REE(III) are released. Ce is highly anomalous as it is not released to seawater. The order of release for the trivalent REEs is MREEs > HREEs = LREEs. This type of fractionation is also observed in the second seawater leach of Mississippi River particles (Figure 6b). As will be discussed in Section 4, the lack of Ce release to seawater may reflect the presence of insoluble Ce(IV) oxides on the surfaces of Mississippi River particles as a result of the *in situ* oxidation of dissolved Ce(III).

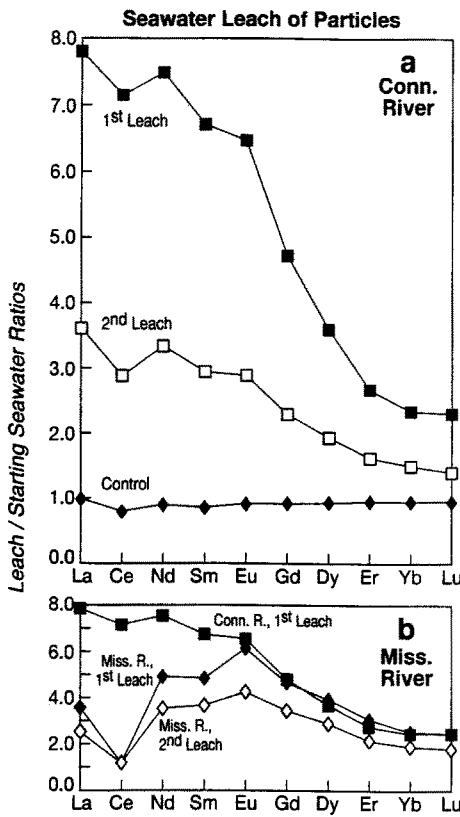


Fig. 6. Seawater leaching experiments using suspended particles from (A) the Connecticut River and (B) the Mississippi River. The y-axes are the dissolved REE concentrations of the seawater leaches normalized to the dissolved REE concentrations of the starting seawater. Both (A) and (B) show a first and second leach of the same filter. Results of a control experiment (Millipak filter and sea water only) are presented in (A).

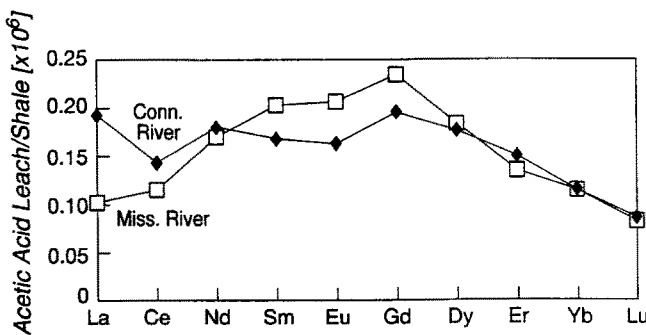


Fig. 7. Acetic acid leach of suspended particles from the Connecticut River and Mississippi River. Leach concentrations ( $< 0.22 \mu\text{m}$ ) are normalized to those shale.

Processes responsible for the concave down distribution to the REE(III) release remain unresolved but will be discussed in Section 5.

### 3.4. SURFACE SORPTION

In order to determine the REE composition associated with the more labile fraction of surfaces, acetic acid (25% solution) was used to leach suspended particles of the Mississippi and Connecticut Rivers. Acetic acid has been used to release adsorbed metals and metals associated with carbonates and oxyhydroxides of Mn and amorphous Fe oxides (Landing and Lewis, 1991). Sholkovitz *et al.* (1994) have shown that acetic acid releases both adsorbed REE(III) and Ce(IV) from marine particles. An acetic acid solution (100 ml) was pumped over a period of 2 h through Millipak filters containing about 100 mg of suspended particles and the leachate was analyzed by TIMS. The REE concentrations of the starting acetic acid solution were found to be very low. One concern is that fractionation of REEs may result from artifacts of chemical leaches. While the use of large solution volume to particle weight ratios will minimize readsorption problems (Sholkovitz, 1989), artifacts cannot be ruled out.

The shale normalized REE(III) pattern of the Mississippi River leachate has a well developed concave down distribution due to a maximum across the MREEs (Figure 7). In contrast, the Connecticut River leachate pattern is flat from La to Gd and then becomes progressively more depleted across the HREEs. This inter-river difference in fractionation is similar to that observed in the seawater leaches where Mississippi River particles have a large concave down distribution and the Connecticut River is progressively depleted from the La to Lu (Figure 6). Hence, there appears to be a fundamental difference in the composition and reactivity of the acetic acid labile, surface-associated REE(III)s. For the Connecticut River the order of association with labile surface phases is LREEs = MREEs > HREEs. Leaching with seawater and lowering the pH releases REEs from Connecticut River particles in the order LREEs > MREEs > HREEs. For the Mississippi River particles, leaching with seawater and acetic acid both yield concave down distributions for the trivalent REEs. In contrast, seawater does not release Ce from the Mississippi River particles while acetic acid does. This reinforces an earlier argument that Ce exists as Ce(IV) oxides on Mississippi River particles.

### 3.5. EFFECTS OF FILTRATION AND COLLOIDS

A series of filtration experiments were carried out using Connecticut River and Hudson River water to ascertain the role of colloids in controlling the absolute concentrations and fractionation of REEs. Fractionation will be quantified by comparing REE compositions to shale and by comparing filtrate and retentate compositions to each other.

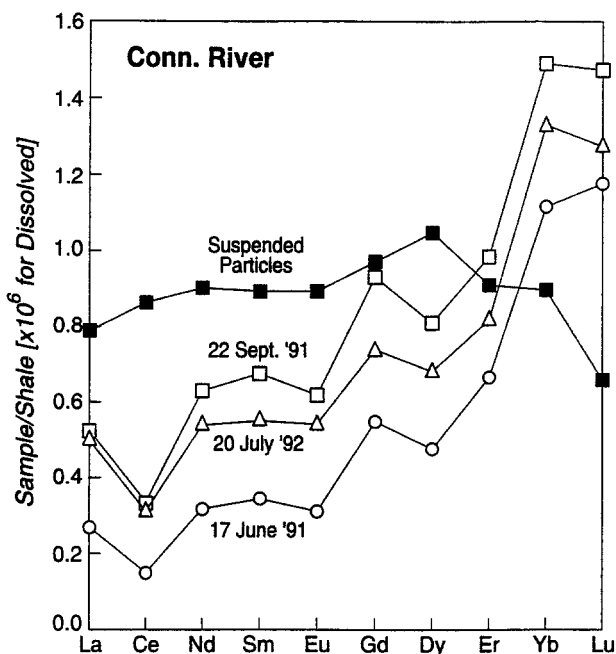


Fig. 8. Filtration experiments. Shale normalized patterns of dissolved ( $< 0.22 \mu\text{m}$ ) REEs collected from the Connecticut River on three dates in 1991 and 1992.

### 3.5.1. Shale-Normalized REE Composition

Figure 8 shows that the  $0.22 \mu\text{m}$  filtrates of the Connecticut River waters are highly fractionated relative to both the REE composition of shale and its own suspended river particles. Connecticut River data for three sampling periods between June 1991 and December 1992 yield a consistent set of HREE-enriched patterns even though the absolute dissolved concentrations vary by a factor of about three. The HREE enrichment is large as indicated by  $(\text{Yb})_n/(\text{La})_n$  ratios ( $n$  signifying a shale normalized ratio) between 3 and 10. The Hudson River water  $0.22 \mu\text{m}$  filtrate is also HREE-enriched relative to shale (Figure 9).

