

**ALUMINUM CONCENTRATIONS IN THE MULLICA
RIVER-GREAT BAY ESTUARY, NEW JERSEY**

A Thesis Submitted
to the Temple University Graduate Board

in Partial Fulfillment
of the Requirement for the Degree

MASTER OF ARTS

by

Mary C. Sleight

December 1978

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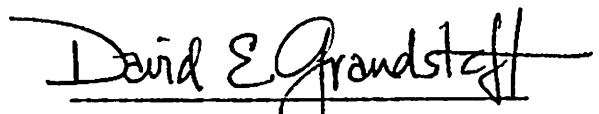
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Mary C. Sleight

A thesis submitted in partial fulfillment
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Master of Arts degree in Geology,
College of Liberal Arts.

December, 1978


Dr. David E. Grandstaff, advisor

ABSTRACT

Dissolved aluminum in filtered water ($0.45 \mu\text{m}$) from the Mullica River-Great Bay Estuary, New Jersey, and from six north-eastern United States rivers was analyzed by a fluorometric method using Manganon as the fluorometric reagent. The aluminum content of the six rivers sampled ranged from 4 to $42 \mu\text{g/l}$, with an average of $15 \mu\text{g/l}$ (corrected for discharge). During the summer and fall of 1977, the aluminum content of the Mullica River averaged approximately $35 \mu\text{g/l}$. The aluminum content of the water during the winter and spring of 1978 was approximately six times that of the previous summer and fall, with a mid-winter high of $237 \mu\text{g/l}$. In Great Bay Estuary, aluminum exhibited definite non-conservative behavior, with more than 80% removal of the aluminum by salinities of less than $10^{\circ}/\text{oo}$. This behavior is similar to that previously observed for iron in this estuary (Coonley et al., 1971). The aluminum concentration appears to be controlled by the solubility of crystalline gibbsite. The estimated flux of dissolved aluminum from the estuary into the ocean is less than $5 \mu\text{g/l}$. Assuming these are representative data, an oceanic residence time for aluminum is calculated to be 25,000 years.

ACKNOWLEDGEMENTS

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Although words are totally inadequate, I would like to express my thanks to my family: my mother, Sarah, and Robert. It was their support, both spiritual and financial, and their belief in me that gave me help and encouragement during the past three years. I would also like to express my appreciation to my room mate, Evelyn Schulz, whose aid was invaluable in so many ways. The fact that she put up with me for three years says it all. I would like to be able to thank individually all the other people and students, both graduate and undergraduate, who helped me meet the daily ups and downs, and made the past three years so interesting.

No acknowledgement would be complete without some mention of Miranda Blau, Evelyn Druding, and Mildred Shapiro. I would like to try to express my appreciation to these ladies for their limitless patience in helping me deal with all the endless

paperwork and problems. It was the countless little things they did that aided me so much during the past three years.

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This work is dedicated to the memory
of my father, I. C. Sleight, whose belief
in me continues to make me live up to it.

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INTRODUCTION

Although aluminum is the third most abundant element in the earth's crust, the concentration and behavior of aluminum in the hydrosphere are not well known. These uncertainties in the geochemical cycle are due to naturally low aluminum concentrations in water and, until recently, inadequate analytical techniques. Early analyses, especially for river water, were performed on unfiltered samples. Consequently, data included aluminum in colloidal and clay particles, and the resulting aluminum concentrations tended to be extremely high. The first accurate aluminum analyses were made by Sackett and Arrhenius (1962) while investigating aluminum concentrations in the Pacific Ocean. More recent work by Hosokawa et al. (1970) in Japan, Hydes and Liss (1976, 1977) in the North Sea, Stoffyn (pers. comm., 1977) in the Chesapeake Bay, and Mackenzie et al. (1978) in the Mediterranean Sea have further examined the behavior and concentration of aluminum in estuarine and oceanic waters. Aluminum concentrations in rivers have been measured by Gibbs (1972) on the Amazon River, Kennedy et al. (1974) and Jones et al. (1974) in the western United States, and Sholkovitz (1976) in several Scottish rivers. However, aluminum concentrations and behavior in natural waters are still inadequately known.

The physical and chemical characteristics of river and ocean water differ greatly. These differences cause estuaries to be regions of rather complex water chemistry. As waters from rivers mix with ocean water in an estuarine environment, dissolved ions

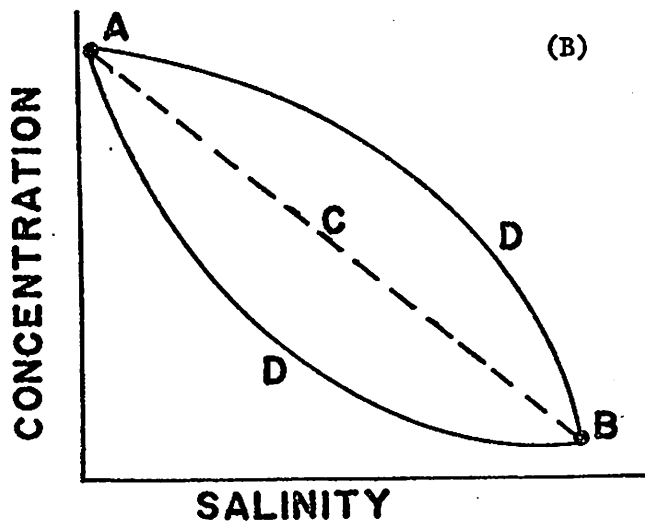
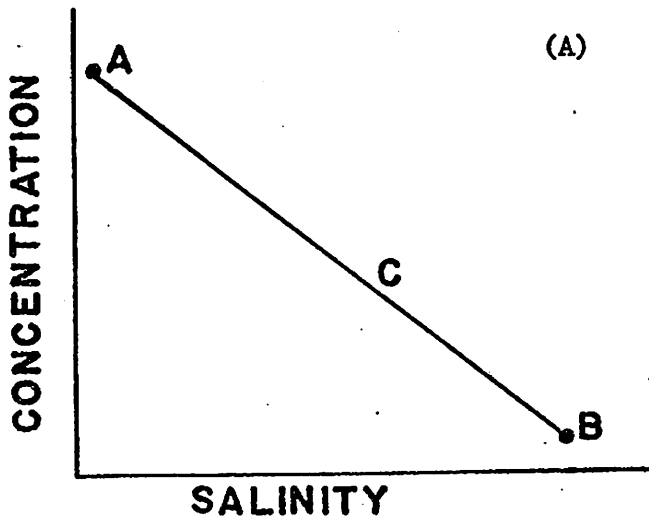


Figure 1 (A). Conservative mixing graph with A being pure river end member, B is the pure oceanic end member, and C is the theoretical dilution line.

(B). Non-conservative mixing graph, with A, B, and C as above. D represents the deviation away from the theoretical mixing line as found in non-conservative mixing.

will exhibit two types of behavior: conservative and non-conservative mixing. Conservative behavior is thought to result from simple dilution, with ion removal or addition being negligible (Boyle et al., 1974). Non-conservative mixing is a result of either addition or removal of ions from solution. A common procedure for the determination of mixing behavior involves a graphic solution. The concentration of the ion being measured is compared to an index of conservative mixing, usually salinity or chlorinity (Liss, 1976). The straight line joining the riverine end member and the oceanic end member is defined as the theoretical dilution line. The theoretical mixing line is used for the determination of mixing behavior.

In conservative mixing, the data points will lie close to the theoretical dilution line, and show little systematic deviation. The relationship between dissolved ion concentration and salinity or chlorinity is linear (Figure 1A). However, if a greater than 10% deviation from the theoretical dilution line occurs, the dissolved ion is said to display non-conservative mixing behavior (Liss, 1976). In non-conservative mixing, the relationship between the ion concentration and the salinity or chlorinity is non-linear (Figure 1B). Changes in some parameter, such as salinity, pH, ionic strength, dissolved organic concentrations, or biological activity cause the addition or removal of ions from the water. The addition of ions could be caused by mineral dissolution, desorption, or halmyrolysis, while removal may be due to flocculation, precipitation, adsorption, or biological removal.

