

AN ABSTRACT OF THE THESIS OF

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DTPA Complexes as Estuarine Hydrological Tracers II. Rare Earth
Elemental Concentrations in some Pacific Northwest Rivers.

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Two studies were conducted involving rare earth elements. In the first study, the use of rare earth diethylenetriaminepentaacetic acid (DTPA) complexes as stable actiabile tracers, a method of stable-isotope tracing with post-sampling neutron activation analysis, was explored. The persistence of rare earth DTPA complexes in estuarine waters was measured in simulated laboratory studies and in two field studies conducted in the South Shore Marina in Newport, Oregon. The ability to use more than one rare earth DTPA tracer simultaneously in a multitracing experiment was also tested in one field experiment.

In the second study, theoretical calculations, laboratory experiments, and field experiments were used to study the solubility of the rare earth elements in river water. The field experiments consisted of measuring the soluble rare earth elemental concentrations for seven Pacific Northwest rivers (Columbia, Fraser, Klamath, Mary's, Rogue, Sacramento, and Willamette) using radiochemical neutron activation

analyses. The laboratory experiments consisted of measuring the soluble rare earth elemental concentrations in a mixture (sediments and water) from the Columbia or Willamette River as the pH was changed from 6 to 8. Also, the absorption of Tm on Willamette River sediments was studied. The theoretical calculations of the solubility of the lanthanum and europium in river water were based upon the solubility of the rare earth phosphate and the speciation of the rare earth elements in rivers. Results of these calculations, using measured field data, were compared to the measured lanthanum and europium concentrations in the river Aare. The results of these studies are consistent with the interpretation that the soluble rare earth elemental concentrations in river water are controlled by the solubility of the rare earth phosphate and the speciation of the rare earth elements with most of the soluble rare earth elements associated with humic substances.

Two Studies Concerning Rare Earth Elements I. Rare Earth DTPA
Complexes as Estuarine Hydrological Tracers II. Rare Earth
Elemental Concentrations in some Pacific Northwest Rivers.

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Two Studies Concerning Rare Earth Elements I. Rare Earth DTPA
Complexes as Estuarine Hydrological Tracer II. Rare Earth Ele-
mental Concentrations In Some Pacific Northwest Rivers

Rare Earth DTPA Complexes As Estuarine Hydrological Tracers

I. Introduction

The pollution of estuaries is of increasing concern to those involved in public health, water pollution control, and water conservation. Most major estuaries in the United States are located near metropolitan areas and receive waste discharges from municipalities, industries, and individuals. Activities of man that alter the hydrologic regimen, such as reduction or regulation of fresh water outflow and extensive paving and storm water collection systems, also influence estuarine water quality.

The development of an optimum water pollution control plan for an estuary must be based on hydraulic, sanitary engineering, and engineering economic factors as well as aesthetic value judgments. Quantitative or semi-quantitative values often are obtained for the first three parameters while the last parameter is a social decision that is best arrived at by the political process.

The amount of dilution in an estuary must be estimated to assess the polluting effects of waste discharges. For existing

estuarine hydrological conditions and waste discharge, the diluting effect of estuarine waters can be estimated by analyzing the estuarine water using a desirable detection characteristic of the waste and comparing this estuarine concentration to the initial waste concentration. Tracers detectable at much lower concentrations than the waste can be added to the discharge if a lower detection limit is needed. Dilution estimates for existing or potential hydrological conditions can be made with numerical or physical models, although verification of model accuracy may require field tracer studies. It may be necessary to use tracers to estimate waste dilutions in several million acre feet of estuarine water and, in such large bodies, tracer costs and quantities become significant.

This research was concerned with the development of stable activable tracers for the estuarine environment. A stable, activable tracer is defined as an element whose concentration is measured by neutron activation analysis, and whose chemical/physical form is such that all the basic criteria for a tracer are satisfied. For a hydrological tracer (a tracer which mimics the flow and dispersion of water), the basic criteria for an "ideal" hydrological tracer are:

1. The tracer should possess a low limit of detection (the smallest concentration or mass which can be detected with a specified degree of confidence) by the particular mode of analysis.^{1,2}
2. The tracer should possess a high sensitivity (the change

in output per change in input) by the particular model of analysis.^{1,2}

3. The tracer should be reasonable in cost in terms of both analysis time and materials.

4. The tracer should have a low natural concentration in the water mass into which it will be introduced.

5. The tracer should not be hazardous at the concentrations or total amount necessary for its use.

6. The tracer should remain in solution, resisting precipitation, adsorption, absorption, etc.

Numerous types of tracers are available and employed in various hydrologic studies, but generally the "classical" tracers fall into three main categories 1) chemical tracers, for example, NaCl, KHSO₄, K₂CO₃, etc., 2) radioactive tracers, for example, ⁸⁶Rb, ³H, ³²P, ¹³¹I, ⁸²Br, etc., 3) dyes, for example, fluorescein, rhodamine B, rhodamine WT, etc.

Chemical tracers^{3,4} have been used successfully on several occasions but usually such tracers have to be added in high concentrations in order to remain detectable after subsequent dilution. When tracers of such high concentrations are used, the density of the tagged materials will exceed that of the natural water and they are no longer hydrologically equivalent.

Radioactive nuclides^{3,4,5,6,7,8,9} have been commonly used as tracers in studying various hydrologic phenomena. Unfortunately, there are situations where the use of radioisotopes is inadvisable

because of safety or public health considerations. The use of long-lived radio-nuclides is usually avoided because their long residence time could cause a long term health hazard. If short-lived nuclides are used, then a rigid time table must be followed. The use of radioactive tracers in many environments is becoming politically infeasible. Typical lead times to do radioactive experiments in open rivers, lakes, estuaries, etc. are fast becoming a year or more due to regulatory problems.

Numerous fluorescent dyes,^{10,11,12} such as rhodamine WT, rhodamine B, fluorescein, etc., are frequently encountered in water resources research. However, there are several factors which affect their usefulness. Some of these factors are temperature, pH, salinity, suspended sediment, background fluorescence, photochemical decay, chemical decay, and biodegradation. Also, when one uses fluorescent dyes one will have an aesthetical problem in that the dye will color the tagged water which will cause some type of public outcry. In this researcher's work with rhodamine WT and B, some of the comments heard when receiving permission to do the field experiment in the South Shore Marina were: "the dye will color the boats red," "the dye will color the piers red," and "the dye will color the fish red" and when the field experiment was in progress, some of the remarks that were heard were "red tide is in" and "someone has killed a whale." In general, the aforementioned comments are a fairly typical community reaction to a large fluorescent tracer experiment.

In brief, the aforementioned classical tracers all have some problems connected with their use and because of these problems and a real need for a good hydrological tracer, a different type of hydrological tracer, a stable activable tracer, was studied. Along with the criteria for a good hydrological tracer, the stable activable tracer nuclide should possess the following nuclear properties:

1. A high thermal neutron capture cross section for the nuclide used.
2. The radioactive nuclide produced by the (n, γ) reaction involving the tracer nucleus should have a suitable half-life (i.e., the half-life should be long enough so that the activity of the radioactive nuclide can be measured).
3. The activation product should emit an easily measurable gamma ray.

Stable activable tracers have been used for a variety of tracer work. Gatz et al.¹³ used indium as a particulate atmospheric tracer in Oklahoma. Shum¹⁴ used dysprosium, samarium, lanthanum, and cerium as tracers to monitor stack effluents of a paper manufacturing company, a metallurgical processing company, and a plywood company in Oregon, while Slinn et al.¹⁵ used dysprosium and indium as tracers to study the wet and dry deposition rate of aerosol particles near Eugene, Oregon.

Channell¹⁶ used stable activable tracers (lanthanum,

and europium) as hydrological tracers in his study of pollutant dispersion in San Francisco Bay. He demonstrated the general feasibility of this technique. Channell did not attempt to measure the stability of the europium and lanthanum tracers in the San Francisco Bay field study. However, in his laboratory study, europium was removed from solution at an alarming rate with approximately 50% of the europium being removed in one hour by the sediments from a "seawater" solution. Considering that in a study by Martin et al.¹⁷ about 50% of the soluble lanthanum from the Dordogne and Garonne Rivers was removed from the estuarine waters of the Gironde estuary, Channell's results are not surprising. Channell and Kruger^{18,19,20} proposed that the tracer should be injected at a very low pH to keep the tagged waters below pH 4 thus keeping adsorption losses very low. However, keeping the pH below 4 is not a realistic idea for both ecological and hydrological reasons. A low pH is harmful to many types of organisms and thus the tracer will be harmful to the environment. When the pH is far below the natural pH of the environment, the tracer will no longer be hydrologically equivalent.

Hanson²¹ did a laboratory study on the stability of indium, scandium, europium, terbium, cesium, cobalt, antimony, and chromium, both complexed and uncomplexed with EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid). He concluded that the uncomplexed elements were relatively unstable and that the complexed elements were stable with the

DTPA complexed elements more stable than the EDTA complexed elements. In a field test, Hanson, through a series of experiments in a small stream (0.5 mile) in Washington, showed that EuDTPA, TbDTPA and InDTPA were all more stable in the stream than Rhodamine B.

Various other uses of stable activable tracers are seen in the literature^{22,23,24,25,26,27,28} with Chick's²⁶ study on the use of stable activable tracers for freshwater tracing being of singular importance. In his study, Chick showed that InDTPA and DyDTPA are stable in a freshwater system (i.e. rivers and lakes).

After the research described in this thesis was completed, a laboratory study on the stability of activable tracers in seawater and freshwater was published. The data described in this study by Drabaek will be discussed in Section III along with my results.

II. Theoretical Considerations

In reviewing the possible elements that would make good stable activable tracers, attention was restricted to the rare earth elements. The reasons for this limitation were that most of the rare earth elements meet the criteria of low natural concentrations in the environment, have low detection limits, and high sensitivities for detection by neutron activation analysis. Since these elements also have very similar chemical behavior, one can devise a single procedure for the analysis of all the rare earth elements. This will give one the potential of having thirteen different elements to be used as stable activable tracers for a given procedure.

In picking the best element(s) for the stable activable tracer one must consider the cost to achieve a certain detection sensitivity (sample radioactivity). One can examine the properties of the various rare earth elements to see which elements produce the greatest amount of activity per dollar of tracer cost (Table I). One concludes that europium and dysprosium are the best candidates on a cost per activity basis. Furthermore, all rare earth elements have very low natural concentrations in the environment (Table II).

Another important aspect to picking a good hydrological tracer is to determine its stability in the environment. Whether the tracer remains in solution and is considered a conservative

Table I. Properties of Some Rare Earth Activation Products

Element	Cost (\$/kg) ^a	Activation Product ^b	$t_{1/2}^b$	$E_\gamma(\text{kev})$	cps/g ^c	cost (\$)/cps
La	23	La-140	40.22 h	487	3.7×10^6	6.0×10^{-9}
Ce	23	Ce-143	33 h	293	7.8×10^4	3.01×10^{-7}
Pr	129	Pr-142	19.2 h	1575	1.5×10^5	8.67×10^{-7}
Nd	70	Nd-148	1.8 h	114	2.3×10^7	3.00×10^{-9}
Sm	128	Sm-153	46.8 h	103	5.5×10^7	2.33×10^{-9}
Eu	2,200	Eu-152	9.3 h	122	1.5×10^{10}	1.40×10^{-10}
Gd	127	Gd-159	18.0 h	363	1.7×10^5	7.26×10^{-8}
Tb	1,209	Tb-160	72.1 h	299	4.2×10^5	2.89×10^{-6}
Dy	115	Dy-165	139.2 h	95	2.6×10^8	4.37×10^{-10}
Ho	659	Ho-166	26.9 h	81	1.9×10^7	3.55×10^{-8}
Er	183	Er-171	7.52 h	112	4.8×10^6	3.82×10^{-8}
Tm	3,426	Tm-170	134 h	84	2.0×10^5	1.75×10^{-2}
Yb	228	Yb-169	318 h	198	5.3×10^6	4.28×10^{-8}
Lu	5,458	Lu-176	3.69 h	88	4.1×10^7	1.32×10^{-8}

a. Research Chemicals, Nucor Corp., Phoenix, Arizona, Jan. 1980

b. C.M. Lederer, J.M. Hollander, I. Perlman, Table of Isotopes, 6th Edition (Wiley, N.Y., 1967)

c. Assume 20 min. irradiation at a flux of 4×10^{12} neutrons/cm²/sec. Delay of 160 min. with the sample being counted one cm away from a 40 cm³ Ge(Li) detector.

TABLE II: Rare Earth Elemental Concentrations in Natural Waters

Element	River Water ¹⁷		Seawater ^{29,30}	
	Dissolved Material (ng/ℓ)	Suspended Solids(ppm)	Dissolved Material (ng/ℓ)	Suspended Solids(ppm)
La	47.5	44	3.4	15
Ce	79.0	93	1.2	35
Pr	7.3	8.2	0.64	-
Nd	37.9	35.8	2.8	-
Sm	7.8	6.2	0.45	1.5
Eu	1.48	1.08	0.13	0.6
Gd	8.5	6.1	0.70	-
Tb	1.24	0.90	0.14	-
Dy	-	-	0.91	-
Ho	1.44	0.90	0.22	-
Er	4.2	2.4	0.87	-
Tm	0.61	0.44	0.17	-
Yb	3.64	2.8	0.82	-
Lu	0.64	0.42	0.15	0.5

tracer will ultimately decide its suitability as a hydrological tracer. The usual causes for non-conservative behavior are that the element has been either precipitated out of solution, and/or has been sorbed by the suspended particles (sediments). In looking at the general adsorption problem, the following trends can be noted:³¹

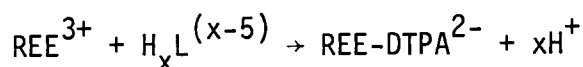
1. The amount of adsorption increases as the grain size of the adsorbant decreases, and, hence, its surface area increases.
2. Adsorption is favored if the adsorbate forms a compound of low solubility with the adsorbant (an example is the adsorption of phosphate ions by ferric hydroxide).
3. The amount of adsorption increases as the charge of the ion increases.

In the case of the rare earth elements, the hydroxide solubility products are very small (Appendix A). This will cause precipitation to occur when the elements are at a concentration of mg/l. According to the statement (2) above, having a low solubility product should cause the rare earth elements to be readily adsorbed by the sediments. From the statement (3) above, it can be seen that the rare earth elements are again predicted to be readily adsorbed since they usually have a +3 charge while the sediments have a negative charge.^{32,33,34,35}

One way to reduce the adsorption problem is to increase the solubility of the rare earth elements and at the same time reduce the +3 charge of the rare earth ion. This can be done by complex-

ing the rare earth elements with an organic ligand which generally will cause the solubility of the rare earth elements to increase and the charge of the ion to decrease.^{36,37,38,39}

Therefore, to overcome possible problems of rare earth adsorption, the rare earth elements were complexed with a strong complexing agent (DTPA). DTPA reacts with the rare earth elements in the following manner to form an anionic complex.



where,

REE = rare earth element

L = DTPA

As discussed previously, anionic tracers are generally more conservative than neutral or cationic tracers.

The stability constants (Table III) are derived from the following equation,

$$K = \frac{[\text{MY}^{x-5}]}{[\text{M}^{x+}][\text{Y}^{5-}]}$$

where M is the metal ion and Y is DTPA. Since in aqueous solution DTPA dissociates as an acid to give five ionic species, the composition of a solution of the compound is thus dependent upon pH. A convenient way of showing this relationship is by means of plots of α -values for the various species as a function of pH where,

$$\alpha_n = \frac{[\text{H}_{(5-n)}\text{Y}^{n-}]}{C_T}$$

Table III: Stability Constants for Various Metals with EDTA,
DTPA, CDTA, and NTA^{40,41}

Metal	EDTA $\log K_s$	DTPA $\log K_s$	CDTA $\log K_s$	NTA $\log K_s$
Ba (II)	7.8	8.6	8.6	6.41
Sr (II)	8.6	9.7	10.0	---
Mg (II)	8.7	9.0	10.3	7.00
Ca (II)	10.7	10.7	12.08	8.17
Sc (III)	23.1	--	---	---
Ti (III)	21.3	--	---	---
V (II)	12.7	15.1	---	---
V (III)	25.9	--	19.40	---
Cr (III)	24.0	--	---	---
Mn (II)	14.0	15.1	16.78	7.44
Fe (II)	14.3	16.5	---	8.84
Fe (III)	25.1	28.6	---	15.87
Co (II)	16.3	18.4	18.92	10.6
Co (III)	~ 36	--	---	---
Ni (II)	18.6	19.6	19.4	11.26
Cu (II)	18.8	21.1	21.30	12.68
Zn (II)	16.5	18.3	18.67	10.45
Cd (II)	16.5	18.9	19.23	---
Hg (II)	21.8	26.7	24.4	---
Al (III)	16.1	--	17.6	---
Ga (III)	20.3	--	22.91	---
In (III)	25.0	--	---	---
Sn (II)	13.5	--	---	---
Pb (II)	18.0	18.8	19.68	11.80
Y (III)	18.0	22.4	19.15	11.48
La (III)	15.5	19.9	16.26	10.36
Ce (III)	15.9	20.4	16.76	10.43
Pr (III)	16.4	21.8	17.31	10.30
Nd (III)	16.6	22.2	17.68	10.49
Sm (III)	17.1	22.8	18.38	11.13
Eu (III)	17.3	22.9	18.62	10.79
Gd (III)	17.3	23.0	18.77	11.17
Tb (III)	17.9	23.2	19.50	11.31
Dy (III)	18.3	23.4	19.69	11.74
Er (III)	18.8	23.1	20.68	11.90
Tm (III)	19.3	22.9	---	11.79
Yb (III)	19.5	23.0	21.12	11.98
Lu (III)	19.8	22.4	---	12.10

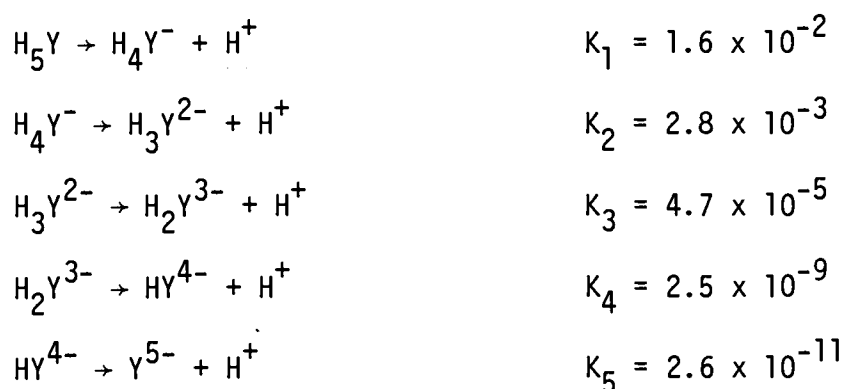
and

$$C_T = [H_5Y] + [H_4Y^-] + [H_3Y^{2-}] + [H_2Y^{3-}] + [HY^{4-}] + [Y^{5-}]$$

The α -value equation can be rearranged to the following equations;

$$\begin{aligned}\alpha_0 &= \frac{[H^+]^5}{[H^+]^5 + K_1[H^+]^4 + K_1K_2[H^+]^3 + K_1K_2K_3[H^+]^2 + K_1K_2K_3K_4[H^+] + K_1K_2K_3K_4K_5} \\ \alpha_1 &= \frac{K_1[H^+]^4}{[H^+]^5 + K_1[H^+]^4 + K_1K_2[H^+]^3 + K_1K_2K_3[H^+]^2 + K_1K_2K_3K_4[H^+] + K_1K_2K_3K_4K_5} \\ &\vdots \\ \alpha_5 &= \frac{K_1K_2K_3K_4K_5}{[H^+]^5 + K_1[H^+]^4 + K_1K_2[H^+]^3 + K_1K_2K_3[H^+]^2 + K_1K_2K_3K_4[H^+] + K_1K_2K_3K_4K_5}\end{aligned}$$

Where the acid-dissociation constants of DTPA are defined by the following equations;⁴⁰



A graph of the α -values vs pH can be seen in Figure I. One can see from this information that the rare earth-DTPA complex is very strong. In fact even at very low concentrations, 1 ng/l, the rare earth elements will be completely complexed (less than 0.04%

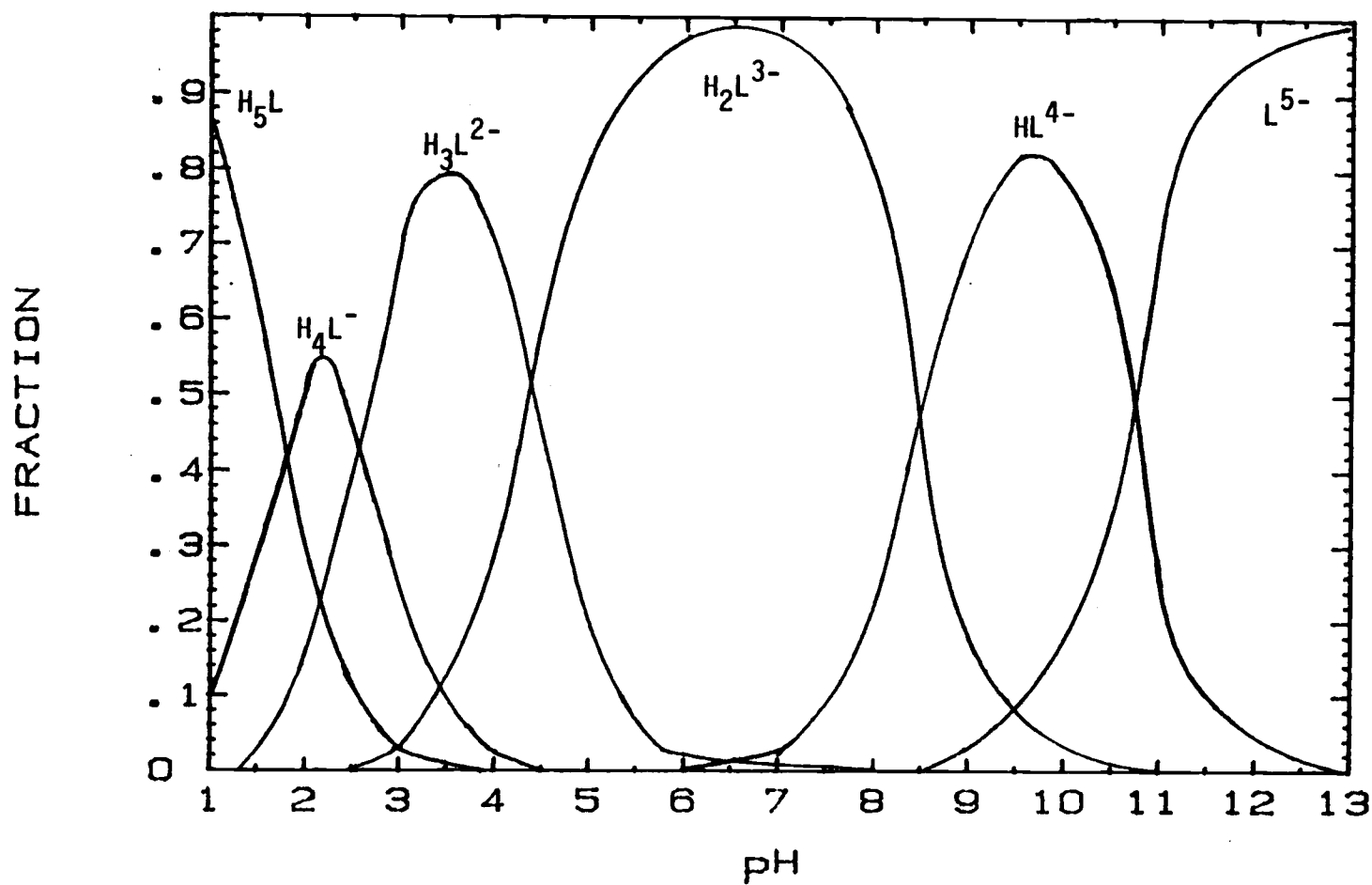
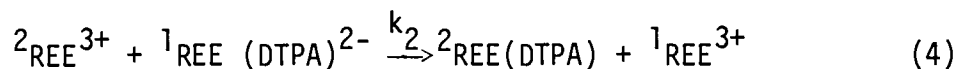
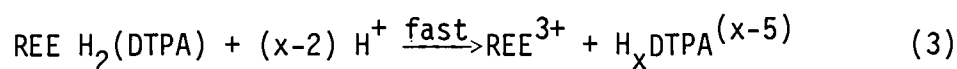
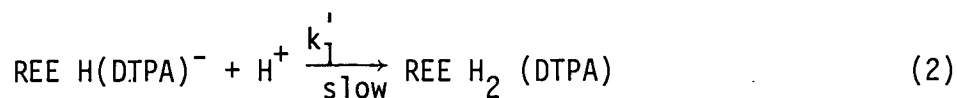


Figure I: Distribution of the DTPA species as a function of pH.

of the rare earth elements being uncomplexed) in estuarine waters.

Along with being a very strong complex, the rare earth-DTPA complex does not break-up very rapidly. In fact, from the following mechanism for the break-up of the rare earth-DTPA complex,^{42, 43,44,45} one can estimate the rate of removal for a rare earth-DTPA tracer from estuarine waters.



where

^1REE = a rare earth element

^2REE = a second rare earth element

From this mechanism, one can conclude that the rate of dissociation for a rare earth-DTPA complex can be defined by the following equation;

$$\text{Rate} = k_1[^1\text{REE}(\text{DTPA})^{2-}][\text{H}^+]^2 + k_2[^2\text{REE}^{3+}][^1\text{REE}(\text{DTPA})^{2-}] \quad (5)$$

where,

$$k_1 = k_1'K''$$

Equation 5 can be rearranged to equation 6 which gives one the rate of the rare earth-DTPA break-up in terms of the fraction

of the total rare earth-DTPA concentration in solution.

$$\frac{\text{Rate}}{[\text{REE}(\text{DTPA})^{2-}]} = k_1[\text{H}^+]^2 + k_2[\text{REE}^{3+}] \quad (6)$$

In seawater, the break-up of the Ce-DTPA complex can be estimated since the concentration of both Pr, $4.5 \times 10^{-12}\text{M}$, and Ce, $8.6 \times 10^{-12}\text{M}$, are known. If one assumes that the value for k_2 at 20°C is $1.3 \text{ l mol}^{-1} \text{ min}^{-1}$ for Pr and $0.31 \text{ l mol}^{-1} \text{ min}^{-1}$ for Ce (See Table IV), then the fraction of the break-up of the Ce-DTPA complex due to Ce and Pr ions in seawater is approximately $3.8 \times 10^{-9} \text{ day}^{-1}$ and $8.4 \times 10^{-9} \text{ day}^{-1}$ respectively. If one assumes that the break-up of a rare-earth-DTPA complex due to rare earth ions in seawater is approximately the same for any given combinations of rare earth elements, then the fraction of the break-up of a rare earth-DTPA complex due to all the rare earth ions in seawater would be approximately equal to $1 \times 10^{-7} \text{ day}^{-1}$. For river water, the rare earth elemental concentrations are much more variable than in seawater. However, the highest rare earth elemental concentrations that one would expect to see in river water would be approximately 100-500 times the rare earth elemental concentration in seawater, with the average rare earth elemental concentration in river water approximately 15-20 times the rare earth elemental concentration in seawater. This would mean that the fraction of the break-up of a rare earth-DTPA complex in river water due to rare earth ions in river water should

TABLE IV: Rate Constants for the Break-up of a Rare Earth-DTPA
Complex^{42,43,44,45}

<u>Rare Earth Element#1</u>	<u>Rare Earth Element#2</u>	<u>Temper- ature(°C)</u>	<u>k₁ (10⁸ l²mol⁻²min⁻¹)</u>	<u>k₂ (l²mol⁻¹min⁻¹)</u>
Ce	Ce	0	0.82	
		15	2.22	1.07
		20	6.20	1.13
		25	3.68	2.13
		35	7.44	4.18
		45	12.8	9.42
Pr	Ce	20	1.67	0.31
Nd	Nd	25	1.1	0.35
Y	Y	25	0.105	0.24

never be greater than $5 \times 10^{-5} \text{ day}^{-1}$. Of course there are many other elements in both seawater and river water which would cause a break-up of a rare earth-DTPA complex by a reaction similar to equation 4. One can crudely estimate the fraction of break-up of a rare earth-DTPA complex due to a non-rare earth ion by comparing the various elemental-DTPA stability constants to the DTPA stability constants and k_2 values for Ce and Pr and by knowing the elemental free ion concentration in both river and seawater. Doing this, one estimates that the fraction of break-up of a rare earth-DTPA complex due to all of the elemental free ions (based upon a reaction similar to equation 4) should be less than $1 \times 10^{-3} \text{ day}^{-1}$. This would mean that the fraction of break-up of a rare earth-DTPA complex, $F_{\text{REE-DTPA}}$, can be estimated from the following equation;

$$F_{\text{REE-DTPA}} = k_1 [\text{H}^+]^2 + 1 \times 10^{-3} \text{ day}^{-1} \quad (7)$$

If one assumes that the break-up of the rare earth-DTPA complex is the rate determining step in the removal of the rare earth-DTPA tracer from estuarine waters, then Figure II would show the estimated rate of removal of the rare earth-DTPA tracer in estuarine water as a function of pH. However, for the following reasons, equation 7 does not accurately calculate the stability of a rare earth-DTPA tracer. First, there is always the probability that once the rare earth-DTPA complex is broken that the rare earth ion and the DTPA ion would recombine. Since this

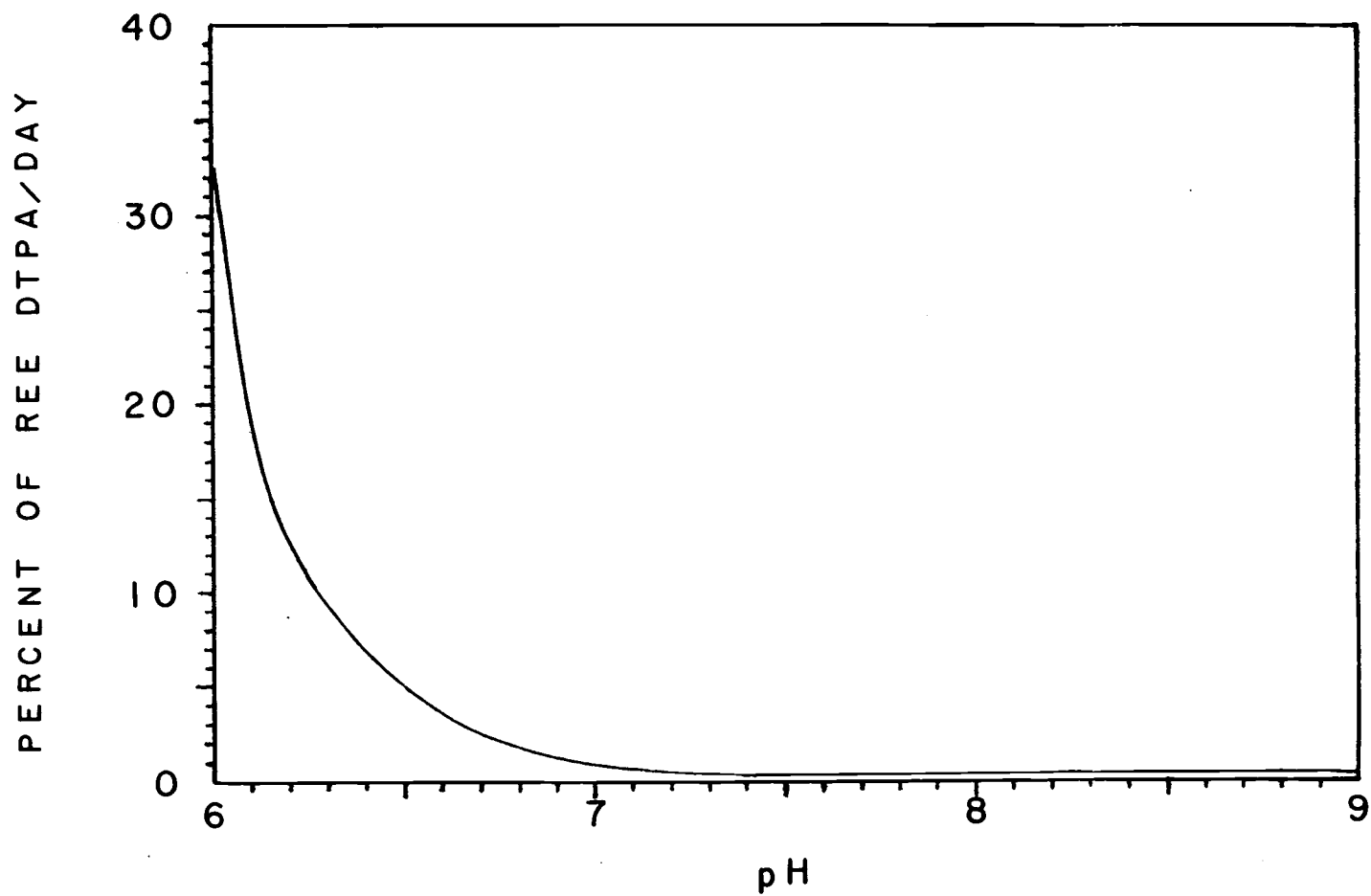


Figure II: Rate of break-up of a rare earth-DTPA complex in estuarine water.

reaction does occur, this would mean that equation 7 would predict a slightly higher rate of break-up than one would expect to see in estuarine waters. Second, the assumption that the rate of break-up of the rare earth-DTPA complex is the rate determining step is not entirely correct for the low pH values. Channell¹⁶ experimentally proved in his thesis that an uncomplexed rare earth element will remain in solution when the estuarine water is kept below a pH value of 4.0. Since the removal of the uncomplexed rare earth element is much slower at low pH values, the stability of the rare earth-DTPA should not mimic the sharp increase in the rate of break-up of a rare earth-DTPA complex seen in Figure II. Finally, the assumption that equations 1-4 show the only mechanisms for the break-up of the rare earth-DTPA complex is not correct. At high pH values, the rare earth element will react with the hydroxide ions to form a rare earth hydroxide precipitate. However, this reaction is not prominent until the pH of the estuarine water is greater than 9.0. Since the pH value of most estuaries falls between 7.0 - 8.2, one would predict from the previous arguments that a rare earth-DTPA complex would be stable with a predicted rate of removal (from Figure II) of less than 0.5% per day.

The economical viability of the stable activable tracer technique can be compared to the other types of tracer in Table V, and in the following examples. If one wants to perform a tracer experiment in the South Beach Marina (2.3×10^2 acre-feet) with

Table V: Relative Cost of Hydrological Tracers

Fluorescent Dye Tracer

Rhodamine B Tracer Concentration	5 ug/l
Cost of Tagging	\$431.72/10 ³ acre-ft
Cost of Analysis	\$1.00/sample

Radioactive Tracer

Tritium Tracer Concentration	1.6 nCi/l
Cost of Tagging	\$108.55/10 ³ acre-ft
Cost of Analysis	\$75.00/sample

Stable Activable Tracer

Eu-DTPA Tracer Concentration	400 ng of Eu/l
Cost of Tagging	\$117.00/10 ³ acre-ft
Dy-DTPA Tracer Concentration	400 ng of Dy/l
Cost of Tagging	\$135.70/10 ³ acre-ft
La-DTPA Tracer Concentration	1.00 ug/l
Cost of Tagging	\$258.71/10 ³ acre-ft
Cost of Analysis	
first element	\$30.00/sample
each additional element	\$5.00/sample

approximately 100 samples, it would cost (to tag the waters and to analyze the samples) approximately \$200 using a rhodamine dye, \$775 using tritium, and \$327 using a stable activable tracer. However, if one wants to perform a tracer experiment in Yaquina Bay ($\sim 2 \times 10^4$ acre-feet) with approximately 200 samples, it would cost (to tag the water and to analyze the samples) \$10,100 using a rhodamine dye, \$17,500 using tritium, and only \$8,700 using a stable activable tracer. Also, if one wanted to do the tracer experiment utilizing two source locations, one could perform both tracing experiments at the same time using the stable activable tracers with the additional cost only being \$4,100. Obviously, the larger the size of the system being studied and the more sites to be studied, the more economically viable the stable activable tracer technique becomes.

The final theoretical consideration that will be reviewed is the tracer toxicity. Even if the tracer meets all the criteria for a good tracer, but if it is harmful to the environment, the tracer will never be used. The rare earth elements are considered as having a low acute toxicity rating (Table VI). Rhodamine B (a commonly used tracer) has a toxicity approximately ten times higher than the rare earth elements. The major toxicity problem of the stable activable tracers comes from the complexing agent DTPA. Its⁴ aquatic toxicity, TLm 96 (the concentration that will kill 50% of the exposed organisms within 96 hours), is between 100-1000 ppm of DTPA. However, DTPA toxicity effects are reduced

Table VI: Oral Toxicity of Rare Earth Elements and Some
Other Tracer Related Compounds⁴⁶

<u>Compound</u>	<u>Subject</u>	<u>Toxicity</u>	<u>Dose</u>
LaCl_3	rat	LD50	4200 mg/kg
$\text{La}(\text{NO}_3)_3$	rat	LD50	4200 mg/kg
CeCl_3	rat	LD50	2111 mg/kg
CeCl_3	mouse	LD50	5277 mg/kg
$\text{Ce}(\text{NO}_3)_3$	rat	LD50	4200 mg/kg
PrCl_3	mouse	LD50	4500 mg/kg
$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	rat	LD50	3500 mg/kg
NdCl_3	mouse	LD50	3693 mg/kg
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	rat	LD50	2750 mg/kg
$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	rat	LD50	2900 mg/kg
EuCl_3	mouse	LD50	5000 mg/kg
$\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	rat	LD50	5002 mg/kg
$\text{Gd}(\text{NO}_3)_3$	rat	LD50	3805 mg/kg
TbCl_3	mouse	LD50	3631 mg/kg
$\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$	mouse	LD50	5100 mg/kg
DyCl_3	mouse	LD50	5443 mg/kg
$\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	rat	LD50	3100 mg/kg
HoCl_3	mouse	LD50	5165 mg/kg
$\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	rat	LD50	3000 mg/kg
ErCl_3	mouse	LD50	4417 mg/kg
TmCl_3	mouse	LD50	4294 mg/kg

Table VI: (Cont)

<u>Compound</u>	<u>Subject</u>	<u>Toxicity</u>	<u>Dose</u>
LuCl_3	mouse	LD50	7074 mg/kg
$\text{In}(\text{SO}_4)_3$	rat	LDL0	1200 mg/kg
$\text{In}(\text{SO}_4)_3$	rabbit	LDL0	1300 mg/kg
DTPA(Na)	fish	TLm96	100-1000 ppm
Rhodamine B	rat	LD50	500 mg/kg

LDL0 - Lethal Dose Low- the lowest dose of a substance introduced over any given period of time in one or more divided portions and reported to have caused death in animals.