Filtration through progressively finer pore-sized filters was carried out for the Connecticut and Hudson Rivers. The starting filtrate had been passed through  $0.22 \mu\text{m}$  Millipak filter, and then aliquots of this "dissolved" fraction were then passed through  $0.025 \mu\text{m}$  disc filters and Filtron ultrafilters with 50K and 5K molecular weight membranes. All filtrations of the  $0.22 \mu\text{m}$  filtrates were done in parallel. The ultrafiltrates are referred to as  $< 50\text{K}$  and  $< 5\text{K}$  solution phase and the retentates as  $> 50\text{K}$  and  $> 5\text{K}$  colloidal phase.

Filtration through filters with progressively smaller pore sizes leads to increasingly lower REE concentrations (Figure 9 and Table II). Hence, a large part of the dissolved REE inventory, the LREEs in particular, is carried by river colloids.

TABLE II. REE concentrations of filtration experiments.

ID#	Filtrate or Retentate	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu	Ce- Anom.	Fe	Color 280nm	DOC
[pmol/Kg]															
<b>A. Connecticut River</b>															
17 JUNE 1991*															
80	0.45 $\mu\text{m}$	195	292	180	36.0	6.92	38.1	27.9	21.6	27.6	4.67	0.74	0.48	0.082	
81	0.22	78.8	85.8	82.9	17.0	3.26	22.0	15.9	14.8	22.6	4.08	0.51	0.23	0.048	
83	0.025 (1)**	38.8	45.6	49.2	10.9	2.00	16.7	11.8	13.1	21.3	3.87	0.51	0.10	0.023	
84	0.025 (2)	42.6	43.8	48.6	11.1	2.08	16.9	12.1	13.4	21.6	3.94	0.47	0.10	0.023	
22 SEPTEMBER 1991*															
105	0.45 $\mu\text{m}$	168	222	178	36.4	7.05	40.3	28.9	22.9	30.7	5.36	0.62	0.15	0.091	
106	0.22	154	196	166	33.5	6.52	37.3	27.2	21.9	30.2	5.11	0.60	0.13	0.090	
107	0.025 (1)***	101	122	112	24.4	4.72	29.2	21.4	19.0	27.5	4.83	0.56	0.08	0.089	
108	0.025 (2)	95.3	119	109	23.5	4.61	28.7	21.0	19.1	27.9	4.60	0.57	0.08	0.089	
20 JULY 1992															
224	< 5 K	12.8	13.5	16.1	3.95	0.90	8.57	7.02	9.70	18.67	3.59	0.462	0.034	0.048	275
223	< 50 K	19.1	22.3	25.7	6.33	1.38	11.9	9.35	11.75	21.23	4.04	0.497	0.049	0.066	282
222	0.22 $\mu\text{m}$	148	184	143	27.6	5.72	29.8	23.0	18.32	26.96	4.44	0.604	0.18	0.073	263
225	> 50 K	2059	2523	1905	354	71.0	324					0.603	11.1	0.231	739
226	> 5 K	3305	4045	3143	590	120	544	412	253	223	31.38	0.597	17.4	0.688	1798
17 DECEMBER 1992															
														Abs@300nm	
339	< 5 K		74.4	87.3	17.1	3.58	27.2	19.1	18.5	29.7	5.00		0.081	0.159	
340	< 50 K		163	179	33.0	7.60	50.4	34.6	28.9	40.0	5.60		0.188	0.204	
394	0.22 $\mu\text{m}$		680	576	89.4	19.6	114	87.7	59.8	68.0	8.83		1.42	0.293	
343	> 50K		5677	4726	815	168	999	673	366	353	40.9		9.78	1.080	
344	> 5K		4852	4099	657	165	837	622	359	360	46.8		9.16	1.160	
<b>B. Hudson River</b>															
23 OCTOBER 1992															
289	< 5K(1)**		110	111	20.8	5.42	34.5	26.4	22.2	22.4	2.77		0.02	0.068	
308	< 5K(2)		102	109	21.9	4.31	32.2	24.7	18.0	21.9	2.95		-	-	
303	< 50K		213	209	41.4	8.22	60.1	46.5	30.3	34.7	4.00		0.12	0.107	
305	0.025 $\mu\text{m}$		320	310	56.4	12.6	89.9	62.8	39.5	44.1	5.19		0.09	0.138	
304	0.22		443	423	78.8	17.0	121	81.6	49.5	52.4	3.91		0.14	0.13	
302	> 50K		2843	2547	492	88.1	593	401	227	221	27.9		0.73	0.369	
301	> 5K(1)**		4142	3903	719	132	981	654	390	363	45.8		1.03	0.791	
309	> 5K(2)		4071	3901	719	144	1028	642	391	370	47.9		-	-	

\*Data previously published in Sholkovitz (1992)

\*\*(1) and (2), replicate analyses of same samples

\*\*\*(2) is refiltration of first (1) filtrate Fe and DOC in  $\mu\text{mol/kg}$

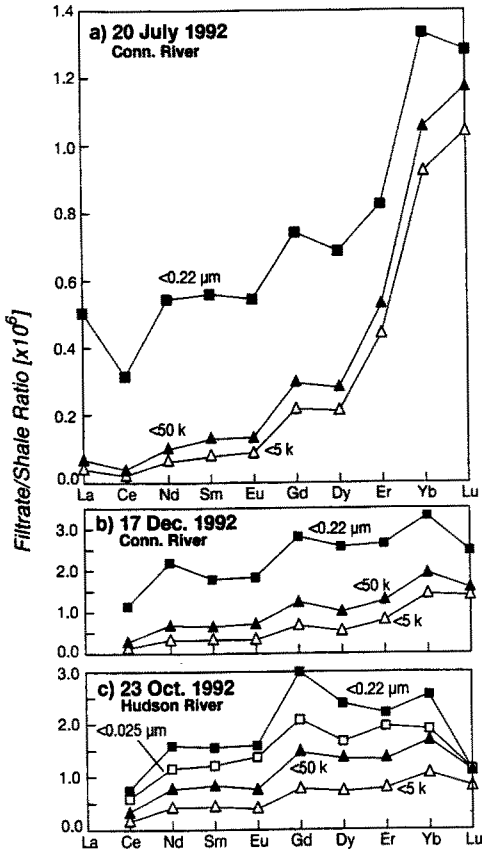


Fig. 9. Filtration experiments. A comparison of shale normalized patterns from three types of filtration ( $< 0.22 \mu\text{m}$ ,  $< 50\text{K}$  and  $< 5\text{K}$  ultrafiltrates) using (A) Connecticut River water collected on 20 July 1992, (B) Connecticut River water collected on 17 December 1992 and (C) Hudson River water collected on 23 October 1992.

Moreover, the extent of removal by ultrafiltration is not similar for each REE but rather varies across the series. That is,  $< 50\text{K}$  and  $< 5\text{K}$  ultrafiltrates are more strongly HREE-enriched (or LREE depleted) than is the  $0.22 \mu\text{m}$  filtrate. As elaborated upon later, the extent of removal of river colloids by ultrafiltration has the order LREEs  $>$  MREEs  $>$  HREEs. The development of fractionated ultrafiltrates is less pronounced for the Hudson River than it is for the Connecticut River.