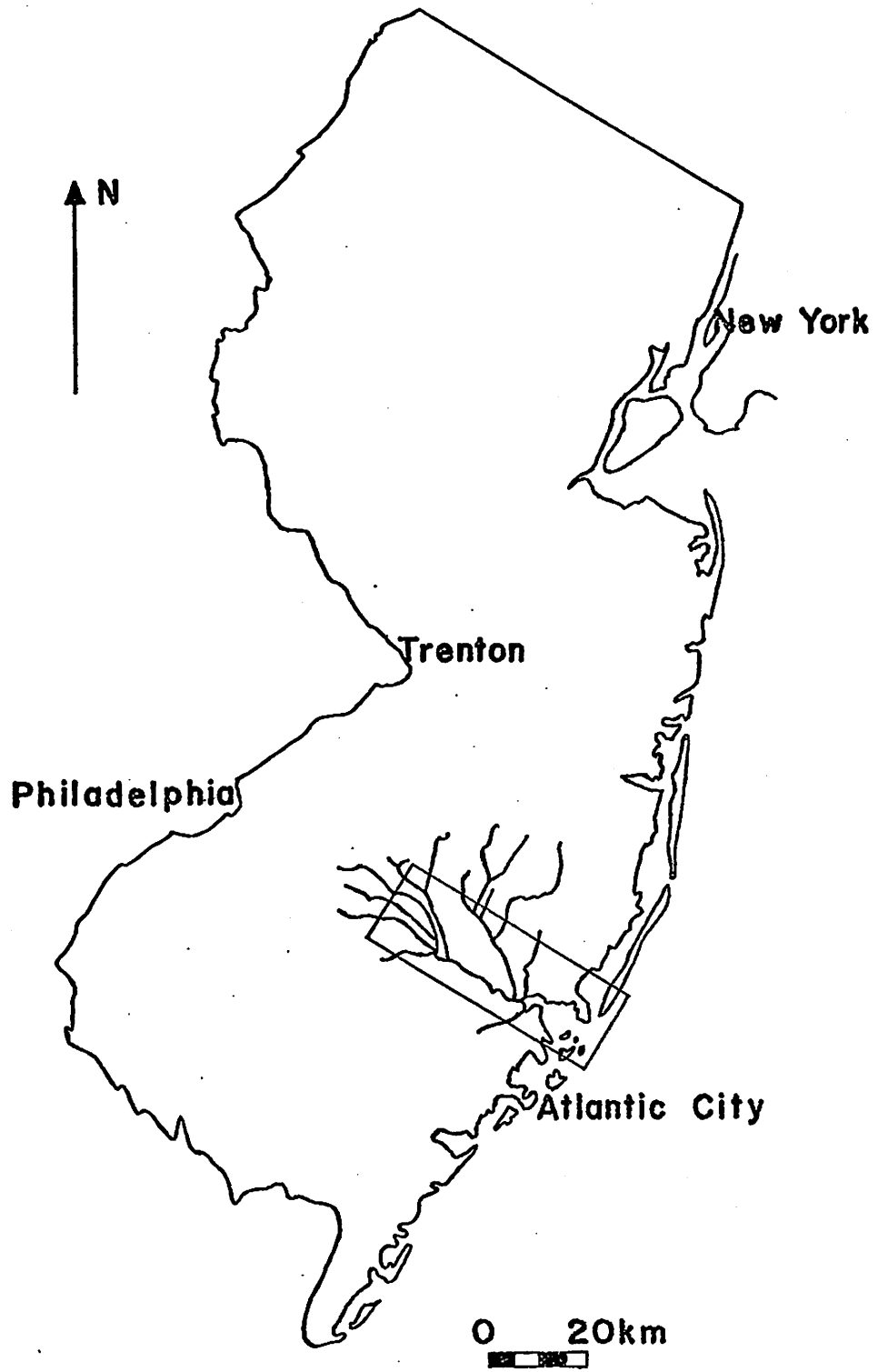


Figure 2 General location map of the Mullica River-Great Bay Estuary.

Previous work has shown fluorine to be the best example of conservative mixing (Liss, 1976), while iron displays non-conservative behavior (Coonley et al., 1971).

In this study, analyses for dissolved aluminum were undertaken to investigate its behavior in estuaries, that is, whether mixing is conservative or non-conservative. Analyses were also undertaken to obtain further data for the determination of an average concentration of dissolved aluminum in rivers. The results of these analyses are used to refine the knowledge of the geochemical cycle for aluminum in the hydrosphere.

STUDY AREA

The area chosen for study was the Mullica River-Great Bay Estuary in New Jersey. This area was chosen because previous work by Coonley et al. (1971) and Boyle et al. (1977) showed that iron exhibits non-conservative behavior in this estuary, and because it has been suggested that aluminum and iron will exhibit similar behavior in an estuarine environment (Sholkovitz, 1976; Boyle et al., 1977; Eckert and Sholkovitz, 1976). The Mullica River-Great Bay Estuary is located in south central New Jersey, about 80 kilometers southeast of Philadelphia and about 20 kilometers north of Atlantic City (Figure 2). The sampling localities are shown in Figure 3. The Mullica River-Great Bay Estuary may be one of the few relatively unpolluted estuaries found in the northeastern United States. The river drains

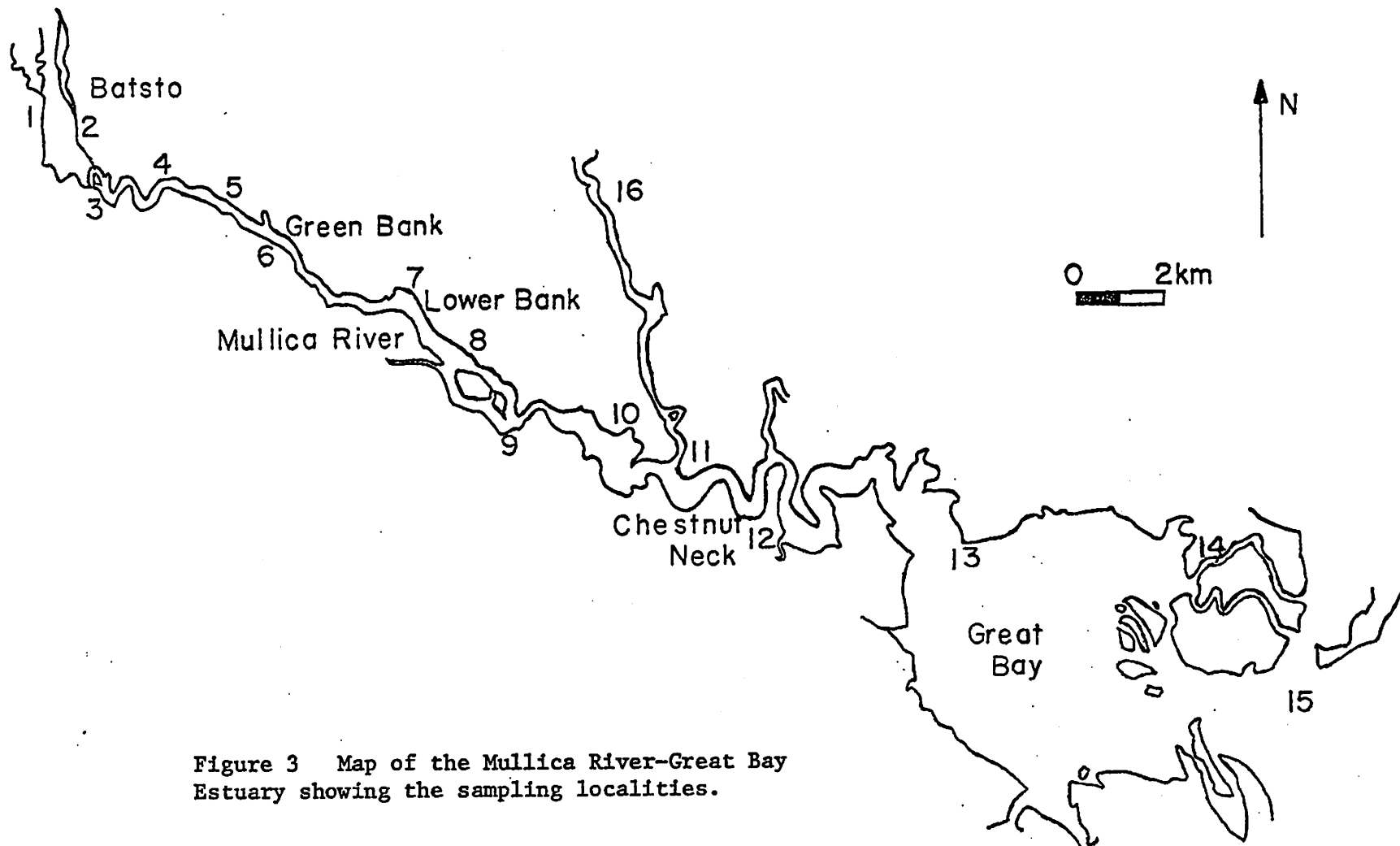


Figure 3 Map of the Mullica River-Great Bay Estuary showing the sampling localities.

approximately 1500 square kilometers of state forest and agricultural land. The entire river system is relatively simple, with only small tributaries running into the main channel. The rainfall in the area averages 115 centimeters per year, with no well defined dry season. Average streamflow is 2.5×10^9 liters per day, with the river flow reaching its minimum in the late summer and fall. The Cohansey Formation, an unlithified Miocene sand, is exposed in most of the study area (Granstrom et al., 1973).

Six other northeastern United States rivers were sampled to obtain additional data to refine the computation of an average river dissolved aluminum concentration. Sampling was done during the fall of 1977. Figure 4 shows the approximate locations of the sampling points. Exact locations are listed in Appendix II. All river samples were taken well above the tidal range in fresh water.