LD50 - Lethal Dose Fifty - A calculated dose of a substance which is expected to cause the death of 50% of an entire defined experimental animal population.

TLm96 - Aquatic Toxicity Rating - The concentration that will kill 50% of the exposed organisms within 96 hours.

DOSE - All doses are given in mg of compound per kilogram of animal weight except for the aquatic toxicity rating which is given in ppm of compound in solution.

when the DTPA is tightly complexed.^{47,48,49,50,51,52} Since the rare earth elements form some of the stablest DTPA complexes, one would estimate that the DTPA toxicity effect in stable activable tracer(s) would be greatly reduced. In general, from the rare earth and DTPA toxicities plus the low tracer concentrations (>10 ug/L) that are used, no health effects from using rare earth elements DTPA complexes are expected, and in fact the rare earth-DTPA tracer is predicted to be at least ten times less toxic than rhodamine dye.

In brief, the advantages of the stable activable tracer technique when compared to fluorescent dyes or radiotracers are:

1. The tracers are nontoxic at concentrations encountered in environmental studies in contrast to the real or imagined problems with radionuclide release in the environment. Also there are no aesthetically objectionable modifications of water color during tracing as with the use of dyes.
2. The sensitivity and the limit of detection of these tracers are very good. For example, for dysprosium one can ideally detect amounts as low as 10^{-12} grams. This allows pollutant tracing over long distances and times not usually possible with fluorescent dyes or radioactive tracers.
3. The tracers can be bound as EDTA or DTPA complexes and thus not suffer appreciable adsorption by sediments, as sometimes plagues the use of various dyes.
4. The detection of these tracers is not affected by the presence of water color or the photochemical decay of the tracer.

5. Their cost effectiveness is extremely competitive.
6. More than one stable activable tracer can be used simultaneously to perform multitracings experiments.

III. Experimental

The overall plan for the research involved the laboratory development and testing of stable activable tracer(s) for use as hydrological tracers in the estuarine environment followed by detailed field studies.

A. Laboratory Studies

Prior to the field studies, several preliminary laboratory experiments were performed to verify the stability of the stable activable tracers in estuarine waters, and to develop a fast and easy way to measure the rare earth content of estuarine water.

1. Tracer Preparation

In the laboratory studies to test the persistence of rare earth element and rare earth diethylenetriaminepentaacetic acid (DTPA) complexes in seawater, radiotracers ^{144}Ce ($t_{1/2} = 284$ days), ^{170}Tm ($t_{1/2} = 128$ days) and ^{169}Yb ($t_{1/2} = 31.8$ days) were used instead of stable rare earth elements. By using the radiotracers, one could simultaneously study the problem of the persistence of the rare earth elements and rare earth DTPA complexes in seawater and work on the development of the analytical procedure to measure the concentration of the rare earth DTPA complexes in estuarine waters. To form the rare earth DTPA complex, the radioactive rare earth element solution (nitrate form) was placed in a 100-ml Nalgene container along with DTPA solution where both the DTPA

and the rare earth element concentration were higher than 0.1 mg/ml. This solution was mixed and allowed to sit for over 24 hours (to allow the rare earth element DTPA complex to form) before the solution was diluted to the desired activity/ml. If the rare earth element and DTPA solution were mixed at a much lower concentration and not allowed sufficient time to react, all of the rare earth element(s) would not be chelated with the DTPA.

2. Stability of the Tracer Under Simulated Estuarine Conditions

An important criterion of a good hydrological tracer is that it should remain in solution and resist losses due to precipitation, adsorption, etc. Prior to the commencement of field studies, preliminary laboratory experiments were performed to investigate the behavior and stability of the chelate tracer under estuarine conditions. Since the salinity, pH, etc. of an estuary change so rapidly with position and time, the stability of the tracer(s) was tested under two widely different conditions, simulated river water conditions and simulated seawater conditions. The experiments involving river water conditions were done by Chick²⁶, Hanson²¹, and Drabaek²⁸. These researchers placed a known quantity of a rare earth element (both complexed and uncomplexed with DTPA) in Erlenmeyer flasks which were agitated continuously for a period of one hour to eight days for Chick²⁶ and Hanson²¹ and one to 35 days for Drabaek²⁸ with various combinations of river water and river sediments. The results and discussion of these experi-

ments can be seen in section IV-A.

Laboratory tests of the stability of chelated and unchelated rare earth elements in simulated seawater conditions were carried out. The test protocols are summarized in Table VII. In each test the rare earth radiotracer was added to a 125-ml Erlenmeyer flask containing the seawater and Pacific Ocean beach sediment collected at Newport, Oregon. The filtered seawater refers to seawater that had been filtered through a 0.45 μm Millipore filter paper to remove suspended particulate matter. The flasks containing the tracer-seawater-sediment mixtures were agitated continuously in a thermostatically controlled shaker bath at a temperature of 10°C for periods up to 21 days. Samples were withdrawn from the flasks for analysis at periodic intervals. (During sampling the shaker was stopped for 2-4 hours, allowing the sediments to settle before an 0.5 ml sample of the solution was withdrawn.) The sample taken for analysis was placed in a 2/5-dram polyvial and its radioactivity was assayed using γ -ray spectroscopy to determine the percentage of the original tracer in solution at the sampling time. The results and discussion of these experiments can be seen in Section IV-A, and Appendix B.

3. Development of an Analytical Procedure for the Analysis of Stable Activable Tracer(s) in Estuarine Waters

In this work, neutron activation analysis was used to determine the abundances of the stable activable tracer(s) in estuarine waters. Because of vast quantities of dissolved elements in sea-

Table VII: Simulated Seawater Conditions Used to Test the Stability of the Rare Earth Element Tracers

<u>Test</u>	<u>Tracer</u>	<u>Amount of Tracer</u>	<u>Seawater</u>	<u>Sediments</u>
1	^{169}Yb	0.1-1 μg	100 ml unfiltered seawater	15g
2	^{144}Ce	1-4 μg	100 ml unfiltered seawater	15g
3	^{144}Ce	1-4 μg	100 ml filtered seawater	0
4	$^{144}\text{Ce-DTPA}$	1-4 μg	100 ml unfiltered seawater	15g
5	$^{144}\text{Ce-DTPA}$	1-4 μg	100 ml filtered seawater	0
6	$^{170}\text{Tm-DTPA}$	0.4-0.5 μg	100 ml unfiltered seawater	15g
7	$^{170}\text{Tm-DTPA}$	0.4-0.5 μg	100 ml filtered seawater	0

water and river water (Table VIII) and the need to concentrate the tracer, pre-irradiation and post-irradiation chemistry was performed. The objectives of the pre-irradiation and post-irradiation chemistry are (1) the removal of the tracer(s) from all elements that interfere with their analysis and (2) to concentrate the tracer for easier analysis. Also, the procedure should conform to the following guidelines:

1. The procedure is inexpensive.
2. The procedure is fast. (≤ 1 hour/sample)
3. Contamination (procedure blank) should be kept as low as possible.
4. An inexperienced analyst can perform the procedure.
5. Radiation exposure doses should be kept as low as possible.

The two procedures commonly used to measure rare earth elements in natural waters are (a) an iron hydroxide precipitation which scavenges the rare earth elements, followed by a series of ion exchange separations and precipitations,¹⁶ and (b) a simple filtration of the water through a filter paper with ion-exchange material incorporated in it.²⁶

For analysis of the rare earth elements, the first technique is good in that the procedure is very accurate with a low contamination blank. This technique does have some problems in that:

1. It is very time consuming (3-6 man-hours per sample).
2. The analysis cost is higher than one might want to pay (greater than \$100 per sample).

Table VIII: Major Elemental Composition of River Water and
Seawater^{53,54,55,56,57,58,59}

Element	River Water (ppm)		Seawater (ppm)	
	Median Concentration	Concentration Range	Median Concentration	Concentration Range
Al	0.34	0.01-2.5	0.002	0.001-0.008
B	0.054	0.009-0.15	4.80	4.44-5.28
Ba	0.010	0.003-0.15	0.02	0.005-0.093
Br	0.021	0.005-140	69.46	68.78-70.18
Ca	15	4-20	425.2	423.0-426.8
Cd	0.08	---	0.00011	---
Cl	7.8	5-35	1.935×10^7	---
Cu	0.01	0.006-0.4	0.00025	---
F	0.10	0.05-2.7	1.34	1.28-1.80
Fe	0.67	0.01-1.4	0.002	---
I	0.002	0.0005-0.007	0.063	0.048-0.080
K	2.3	1.4-10	412	406.0-418.0
Mg	4.1	1.5-5	1,340	1,330-1,340
Na	6.3	3-25	11,100	11,070-11,140
Se	0.02	---	0.0002	---
Si	7.0	0.50-12	2.0	0.00-4.90
Sr	0.08	0.003-0.8	8.0	7.6-8.2
Zn	0.01	0.0002-1	0.0123	0.0039-0.0484

3. The procedure measure uncomplexed rare earth elements and may not be able to measure rare earth elements complexed with DTPA.

The second procedure meets all the aforementioned criteria except that the procedure does not work in high salinities. This can be seen in Table IX, where a ^{169}Yb -DTPA seawater solution (approximately $1.3 \mu\text{g Yb/l}$) was filtered through two Nuclepore anion-exchange papers (SB-6407). The filtrate and the anion-exchange paper were analyzed for the activity of the radiotracer and the pickup efficiency % was determined by the equation below:

$$\text{pickup efficiency \%} = \frac{A_{\text{paper}}}{A_{\text{paper}} + A_{\text{sol}}} \times 100$$

where

A_{paper} = ^{169}Yb activity of the anion-exchange papers

A_{sol} = total ^{169}Yb activity of the filtrate

The pH of the solution was changed by adding ammonium hydroxide and/or acetic acid.

Because of the above problems, a new separation procedure involving a pre-irradiation precipitation of the rare earth element-DTPA complex with potassium hydroxide followed by a post-irradiation HAP (hydrated antimony pentoxide) batch extraction of the remaining sodium, was developed in this study to measure the stable activable tracer(s) in estuarine waters. This procedure is quick (45-60 man-minutes per sample), cheap, an easy procedure to perform, and leads to a low radiation dose for the analyst

Table IX: Variation of Pickup Efficiency of ^{169}Yb -DTPA on Anionic Filters with pH

<u>pH</u>	<u>Percent Pick-up in Distilled Water</u>	<u>pH</u>	<u>Percent Pick-up in Seawater</u>
4.89	97.9	4.78	2.09
4.93	97.2	4.96	3.53
6.95	97.6	5.00	1.69
7.93	99.2	6.69	2.28
8.49	97.1	6.78	2.00
8.57	99.2	6.92	0.94
8.69	99.3	7.06	1.66
8.71	98.7	8.44	7.90
		8.45	5.54

(total hand dose of less than 0.25 mrem per sample). The analytical procedure used to measure the concentration of the rare earth DTPA tracer is described in detail in Section III-B-7.

It is of interest to note that Drabaek²⁸ also decided to use a co-precipitation method in his analysis of the concentration of the rare earth DTPA tracer. In his analytical procedure, he used a series of acidification and precipitation steps (using $\text{Bi}(\text{OH})_3$ as the co-precipitation agent) to preconcentrate the tracer and to remove all interfering elements from the sample. His procedure to analyze the concentration of the rare earth-DTPA tracer is comparable to the analytical procedure used in this research in both analysis time and estimated expense. His method is an apparent improvement over the analytical procedure used in this report in the fact that it greatly reduces the amount of radiation exposure for the analyst, and the procedure also has a very low procedural background. His method does have serious problems in determining the tracer yield. He found that the estimated tracer yield must be determined for each element for each given composition of water. For example, the analytical procedure yield for lanthanum in demineralized water, salinity of 9.5%, and a salinity of 18.9% is 0.92, 0.77, and 0.84 respectively. Since the composition of the water varies widely in an estuary, Drabeck's analytical procedure would not be very useful in an estuarine experiment. Also, he reported that the precision of the yield is between 4.2 to 19.7% which is a larger yield uncertainty than one would normally like

to have for an analytical procedure to measure the rare earth DTPA tracer concentration. In conclusion, it is interesting that Drabaek used the same general approach (co-precipitation) to measure the concentration of the rare earth DTPA tracer as the one used in this thesis.

a. Development of a Pre-Irradiation Chemistry

In the pre-irradiation chemical procedure, one would like to concentrate the tracer as much as possible and also remove as much as possible all interfering elements without increasing the blank contamination of the procedure. The way this researcher accomplished this goal was by a hydroxide precipitation of the rare earth elements with potassium hydroxide. For the precipitation to occur the pH must be high enough to break the metal-DTPA bond. At a pH greater than 12, the cerium-DTPA complex is completely ionized and a rare earth hydroxide forms (Figures III and IV).

This was determined in two laboratory experiments using ^{144}Ce radiotracer which was complexed with DTPA. In the first experiment (Figure III), a 6M sodium hydroxide solution was added to a Ce-DTPA river water solution (approximately 9-10 $\mu\text{gCe}/\ell$) and the resulting solution was filtered through two Nuclepore filter papers (0.2 μm pore size). The filtrate and the precipitate were analyzed for the activity of the cerium radiotracer, and the fraction of the cerium radiotracer in the precipitate was calculated using the following equation:

$$\text{Fraction of Ce in Precipitate} = \frac{A_{\text{ppt}}}{A_{\text{ppt}} + A_{\text{sol}}}$$

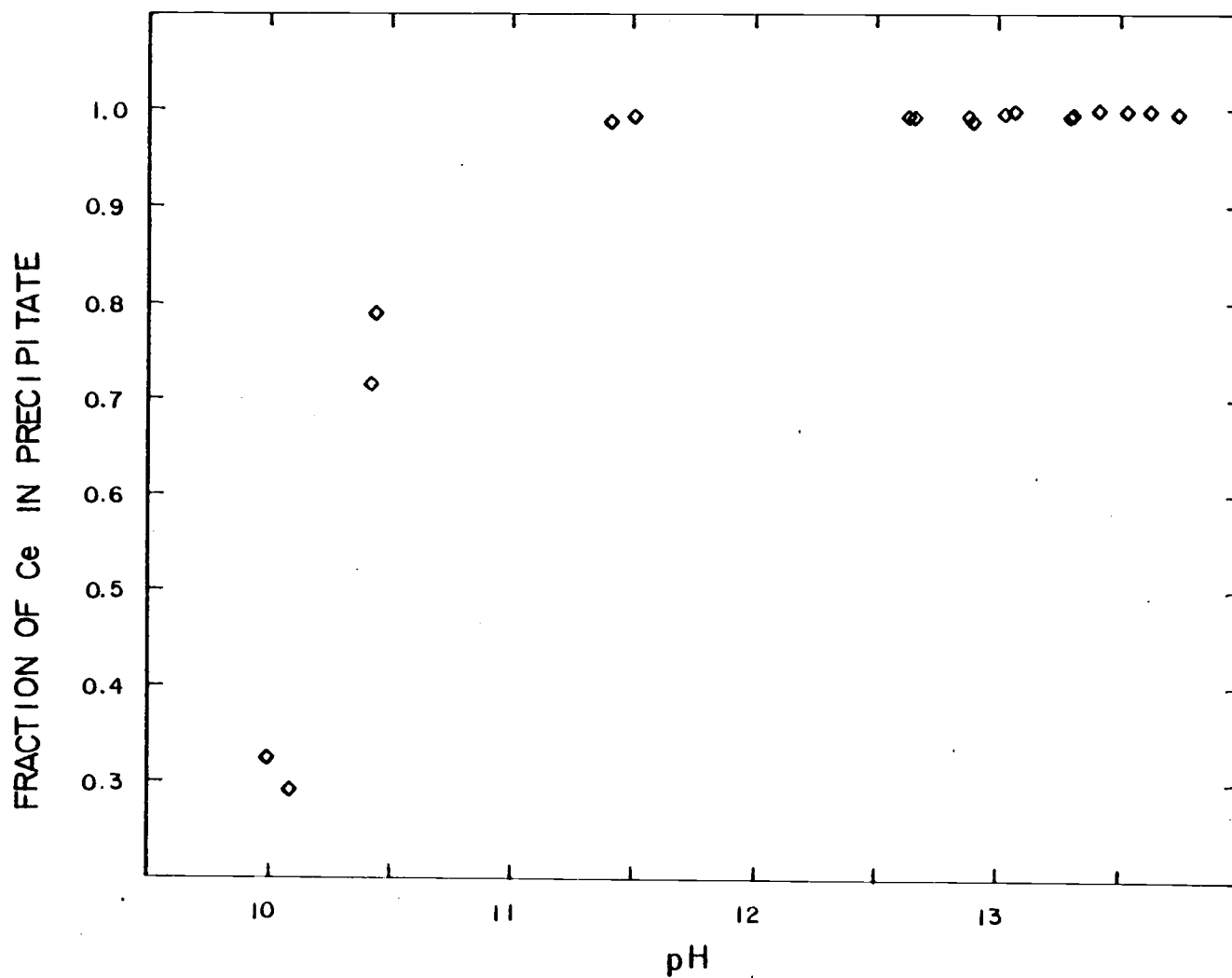


Figure III: The pH dependence of the precipitation of Ce-DTPA in river water.

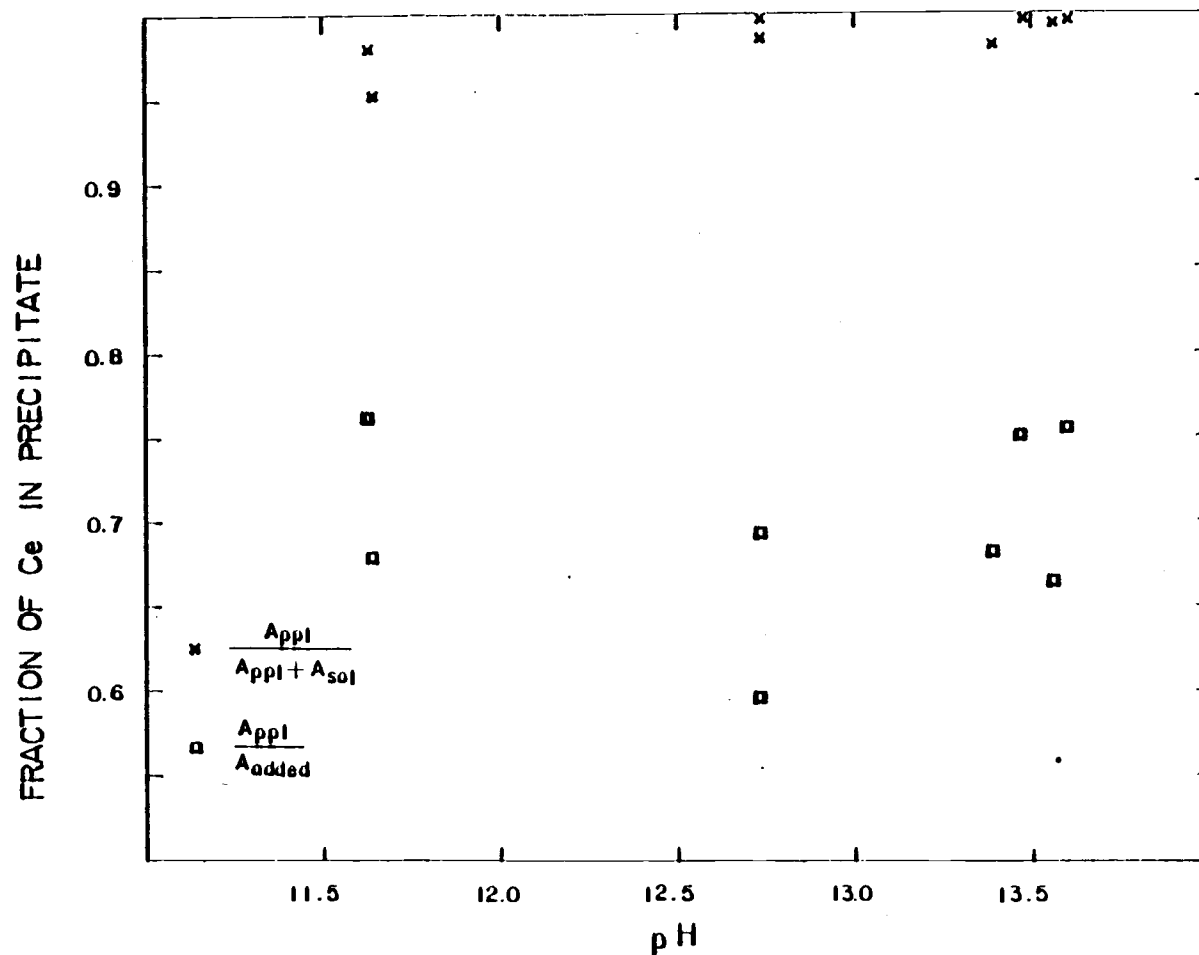


Figure IV: The pH dependence of the precipitation of Ce-DTPA in seawater; where $A_{ppt} = {}^{144}\text{Ce}$ activity in the precipitate, $A_{sol} = {}^{144}\text{Ce}$ activity in the solution after precipitate, and $A_{added} = {}^{144}\text{Ce}$ activity in the solution before precipitation.

where

$A_{\text{ppt}} = {}^{144}\text{Ce}$ activity in the precipitate

$A_{\text{sol}} = {}^{144}\text{Ce}$ activity in the filtrate

It was determined (Figure III) that a pH of greater than 12, essentially all (greater than 98%) the cerium radiotracer was in the precipitate.

In the second experiment, the same procedure was followed with the exceptions that seawater was used instead of river water and the cerium radiotracer activity of the original solution was determined. The fraction of the cerium radiotracer in the precipitate was calculated by the previous equation and by the following equation:

$$\text{Fraction of Ce in Precipitate} = \frac{A_{\text{ppt}}}{A_{\text{added}}}$$

where

$A_{\text{ppt}} = {}^{144}\text{Ce}$ activity in the precipitate

$A_{\text{added}} = {}^{144}\text{Ce}$ activity in the original solution

It was again determined (Figure IV) that at a high pH (greater than 12), essentially all (greater than 98%) the cerium radiotracer was in the precipitate. It was also determined by comparing the amount of the cerium radiotracer added to the original solution to the amount found in the precipitate ($A_{\text{ppt}}/A_{\text{added}}$), approximately 30% of the

radiotracer did not go into the precipitate. Because of this loss of radiotracer (from adsorption of cerium on the glass walls), a 0.5 mg carrier of praseodymium was added to the solution to reduce losses of the radiotracer.

When I repeated the previous procedure with a praseodymium carrier (Table X), it was determined that the fraction of the cerium radiotracer ($A_{\text{ppt}}/A_{\text{added}}$) did not change as a function of concentration. Also, the precipitate yield ratio of greater than 1.0 is not surprising due to the combination of matrix and geometry effects. The major matrix and geometry effect which was seen in this analysis was the attenuation of the gamma ray as it travels through the sample. In the determination of A_{ppt} , the precipitate (0.2-0.5 grams) was placed in a 2-dram polyvial and counted. One would predict that there would be almost no attenuation effect since the gamma ray travels through a very thin section of the solid sample and thus should not be attenuated. In the determination of A_{added} , one ml of the original solution was placed in a 2.5-dram polyvial and one would predict that there will be some attenuation of the gamma ray as it travels through the solution. The reason for this attenuation effect is that the gamma ray had to travel through as much as 1.4 cm of solution. The ratio of 1.19 does indicate that most if not all the cerium radiotracer was found in the precipitate and that the praseodymium carrier does prevent adsorption of the rare earth elements on the glass walls of the beaker.

Table X: Precipitate Yield Ratio of Ce-DTPA at Various Concentra-
tions Using a Praseodymium Carrier

<u>Concentration</u> <u>of Ce-DTPA</u>	<u>pH</u>	<u>Activity of Precipitate/</u> <u>Activity Added to Sample</u>
80 ng/L	13.6-13.7	$1.187 \pm .034$
104 ng/L	13.0-13.7	$1.189 \pm .066$
4000 ng/L	13.6-13.7	$1.187 \pm .037$

In conclusion, the pre-irradiation chemistry has the qualities of being fast, inexpensive, and easy. Most of the interfering elements have been removed except for sodium, and a concentration factor of the rare earth elements of about 200-400 is achieved. Approximately 10-20 mg of sodium remained in the precipitate and because of this quantity, a post-irradiation procedure was developed.

b. Development of a Post-Irradiation Chemistry

The post-irradiation chemical procedure was developed to remove the remaining solution from the samples. The remaining amount of sodium in the samples had to be removed before the samples were analyzed by gamma spectroscopy since after neutron activation analysis, the activity of the activated sodium would mask the activity from the activated rare earth elements. The post-irradiation procedure has essentially the same constraints as the pre-irradiation chemistry except for the blank contamination problem. Since this procedure is to be done after irradiation, the concentration of rare earth elements in common reagents will not affect the procedure blank. The major restriction in doing post-irradiation chemistry is that the chemistry must be fast in both man-hours per sample and total elapsed time per sample. A procedure similar to the pre-irradiation chemistry could be done, but the man-hours per sample and the total elapsed time per sample would be higher than one would like. With this in mind, a HAP (hydrated antimony pentoxide) batch extraction was developed. This procedure only takes approximately 5-7 man-minutes per sample with a total elapsed time per

sample of only 15-20 minutes.

HAP has the capacity to retain approximately 30 mg of sodium per g of HAP, with a decontamination factor as high as 10^{10} in columns with less than 5% retention of the rare earth elements in 6 molar or higher hydrochloric acid.^{60,61} In batch equilibrium, the decontamination factor is only 10^3 .^{60,61} However, unlike the column method, the batch method can be done in five minutes while the column method takes 1-2 hours.

With this in mind, the activated precipitate (1-3 grams) was dissolved in excess amounts of concentrated hydrochloric acid (15 ml) and 2-4 grams of HAP were added to the solution. It was ascertained that after five minutes of heating (70-90°C) and stirring, essentially all the sodium was removed from the sample with no loss of the rare earth element(s). Without either heating and/or stirring, the decontamination factor was drastically reduced and some sodium activity remained in the solution.

c. Measuring the Tracer Concentration

The gamma ray emitted by the activated tracer nuclide was detected using a Ge(Li) detector connected to a multichannel analyzer. The Ge(Li) detectors which were used in this research were two 40cm Nuclear Diodes closed-end coaxial Ge(Li) detectors. The characteristics and shape of the Ge(Li) detectors can be seen in Appendix C. The multichannel analyzers which were used in this research were a Nuclear Data 4420 and a Nuclear Data 2200. Prior to all sample analysis, the gamma ray spectrometer was calibrated

using point source standards of ^{137}Cs (661.661 keV) and ^{60}Co (1173.238 and 1332.513 keV).⁶² All samples were counted 10.5 cm from the germanium crystal in detector A and 4.5 cm from the germanium crystal in detector B.

From Table XI, one can see the predominant gamma rays which were detected by the gamma ray spectrometer in a typical tracer sample. Because of the activity from radioactive nuclides in the tracer sample (^{42}K , ^{38}Cl , ^{56}Mn , ^{35}Br , etc.), the ideal detector would have the following characteristics:

1. a relatively high efficiency for low energy gamma rays (<300 keV) with a relatively low efficiency for high energy gamma rays (>1 MeV)
2. good resolution (a full width half maximum of <2 keV for a 1332 keV gamma ray)
3. high peak to Compton ratio (>50/1 for a 1332 keV gamma ray)

With these characteristics (plus a cadmium sheet around the detector to protect the detector from Pb X-rays), one could easily measure the low energy gamma rays from ^{165}Dy (95 keV) and $^{152\text{m}}\text{Eu}$ (122 keV). If one compares the characteristics of the two detectors used in this experiment with the characteristics of the ideal detector, one would notice that the two detectors used in this research do not meet all the criteria for an ideal detector. However, the detectors were adequate for detecting and measuring the low energy gamma rays of ^{165}Dy and $^{152\text{m}}\text{Eu}$.

Table XI: Typical Gamma Ray Peaks of the Major Radionuclides
Detected by the Gamma Ray Spectrometer

<u>Radionuclide</u>	<u>Compton Background*(counts)</u>	<u>Peak Area(counts)</u>	<u>Energy (keV)</u>
^{165}Dy	18,328	5,807	94.5
Positron Annihilation	7,341	3,017	511
^{80}Br	11,075	2,246	619.1
^{56}Mn	6,353	13,972	846.7
^{42}K	1,987	1,230	1524.7
^{142}Pr	2,477	2,619	1575.6
^{38}Cl	3,159	19,749	1642.7
^{38}Cl	939	19,826	2167.6

*The sum of the background below the gamma ray peak

Since neutron activation was used as the mode of analysis, the basic equation of quantitative activation analysis is:^{63,64,65}

$$W = \frac{AM}{\sigma f \Phi N_0 \{1 - e^{-\lambda t}\}}$$

where

W = weight of the element in the sample

A = induced activity of the particular isotope of the element concerned at E.O.B. (End of Bombardment)

Φ = neutron flux in neutrons/cm²/sec

σ = thermal neutron capture cross-section in cm²

f = fractional abundance of the particular isotope of the element concerned

λ = decay constant of the induced radionuclide

t = irradiation time

M = atomic weight of the element

N_0 = Avogadro's number (6.022×10^{23} atoms/mole)

In this experiment where all the samples and standards were irradiated under the same conditions, the aforementioned equation simplifies so that the stable activable tracer concentration(s) can be determined by the following equation:

$$C_{SAT} = \frac{(W_{std})(A_{unk})(A'_{std})(fg)}{(V_{sample})(A'_{unk})(A_{std})}$$

where

C_{SAT} = concentration of the stable activable tracer

W_{std} = weight of the element in the standard

A_{unk} = sample's activity of the tracer nuclide at E.O.B.

A_{std} = standard activity of the tracer nuclide at E.O.B.

A'_{unk} = praseodymium (carrier) activity of the sample at E.O.B.

A'_{std} = praseodymium (carrier) activity of the standard at
E.O.B.

V_{sample} = volume of the sample

fg = geometry correction (mostly due to the difference in the
amount of attenuation of the gamma rays in the standards
vs the samples)

Since the activated sample and elemental standards have different volumes (15 and 1 ml, respectively), a correction for differing counting geometries was made. To obtain the geometry correction, a known amount of dysprosium and europium-DTPA was added to 500 ml of filtered (through a 0.45 μ m Millipore filter paper) seawater and river water. This solution was analyzed by the pre- and post-irradiation procedures and compared to the known standards. The geometry correction, fg , was determined for this data by taking the rare earth element yield and dividing it by the praseodymium carrier yield. For detector A, the geo-

metry correction is 0.8380 ± 0.0085 for dysprosium and 0.8551 ± 0.0077 for europium, and for detector B the geometry correction is 0.8640 ± 0.0055 for dysprosium and 0.8834 ± 0.0094 for europium. As can be seen in the following equation, the fraction of gamma rays which are attenuated is a function of the attenuation coefficient (constant for a given medium) and the path length.

$$\frac{I}{I_0} = e^{-ux}$$

where

I_0 = initial intensity of a beam of gamma rays

I = intensity of a beam of gamma rays after passing through an absorbing medium

u = attenuation coefficient

x = path length of gamma ray as it travels through the absorbing medium

Since the attenuation coefficient for water is approximately 0.18 cm^{-1} for dysprosium (95 keV gamma ray), and 0.15 cm^{-1} for europium (134 keV gamma ray), and 0.028 cm^{-1} for praseodymium (1575 keV gamma ray),⁶⁶ the geometry correction calculated in the aforementioned experiment does qualitatively agree with the theory that most of the geometry correction comes from the attenuation of the gamma ray as it travels through the solution in that the lower energy gamma rays seem to be attenuated more than the higher energy gamma rays.

B. Field Study

This phase of the research involves field studies to test the conservative nature of the stable activable tracer(s) in estuaries. One can test the conservative nature of the tracer(s) by the following methods:

1. A comparison of the tracer(s) dispersion pattern to a hydrological model of the estuary.
2. A comparison of the tracer(s) dispersion pattern to that of a recognized conservative element.
3. A comparison of the tracer(s) behavior to that of another tracer whose characteristics are known.

Given very precise and accurate physical data inputs, hydrological models yield fairly accurate prediction as to the dispersion of elements in the whole estuary, but their predictions are generally inaccurate in localized and/or small regions of an estuary. The only estuary near Corvallis, Oregon that is sufficiently well characterized (tide height measurements, wind velocity, etc.) to allow hydrological modeling is Yaquina Bay, Oregon.

At the present time, there is no good hydrological model for Yaquina Bay. However, there is a model for a marina (South Beach Marina) in Yaquina Bay.^{67,68} The model calculations are based upon the assumption that the tracers are uniformly mixed throughout the marina and thus the mass of the marina decreases only when the tide goes out and the concentration of the tracer decreases when the tide comes in. It follows that one can calculate the

concentration of the tracer at high tide from the concentration of the tracer from the previous low tide by the following equation:

$$C_h = C_l(V_l/V_h)$$

where

C_h = concentration of the tracer at high tide

C_l = concentration of the tracer at the previous low tide

V_h = volume of the marina at high tide

V_l = volume of the marina at low tide

Because of the existence of this model which has

proven fairly reliable in predicting the flushing rate of tracers in the marina, I compared the stable activable tracer flushing rate with the flushing rate predicted by the model. From this comparison, the persistence of the stable activable tracer was estimated. However, this comparison between the experimental flushing rate and the model predicted flushing rate should be taken as only an approximation, since it has been experimentally determined that the model will occasionally underestimate the amount of tracer which has been removed from the marina by as much as 30%.

The second method is a very good and precise way to test the tracer's conservative nature. Estuaries contain a readily usable internal tracer (chlorine) which is conservative, whose content is easily measured, and which has a broad natural concentration range (less than 0.01‰ - 34‰). The major problem with using

chlorine as a tracer is one will have to tag with the stable activable tracer(s) all freshwater inputs to the estuary and allow the whole estuary to equilibrate before taking samples. This will cause two problems; (a) a large quantity of tracer is needed (50-100 kg of dysprosium and 50-100 kg of DTPA) and (b) the measurement will only show the conservative nature of the tracer(s) for the mean residence time of the estuary. For these reasons, chlorine was not used to test the conservative nature of the tracer.

For various reasons, the procedure which compares the stable activable tracer hydrological behavior to that of another tracer whose hydrological characteristics are known was used to test the conservative nature of the stable activable tracer(s). By mixing a tracer whose hydrological characteristics are known (rhodamine B or WT) with the stable activable tracer(s), the necessity of waiting for complete equilibrium in the estuary is eliminated. By measuring the ratio of the concentrations of the two types of tracers, the time dependence of the stability of the stable activable tracer can be determined. Rhodamine B or WT was used as the known tracer (rhodamine B and WT can be considered conservative under the experimental conditions encountered in the field studies) since these dyes are cheap, well tested, and permission to use them is attainable.

1. Location

The ideal location for the testing of the conservative nature

of the tracer in the field, would have the following characteristics:

1. Proximity to Corvallis, Oregon (lab location of experimenter).
2. Small exchange of untagged water with tagged water (a low flushing rate).
3. Small volume of water to be tagged.
4. The physical characteristics (salinity, pH, etc.) cover the normal estuarine range.