The colloids retained behind the ultrafilters have high concentrations of REEs and have shale normalized patterns which are quite distinct from those of the ultrafiltrates (Figure 10). The  $> 50\text{K}$  and  $> 5\text{K}$  fractions from both rivers have shale patterns which are either fairly flat or slightly elevated in the MREEs. The Connecticut River retentate of July 1990 has a large negative Ce anomaly. Hence, the removal of colloids with shale-like composition of REE(III) leads to ultrafiltrates with large depletion in the LREEs (Figure 9). The flat patterns of the retentates are



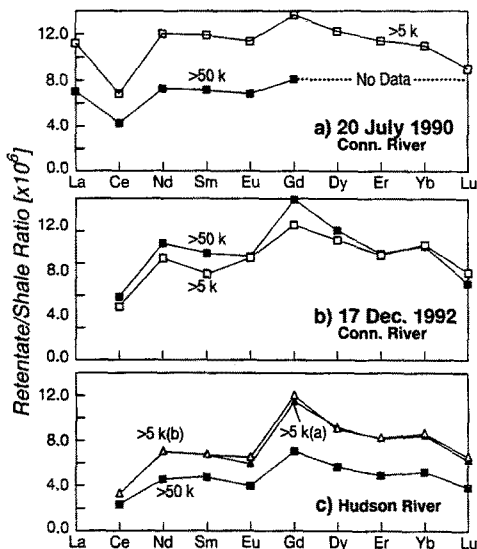


Fig. 10. Filtration experiments. Shale normalized REE patterns of retentates (colloids) collected by ultrafiltration using (A) Connecticut River water collected on 20 July 1992, (B) Connecticut River water collected on 17 December 1992 and (C) Hudson River water collected on 23 October 1992. (C) shows a replicate measurement of one retentate.

not interpreted to mean that the river colloids are composed of minerals representative of the crust. Rather these colloids are composed mainly of organic matter and Fe oxyhydroxides which have a shale-like composition.

Fe, DOC, and color (absorbance at 280 nm) were also measured on the ultrafiltration experiment of 20 July 1992 Connecticut River water. The latter three components of the 0.22  $\mu\text{m}$  filtrate are highly enriched in the > 50K and > 5K retentates (Table II), as are the REEs. Fe and color decrease in the ultrafiltrates; DOC, in contrast, is essentially constant in all filtrates and ultrafiltrates. The high organic carbon and Fe content of river colloids is confirmed by this experiment. Hence, REEs are strongly associated with river colloids, a conclusion deduced by earlier studies of river water (Goldstein and Jacobsen, 1988; Sholkovitz and Elderfield, 1988; Elderfield *et al.*, 1990; Sholkovitz, 1993).

### 3.5.2. River Water-Normalized REE Compositions

The aquatic chemistry responsible for fractionation is better understood by directly comparing the REE compositions of dissolved, colloidal and solution fractions to each other. Figures 11 and 12 compare the REE composition of the 0.025  $\mu\text{m}$  filtrate and < 5K ultrafiltrate to that of the dissolved (< 0.22  $\mu\text{m}$ ) fraction of the Connecticut River water. The 0.025  $\mu\text{m}$  filtrate is progressively depleted in going from the heaviest REE (Lu) to the lightest REE (La). This LREE depletion is more pronounced when comparing the < 5K ultrafiltrate to the 0.22  $\mu\text{m}$  filtrate

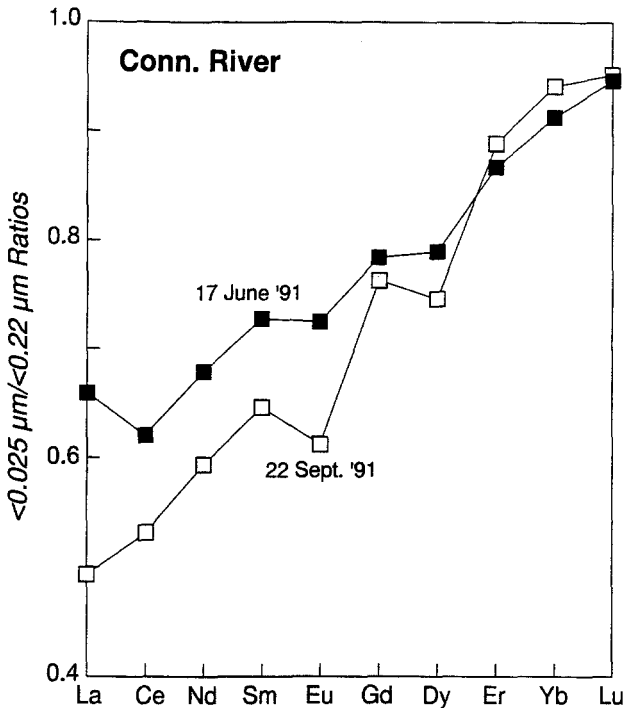


Fig. 11. Filtration experiments. The REE concentrations of the  $0.025 \mu\text{m}$  filtrate are normalized against the REE concentrations of the  $0.22 \mu\text{m}$  filtrate (*dissolved* form) for Connecticut River water collected on 17 June 1991 and 22 Sept. 1991. These data were previously reported in Sholkovitz (1993).

(Figure 12). In general, the fractionation between filtrates is less developed for the Hudson River sample.

As illustrated in Figures 13 to 15, a major observation of the filtration experiments is that the colloids are highly LREE-enriched relative to both the  $0.22 \mu\text{m}$  filtrate and to the ultrafiltrates. Plots of  $> 5\text{K}/ < 5\text{K}$  and  $> 50\text{K}/ < 50\text{K}$  ratios demonstrate that the colloids of the Connecticut and Hudson Rivers are highly fractionated (LREEs  $>$  MREEs  $>$  HREEs) when compared to the solution form. In this type of normalization Ce anomalies are not prominent with the exception of the 20 July 1992 where the  $> 5\text{K}$  retentate has a positive anomaly when compared to the  $< 5\text{K}$  ultrafiltrate (Figure 14a).

### 3.5.3. Ultrafiltration: Inventories, Mass Balances and Colloid Composition

This section will deal with two additional aspects: the inventory of REEs, Fe, DOC and color carried in the colloidal fraction and the mass balance of the ultrafiltration experiments. The latter will shed light on artifacts associated with ultrafiltration.

If one assumes that ultrafilters work perfectly, then the inventory of REEs and other components in the colloid pool of the river water can be calculated by knowing

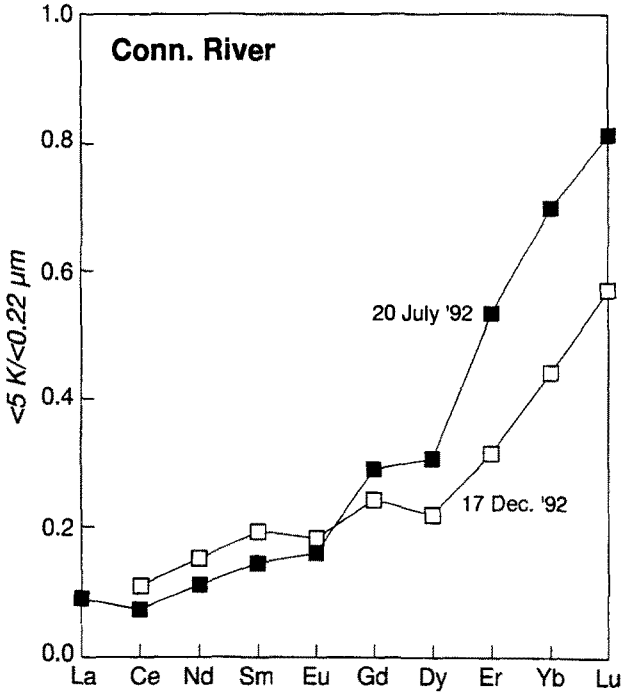


Fig. 12. Filtration experiments. The REE concentrations of the < 5K ultrafiltrate are normalized against the REE concentrations of the 0.22 μm filtrate (*dissolved* form) for Connecticut River water collected on 20 July 1992 and 17 December 1992.