ANALYTICAL METHODS

Water samples were collected on thirteen occasions between June 1977 and May 1978. The sampling localities are shown in Figure 3. All samples were collected in one liter polyethylene bottles from a boat or from the shore. All bottles were rinsed well with in situ water to pre-adsorb the aluminum ions onto the surface of the bottle. The pre-adsorption onto the surface of the bottle reduces the aluminum loss in the sample during storage. Samples were refrigerated upon collection, and all samples were

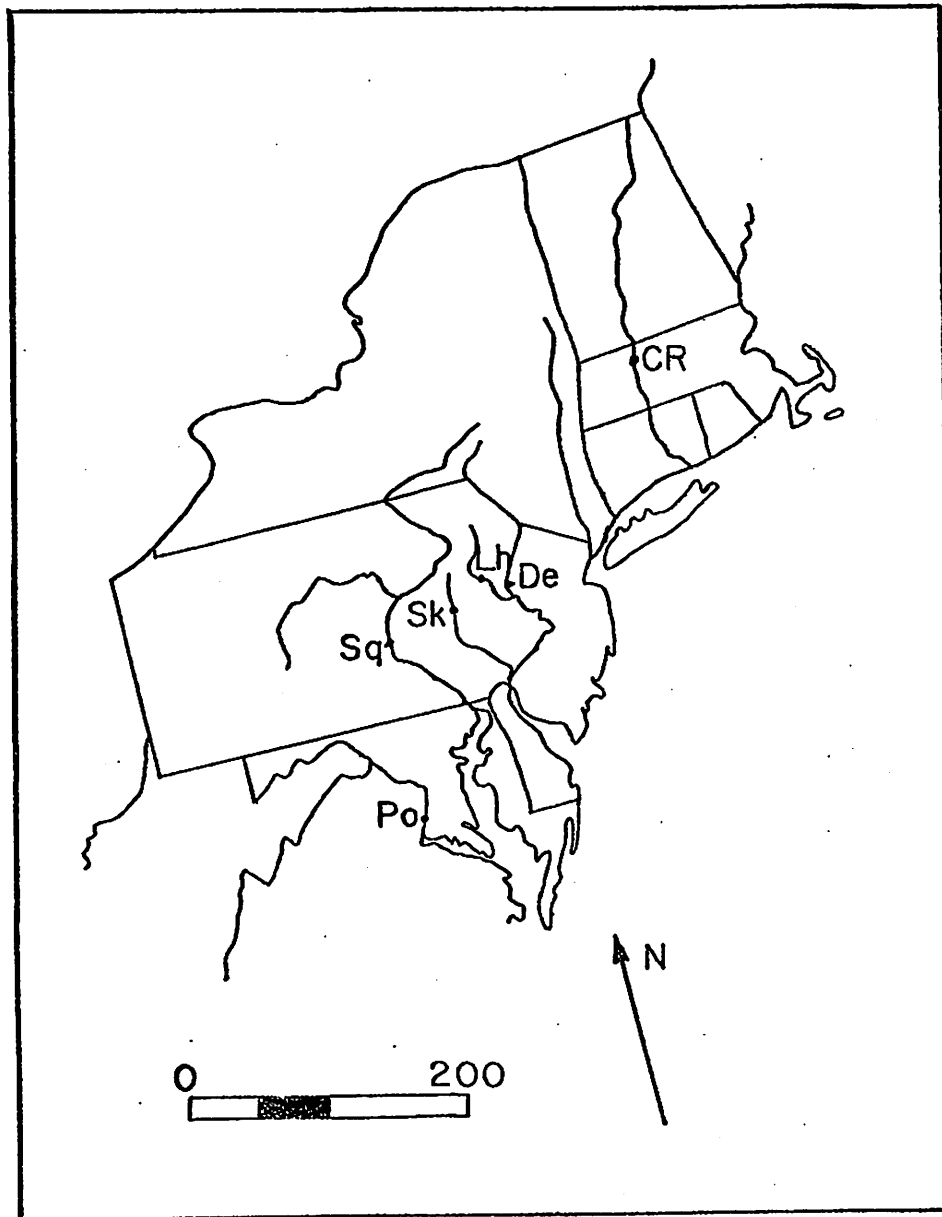


Figure 4 Location map showing the approximate locations of the sampling points for the six northeastern United States rivers. (The exact locations are listed in Appendix II.)

analyzed within 36 hours of collection. Samples were filtered by vacuum through a 0.45 μm filter. This filter size is the one accepted as the arbitrary boundary between dissolved and colloidal or particulate constituents (Kennedy et al., 1974). Several samples were filtered through a 0.22 μm filter to determine the possible effects of filter size on the dissolved aluminum concentration.

Temperature and pH measurements were made in the field. The pH measurements were made with a portable Soiltest ^(TM) model L-180 pH meter, and rechecked in the laboratory. Iron analyses were performed by a flame atomic adsorption technique. Salinity was calculated from chlorinity using the standard relationship:

$$\text{Salinity}(\text{‰}) = 1.80655 \times \text{Chlorinity}(\text{‰}). \quad (1)$$

Chlorinity was measured using a chloride specific ion electrode. Silica was analyzed by the yellow molybdosilicate technique.

Dissolved aluminum was determined by a fluorometric method modified from Dagnall et al. (1966) (see Appendix I). Manganon, also known as 2,2'(methylidene-nitrilo)diphenol, or as salicyliden-o-aminophenol, was used as the fluorometric reagent. Most cations that could cause possible interference were removed before the addition of the Manganon with a double extraction using sodium diethyldithiocarbamate. After a 20 minute developing time, the samples were analyzed on a Turner Fluorometer using filters to allow the passage of the 410 m μ excitation wavelength and the 520 m μ emission wavelength. Blanks were run through the entire procedure. Water from a Millipore-Milli-Q ^(TM) deionizer was used to prepare all solutions. An estimated detection limit for

aluminum of approximately 1 $\mu\text{g}/\text{l}$ was determined by the concentration of aluminum in the water provided by the deionizer system. The procedure is specific for dissolved aluminum. The estimated relative standard deviation for samples with a concentration of more than 5 $\mu\text{g}/\text{l}$ is less than approximately 5%.

RESULTS

Results of the individual analyses are listed in Appendix II. Samples collected from the lower portions of Great Bay and the oceanic inlet averaged approximately 2 $\mu\text{g}/\text{l}$ of aluminum. Although near shore aluminum concentrations should be higher due to suspended clay and mineral materials (Hydes, 1977), this value is consistent with the oceanic aluminum concentration of 1-3 $\mu\text{g}/\text{l}$ for surface waters determined by Sackett and Arrhenius (1962) and Mackenzie et al. (1978). Samples considered to be "river" water were taken above Green Bank, and had salinities of less than 0.01 to about 5‰. The river concentrations averaged about 35 $\mu\text{g}/\text{l}$ of aluminum during the summer and fall, with an early summer high of 45 $\mu\text{g}/\text{l}$. Late winter and early spring river samples contained much higher concentrations of aluminum, about six times larger than the summer samples and averaging about 190 $\mu\text{g}/\text{l}$ of aluminum (Figure 5A and 5B). The middle estuary, geographically located between Green Bank and Chestnut Neck, displayed the greatest variation in both salinities and aluminum concentrations. This area is influenced by tidal variation and streamflow, allowing