Since the tidal effect is the major factor in the mixing and flushing of estuaries, points 2 and 3 are in conflict. Normally in an estuary, if only a small amount of flushing occurs, the volume of the estuary is usually large. Therefore, one must balance the need for point 2 against the need for point 3. The South Beach Marina at Yaquina Bay, Oregon was picked as the site for the field experiments for the following reasons:

1. Close to Corvallis, Oregon (50 miles)
2. The marina is approximately one tenth the volume of Yaquina Bay.
3. Its flushing rate is approximately that of Yaquina Bay.
4. Its salinity range is almost that of the whole estuary (approximately 15-34‰).
5. A hydrological study of the marina was done recently.^{67,68}

From Figure V, one can see the size and shape of the marina and its location in Yaquina Bay. Some of the general information

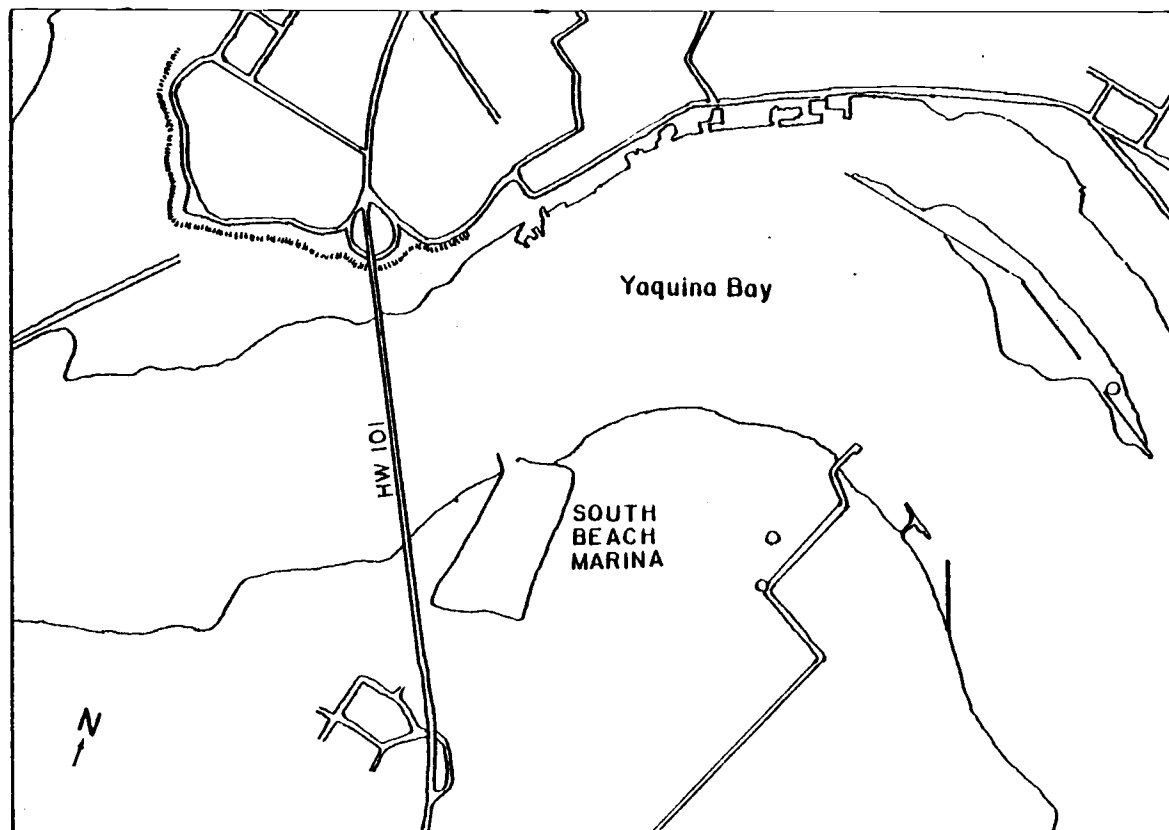


Figure V: Map of Yaquina Bay and the South Beach Marina.

about the South Beach Marina is that the entrance of the marina is 1.5 nautical miles (2.8 km) upstream of the end of the north jetty at Newport, Oregon. The approximate marina dimensions are length = 1,574 ft (480 m), width = 623 ft (190 m), depth at mean tide level = 13.4 ft (4.1 m). The mean tide range is equal to 6.0 ft (1.83 m) and the entrance/exit width is 157 ft (48 m). The marina is designed to hold 600 boats.

2. Sample Containers and Cleaning of the Containers

In choosing a container to store the estuarine water samples, one must pick a container which is easily transported and stored, and which does not affect the integrity of the sample. One usually worries about metals being leached from the container walls or the metals in solution being sorbed on the container walls. Since Nalgene containers are considered one of the best containers to prevent those problems, Nalgene containers were used in this field study.

The cleaning of the Nalgene containers prior to use has two purposes, to remove all leachable metals from the containers, and to remove all activated adsorption sites on the containers. There are various methods in use for the cleaning of these jars.^{69,70,71} All methods recommend a soaking in nitric acid (to leach all the metals from the containers) followed by a meticulous job of washing the containers with distilled water (to "remove" the activated adsorption sites). Since the nitric acid creates activated adsorption sites in the containers, the concentration

and length of time of soaking the containers in nitric acid varies within the different procedures. A 12-24 hour soaking of the containers in 0.5 M nitric acid bath followed by two washings with distilled-deionized water was used in this study.

3. Tracer Preparation

The stable activable tracers chosen for this work included the rare earth elements dysprosium and europium. Oxides of the elements were dissolved in a minimum amount of hot concentrated nitric acid and a solution of diethylenetriamine pentaacetic acid (DTPA) was added to form a 1:1 complex of the rare earth element(s) and DTPA. The pH of the metal chelate solution was adjusted to approximately the natural pH of 7.0-8.0 of the estuarine water and the rhodamine B or WT was added to the solution and mixed. If necessary, the volume of the tracer solution was adjusted with distilled water.

For the first field study, the tracer solution consisted of 2.2 kg of DTPA, 0.902 kg of dysprosium, and 2.053 kg of rhodamine B in approximately 38 liters. For the second field study, the tracer solution consisted of 3.3 kg of DTPA, 0.874 kg of dysprosium, 0.1448 kg of europium, and 3.26 kg of rhodamine WT in approximately 38 liters.

4. Tracer Injection into the South Beach Marina

Since the major idea behind the testing of the stable acti-

vable tracer is to test its conservative nature as a function of time, the tracer was placed in the South Beach Marina in a way to keep the tracer inside the marina as long as feasible. To achieve this goal, the tracer was dumped as a slug in the southeast corner of the marina. From previous field work,^{67,68} the water in the southeast corner is recognized as having the longest residence time in the marina (i.e., this spot has the slowest diffusion rate in the marina). Also the southeast corner is the farthest distance from the entrance/exit of the marina and therefore any material added to this spot will be hydrologically removed from the marina slower than any other spot.

5. Sampling Procedure

The samples were taken at the times when it was either high or low tide. The marina was sampled at eight different sites which were uniformly distributed so that a total picture of tracer dispersal was obtained. With the anticipation of finding a partial stratified hydrological environment in the marina, three depths were sampled, which are surface, middle, and one foot above the bottom. At the surface, the sample was taken by rinsing the Nalgene container with the surface estuarine water followed by the taking of a grab sample with the container at the surface of the estuarine water. For both the middle and bottom samples, the procedure involved the use of a commercial messenger-

operated Nansen type trace metal water sampling bottle.⁷² As with the surface sample, a portion of the water collected in the Nansen sampler was used to rinse the Nalgene container before the remaining water was poured into the container.

6. Sample Storage

It may be worthwhile to point out that there is no technique of preservation that can maintain complete stability for every constituent after the sample is removed from the parent source.⁷³ Traditionally, the acidification of water samples is considered by many as the way of preserving metallic ions in solution.^{69,70,74} However, acidification of the water samples will not be indicative of the true metal content of the water samples at its source, since most inorganic constituents will have been desorbed from the suspended particles during acid storage. However, it is also important to consider the adsorption and leaching of soluble materials upon and from the walls of the sample containers, which can be prevented by acidifying the water prior to storage.⁷⁵ This may seem paradoxical (since one must acidify and yet cannot). The obvious solution is to filter the water to remove suspended particulates and then acidify or otherwise prevent container surface adsorption. In addition, it is most unfortunate that a wide variety of solvents, reagents, and other materials encountered in trace analysis contain extremely high levels of various elemental impurities.⁷⁶

In our case, we elected to freeze the samples (at -20°C)

as soon as possible after sampling to eliminate the adsorption and leaching of soluble materials upon and from the walls of the containers as well as desorption of inorganic constituents from the suspended particles. Indeed, it has been demonstrated by the Battelle Pacific Northwest Laboratories and National Bureau of Standards that rapid freezing of the sample provide a better alternative to chemical preservation.^{77,78} This procedure has also been shown to be a reliable method for storage of stable activable tracer(s) in Nalgene containers.²⁶

7. Sample Analysis

The samples were removed from cold storage (-20°C) and allowed to melt in the Nalgene containers. After all the samples were melted, 500 ml of the estuarine water was removed and filtered through a $0.45\text{ }\mu\text{m}$ poresize Millipore filter paper (to remove all suspended particulates). The filtrate was poured into a one-liter beaker with 0.5 mg of praseodymium being added and thoroughly mixed. Twenty ml of a 45 weight % solution of potassium hydroxide was added to the solution, and the solution was then heated until boiling followed by a gentle cooling period (digestion of the precipitate).⁷⁹ When the solution reached room temperature, all but 100-200 ml of the supernatant was decanted and filtered through two $0.8\text{ }\mu\text{m}$ Nuclepore filter papers. The remaining solution was transferred to a 250 ml centrifuge tube and centrifuged for ten minutes at a force of 9 G's. After centrifuging, the remaining supernatant was decanted and filtered through the same previously mentioned

0.8 μm filter papers. Using 50 ml of a 1.6 N ammonium hydroxide solution, the precipitate was transferred to the filtering apparatus and filtered through the two 0.8 μm filter papers. The filter paper and the precipitate was allowed to air dry before being placed inside a 2-dram polyvial.

The samples were placed in the rotating rack of a TRIGA Mark II reactor and were irradiated for 20 minutes in a neutron flux of 1.2×10^{12} neutron/cm²/sec. The samples were allowed to decay (for 100 minutes) before they were dissolved in 15 ml of concentrated hydrochloric acid (the solution was gently heated to aid in dissolving the precipitate). When all the precipitate was dissolved, 2-4 grams of HAP (hydrated antimony pentoxide) were added to the solution. After five minutes of gently heating and stirring, the slurry was transferred to a 25-ml centrifuge tube and centrifuged for three minutes. At this point, the supernatant was decanted into 7-dram polyvial which was then sealed with a soldering iron. The activated samples were then analyzed by γ -ray spectroscopy.

The rhodamine B or WT samples were analyzed with a Turner Model 10-005R fluorometer at Newport, Oregon. The equipment set-up was as follows, 10-046 clear quartz lamp (excitation lamp), 10-056 color specification (green) 546 filter (excitation filter), 10-053 color specification (yellow) 16 filter (reference filter), 10-057 color specification (reddish-orange) 23A filter (emission filter), and a 10-052 color specification (light blue) 3-66

(emission filter). With this equipment arrangement, it was determined that the calibration curve is a straight line until approximately 23 ppb. Therefore, the following equation was used to calculate the concentration of the dye in the samples.

$$\frac{\text{Concentration of Sample}}{\text{Concentration of Standard}} = \frac{\text{Sample's Fluorescent Signal}}{\text{Standard's Fluorescent Signal}}$$

The temporal stability of the stable activable tracer(s) (Dy-DTPA and Eu-DTPA) compared to a fluorescent dye (rhodamine B or WT) in the South Beach Marina experiments was determined by comparing the experimentally determined marina averages for the two stable activable tracer concentration to the experimentally determined marina average fluorescent dye concentration as a function of time. The experimentally determined marina average tracer concentrations were determined by summing the tracer concentrations over all the sampling sites for a given time and dividing this number by the number of sampling sites. Since each sample represents a certain fraction of the marina volume with each sample designed to represent an equal volume of the marina, this procedure of comparing the marina average concentration of the individual tracers to each other is essentially equal to comparing the mass of the individual tracers in the marina to each other. This argument can be shown to be true from the following relationships.

$$M^t = \sum_{i=1}^n t_{C_i} V_i$$

$$\frac{M_{SAT}^t}{M_F^t} = \frac{\sum_{i=1}^n t_{C_i}^{SAT} V_i}{\sum_{i=1}^n t_{C_i}^F V_i}$$

however,

$$V_i \approx \frac{1}{n} \sum_{i=1}^n V_i$$

therefore

$$\frac{M_{SAT}^t}{M_F^t} = \frac{\sum_{i=1}^n t_{C_i}^{SAT}}{\sum_{i=1}^n t_{C_i}^F}$$

or

$$\frac{M_{SAT}^t}{M_F^t} = \frac{\sum_{i=1}^n t_{C_i}^{SAT} / n}{\sum_{i=1}^n t_{C_i}^F / n}$$

where

M^t = mass of tracer in the marina at time t

t_{C_i} = tracer concentration in sample i at time t

V_i = marina volume which sample i represents

M_{SAT}^t = mass of stable activable tracer in the marina at time t

M_F^t = mass of fluorescent dye in the marina at time t

$t_{C_i}^{SAT}$ = stable activable tracer concentration in sample i at
time t

$t_{C_i}^F$ = fluorescent dye concentration in sample i at time t

t = the difference in time between when the tracers were added
to the marina and when the samples were taken

n = number of sampling sites

IV. Results and Discussion

All tracers suffer losses in the natural environment due to various mechanisms. Some of the mechanisms which could cause the stable activable tracer to be removed from an estuary are as follows:

1. Biodegradation of the complexing agent (DTPA).
2. Adsorption reaction with solid phases including sediments, organisms, and/or sample containers.
3. Breakup of the rare earth element(s) - DTPA complex.
4. Biological-uptake of the stable activable tracer(s).

A. Laboratory Studies

Biodegradation of the chelate (DTPA) is expected to have no effect on the rare earth element(s) - DTPA stability. In laboratory studies,⁸⁰ DTPA, in the presence of settled sewage and yeast extract, lost no chelating ability for up to three weeks. Also from this study on compounds with similar chemical structures,⁸⁰ one would predict that DTPA would not lose any chelating ability for a much longer time than the three weeks in which it was tested. Since the DTPA chelating ability is reduced as DTPA biodegrades, this would mean that DTPA would not biodegrade to any appreciable degree for over 3 weeks. With such a low biodegradability potential, one can assume that biodegradation of the chelate (DTPA) will have no effect on the rare earth element(s) - DTPA stability during a typical (less than one month) hydrological tracing experiment.

The potential sorption reactions involving the Nalgene sample container walls have been discussed previously (Section III-B-2). It was concluded that such a reaction will have almost no effect on the stability of the rare earth element DTPA complex in an estuarine environment.^{26,77,78}

In the laboratory stability tests (see Figures VI and VII), it was demonstrated that the rare earth DTPA complex is not readily sorbed by the suspended particulates and sediments while the uncomplexed rare earth elements are readily sorbed by the suspended particulates and sediments. These results have recently been confirmed to hold true at high tracer concentrations (100-600 $\mu\text{g}/\ell$) in river water (Figure VI-b) and in seawater where the mean % tracer recovery was 100.9, 99.4, and 105.2 for samarium, dysprosium and lanthanum respectively.²⁸ The fact that the laboratory tests showed only a small loss of rare earth DTPA tracer over time, approximately 3-5% per week, which is in good agreement with the theoretical rare earth DTPA rate of break-up calculated in Section II, approximately 0.7% per week, one can infer that the rare earth DTPA complex is not readily broken by the competition from other estuarine elements for the chelates, DTPA. One can also infer from the laboratory results that the rare earth-DTPA complex should essentially remain in solution for the lifetime of most hydrological experiments with only negligible losses due to sorption reactions.

Biological-uptake will usually have only a small effect on

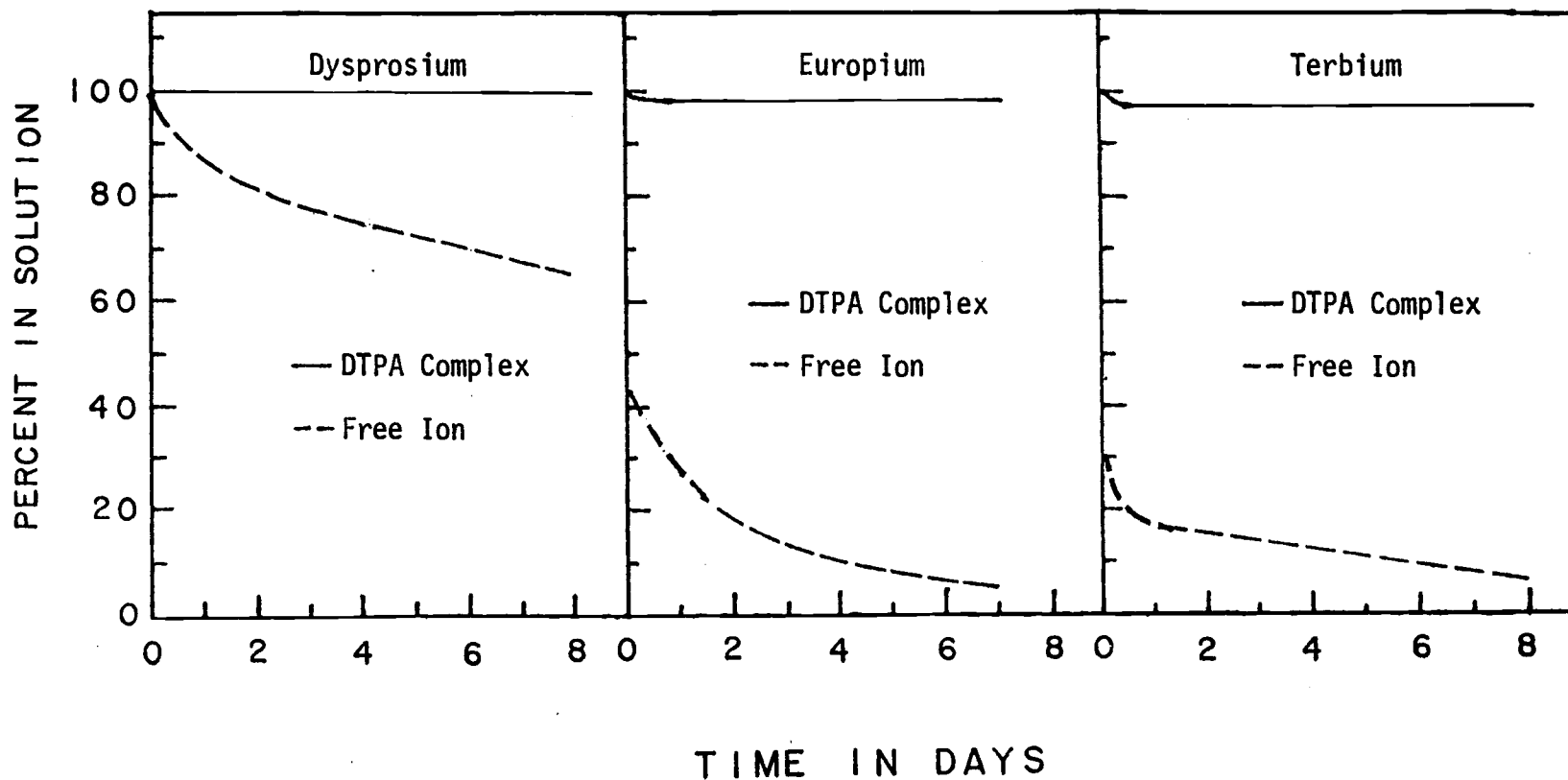


Figure VI-a: Time dependence of rare earth tracer stability test in simulated river water conditions.^{21,26}

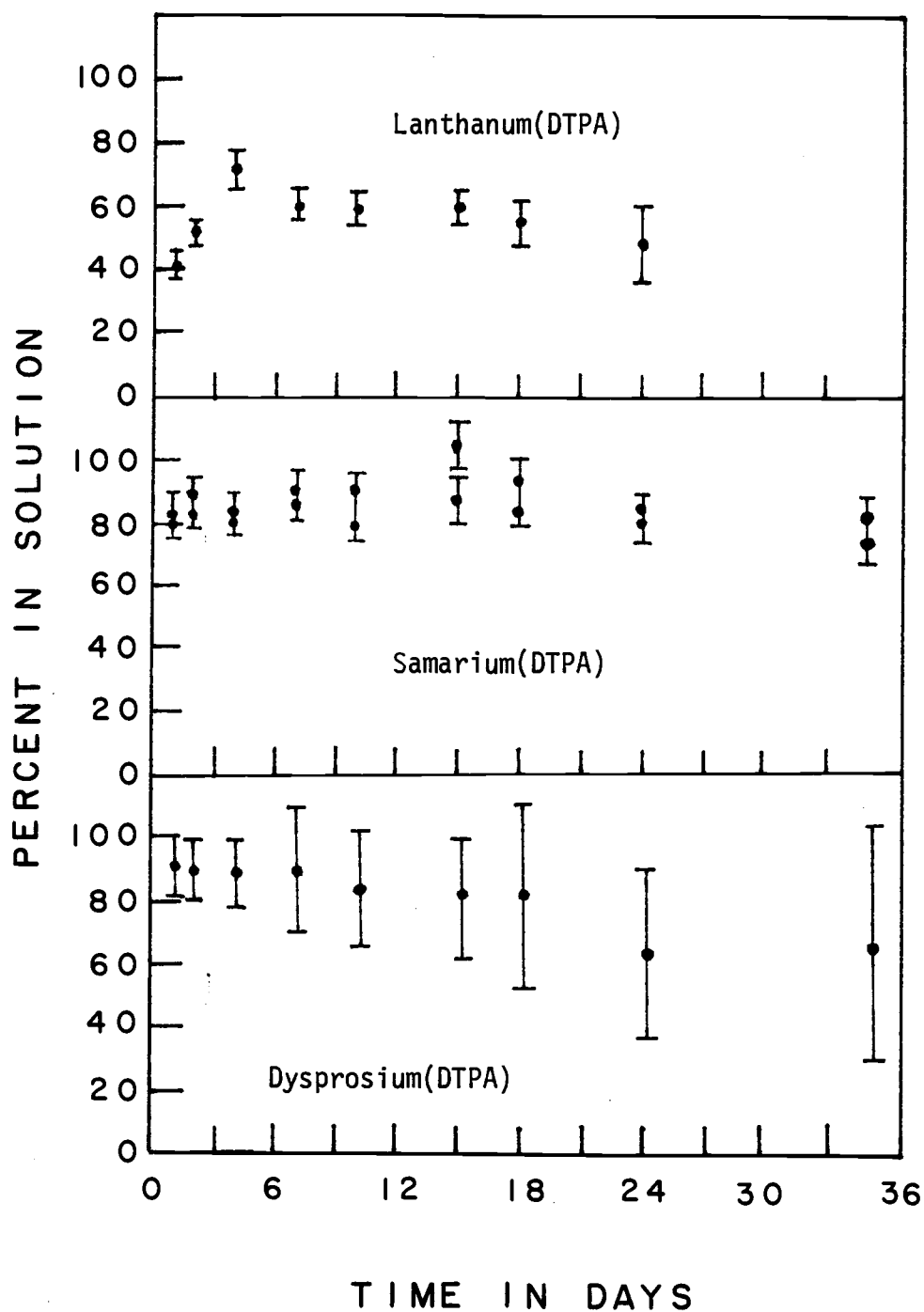


Figure VI-b: Time dependence of rare earth tracer stability test in simulated river water conditions.²⁸

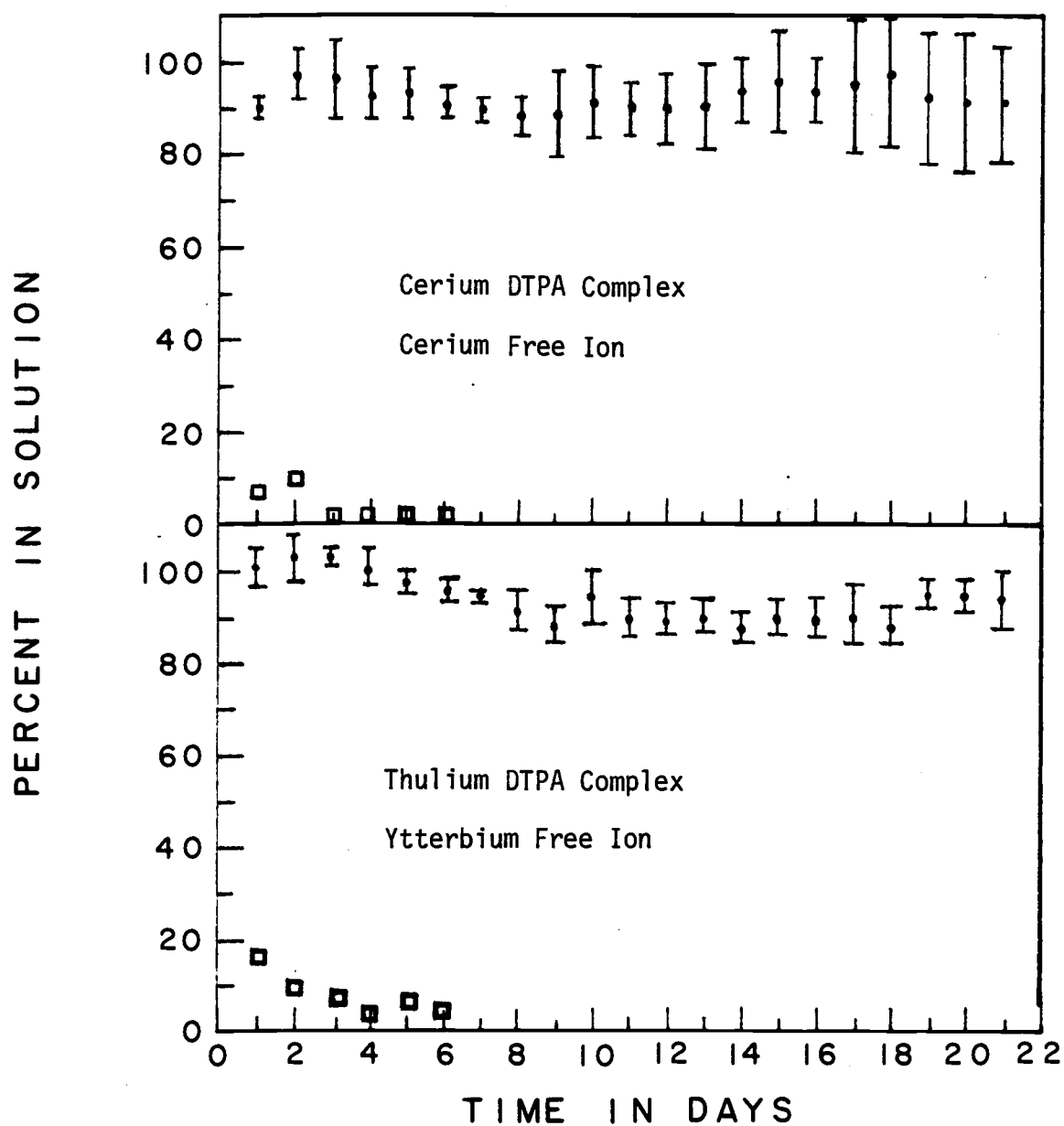


Figure VII: Time dependence of rare earth tracer stability in simulated seawater conditions.

the stability of the rare earth-DTPA complex since the mass of most tagged waters is usually many orders of magnitude higher than the mass of the biological material in most hydrological studies. However, estuaries are known to have areas of extremely high biological activity and in these zones, biological-uptake can have a pronounced effect on the transport of dissolved species. For example, in the Newport Bay estuary, Beaufort, North Carolina, it is estimated that bio-uptake accounts for 10% of the total zinc transport through the estuary.^{81,82} Also, one type of fish (menhaden) which represents approximately 17% of the total fish biomass in the estuary, ingests daily both particulate and dissolved form, about 0.3% of the zinc, 0.7% of the iron and 0.06% of the manganese in the water.⁸³ As for plant life, it was found that marine plankton can remove iron at a rate of 1-8% per hour and zinc at a rate of 1-5% per hour.⁸⁴

Unfortunately, nobody has looked at the effects that biological-uptake has on the transportation of the rare earth elements through estuaries. However, Turekian et al.⁸⁵ has proposed that rare earth elements are removed from the estuaries by planktonic adsorption. An approximation of the rate of removal of rare earth elements in estuaries can be estimated from the relative bioconcentration of some rare earth elements to iron. Some of the bioconcentration factors are 8,300 for lanthanum which compares to 17,000 for iron in brown algae in seawater, and 7,100 for cerium which compares to 4,935 for iron in 19 plant species in freshwater.⁸⁶

From this limited data, one could conclude that the rare earth element(s) are removed from solution by biological processes at approximately the same rate as iron. However, since the rare earth element(s) are complexed with DTPA for the hydrological tracer, one would like to have some comparison between the complexed and uncomplexed rare earth elements. One comparison that is known is for red alder roots, in which nonchelated dysprosium is accumulated eight times faster than the dysprosium-DTPA complex.⁸⁷ From all the bioconcentration for the rare earth elements and iron plus the measured rate of removal of iron by bio-uptake in Newport Bay, one can estimate that the removal rate for the rare earth element(s)-DTPA complexes in estuarine waters should be less than 0.02% per hour.

B. South Shore Marina Experiments

To check the validity of the laboratory tests on the persistence of stable activable tracer in estuarine waters, two field studies were conducted in the South Beach Marina in Yaquina Bay, Newport, Oregon. In the first field study, Dy-DTPA and rhodamine B were mixed together and dumped into the marina. Samples were taken at low and high tides (tidal data can be seen in Table XII), and analyzed for their tracer concentrations (see Appendix D for the measured tracer concentrations). By comparing the marina average concentration of Dy-DTPA to the marina average concentration of rhodamine B as a function of time (Table XIII and Figure

Table XII: Tide Height Measurements for Yaquina Bay during the first
South Beach Marina Experiment

<u>Date</u>	<u>Time (PST)</u>	<u>Tide Height</u>	<u>Change in Height</u>	<u>Elapsed Time in Experiment</u>
August 14, 1980	2130	1.7 ft		0.00 hr
August 15, 1980	0330	6.8 ft	5.1 ft	6.00 hr
	1000	0.7 ft	6.1 ft	13.50 hr
	1615	7.0 ft	6.3 ft	19.75 hr
	2215	1.6 ft	5.4 ft	24.75 hr
August 16, 1980	0415	6.0 ft	4.4 ft	30.75 hr
	1030	1.0 ft	5.0 ft	37.00 hr
	1700	6.9 ft	5.9 ft	43.50 hr

Table XIII: Temporal Stability of Dy-DTPA Relative to Rhodamine B in the first South Beach
Marina Experiment (Aug. 14-16, 1980)

<u>Elapsed Time in Experiment (hrs)</u>	<u>Marina Average Dysprosium - DTPA Concentration (ngDy/ℓ)</u>	<u>Marina Average Rhodamine B Concentration (ng/ℓ)</u>	<u>Dysprosium-DTPA Concentration* Rhodamine B Concentration</u>
19.75 hours	453 ± 13	878 ± 73	1.227 ± 0.109
24.75 hours	547 ± 8	1,176 ± 55	1.057 ± 0.051
37.00 hours	494 ± 7	1,002 ± 41	1.121 ± 0.049
43.50 hours	359 ± 7	734 ± 31	1.113 ± 0.051

*A Dy-DTPA/rhodamine B ratio of 1.0 is equal to the ratio of the amounts of tracer added to the marina.

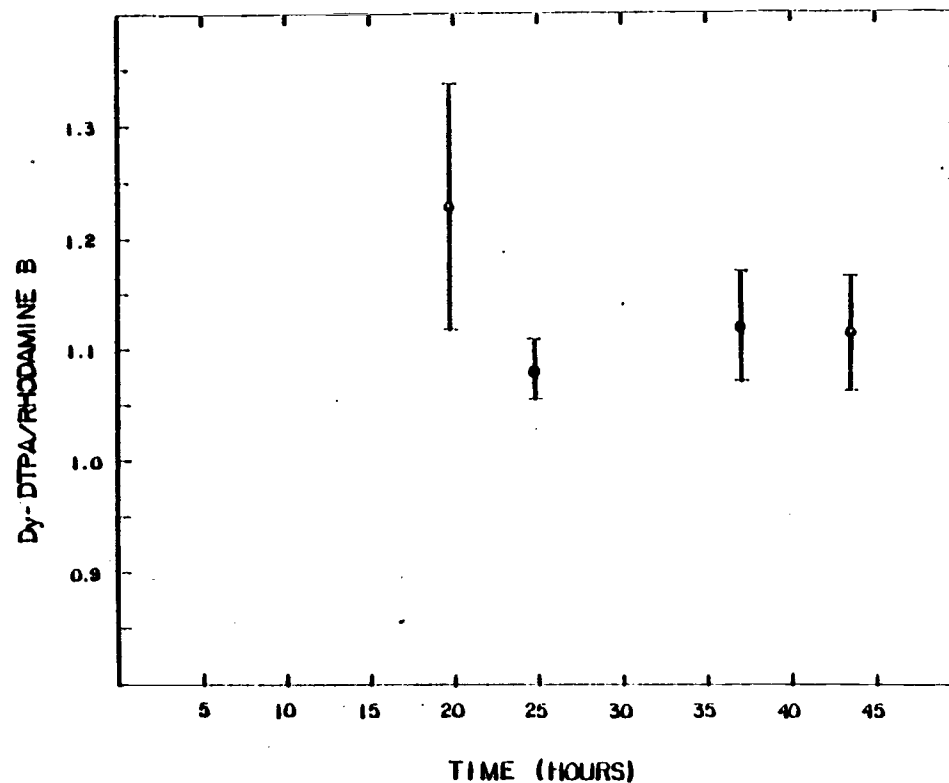


Figure VIII. The persistence of Dy-DTPA tracer relative to rhodamine B tracer in a field study done in the South Beach Marina (Aug. 14-16, 1980); A Dy-DTPA/rhodamine B ratio of 1.0 is equal to the ratio of the amounts of tracer added to the marina

VIII), one would conclude that Dy-DTPA is just as conservative as rhodamine B since the tracer ratio was constant (within experimental uncertainties) over the sampling time. In fact, using a weighted linear regression technique⁸⁸ in which the weighting factor is based on the uncertainty of the experimental data, one would derive that the equation which fits the experimental data is the following:

$$[\text{Dy-DTPA}]/[\text{rhodamine B}] = 1.0825 + 0.00070 (t) \\ \pm 0.1164 \pm 0.00332$$

where

$[\text{Dy-DTPA}]$ = Dy-DTPA marina average concentration at time t

$[\text{rhodamine B}]$ = rhodamine B marina average concentration at
time t

t = the difference in time between when the tracer was added
to the marina and when the samples were taken (hours)

This equation states that the initial $[\text{Dy-DTPA}]/[\text{rhodamine B}]$ ratio is equal to 1.0825 ± 0.1164 with a slope of 0.00070 ± 0.00332 . As can be seen, the slope can be taken as approximately zero since the uncertainty of the slope is much larger than the calculated slope value. The $[\text{Dy-DTPA}]/[\text{rhodamine B}]$ ratio in the slug initially added to the marina (calculated by dividing the mass of Dy-DTPA added to the original tracer solution by the mass of rhodamine B added to the original tracer solution) was normalized to 1.00. The fact that subsequent measurements of this ratio exceed 1.00 is not thought to be significant because

of difficulties in assessing the initial stable activable tracer/dye ratio. However, the calculated value (based upon the weighted linear regression) of the initial $[\text{Dy-DTPA}]/[\text{rhodamine B}]$ ratio (1.083 ± 0.116) does agree within the uncertainty of the calculation with the $[\text{Dy-DTPA}]/[\text{rhodamine B}]$ ratio in the slug initially added to the marina.