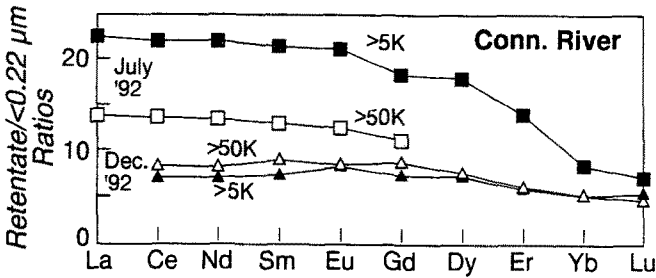


Fig. 13. Filtration experiments. The REE concentrations of the > 50K and > 5K retentates (colloids) are normalized against the REE concentrations of the 0.22 μm filtrate (*dissolved* form) for Connecticut River water collected on 20 July 1992 and 17 December 1992. There are no HREE data for the > 50K July sample.

the elemental concentrations and the weight percent of each pair of retentates and ultrafiltrates. This has been done in Table III for the > 50K and > 5K retentates of the two Connecticut River studies. For example, the > 5K colloidal matter of the July 1992 sample carries between 90 and 24% of the REEs. These percentages decrease across the series from La to Lu, consistent with the colloids being LREE-enriched relative to the dissolved pool. Like the LREEs, Fe (95%) is also carried predominantly in the > 5K colloids. DOC (19%) and color (33%) have smaller

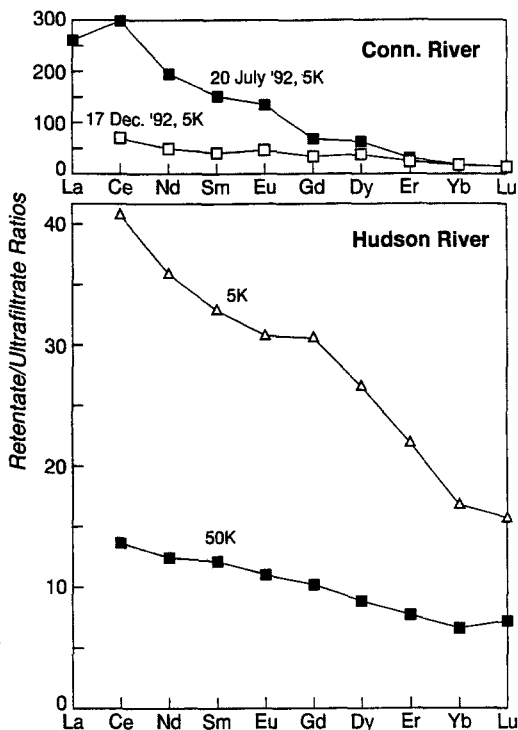


Fig. 14. Filtration experiments. (A) The REE concentrations of the  $> 5K$  retentates (colloids) are normalized against the REE concentrations of the  $< 5K$  ultrafiltrate (*solution* form) for Connecticut River water collected on 20 July 1992 and 17 December 1992. (B) Same as (A) for the Hudson River but including ( $> 50K$  retentate)/( $< 50K$  ultrafiltrate) normalization.

colloidal inventories. The same observations hold for the December 1992 sample except that the colloidal inventories of the LREEs are significantly smaller (70%) than their July 1992 counterparts. These inventory calculation shows that colloids are the major carriers of Fe, LREEs, and MREEs in the Connecticut River.

Because ultrafiltration may lead to imperfect recovery, it is important to make a mass balance between the starting water ( $0.22 \mu\text{m}$  filtrate in this case) and the retentate and ultrafiltrate. Percent recoveries are presented in Table III; they represent the sum of the retentate and ultrafiltrate inventories, compensated for their weight percentages, divided by the  $0.22 \mu\text{m}$  inventory. For the July 5K experiment the recoveries range from a low 82–86% for the LREEs to a high of 95–102% for the HREEs. Hence, a significant fraction of the LREEs are not accounted for. The July 50K experiment had excellent recoveries, 91–101% for La through Gd. While there are no HREE data for this experiment, I would expect HREE recoveries to be near 100% as HREEs are less colloidal. For the December 1992 experiment the recoveries of the 50K experiment all lie above 96%, with some as high as 118%. The biggest discrepancy occurs in the December 5K experiment where all recoveries except Lu (at 83%) range from 50–70%. Only 50% of the Ce and Nd are

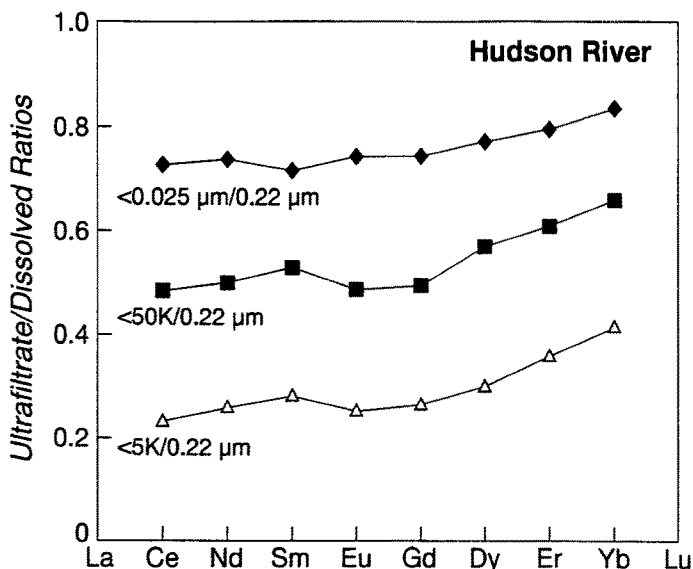


Fig. 15. Filtration experiments using Hudson River water. The REE concentrations of the 0.025 μm filtrate and the < 50K and < 5K ultrafiltrates are normalized against the REE concentrations of the 0.22 μm filtrate. No Lu are available.

TABLE III. Colloidal inventory and recoveries for ultrafiltration experiments.

	Weight % 5K and 50K Retentates	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu	Fe	Color [Abs. 280nm]	DOC
Connecticut River: 20 JULY 1992														
% Inventory of > 50K	5.8	87	87	82	77	76	63	no data			93	17	14	
% Inventory of > 5K	3.4	90	87	91	83	82	69	67	48	30	24	95	33	19
% Recovery in 50K Experiment		93	91	94	96	95	101	no data			91	103	117	
% Recovery in 5K Experiment		84	82	86	87	87	90	90	102	95	102	82	95	124
Connecticut River: 17 DECEMBER 1992														
% Inventory of > 50K colloid	8.9	77	72	71	68	66	66	55	46	42	-	-	34	
% Inventory of > 5K colloids	5.5	79	73	69	73	64	65	53	41	35	-	-	30	
% Recovery in 50K Experiment		-	96	101	115	112	118	104	98	100	99	-	96	
% Recovery in 5K Experiment		-	50	53	58	64	60	62	70	83	-	-	73	

Inventory refers to percentage of dissolved REEs, Fe etc. carried as > 5K and > 50K colloids

% inventory = (retentate conc. × wt. % retentate)/((retentate conc. × wt. % retentate) + ultrafiltrate conc. × wt. % ultrafiltrate)

Recovery refers to a mass balance calculation; 100% means that all the starting dissolved inventory can be accounted by summing ultrafiltrate and retentate.

% recovery = (retentate conc. + ultrafiltrate conc.) × 100/(starting 0.22 μm filtrate conc.)

accounted for. Even color, with nearly a 100% recovery in the other experiments, was only 73%. There appears to have been a recovery problem associated with the 5K retentate of the December 1992 experiment. One can see this in several of the earlier figures which use the > 5K data (Figures 10b, 13, 14a). In Figure 14a, for example, the > 5K retentate of the December sample is greatly depleted in MREEs and LREEs when compared to its July counterpart.