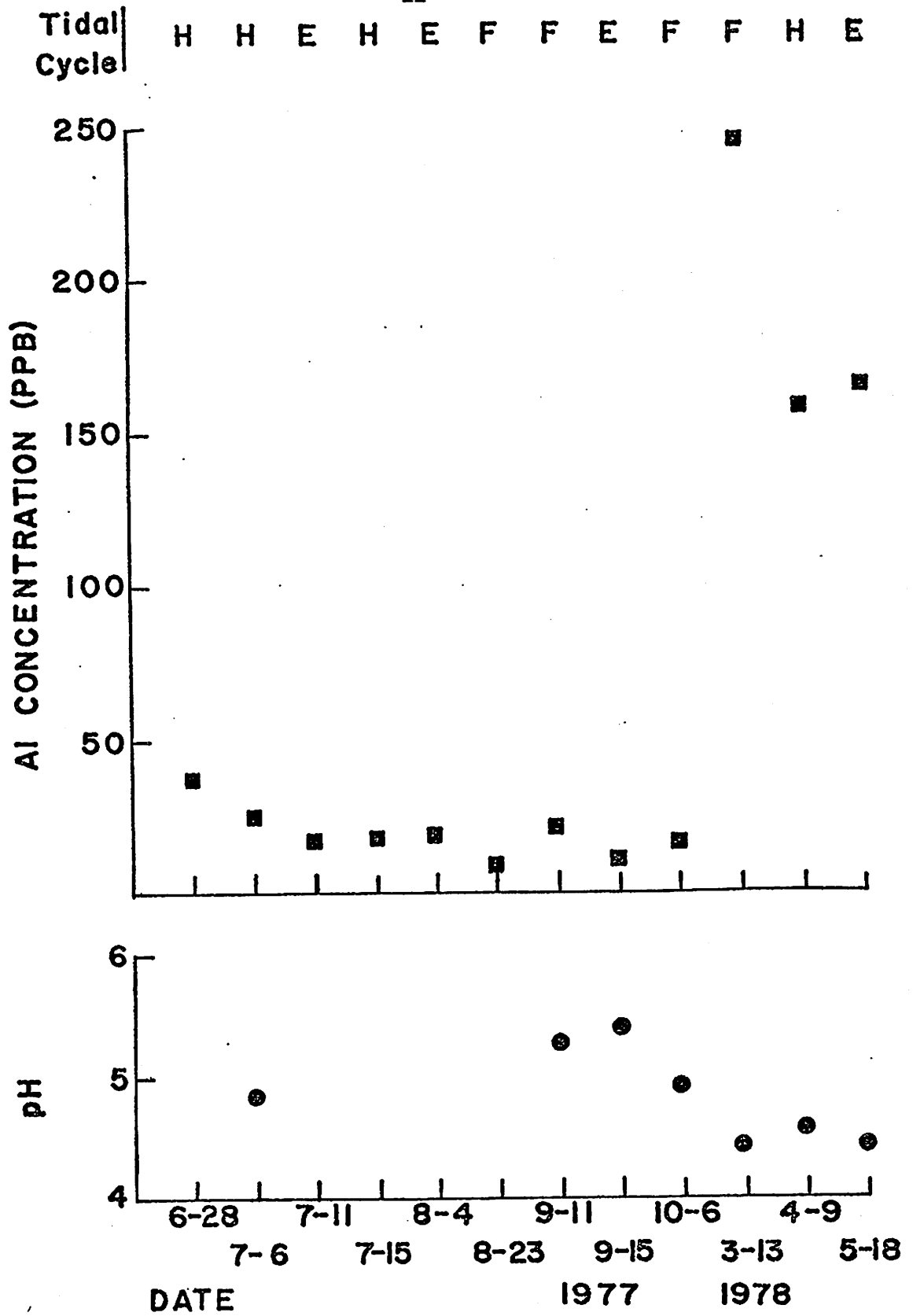


Figure 5A Variation of pH, aluminum concentration, and tidal cycle through time for sampling point 3 (Batsto).

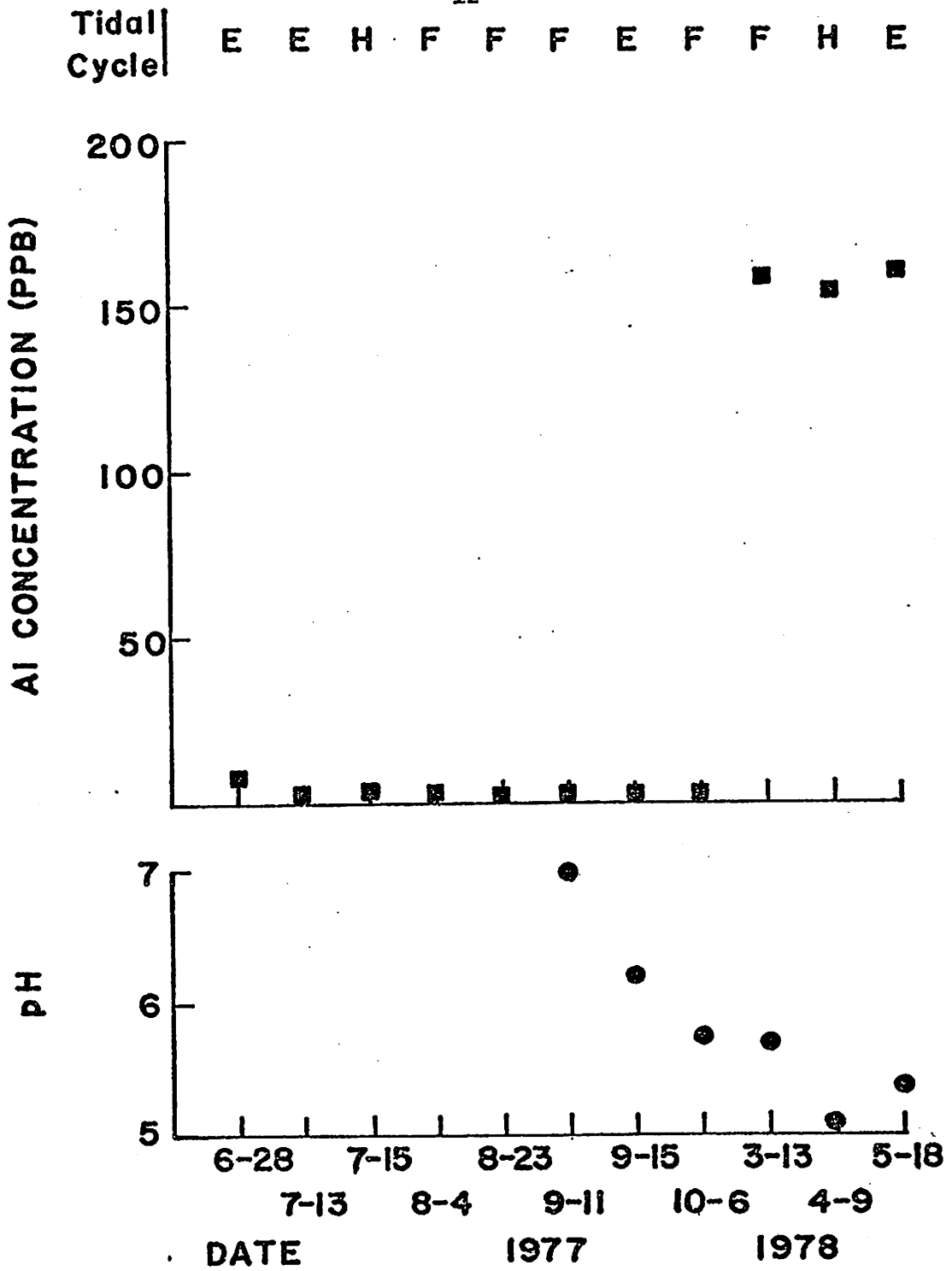


Figure 5B Variation of pH, aluminum concentration, and tidal cycle through time for sampling point 7 (Lower Bank).

salinities to range from 1 to 20⁰/∞. During the summer and fall, the middle estuary aluminum concentrations ranged from 1 to 15 µg/l, while the winter and spring samples had much higher aluminum concentrations, averaging about 150 µg/l.

The variation through time of aluminum concentrations at a given sampling locality is shown in Figures 5A and 5B. This variation indicates the possibility of seasonal variation in dissolved aluminum concentrations. The variation in dissolved aluminum concentrations may be caused by seasonal variation in such parameters as temperature, runoff, pH, or dissolved organic material. Schofield (1971) shows seasonal changes in the dissolved aluminum concentration in several lakes in the Adirondack Mountains. Acidic pollutants collect in the snow during the winter and are released during the spring thaw. These acidic runoffs cause the increase in the dissolved aluminum concentration in the late winter and spring. In the Mullica River-Great Bay Estuary, the observed increase in the aluminum concentration is probably due to a combination of several factors, with changes in the pH of the water being most important (Figures 5A and 5B). A noticeable drop in the pH of the river water seems to coincide with increased runoff due to the spring thaw. The nature of the drainage basin (low lying forest and farmland) allows high concentrations of dissolved organic material. The pH changes in the estuary may correlate with seasonal variation in these organic materials. The concentration of acidic pollutants from Philadelphia and New York during the winter may also cause the pH

drop, similar to the effect that Schofield (1971) found in the Adirondacks. The cause of the increase of dissolved aluminum concentration may be some combination of several factors, with pH changes giving the best explanation.

The type of mixing behavior of aluminum in the Mullica River-Great Bay Estuary was determined by graphing the aluminum concentrations versus salinity (Figure 6). The graph, using data from the summer of 1977, shows that in the Mullica River-Great Bay Estuary, aluminum exhibits definite non-conservative behavior. More than 80% is removed at salinities of less than 10⁰/oo, with most of the aluminum removal taking place in the upper estuary around Green Bank. Previous work by Hosokawa et al. (1970) on the Chikogogawa Estuary in Japan, and by Hydes and Liss (1976, 1977) on the Conway and Ouse Estuaries in Great Britain, also suggest non-conservative mixing of aluminum. However, because of lower initial aluminum concentrations, the percentage of aluminum removal was not as large as in this study. After non-conservative mixing in the upper estuary, the concentration of dissolved aluminum is reduced from 35 µg/l to 1-5 µg/l. Previous work by Hydes and Liss (1976, 1977) on the Conway Bay, and unpublished data from Stoffyn (pers. comm., 1977) from the Chesapeake Bay, also shows similar low aluminum concentrations in lower estuaries, varying from 0.4 to 7 µg/l. The aluminum concentrations for spring 1978 analyses, although higher in the low salinity end, also exhibited the expected non-conservative behavior with approximately 95% removal by salinities of 10⁰/oo. The final flux from the estuary

remained the same for the winter and spring samples, averaging between 1 to 5 $\mu\text{g}/\text{l}$.

It has been suggested that aluminum and iron will exhibit similar behavior in an estuary (Sholkovitz, 1976; Boyle et al., 1977; Eckert and Sholkovitz, 1976). Previous studies have shown that in the Mullica River-Great Bay Estuary, iron exhibits non-conservative behavior (Coonley et al., 1971; Boyle et al., 1977). Because of the proposed similarity in estuarine behavior, dissolved iron analyses were performed on four sets of samples. (Appendix II). Figure 7 compares aluminum and iron concentrations plotted against salinity. Both iron and aluminum exhibit similar non-conservative behavior in the Mullica River-Great Bay Estuary. The major removal of both species of ions occurs at salinities of less than $10^{\circ}/\text{oo}$.