In the second field study, Dy-DTPA, Eu-DTPA, and rhodamine WT were placed in the marina to demonstrate the feasibility of using stable activable tracer(s) in a multitracing experiment, and to demonstrate that the stable activable tracers do persist in estuarine waters when compared to the persistence of rhodamine WT. Samples were taken at low and high tides (tidal data can be seen in Table XIV), and analyzed for their tracer concentration (see Appendices D-4, 5, and 6 for the measured tracer concentrations). The general feasibility of performing a multitracing experiment was shown in the second experiment (Table XV and Figure IX) in that one is able to simultaneously determine the concentration of both the stable activable tracers (Dy-DTPA and Eu-DTPA) in the study. Also from Figure IX, one can estimate the general hydrological behavior of the two stable activable tracers relative to each other. One would ideally want all the stable activable tracers to mimic the hydraulic behavior of one another in a multitracing experiment. As one can see from Figure IX and Table XV, the $[\text{Eu-DTPA}]/[\text{Dy-DTPA}]$ ratio does decrease during the time span of the experiment. In fact, using a weighted linear regression⁸⁷

Table XIV: Tide Height Measurements for Yaquina Bay during the
Second South Beach Marina Experiment (Jan 16-18, 1981)

<u>Date</u>	<u>Time (PST)</u>	<u>Tide Height</u>	<u>Change in Height</u>	<u>Elapsed Time in Experiment</u>
January 16, 1981	0200	3.4 ft		0.00 hr
	0830	9.8 ft	6.4 ft	6.50 hr
	1515	0.1 ft	9.7 ft	13.25 hr
	2200	7.3 ft	7.2 ft	20.00 hr
January 17, 1981	0305	3.8 ft	3.5 ft	25.08 hr
	0930	10.2 ft	6.4 ft	31.50 hr
	1615	-0.1 ft	10.3 ft	38.25 hr
	2300	8.0 ft	8.1 ft	45.00 hr
January 18, 1981	0430	4.0 ft	4.0 ft	50.50 hr
	1030	10.3 ft	6.3 ft	56.50 hr

Table XV: Temporal Stability of Dy-DTPA and Eu-DTPA Relative to Rhodamine WT in the Second South Beach Marina Experiment (Jan 16-18, 1981)

<u>Elapsed Time in Experiment</u>	<u>Marina Average Dysprosium - DTPA Concentration (ngDy/l)</u>	<u>Marina Average Europium - DTPA Concentration (ngEu/l)</u>	<u>Marina Average Rhodamine WT Concentration (ng/l)</u>
13.25 hours	832.0 ± 8.3	132.2 ± 1.7	3,758 ± 33
20.00 hours	414.1 ± 6.0	62.9 ± 1.3	1,620 ± 12
31.50 hours	280.5 ± 5.7	56.2 ± 1.5	1,138 ± 9
38.25 hours	311.3 ± 6.5	40.8 ± 1.4	970 ± 8
45.00 hours	70.4 ± 4.6	9.2 ± 0.9	389 ± 4
56.50 hours	44.9 ± 4.9	5.7 ± 1.1	267 ± 3

<u>Elapsed Time in Experiment</u>	<u>Dysprosium-DTPA Concentration* Europium-DTPA Concentration</u>	<u>Dysprosium-DTPA Concentration* Rhodamine WT Concentration</u>	<u>Europium-DTPA Concentration* Rhodamine WT Concentration</u>
13.25 hours	0.959 ± 0.015	0.826 ± 0.011	0.793 ± 0.012
20.00 hours	0.917 ± 0.024	0.954 ± 0.015	0.874 ± 0.020
31.50 hours	1.209 ± 0.041	0.920 ± 0.020	1.113 ± 0.031
38.25 hours	0.791 ± 0.032	1.198 ± 0.027	0.947 ± 0.034
45.00 hours	0.787 ± 0.093	0.674 ± 0.045	0.531 ± 0.053
56.50 hours	0.769 ± 0.170	0.628 ± 0.069	0.483 ± 0.093

*Normalized to where a ratio of 1.0 is equal to the ratio of the amounts of tracers added to the marina

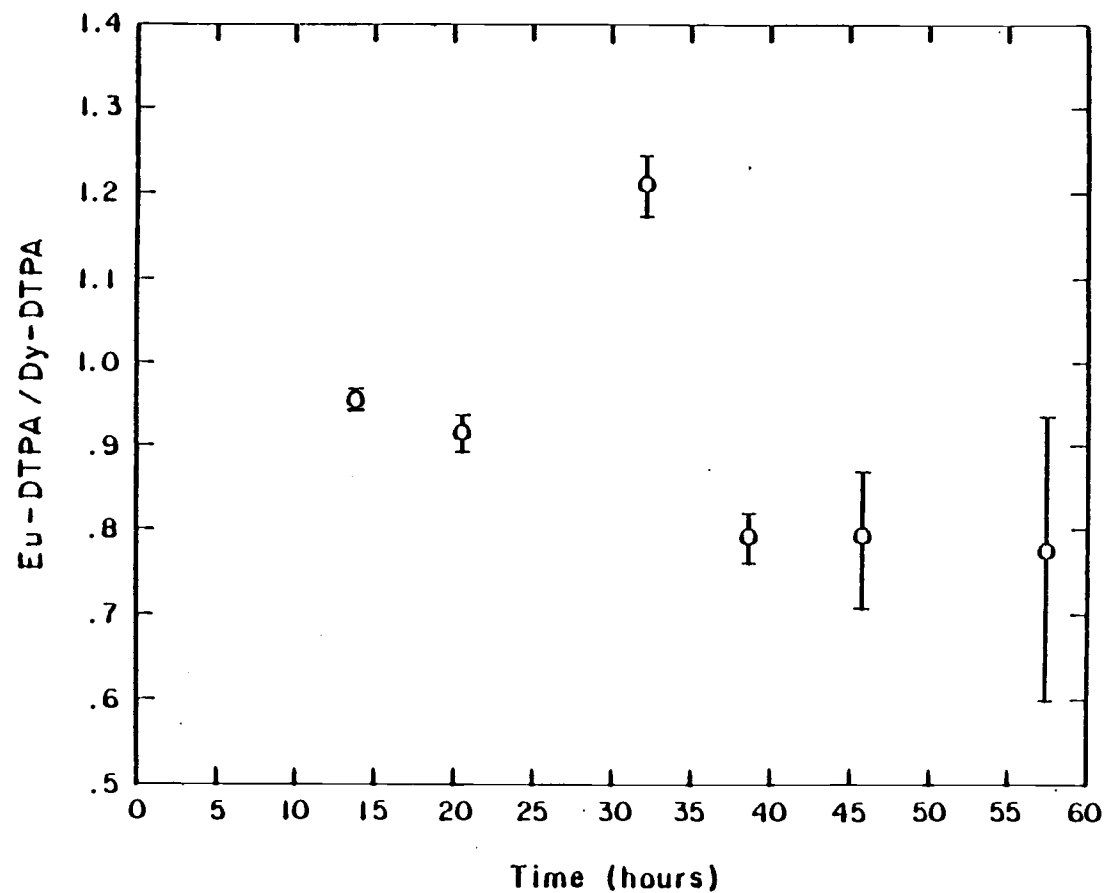


Figure IX: The persistence of Eu-DTPA tracer relative to Dy-DTPA tracer in a field study done in the South Beach Marina (Jan. 16-18,1981); an Eu-DTPA/Dy-DTPA ratio of 1.0 is equal to the ratio of the amounts of tracer added to the marina.

technique in which the weighting factor is based on the uncertainty of the experimental data, one would derive that the equation which fits the experimental data is the following:

$$\begin{aligned} [\text{Eu-DTPA}]/[\text{Dy-DTPA}] = 1.035 - 0.0038 (t) \\ \pm 0.038 \pm 0.0015 \end{aligned}$$

where

$[\text{Eu-DTPA}]$ = Eu-DTPA marina average concentration at time t

$[\text{Dy-DTPA}]$ = Dy-DTPA marina average concentration at time t

t = the difference in time between when the tracers were added to the marina and when the samples were taken (hours)

This equation states that the initial $[\text{Eu-DTPA}]/[\text{Dy-DTPA}]$ ratio is equal to 1.035 ± 0.038 with a slope of -0.0038 ± 0.0015 . Since the $[\text{Eu-DTPA}]/[\text{Dy-DTPA}]$ ratio in the slug initially added to the marina (calculated by dividing the mass of the Eu-DTPA added to the tracer solution by the mass of the Dy-DTPA added to the tracer solution) was normalized to 1.00, the calculated initial $[\text{Eu-DTPA}]/[\text{Dy-DTPA}]$ (based on the weighted linear regression) is in good agreement with the initial $[\text{Eu-DTPA}]/[\text{Dy-DTPA}]$ ratio in the original tracer solution. From the slope of the line, it would indicate that Eu-DTPA was being removed 0.38% per hour faster than Dy-DTPA. This would mean that Dy-DTPA and Eu-DTPA do not have the same hydraulic behavior. However, this difference in the hydraulic behavior can be considered small when one remembers that only about 5% of the mass of the original tracer still

remained in the marina at the end of the experiments (56.50 hours). Also for the last two sampling times, the tracer concentrations were fairly close to the tracer background level, 33.8 ± 7.5 ngDy/l and 4.2 ± 1.0 ngEu/l (determined from samples taken in the marina before the tracer solution was added to the marina), and thus the uncertainty in the background level could easily cause the trend seen in Figure IX. In conclusion, Eu-DTPA and Dy-DTPA tracers do have similar hydraulic behavior, and thus they can be used together in a multitracing experiment.

When one compares the persistence of the stable activable tracer (Dy-DTPA and Eu-DTPA) to the persistence of the rhodamine WT dye (Figures X and XI), the picture is not as clear as was seen in the first field experiment. If one uses the weighted linear regression technique⁸⁷ on this data, one would derive that the linear equations which fit this experimental data are the following:

$$[\text{Dy-DTPA}]/[\text{rhodamine WT}] = 0.806 + 0.0043 (t) \\ \pm 0.018 \pm 0.0008$$

$$[\text{Eu-DTPA}]/[\text{rhodamine WT}] = 0.788 + 0.0026 (t) \\ \pm 0.021 \pm 0.0010$$

where

[Dy-DTPA] = Dy-DTPA marina average concentration at time t

[Eu-DTPA] = Eu-DTPA marina average concentration at time t

[rhodamine WT] = rhodamine WT marina average concentration
at time t

t = the difference in time between when the tracers were

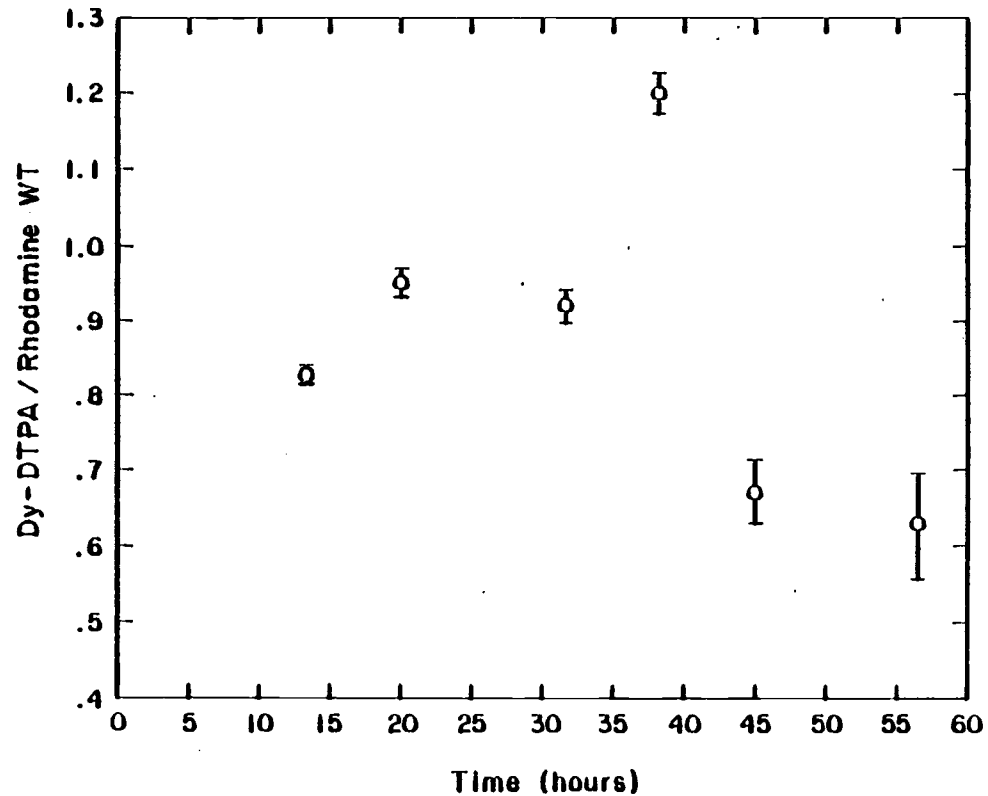


Figure X: The persistence of Dy-DTPA tracer relative to rhodamine WT tracer in a field study done in the South Beach Marina (Jan. 16-18,1981); A Dy-DTPA/rhodamine WT ratio of 1.0 is equal to the ratio of the amounts of tracer added to the marina.

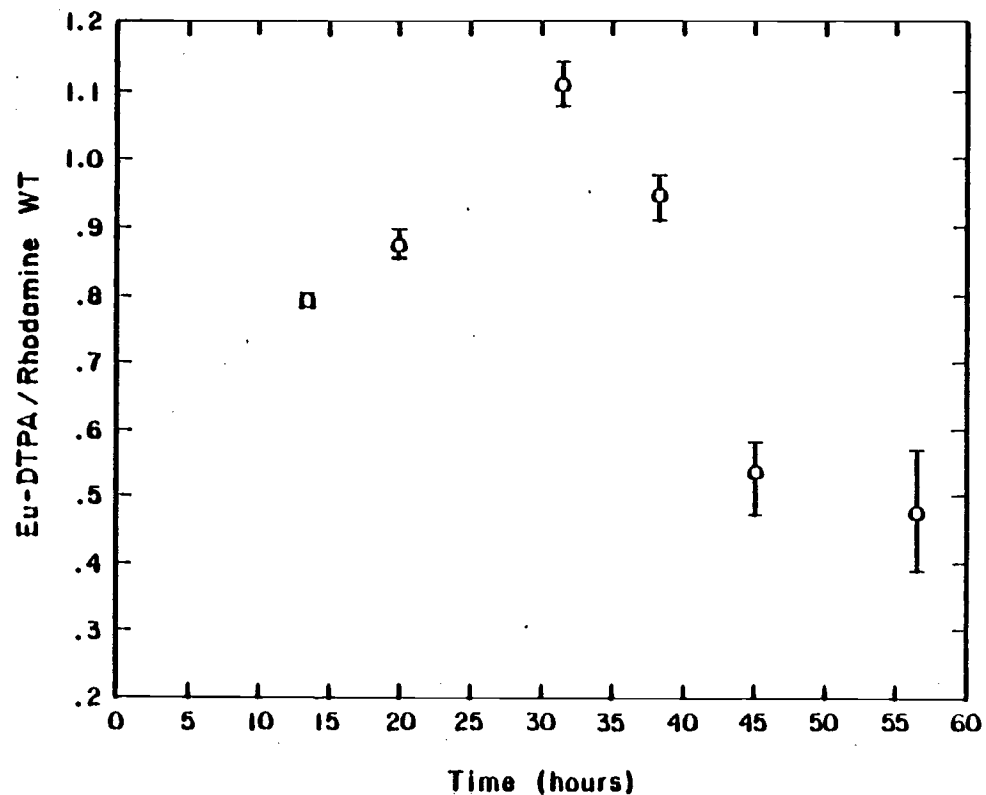
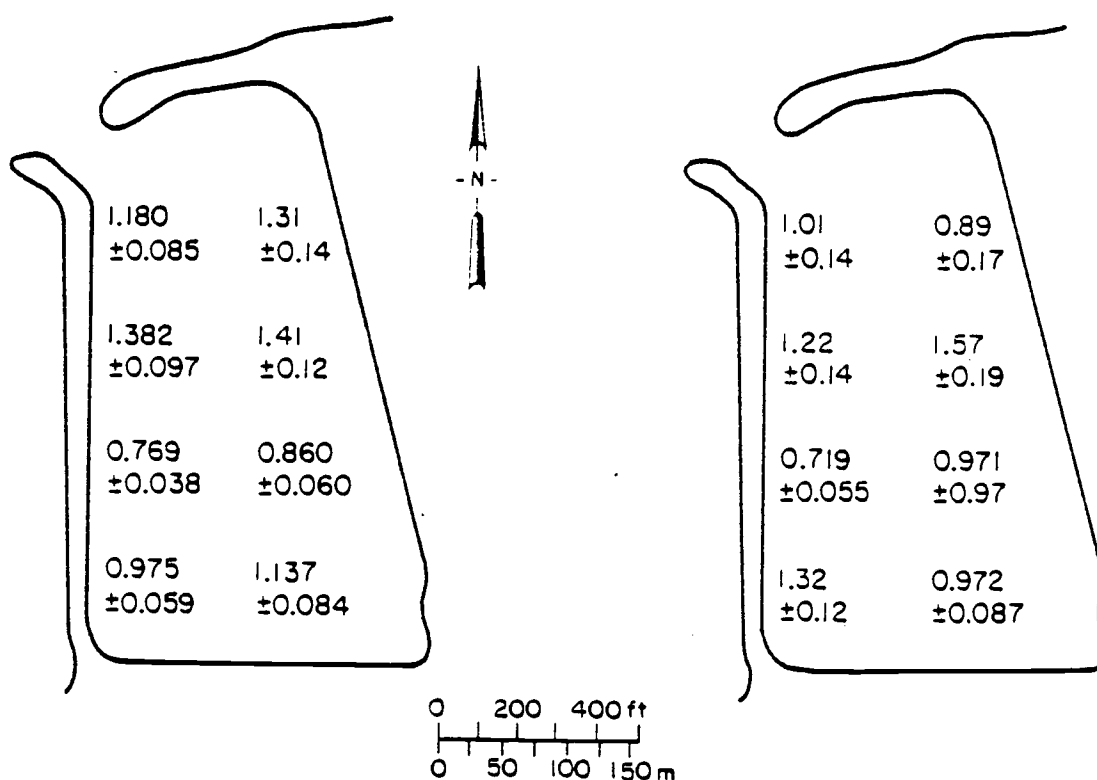


Figure XI: The persistence of Eu-DTPA tracer relative to rhodamine WT tracer in a field study done in the South Beach Marina (Jan. 16-18, 1981); An Eu-DTPA/rhodamine WT ratio of 1.0 is equal to the ratio of the amounts of tracer added to the marina.

added to the marina and when the samples were taken
(hours)

These equations state that the initial $[\text{Dy-DTPA}]/[\text{rhodamine WT}]$ ratio is 0.806 ± 0.018 and that the initial $[\text{Eu-DTPA}]/[\text{rhodamine WT}]$ ratio is 0.788 ± 0.021 . The $[\text{Dy-DTPA}]/[\text{rhodamine WT}]$ and $[\text{Eu-DTPA}]/[\text{rhodamine WT}]$ ratio in the slug initially added to the marine (calculated by dividing the mass of the Dy-DTPA or Eu-DTPA added to the tracer solution by the mass of the rhodamine WT added to the tracer solution) was normalized to 1.00. The fact that the weighted linear regression technique says that the initial $[\text{Dy-DTPA}]/[\text{rhodamine WT}]$ or $[\text{Eu-DTPA}]/[\text{rhodamine WT}]$ ratio is closer to 0.80 is not thought to be significant because of the difficulties in assessing the initial stable activable tracer/rhodamine ratio. It seems of interest that the linear regression technique indicates that the Dy-DTPA and Eu-DTPA tracers are more stable than rhodamine WT. However, this equation does not fit the data points very well, especially the last two sampling times. In fact, the $[\text{Dy-DTPA}]/[\text{rhodamine WT}]$ and $[\text{Eu-DTPA}]/[\text{rhodamine WT}]$ ratios with the tracer ratios generally increasing for the first 38 hours of the experiment and then drastically decreasing for the next 18 hours. Part of the spread of the tracer ratio can be attributed to the problem of estimating the dye background (mostly due to turbidity) during the experiment. The problem was more acute in the second experiment since in the second experiment a much lower dye tracer concentration was used compared

to the first experiment and the marina was open to boat traffic. With the boating activity in the marina during the second field experiment, one would expect the turbidity should widely fluctuate due to local turbulence caused by the boat propellers. This would cause the dye background to also fluctuate. In the case of this marina, as the turbidity increases the measured dye background will also increase due to the light scattering property of the white suspended particulates of the marina and the technique used to measure the dye concentrations. This would cause a large inaccuracy in measuring the dye concentrations and could conceivably cause part of the fluctuation seen in Figures X and XI. Another reason for the fluctuation is that the stable activable tracers seem to have dispersed slightly differently than the rhodamine WT dye tracer in the second experiment. A good example of this difference in dispersion can be seen in Figure XII, where the tracer ratio for each sampling site is plotted for a given sampling time (38 hours). In this Figure, the $[Dy-DTPA]/[rhodamine\ WT]$ and $[Eu-DTPA]/[rhodamine\ WT]$ ratio is normalized to make the measured marina average tracer ratio for that sampling time be unity. As can be seen in Figure XII, the tracer ratios do vary widely from one sampling to another. One can see a plausible reason why the drastic drop in the rare earth-DTPA/dye ratio was seen at the 45.00 and 56.50 hour sampling time. One can see that there is a disproportionate amount of rare earth-DTPA tracer near the exit/entrance of the marina when compared to the



Dy-DTPA / Rhodamine WT

Eu-DTPA / Rhodamine WT

Figure XII: Dy-DTPA/ rhodamine WT and Eu-DTPA/rhodamine WT ratio at the different sampling sites 38.25 hours after injection of the tracers in the marina; a Dy-DTPA or Eu-DTPA/rhodamine WT ratio of 1.0 is equal to the measured marina average Dy-DTPA or Eu-DTPA/ rhodamine WT ratio.

rhodamine WT tracer. Since the tide is going out after this sampling time, this would mean that a disproportionate amount of the rare earth-DTPA tracers would be removed from the marina. This would cause the rare earth-DTPA/rhodamine WT ratio to decrease in the subsequent sampling times, which can be seen from Figures X and XI. The most likely reason behind the different dispersion pattern of the tracers can be attributed to the mixing of the original solution. It is very likely that the rare earth-DTPA/dye solutions were not adequately mixed in the containers used in the experiment before the tracers were dumped into the marina. This would affect where the different tracers were placed in the marina and thus the subsequent dispersion of the different tracers in the marina.

Since this marina had been studied previously^{67,68} resulting in a mathematical model of this marina, one would like to see how the measured flushing rate of the tracers in these field experiments compared to the calculations of the marina model. The model calculation is based upon the assumption that the tracers are uniformly mixed throughout the marina and thus the mass of the tracers in the marina decreases when the tide goes out and the concentration of the tracers decreases when the tide comes in. Unfortunately, in the first experiment the tracers were not adequately mixed throughout the marina to justify the use of the model. However in the second experiment, by the first low tide (13.25 hours) after the tracers were dumped into the marina, the tracers were

evenly distributed throughout the marina such that one could use the model to predict the tracer concentrations for the subsequent sample times. For example, using the tidal data (Table XIV) for this experiment and the marina model, one can calculate the predicted tracer concentrations for the various remaining sampling times (Figure XIII). As one can see from Figure XIII where the experimental and predicted tracer concentrations are compared, the model did predict fairly closely the average measure tracers concentrations. The difference between the measured and predicted values is not surprising since in all three dye experiments performed by Calloway to check the model for this marina,⁶⁸ he found that the model routinely underestimated the tracer removal by as much as 30-40%. Therefore, to the first approximation, the model for the marina does predict that the stable activable tracers are conservative in estuarine waters.

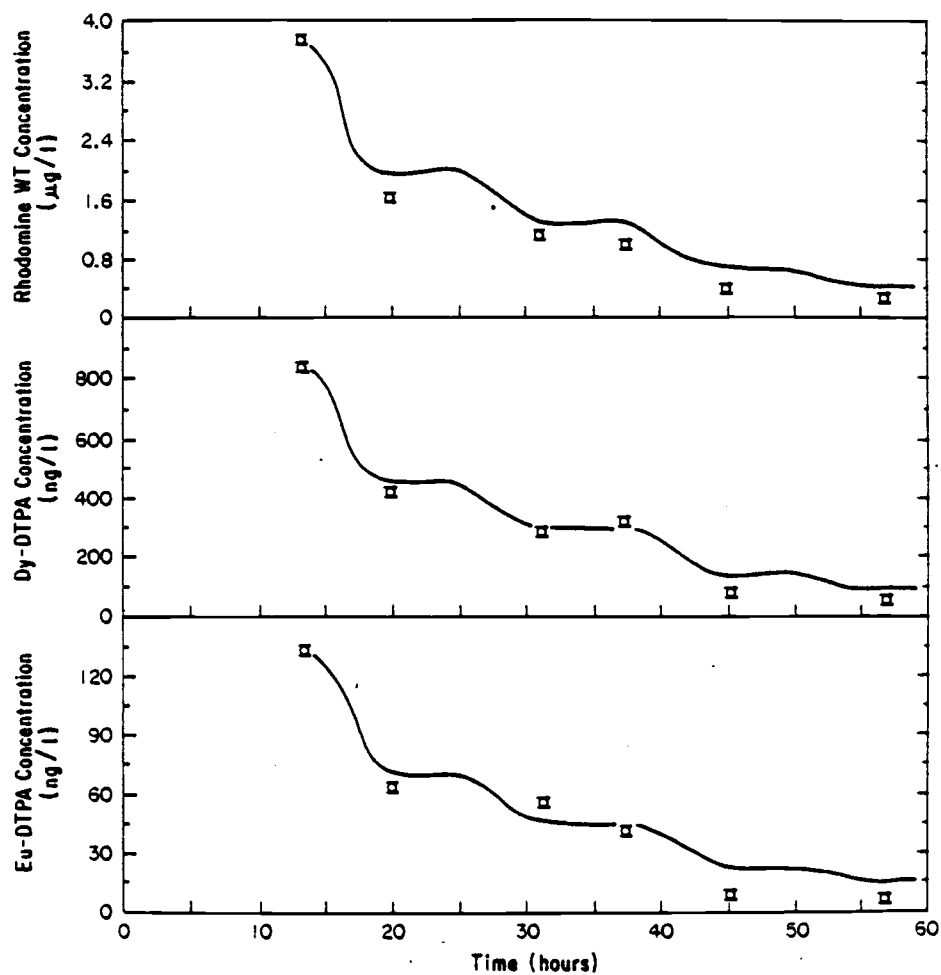


Figure XIII: A comparison between the experimental and model predicted tracer concentrations in the field study done in the South Beach Marina (Jan. 16-18,1981).

V. Conclusion

The use of stable activable tracer(s) as hydrological tracer(s) in an estuarine environment shows much promise and versatility. It has been shown that stable activable tracers are non-toxic at tracer concentrations (less than 100 $\mu\text{g}/\ell$), are economically viable, and are conservative in laboratory studies for up to three weeks. In the field studies which were performed, the feasibility of performing multi-tracing experiments was demonstrated. The field work also indicated that the stable activable tracers are fairly conservative in estuarine waters. In conclusion, stable activable tracer(s) are a viable form of hydrological tracer which can be used in an estuarine environment.

RARE EARTH ELEMENTAL CONCENTRATIONS
IN SOME PACIFIC NORTHWEST RIVERS

I. Introduction

Chemical oceanography has dealt mostly with the study of dissolved and particulate matter in the open ocean; the important interactions, i.e., ocean-atmosphere, sediment-water, as well as river-ocean, have only been recognized recently. There are but a few studies on the river-ocean interface, especially the river inputs to the ocean, which are by far the most important type of continent-ocean interaction. The geochemical cycle of many elements is poorly known, i.e., the total elemental input to the ocean as well as elemental speciation and subsequent oceanic reactivity.

In the case of the rare earth elements, their geochemical behavior in natural waters is essentially unknown. In order to have a better estimate of the global geochemical cycle of rare earth elements, it is of interest to determine their soluble input into the ocean and to compare this input with the output of rare earths from the ocean by authigenic and biogenic material in ocean sediments. Owing to the large uncertainty associated with most of the data used to calculate the rare earth input/output rate from the oceans, this kind of balance must be taken as a first approximation. As an example, we should consider lanthanum. Taking into account the occurrence of calcium carbonate, polymetallic nodules, fish bones, montmorillonite, phillipsite, and barite on the sea floor, one can estimate that the total lanthanum output from the oceans is $2.26 \times 10^{-9} \text{gcm}^{-2}\text{y}^{-1}$,

as shown in Table XVI. From a study on the Gironde estuary,¹⁷ one can estimate the rate of input of lanthanum into the oceans as $0.25 \times 10^{-9} \text{gcm}^{-2}\text{y}^{-1}$. If both the estimated input and output rates are accurate predictors of the true input/output rate for lanthanum in the oceans, then one would conclude that lanthanum is being removed from the oceans nine times faster than it is entering into the oceans. If this global imbalance is true, then one would expect to see a steady decline in the concentrations of rare earth elements in the oceans. However, there is no evidence that this trend is occurring.¹⁰⁰ Therefore, one would conclude that either the calculated output rate is wrong or that the calculated input rate is in error.

The calculated global lanthanum output rate from the oceans (Table XVI) is considered fairly accurate. However, the calculated global lanthanum input rate into the oceans is not considered very accurate. The reason for its questionable accuracy is that only one measurement¹⁰⁰ of soluble lanthanum concentration of two rivers (Dordogne and Garonne) from the same estuary (Gironde) was used to estimate the average global river concentration of lanthanum. Also, the average global lanthanum behavior in estuaries was estimated from only one study from the aforementioned estuary.¹⁷ In that study, they concluded that approximately 50% of the lanthanum supply in the rivers was removed in the estuaries before it reaches the oceans, and thus only one-half of the rare earth supply from the rivers can be considered

Table XVI: Lanthanum Output from the Ocean¹⁷

Method of Removal	Accumulation Rate ($10^{-6}\text{gcm}^{-2}\text{yr}^{-1}$)	Lanthanum Concentration (ppm) ^{85,96,97,98}	Lanthanum Accumulation Rate ($10^{-9}\text{gcm}^{-2}\text{yr}^{-1}$)
CaCO_3^{a}	60	1	0.06
Polymetallic nodules ^b	0.2	250	0.05
Fish bones ^c	0.15	2000	0.30
Montmorillonite ^d	15	100	1.60
Barite ^e	1	--	--
Phillipsite ^f	1.5	150	0.25
Total Output			2.26

a: CaCO_3 equals 40% of the pelagic sediment⁸⁹ which is deposited at a rate of $2 \times 10^{-3}\text{mmyr}^{-1}$,⁹⁰ i.e., $150 \times 10^{-6}\text{gyr}^{-1}$ assuming a sediment concentration of 0.7 g/cm^3 .

b: Polymetallic nodules accretion rate is $10^{-6}\text{gcm}^{-2}\text{yr}^{-1}$.^{91,92}
They cover 20% of the sea floor.⁹³

c: Fish bones equal 0.1% of the total sediment.

d: Montmorillonite equals 30% of the clay materials, half of which is assumed to be authigenic.⁹⁴

e: Barite equals 1% of the sediment on a carbonate free basis.⁹⁵

f: Phillipsite equals 1% of the total sediment.⁸⁵

to ever reach the oceans. The removal of the soluble rare earth elements in estuaries has recently been confirmed in a laboratory experiment performed by Hoyle and Elderfield.¹⁰¹ In their study, they found that between 50-80% of the soluble rare earth elements are removed over a salinity range of 0-10% during estuarine mixing.

The validity of using only two measurements of soluble lanthanum concentration to estimate the global average soluble lanthanum concentration in rivers is, of course, questionable. However in this case, it was necessary for Piper⁹⁸ and Martin *et al.*¹⁷ to use these measurements in their estimation of the lanthanum input rate into the oceans, since most of the other measurements of lanthanum in rivers are of questionable accuracy. For example, in one study of the Columbia River,^{102a,b} the lanthanum concentration was measured by neutron activation analysis without removing the uranium from the samples. Thus part of the measured lanthanum concentration was due to uranium which had fissioned during the neutron activation. The greatest common error in previous studies involved acidifying the water samples before removing the suspended particulates.^{103,104,105} This procedure could cause leaching of the REE from the particulates leading to artificially elevated REE levels. To illustrate the possible implication of this procedure, one can look at the study by Kolesov *et al.*¹⁰⁵. In that study, they demonstrated that the total rare earth concentration is correlated to the amount of suspended material in the river

water. It is possible that this correlation does occur, but it is more likely that part of the correlation comes from the rare earth elements being leached from the suspended material as part of the analytical procedure used in the aforementioned studies. 103,104,105

Because of the lack of good experimental data on the concentrations of soluble rare earth elements in rivers, this researcher decided to measure the rare earth elemental concentrations in seven Pacific Northwest rivers (Columbia, Fraser, Klamath, Marys, Rogue, Sacramento, and Willamette). Some laboratory experiments were also concurrently conducted in an attempt to identify any rare earth elemental adsorption behavior in the rivers and to identify any correlation between soluble rare earth elemental concentrations and pH. Also, some theoretical calculations based upon the solubility of lanthanum and europium complexes were done in an attempt to correlate this information to the measured soluble rare earth elemental concentrations in river water. Using all this information, the geochemistry of the rare earth elements will be conceptually explained, and also the lanthanum input/output rate in the oceans will be discussed.

II. Experimental

A. Field Experiments

The rivers studied in this work (see Table XVII for a description) represent a typical cross section of major rivers in the Pacific Northwest region of the United States. They range in annual flow rate from 457-193,500 cfs. Four of the rivers (Columbia, Mary, Sacramento, and Willamette) are used extensively for irrigation while two of them (Klamath and Rogue) drain more remote, heavily wooded areas.

1. Sampling Procedure

In the first set of experiments (April 25-May 2, 1981), three 10 liter samples were collected from the surface of each river with clean Nalgene containers (see Tables XVII and XVIII for a description of the sampling location and conditions). These samples were rushed to a laboratory near the collection site where the samples were filtered within 2-14 hours after sampling through a 0.45 μ m Millipore filter paper to remove the suspended particulates. After filtration, the filtrate was acidified using hydrogen chloride gas and transported to Corvallis, Oregon.

In the second set of experiments (Sept. 1-Sept. 24, 1982), two 10 liter samples were collected from the surface of each river with clean Nalgene containers (see Tables XVII and XVIII for a description of the sampling location and conditions). These samples were rushed to the Corvallis laboratory where one 10 liter

Table XVII: Information about the Pacific Northwest Rivers Studied in this Report

River	Annual Flow Rate (cfs)	Drainage Area (sq. miles)	Comments
Columbia	193,500	259,000	Used very heavily for irrigation upstream of sample site
Fraser	103,120	91,000	Glacier-fed river with some irrigation near sample site
Klamath	8,121	15,640	Drains area with dense timber
Marys	457	329	Used very heavily for irrigation
Rogue	3,486	5,160	Drains wooded area
Sacramento	11,440	26,000	Used very heavily for irrigation
Willamette	37,830	12,045	Used very heavily for irrigation

Table XVIII: Sampling Location and Conditions

River	Location*	Date	Temperature (°C)	pH	Dissolved O ₂ (ppm)	Total Filterable Material (mg/ℓ)	Inorganic† Filterable Material (mg/ℓ)	Flow Rate at Sampling Time (cfs)
Columbia	Vancouver, WA	5/2/81	18.0±.5	7.85±.02				209,800
	"	" 9/1/82	25.5±.5	6.88±.02	7.9		2.3	82,000
	"	" 9/8/82	23.8±.5	6.90±.02	8.5	1.9	1.1	113,000
	Portland, OR	9/15/82	21.0±.5	6.81±.02	9.0	4.6	2.9	107,000
	"	" 9/22/82	23.0±.5	7.75±.02	8.7	2.2	1.6	217,000
Fraser	Agassiz, B.C.	5/1/81	15.0±.5	7.15±.02				111,240
Klamath	Orleans, CA	4/27/81	19.0±.5	7.48±.02				5,930
Marys	Corvallis, OR	9/10/82	19.0±.5	6.66±.02	9.2	6.5	4.1	19
	"	" 9/17/82	20.0±.5	7.45±.02	9.3	5.7	2.7	18
Rogue	Grants Pass, OR	4/27/81	18.0±.5	7.27±.02				2,280
Sacramento	Colusa, CA	4/25/81	19.0±.5	7.55±.02				8,900
Willamette	Corvallis, OR	9/3/82	19.5±.5	6.18±.02	8.8		0.94	6,050
	"	" 9/13/82	19.0±.5	6.24±.02	9.4		1.3	7,360
	"	" 9/20/82	18.8±.5	7.12±.02	9.2	1.3	1.3	7,610
	"	" 9/24/82	20.0±.5	7.21±.02	9.1	1.6	1.6	8,520

*Nearest town to location where sample was taken

†Based upon the weight of the filterable material after ashing at 600°C

sample was filtered through a 0.2 μm Nucleopore filter paper, and the other 10 liter sample was filtered through a 0.45 μm Millipore filter paper to remove the suspended particulates. After filtration, the filtrate was acidified using hydrogen chloride gas.

2. Determination of the Soluble Rare Earth Elemental Concentration

a. Pre-Irradiation Chemistry

The analytical procedure used to measure the soluble rare earth elements concentration in river water was a modified version of the Goldberg *et al.*²⁹ procedure. The procedure consists of adding ^{144}Ce (0.0033 μCi) and ^{170}Tm (0.024 μCi) radiotracers along with 75 mg iron carrier to the water samples immediately after arrival in Corvallis. The radioactive tracers and iron carrier were allowed to equilibrate with the river water for a minimum of one week before the iron was precipitated. The precipitation was done with ammonia gas which was bubbled through the river water until the pH was between 8.6 and 9.4. A pH of 8.6 or greater was needed to precipitate the iron carrier from the solution and also to efficiently scavenge the rare earth elements. The pH was kept below 9.4 to ensure that no other elements (i.e. magnesium and calcium) would also precipitate out of solution. The precipitate was allowed to settle with occasional decanting of some of the supernatant. When only 1-2 liters remained of the solution, the solution was centrifuged and the final supernatant was decanted.

The precipitate was dissolved in a minimum amount of Baker

ultrapure concentrated hydrochloric acid or concentrated hydrochloric acid made by bubbling hydrogen chloride gas through doubled deionized water (4 ml), and the resulting solution was poured into an anion exchange column (1 1/2 diameter x 15 cm, Dowex 1 x 8, 100-200 mesh). This column was prepared by conditioning the column with 100 ml of 0.05 N hydrochloric acid and 50 ml of 10 N hydrochloric acid. The samples were eluted with approximately 45 ml of 10 N hydrochloric acid. This procedure allows the REE to pass through the column while retaining on the column iron and uranium. Three mg of iron was added to the eluate and the rare earth elements were re-precipitated by bubbling ammonia gas through the solution. After centrifuging the samples, the supernatant was removed and the precipitate was washed several times with double-distilled deionized water. The samples were air dried and placed in 2/5 dram polyvials for irradiation.

b. Irradiation

The first set of samples (1981) were irradiated in the rotating rack of the OSU TRIGA research reactor for 6.5 hours in a neutron flux of 3×10^{12} neutrons/cm²/sec. Due to instrumental failure, I was not able to analyze the samples until many days later, and since there are many short-lived rare earth products which one wants to use to analyze for the rare earth elemental concentration, the samples were re-irradiated 14 days later for 7.0 hours at the same neutron flux. The samples were allowed to decay overnight before post-irradiation chemistry was per-

formed. The second set of river samples (1982) were irradiated for 7.0 hours at a neutron flux of 3×10^{12} neutrons/cm²/sec.

c. Post-Irradiation Chemistry

The activated samples were dissolved in concentrated hydrochloric acid and to the resulting solution 3 ml of rare earth elemental carrier (Appendix E-1), 5 ml of iron (3 mg/ml), and 1 ml of sodium hydrogen sulfite (1M) were added. Ammonia gas was used to precipitate the iron carrier which scavenged the rare earth elements. The samples were centrifuged and the supernatant decanted from the precipitate.

The following procedure was repeated 3-4 times to remove all the scandium, iron, etc. from the samples. It consisted of dissolving the precipitate from the previous steps in a minimum amount of concentrated hydrochloric acid and transferring the solution to polycarbonate centrifuge tubes. Precipitation of the rare earth fluorides was accomplished by the addition of 1 ml of concentrated hydrofluoric acid and 2 ml of saturated ammonium bifluoride. The supernatant was discarded after centrifuging. Two ml of saturated boric acid and 0.5 ml of concentrated nitric acid were added to the precipitate and the resulting solution was heated for 15 minutes to dissolve the rare earth fluoride precipitate. The rare earths were re-precipitated with ammonia gas, and the supernatant was again discarded after centrifuging. After this procedure was repeated 3-4 times, the precipitate was washed twice with double-distilled deionized water, and was dis-

solved in minimum amount of nitric acid. One ml of the resulting solution was placed in a 2/5 dram polyvial, and was analyzed by gamma ray spectroscopy approximately 1 day, 3-6 days, 7-16 days, and 26-37 days after activation. The equipment used consisted of a multichannel analyzer (2048 or 4096 channels) coupled with a Ge(Li) detector. The gamma rays and half-lives used in the determination of the soluble rare earth elemental concentrations can be seen in Appendix F-1.

d. Yield Determination

The chemical yield for this procedure was determined by calculating the yield for the ^{144}Ce and ^{170}Tm radioactive tracers with the determination of the post-irradiation yield of the rare earth carrier (determined by reactivating the samples several months later). Although in this study the chemical yield for all the REE could have been determined using only the ^{144}Ce tracer yield, the ^{170}Tm and post-irradiation yields were determined to ensure no fractionation or anomalies occurred during the experimental procedure.

