CHAPTER IV
Chemical Kinetics of Dissolved Aluminium in Estuarine Waters

4.1 Introduction

The reactive nature of Al has been observed in many estuarine environments and the riverine input is known to be modified by several estuarine processes (Hosakowa et al., 1970; Hydes & Liss, 1977; Van Bennekom & Jager, 1978; Mackin & Aller, 1984a,c; Morris et al., 1986; Hydes 1989). One of these processes is salt-induced flocculation of riverine colloidal Al as demonstrated by Sholkovitz (1976, 1978) and Eckert & Sholkovitz (1976). In this case, riverine dissolved Al which exists as colloid, is removed in an estuary together with other dissolved constituents during the mixing of river water and seawater. Thus, flocculation of colloidal material may cause a net consumption of dissolved Al in estuaries. In estuaries with low dissolved iron and organic matter, Mackin & Aller (1984a) and Mackin (1986, 1989) have demonstrated that authigenic aluminosilicate formation is the major mechanism controlling the concentration of dissolved Al. Their authigenic aluminosilicate equilibrium model can explain the removal of dissolved Al at low salinities as well as an addition of dissolved Al at high salinities.

It is now established that reactions do occur within estuaries to alter the flux of dissolved Al from rivers into the oceans and sediment-water interactions have a significant influence on dissolved Al distribution in estuaries. Undisturbed sediments will act as a sink for dissolved Al because of diffusion across the sediment-water interface and reaction of Al within the sediment. Resuspension of sediment will cause a release of dissolved Al into relatively Si-depleted estuarine waters (Mackin & Aller, 1984b). In contrast, Morris et al., (1982) proposed that suspended sediment dynamics control the distribution of Al in an estuary based on their results from the Tamar estuary. In this case, riverine dissolved Al is removed in a well-developed turbidity maximum zone and some input of Al flux is expected from mid-estuarine sediments.

As regards estuarine Al cycling, previous studies have reported a generalized pattern of removal in low salinity regions (Van Bennekom & Jager, 1978, Mackin &
Aller, 1984b). Morris et al., (1982) have found evidence of dissolved Al removal closely associated with the development of turbidity maxima in estuaries and particulate interaction. In micro-tidal systems (e.g. Rhone), Al was found inactive and a linear dilution against salinity was reported; in the meso- and/or macro-tidal estuaries (e.g. Tamar & Mandovi), however reactive behaviour of Al has been identified, which can be summarised as removal of Al due to sorption in low salinity area and regeneration of this element in the middle and lower estuary following resuspension of bottom sediments (Mackin & Aller, 1984a,c; Lin et al., 1985; Morris et al., 1986; Chou & Wollast, 1990; Benoit et al., 1994; Upadhyay & Sen Gupta, 1995). This suggests that estuarine geochemistry of Al could be strongly controlled by particle-solution interactions. It has been shown that fine mineral particles (e.g. clay) provide sites for aqueous Al adsorption followed by the formation of Al-clay complexes, which in turn regulates Al concentrations in solution (Walker et al., 1988).

It seems that Al-enrichment in intermediate and/or high salinity waters is almost common in micro-tide and meso-tide systems, where Al can be released from solid phases following the resuspension of bottom sediments. The significance of particle and solution reactions on the estuarine mass balance of Al has been recognised in other shelf regions such as the Zaire and estuaries from South Carolina of United States, where remobilisation and sediment water exchange may supply micromoles of Al and sustain high concentrations in water column (Van Bennekom & Jager, 1978; Mackin & Aller, 1984c).

These processes may not, in many cases be the primary cause. Laboratory experiments simulating estuarine processes were conducted in order to examine possible mechanisms controlling Al distribution. Principal mechanisms responsible for Al removal inferred from laboratory experiments were flocculation and adsorption onto suspended matter. Generally, Al distribution is controlled by a combination of three removal mechanisms: flocculation, authigenic aluminosilicate formation, and adsorption. Each mechanism can become a dominant factor depending on the concentration level and speciation of dissolved Al in the river water. Here, the results of laboratory experiments simulating estuarine processes are reported, in order to further elucidate the geochemical cycling of dissolved Al in the coastal marine environment.
4.2 Laboratory Experiments

Flocculation Experiment

Laboratory experiments were conducted to estimate the removal of dissolved Al by flocculation due to induced ionic strength changes. Filtered river water and seawater were mixed together at room temperature in different proportions to give salinity 5, 10, 15, 20, 25 & 30 psu. The seawater had a salinity of 30 psu and the river water, 3 psu. The mixtures were agitated intermittently for 4 hours and then filtered and the filtrate analysed for dissolved Al. The results are reported in fig.13.