Unpublished work by Stoffyn (pers. comm., 1977) in Chesapeake Bay has shown a 2 $\mu\text{g}/\text{l}$ increase in aluminum concentrations from the surface down to depths of 25 meters. Mackenzie et al. (1978) suggest that sediment-water interactions in bottom waters may account for most of the increase in ion concentration. In the Mullica River-Great Bay Estuary, aluminum concentrations did not vary with depth. However, the Mullica River-Great Bay Estuary is a shallow system, generally less than 4 meters in depth. The shallow nature of the estuary probably allows complete vertical mixing of the water.

Most of the Mullica River is tidally influenced, with saline waters occurring as far inland as Greenbank. However, the aluminum concentrations do not appear to be influenced by tidal action.

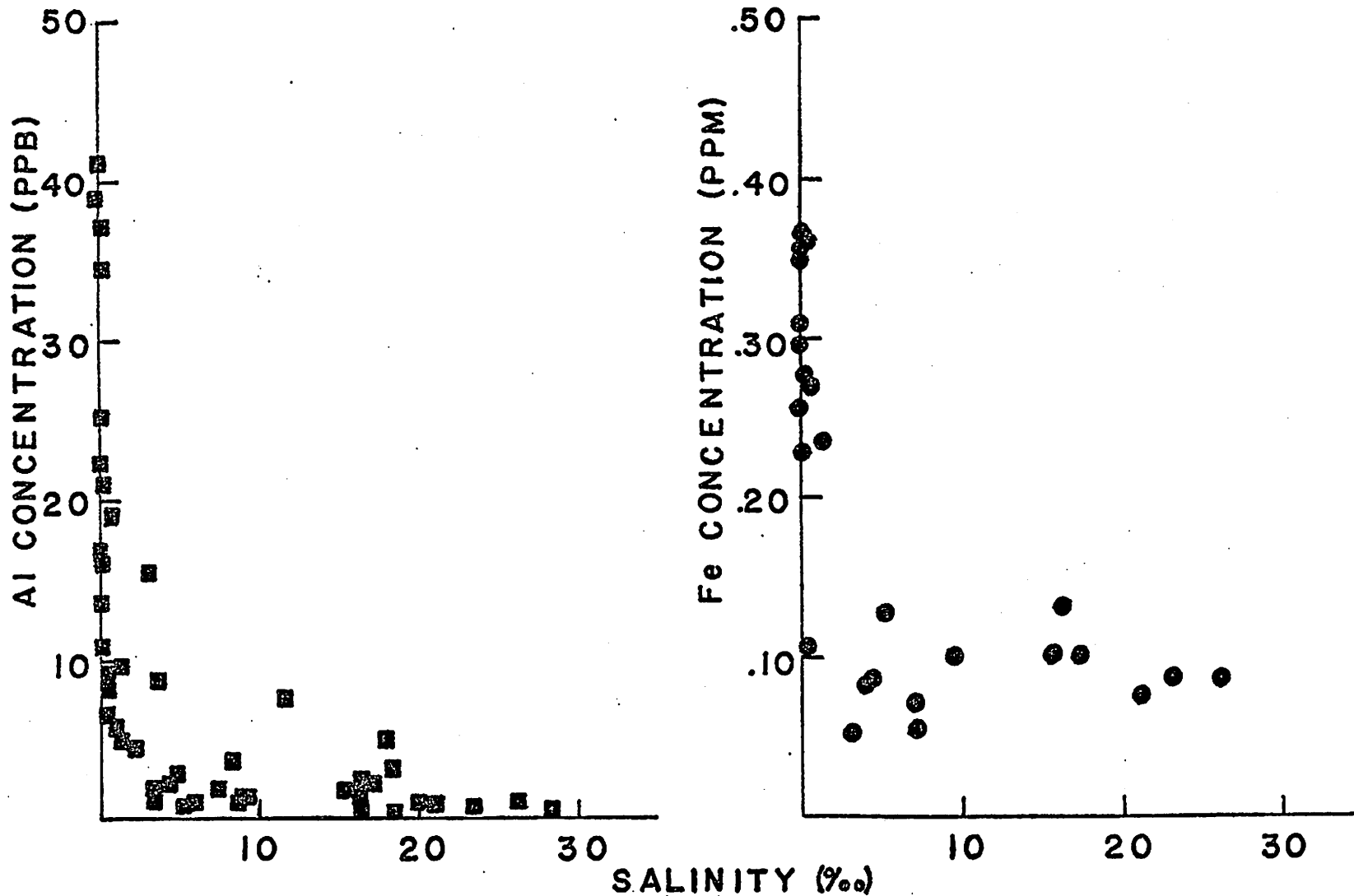


Figure 7 Comparison of aluminum and iron concentrations versus salinity in the Mullica River-Great Bay Estuary. Both ions exhibit definite non-conservative behavior, with major removal of the ions occurring at salinities of less than 10‰.

Figure 5A and 5B compare aluminum concentration to the tidal cycle. The small variations in aluminum concentration is probably due to fluctuations in pH which are influenced by climatic variation such as rainfall and runoff fluctuations. These factors are all closely related, and their individual importance cannot be determined.

The apparent ion concentrations may be influenced by filter pore size. The relationship between filter size and ion concentration has been studied by Kennedy et al. (1974). Their work shows a decrease in both aluminum and iron concentrations with decreasing filter size. Boyle et al. (1977) also noted decreases in ion concentration with smaller filter pore size. The concentration decrease is due to the more complete removal of suspended colloidal and fine clay particles by the finer filter pore size.

Possible variation of aluminum concentrations caused by the inclusion of these suspended solids was examined (Table 1). Selected samples were analyzed unfiltered, and filtered through a 0.45 μm and 0.22 μm filters. The variation between unfiltered and filtered water was large, with the unfiltered water averaging about 10 $\mu\text{g}/\text{l}$ more of aluminum than filtered (0.45 μm) water. This difference is due to the suspended solids that are removed during the filtration process. The aluminum concentration difference between samples filtered through a 0.45 μm and a 0.22 μm filter were negligible. This suggests that the 0.45 μm filter effectively removed most suspended and colloidal particles.

The mode of transportation of chemical species is important

DATE	SAMPLE	.22 μm	.45 μm	unfiltered
10/6/77	5	--	39.0	53.2
	6	---	22.5	50.75
4/9/78	3	152.0	154.0	--
	5	158.0	158.0	--
	7	158.0	150.0	--

Table 1 Differences in the aluminum concentration ($\mu\text{g}/\text{l}$) caused by various filter pore sizes.

in determining the possible removal mechanisms. Gibbs (1973), working with Amazon and Yukon River water, distinguished five different transportation mechanisms: (1) the dissolving of species and the resulting inorganic and organic associations, (2) the adsorption onto solids, (3) metallic coatings on pre-existing solids, (4) use in biological material, and (5) the formation of new crystalline structures. Less than 10% of most trace metals are carried in solution. Reuter and Perdue (1977) have found that both aluminum and iron exhibit a good linear correlation with dissolved organic concentrations. The actual method of transportation for aluminum is probably not distinguishable, but it is probably a combination of organic and inorganic associations and complexing.

Several mechanisms for the removal of ions during estuarine mixing have been proposed. Eckert and Sholkovitz (1976) suggest that the increasing electrolyte concentration in an estuary may cause the precipitation of dissolved organic complexes. The positive cations are associated with the negatively charged organic molecules, and are removed as the organic complexes flocculate in increasingly saline waters. Hydes and Liss (1977) propose that aluminum removal is accomplished by adsorption onto very fine clay particles. As the clay particles start to flocculate due to the increasing electrolyte concentrations, the aluminum becomes trapped on the clay surface. The formation of authigenic aluminum hydroxides and alumino-silicates is another possible mechanism for removal of aluminum. Authigenic formation

of these substances could occur as epitaxial growth on previous clay particles, or could create new particles. However, nucleation and growth of authigenic aluminum hydroxides is slow. Laboratory experiments by Hem and Roberson (1967) show that nucleation and growth processes take three or more months. Removal of aluminum by authigenic clay formation is possible. Pačes (1978) has proposed that at high silica concentrations, aluminum removal may be due to the formation of an amorphous aluminosilicate, while at low silica concentration, gibbsite would be the authigenic mineral phase controlling aluminum solubility. The silica concentration in the Mullica River-Great Bay Estuary is low, varying from 0.5 to 3 $\mu\text{g/ml}$ ($5 \times 10^{-5} \text{M}$). While these silica concentrations lie in the kaolinite stability field, it is uncertain whether authigenic kaolinite actually forms. Authigenic clays, if formed, would represent only approximately 0.01% of the total sediment flux. The authigenic clays would be an insignificant source of sediments, but could be a significant removal mechanism for aluminum. The removal of aluminum from ocean water by biological means has been supported by Mackenzie et al. (1978). The aluminum could be incorporated into silicious tests as a substitute for silicon. The noticeable lack of tests in the middle and upper estuary (Jahnke, unpublished data) is an indication that, at least in the estuary, this is not a major removal mechanism.