3. Determination of the Elemental Concentrations in the Filterable Material

a. Pre-Irradiation Procedure

The elemental concentrations in the filterable material from the river water samples were determined by filtering a known amount of river water through a tared $0.45\ \mu\text{m}$ Millipore filter

paper. The filtered solid sample was allowed to air dry over several days before the filter was reweighed to determine the concentration of the suspended particulates in the river water sample. The filter paper was then ashed at 600°C overnight in a porcelain crucible to determine the percent of inorganic particulates in the filterable material. The ashed sample was then prepared for irradiation by placing the sample in a 2/5 dram polyvial.

b. Irradiation and Analysis

Because of the wide range of half-lives of the radionuclides used to determine the elemental concentration in the filterable material (see Appendix F-2), two analysis procedures were used. In the first analysis procedure, the samples were irradiated in the pneumatic tube of the OSU TRIGA research reactor for one minute in a neutron flux of 1×10^{13} neutrons/cm²/sec. These samples were analyzed by gamma ray spectroscopy approximately 5-10 minutes, 1-2 hours, 4-8 hours, and 3 days after irradiation. Six days after the first irradiation, the samples were re-irradiated in the rotating rack of the OSU TRIGA research reactor for 6.0 hours in a neutron flux of 3×10^{12} neutrons/cm²/sec. These samples were analyzed by gamma ray spectroscopy approximately 2-3 days and 4-6 weeks after irradiation. Roughly, the first analysis procedure was used to determine the elemental concentration of elements whose product radionuclide have a half-life of less than 2 days, while the second analysis procedure was used

to determine the elemental concentration of elements whose product radionuclide have a half-life of greater than 12 hours. The gamma rays and half-lives used in the determination of the elemental concentrations in the filterable material can be seen in Appendix E-2.

B. Laboratory Experiments

1. Rare Earth Elemental Concentration at Different pH Values

In this study, the pH of the river water in contact with river sediments was varied in the attempt to see if pH has any effect on the solubility of the rare earth elemental concentrations in river water.

The procedure which was used consisted of taking 3 kg of river sediment and 10 liters of river water and placing them into a Nalgene container. The pH of the solution was adjusted to a given pH value by bubbling either hydrogen chloride or ammonia gas through the solution. The mixture was periodically agitated and the pH of the solution was measured over time. When the pH of the solution remained constant (a pH change of less than 0.05) for at least two days, the solution was then analyzed for its soluble rare earth elemental concentrations. The procedure which was used for the analysis of the soluble rare earth elemental concentrations consisted of the same procedure as in the field work with the exception that only a 0.45 μm Millipore filter paper was used to filter out the filterable material and

no post-irradiation chemistry was performed on these samples.

2. Adsorption Studies

Adsorption studies were conducted with a ^{170}Tm radiotracer in order to tell whether or not adsorption phenomenon has anything to do with controlling the soluble rare earth elemental concentration in river water.

The procedure which was used consisted of taking 10 grams of Willamette River sediment (sieved through a 297 micron sieve) and 100 ml of the Willamette River water and placing them into a 125 ml erlenmeyer flask. The pH of the solution was adjusted to a given pH value by adding drops of either sodium hydroxide or nitric acid solution. The mixture was periodically agitated and the pH of the solution was measured over time. When the pH of the solution remained fairly constant (a pH change of less than 0.10) for at least two days, a ^{170}Tm radiotracer (4.4 μg of Tm) was added to the solution and the pH of the solution was readjusted to the same pH value as occurred before addition of the ^{170}Tm radiotracer. A one ml sample of the solution was taken and analyzed in a NaI well-type detector for the ^{170}Tm radiotracer activity. After a specified period of time (1 or 2 days), another one ml sample was removed from the solution and analyzed for the ^{170}Tm radiotracer activity. The pH of the solution was measured again after the adsorption studies were completed, and any sample in which the change of pH of the solution was greater than 0.25,

the sample was thrown out of the data set. From kinetic experiments reported in Section IV-A of the stable activable tracer part of this thesis, one would estimate that after one day the ^{170}Tm radiotracer concentration should reach 70-80% of its equilibrium value while after two days the ^{170}Tm radiotracer concentration should reach 85-95% of its equilibrium value.

III. Results and Discussion

In the literature, one finds many plausible mechanisms for the controlling factor in the soluble rare earth elemental concentrations in river water. In fact, the number of proposed mechanisms is so large that one has the feeling that the number is limited only by the author's imagination. In reviewing the literature, this author feels that there are only two viable controlling reactions for the soluble rare earth elemental concentrations in river water. These reactions are:

1. an adsorption reaction with the suspended particulates.
2. the solubility of the rare earth phosphate.

The following discussion will talk about each mechanism in light of the research presented in this thesis and the results done by others. Also, a brief discussion concerning the lanthanum input/output rate in the oceans will be presented at the end of this section.

A. Adsorption

Particulates present in rivers, estuaries, and oceans are comprised of a diverse mixture of component "phases" ranging from clays to metal oxides to organic detritus.^{106,107,108} A mixture of such materials would be expected to have a wide range of surface chemical properties and, by inference, a wide range of trace-metal adsorption characteristics. This complex situation might be simplified if most particulate surfaces were coated with

a limited array of materials, thereby occluding the underlying bulk material matrix and decreasing the degree of surface chemical heterogeneity. Substantial evidence exists suggesting that natural organic compounds (e.g., humics) and the hydrous oxides of iron and manganese are important surface phases in environments ranging from seawater to soils.^{109,110,111,112,113}

Hydrous metal oxide and organic coatings, together with the underlying bulk material matrix, may be combined conceptually to create a model particulate phase with a given metal adsorption behavior. Overall adsorption characteristics of a natural material for a particular trace metal would be expected to vary as the relative proportioning of surface sites among the component metal adsorbing phases changes. This conceptual approach suggests that information concerning the metal adsorption behavior of a single adsorbant phase system might be used to understand the behavior of more complex natural materials. Adsorption studies of single component systems have been accomplished for a range of model solids, and the observed experimental behavior has been shown to be consistent with fundamentally based conceptual models.¹¹⁹ Pertinent studies have investigated the adsorption/complexation characteristics of humic and hydrous oxide coating materials and have defined their intensity and capacity factors for binding with a number of trace metals. Specifically, natural organic isolates such as humic and fulvic acid compounds have been characterized as to their complexation of Cu, Cd, Pb,

and other metals.^{115,116,117} The adsorption of Cd, Cu, Pb, Zn onto amorphous $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and other hydrous oxides has been studied over a wide range of adsorbate-to-metal concentrations as a function of variable pH.^{114,118} These studies suggest general characteristics likely to be observed in multicomponent natural solid systems. The results for cation adsorption by hydrous oxide^{118,119} can be summarized as follows:¹²⁰

1. Fractional trace-metal adsorption as a function of pH typically increases sharply over a narrow range of 1 to 2 pH units (the "pH adsorption edge").
2. The fraction of metal adsorbed increases with increasing solid concentration at fixed total metal concentration and constant pH. This behavior is directly analogous to the titration of a metal cation with a dissolved complexing ligand.¹¹⁹
3. At a fixed solid concentration and very low adsorption site occupancies (e.g., less than 1%), fractional metal adsorption increases as the total metal concentration decreases at constant pH. This behavior is attributed to variations in site-metal binding energies due to differences in the nature of surface sites present.^{118,119}
4. For the same adsorbant and pH the fraction of metal adsorbed varies with differing metal cations (at equivalent total metal - adsorbant concentrations ratios). This is attributed to differences in the site bonding energies for different trace metals.¹¹⁹

By comparing these expected results for cation adsorption to field and laboratory rare earth elemental results, one should be able to accurately postulate whether or not adsorption is the controlling factor for the soluble rare earth elemental concentrations in natural water. For example, according to the second statement, the rare earth elemental concentrations should decrease as the suspended particulate concentration increases if adsorption is the dominant mechanism. However, there have been two rare earth elemental studies in which the opposite correlation has been noticed. In the first study by Kolesov *et al.*¹⁰⁵, the correlation was very questionable due to the analytical procedure that was used to analyze the soluble rare earth elemental concentrations in river water. The particular problems with this correlation has already been discussed in detail in the Introduction section. In the second study,^{121,122} the soluble lanthanum concentration in seawater has roughly the same profile as the suspended particulate concentration in seawater. Since the rare earth elemental concentration exhibits the opposite correlation with the suspended particulate concentration which one would expect to see for an adsorption mechanism, one concludes that this study is a good indication that adsorption does not control the soluble rare earth elemental concentration in natural water. Unfortunately, this study is not conclusive since many parameters were not measured in the study. For example, the concentration of sulphate, humic substances, carbonate and hydronium ions, could

effect the adsorption process. Because of the problems associated with the first study and the paucity of data in the second study, one should consider these studies as good but not conclusive evidence that the rare earth elemental concentrations in natural waters are not controlled by adsorption.

A more convincing argument that the soluble rare earth elemental concentrations in river water are not controlled by the adsorption of the rare earth elements on the suspended particulates is based upon the first general characteristics of cation adsorption which is that the fractional trace-metal adsorption as a function of pH typically increases sharply over a narrow range of one to two pH units. This characteristic is called the adsorption edge and has been observed in metal oxide surfaces and for soil systems.^{120,123,124,125,126,127,128,129} A theoretical explanation of this observed phenomenon is that the hydronium ion is competing with the metal cation for the adsorbing sites.¹³⁰ Other important factors which could cause this observable phenomenon is the change in the metal speciation and the adsorption sites (i.e. effective bonding energies) as a function of pH.^{120,124} From the ^{170}Tm adsorption experiment, one can see, Figure XIV or Appendix G, that there is no evidence for an adsorption edge. This observation is very convincing but not necessarily conclusive evidence that the soluble rare earth elemental concentrations are not controlled by the adsorption of rare earth elements on the suspended particulates. In conclusion, from

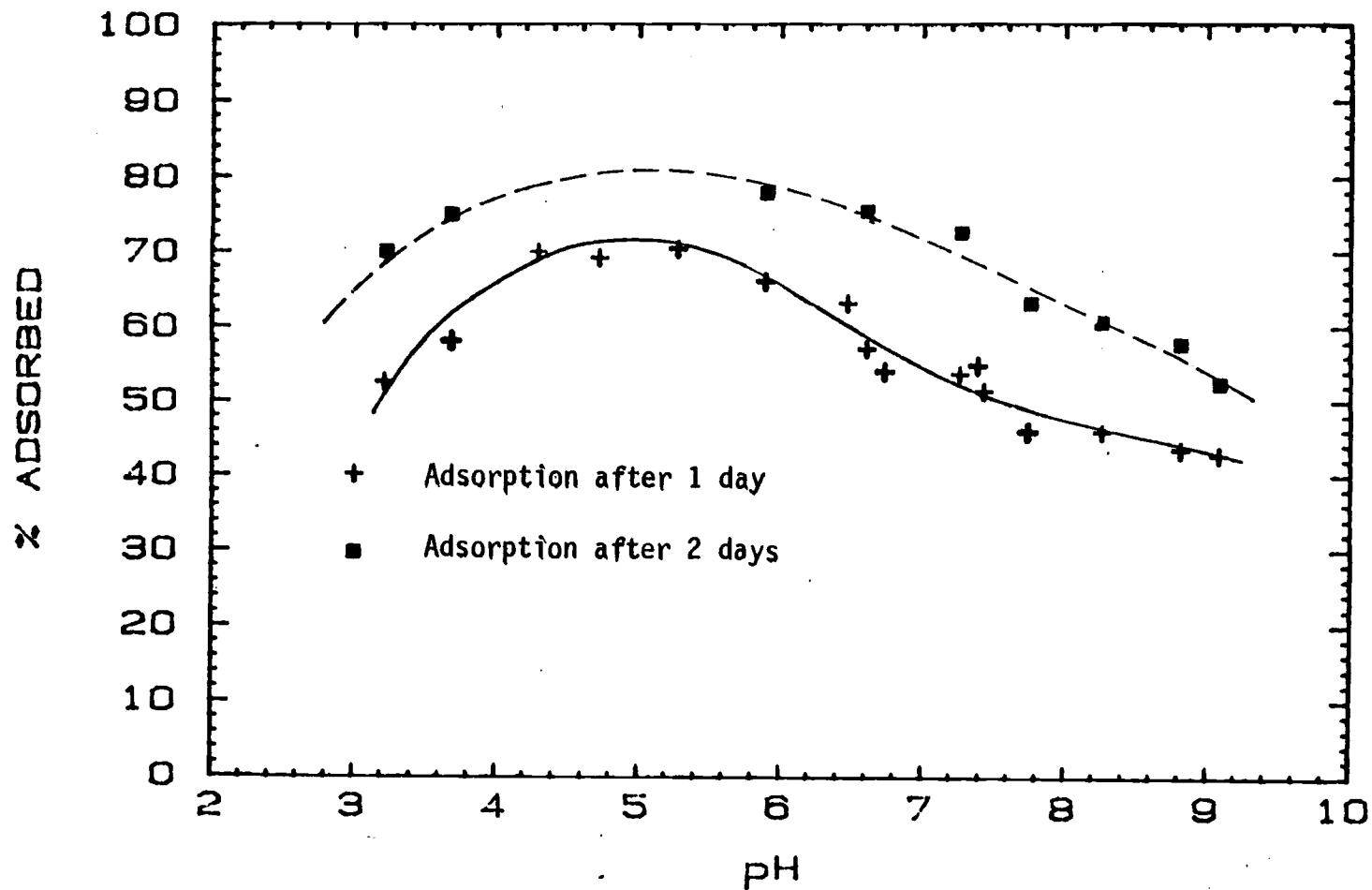


Figure XIV: Adsorption of ^{170}Tm on river sediments as a function of pH. The lines drawn through the data point are to guide the eye and do not reflect results from either a theoretical model or statistical manipulation of the data.

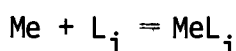
all the circumstantial evidence mentioned in this section, one concludes that adsorption is not the controlling mechanism for the soluble rare earth elemental concentrations in river water.

B. Theoretical Speciation Calculation

At the present time, there seems to be no good theoretical calculation of the equilibrium speciation of the rare earth elements. In fact, this researcher has found only one paper by Turner et al.¹³¹ which even addresses the question of the speciation of the rare earth elements in river water. In this paper, Turner et al. were forced to use many extrapolated and questionable values for the stability constants of many rare earth complexes. Also, Turner et al. were more interested in calculating the major speciation pattern of 58 elements in natural waters than the specific speciation of a given element or group of elements. Thus, they did not take into account many rare earth complexes which could effect the calculation of the speciation of the rare earth elements in river water. Because of the aforementioned reasons, their calculation on the speciation of the rare earth elements should be considered as a first approximation. Since this paper, new values of the stability constants of many rare earth complexes have been published.¹³² This allows one to extrapolate from this new data base a more accurate value for the unmeasured stability constant of some rare earth complexes, and in many cases this new data base has a measured stability constant for some of the previously unmeasured rare earth com-

plexes. Using this extended data base, this researcher calculated the speciation of lanthanum and europium in river water by the following mathematical procedure.

The general equations used for speciation calculations are well known and are only briefly summarized here. Consider a system consisting of free (uncomplexed) species Me and complexes MeL. The formation reaction for MeL can be written



where

$$K = \frac{[\text{MeL}_i]}{[\text{Me}][\text{L}_i]} \frac{f_{\text{MeL}_i}}{f_{\text{Me}}f_{\text{L}_i}}$$

where f_{MeL_i} , f_{Me} , and f_{L_i} is the activity coefficient of the free metal species, the ligand (L_i), and the metal complex respectively. The total concentration of the metal, both free and complexed, can be defined as

$$[\text{Me}]_T = [\text{Me}] + \sum [\text{MeL}_i]$$

where the fraction of any species can be defined as

$$\alpha = [\text{MeL}_i]/[\text{Me}]_T$$

Using the lanthanum and europium stability constants in Appendices H-2 and H-3, one can calculate the variation of α as a function of pH for all the major species of lanthanum and europium. The assumed values for the concentration of the

various ions used in this calculation can be seen in Appendix H-7. This researcher realized that the concentration of some of these ions (Ca^{2+} and Mg^{2+}) do drastically change as a function of pH. However, this researcher felt that the changes do not effect the α value enough to warrant the extra work involved to incorporate the change of the concentration of these ions as a function of pH in the α calculations. Also in many cases, the variation of these ion concentrations varies less as a function of pH then the observed change seen in the ion concentration from river to river. Because of the aforementioned reasons, the free ion concentration for calcium, chloride, fluoride, magnesium, and sulfate were assumed to remain constant as the pH of the model solution varies from 5 to 9. In the case of the H_2PO_4^- and CO_3^{2-} ions, one must calculate the variation of the concentration of these ions as a function of pH since their concentrations drastically change as a function of pH. For the CO_3^{2-} ion, this researcher calculated its concentration as a function of pH based upon the stability constants in Appendix F-5 and assuming that the river water was in equilibrium with the atmosphere. For the H_2PO_4^- ion, I calculated its concentration as a function of pH based upon the stability constants in Appendix F-4, with the assumption that the total phosphate concentration is constant, 20 μg of phosphorus per liter, and that the Fe^{3+} ion concentration is controlled by the solubility of iron hydroxide.

The individual ion activity coefficient was calculated using

the extended Debye-Huckel equation.

$$\log f = -Az^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}}$$

where,

f = activity coefficient

$A = 0.5085$ for water at 25°C

z = charge of the ion

I = ionic strength of the solution

$B = 0.3281$ for water at 25°C

a = adjustable parameter (\AA) corresponding to the size of the hydrated ion

The parameter a values used in the ion activity coefficient calculation can be found in Appendix H-6. The results of these calculations can be seen in Figures XV and XVI, where one can see that the predicted major lanthanum and europium species in river water are the free rare earth ion and the rare earth carbonate ion.

C. Theoretical Solubility of Lanthanum and Europium in River Water

As mentioned before, one possible mechanism for controlling the soluble rare earth concentrations in river water is based upon the solubility of the rare earth phosphate. In this section, the expected soluble concentration of lanthanum and europium in river water will be calculated based upon the solubility of lan-

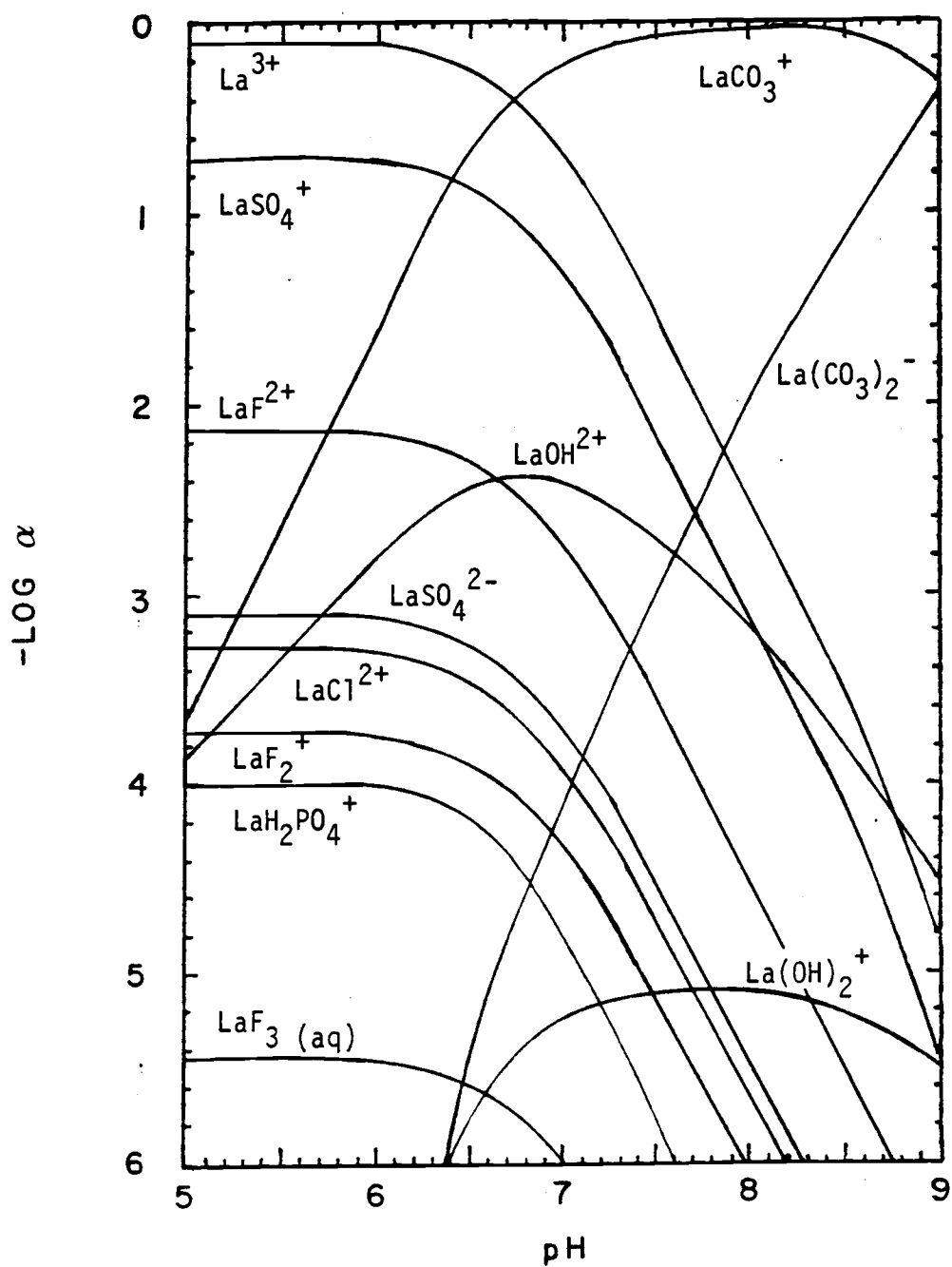


Figure XV: Speciation of lanthanum in river water as a function of pH.

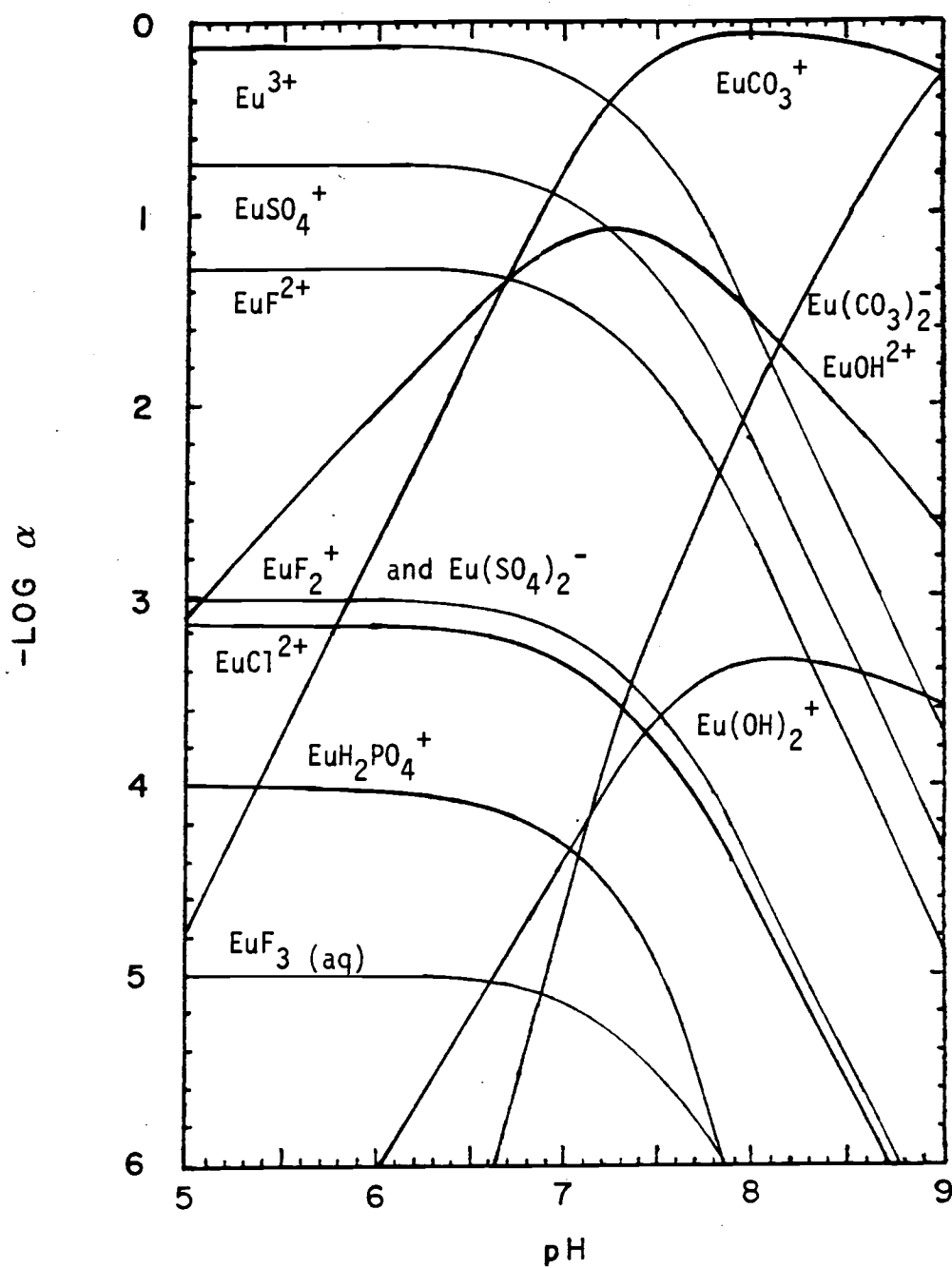


Figure XVI: Speciation of europium in river water as a function of pH.

thanum or europium phosphate as the controlling phase.

The first thing one wants to do, is to calculate the concentration of the PO_4^{3-} ion as a function of pH. From the data in Appendix H-4, one can see that there are many possible controlling reactions. However, if one calculates the respective PO_4^{3-} ion concentrations for each reaction, one can see that aluminum phosphate seems to control the PO_4^{3-} ion concentration at low pH values and hydroxylapatite seems to control the PO_4^{3-} ion concentration at high pH values. The Ca^{2+} and Al^{3+} ion concentrations were calculated as a function of pH assuming that the solubility of calcite and gibbsite, respectively, were the controlling reactions.

The results of these calculations can be seen in Figure XVII, where one can see that the calculated total phosphate concentration in river water varies from 4×10^{-2} to 1×10^{-9} M. However, the observed range of values for the total concentration of phosphate in river water is from 1×10^{-5} to 3×10^{-8} M.⁵⁹ The difference between the observed and calculated values seem to indicate that these solids do not control the total phosphate concentration, but one should not jump to this obvious conclusion. For example, if one uses the solubility constant of freshly precipitated aluminum hydroxide, $\log K = 33$, instead of the solubility constant of aged aluminum hydroxide (gibbsite), $\log K = 36.3$,^{35,133} the calculated total phosphate concentration will be reduced by a factor of two thousand. This correction alone is

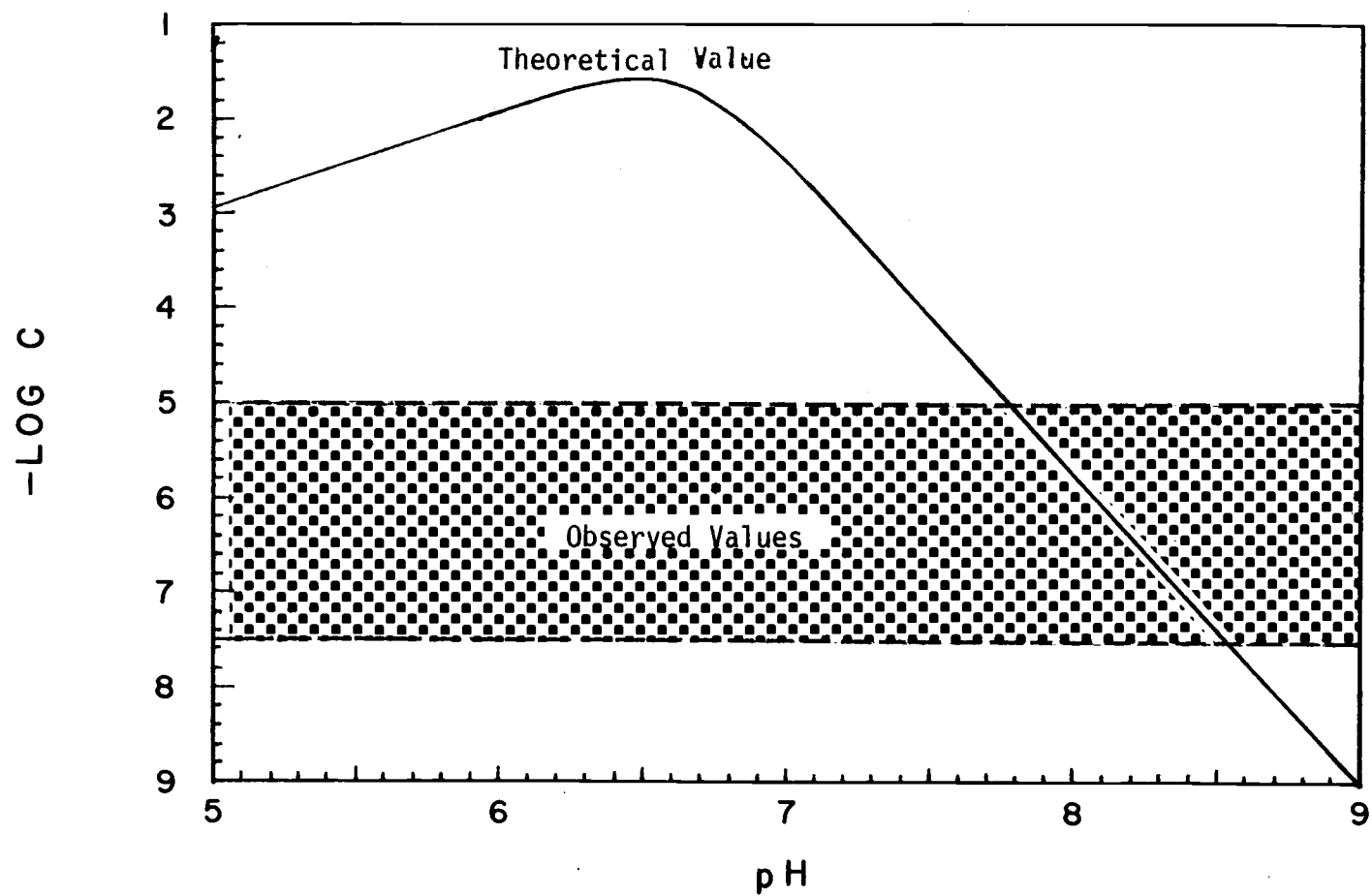


Figure XVII: Concentration of phosphate in river water as a function of pH.

almost enough to place the calculated phosphate concentration in the range of observed concentration values of phosphate in river water. Another consideration that one must consider, is that the ions may not be in equilibrium with the solubility of the respective solid, which could cause a shift in the calculated phosphate ion concentration in river water. Also, one must consider photosynthesis and respiration reaction in controlling the total concentration of phosphate in river water. Although it is believed that photosynthesis and respiration are not a factor in controlling the phosphate concentration in river water,³⁵ it has been noted that in lakes and in the oceans, the total phosphate concentration is correlated to photosynthesis and respiration.^{134,135,136,137} Finally, one must consider the possibility of a sorption reaction in controlling the total phosphate concentration in river water. It has been noted that phosphate anions are taken up from water by kaolinites, montmorillonites,¹³⁸ and by freshly precipitated ferric and aluminum hydroxide.³⁵ The upshot of the above statements is that an accurate theoretical calculation of the PO_4^{3-} ion concentration as a function of pH in river water is beyond the scope of this research. In conclusion, the theoretically calculated solubility of lanthanum and europium (Figures XVIII and XIX) are based upon the low and high observed values for the total phosphate concentrations measured in river water, the solubility of lanthanum or europium phosphate (Appendices H-2 and H-3), and the speciation calculations in the

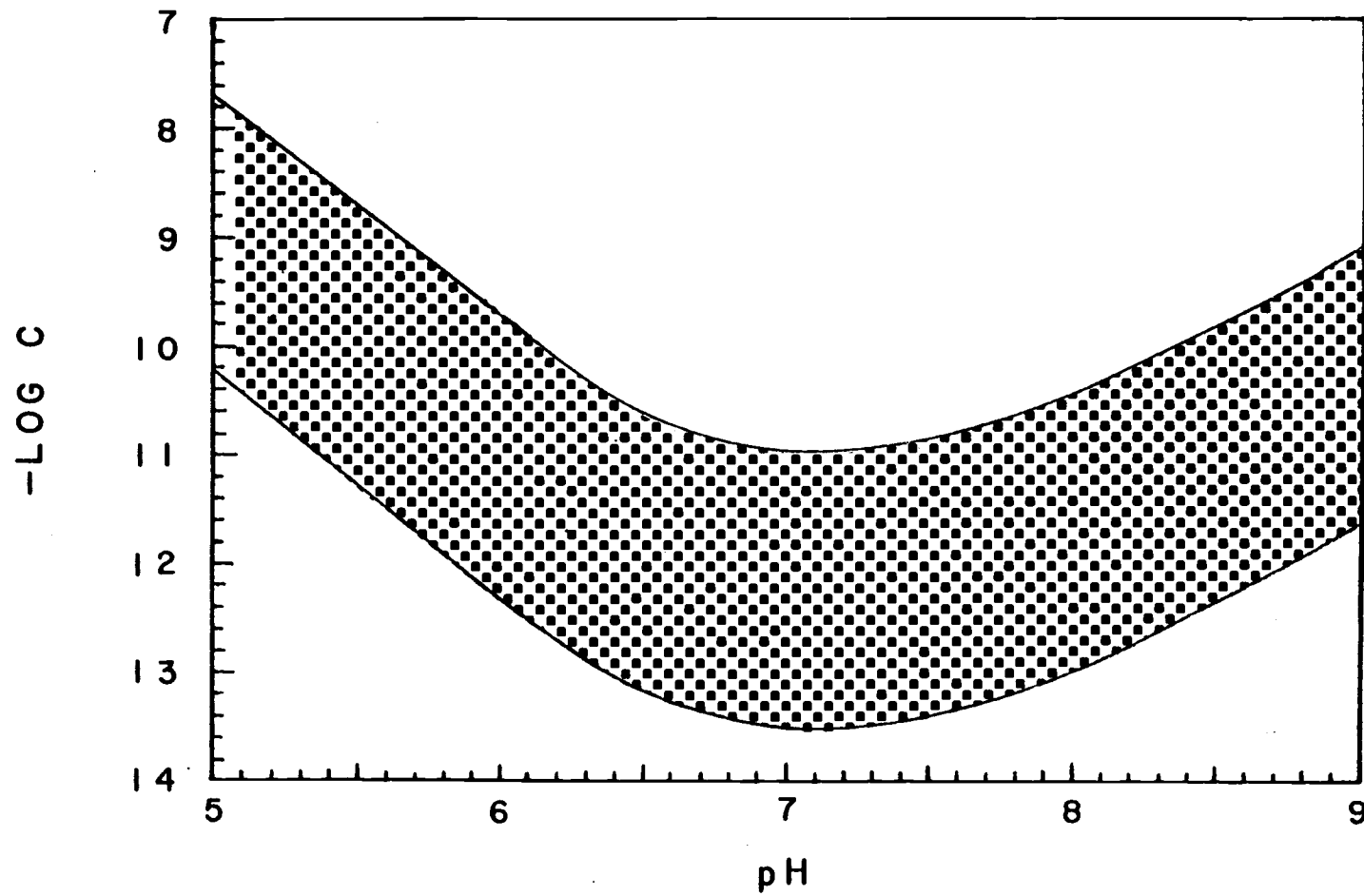


Figure XVIII: Theoretical lanthanum concentration in river water as a function of pH.

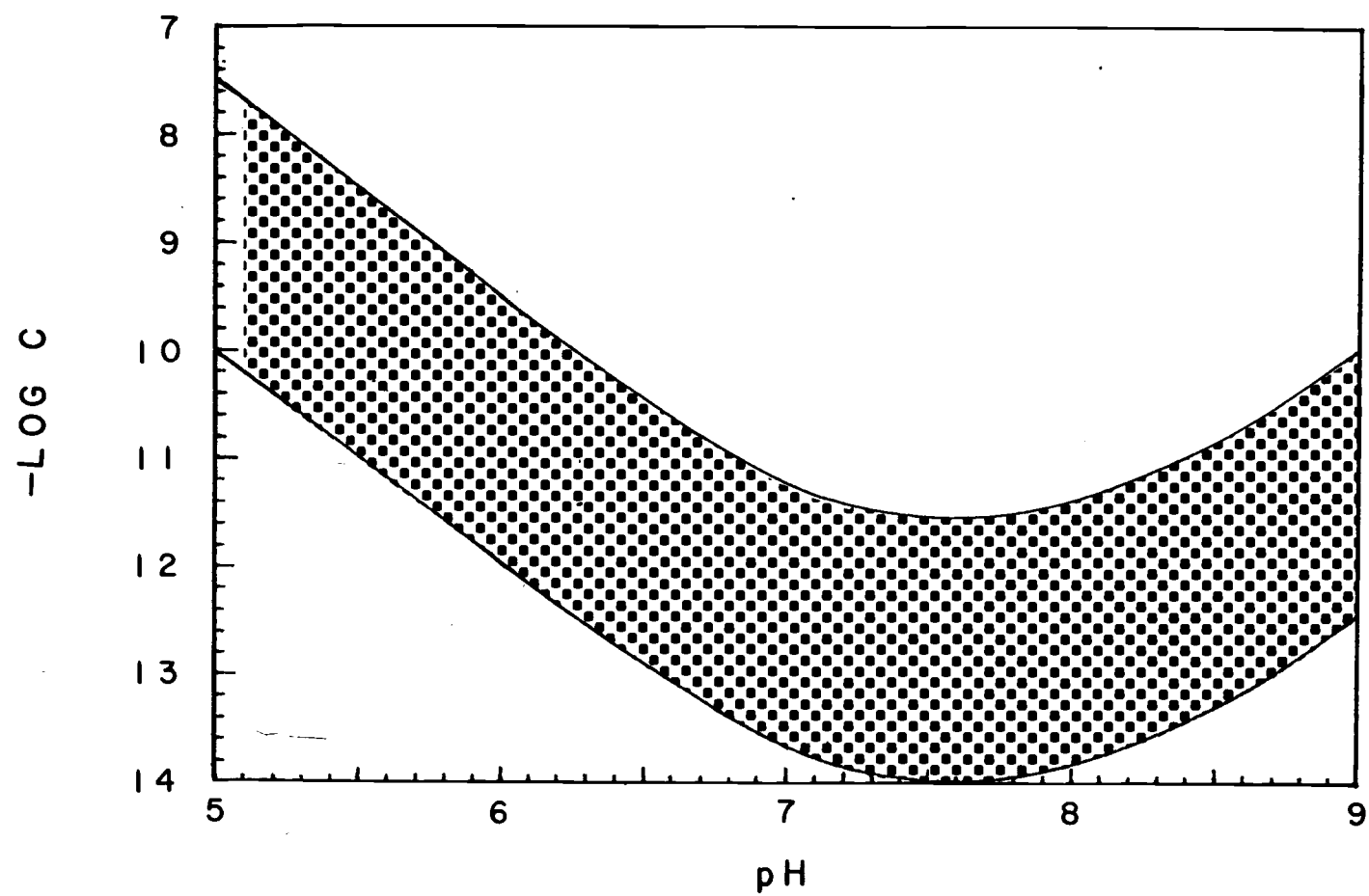


Figure XIX: Theoretical europium concentration in river water as a function of pH.

previous section.