Clearly, there was an artifact associated with the 5K ultrafiltration of the December 1992 Connecticut River water. One can speculate that there was a wall and/or filter effect. It is also possible that the > 5K retentate was not totally recovered from the ultrafilter. Since the LREEs and MREEs are more extensively carried as colloids than are the HREEs; they could preferentially "stick" to the walls and filter. Artifacts of this type can be viewed in two ways. They could preclude any geochemical interpretation of the data or they could be indicators of the processes being studied. As argued next, the poor recoveries reflect the presence of river colloids enriched in LREEs and MREEs and stuck to the ultrafilters.

Since a key aspect of this study is to determine the REE composition of river colloids, it is important to return to this subject in the context of possible wall/filter artifacts. The REE composition of river colloids was previously reported by using the REE measurements of the retentates (Figures 10, 13 and 14). Alternatively, the colloidal composition can be calculated by subtracting the concentrations of ultrafiltrates from those of the starting  $0.22 \mu\text{m}$  filtrate. This calculation of the colloidal composition by difference does not rely on knowing the retentate composition. If one assumes that the poor recoveries result from colloids stuck to the filter or walls, then the method of difference should give a reliable measure of colloidal composition. Figure 16 shows the *calculated* REE compositions of colloids normalized to the dissolved ( $< 0.22 \mu\text{m}$ ) phase. The resulting patterns for all three experiments, including the previously suspect data of > 5K experiment of December 1992, are smooth and consistent. They reconfirm that the colloids are HREE-depleted when compared to the dissolved form. The extent of fractionation is greatest for the 20 July sample of the Connecticut River and smallest for the Hudson River. The shale normalized patterns of the *calculated* colloid composition are presented in Figure 17; they can be compared to the patterns derived from the retentates (Figure 10). The *calculated* patterns reconfirm that the river colloids have shale-like compositions for the REE(III) and negative Ce anomalies. The artifact of the 5K December experiment is no longer apparent.

#### 4. The Mississippi and Amazon Rivers

A comparison of these two major world rivers highlights key features of REE fractionation in river systems (Table IV). Shale normalized REE compositions of the dissolved phase and suspended particles are presented in Figures 18 and 19. The suspended particles (total dissolution by fusion) of the Mississippi River have a flat pattern while Amazon particles are slightly HREE depleted. This slight HREE

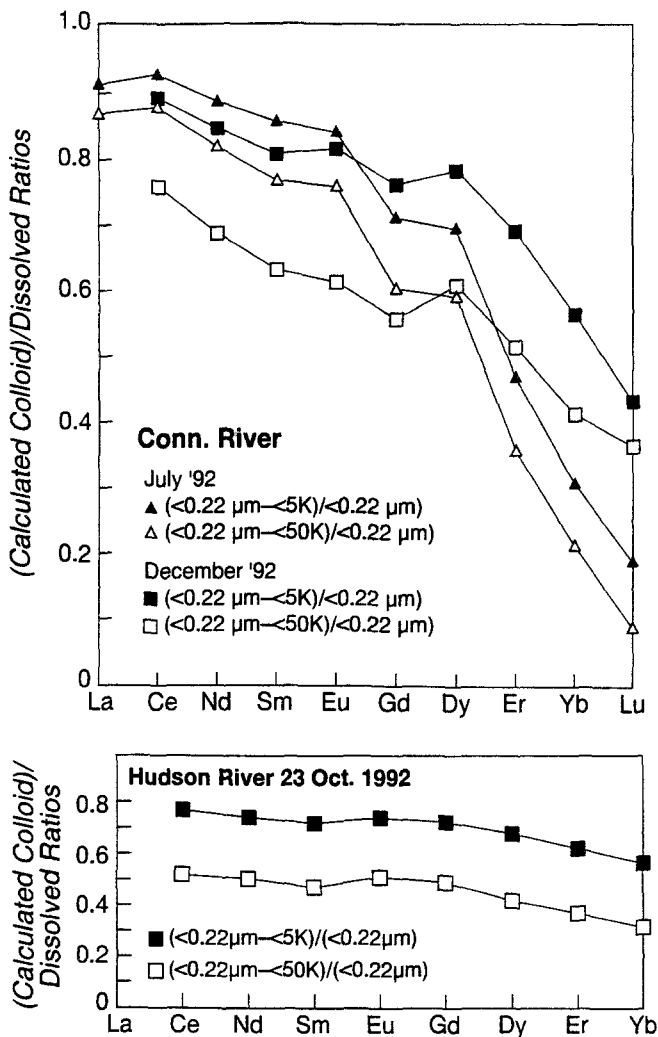


Fig. 16. Filtration experiments. The "calculated" REE concentrations of colloids are normalized against the dissolved (< 0.22 μm filtrate) REE concentrations for (A) Connecticut River water collected on 20 July 1992 and (B) Hudson River water collected on 23 October 1992. See insert on figure and text for definition of "calculated" colloid composition.

depletion is consistent with Goldstein and Jacobsen's (1988) observation for the averaged composition of suspended particles in the world's rivers. In general, the Mississippi and Amazon River suspended particles have crust-like REE compositions. In marked contrast, the dissolved REE(III) composition of the Mississippi River water is systematically enriched from La to Lu. Being strongly enriched in HREE, the REE(III)s are highly fractionated with respect to the upper crust and suspended particles. A large (0.37) negative Ce anomaly also characterizes this river. As documented in Figure 18, Goldstein and Jacobsen (1988) also noted these same features in their Mississippi River filtrate (0.22 μm). The outstanding features

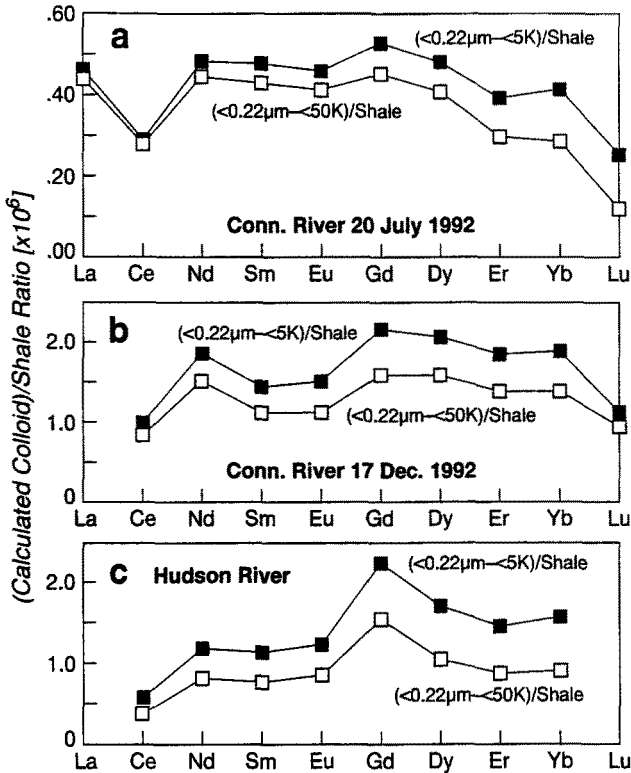


Fig. 17. Filtration experiments. The “calculated” REE concentrations of colloids are normalized against shale for (A) Connecticut River water collected on 20 July 1992, (B) Connecticut River water collected on 17 December 1992 and (C) Hudson River water collected on 23 October 1992. See insert on figure and text for definition of “calculated” colloid composition.

TABLE IV. REE concentrations of the Amazon and Mississippi Rivers.