The data from this study can not distinguish between the various mechanisms of removal. It does appear, however, that pH

controls the aluminum concentrations in the upper estuary, as well as the extent of removal. The relationship between aluminum activity and pH is shown in Figure 8. The solubility graph suggests that aluminum concentrations, at least in the upper and middle estuary, are similar to that predicted from the solubility of crystalline gibbsite. Although the gibbsite thermodynamic data best fit the natural aluminum concentrations, it has been suggested that other aluminum hydroxides such as boehmite, bayerite, or amorphous gibbsite are precipitated (Hem and Roberson, 1967). However, recent work by Pačes (1978) indicates that natural waters are only saturated with respect to gibbsite and kaolinite. Using data from ground water, Pačes determined that natural waters are undersaturated with respect to amorphous aluminum hydroxides, amorphous aluminosilicates, and microcrystalline gibbsite. Pačes suggests that the aluminum concentrations indicate that gibbsite would be the major mineral formed by precipitation at low silica concentrations.

Aluminum activity decreases sharply with increasing pH. Major removal of aluminum from the water is completed by a pH of 5 to 6, approximately the pH of the minimum gibbsite solubility. Although the solubility of the aluminum hydroxides increases above pH 5.9, only small increases of aluminum concentration in the lower estuary were observed. This may be due to the possible inhibition of the dissolution of the precipitated aluminous phases. The formation of more stable phases may be favored, also accounting for the low aluminum values. Hosokawa et al. (1970) observed an

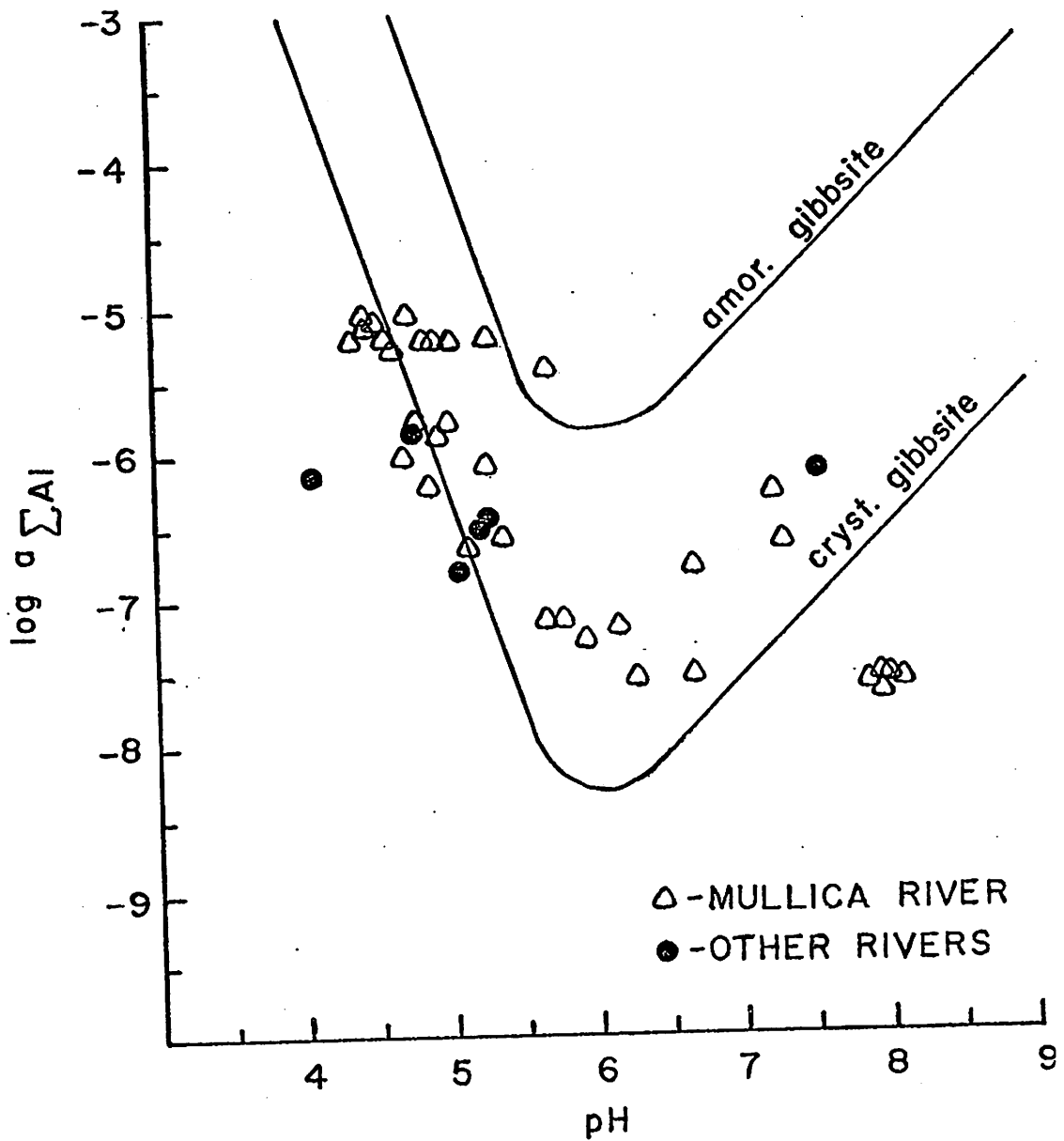


Figure 8 Gibbsite solubility graph plotting aluminum activity versus pH. The graph compares the theoretical solubility field and the natural concentrations.

increase in the dissolved aluminum concentrations in more saline waters. This concentration increase can be explained by the passage through the pH of minimum solubility, with the subsequent dissolution of the aluminous phases in the lower estuary. This would increase the aluminum concentration in the middle and lower estuary.

There is still considerable uncertainty concerning the Gibbs Free Energies of the various aluminous phases. The thermodynamic data and the Gibbs Free Energies for aluminum and its ions and hydroxides are still being revised and corrected. Figure 8 was constructed using the most recent thermodynamic data. The gibbsite Gibbs Free Energy data are from May et al. (1978 and pers. comm., 1978), while the aluminum ion (Al^{+3} , $\text{Al}(\text{OH})_4^-$) thermodynamic data was taken from Hemingway et al. (1978).

ALUMINUM IN NATURAL WATERS

Knowledge of aluminum concentrations and behavior in natural waters is deficient, and estimates of the world wide average for dissolved aluminum in water are inaccurate. To help gain further information about average dissolved aluminum values, water samples were obtained from six northeastern United States rivers in the fall of 1977 (Table 2). The dissolved aluminum concentrations ranged from a low of 4 $\mu\text{g}/\text{l}$ for the Delaware River, to a high of 42 $\mu\text{g}/\text{l}$ for the Lehigh River. The average aluminum concentration for these six rivers is 15 $\mu\text{g}/\text{l}$, corrected for discharge. The

RIVER	SALINITY(°/oo)	pH	Al Conc (µg/l)
Connecticut	.025	7.6	17.5
Delaware	.015	5.1	4.25
Lehigh	.012	4.8	42.0
Schuylkill	.026	5.25	7.75
Susquehanna	.016	4.1	18.75
Potomac	--	5.3	9.75
Average			15

Table 2 Aluminum concentrations for six northeastern United States rivers.

aluminum concentrations of these six rivers are also plotted on the gibbsite solubility diagram (Figure 8). These rivers also seem to exhibit the same pH control of aluminum concentrations.

Aluminum concentrations from this study are similar to recent aluminum concentrations obtained by various researchers on different types of surficial waters (Table 3). The first eleven values listed in Table 3 are for river water. Aluminum concentrations range from 1 $\mu\text{g}/\text{l}$ to approximately 250 $\mu\text{g}/\text{l}$. Lower values are usually summer and fall samples, while higher concentrations tend to be winter and spring samples, reinforcing the suggestion of a seasonality to aluminum concentrations. Most of the river concentrations of aluminum are less than 100 $\mu\text{g}/\text{l}$. Although there is still considerable uncertainty, it appears that average river aluminum concentrations are approximately 30 $\mu\text{g}/\text{l}$. This value is similar to the river aluminum concentration of 25 $\mu\text{g}/\text{l}$ recently proposed by Mackenzie et al. (1978), but considerably higher than the value of 10 $\mu\text{g}/\text{l}$ suggested by Garrels and Mackenzie (1971), and much lower than the value of 400 $\mu\text{g}/\text{l}$ given by Turekian (1969). The last four values listed in Table 3 are for estuarine and ocean water. These are considerably lower, and range from 1 to 10 $\mu\text{g}/\text{l}$. Sackett and Arrhenius (1962) suggested an average oceanic concentration of 1 $\mu\text{g}/\text{l}$. Recently, Hydes and Liss (1976, 1977) and Mackenzie et al. (1978) have found oceanic aluminum concentrations ranging from 1 to 10 $\mu\text{g}/\text{l}$. It appears that a value of 3 $\mu\text{g}/\text{l}$ is closer to an average oceanic aluminum concentration.

LOCATION	Al CONC($\mu\text{g}/\text{l}$)	AUTHOR
RIVERS		
Mullica, New Jersey	35	This Report (1978)
N.E. United States	15(ave.)	
Chikugogawa, Japan	15	Hosokawa et al. (1970)
Scotland (4 rivers)	30-70	Sholkovitz (1976)
N. California (7 rivers)	1-10	Jones et al. (1974)
United States (10 rivers)	5-250	Kennedy et al. (1974)
Amazon, South America	20-60	Gibbs (1972)
Fischbach, Great Britain	200	Hydes and Liss (1976)
Weende, Great Britain	39	
Leine, Great Britain	14	
Conway, Great Britain	12-20	
ESTUARIES		
Conway Bay, Great Britain	4-6	Hydes and Liss (1976)
Chesapeake, U.S.	.4-7	Stoffyn (pers. comm. 1977)
OPEN OCEAN		
Pacific	1-10	Sackett and Arrhenius (1962)
Mediterranean	1-6	Mackenzie et al. (1978)

Table 3 Some aluminum concentrations in rivers and estuaries reported since 1970.