D. Observed Rare Earth Elemental Concentrations in River Water

The soluble rare earth elemental concentrations were measured for seven Pacific Northwest rivers (Columbia, Fraser, Klamath, Marys, Rogue, Sacramento, and Willamette). The river water condition and the experimental procedure used to analyze for the rare earth elemental concentrations are reported in detail in the experimental section. The measured rare earth elemental concentration for any given sampling time are reported in Appendix I-1, while the run-off weighted average rare earth elemental concentration for the river samples can be found in Table XIX. From Table XIX, one can see that the measured soluble lanthanum concentration (as defined by filtration through a 0.45 μm pore-size filter paper) in river water is quite variable, 5.5-97 ng/ ℓ . For the seven Pacific Northwest rivers sampled in this thesis, the soluble lanthanum concentration (as defined by filtration through a 0.45 μm poresize filter paper) ranges from 8.1 to 97 ng/ ℓ with a run-off weighted average of 42.3 ng/ ℓ . This run-off weighted average is comparable to the measured soluble lanthanum concentration for the Dordogne (48.3 ng/ ℓ) and Gargonne (47.1 ng/ ℓ) Rivers in France¹⁰⁰ but is not comparable to the measured soluble lanthanum concentration for the Aare River (5.5 to 11 ng/ ℓ) in Switzerland.

From this data, one will notice two important trends. First,

Table XIX: Concentrations* of Rare Earth Elements in Some Rivers and Seawater (ng/l)

River**	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Aare (at Bern) ¹³⁹	7.8					0.3								
(at Geneva)	9.3					18								
(at Hagneck)	7.8					1.1								
(at Merringen)	11					0.51								
(at Thun)	5.5					0.08								
Dordogne ¹⁰⁰	48.3	76.5	10.5	37.4	7.3	1.3	8.1	1.3	--	1.2	4.3	0.60	3.7	0.69
Garonne ¹⁰⁰	47.1	81.0	5.2	38.4	8.2	1.6	8.8	1.2	--	1.6	4.1	0.62	3.6	0.60
Columbia	21.3±.3†	47±2	7±2†	22±2	4.5±.1	1.22±.04	15±2	0.76±.05	--	--	--	--	2.8±.3	0.43±.02
Columbia-8	15.1±.8†	37±2	--	8±2†	3.44±.09	0.74±.05	12±3†	0.38±.05	--	--	--	--	2.0±.2	0.34±.02
Fraser	97±1	155±3	28±2	88±4	25.3±.4	7.19±.09	53±3	4.34±.09	--	6.90±.04	14±2	--	15.7±.6	2.13±.07
Klamath	15.1±.2	26±1	5.1±.7	9±2	3.2±.2	1.25±.03	4±1	0.54±.03	--	0.72±.05	5±1	--	3.1±.4	0.28±.03
Marys	32.4±.8	82±3	--	37±3†	9.4±.3	2.41±.08	25±6†	1.54±.08	--	--	--	--	4.6±.2	0.67±.04
Marys-8	17.6±.5	33±3	--	6±2†	6.7±.2	1.20±.07	14±2†	0.5±.1	--	--	--	--	2.2±.3	0.31±.03
Rogue	25.0±.3	47±1	19±1	23±2	8.3±.2	2.94±.04	8±1	1.20±.04	--	1.92±.09	--	--	6.3±.7	0.79±.03
Sacramento	8.1±.1	11.4±.8	7.2±.9	11±2	2.5±.2	0.98±.02	5±1	0.53±.03	--	0.38±.06	--	--	2.5±.3	0.32±.03
Willamette	18.8±.4	41.3±.4	--	19±2	6.7±.6	1.5±.3	6±1†	0.75±.05	--	--	--	--	2.8±.4	0.47±.04
Willamette-8	20.1±.7	41±5	--	12±3†	2.8±.4	0.8±.1	--	0.9±.4	--	--	--	--	1.0±.3†	0.38±.07†
Runoff Weighted														
Average of the														
PNW Rivers (A)	42.3	75.9	13.9	39.7	10.5	3.0	24	1.8	--	--	--	--	6.5	0.92
Seawater ³⁰	3.4	1.2	0.64	2.8	0.45	0.45	0.13	0.14	0.14	0.22	0.87	0.17	0.82	0.15

*The uncertainties in the concentrations only reflect counting statistics and not systematic errors. I would estimate the systematic error due to sampling, chemical manipulations, etc. to be approximately 10-20% of the reported values.

**The 8 designates samples were filtered through a 0.20 µm filter paper, while the other river samples were filtered through a 0.45 µm filter paper.

†On rivers with multiple sampling times, a extrapolated value was used for the rare earth elemental concentration for a given sampling time if it was missing from the data set.

the measured values for the soluble rare earth elemental concentrations are generally higher in value than the highest possible value theoretically calculated in the previous section. This is exemplified in Table XX, where the run-off weighted average soluble lanthanum and europium concentrations are compared to the corresponding theoretically calculated lanthanum and europium concentrations in the seven Pacific Northwest river samples. The actual phosphate ion concentration for each river water sample was not measured for various reasons. The major reasons why the phosphate ion concentration was not measured are because of the enormous difficulties in accurately measuring the phosphate ion concentration in river water and that the only data which this researcher knew about when the field experiments were in progress¹⁰² predicted that the solubility of the rare earth phosphate was not the controlling phase. Because of these reasons and other reasons, this researcher felt that his time could be spent more wisely on other studies. Secondly, the soluble rare earth elemental concentrations as defined by filtration through a 0.20 μm poresize filter paper are generally less than the rare earth elemental concentrations as defined by filtration through a 0.45 μm poresize filter paper. The difference between these two measurements is quite variable from sample to sample but for the river water samples that were filtered through a 0.20 μm poresize filter paper, the lanthanum concentration is on the average approximately the same for the Willamette River, 30% less for the Columbia River, and

Table XX: Measured and Theoretical Lanthanum and Europium Concentration in the Seven Pacific Northwest Rivers

River	Measured Lanthanum Concentration (ng/ℓ)	Theoretically Calculated La Concentration (ng/ℓ)	Measured Europium Concentration (ng/ℓ)	Theoretically Calculated Europium Concentration (ng/ℓ)
Columbia	21.3±.3	3.0-0.0096	1.22±.04	0.94-.0030
Columbia-B	15.1±.8	3.0-0.0096	0.74±.05	0.94-.0030
Fraser	97±1	1.7-0.0053	7.19±.09	0.69-.0022
Klamath	15.1±.2	2.5-.0078	1.25±.03	0.48-.0015
Marys	32.4±.8	2.6-.0083	2.41±.08	1.72-.0054
Marys B	17.6±.5	2.6-.0083	1.20±.07	1.72-.0054
Rogue	25.0±.3	1.8-.0058	2.94±.04	0.56-.0018
Sacramento	8.1±.1	2.6-.0084	0.98±.02	0.48-.0015
Willamette	18.8±.4	6.3-.020	1.5±.3	8.7-.028
Willamette-B	20.1±.7	6.3-.020	0.8±.1	8.7 .028

50% less for the Marys River when compared to the lanthanum concentration of the river water samples that were filtered through a 0.45 μm poresize filter paper. The implication of these two trends will be discussed in detail after the presentation of the theoretical and measured lanthanum and europium concentrations in the Aare River (Switzerland).

In a study conducted at four locations (Hagneck, Bern, Thun, and Merringen) on the Aare River, Bart and von Gunten¹⁴⁰ measured the soluble lanthanum and europium concentrations (as defined by filtration through a 0.45 μm poresize filter paper) in the Aare River. At the same time, they measured the pH, temperature, and conductivity of the river water along with the respective concentration of nitrate, sulphate, phosphate, chloride, calcium and magnesium. Using these measured values, which are reported in Appendix J-1, one can calculate the theoretical lanthanum and europium concentration using the calculations seen in the previous section. The CO_3^{2-} ion concentration was calculated from the assumption that the river water was in equilibrium with the atmosphere with the atmospheric pressure for each given location being assumed to be the average atmospheric pressure seen at that altitude as reported in the CRC Handbook of Chemistry and Physics. The ionic strength of the river water was calculated using the following equation which is based upon the observed correlation between ionic strength and conductivity in river water.¹⁴¹

$$\text{Ionic Strength} = (1.65 \times 10^{-5})(\text{Conductivity in } \mu\text{S/cm})$$

The measured and theoretical lanthanum and europium concentrations in the Aare River can be seen in Table XXI, while the calculated fraction ($-\log \alpha$) of each lanthanum and europium species can be found in Appendices J-2 and J-3. One can see from Table XXI, that the observed ratio of measured lanthanum or europium concentration to the theoretical lanthanum or europium concentration is quite variable. However, the ratio is generally greater than one, which would mean that the river water is oversaturated with respect to the rare earth elements, but one should not make this conclusion at this time for several reasons.

First of all, the temperature of the water samples from the Aare River is between 3.4 to 18.6°C while the theoretical calculated lanthanum and europium concentrations were calculated at 25°C. One would ideally like to recalculate the theoretical concentrations and take into account this temperature difference, but unfortunately the theoretical data is not there to accurately calculate the lanthanum and europium concentrations at any other temperature. However, one can approximately estimate the effect the difference in temperature will make on the calculated theoretical concentration value using the basic principles of thermodynamics. For the Aare River samples, one only has to look at the effect of temperature on two rare earth reactions, which are for lanthanum,

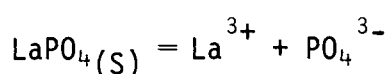
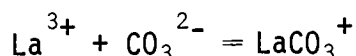


Table XXI: Measured and Theoretical Lanthanum and Europium Concentration in the Aare River (ng/ℓ)

River	Date	Measured La Concentration	Theoretical La Concentration	La Ratio Measured/ Theoretical	Measured Eu Concentration	Theoretical Eu Concentration	Eu Ratio Measured/ Theoretical
Hagneck	7/8/74	64±5	0.223	290±20			
	9/3/74	110±10	0.392	250±30			
	12/11/74	5.0±.8	0.238	21±3	0.38±.08	0.040	9±2
	2/11/75	17±2	0.283	61±6	0.16±.05	0.057	2.8±.9
	4/11/75	10±2	0.202	50±10			
	5/29/75	4.7±.7	0.292	16±3	4±2	0.030	140±60
	6/26/75	5.8±.9	0.379	15±2	0.18±.05	0.024	7±2
	8/11/75	4.2±.7	0.253	17±3	0.33±.04	0.038	9±1
Bern	7/8/74	33±3	0.291	110±10			
	9/3/74	18±2	0.556	32±3			
	12/11/74	4.0±.7	0.631	6±1	0.40±.05	0.082	4.9±.6
	4/11/75	5.5±.7	1.82	3.0±.4	0.24±.04	0.273	0.9±.2
	5/29/75	4.7±.7	0.672	7±1			
	6/26/75	3.6±.7	1.64	2.2±.4	0.60±.05	0.21	2.9±.2
	8/11/75	11±1	0.339	33±3	0.09±.05	0.044	2±1
Thun	7/8/74	11±1	4.19	2.6±.2			
	4/11/75	4.0±.5	1.90	2.1±.3			
	8/11/75	6.6±.9	16.1	0.41±.06			
Merringen	7/8/74	850±70	0.099	8,600±700			
	9/3/74	8±1	0.341	23±3			
	4/11/75	19±4	0.639	30±6			
	8/11/75	1.2±.9	0.872	1±1	0.60±.05	0.12	4.8±.4

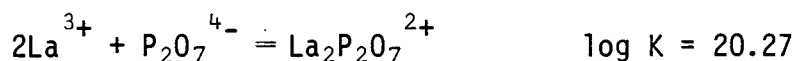
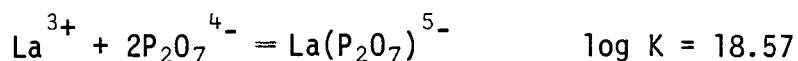
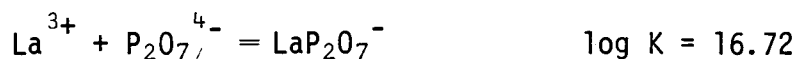
and



At constant PO_4^{3-} and CO_3^{2-} ion concentrations, one would expect, due to entropy effects, the solubility constant for lanthanum phosphate to decrease as the temperature decreases while the stability constant for the formation of LaCO_3^+ should increase as the temperature decreases. The net effect should be close to zero which translates that there should only be a small to no change in the calculated theoretical value for the lanthanum and europium concentrations as the temperature decrease if the PO_4^{3-} and CO_3^{2-} ion concentration remains constant. However, one would expect that both the PO_4^{3-} and CO_3^{2-} ion concentration to change as the temperature decreases. For a given total phosphate concentration, one would expect to see a decrease in the PO_4^{3-} ion concentration as the temperature decreases due to the decrease in the acid dissociation constants for phosphoric acid. While for the CO_3^{2-} ion concentration, one should see the same trend except that one will not expect to see as large as a decrease in the CO_3^{2-} ion concentration as one will expect to see for the PO_4^{3-} ion concentration since carbon dioxide becomes more soluble in river water as the temperature decreases. In fact, one can calculate that the CO_3^{2-} ion concentration in river water will be 18% lower at 10°C than at 25°C due to the differences in the stability constants for the carbonate species at 10°C and 25°C.³⁵ The final conclusion to

these arguments is that the calculated speciation for lanthanum and europium in the Aare River water samples should be affected as the temperature decreases, but that the total concentration for lanthanum and europium should either remain constant or increase slightly as the temperature decreases if all the reactions are in equilibrium.

Another problem in the calculations for the theoretical lanthanum and europium concentration in river water is that several rare earth species were not considered. For example, there are many phosphorus compounds found in natural river water which reacts with rare earth elements to form some very stable species. Some of these phosphorus compounds are pyrophosphate, tripolyphosphate, trimetaphosphate, organic orthophosphates, organic condensed phosphates, and phosphorus-containing pesticides. Many of the species form very stable species which can be illustrated by the high stability constants of the following reactions between lanthanum and pyrophosphate.^{132,142}



These phosphorus compounds enter the river water from a wide variety of sources. For example, condensed inorganic phosphates (pyrophosphate, tripolyphosphate, and trimetaphosphate) are

not found to occur naturally in minerals but they are found in all plants and animals where they are synthesized enzymatically and constitute a part of the polyphosphate pool. Another source of condensed inorganic phosphates is from man-made sources where it is produced by dehydration and condensation of orthophosphates. Some of these condensed inorganic phosphates are used as substantial components of synthetic detergents, while some other compounds are used in water conditioning operations for scale prevention and corrosion control. The organic phosphorus compounds in river water are products of biological growth. Although there is no available information to identify the specific compounds or group of compounds which may make up the dissolved organic phosphorus fraction in river water, the dissolved organic phosphorus amount to as much as 25-30% of the total phosphorus in some river water.^{143,144} From all this information, one concludes that the soluble rare earth elemental concentration could greatly depend on the concentration of these phosphorus compounds.

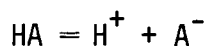
Another interaction which was not considered in the theoretical calculation of lanthanum and europium concentration in river water was the rare earth elements reacting with humic substances. Humic substances are generally divided into three groups based upon their respective solubility in dilute acid ($\text{pH} = 1$) and dilute base. These groups are:

1. Fulvic acids - soluble in both dilute acid and dilute base

2. Humic acids - soluble in dilute base and insoluble in dilute acid

3. Humin - insoluble in both dilute acid and dilute base

The interaction between the rare earth elements and humic substances in river water are dependent on three reactions. From the first reaction, we can see that the concentration of the fulvic/humic anion available to react with the rare earth element is dependent on the concentration of fulvic/humic acid, the pH of the river water, and the acid-dissociation constant as defined by the following reaction,



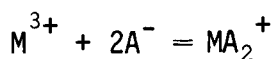
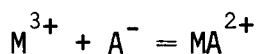
where

HA = fulvic acid or humic acid

H^+ = hydronium ion

A^- = fulvic anion or humic anion

Secondly, the fraction of rare earth elements which are complexed with the fulvic/humic anion are dependent on the concentration of the fulvic/humic anion and the stability constant of the following reactions,



where

M^{3+} = uncomplexed rare earth element ion

MA^{2+} or MA_2^+ = complexed rare earth element

Although the major functional groups in both fulvic acid and humic acid are fairly well defined, the stability constant for the acid-dissociation of fulvic acid and humic acid is not well defined. This is in part because of the complexity of the functional groups in fulvic acid and humic acid and also because the relative amount of each functional group in fulvic acid or humic acid changes as the location changes. Because of these problems, conditional stability constants will be used in the discussion on forming a rare earth-humic substance complex. The conditional stability constant (measured at a pH of 4.50) for the reaction of uncomplexed europium ions with fulvic acid is 8×10^6 for the formation of a 1:1 complex and 9×10^{10} for the formation of a 1:2 complex, while the conditional stability constant for the reaction of uncomplexed europium ions with humic acid is 6×10^5 and 5×10^{10} for the 1:1 and 1:2 complex respectively.^{145,146} From these arguments, one would expect that the concentration of fulvic acid and humic acid would play a very active role in determining the concentration of lanthanum and europium in river water. In fact, a laboratory study recently published comes to the same conclusion.¹⁰¹ In the studies of Hoyle and Elderfield¹⁰¹, they concluded that somewhere between 50 to 80% of the soluble rare earth elements in the Water of Luce are associated with humic substances.

Finally, the possibility that one is actually measuring the concentration of the suspended particulates which passes through the 0.45 μm poresize filter paper than the actual soluble rare

earth elemental concentrations in river water has to be considered. As has already been mentioned, the Pacific Northwest river samples which were filtered through a 0.20 μm poresize filter paper generally show a reduction in the measured rare earth elemental concentrations when compared to the measured rare earth elemental concentration of samples filtered through a 0.45 μm poresize filter paper. From this observed reduction in the measured rare earth elemental concentration, one concludes that a certain fraction of the suspended particulates are getting through the 0.45 μm poresize filter paper. It is of interest to note that the observed reduction in the measured soluble lanthanum concentration seen in the Pacific Northwest river samples which were filtered through a 0.20 μm poresize filter paper instead of a 0.45 μm poresize filter paper roughly corresponds to the observed loss in weight in the respected Pacific Northwest river suspended particulate samples after the samples were ashed at 600°C. From this correlation, one would assume that the mass of the rare earth elements which passed through the 0.45 μm poresize filter paper but not the 0.20 μm poresize filter paper is associated with the organic fraction, humin, of the suspended particulates. However, due to the paucity of the data base this correlation may be coincidental.

In conclusion, the fact that the soluble rare earth elemental concentrations for the Pacific Northwest rivers and for the Aare River are higher than the theoretical calculated values is very encouraging. From the aforementioned arguments, one would

expect that a certain fraction of the soluble rare earth elemental concentrations to be associated with the phosphorus compounds already mentioned and also associated with humic acid and fulvic acid. This would cause the measured soluble rare earth elemental concentrations to be higher in value than the theoretically calculated rare earth elemental concentrations. Also as was seen in the Pacific Northwest river samples, a certain but variable fraction of the suspended particulates do get through the 0.45 μm poresize filter paper. This would also cause the measured soluble rare earth elemental concentrations to be higher in value than the theoretical calculated soluble rare earth elemental concentrations. This roughly translates to the conclusion that the solubility of the rare earth phosphate could easily be the controlling reaction for the soluble rare earth elemental concentration, but more data is needed before this can be confirmed.

E. Variation of the Rare Earth Elemental Concentration as a Function of pH

In this section, the results of the laboratory experiments with river water and sediments from either the Columbia or Willamette river will be discussed. In brief, the experiment consisted of taking a mixture of river water and sediment and adjusting the mixture's pH to a desired new pH. The soluble rare earth elemental concentrations of this solution was consequently measured, and are reported in Table XXII.

Table XXII: Soluble Rare Earth Elemental Concentrations, ng/l,
in River Water as a Function of pH (A Laboratory
Experiment Involving River Water and Sediments)

Columbia River:

<u>pH</u>	<u>La</u>	<u>Pr</u>	<u>Sm</u>	<u>Eu</u>	<u>Lu</u>
5.98	29±1	47±4	28±1	31±2	1.4±.2
6.19	89±4	170±10	78±4	107±7	2.2±.3
6.51	39±1	67±5	34.3±.9	45±2	1.1±.2
6.75	9.7±.4	--	3.0±.1	1.03±.08	--
6.95	8.7±.3	7±2	2.63±.07	1.37±.05	--
7.24	11.2±.4	11±3	3.9±.1	0.96±.04	--
7.50	5.4±.2	--	1.21±.06	1.45±.03	--
7.76	16.8±.5	28±2	14.4±.3	18.9±.7	--
7.91	12.2±.7	19±3	9.1±.5	11.1±.8	0.5±.2

Willamette River:

6.11	34.6±.7	12±2	15.6±.3	5.5±.2	2.2±.2
6.27	31.6±.6	17±2	15.5±.3	8.3±.3	1.7±.1
6.40	18.4±.4	7±2	7.6±.2	2.27±.09	1.1±.1
6.55	32.7±.8	15±4	14.0±.3	5.7±.1	1.9±.1
7.02	20.6±.4	6±2	7.9±.2	2.7±.1	0.9±.1
7.17	18.1±.4	--	6.8±.1	1.96±.09	1.0±.1
7.57	25.9±.8	15±4	10.9±.3	4.1±.2	1.5±.1
7.77	19.6±.6	--	7.2±.2	2.3±.1	1.1±.1
7.90	17.6±.4	5±2	6.9±.2	2.1±.1	0.9±.1

In reviewing the results, one can see that there is considerable fluctuation in the data. Although every attempt was made to keep the characteristics of the water samples the same, it is believed that the dispersion in the data is caused by the variation of the individual ion concentrations (i.e. phosphate, sulphate, humic, fulvic, etc.) in the individual samples. Because of this fluctuation and the paucity of the data, it is very difficult to see any correlation between the soluble rare earth elemental concentrations and pH. However, the following conclusions seem to be reasonable. First, the soluble rare earth elemental concentrations in river water will not fluctuate widely (i.e. changes in order of magnitudes) as the river water pH varies from 6.0 to 8.0. Secondly, the rare earth elemental concentrations are generally higher at low pH values, less than 6.5, than at high pH values, greater than 7.0.

It is of interest to note that if one combines the predicted variation of phosphate in pond water as a function of pH¹⁴⁷ and the theoretical variation of the rare earth elemental concentrations as a function of pH, one would qualitatively get the same correlation as was seen in the laboratory experiments. This is in agreement with the conclusion that the solubility of the rare earth phosphate is the controlling reaction for the soluble rare earth elemental concentrations in river water.

F. Rare Earth Elemental Pattern

Because of the similarity of the chemical properties of the

rare earth elements, the rare earth elemental concentrations usually form a noticeable pattern. Unfortunately, the rare earth elemental pattern which one will get if the rare earth elemental concentrations are plotted against the rare earth ionic radius is a jig-saw pattern. This is caused by the fact that even atomic number rare earth elements are higher in concentration than the odd atomic number rare earth elements. To smooth out this effect, most researchers normalize their rare earth elemental concentrations to some known source (i.e. sedimentary type rocks, chondrites, shale, etc.). If one would plot this normalized rare earth values against the rare earth ionic radius, one will usually get a very smooth pattern.

In the case of the rare earth elemental concentrations in the suspended particulates (ashed at 600°C) of some rivers, Table XXIII, one can see that their normalized values, Table XXIV, illustrate that most of the rare earth elemental concentrations in the rivers suspended particulates have a rare earth elemental pattern similar to the rare earth elemental pattern for the average sedimentary rock type.¹⁴⁸ Specifically, the suspended particulates of the Amazon, Columbia, Congo, Ganges, Marys, Mekong, Sacramento, and Willamette Rivers all have a rare earth elemental pattern, within experimental error, similar to the rare earth elemental pattern of the average sedimentary type rock. The suspended particulates of the Klamath and Rogue Rivers have a rare earth elemental pattern in which the normalized values

Table XXIII: Concentration of Rare Earth Elements in Some Rivers' Suspended Particulates (ppm)

River	Sample Date	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Yb	Sc
Columbia	5/2/81	34±5	65±2	28±6	6.9±.4	1.8±.1	13.7±.7	0.91±.05	5.8±.6	3.1±.3	23±1
	5/2/81	37±3	82±2	34±9	7.1±.3	1.6±.1	12.6±.7	1.16±.05	6.0±.6	3.8±.2	23±1
	9/1/82	42±9	60±2	21±8	7.4±.5	2.1±.3	15±1	0.94±.07	7±2	3.3±.5	18±1
	9/8/82	53±7	121±7	60±20	7.8±.7	3.4±.7	25±2	2.6±.2	7±3	3.3±.2	--
	9/15/82	43±4	54±5	--	8.5±.6	3.1±.8	11±1	3.1±.7	8±2	6.0±.5	21.8±.9
	9/22/82	44±6	50±7	--	10.8±.9	2.3±.5	11±1	--	8±3	2.8±.4	22±1
Fraser	5/1/81	55±7	47±4	10±4	5.9±.4	1.4±.2	10.3±.6	2.1±.3	5.0±.5	2.1±.1	19.9±.7
	5/1/81	43±6	50±5	14±5	5.9±.4	1.2±.1	10.5±.6	2.1±.3	4.0±.4	2.0±.1	20.3±.7
Klamath	4/27/81	21±2	43±1	25±5	4.7±.2	1.5±.1	6.8±.4	0.71±.04	4.7±.8	2.7±.1	27±1
Marys	9/10/82	43±5	73±3	--	8.7±.6	2.2±.2	10.0±.7	1.31±.08	5±3	4.1±.4	38±2
	9/17/82	42±5	--	41±15	8.2±.5	1.8±.4	--	1.8±.6	8±3	--	9.1±.4
Rogue	4/27/81	19±2	42±1	19±5	4.9±.2	1.3±.2	6.1±.3	0.73±.03	5.7±.9	2.6±.1	26±1
Sacramento	4/25/81	25±3	47±2	15±6	6.0±.3	1.7±.1	8.8±.6	0.84±.06	--	--	29±2
	4/25/81	25±2	69±7	--	4.8±.4	--	4.8±.7	--	4±1	3.3±.5	23±1
Willamette	9/3/82	61±9	86±7	20±10	5.7±.9	1.5±.2	4.8±.8	0.79±.09	6±4	6.5±.7	22±2
	9/13/82	36±5	25±5	--	6.5±.6	1.3±.1	4±1	--	6±4	3.5±.7	27±2
	9/20/82	43±6	25±6	--	6.6±.7	1.7±.2	--	--	7±3	--	--
	9/24/82	45±6	132±8	60±20	5.9±.5	1.9±.2	5.8±.8	--	--	3.8±.4	22±2
Amazon ¹⁷		48	112	--	9.7	1.8	--	--	--	3.7	--
Congo ¹⁷		47	104	--	--	1.5	--	1.6	--	2.4	--
Ganges ¹⁷		42	98	48	9.7	1.2	--	0.7	--	3.2	--
Mekong ¹⁷		48	93	47	5.4	1.5	5.3	0.9	--	3.6	--
Garrone ¹⁷		44	92	35	6.1	1.04	5.9	0.86	--	2.8	--
Dordogne ¹⁷		--	96	39	6.6	1.26	7.0	1.05	--	3.0	--

Table XXIV: Rare Earth Elemental Concentrations in Some River Suspended Particulates Normalized
to Sedimentary Type Rock¹⁰⁶

River	Sample Rock	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Yb
Columbia	5/2/81	1.2±.2	1.14±.04	1.1±.2	1.15±.07	1.50±.08	2.5±.1	1.30±.07	1.5±.2	1.4±.1
	5/2/81	1.3±.1	1.44±.04	1.3±.3	1.19±.05	1.33±.08	2.3±.1	1.59±.07	1.5±.2	1.73±.09
	9/1/82	1.5±.3	1.05±.04	0.8±.3	1.23±.08	1.75±.25	2.8±.2	1.3±.1	1.7±.5	1.50±.09
	9/8/82	1.8±.2	2.1±.1	2.3±.8	1.3±.1	2.8±.6	4.6±.4	3.7±.3	1.8±.8	2.7±.2
	9/15/82	1.5±.1	0.95±.09	--	1.4±.1	2.6±.7	2.0±.2	4±1	2.0±.5	1.3±.2
	9/22/82	1.5±.2	0.9±.1	--	1.8±.2	1.9±.4	2.0±.2	--	2.0±.8	--
Fraser	5/1/81	1.9±.2	0.82±.07	0.4±.2	0.98±.07	1.2±.2	1.9±.1	3.0±.4	1.3±.1	0.95±.05
	5/1/81	1.5±.2	0.88±.09	0.5±.2	0.98±.07	1.0±.1	1.9±.1	3.0±.4	1.0±.1	0.91±.05
Klamath	4/27/81	0.72±.07	0.75±.02	0.9±.2	0.78±.03	1.25±.08	1.26±.07	1.01±.06	1.2±.2	1.23±.05
Marys	9/10/82	1.5±.2	1.28±.05	--	1.5±.1	1.8±.2	1.9±.1	1.9±.1	1.3±.8	1.9±.2
	9/17/82	1.5±.2	--	1.5±.6	1.37±.08	1.5±.3	--	2.6±.9	2.0±.8	--
Rogue	4/27/81	0.66±.07	0.74±.02	0.7±.2	0.82±.03	1.1±.2	1.13±.06	1.04±.04	1.4±.2	1.18±.05
Sacramento	4/25/81	0.9±.1	0.82±.04	0.6±.2	1.00±.05	1.42±.08	1.6±.1	1.20±.09	--	--
	4/25/81	0.86±.07	1.2±.1	--	0.80±.07	--	0.9±.1	--	1.0±.3	1.5±.2
Willamette	9/3/82	2.1±.3	1.5±.1	0.8±.4	0.9±.2	1.3±.2	0.9±.2	1.1±.1	1.5±1.0	2.9±.3
	9/13/82	1.2±.2	0.4±.1	--	1.1±.1	1.08±.08	0.7±.2	--	1.5±1.0	1.6±.3
	9/20/82	1.5±.2	0.4±.1	--	1.1±.1	1.4±.2	--	--	1.7±.8	--
	9/24/82	1.5±.2	2.3±.1	2.3±.8	0.98±.08	1.6±.2	1.1±.2	--	--	1.7±.2
Amazon		1.66	1.96	--	1.62	1.50	--	--	--	1.68
Congo		1.62	1.82	--	--	1.25	--	2.29	--	1.09
Ganges		1.45	1.72	1.82	1.62	1.00	--	1.00	--	1.45
Mekong		1.66	1.63	1.78	0.90	1.25	0.98	1.29	--	1.64
Garrone		1.52	1.61	1.33	1.02	0.87	1.09	1.23	--	1.27
Dordogne		--	1.68	1.48	1.10	1.05	1.30	1.50	--	1.36

increase from lanthanum to lutetium, while the suspended particulates of the Dordogne and Garrone Rivers have a rare earth elemental pattern in which the normalized values decrease from lanthanum to lutetium. This observed fluctuation in the rare earth elemental pattern in the suspended particulates is not surprising since the specific mixture of shales, sandstones, limestones, etc. which makes up the composition of the sedimentary type rock should vary from river to river, and thus the rare earth elemental pattern for the suspended particulates should also vary from river to river.

In the case of the rare earth elemental pattern for the soluble rare earth elemental concentrations in river water, there are three theoretical patterns possible. In the first possibility, one assumes that an adsorption or leaching process would control the soluble rare earth elemental pattern in river water. If this is the case, one would expect to see the same correlation between the rare earth elemental concentration in the suspended particulates and the rare earth elemental concentrations in the various rivers. In the second possibility, one assumes that the relative ratio of the stability constants for the rare earth elements would control the rare earth elemental pattern. If this is the case, one would expect to see the same correlation between the rare earth elemental concentrations in the various rivers, and the rare earth elemental concentrations in the average sedimentary type rock. In the last possibility, one assumes that the ionic

strength, pH, and various ion concentrations would effect the rare earth elemental pattern in the various rivers. If this is the case, one would expect to see the correlation between the soluble rare earth elemental concentrations and the rare earth elemental concentrations in either the suspended particulates or the average sedimentary type rock to change as the composition of the river water changes.

In reviewing the soluble rare earth elemental concentrations normalized to the rare earth elemental concentrations in the respective suspended particulates, Table XXV, or to the rare earth elemental concentrations in the average sedimentary type rock, Table XXVI, one can see that the rare earth elemental pattern for each river sample is generally smooth, and that the pattern is not the same for every river water sample. From this one can either postulate that the enormous difficulties in accurately measuring the rare earth elemental concentrations in natural waters are responsible for the observed fluctuations in the rare earth pattern, or that this data is in fact accurate and one is actually seeing evidence that the third possibility for controlling the rare earth elemental pattern is the correct scenario. This researcher feels that this data is qualitatively good and that it is good evidence that ionic strength, pH, and various ion concentrations do effect the soluble rare earth elemental pattern in river water. However, this researcher also realizes that some of the fluctuation seen in the observed rare earth elemental pattern is caused by the

Table XXV: Soluble Rare Earth Elemental Concentrations in Some Rivers Normalized to the Rare Earth Elemental Concentration in the Rivers' Suspended Particulates and Lanthanum equal to 1.0.

River	Sample Date	La	Ce	Nd	Sm	Eu	Gd	Tb	Yb
Columbia	1A 5/2/81	1.00±.05	0.9±.1	0.9±.1	--	1.10±.08		1.4±.2	1.5±.3
	3A 9/8/82	1.0±.2	0.9±.1	--	1.6±.3	0.5±.1	1.7±.3	0.33±.06	1.7±.2
	4B 9/15/82	1.0±.2	0.7±.1	--	0.28±.04	0.17±.05	--	0.10±.04	0.29±.05
	5A 9/22/82	1.0±.2	2.8±.6	--	1.0±.2	1.4±.4	6±1	--	2.5±.6
	5B 9/22/82	1.0±.2	3.8±.8	--	1.2±.2	1.4±.4	--	--	4.2±.9
Fraser	A 5/1/81	1.0±.2	1.6±.2	3.7±.8	2.2±.3	2.8±.4	2.6±.4	1.0±.2	3.9±.5
Garrone	A	1.0	0.82	1.0	1.3	1.4	1.4	1.3	1.2
Klamath	A 4/27/81	1.0±.1	0.84±.09	0.5±.2	0.9±.1	1.2±.1	0.8±.2	1.1±.1	1.6±.3
Marys	1A 9/10/82	1.0±.2	1.6±.2	--	1.5±.2	1.6±.2	--	1.6±.2	1.6±.3
	1B 9/10/82	1.0±.2	0.8±.1	--	1.1±.2	0.9±.1	4±1	0.5±.3	1.1±.2
	2A 9/17/82	1.0±.2	--	1.1±.4	1.5±.2	1.7±.4	--	1.1±.4	--
	2B 9/17/82	1.0±.2	--	0.6±.3	4.1±.6	2.9±.7	--	1.2±.5	--
Rogue	A 4/27/81	1.0±.1	0.68±.08	0.9±.3	1.3±.1	1.7±.3	1.0±.2	1.2±.1	1.8±.3
Sacramento	A 4/25/81	1.0±.1	0.6±.1	2±1	1.4±.2	1.8±.2	2.3±.8	--	2.3±.5
Willamette	1A 9/3/82	1.0±.2	0.7±.1	2±1	1.8±.4	1.7±.4	--	2.4±.6	1.5±.4
	1B 9/3/82	1.0±.2	0.8±.1	0.9±.5	0.6±.1	0.6±.1	--	0.6±.3	0.3±.1
	2A 9/13/82	1.0±.2	3±2	--	1.2±.3	1.1±.6	--	--	--
	2B 9/13/82	1.0±.2	5±4	--	1.8±.5	2.8±.8	--	--	--
	3A 9/20/82	1.0±.2	4±1	--	1.6±.3	1.7±.3	--	--	--
	3B 9/20/82	1.0±.3	13±5	--	4±1	6±1	--	--	--
	4A 9/24/82	1.0±.2	1.0±.1	0.9±.3	3.0±.5	0.7±.1	2.1±.6	--	1.3±.3
	4B 9/24/82	1.0±.2	1.4±.6	--	1.1±.3	1.0±.3	--	--	--

Table XXVI: Soluble Rare Earth Elemental Concentrations in Some Rivers Normalized to Sedimentary
Type Rock and Lanthanum equal to 1.0

Sample†	Sample Date	La	Ce	Pr	Nd	Sm	Eu
Columbia	1A 5/2/81	1.00±.01	0.98±.02	1.3±.3	0.84±.07	--	1.28±.03
	3A 9/8/82	1.00±.02	1.05±.03	--	--	1.16±.02	0.85±.04
	4B 9/15/82	1.00±.08	0.45±.04	--	0.21±.01	0.27±.02	0.29±.03
	5A 9/22/82	1.00±.05	1.6±.1	--	2.1±.1	1.16±.06	1.8±.1
	5B 9/22/82	1.0±.1	2.2±.3	--	1.5±.4	1.4±.2	1.8±.3
Dordogne	A	1.00	0.83	0.86	0.87	0.75	0.67
Fraser	A 5/1/81	1.00±.01	0.81±.02	1.12±.08	1.00±.05	1.26±.02	1.79±.02
Garrone	A	1.00	0.87	0.43	0.90	0.84	0.82
Klamath	A 4/27/81	1.00±.03	0.88±.04	1.3±.2	0.7±.1	1.02±.07	2.00±.07
Marys	1A 9/10/82	1.00±.03	1.36±.06	--	--	1.43±.08	1.83±.07
	1B 9/10/82	1.00±.05	0.68±.09	--	--	1.08±.06	1.13±.08
	2A 9/17/82	1.00±.03	1.22±.05	--	1.19±.09	1.37±.03	1.76±.08
	2B 9/17/82	1.00±.06	1.7±.1	--	0.7±.2	3.8±.2	3.0±.2
Rogue	A 4/27/81	1.00±.02	0.96±.02	2.9±.2	1.01±.09	1.60±.04	2.84±.06
Sacramento	A 4/25/81	1.00±.05	0.72±.06	3.4±.5	1.5±.3	1.5±.1	2.9±.1
Willamette	1A 9/3/82	1.0±.1	0.50±.08	--	0.8±.2	0.8±.1	1.0±.2
	1B 9/3/82	1.00±.01	0.54±.04	--	0.32±.04	0.27±.01	0.35±.02
	2A 9/13/82	1.0±.5	1.0±.6	--	--	1.1±.3	1.0±.5
	2B 9/13/82	1.0±.1	2±1	--	--	1.6±.3	2.4±.7
	3A 9/20/82	1.00±.03	1.13±.05	--	1.10±.09	1.19±.03	1.64±.07
	3B 9/20/82	1.0±.1	3.9±.6	--	--	3.3±.4	5.3±.6
	4A 9/24/82	1.00±.02	1.43±.06	--	1.3±.1	1.89±.04	2.23±.07
	4B 9/24/82	1.0±.2	2.1±.9	--	--	0.7±.2	1.0±.3

†The A designates samples were filtered through a 0.45 μ m poresize filter paper, while the B designates samples were filtered through a 0.20 μ m poresize filter paper.