SAMPLE	Ce Anom.	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
A. Filtrates [pmol/kg]											
Miss.	0.37	59.9	52.5	80.0	19.9	4.3	27.0	27.1	25.4	25.3	3.51
Amazon (b)*	1.00	373	930	579	146	35	150	130	70.4	56.8	7.25
Amazon (a)*	0.99	305	754	471	123	29.8	137	111	61.3	50.2	6.44
Sarg SW **	0.46	15.5	15	15.6	3.49	0.92	5.12	6.02	4.71	4.07	0.56
B. Suspended particles *** [pmol/mg particle]											
Miss.	1.01	60.8	125.4	56.4	9.93	2.11	9.86	7.46	4.94	3.94	0.47
Amazon	0.99	349	707	335	57.9	10.9	46.3	39.7	21.7	20.5	3.02

\*Two river water samples, Sholkovitz (1993)

\*\*30 m Sargasso Sea sample, Sholkovitz and Schneider (1991)

\*\*\*Dissolution by lithium metaborate fusion

All filtration with 0.22  $\mu\text{m}$  pore size



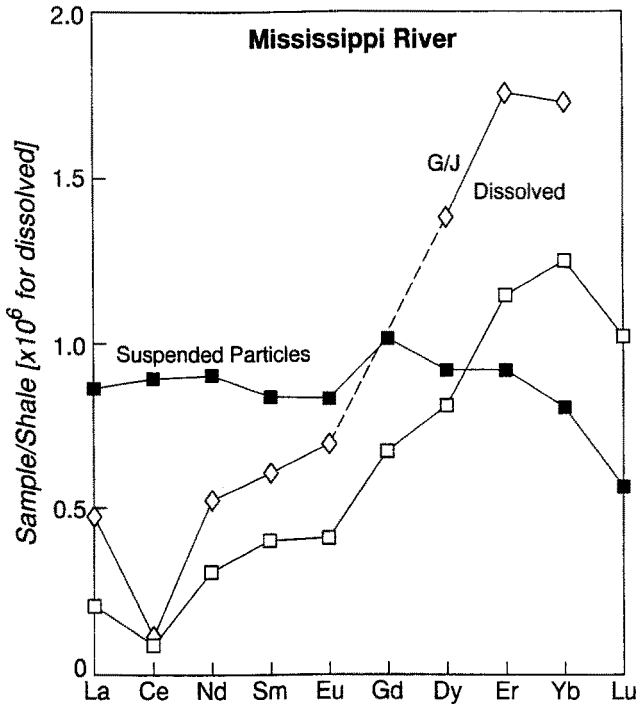


Fig. 18. Mississippi River. Shale normalized REE patterns of filtered river water and suspended particles. The author's sample is compared to river water data (G/J) reported by Goldstein and Jacobsen (1988,  $< 0.22 \mu\text{m}$ ). Note that the filtrate data are scaled by  $10^6$ . Particles were totally dissolved by fusion with lithium metaborate.

of the Amazon River's shale pattern are a lack of a Ce anomaly (value equals 1) and a large maximum in the region of the MREEs. This maximum, called here the "MREE downward concavity", is characterized by shale ratios which increase steadily and by a factor of three from La to Gd-Dy and then decrease by a factor of 1.5 to Lu. This MREE downward concavity is a reproducible feature of Amazon River water as it has been observed in two 0.30 salinity samples (Sholkovitz, 1993) and independently by Goldstein and Jacobsen (1988) and Elderfield *et al.* (1990) (Figure 19). Thus the dissolved REE(III)s of the Amazon River are highly fractionated with respect to the upper crust and to its own suspended particles. Processes responsible for the fractionation will be discussed below.

Figure 20 shows that the dissolved REE(III)s of the Mississippi and Amazon Rivers have compositions which are as evolved as North Atlantic Ocean surface seawater. Moreover, the negative Ce anomaly of the Mississippi River is comparable in magnitude to that of Atlantic surface seawater. While there are no data on the REE composition of colloids and ultrafiltrates for the Amazon and Mississippi Rivers, the removal of river colloids should lead to even more fractionated (HREE-enriched) REE compositions as illustrated in Figure 9 for the Connecticut River. As inferred from the Amazon and Mississippi River data of Stordal and Wasserburg

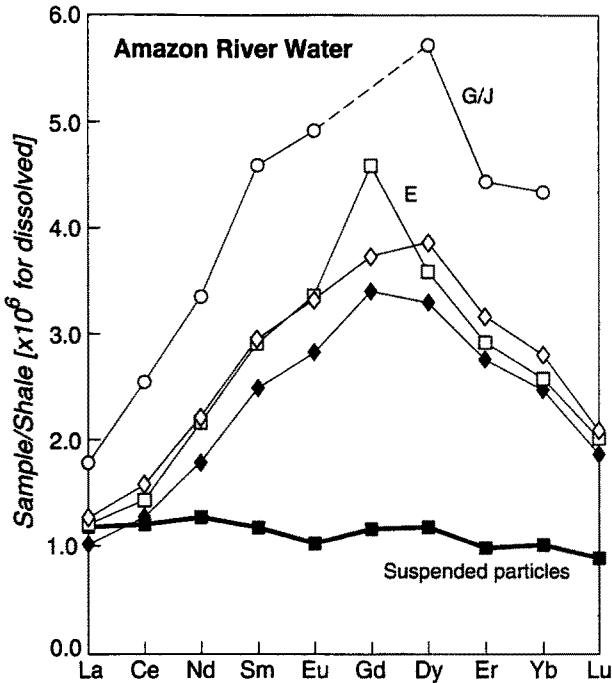


Fig. 19. Amazon River. Shale normalized REE patterns of filtered river water and suspended particles. Two dissolved ( $< 0.22 \mu\text{m}$ ) samples at 0.3 salinity from the author's laboratory are compared to river water data (G/J and E) reported by Goldstein and Jacobsen (1988,  $< 0.22 \mu\text{m}$ ) and Elderfield *et al.* (1990,  $< 0.22 \mu\text{m}$ ). Note that the filtrate data are scaled by  $10^6$ . Particles were totally dissolved by fusion with lithium metaborate.

(1986), colloids comprise a large proportion of the dissolved ( $< 0.4 \mu\text{m}$ ) Nd and Sm inventories. Their  $0.1 \mu\text{m}$  filtrates have much smaller Nd and Sm concentrations than do their  $0.4 \mu\text{m}$  filtrates. For the Mississippi River the  $0.1 \mu\text{m}/0.4 \mu\text{m}$  ratios for Nd and Sm are 0.40 and 0.39 respectively. These ratios decrease to 0.18–0.23 for the Amazon River. At minimum, 80% and 60% of the dissolved Nd and Sm in the Amazon and Mississippi Rivers respectively are colloidal.