GEOCHEMICAL CYCLE OF ALUMINUM

Over long periods of time, the oceans probably exist in steady state, with no change in the concentration of the chemical species dissolved in the water. The probable steady state of the composition of ocean water has created the need for further studies of the geochemical cycling of various elements. Rivers are continually delivering large concentrations of dissolved ions to the oceans. In order to remain in a steady state, the rate of removal of these ions from the oceans must be equal to the rate of input from rivers. Knowledge of river input and oceanic concentrations permits the calculation of the residence time (τ) for various elements. The residence time is the average length of time an ion will remain in solution in the reservoir of a system. The oceanic residence time of an ion is found by dividing the total mass of the oceanic reservoir (or the oceanic mass of an ion) by the river flux, or the total removal rate of an ion.

$$\tau = \frac{\text{total mass of element in ocean (grams)}}{\text{input to or output from ocean (grams/year)}} \quad (2)$$

For most elements, it is easier to measure the rate of input rather than the rate of removal. Therefore, equation 2 may be expanded to the form of equation 3 to calculate the oceanic residence time:

$$\tau = \frac{(\text{mass of ocean})(\text{concentration of ion in ocean})}{(\text{river flux})(\text{concentration of ion in river})} \quad (3)$$

Until recently, most of the accepted values for the oceanic residence time of aluminum were on the order of hundreds of years.

Goldberg and Arrhenius (1958) calculated an oceanic residence time for aluminum of 100 years. However, most of these early calculations greatly overestimated the concentration of aluminum in rivers, and underestimated the oceanic residence time for aluminum.

The data from this study can be applied toward an understanding of aluminum in the geochemical cycle, and a recalculation of the oceanic residence time. Because of the behavior of aluminum in the estuary, two models of the global cycle are proposed. In the first model (Figure 9A) an estimated river concentration of 30 $\mu\text{g}/\text{l}$ and the annual river flux of 3.2×10^{19} grams/year are used to calculate the total river flux of 9.6×10^{11} grams of aluminum delivered to the oceans annually. This river flux is still poorly known, but it is probably considerably lower than previously proposed. Using the tentative oceanic aluminum concentration of 3 $\mu\text{g}/\text{l}$ and an oceanic mass of 1.35×10^{24} grams, an oceanic reservoir of 4×10^{15} grams of aluminum is calculated. For the simple model, the oceanic residence time of aluminum is approximately 4,000 years. This value is approximately the same order of magnitude as the most recently calculated aluminum oceanic residence time (Yokoyama et al., 1978)

This simple method for calculation of residence time would be valid for elements displaying conservative chemical behavior in estuaries. However, if material is precipitated and permanently removed from solution during non-conservative mixing, this simple model will greatly overestimate the dissolved river water flux to the oceans. For example, Benninger (1978), working with ^{210}Pb in

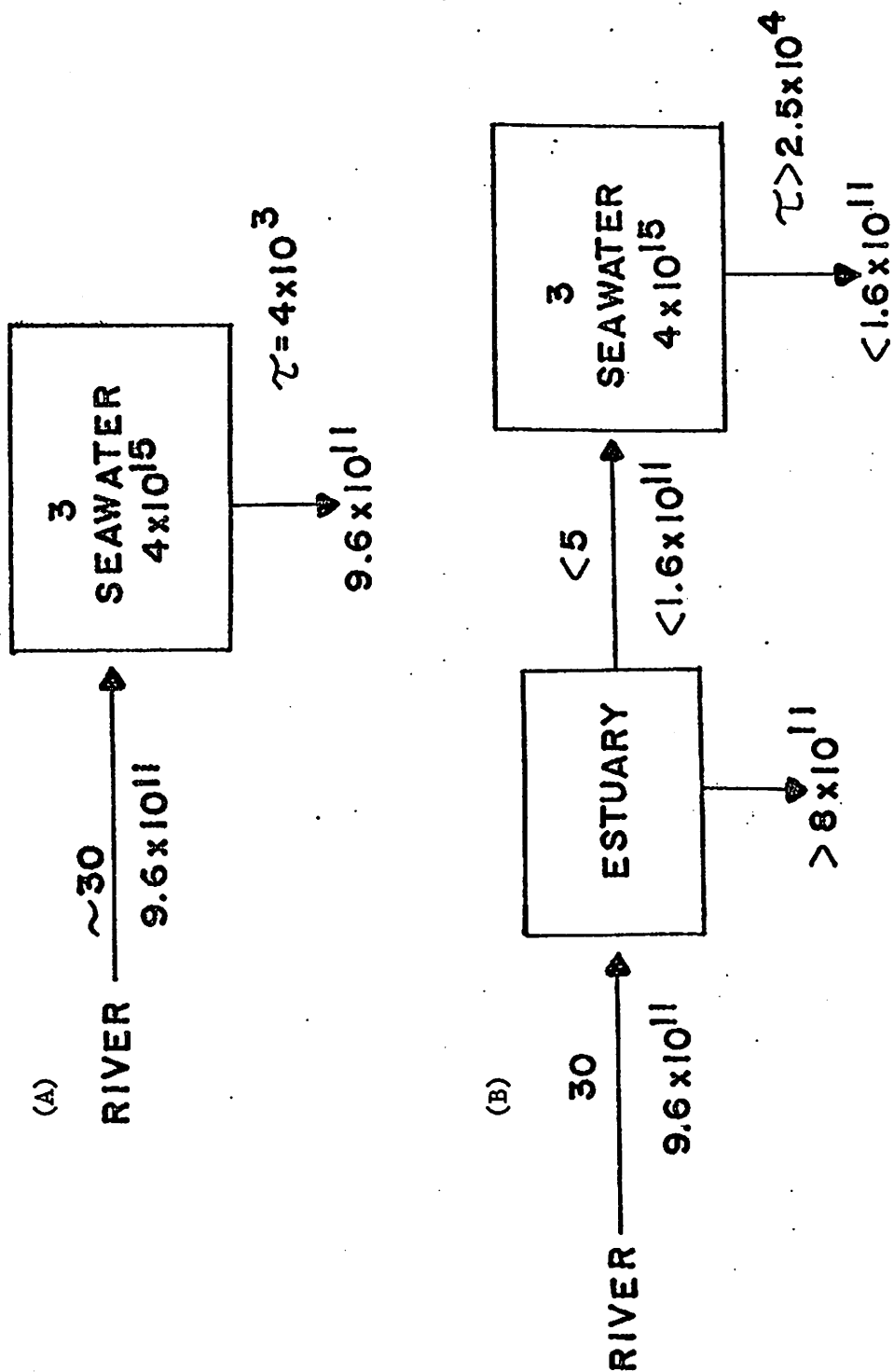


Figure 9A Geochemical cycle for the conservative mixing of aluminum.

9B Geochemical cycle for the non-conservative mixing of aluminum.

Long Island Sound, has shown that ions are permanently removed from the water and trapped in the sediment. Therefore, a modified, three box model is proposed to account for the aluminum removal in the upper estuary. In the non-conservative model (Figure 9B), an intermediate box is added to represent the estuary and its processes. In this model, the same initial river flux of 30 $\mu\text{g}/\text{l}$ allows the calculation of an annual flux of 9.6×10^{11} grams of aluminum into the estuary. Non-conservative mixing in the estuary reduces the aluminum concentration by about 80%, or a removal in excess of 8.0×10^{11} grams of aluminum annually. This removal provides a final estuary flux of less than 5 $\mu\text{g}/\text{l}$, or a total estuarine flux to the ocean of less than 1.6×10^{11} grams of aluminum per year. The calculated residence time for this non-conservative model is approximately 25,000 years. This value is approximately two orders of magnitude greater than most previously calculated residence times for aluminum (Goldberg and Arrhenius, 1958).

Recent work by Yokoyama et al. (1978) also supports the hypothesis of a longer oceanic residence time for aluminum. Yokoyama and his co-workers, using $^{26}\text{Al}/\text{Al}$ ratios from aluminum in manganese nodules, have calculated a minimum oceanic residence time for aluminum of 1,400 years. This value is more consistent with the residence time determined in this study, but is in sharp contrast to the residence time of 100 years calculated by Goldberg and Arrhenius (1958).

Mackenzie, Stoffyn, and Wollast (1978) recently suggested that

a major mechanism of aluminum removal from the oceans is the biogenic removal by silico-flagellates. These organisms incorporate aluminum as a substitute for silicon in their tests. If this is the major oceanic removal mechanism, the residence times of silica and aluminum in ocean water should be similar. The oceanic residence time for silica of 20,000 years is the same order of magnitude as the calculated residence time for aluminum of 25,000 years. In spite of the uncertainties of the aluminum residence time, the two values are similar. This similarity supports the idea of similar behavior of silica and aluminum in the oceans, as well as the possible biological removal mechanism for aluminum.