Table XXVI: (Continued)

Sample		Gd	Tb	Ho	Er	Yb	Lu
Columbia	1A	1.2±.1	1.69±.06	1.00±.08	--	2.0±.3	1.6±.1
	3A	4.4±.5	0.68±.05	--	--	1.37±.04	1.31±.07
	4B	--	0.31±.08	--	--	0.54±.05	0.52±.05
	5A	9±1	1.4±.2	--	--	2.1±.3	1.6±.1
	5B	--	1.9±.3	--	--	3.5±.5	3.1±.4
Dordogne	A	0.92	1.1	0.82	0.95	1.0	1.1
Fraser	A	2.9±.2	1.85±.04	2.29±.02	1.5±.2	2.13±.08	1.59±.05
Garrone	A	1.0	1.1	1.1	0.90	1.0	1.1
Klamath	A	1.4±.4	1.48±.09	1.5±.1	1.3±.3	2.7±.4	1.3±.1
Marys	1A	--	2.0±.1	--	--	2.0±.1	1.6±.1
	1B	5±1	0.7±.3	--	--	1.3±.2	1.0±.1
	2A	2.0±.3	1.9±.1	--	--	1.82±.05	1.39±.08
	2B	--	2.2±.4	--	--	2.5±.3	2.0±.2
Rogue	A	1.7±.2	1.99±.07	2.5±.1	--	3.3±.4	2.29±.09
Sacramento	A	3.3±.7	2.7±.2	1.5±.2	--	4.1±.5	2.9±.3
Willamette	1A	--	1.3±.2	--	--	2.1±.5	1.9±.3
	1B	--	0.3±.1	--	--	0.36±.13	0.44±.08
	2A	--	--	--	--	--	--
	2B	--	--	--	--	--	--
	3A	1.3±.2	1.39±.09	--	--	2.4±.3	2.2±.2
	3B	--	7±2	--	--	1.9±.4	--
	4A	1.5±.3	2.2±.1	--	--	1.5±.1	1.24±.05
	4B	--	5±3	--	--	--	--

difficulties in measuring the rare earth elemental concentrations due to sampling, chemical manipulations, etc. (which were previously estimated to be 10-20%).

G. Material Balance in the Oceans

As has already been discussed in detail, in the Introduction, the lanthanum rate of removal from the oceans has been calculated to be approximately nine times faster than the lanthanum rate of input into the oceans from the rivers. It was also mentioned that no sign of this calculated imbalance has been seen in the oceans. One possible reason for this calculated imbalance is that the lanthanum concentration, 47.5 ng/ℓ, used for the average lanthanum concentration in river water was based upon only two river water measurements. In this thesis, seven Pacific Northwest rivers were measured for their soluble rare earth elemental concentrations, Table XIX. From this data, one can see that the measured soluble lanthanum concentration for these Pacific Northwest rivers range from 8 to 97 ng/ℓ with a run-off-weighted average lanthanum concentration of 42 ng/ℓ. This data is fairly good evidence that the lanthanum concentration used in the calculation of the river water lanthanum input rate into the oceans is qualitatively correct. From this data, one either concludes that there is a lanthanum material imbalance in the oceans or that there is another major source of lanthanum input into the oceans.

Recently there has been a study which seems to solve this dilemma. In this study,¹²¹ Elderfield and Greaves used neodymium isotope ratios,^{149,150} the rare earth elemental concentrations in marine aerosols,¹⁵¹ and the rare earth elemental concentrations as a function of depth to speculate on the possibility that the major lanthanum input into the oceans is from the atmosphere. From their data, they concluded that indeed the major source of lanthanum in the oceans appears to be atmospheric. They also concluded that the rare earth elements are leached from the aeolian particles without significant fractionation at the surface, and then are scavenged from the surface waters with preferential removal of the light rare earth elements. At first glance, this scenario seems unlikely since the rare earth elements must be leached fairly quickly from the aerosol particulates at the surface, and then they are subsequently removed from the surface water at the next instant. However, there is a theory which predicts that this phenomenon could indeed happen. The theory is inferred from the rare earth elemental experiments done in this thesis, which simply states that the solubility of the rare earth phosphate seems to control the soluble rare earth elemental concentrations in river water. If this is the case, one would expect that the soluble rare earth elemental concentrations in the oceans are also qualitatively controlled by the phosphate concentration. Since the ocean surface waters are known to be depleted of phosphates at the ocean surface due

to photosynthesis reactions,^{35,121,133} one would expect to see larger rare earth elemental concentrations at the surface than at lower ocean depths since the photosynthesis reaction only occurs near the surface of the oceans. This expected results is indeed observed in the Elderfield and Greaves study,¹²¹ which seems to prove that the rare earth elements are indeed leached from the marine particulates. However, there is an alternative explanation to the aforementioned rare earth elemental data. The observed increase in the rare earth elemental concentrations seen near the ocean surface could be caused by the amount of suspended particulates passing through the 0.45 μm poresize filter paper. This observed change in the soluble rare earth elemental concentrations as a function of depth could then be related to the absolute amount of suspended particulates passing through the 0.45 μm poresize filter paper. If this is the case, then the absolute amount of suspended particulates passing through the filter paper as a function of depth could reflect the time it takes for the individual particles to flocculate in the low suspended particulate concentration seen in the oceans. However this researcher feels that the increase of the lanthanum concentration observed at the ocean surface is mostly due to the decrease in the phosphate concentration at the oceans surface than in the amount of suspended particulates passing through the 0.45 μm poresize filter paper. In conclusion, the research reported in this thesis support the conclusion that

most of the soluble lanthanum supply into the oceans is derived from atmospheric sources, and that the rare earths are indeed leached from the marine particulates.

IV. Conclusion

Since the total water discharge of the rivers investigated in this work represents only a small fraction of the world river discharge to the oceans and since the number of reliable data on dissolved rare earth elements content in rivers is very limited, it is hardly possible to accurately establish a model for the soluble rare earth elements content of natural waters. However, the following conclusions appear reasonable even though the analyses have been limited.

1. The soluble rare earth elemental concentrations in river water is dependent on the solubility of the rare earth phosphate.

2. A variable but noticeable fraction of the suspended particulates passes through the 0.45 μm poresize filter paper and thus increases the measured soluble rare earth elemental concentration (as defined by filtration through a 0.45 μm poresize filter paper) in river water.

3. A large fraction of the soluble rare earth elements in river water are associated with fulvic acid, humic acid, and an assorted number of phosphorus compounds.

4. The world wide average lanthanum concentration in river water is approximately 45 ng/l which is in good agreement with the predicted world wide average lanthanum concentration, 47.5 ng/l, of Martin et al.¹⁷

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APPENDICES

Appendix A: Solubility of some rare earth hydroxides^{152,153,154,155}

<u>Element</u>	<u>Solubility Product Constant</u>
La	1.0×10^{-19}
Ce	1.5×10^{-20}
Pr	2.7×10^{-20}
Nd	1.9×10^{-21}
Sm	6.8×10^{-22}
Eu	3.4×10^{-22}
Gd	2.1×10^{-22}
Er	1.3×10^{-23}
Tm	3.3×10^{-24}
Yb	2.5×10^{-24}

Appendix B: Time dependence of tracer stability under simulated seawater conditions as determined by radiotracers. Complete details of the experimental procedure used in the determination of the tracer stability can be seen in Section III-A, while the discussion of these results is in Section IV-A.

APPENDIX B-1: Time Dependence of Tracer (Yb) Stability in Simulated Seawater Condition (Test 1: Unfiltered Seawater and Sediments)

<u>Time of Sampling (days)</u>	<u>Percent of Yb Tracer Remaining in Solution</u>
1	16.5 ± 1.0
2	10.6 ± 1.0
3	7.4 ± 3.5
4	3.4 ± 1.8
5	6.7 ± 0.2
6	4.8 ± 0.2

APPENDIX B-2: Time Dependence of Tracer (Ce) Stability in
Simulated Seawater Conditions

<u>% of Ce Tracer Remaining in Solution</u>			
<u>Time of Sampling (days)</u>	<u>Unfiltered</u>	<u>Filtered</u>	<u>Estimated*</u>
	<u>Water and Sediments (Test 2)</u>	<u>Water (Test 3)</u>	<u>Tracer Stability</u>
1	6.52 ± .31	94.7 ± 5.2	6.88 ± .50
2	2.03 ± .08	92.6 ± 5.7	2.19 ± .16
3	1.94 ± .28	87.9 ± 9.6	2.21 ± .40
4	1.86 ± .09	82.9 ± 13.2	2.24 ± .37
5	1.38 ± .27	86.9 ± 12.7	1.59 ± .39
6	1.36 ± .07		1.60 ± .40**

*Calculated by dividing the percent of tracer remaining in solution
in Test 2 by the fraction of tracer remaining in solution in Test 3

**Estimated by extrapolating existing data

APPENDIX B-3: Time Dependence of Tracer (Ce-DTPA) in Simulated
Seawater Conditions

<u>Time of Sampling</u> <u>(days)</u>	<u>Unfiltered</u> <u>Water and</u> <u>Sediments (Test 4)</u>	<u>Filtered</u> <u>Water (Test 5)</u>	<u>Estimated*</u> <u>Tracer Stability</u>
1	89.6 ± .4	99.7 ± 2.6	90.1 ± 2.4
2	93.2 ± 3.8	96.0 ± 3.5	97.1 ± 5.3
3	93.9 ± 7.0	97.9 ± 4.9	95.9 ± 8.6
4	90.0 ± 5.1	97.5 ± 3.1	92.3 ± 6.0
5	88.9 ± 4.4	95.8 ± 2.8	92.8 ± 5.3
6	88.8 ± 2.2	98.0 ± 2.6	90.6 ± 3.3
7	88.4 ± 4.2	99.1 ± 1.8	89.2 ± 2.7
8	87.2 ± 3.7	99.2 ± 1.9	87.9 ± 4.1
9	83.8 ± 8.6	95.0 ± 2.7	88.2 ± 9.4
10	83.9 ± 6.3	92.3 ± 3.3	90.9 ± 7.5
11	82.9 ± 4.5	92.7 ± 3.0	89.4 ± 5.7
12	82.7 ± 5.0	92.3 ± 5.3	89.6 ± 7.5
13	82.7 ± 2.7	91.9 ± 8.5	90.0 ± 8.8
14	82.0 ± 4.6	87.9 ± 7.8	93.3 ± 7.0
15	84.4 ± 6.0	88.5 ± 7.8	95.4 ± 10.8
16	85.4 ± 5.4	91.3 ± 3.7	93.5 ± 7.0
17	81.2 ± 3.4	86.1 ± 13.0	94.3 ± 14.8
18	80.2 ± 6.2	82.7 ± 11.9	97.0 ± 15.8
19	74.9 ± 2.5	- -	91.8 ± 14.2**
20	- -	80.5 ± 12.7	90.8 ± 14.9**
21	71.3 ± 2.5	78.5 ± 10.1	90.8 ± 12.9

* Calculated by dividing the percent of tracer remaining in Test 4
 by the fraction of tracer remaining in Test 5.

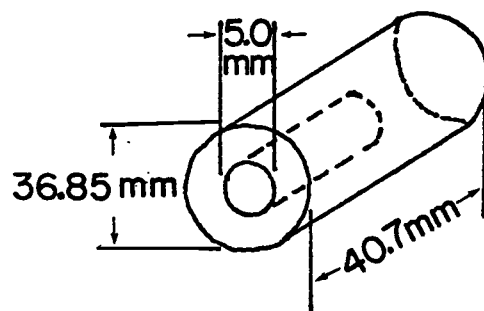
** Estimated by interpolating existing data.

Appendix B-4: Stability of Tm-DTPA Under Simulated Seawater

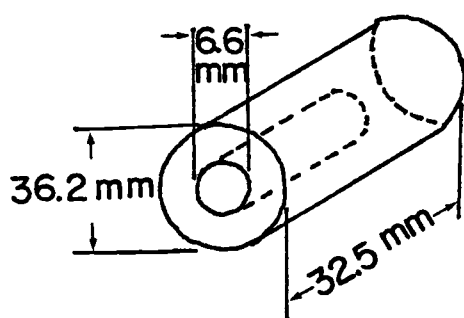
Conditions			
Day	Unfiltered Water and Sediments (Test 6)	Filtered Water (Test 7)	Estimated Tracer Stability
1	101.1 ± 3.3	100.0 ± 2.6	101.1 ± 4.2
2	102.6 ± 4.6	99.3 ± 2.6	103.3 ± 5.4
3	99.5 ± 2.0	97.0 ± 0.8	102.6 ± 2.2
4	97.0 ± 1.7	96.6 ± 3.6	100.4 ± 4.1
5	95.7 ± 2.4	97.8 ± 2.5	97.9 ± 3.5
6	95.1 ± 0.4	99.6 ± 2.8	95.5 ± 2.7
7	94.6 ± 1.3	100.5 ± 1.2	94.1 ± 1.7
8	90.1 ± 1.3	98.7 ± 4.2	91.3 ± 4.1
9	90.7 ± 3.5	102.8 ± 1.9	88.2 ± 3.8
10	94.2 ± 4.3	99.8 ± 4.2	94.4 ± 5.9
11	90.7 ± 2.3	101.3 ± 3.8	89.5 ± 4.1
12	89.1 ± 2.2	99.9 ± 2.0	89.2 ± 2.8
13		97.9 ± 2.2	89.8 ± 3.7*
14	86.7 ± 3.2	99.0 ± 2.2	87.6 ± 3.8
15	86.1 ± 2.8	96.1 ± 2.4	89.6 ± 3.7
16	85.9 ± 3.1		89.3 ± 4.3*
17	86.6 ± 5.6	96.3 ± 3.0	89.9 ± 6.5
18	83.3 ± 4.4	94.6 ± 1.8	88.1 ± 4.9
19	82.7 ± 3.2	86.9 ± 0.9	95.2 ± 3.8
20	81.7 ± 2.8	86.3 ± 1.3	94.7 ± 3.5
21	81.4 ± 4.6	86.9 ± 2.6	93.7 ± 6.0

Appendix C: Characteristics of the two Ge(Li) detectors used in the analysis of the stable activable tracer concentration. Discussion concerning the characteristics of these detectors can be seen in Section III-A-6.

Characteristics of the
detector relative to the
 ^{60}Co 1332 keV gamma ray



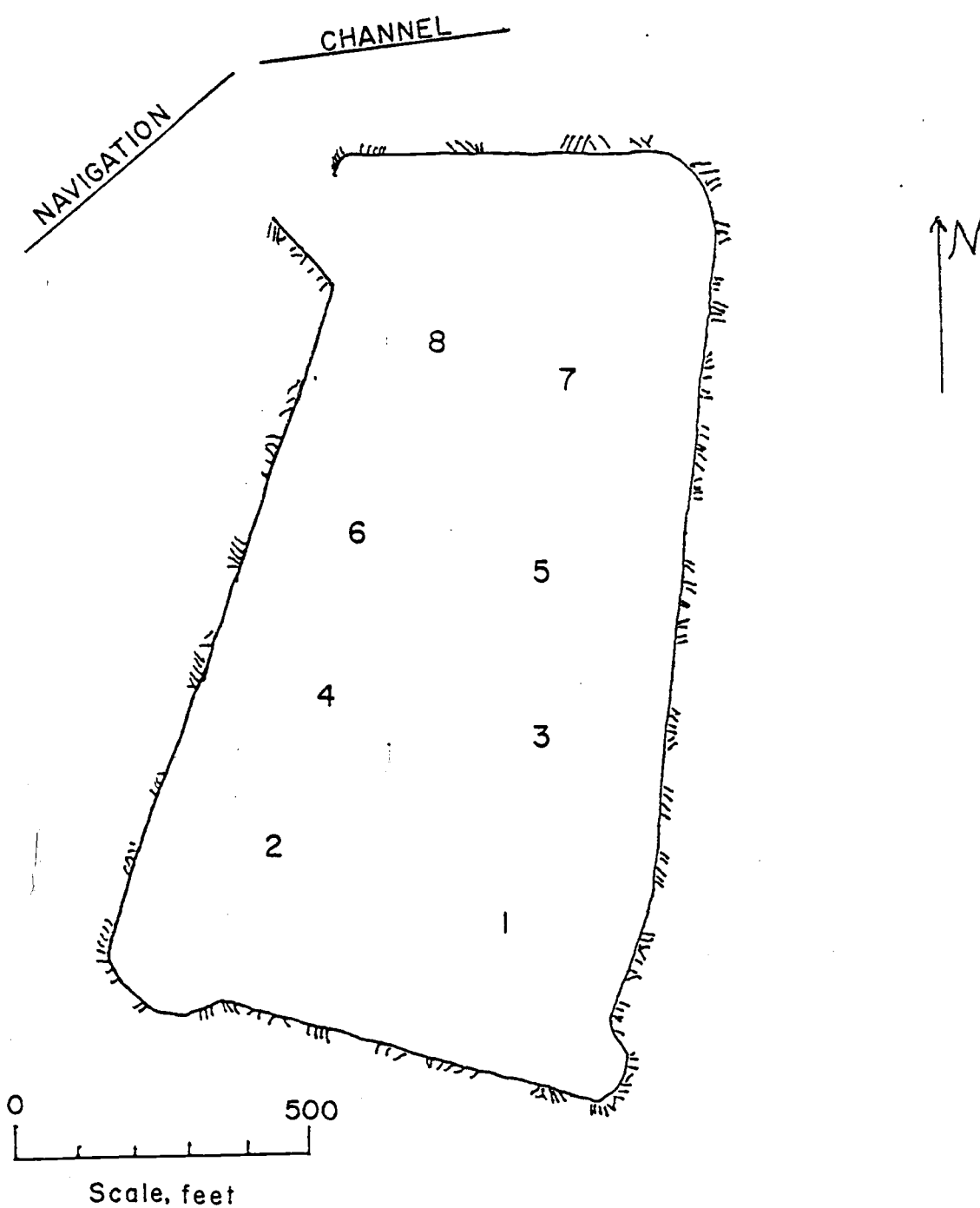
peak efficiency relative to a 3" x 3" NaI detector	5.65%
full width half maximum	1.90 keV
peak to compton ratio	32.5/1



peak efficiency relative to a 3" x 3" NaI detector	6.1%
full width half maximum	2.90 keV
peak to compton ratio	21.5/1

Appendix D: Measured tracer concentration in the field experiments conducted in the South Beach Marina. The procedure used to measure the tracer abundances is described in Section III-B-7 while the results are discussed in Section IV-B.

APPENDIX D-1: Sampling Sites in the South Beach Marina



APPENDIX D-2: Measured Rhodamine B Concentrations (ug/l) in the first
South Beach Marina Experiment (Aug. 14-16, 1980)

Sampling* Site	Elapsed Time in Experiment (hours)			
	<u>19.75</u>	<u>24.75</u>	<u>37.00</u>	<u>43.50</u>
1-T		2.16±0.06	1.75±0.05	1.91±0.06
1-M		5.29±0.16	1.33±0.04	0.75±0.02
1-B	1.02±0.03	1.01±0.03	0.89±0.03	1.91±0.06
2-T	2.07±0.06	1.82±0.05	1.82±0.05	1.98±0.06
2-M		2.27±0.07	1.71±0.05	0.35±0.01
2-B		1.60±0.05	3.01±0.09	0.96±0.03
3-T	0.65±0.02	1.61±0.05	1.56±0.05	1.40±0.04
3-M	0.45±0.01	0.72±0.02	1.36±0.04	0.86±0.03
3-B	0.45±0.01	0.75±0.02	0.44±0.01	0.50±0.02
4-T		1.19±0.04	1.31±0.04	1.15±0.03
4-M		1.00±0.03	1.24±0.04	0.37±0.01
4-B		0.70±0.02	1.68±0.05	0.21±0.01
5-T		0.92±0.03	1.50±0.05	1.22±0.04
5-M		0.53±0.02	0.55±0.02	0.38±0.01
5-B		0.51±0.02	0.62±0.02	0.13±0.01
6-T		0.95±0.03	1.28±0.04	1.15±0.03
6-M		1.06±0.03	0.53±0.02	0.66±0.02
6-B		0.22±0.01	0.34±0.01	0.34±0.01
7-T	0.41±0.01	0.65±0.02	0.66±0.02	1.10±0.03
7-M		1.06±0.03	0.49±0.01	0.47±0.01
7-B		0.41±0.01	0.73±0.02	0.32±0.01
8-T		0.81±0.02	0.82±0.02	1.09±0.03
8-M		0.43±0.01	0.41±0.01	0.43±0.01
8-B		0.56±0.02	0.43±0.01	0.40±0.01

* The number corresponds to the sampling site in the Marina (Appendix I), and the letter corresponds to the sampling depth i.e., T = surface, M = middle, and B = one foot above the bottom of the marina)

APPENDIX D-3: Measured Dysprosium-DTPA Concentrations (ngDy/l) in the
First South Beach Marina Experiment (Aug. 14-16, 1980)

Sampling* Site	Elapsed Time in Experiment (hours)			
	19.75	24.75	37.00	43.50
1-T		1,623 49	962 45	1,108 41
1-M		477 37	868 45	193 32
1-B	332 37	175 28	222 34	199 32
2-T	1,153 39	1,375 51	992 41	1,266 54
2-M		545 41	575 34	68 30
2-B		287 32	293 30	90 34
3-T	432 30	635 37	960 45	813 39
3-M	383 34	458 37	836 37	297 28
3-B	128 30	199 34	167 32	199 37
4-T		900 41	791 34	543 32
4-M		161 30	774 45	109 28
4-B		167 30	98 28	45 28
5-T		742 47	1,193 55	764 34
5-M		347 32	280 32	192 30
5-B		680 51	71 28	- 2 28
6-T		663 45	1,061 51	622 34
6-M		721 34	269 30	257 34
6-B		146 38	133 28	69 28
7-T	293 28	462 36	359 36	537 34
7-M		813 34	195 30	163 28
7-B		312 30	124 26	34 26
8-T		530 41	357 30	701 39
8-M		287 30	212 36	252 34
8-B		417 41	58 32	103 28

*The number corresponds to the sampling site in the marina (Appendix I) and the letter corresponds to the sampling depth (i.e., T = surface, M = middle, and B = one foot above the bottom of the marina).

APPENDIX D-4: Measured Rhodamine WT Concentrations (ug/l) in the Second South Beach Marina Experiment
(Jan. 16-18, 1981)

Sampling* Site	Elapsed Time in the Experiment (hours)					
	<u>13.25</u>	<u>20.00</u>	<u>31.50</u>	<u>38.25</u>	<u>45.00</u>	<u>56.50</u>
1-T	5.70±0.20	2.10±0.10	2.10±0.10	1.90±0.10	0.41±0.02	0.79±0.03
1-M	2.00±0.10	1.70±0.10	1.60±0.10	0.86±0.03	0.21±0.01	0.38±0.01
1-B	0.07±0.01	0.63±0.02	2.30±0.10	0.86±0.03	1.30±0.10	0.30±0.01
2-T	6.10±0.20	1.90±0.10	2.30±0.10	1.30±0.10	0.25±0.01	
2-M	0.02±0.01	1.30±0.10	-0.08±0.03	0.54±0.02	0.19±0.01	0.52±0.02
2-B	0.05±0.01	0.75±0.02	1.30±0.10	0.81±0.03	0.69±0.02	0.16±0.01
3-T	4.30±0.10	2.10±0.10	2.10±0.10	2.50±0.10	0.32±0.01	0.43±0.02
3-M	1.30±0.10	2.30±0.10	1.30±0.10	2.80±0.10	1.60±0.10	
3-B	0.06±0.01		0.78±0.02	0.91±0.03	0.49±0.02	0.09±0.01
4-T	8.10±0.03	1.90±0.10	2.10±0.10	1.10±0.10	0.22±0.01	0.32±0.01
4-M	0.72±0.03	3.30±0.10	0.37±0.01	1.80±0.10	0.17±0.01	0.21±0.01
4-B	0.57±0.02	1.10±0.10	0.57±0.02	0.50±0.02	0.09±0.01	
5-T	7.70±0.20	2.70±0.10	1.70±0.10	1.10±0.10	0.35±0.01	0.40±0.02
5-M	8.80±0.30	1.10±0.10	0.46±0.02	0.46±0.02	0.40±0.01	0.14±0.01
5-B	5.90±0.20	0.82±0.03	0.50±0.02	0.68±0.02		0.07±0.01
6-T	9.90±0.30	2.70±0.10	1.90±0.10	0.18±0.01	0.19±0.01	0.28±0.01
6-M	5.50±0.20	1.50±0.10	0.37±0.01	0.67±0.02	0.17±0.01	0.21±0.01
6-B	0.15±0.01	0.48±0.02	0.26±0.01	0.52±0.02		0.04±0.01
7-T	1.30±0.10	1.50±0.10	1.50±0.10	0.26±0.01	0.43±0.02	0.40±0.02
7-M	10.0±0.30	1.20±0.10	1.50±0.10	1.60±0.01	0.31±0.01	0.21±0.01
7-B	0.23±0.01	1.10±0.10	0.23±0.01	0.37±0.01	0.17±0.01	0.05±0.01
8-T	9.10±0.30	2.10±0.10	1.50±0.10	-0.01±0.01	0.22±0.01	0.34±0.01
8-M	2.40±0.10	2.50±0.10	0.49±0.02	1.10±0.10	0.03±0.01	0.23±0.01
8-B	0.26±0.01	0.49±0.02	0.15±0.01	0.46±0.02	0.36±0.01	0.03±0.01

* The number corresponds to the sampling site in the marina (Appendix I), and the letter corresponds to the sampling depth (i.e., T = surface, M = middle, and B = one foot above the bottom of the marina).

APPENDIX D-5: Measured Dysprosium-DTPA Concentrations (ngDy/L) in the Second South Beach Marina Experiment
(Jan. 16-18, 1981)

Sampling* Size	Elapsed Time in the Experiment (hours)					
	<u>13.25</u>	<u>20.00</u>	<u>31.50</u>	<u>38.25</u>	<u>45.00</u>	<u>56.50</u>
1-T	1168±39	545±35	663±41	569±29	105±24	109±19
1-M	425±25	432±35	400±24	259±37	60±18	44±22
1-B	111±39	151±18	544±24	306±37	168±16	24±22
2-T	389±39	433±25	584±43	515±48	118±14	
2-M	21±14	293±27	194±19	246±29	21±29	98±30
2-B	130±34	454±19	223±30	207±21	96±27	52±24
3-T	1153±43	540±23	293±23	466±25	43±24	74±23
3-M	1352±58	569±27	250±27	445±35	257±29	
3-B	48±21		280±30	622±52	62±17	4±17
4-T	1309±41	644±39	573±27	235±19	54±18	60±29
4-M	215±24	800±29	80±19	464±28	21±17	17±21
4-B	146±19	217±24	120±18	240±39	60±24	
5-T	1290±39	614±35	285±29	513±39	100±29	14±19
5-M	1502±43	181±17	158±30	300±25	60±22	88±21
5-B	1226±35	125±17	149±19	181±25		- 4±23
6-T	2177±61	684±29	499±23	150±35	96±23	77±23
6-M	388±22	415±32	122±27	306±30	22±13	- 4±18
6-B	35±23	163±32	105±27	164±18		- 5±18
7-T	922±37	454±35	223±39	187±26	53±17	115±24
7-M	2160±78	349±27	260±18	595±35	16±16	57±22
7-B	87±21	270±25	177±35	63±14	37±19	47±35
8-T	2520±80	565±27	411±27	123±23	36±25	22±19
8-M	569±32	402±18	103±29	295±80	1±16	26±19
8-B	120±23	225±43	37±23	192±27	62±25	27±16

* The number corresponds to the sampling site in the marina (Appendix I), and the letter corresponds to the sampling depth (i.e., T = surface, M = middle, and B = one foot above the bottom of the marina)

APPENDIX D-5: Measured Europium-DTPA Concentrations (ngEu/l) in the Second South Beach Marina Experiment
(Jan. 16-18, 1981)

Sampling* Site	Elapsed Time in the Experiment (hours)					
	13.25	20.00	31.50	38.25	45.00	56.50
1-T	181.6±10.5	79.0± 6.9	121.0± 9.3	88.5± 7.3	15.7± 3.9	15.2± 3.6
1-M	70.0± 5.3	78.7± 7.9	73.1± 7.2	31.5± 7.4	4.3± 3.9	4.5± 3.3
1-B	5.0± 6.4	21.5± 4.0	85.2± 4.7	28.0± 7.0	31.8± 6.1	4.2± 3.6
2-T	46.2± 6.5	74.5± 6.3	95.8± 8.9	82.0± 9.6	11.5± 6.0	
2-M	6.3± 4.7	38.1± 5.6	29.2± 3.9	25.6± 4.7	1.6± 3.3	0.7± 5.1
2-B	0.1± 3.1	26.0± 4.7	44.4± 6.8	39.4± 5.9	21.5± 7.3	0.5± 4.7
3-T	189.5± 6.9	83.8± 4.8	58.9± 6.8	75.0± 5.6	-2.9± 3.3	8.2± 4.0
3-M	310.6± 8.4	89.9± 4.3	24.3± 5.3	72.3±10.5	32.4± 5.3	
3-B	11.3± 6.4		35.5± 6.4	40.6± 6.8	8.4± 3.4	7.7± 5.7
4-T	222.4± 8.7	105.3± 9.7	87.8± 6.8	38.5± 6.9	12.7± 3.1	1.6± 5.2
4-M	32.5± 4.5	136.3± 6.9	21.8± 4.5	76.6± 5.9	5.2± 3.6	-1.4± 4.8
4-B	26.9± 4.0	35.3± 5.4	24.1± 4.3	23.8± 8.7	0.9± 1.8	
5-T	220.1± 8.7	92.6± 7.3	64.1± 6.5	45.8± 8.9	12.9± 6.2	-0.3± 5.1
5-M	242.0± 9.5	27.9± 4.0	62.1±13.2	31.7± 6.8	6.3± 3.6	2.8± 4.0
5-B	193.9± 7.9	23.5± 3.8	23.4± 5.3	37.8± 5.4		-0.7± 3.1
6-T	357.8± 9.0	132.3± 6.5	88.0± 6.5	23.1± 7.0	2.8± 3.7	17.0± 5.6
6-M	52.4± 4.3	62.4± 7.8	162.7± 6.3	38.0± 6.6	10.7± 3.4	7.1± 4.6
6-B	- 1.3± 3.4	12.9± 4.8	26.0± 9.2	29.2± 4.8		6.7± 7.6
7-T	149.3± 6.3	76.4± 7.8	66.8± 6.6	3.2± 4.8	8.8± 1.8	15.4± 6.1
7-M	376.0±14.0	55.8± 5.2	48.4± 6.3	77.2±10.3	5.0± 3.8	2.9± 4.5
7-B	4.4± 4.8	32.7± 6.1	3.3± 8.1	14.7± 4.9	-1.2± 2.7	1.9± 5.0
8-T	393.0±20.0	82.0±13.0	81.7±10.3	4.7± 4.4	10.1± 5.5	9.9± 3.8
8-M	69.8± 7.9	62.3± 3.8	20.6± 8.7	30.6± 5.9	1.1± 4.7	16.1± 7.8
8-B	13.3± 4.0	18.0± 6.2	1.1± 6.7	21.3± 6.9	2.2± 3.7	-0.1± 4.5

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* The number corresponds to the sampling site in the marina (Appendix I), and the letter corresponds to the sampling depth (i.e., T = Surface, M = Middle, and B = one foot above the bottom of the marina)

Appendix E: Elemental concentrations in the carrier used in the procedure to measure the soluble rare earth elements in the various Pacific Northwest river samples.

<u>Rare Earth Element</u>	<u>Concentration (mg/ml)*</u>	<u>Concentration (mg/ml)[†]</u>
La	0.813	0.437
Ce	0.946	0.508
Pr	1.550	0.833
Nd	0.100	0.054
Sm	0.959	0.515
Eu	0.975	0.524
Gd	0.050	0.027
Tb	0.050	0.072
Dy	1.043	0.561
Ho	0.050	0.027
Er	0.050	0.027
Tm	1.057	0.568
Yb	0.050	0.096
Lu	0.230	0.162

*The carrier used in the analysis of the 1981 samples

[†]The carrier used in the analysis of the 1982 samples

Appendix F: Properties of the radionuclides used in the procedure to measure the elemental abundances of the suspended and the soluble rare earth elements in the Pacific Northwest river samples.

Appendix F-1: Properties of Some Rare Earth Elements Activation
Products Used in the Analysis of the Rare Earth
Concentration in River Water¹⁵⁶

<u>Isotope</u>	<u>Half-Life</u>	<u>Gamma Ray Energy (keV)</u>
¹⁴⁰ La	40.2h	487,1597
¹⁴¹ Ce	32.5d	146
¹⁴⁴ Ce	284d	134
¹⁴² Pr	19.2h	1576
¹⁴⁷ Nd	11.1d	91
¹⁵³ Sm	46.8h	103
^{152m} Eu	9.30h	842
¹⁵² Eu	12.7y	344
¹⁵³ Gd	242.0d	98
¹⁵⁹ Gd	18.0h	363
¹⁶⁰ Tb	72.1d	299
¹⁶⁶ Ho	26.8h	81
¹⁷¹ Er	7.52h	308
¹⁷⁰ Tm	129.0d	84
¹⁶⁹ Yb	31.8d	198
¹⁷⁵ Yb	4.21d	283
¹⁷⁷ Lu	6.74d	208
¹⁴⁰ Ba	U 12.8d	1597
¹⁴⁰ La		

Appendix F-2: Properties of Some Elemental Activation Products
 Used in the Analysis of the Filterable Material in
 River Water¹⁵⁶

<u>Element</u>	<u>Product Radionuclide</u>	<u>Half-Life</u>	<u>E_γ Measured (keV)</u>
Al	Al-28	2.241m	1778.9
Ce	Ce-141	32.50d	145
Co	Co-60	5.26y	1173.2, 1332.5
Cr	Cr-51	27.7d	320
Cs	Cs-134	2.06y	605
Dy	Dy-165	2.334h	94.7
Eu	Eu-152m	9.30h	842
	Eu-152	12.7y	344
Fe	Fe-59	44.60d	1099
Gd	Gd-159	18.0h	363
	Gd-153	242.0d	99
Hf	Hf-181	42.50d	482
K	K-42	12.401h	1542.7
La	La-140	1.675d	1596.4, 487
Mg	Mg-27	9.46m	1014
Mn	Mn-56	2.58h	846.6, 1810
Na	Na-24	15.00h	1368.5
Nd	Nd-147	11.1d	91
Sc	Sc-46	83.80d	889
Sm	Sm-153	1.933d	103.2
Ta	Ta-182	115.00d	1221

Appendix F-2 (continued)

<u>Element</u>	<u>Product Radionuclide</u>	<u>Half-Life</u>	<u>E_γ Measured (keV)</u>
Tb	Tb-160	72.1d	299
Th	Pa-233	27.00d	311.9
Ti	Ti-51	5.80m	319.8
V	V-52	3.77m	1434
Yb	Yb-175	4.21d	283
	Yb-169	31.8d	198
Zn	Zn-65	244.00d	1115.5

Appendix G: Adsorption of Tm-170 on Willamette River sediments as a function of pH. Details of the experimental procedure used in the determination of the Tm-170 adsorption behavior can be seen in Section II-B-2 while the results are discussed in Section III-A of the rare earth elemental concentration in river water section of this thesis.