The Mississippi River is an excellent example of a high pH (8.0), high colloid and high carbonate river. These conditions lead to low concentrations of dissolved REEs (Figure 20), strongly HREE-enriched shale normalized patterns and the largest (0.37) Ce anomaly reported for rivers (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990). As previously shown in Figure 6, Ce is anomalous in that it is the only REE not released to the dissolved phase when Mississippi River particles are leached with seawater. By contrast, Ce is released along with its neighbors La and Nd when Mississippi River particles are leached with acetic acid (Figure 7). These observations suggest that Mississippi River particles contain Ce(IV) which is insoluble in seawater but soluble in acetic acid. This feature has been reported for oceanic particles (Sholkovitz *et al.*, 1994). One explanation is that there is oxidation of dissolved Ce(III) to particulate Ce(IV) oxides in the Mississip-

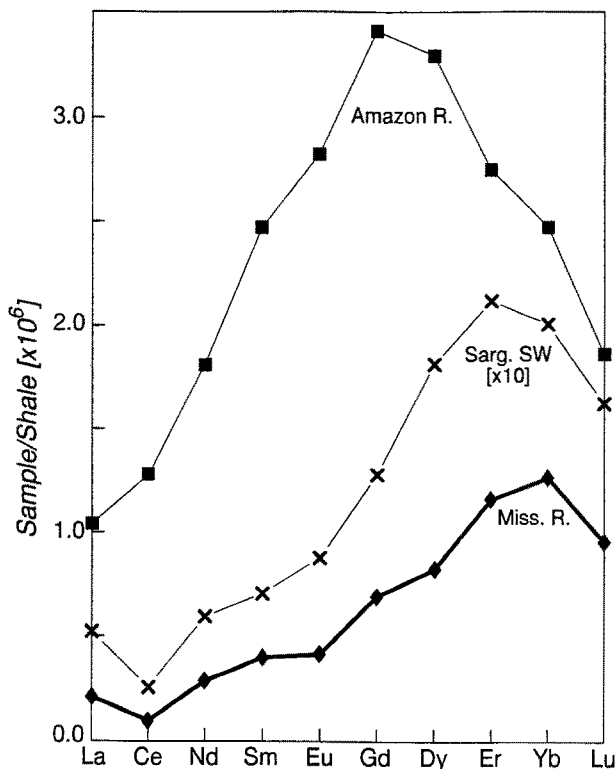


Fig. 20. The shale normalized REE compositions of 0.22 mm filtrates of the Amazon and Mississippi River waters are compared to that of Sargasso Sea surface water (<math>< 0.22 \mu\text{m}</math> filtered sample from 30 m; Sholkovitz and Schneider, 1991). The river data are those from the author's laboratory. Note that the sea water data are scaled by a factor of 10.

pi River where high pH and an abundance of surface sites promote the reaction and yield large negative Ce anomalies in the dissolved pool. The microbial oxidation of Ce(III) to Ce(IV) has been measured in seawater (Moffett, 1990) and estuarine waters (Moffett, 1994) and inferred for the Amazon River estuary (Sholkovitz, 1993). The oxidation kinetics of Ce(III) in freshwater remains unstudied.

## 5. Discussions, Implications and Conclusions

The aims of this final section are to summarize results and to show that the field, laboratory and model studies yield a coherent picture of the aquatic geochemistry of REEs. In order to integrate these studies, it is important to first briefly describe the chemical properties of REEs and model calculations of their speciation.

With the exception of multiple oxidation states for cerium, the other REEs have a trivalent oxidation state in most natural waters; Eu(II) in hydrothermal waters is a special case (Michard *et al.*, 1983). As a result of the f-electron shell being progressively filled, there is a gradual decrease in ionic radius ("lanthanide

contraction"). This leads to small but systematic changes in the chemical properties across the REE(III) series from the lightest REE (La) to the heaviest REE (Lu), the most important one being increased complexation with ligands. With respect to seawater, where REE-carbonate ion complexes are the dominant dissolved species, the most important property is the systematic increase in carbonate complexation from the light to heavy REE(III) (Cantrell and Byrne, 1987; Byrne and Kim, 1990, Lee and Byrne, 1992, 1993; Millero, 1992). Increased complexation from La to Lu leads to a decrease in the proportions of free REE(III) ions in sea water and fractionation, whereby the LREEs are preferentially adsorbed to surfaces as the HREE are preferentially retained in solution.

The chemical properties of REEs have been used to model their particle/solution interactions in seawater (Turner *et al.*, 1981; Elderfield, 1988; Kim and Byrne, 1990; De Baar *et al.*, 1991; Erel and Morgan, 1991; Lee and Byrne, 1992, 1993; Erel and Stopler, 1993; Koeppenkastrup and De Carlo, 1993). These models employed complexation constants for REE(III)-solution interactions and estimated binding constants for surface interactions. They concluded that fractionation occurs because of differences in the relative affinity of REE(III) for surface adsorption to particles and for complexation with ligands in seawater. In models of seawater this difference in relative affinities results in the adsorption to particles being ordered as follows, LREEs > MREEs > HREEs. While these models do not consider colloidal particles, a good first assumption is that the surface properties of colloids are similar to those of particles.

The majority of studies cited above have focused on seawater. Models of REEs in freshwater are much less elaborate as they only considered complexes with inorganic anions (Turner *et al.*, 1981; Goldstein and Jacobsen, 1988; Wood, 1990; Byrne *et al.*, 1991; Lee and Byrne, 1992). Unlike seawater where REE-carbonate complexes dominate, river waters contain a more complex set of inorganic and organic ligands and surfaces acting on the REEs. Building on the chemical models of ground water by Wood (1990), Byrne *et al.* (1991) and Lee and Byrne (1992) concluded that between pH 7.0 and 9.0 for freshwater, heavy REE complexes with dissolved phosphate can be more important than carbonate complexes. They showed that the competition between phosphate and carbonate complexation with REEs in freshwater is pH-sensitive and varies across the series of trivalent REEs. Models, which incorporate complexation with mixed inorganic ligands and organic matter and adsorption onto surfaces of colloids and suspended particles, are required to accurately simulate freshwater conditions. Nevertheless, these models do suggest that there should be pH-dependent REE fractionation between dissolved and surface phases in river waters as a result of solution/surface chemistry.

The following points summarize the main results and geochemical implications of this study.

1. The concentration and fractionation of REEs dissolved in river waters are highly pH dependent. Higher pH results in lower concentrations and more fractionated composition relative to the crustal abundance. With increasing pH the order

of REE adsorption onto river particle surfaces is LREEs > MREEs > HREEs. With decreasing pH REEs are released from surfaces in the same order, LREEs > MREEs > HREEs. Hence, the composition of REEs in the dissolved form (< 0.22  $\mu\text{m}$  filtrate) of river waters is mainly controlled by surface reactions. The pH controlled fractionation order of adsorption and release is consistent with chemical models of REE partitioning between solutions and surfaces. This conclusion supports earlier studies which argued that solution chemistry, not rock composition of the drainage basin, is the most important factor in establishing the REE composition of river waters (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990).

2. Within the dissolved form of river waters, Fe-organic colloids are major carriers of REEs (Table II). This explains the close and direct relationship between the concentrations of REEs and Fe in river and estuarine waters (Goldstein and Jacobsen, 1987; Elderfield *et al.*, 1990). Filtration through filters with progressively finer pore sizes results in filtrates which are more fractionated with respect to the REE composition of the upper crust. Fractionation with respect to shale, HREEs > MREEs > LREEs, is most pronounced in the < 5K and < 50K ultrafiltrates of river water. Colloidal particles have shale-like REE compositions and are highly LREE enriched relative to the REE composition of the solution phase. The order of fractionation (LREEs > MREEs > HREEs) between colloidal and solution phases is consistent with relative affinity models of REEs in natural waters. Lower pHs result in river waters with colloidal REEs which are less abundant and less fractionated with respect to the dissolved REE composition. This explains observations to that effect for river waters (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990).

3. The addition of seawater to river water causes the coagulation of colloidal REEs from the dissolved (< 0.22  $\mu\text{m}$ ) pool. Fractionation accompanies coagulation with the order of salt-induced removal being LREEs > MREEs > HREEs. This observation is compatible with the chemical models and the measurements which show that river colloids are LREE enriched. It also explains the estuarine data which indicate the order of removal to be LREEs > MREEs > HREEs (Table I). While the large scale removal of dissolved river REEs in estuaries is well established, the release of dissolved REEs off river particles is a less studied process. Laboratory experiments in this paper show, for the first time, that there is both release and fractionation of REEs when river particles are leached with seawater (Figure 6). The order of release of REE(III) (LREEs > MREEs > HREEs) from the Connecticut River particles is similar to that associated with lowering the pH and the same as that associated with colloidal particles. This is further evidence for fractionation in the dissolved form being controlled by surface/solution reactions. The balance between coagulation and release from particles will determine the net flux and fractionation during estuarine mixing. Field results indicate that coagulation and preferential removal order of LREEs > MREEs > HREEs are dominant (Table I). It is difficult to identify and quantify the release of dissolved REEs in estuaries from sediments and suspended particles as this is a more spatially-diffuse process than is coagulation in the low salinity region.