CONCLUSIONS

In the Mullica River-Great Bay Estuary, dissolved aluminum exhibits definite non-conservative behavior, with more than 80% removal occurring at salinities of less than 10⁰/oo. The works of Hosokawa et al. (1970), Hydes and Liss (1976, 1977), and Stoffyn (pers. comm., 1977) also suggest that non-conservative mixing of aluminum occurs in other estuaries. Although the mechanism of aluminum removal is undetermined, the solubility of aluminum, as well as the extent of aluminum removal, appears to be controlled by the solubility of crystalline gibbsite. A seasonal variation of aluminum concentrations is suggested by the data of this study. The Mullica River averaged approximately 35 µg/l of aluminum during the summer and fall, with winter and spring samples averaging approximately 190 µg/l.

The fall aluminum concentrations for six northeastern United States rivers ranged from 4 to 42 µg/l, averaging approximately 15 µg/l (corrected for discharge). An estimate for a world wide average river aluminum concentration appears to be approximately 30 µg/l. After non-conservative mixing in the estuary, the final aluminum flux to the oceans is less than 5 µg/l. The data from Mackenzie et al. (1978), Sackett and Arrhenius (1962), and Hydes and Liss (1976, 1977) suggest an average oceanic aluminum concentration of approximately 3 µg/l. Assuming these data are representative, an oceanic residence time for aluminum is calculated to be approximately 25,000 years.

APPENDIX I--ANALYTICAL PROCEDURE

The method used for the analysis of dissolved aluminum was modified from Dagnall, Smith and West (1966).

REAGENTS

0.1% Manganon (salicylidene-o-aminophenol, or 2,2'(methylidyn-entrilo)diphenol)--Dissolve 0.5 grams of solid in 500 mls of acetone. The reagent is stable for several weeks. The fluorescence increased as the solution ages due to the evaporation of the acetone.

Buffer Solution (pH 5.6 ± 0.1)--Dissolve 50 grams of ammonium acetate in 400 mls of water. Add sufficient glacial acetic acid (approximately 10 mls) to bring the solution to a pH of 5.6 ± 0.1 .

0.4% Sodium Diethyldithiocarbamate--Dissolve 1 gram of solid in 250 mls of water. This solution is double the strength of the original, allowing for a more complete removal of interfering ions. The original procedure was designed for fresh water, and the double strength solution is needed because of the nature of the seawater. The solution is unstable, and must be made fresh daily.

Carbon Tetrachloride

Ethyl Acetate

All glass apparatus was soaked overnight in an acid bath of H_2SO_4 , and rinsed in distilled and deionized water. All solutions were made using deionized water from a Millipore-Milli-Q^(TM) deionizer.

PROCEDURE

A 20 ml aliquot of sample was added to a 250 ml separatory

funnel containing 10 mls of buffer and 15 mls of carbon tetrachloride. Five mls of sodium diethyldithiocarbamate solution was added, and the funnel was shaken for 30 seconds. After sitting 5 minutes, the solution was shaken again for 30 seconds. The organic phase was removed. Thirty mls of ethyl acetate was added, and the mixture was again shaken twice for 30 second periods. The aqueous phase was removed to a 50 ml volumetric flask. Two mls of the Manganon was added, and the solution was diluted to 50 mls with water. After a developing period of 20-30 minutes, the fluorescence was measured using a Turner Fluorometer Model 111. The excitation beam was passed through the 47B filter to select a wavelength of 410 m μ . The emission beam was passed through a combination of the 2A-12 and 58 filters to allow the passage of the 520 m μ wavelength. The procedure is sensitive to approximately 1 μ g/l, with the lower detection limit being set by the aluminum concentration of the deionized water.

APPENDIX II--RESULTS OF WATER ANALYSES

Date	Sample	Location (Fig. 3)	Temp. ($\pm .5^{\circ}\text{C}$)	Salinity ($\pm .5^{\circ}/\text{oo}$)	pH	Al Conc ($\mu\text{g}/\text{l}$)*	Fe Conc ($\mu\text{g}/\text{ml}$)*	Silica Conc ($\mu\text{g}/\text{ml}$)*
6/28/77	1	4	25.0	.36	--	37.5		
	2	13	24.0	20.7	--	1.5		
	3	16	25.0	18.0	--	5.0		
	4	7	26.0	4.0	--	8.75		
7/6/77	1	4	26.0	.13	4.6	25.5		
	2	12	25.2	16.8	--	2.5		
	3	16	23.0	18.75	--	3.75		
7/11/77	1	15	23.0	28.2	--	1.0		
	2	16	26.8	3.2	--	15.75		
	3	6	26.3	1.0	--	19.75		
	4	4	25.4	.05	--	17.0		
7/13/77	1	16	26.0	18.8	--	0.5		
	2	8	26.0	9.9	--	1.0		
	3	7	25.0	6.4	--	0.5		
	4	6	25.0	1.7	--	9.6		
	5	9	24.0	6.7	--	0.5		
	6	12	25.0	16.4	--	0.5		

*Filtered through a 0.45 μm filter unless otherwise noted.

Date	Sample	Location	Temp	Salinity	pH	Al Conc	Fe Conc	Silica Conc
7/15/77	1	10	26.1	11.9	--	7.25		
	2	7	27.0	8.3	--	3.75		
	3	6	27.1	2.7	--	4.25		
	4	4	27.8	0.2	--	19.0		
	5	3	27.0	.007	--	13.75		
8/4/77	1	15	--	22.9	--	16.0		
	2	12	--	21.6	--	5.0		
	3	11	--	17.0	--	2.0		
	4	11	--	17.4	--	3.1		
	5	7	--	11.9	--	1.0		
	6	6	--	10.5	--	1.0		
	7	5	--	2.4	--	3.0		
	8	4	--	1.1	--	18.0		
8/23/77	1	12	--	15.8	--	2.0	.11	
	2	16	--	16.4	--	1.5	.13	
	3	9	--	9.3	--	1.5	.10	
	4	7	--	4.9	--	2.75	.09	
	5	7	--	4.2	--	2.0	.08	
	6	6	--	1.1	--	5.5	.27	
	7	5	--	0.6	--	9.75	.36	
	8	4	--	.46	--	8.5	.35	

Date	Sample	Location	Temp	Salinity	pH	Al Conc	Fe Conc	Silica Conc
9/11/77	1	14	21.5	23.6	7.93	1.0	.09	
	2	16	22.5	2.9	6.67	14.0	.09	
	3	7	23.0	5.4	7.03	1.0	.13	
	4	6	23.0	1.5	6.46	4.75	.25	
	5	4	23.0	.06	5.28	21.0	.27	
	6	2	20.5	.005	4.95	34.75	.11	
9/15/77	1	14	20.5	26.3	6.75	1.0	.09	
	2	12	21.5	21.35	6.3	1.0	.08	
	3	7	21.0	7.6	6.2	2.0	.07	
	4	6	20.5	3.7	5.9	1.0	.06	
	5	4	20.5	.21	5.4	11.0	.37	
	6	2	19.5	.005	5.05	41.0	.05	
10/6/77	1	12	17.0	15.0	5.8	2.5		
	2	7	16.5	3.45	5.7	2.25		
	3	6	16.0	.64	5.15	6.8		
	4	4	15.5	.015	4.9	16.0		
	5	2	14.3	.006	4.8	39.0		
	6	1	13.9	.007	4.7	22.5		
						53.2a		
						50.75a		

a denotes unfiltered samples.

Date	Sample	Location	Temp	Salinity	pH	Al Conc	Fe Conc	Silica Conc
3/13/78	1	14	0.5	17.8	8.0	1.0	.11	.73
	2	12	0.5	7.4	7.37	9.0	.04	1.87
	3	7	0.5	.17	5.72	158.0	.24	2.87
	4	6	0.5	.09	4.76	334.0	.30	2.67
	5	4	0.5	.04	4.43	245.0	.35	2.60
	6	2	0.5	.03	4.55	210.0	.25	2.60
	7	1	0.5	.04	4.45	237.0	.31	2.30
4/9/78	1	14	8.0	15.0	8.05	1.0		
	2	12	10.0	8.6	7.24	17.0		
	3	7	13.0	.054	5.05	154.0		
						152.0b		
	4	6	13.0	.011	4.94	153.0		
	5	4	13.0	.006	4.58	158.0		
						158.0b		
5/18/78	1	7	--	--	5.36	160.0		
	2	3	--	--	4.41	165.0		

b denotes samples filtered through a 0.22 μ m filter.

Date	Sample	Location	Temp	Salinity	pH	Al Conc	Fe Conc	Silica Conc
9/29/77	Little Beach, N.J.	--		30.4	8.15	1.0		
10/14/77	CR Conneticut River	Turners Falls, MA	--	0.025	7.6	17.5		
11/5/77	Sq Susquehanna River	Deposit, PA	15.0	.02	4.1	18.75		
	Sk Schuylkill River	Hamburg, PA	15.0	.03	5.25	7.75		
	Lh Lehigh River	Bowmanstown, PA	13.8	.012	4.8	42.0		
	De Delaware River	Martins Creek, PA	14.5	.015	5.1	4.25		
11/26/77	Po Potomac River	Great Falls, VA	7	.02	5.3	9.75		

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