<u>pH</u>	<u>% Adsorbed (Day 1)</u>	<u>% Adsorbed (Day 2)</u>
3.14	52.4 ± .4	70.3 ± .3
3.70	57.4 ± .5	75.0 ± .4
4.28	70.8 ± .4	-
4.76	69.5 ± .3	-
5.30	70.2 ± .3	-
5.90	66.0 ± .3	77.7 ± .2
6.48	63.1 ± .3	-
6.57	56.7 ± .3	76.5 ± .2
6.72	53.7 ± .4	-
7.25	53.7 ± .4	-
7.45	55.1 ± .3	74.8 ± .2
7.47	51.3 ± .4	-
7.74	46.3 ± .4	63.4 ± .3
8.26	46.2 ± .4	58.7 ± .3
8.80	43.4 ± .4	57.8 ± .3
9.12	43.1 ± .4	52.7 ± .3

Appendix H: Data used in the theoretical calculation of the speciation of lanthanum and europium in river water. Discussion of the mathematical procedure used in the theoretical calculation can be seen in Section III-B of the river water study.

Appendix H-1: Compilation of the Stability Constant Data Base

General Approach

The most difficult problem encountered in the preparation of any speciation model is undoubtedly the selection of stability constants (K_w^*) to describe the interactions involved. Owing to the complexity of natural systems it is necessary to adapt stability constants determined in simple ionic media (K_m^*) for use in the speciation model. The most rigorous procedure would undoubtedly be to correct the stability constant (K_m^*) values measured in simple media to infinite dilution (K°) using a particular ionic interaction theory. This same theoretical approach could then be used to adjust the K° value to provide a corrected stability constant appropriate to the natural medium (K_w^*) taking into account all of the interactions not specifically included in the speciation model. Unfortunately there are very few systems for which the necessary ionic interaction parameters are available and only a small minority of the measured K^* values are presented in sufficient detail for the initial extrapolations to be made. An alternative approach is to make some simplifying assumptions concerning the interactions in the ionic medium and in the natural system that enable the measured K_m^* values to be used for speciation calculations with the minimum of manipulation. In applying such a procedure it is customary to make the following assumptions:

1. That any strong specific interaction between the medium ions and the trace element ion or ligand have been taken into ac-

count in the interpretation of the original measurement of K_m^* .

2. That the activity coefficients of the free metal ion, free ligand and complex are unaffected by changes in the medium composition at constant ionic strength.

3. That K_m^* can be reliably corrected for the difference in ionic strength between the medium in which the original measurement was carried out and the system which is being modelled.

Since this researcher is interested in elucidating the lanthanum and europium speciation patterns, the latter course was chosen. The most rigorous course of refitting the primary data is not only unacceptably time consuming with such a body of data but, as have been indicated, the interaction parameters are not generally available for these rare earth compounds.

Clearly the assumptions listed above will become more acceptable the more closely the ionic medium corresponds to the natural system but most experimental measurements are made in perchlorate or nitrate media. In the introduction to their critical compilation of stability constants, Smith and Martell^{132,142} state that the constants listed have not been corrected for the interaction of trace components with medium ions since, in the majority of cases, insufficient data are available to make such corrections. I have consequently taken the measured values compiled by Smith and Martell and fitted them directly to a function of the ionic strength. The original compilation of K_m^* values is necessarily a rather heterogenous collection of data gathered by numerous

authors using different experimental techniques in a variety of media and the fitting parameters obtained are best considered as providing a summary of the available data. Hopefully as the experimental data base expands and theoretical procedures improve, a more rigorous approach may be adopted and some of the inconsistencies of this simple approach may be removed. In the meantime it will be useful to extract as much information as is feasible from the data we have.

Primary Data Base

With a few exceptions, data for the complexation reactions were obtained from the critical compilation of Smith and Martell.^{132,142} Since our aim was to summarize the available data in a convenient form the critically selected constants listed at ionic strengths different from zero were corrected to ionic strength equal to zero using the Davies equation,³⁵

$$\log f = Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

where,

f = activity coefficient

$A = 0.5085$ for water at 25°C

z = charge of ion

I = ionic strength of the solution

Extension of Primary Data Base

In a few cases the stability constant for some europium and

lanthanum complexes were not available, and in these cases the stability constant was extrapolated from the stability constant of other rare earth complexes. In the extrapolation procedure which was used, one plotted the log of the stability constant for a given complex versus the ionic radii of the respected rare earth element. One then drew the best line through these data points and subsequently read the stability constant for the europium or lanthanum complex from the graph. This extrapolation procedure was based upon the fact that approximately one-half of the ligands that have been studied in complexes with all of the rare earth elements can be explained by a simple electrostatic or acid-base concepts of size and charge (a more or less uniform increase in stability accompanying the decrease in ionic radii).
157,158

Clearly the extrapolation procedure outlined above will be more acceptable if the ligand does obey the simple electrostatic or acid-base concepts of size and charge than if the ligand forms a complex which shows discrepancies from this simple picture. However even if the ligand forms a complex with the rare earth elements that does not obey the aforementioned theory, there still should be some correlation between the stability constant for the complex and the rare earth ionic radii. So this procedure should still predict a fairly accurate stability constant.

Appendix H-2: Stability Constants for Some Lanthanum Compounds

(at 25°C and Ionic Strength = 0.0)^{132,142}

<u>Reaction</u>	<u>log K</u>
$\text{La}^{3+} + \text{PO}_4^{3-} \rightarrow \text{LaPO}_4(\text{S})$	25.26
$\text{La}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{LaH}_2\text{PO}_4^{2+}$	2.57
$\text{La}^{3+} + \text{SO}_4^{2-} \rightarrow \text{LaSO}_4^+$	3.64
$\text{La}^{3+} + 2\text{SO}_4^{2-} \rightarrow \text{La}(\text{SO}_4)_2^-$	5.29
$\text{La}^{3+} + \text{OH}^- \rightarrow \text{LaOH}^{2+}$	5.5
$\text{La}^{3+} + 2\text{OH}^- \rightarrow \text{La}(\text{OH})_2^+$	9.6
$\text{La}^{3+} + 4\text{OH}^- \rightarrow \text{La}(\text{OH})_4^-$	17.9
$\text{La}^{3+} + \text{F}^- \rightarrow \text{LaF}^{2+}$	3.6
$\text{La}^{3+} + 2\text{F}^- \rightarrow \text{LaF}_2^+$	7.3
$\text{La}^{3+} + 3\text{F}^- \rightarrow \text{LaF}_3(\text{aq})$	10.9
$\text{La}^{3+} + 4\text{F}^- \rightarrow \text{LaF}_4^-$	13.8
$\text{La}^{3+} + \text{Br}^- \rightarrow \text{LaBr}^{2+}$	0.7
$\text{La}^{3+} + 2\text{Br}^- \rightarrow \text{LaBr}_2^+$	1.1
$\text{La}^{3+} + \text{Cl}^- \rightarrow \text{LaCl}^{2+}$	0.8
$\text{La}^{3+} + 2\text{Cl}^- \rightarrow \text{LaCl}_2^+$	0.9
$\text{La}^{3+} + \text{NO}_3^- \rightarrow \text{LaNO}_3^{2+}$	1.02
$\text{La}^{3+} + 2\text{NO}_3^- \rightarrow \text{La}(\text{NO}_3)_2^+$	0.26
$\text{La}^{3+} + \text{CO}_3^{2-} \rightarrow \text{LaCO}_3^+$	8.21
$\text{La}^{3+} + 2\text{CO}_3^{2-} \rightarrow \text{La}(\text{CO}_3)_2^-$	11.7
$\text{La}^{3+} + \text{P}_2\text{O}_7^{4-} \rightarrow \text{LaP}_2\text{O}_7^-$	16.72

Appendix H-3: Stability Constants for Some Europium Compounds

(at 25°C and Ionic Strength = 0.0)^{132,142}

<u>Reaction</u>	<u>log K</u>
$\text{Eu}^{3+} + \text{PO}_4^{3-} \rightarrow \text{EuPO}_4(\text{S})$	25.11
$\text{Eu}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{EuH}_2\text{PO}_4^{2+}$	2.49
$\text{Eu}^{3+} + \text{SO}_4^{2-} \rightarrow \text{EuSO}_4^+$	3.67
$\text{Eu}^{3+} + 2\text{SO}_4^{2-} \rightarrow \text{Eu}(\text{SO}_4)_2^-$	5.41
$\text{Eu}^{3+} + \text{OH}^- \rightarrow \text{EuOH}^{2+}$	6.2
$\text{Eu}^{3+} + 2\text{OH}^- \rightarrow \text{Eu}(\text{OH})_2^+$	10.3
$\text{Eu}^{3+} + 4\text{OH}^- \rightarrow \text{Eu}(\text{OH})_4^-$	18.4
$\text{Eu}^{3+} + \text{F}^- \rightarrow \text{EuF}^{2+}$	4.3
$\text{Eu}^{3+} + 2\text{F}^- \rightarrow \text{EuF}_2^+$	8.0
$\text{Eu}^{3+} + 3\text{F}^- \rightarrow \text{EuF}_3(\text{aq})$	11.4
$\text{Eu}^{3+} + 4\text{F}^- \rightarrow \text{EuF}_4^-$	14.3
$\text{Eu}^{3+} + \text{Br}^- \rightarrow \text{EuBr}^{2+}$	0.7
$\text{Eu}^{3+} + 2\text{Br}^- \rightarrow \text{EuBr}_2^+$	1.1
$\text{Eu}^{3+} + \text{Cl}^- \rightarrow \text{EuCl}^{2+}$	0.76
$\text{Eu}^{3+} + 2\text{Cl}^- \rightarrow \text{EuCl}_2^+$	0.8
$\text{Eu}^{3+} + \text{NO}_3^- \rightarrow \text{EuNO}_3^{2+}$	1.23
$\text{Eu}^{3+} + 2\text{NO}_3^- \rightarrow \text{Eu}(\text{NO}_3)_2^+$	0.47
$\text{Eu}^{3+} + \text{CO}_3^{2-} \rightarrow \text{EuCO}_3^+$	7.11
$\text{Eu}^{3+} + 2\text{CO}_3^{2-} \rightarrow \text{Eu}(\text{CO}_3)_2^-$	10.6
$\text{Eu}^{3+} + \text{P}_2\text{O}_7^{4-} \rightarrow \text{EuP}_2\text{O}_7^-$	20.27

Appendix H-4: Stability Constants for Some Phosphate Compounds
(at 25°C and Ionic Strength = 0)^{35,132,133,142}

<u>Reaction</u>	<u>log K</u>
$\text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{PO}_4^- + \text{H}^+$	-2.148
$\text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}^+$	-7.199
$\text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}^+$	-12.35
$\text{Ca}^{2+} + \text{PO}_4^{3-} \rightarrow \text{CaPO}_4^-$	6.46
$\text{Ca}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{CaHPO}_4(\text{aq})$	2.74
$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{CaH}_2\text{PO}_4^+$	1.4
$\text{Mg}^{2+} + \text{PO}_4^{3-} \rightarrow \text{MgPO}_4^-$	5.3
$\text{Mg}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{MgHPO}_4(\text{aq})$	2.91
$\text{Mg}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{MgH}_2\text{PO}_4^+$	0.99
$\text{Fe}^{3+} + \text{HPO}_4^{2-} \rightarrow \text{FeHPO}_4^+$	9.96
$\text{Fe}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{FeH}_2\text{PO}_4^{2+}$	4.30
$\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{S}) \rightarrow 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^-$	-55.6
$\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{S}) + 3\text{H}_2\text{O} \rightarrow$ $2[\text{Ca}_2\text{HPO}_4(\text{OH})_2]_{\text{surface}} + \text{Ca}^{2+} + \text{HPO}_4^{2-}$	-8.5
$\beta\text{-Ca}_3(\text{PO}_4)_2(\text{S}) \rightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	-24.0
$[\text{Ca}_2\text{HPO}_4(\text{OH})_2]_{\text{surface}} \rightarrow$ $2\text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{OH}^-$	-27
$\text{FePO}_4(\text{S}) \rightarrow \text{Fe}^{3+} + \text{PO}_4^{3-}$	-21.9
$\text{AlPO}_4(\text{S}) \rightarrow \text{Al}^{3+} + \text{PO}_4^{3-}$	-21.0

Appendix H-5: Stability Constants of Some Miscellaneous Compounds (at 25°C and Ionic Strength = 0.0)^{35,132,133,142}

<u>Reaction</u>	<u>log K</u>
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3(\text{aq})$	-1.464
$\text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+$	-6.352
$\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$	-10.329
$\text{Ca}^{2+} + \text{OH}^- \rightarrow \text{Ca}(\text{OH})^+$	1.3
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(\text{aq})$	3.15
$\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaHCO}_3^+$	1.0
$\text{Mg}^{2+} + \text{OH}^- \rightarrow \text{Mg}(\text{OH})^+$	2.58
$\text{Mg}^{2+} + \text{CO}_3^{2-} \rightarrow \text{MgCO}_3(\text{aq})$	2.88
$\text{Mg}^{2+} + \text{HCO}_3^- \rightarrow \text{MgHCO}_3^+$	0.95
$\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3(\text{S})$	38.8
$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3(\text{S})$	36.3
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(\text{S})$	-8.34
$\text{Mg}^{2+} + \text{CO}_3^{2-} \rightarrow \text{MgCO}_3(\text{S})$	-4.90

Appendix H-6: The Effective Diameter of the Hydrated Ion¹⁵⁹
 Used in the Extended Debye-Huckel Activity
 Coefficient Calculation

<u>Inorganic Ion</u>	<u>Ion Size (a)</u>
Cl^- , Br^- , I^- , NO_3^-	3
F^-	3.5
SO_4^{2-} , HPO_4^{2-} , PO_4^{3-}	4
H_2PO_4^- , HCO_3^-	4.4
CO_3^-	4.5
Ca^{2+}	6
Mg^{2+}	8
Al^{3+} , Fe^{3+} , La^{3+} , Eu^{3+}	9

Appendix H-7: Concentrations for the Major Components Used in
the Speciation Calculation of Lanthanum and
Europium

<u>Component</u>	<u>Concentration</u>
Ionic Strength	4×10^{-3}
Cl^-	$2.19 \times 10^{-4} \text{ M}$
F^-	$4.9 \times 10^{-6} \text{ M}$
SO_4^{2-}	$1.2 \times 10^{-4} \text{ M}$
Ca^{2+}	$3.8 \times 10^{-4} \text{ M}$
Mg^{2+}	$3.4 \times 10^{-4} \text{ M}$
P	$6.46 \times 10^{-7} \text{ M}$
CO_2	$3.3 \times 10^{-4} \text{ atm}$

Appendix I: Elemental abundances of the suspended particulates and the soluble rare earth elements in seven Pacific Northwest rivers. The procedure used in the analysis can be seen in Sections II-B and II-C.

Appendix I-1: Concentrations* of Rare Earth Elements in Some Pacific Northwest Rivers (ng/l)

Sample [†]		Sample Date	La	Ce	Pr	Nd	Sm	Eu
Columbia	1A	5/2/81	30.1±.3	58±1	10±2	23±2	--	1.59±.03
	2A	9/1/82	--	48±1	--	16±1	4.4±.2	1.52±.05
	2B	9/1/82	--	41±2	--	--	6.2±.2	1.17±.05
	3A	9/8/82	23.3±.3	46±2	--	--	5.60±.06	0.82±.04
	3B	9/8/82	--	56±2	--	--	5.90±.07	1.24±.06
	4A	9/15/82	--	--	--	--	6.6±.1	1.37±.07
	4B	9/15/82	32±2	28±2	--	6.1±.2	1.79±.08	0.39±.03
	5A	9/22/82	11.8±.2	37±2	--	23±1	2.84±.09	0.89±.04
Fraser Klamath Marys	5B	9/22/82	6.7±.2	29±1	--	9±2	1.92±.06	0.49±.05
	A	5/1/81	97±1	155±3	28±2	88±4	25.3±.4	7.19±.09
	A	4/27/81	15.1±.2	26±1	5.1±.7	9±2	3.2±.2	1.25±.03
	1A	9/10/82	28.1±.6	75±3	--	--	8.3±.4	2.13±.07
	1B	9/10/82	24.7±.8	33±4	--	--	5.5±.2	1.16±.07
	2A	9/17/82	37±1	89±3	--	40±3	10.5±.1	2.7±.1
	2B	9/17/82	10.1±.2	33±2	--	6±2	8.0±.2	1.24±.07
	A	4/27/81	25.0±.3	47±1	19±1	23±2	8.3±.2	2.94±.04
Rogue	A	4/25/81	8.1±.1	11.4±.8	7.2±.9	11±2	2.5±.2	0.98±.02
Sacramento Willamette	1A	9/3/82	13.3±.8	13±1	--	10±2	2.20±.08	0.57±.04
	1B	9/3/82	62.2±.6	66±5	--	18±2	3.54±.05	0.90±.06
	2A	9/13/82	50±20	100±50	--	--	11±2	2±1
	2B	9/13/82	11.9±.6	40±30	--	--	3.9±.7	1.2±.3
	3A	9/20/82	23.9±.4	53±2	--	24±2	5.9±.1	1.62±.06
	3B	9/20/82	3.5±.5	27±4	--	--	2.4±.1	0.77±.08
	4A	9/24/82	18.1±.2	51±2	--	21±2	7.07±.08	1.67±.04
	4B	9/24/82	12±1	50±20	--	--	1.7±.3	0.49±.09

*The uncertainties in the concentrations only reflect counting statistics and not systematic errors. We would estimate the systematic error due to sampling, chemical manipulations, etc. to be approximately 10-20% of the reported values.

†The A designates samples were filtered through a 0.45µm pore size filter paper, while the B designates samples were filtered through a 0.20µm pore size filter paper.

Appendix I-1: (continued)

Sample		Gd	Tb	Ho	Er	Yb	Lu
Columbia	1A	6.5±.7	1.23±.04	0.93±.07	--	4.5±.6	0.67±.04
	2A	16±1	0.55±.03		--	2.3±.1	0.38±.01
	2B	21±2	0.31±.09		--	1.9±.3	0.29±.02
	3A	19±2	0.38±.03		--	2.43±.05	0.42±.02
	3B	--	0.69±.05		--	3.0±.4	0.57±.05
	4A	16±2	1.16±.08		--	2.3±.1	0.364±.008
	4B	--	0.24±.06		--	1.3±.1	0.23±.02
	5A	19±2	0.39±.06		--	1.9±.3	0.26±.02
	5B	--	0.31±.03		--	1.8±.1	0.29±.01
Fraser	A	53±3	4.34±.09	6.90±.04	14±2	15.7±.6	2.13±.07
Klamath	A	4±1	0.54±.03	0.72±.05	5±1	3.1±.4	0.28±.03
Marys	1A	--	1.36±.08		--	4.2±.3	0.63±.04
	1B	25±6	0.41±.2		--	2.5±.3	0.33±.04
	2A	14±2	1.74±.09		--	5.1±.1	0.71±.04
	2B	--	0.53±.08		--	1.9±.2	0.28±.02
Rogue	A	8±1	1.20±.04	1.92±.09	--	6.3±.7	0.79±.03
Sacramento	A	5±1	0.53±.03	0.38±.06	--	2.5±.3	0.32±.03
Willamette	1A	--	0.42±.05			2.1±.4	0.35±.03
	1B	--	0.5±.2			1.7±.6	0.38±.07
	2A	--	--			--	--
	2B	--	--			--	--
	3A	6±1	0.80±.05			4.3±.6	0.74±.08
	3B	--	0.6±.2			0.5±.1	--
	4A	5±1	0.94±.04			2.0±.2	0.31±.01
	4B	--	1.5±.7			--	--

Appendix I-2: Elemental Abundances of the Filterable Material from River Water (%)

Sample	Al ₂ O ₃	FeO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO
<u>Columbia</u>							
May 2, 1981	21.9±.6	8.6±.5	3.7±.5	1.40±.01	1.6±.1	1.5±.2	0.247±.004
May 2, 1981	21.2±.5	8.9±.5	4.2±.4	1.41±.01	1.56±.07	1.3±.2	0.249±.003
Sep. 1, 1982	--	7.2±.5	4±1	1.28±.03	1.9±.2	1.4±.5	0.277±.009
Sep. 8, 1982	16.2±.9	--	5±1	1.45±.06	1.7±.2	0.9±.3	0.37±.02
Sep. 15, 1982	16.6±.4	8.7±.5	3.9±.7	1.56±.03	2.3±.2	0.9±.1	0.308±.08
Sep. 22, 1982	17.5±.7	8.2±.6	4±1	1.79±.05	1.7±.2	0.8±.2	0.39±.03
<u>Fraser</u>							
May 1, 1981	19.9±.3	7.6±.4	4.3±.3	1.73±.05	2.8±.2	0.81±.08	0.141±.002
May 1, 1981	20.3±.6	7.8±.4	4.7±.4	1.76±.01	3.4±.1	1.1±.1	0.0941±.0005
<u>Klamath</u>							
April 27, 1981	17.3±.3	8.9±.5	2.7±.3	0.663±.005	0.620±.006	0.7±.1	0.431±.003
<u>Marys</u>							
Sept. 10, 1982	17±1	12.9±.8	4±1	0.57±.01	1.2±.1	2.2±.7	0.83±.02
Sept. 17, 1982	23±2	4.4±.3	3±1	0.42±.01	1.7±.1	2.1±.7	0.57±.02
<u>Rogue</u>							
April 27, 1981	19±3	8.9±.5	3.3±.7	0.825±.007	1.01±.06	1.2±.4	0.373±.003
<u>Sacramento</u>							
April 25, 1981	19.2±.5	11.0±.6	4.0±.6	1.58±.02	1.6±.1	0.9±.2	0.172±.003
April 25, 1981	14.8±.5	8.8±.5	3.0±.7	1.12±.02	1.4±.1	0.6±.2	0.124±.003
<u>Willamette</u>							
Sept. 3, 1982	18±1	8.3±.7	--	1.31±.07	0.6±.2	--	0.25±.02
Sept. 13, 1982	17.9±.9	9.7±.7	--	1.11±.04	1.0±.1	3.0±.7	0.49±.02
Sept. 20, 1982	19±1	9.2±.8	8±2	0.90±.06	0.3±.2	1.0±.4	0.26±.02
Sept. 24, 1982	19±1	8.8±.6	--	0.86±.07	0.9±.2	--	0.25±.02

Appendix I-3: Elemental Abundances of the Filterable Material from River Water (ppm)

Sample	Co	Cr ₂ O ₃	Cs	Hf	Sc	Th	V	Zn	Ta
<u>Columbia</u>									
May 2, 1981	26±1	120±20	3.7±.2	5.0±.3	23±1	8.9±.4	170±10	370±50	1.3±.1
May 2, 1981	27±1	110±20	4.3±.2	5.6±.4	23±1	8.7±.4	200±10	330±50	1.14±.08
Sep. 1, 1982	22±1	80±30	3.3±.2	4.1±.3	18±1	8.8±.5	150±20	270±50	1.2±.1
Sep. 8, 1982	--	500±100	5.3±.6	6.3±.7	--	14±1	180±20	400±80	2.3±.4
Sep. 15, 1982	26±1	30±30	2.5±.4	3.8±.5	21.8±.9	9.4±.7	160±10	140±10	--
Sep. 22, 1982	22±2	130±50	--	4.8±.2	22±1	9.5±.9	160±20	160±20	--
<u>Fraser</u>									
May 1, 1981	25.7±.9	120±30	2.7±.4	2.7±.2	19.9±.7	9.0±.6	165±9	77±4	1.0±.2
May 1, 1981	26.3±.9	120±30	2.7±.4	2.7±.2	20.3±.7	9.2±.6	180±10	162±6	0.27±.07
<u>Klamath</u>									
April 27, 1981	29±1	180±20	3.4±.2	3.4±.2	27±1	4.0±.2	160±10	140±20	0.59±.08
<u>Marys</u>									
Sep. 10, 1982	47±3	230±50	3.5±.3	3.3±.3	38±2	7.3±.4	310±50	250±40	1.0±.2
Sep. 17, 1982	10.6±.9	--	--	1.5±.3	9.1±.4	3.6±.4	430±60	150±20	--
<u>Rogue</u>									
April 27, 1981	26±1	140±20	3.4±.2	3.2±.2	26±1	4.1±.2	180±40	140±20	0.55±.07
<u>Sacramento</u>									
April 25, 1981	44±2	310±50	3.3±.2	3.6±.3	29±2	5.7±.3	290±20	1,800±300	0.5±.1
April 25, 1981	25±1	160±60	--	2.3±.5	23.0±.9	4.9±.6	260±20	2,010±80	--
<u>Willamette</u>									
Sep. 3, 1982	19±2	--	2.5±.3	3.9±.5	22±2	4.1±.4	210±30	140±50	--
Sep. 13, 1982	30±2	--	1.6±.4	4.8±.8	27±2	3.6±.6	250±20	--	--
Sep. 20, 1982	23±3	--	2.7±.6	2.3±.9	--	5.2±.9	220±30	--	--
Sep. 24, 1982	18±2	330±90	2.3±.3	4.6±.5	22±2	3.5±.4	130±30	--	0.8±.2

Appendix J: Calculated speciation of lanthanum and europium in the Aare River along with the measured values used in this theoretical calculation. Details of the procedure used in the speciation calculation can be seen in Section III-B while the discussion on the results of these calculations are in Section III-D.

Appendix J-1: Measured Concentrations for Some Major Components in the River, Aare¹³⁹

Sample	pH	Temperature (°C)	Conductivity (µS/cm)	NO ₃ ⁻ (mg/ℓ)	SO ₄ ²⁻ (mg/ℓ)	PO ₄ ³⁻ (mg/ℓ)	Cl ⁻ (mg/ℓ)	Ca ²⁺ (mg/ℓ)	Mg ²⁺ (mg/ℓ)
<u>Hagneck</u>									
July 8, 1974	7.95	15.4	251	2.3	34	0.18	3.1	176	34
Sep. 3, 1974	8.19	15.4	250	2.9	33	0.18	3.2	168	34
Dec. 11, 1974	8.08	6.6	349	5.2	38	0.31	4.7	256	44
Feb. 11, 1975	8.09	5.7	336	5.3	40	0.25	5.8	240	39
April 11, 1975	8.02	7.2	365	6.4	42	0.33	11	248	49
May 29, 1975	8.14	11.8	288	2.6	28	0.20	2.6	168	24
June 26, 1975	8.12	14.0	262	2.6	32	0.17	1.8	200	34
Aug. 11, 1975	8.07	18.4	210	2.3	40	0.18	1.4	160	24
<u>Bern</u>									
July 8, 1974	7.97	13.4	235	1.8	32	0.13	2.4	160	29
Sep. 3, 1974	8.28	15.4	227	2.1	32	0.15	2.4	152	34
Dec. 11, 1974	8.26	6.6	282	3.7	39	0.15	2.8	176	44
April 11, 1975	8.68	7.0	288	4.1	40	0.17	8.1	200	39
May 29, 1975	8.15	11.0	244	1.9	33	0.06	3.3	168	34
June 26, 1975	8.35	14.1	218	1.9	29	0.06	1.0	168	24
Aug. 11, 1975	8.24	17.0	192	2.0	26	0.20	1.2	152	24
<u>Thun</u>									
July 8, 1974	8.03	13.0	221	1.2	32	0.01	1.5	152	29
April 11, 1975	8.10	6.2	248	1.6	40	0.03	4.3	168	39
Aug. 11, 1975	8.57	18.6	176	1.0	25	0.01	0.6	136	19
<u>Merringen</u>									
July 8, 1974	7.66	8.6	49	1.0	6	0.07	0.4	32	5
Sep. 3, 1974	7.85	7.6	39	0.9	5	0.03	0.6	24	5
April 11, 1975	7.62	3.4	50	1.4	7	0.01	3.9	32	5
Aug. 11, 1975	7.85	6.2	33	0.8	4	0.01	0.4	32	--

Appendix J-2: Calculated Speciation of Lanthanum in the River, Aare (-log α)

Sample	La ³⁺	LaSO ₄ ⁺	La(SO ₄) ₂ ⁻	LaH ₂ PO ₄ ²⁺	LaOH ²⁺	La(OH) ₂ ⁺	La(OH) ₄ ⁻
<u>Hagneck</u>							
July 8, 1974	2.37	2.39	4.31	6.49	3.06	5.09	8.89
Sep. 3, 1974	2.85	2.88	4.82	7.17	3.30	5.09	8.41
Dec. 11, 1974	2.62	2.77	4.66	6.63	3.19	5.11	8.65
Feb. 11, 1975	2.64	2.76	4.63	6.75	3.20	5.10	8.62
April 11, 1975	2.50	2.62	4.47	6.44	3.14	5.12	8.78
May 29, 1975	2.75	3.00	5.01	6.99	3.25	5.10	8.52
June 26, 1975	2.71	2.89	4.84	7.00	3.23	5.09	8.55
Aug. 11, 1975	2.62	2.67	4.51	6.82	3.17	5.08	8.64
<u>Bern</u>							
July 8, 1974	2.41	2.57	4.52	6.68	3.07	5.08	8.84
Sep. 3, 1974	3.03	3.19	5.13	7.52	3.39	5.08	8.22
Dec. 11, 1974	2.99	3.09	4.96	7.46	3.37	5.09	8.27
April 11, 1975	3.81	3.91	5.77	8.63	3.78	5.08	7.42
May 29, 1975	2.57	2.65	4.49	7.34	3.06	4.89	8.29
June 26, 1975	3.18	3.38	5.36	8.12	3.46	5.09	8.09
Aug. 11, 1975	2.96	3.19	5.21	7.27	3.34	5.07	8.29
<u>Thun</u>							
July 8, 1974	2.53	2.68	4.62	7.96	3.13	5.07	8.71
April 11, 1975	2.66	2.74	4.59	7.68	3.20	5.08	8.58
Aug. 11, 1975	3.66	3.89	5.92	9.57	3.72	5.12	7.68
<u>Merringen</u>							
July 8, 1974	1.83	2.56	5.17	6.06	2.74	5.02	9.40
Sep. 3, 1974	2.26	3.05	5.73	6.99	2.97	5.06	9.06
April 11, 1975	1.75	2.41	4.96	6.79	2.70	5.02	9.48
Aug. 11, 1975	2.22	3.09	5.87	7.42	2.92	5.00	9.00

Appendix J-2: (Continued)

Sample	LaF^{2+}	LaF_2^+	$\text{LaF}_3(\text{aq})$	LaF_4^-	LaBr^{2+}	LaBr_2^+
<u>Hagneck</u>						
July 8, 1974	4.25	5.97	7.74	10.15	8.42	14.71
Sep. 3, 1974	4.73	6.45	8.21	10.63	8.90	15.19
Dec. 11, 1974	4.52	6.26	8.03	10.45	8.69	15.00
Feb. 11, 1975	4.54	6.27	8.05	10.46	8.71	15.01
April 11, 1975	4.41	6.15	7.93	10.34	8.58	14.89
May 29, 1975	4.63	6.36	8.13	10.54	8.81	15.10
June 26, 1975	4.59	6.31	8.08	10.49	8.76	15.05
Aug. 11, 1975	4.48	6.19	7.95	10.37	8.65	14.93
<u>Bern</u>						
July 8, 1974	4.28	6.00	7.76	10.18	8.45	14.74
Sep. 3, 1974	4.90	6.62	8.38	10.78	9.07	15.36
Dec. 11, 1974	4.87	6.60	8.37	10.78	9.04	15.34
April 11, 1975	5.70	7.43	9.20	11.61	9.87	16.17
May 29, 1975	4.45	6.17	7.93	10.35	8.62	14.91
June 26, 1975	5.05	6.76	8.53	10.94	9.22	15.50
Aug. 11, 1975	4.82	6.53	8.29	10.70	8.99	15.27
<u>Thun</u>						
July 8, 1974	4.39	6.11	7.87	10.28	8.56	14.85
April 11, 1975	4.54	6.26	8.02	10.43	8.71	15.00
Aug. 11, 1975	5.51	7.22	8.97	11.38	9.68	15.96
<u>Merringen</u>						
July 8, 1974	3.62	5.29	7.02	9.43	7.79	14.03
Seo. 3, 1974	4.04	5.70	7.43	9.84	8.21	14.44
April 11, 1975	3.54	5.21	6.94	9.36	7.71	13.95
Aug. 11, 1975	3.99	5.65	7.38	9.79	8.16	14.39

Appendix J-2: (Continued)

Sample	LaCl ²⁺	LaCl ₂ ⁺	LaNO ₃ ²⁺	La(NO ₃) ₂ ⁺	LaCO ₃ ⁺	La(CO ₃) ₂ ⁻
<u>Hagneck</u>						
July 8, 1974	5.80	9.87			0.0094	2.15
Sep. 3, 1974	6.26	10.32			0.0081	1.67
Dec. 11, 1974	5.89	9.79			0.0083	1.87
Feb. 11, 1975	5.81	9.63			0.0081	1.85
April 11, 1975	5.41	8.95			0.016	1.53
May 29, 1975	6.26	9.41			0.0091	1.76
June 26, 1975	6.38	10.68			0.0086	1.81
Aug. 11, 1975	6.37	10.78			0.0076	1.92
<u>Bern</u>						
July 8, 1974	5.94	10.12			0.0067	2.11
Sep. 3, 1974	6.56	10.74			0.013	1.50
Dec. 11, 1974	6.47	10.58			0.014	1.53
April 11, 1975	6.83	10.49			0.00075	2.88
May 29, 1975	5.97	10.01			0.015	1.56
June 26, 1975	7.09	11.64			0.020	1.37
Aug. 11, 1975	6.78	11.25			0.013	1.59
<u>Thun</u>						
July 8, 1974	6.26	10.64			0.0055	2.24
April 11, 1975	5.94	9.87			0.0075	1.85
Aug. 11, 1975	7.77	12.54			0.098	0.98
<u>Merringen</u>						
July 8, 1974	6.06	10.96			0.0095	2.80
Sep. 3, 1974	6.30	11.02			0.0059	2.47
April 11, 1975	4.99	8.91			0.011	2.88
Aug. 11, 1975	6.43	11.32			0.0047	2.43

Appendix J-3: Calculated Speciation of Europium in the River, Aare (-log α)

Sample	Eu^{3+}	EuSO_4^+	$\text{Eu}(\text{SO}_4)_2^-$	$\text{EuH}_2\text{PO}_4^{2+}$	EuOH^{2+}	$\text{Eu}(\text{OH})_2^+$	$\text{Eu}(\text{OH})_4^-$
<u>Hagneck</u>							
Dec. 11, 1974	1.66	1.78	3.58	5.75	1.54	3.45	7.19
Feb. 11, 1975	1.76	1.85	3.62	5.95	1.62	3.52	7.24
May 29, 1975	1.56	1.78	3.71	5.89	1.37	3.21	6.83
June 26, 1975	1.33	1.48	3.34	5.70	1.15	3.01	6.67
Aug. 11, 1975	1.60	1.62	3.38	5.89	1.46	3.36	7.12
<u>Bern</u>							
Dec. 11, 1974	1.91	1.99	3.76	6.47	1.60	3.32	6.70
April 11, 1975	2.80	2.87	4.64	7.70	2.07	3.37	5.91
June 26, 1975	2.10	2.26	4.16	7.12	1.68	3.30	6.50
Aug. 11, 1975	1.88	2.08	4.01	6.27	1.56	3.30	6.72
<u>Merringen</u>							
Aug. 11, 1975	1.18	2.03	4.71	6.46	1.19	3.27	7.47

Appendix J-3: (Continued)

Sample	EuF^{2+}	EuF_2^+	$\text{EuF}_3(\text{aq})$	EuF_4^-	EuBr^{2+}	EuBr_2^+
<u>Hagneck</u>						
Dec. 11, 1974	2.86	4.60	6.57	8.99	7.73	14.04
Feb. 11, 1975	2.96	4.69	6.67	9.08	7.83	14.13
May 29, 1975	2.75	4.48	6.45	8.86	7.62	13.92
June 26, 1975	2.51	4.23	6.20	8.61	7.38	13.67
Aug. 11, 1975	2.76	4.47	6.44	8.85	7.63	13.92
<u>Bern</u>						
Dec. 11, 1974	3.10	4.82	6.79	9.20	7.97	14.26
April 11, 1975	3.99	5.72	8.69	10.10	8.86	15.16
June 26, 1975	3.27	4.98	6.94	9.36	8.14	14.42
Aug. 11, 1975	3.04	4.75	6.71	9.12	7.91	14.19
<u>Merringen</u>						
Aug. 11, 1975	2.26	3.91	5.85	8.25	7.13	13.35

Appendix J-3: (Continued)

Sample	EuCl^{2+}	EuCl_2^+	EuNO_3^{2+}	$\text{Eu}(\text{NO}_3)_2^+$	EuCO_3^+	$\text{Eu}(\text{CO}_3)_2^-$
<u>Hagneck</u>						
Dec. 11, 1974	4.97	8.93	4.70	9.66	0.15	2.01
Feb. 11, 1975	4.97	8.84	4.78	9.74	0.23	2.07
May 29, 1975	5.11	9.33	4.89	10.14	0.074	1.68
June 26, 1975	5.03	9.40	4.65	9.90	0.27	1.53
Aug. 11, 1975	5.40	9.86	4.95	10.25	0.091	2.00
<u>Bern</u>						
Dec. 11, 1974	5.43	9.61	5.08	10.18	0.036	1.55
April 11, 1975	5.86	9.58	5.93	10.99	0.089	0.76
June 26, 1975	6.05	10.66	5.54	10.92	0.035	1.39
Aug. 11, 1975	5.74	10.27	5.29	10.64	0.034	1.61
<u>Merringen</u>						
Aug. 11, 1975	5.44	10.39	4.91	10.60	0.071	2.49