4. River waters have dissolved REE compositions which are strongly fractionated (HREE-enriched) and evolved with respect to the continental crust. River waters, stripped of their colloidal particles by coagulation in estuaries, have even more highly evolved REE composition (Figure 9). That is, REEs in solution form in river waters are strongly HREE-enriched and are fractionated to the same extent as Atlantic surface water (Figure 20). This result strengthens a major conclusion of Goldstein and Jacobsen (1988) and Elderfield *et al.* (1990) that the evolved REE composition of sea water is coupled to chemical weathering on the continents, and oceanic chemical cycles are not the solely responsible for the evolved REE composition of sea water.

5. One conclusion reached in many studies is that there is fractionation of REEs during the formation of weathering products from parent rocks (e.g., Nesbitt, 1979; Duddy, 1980; Banfield and Eggleton, 1989; Braun *et al.*, 1990, 1993). Weathered products accumulate REEs and tend to be LREE-enriched relative to the parent rock. These studies have suggested that fractionation is due, in part, to the formation of more soluble HREE-complexes which are transported away from the weathering zone and to the preferential retention of the LREE by adsorption to or incorporation into secondary minerals. Braun *et al.* (1990) showed that the surface waters are HREE-enriched relative to REE composition of syenite, the parent rock of their laterite soil. Also, the reductive dissolution of Ce(IV) to the more soluble Ce(III) and its subsequent transport and oxidation to a Ce(IV) oxide is also an active process in chemical weathering as noted by lateritic soils with positive Ce anomalies (Braun *et al.*, 1990). Obviously, weathering systems are geochemically complex and difficult to interpret with only solid phase data and without fluid composition. Modern rivers have properties which are consistent with concepts of REE fractionation during weathering, specifically solutions with HREE-enriched compositions. pH and the composition and transport properties of colloids in weathering waters will be critical parameters in the reconstruction of rock weathering.

6. The concave down shape to the shale normalized patterns of dissolved REE(III) in river water is an interesting feature, the Amazon River being a striking example (Figure 19). Many other rivers have less well developed concave down patterns (Elderfield *et al.*, 1990). Knowing its cause will enhance our understanding of REE aquatic chemistry. The absence of a MREE downward concavity is equally important in this respect. Except for the Amazon River, Goldstein and Jacobsen (1988) did not observe a concave down pattern in other major rivers. None are observed for the Connecticut and Hudson Rivers (Figures 8 and 9). Elderfield *et al.* (1990, their Figure 10) reported a well developed MREE downward concavity for the labile fraction of suspended particles and sediments from the Tamar Estuary (England). Here labile is defined as REEs released by leaching with 1.75N HCl. In this case labile refers to both surface-adsorbed REEs and REEs in acid soluble minerals such as carbonates and phosphates. The seawater and acetic acid leaches of Mississippi River particles yield MREE downward concavities (Figures 6 and 7), suggesting MREEs are more labile than both LREEs and HREEs. Yet the dis-

solved REE composition of the Mississippi River is progressively enriched relative to shale from La to Lu (Figure 18). No MREE downward concavities appear when Connecticut River particles are leached with seawater or when desorbing REEs off suspended particles by lowering the pH of Connecticut and Hudson Rivers.

Two broad types of processes are possible. Concave down distributions may reflect the reactions of river water with mineral components of suspended particles and/or fractionation between surfaces and solutions. Elderfield *et al.* (1990) suggested the binding of REE(III)s to surfaces increases in a non-linear fashion from Lu to La resulting in a strongly depleted LREE sector. This process does not explain the Amazon-type pattern where large depletion exist at both the LREE and HREE ends.

The fractionation of REEs in rivers may be related to phosphorus geochemistry. Studies of P in rivers by Fox *et al.* (1986) and Fox (1989, 1990, 1991) conclude that "... phosphate concentrations in major rivers are controlled through equilibration with a solid-solution amorphous ferric phosphate in amorphous ferric hydroxide." (from Fox, 1989, p. 417). There is a strong dissolved Fe-REE relationship in river waters (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990). Moreover, large scale desorption of dissolved phosphate from river particles and suspended sediments has been reported for many estuaries including the Amazon (Chase and Sayles, 1980; Edmond *et al.*, 1981; Fox *et al.*, 1986; Froelich, 1988). The MREE downward concavity reported here for desorption experiments with seawater (Figure 6) and acetic acid (Figure 7) and for Amazon River water (Figure 19) may be related to P speciation and reactivity. As noted earlier, the speciation models of Byrne *et al.* (1991) and Lee and Byrne (1992) show there is a shift from carbonate to phosphate complexation in freshwater. This shift in speciation varies across the series of REEs and depends on pH and the relative concentrations of both anions. Fractionation leading to a MREE concavity in freshwater may reflect this shift and should vary between rivers with different compositions and pH. For example, the Amazon and Mississippi Rivers (near the heads of their estuaries) differ in pH (7.0 vs. 8.0), phosphate concentration (0.6 to 1.0 mM vs. 1–3 mM) and alkalinity (300 mM vs. 1300–2000 mM) (Stallard and Edmond, 1983; Fox *et al.*, 1986; Plunkett *et al.*, 1992). Deciphering the actual processes behind the fractionation of REEs in freshwater awaits more complex speciation models and laboratory experiments.

If solution/surface chemistry is ruled out, then a solution/mineral reaction is an alternative explanation. Phosphatic minerals stand out as having large MREE downward concavities when normalized against shale (e.g., Elderfield *et al.*, 1981; Wright *et al.*, 1987; Grandjean *et al.*, 1993; Grandjean-Lecuyer *et al.*, 1993). The diagenetic accumulation of REEs into fish teeth and other biogenic apatites leads to high concentrations and very fractionated patterns. These same features have been reported for secondary carbonate minerals and ground waters from a brine aquifer (Gosselin *et al.*, 1992). The preferential incorporation of LREE and MREEs into minerals is attributed to the substitution of  $\text{Ca}^{2+}$  by similar sized REEs. This explanation is not totally satisfactory as a size-controlled process should favor

the LREE (La, Ce and Nd). Biogenic apatite, on the other hand, show concave down shale patterns centered around Sm to Dy. This complexity persists when one considers that a large number of phosphatic minerals do not exhibit MREE concavities (e.g., McArthur and Walsh, 1984/1985).

7. The seawater-induced release of dissolved REEs from river suspended particles is potentially a large source of Nd to the oceans. The solubilization of less than 1% of Nd off river particles would exceed the effective river flux of dissolved Nd to the oceans (Goldstein and Jacobsen, 1987, 1988). They calculate a long (7100 yr) ocean residence-time for Nd based on the effective river flux to the oceans (total dissolved flux minus removal in estuaries). To reconcile a long residence-time with the inter-ocean variations in the isotopic composition of Nd, they argued that there must be a missing source of Nd to the oceans. They eliminated atmospheric dust and hydrothermal input as significant sources. The release of dissolved Nd from river particles (Figure 6) and from shelf sediments (Sholkovitz, 1993), in principle, would shorten the residence-time and maintain the inter-ocean isotopic variations. Quantifying these release fluxes remains a challenge.

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