Sorption Experiment

Another set of two experiments were conducted to estimate the Al addition/removal by sorption in the presence of SPM. Dried suspended particulate matter obtained from the turbidity maximum zone of the estuary was added to two aliquots of filtered river water to give SPM concentrations of 150 and 300 mg/l and they were agitated at room temperature for 15 minutes. The concentration of dissolved Al was monitored for 48 hours and results are reported in fig.14.

Sediment-water Al interactions

Three sediment samples representing riverine, brackish and marine and five water samples of distilled water, tap water, river water, brackish water and seawater were utilised for the interaction studies. Each of the sediment samples was allowed to interact with all the five different water types.

Aliquots of the wet sediment (~2.0 gm) were added to separate glass jars containing 500 ml each of the above water samples. Agitation was started immediately after the addition of sediment samples. The mixture was agitated for 15 minutes using plastic coated stir bars and allowed to settle. The concentration of dissolved Al was monitored for 48 hours; the results are consolidated in fig.15a-o.

In all experiments, the kinetics of the reactions was followed by abstracting 50 ml sub-samples at appropriate intervals for analysis of soluble Al by the fluorimetric method as described in Chapter II.
Leaching Experiment

Acetic acid leaching technique was used to extract labile Al in sedimenting particulate material (top 2 cm layer of sediment), which was collected from riverine side, mid-estuarine and seaward side for the measurement of acetic acid-leachable particulate Al. A series of experiments have been carried out to determine the acetic acid leaching conditions. The finally adopted procedure is summarised as follows. The particulate sediment samples were dried in an oven (60°C) and powdered. The powdered sediment was sieved (mesh size 175) and stored in airtight containers. About 5.0 gm was suspended in 100 ml 1N acetic acid solution in a conical flask and was kept in a shaker for 24 hours at room temperature. The leachate was then separated from the sediments by filtering. The leachate was buffered with sodium acetate and 2.5 ml of the leachate was made up to 50 ml and analysed for dissolved Al by fluorimetric method. The results are presented in fig.16.

4.3 Results and Discussion

Estimation of Al removal by flocculation

The results of mixing experiments using filtered river water and seawater are shown in fig.13. From the graph of dissolved Al concentration vs. salinity, it can be noted that in low saline waters, the removal of Al is rapid. Up to salinity 10 psu, the removal is rapid; thereafter, in high saline waters the removal mechanism is slow. The following table provides consolidated data on Al decrease on salinity change:

<table>
<thead>
<tr>
<th>Salinity range (psu)</th>
<th>% Aluminium decrease (independent of initial value)</th>
<th>Slope (difference in concentration at lower and higher salinities vs. salinity variation)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-5</td>
<td>6.14</td>
<td>4.4</td>
<td>Mild change</td>
</tr>
<tr>
<td>5-10</td>
<td>52.80</td>
<td>37.0</td>
<td>Very rapid variation</td>
</tr>
<tr>
<td>10-15</td>
<td>6.60</td>
<td>2.2</td>
<td>Mild change</td>
</tr>
<tr>
<td>15-20</td>
<td>4.50</td>
<td>1.6</td>
<td>Mild change</td>
</tr>
<tr>
<td>20-25</td>
<td>27.70</td>
<td>8.2</td>
<td>Moderate change</td>
</tr>
<tr>
<td>25-30</td>
<td>61.80</td>
<td>13.2</td>
<td>Considerable variation</td>
</tr>
</tbody>
</table>
Fig. 13. Mixing experiment: Dissolved Al vs. salinity. The broken line indicates the theoretical dilution line between the two end members. The solid line is drawn by polynomial curve fit.

Fig. 14. Dissolved Al vs. time for different concentrations of added SPM.
A salinity change from 5 psu to 10 psu led to a 52.80% decrease in dissolved Al concentration; similarly, for salinities changing between 20 and 25 or 25 and 30, 27.7% and 61.80% decrease in Al was witnessed. This decrease, however, does not reflect the rate of change in Al content, but in fact is independent of the initial Al concentration. In this scenario, one should expect considerable to rapid variations in Al content at the above stated salinity ranges in normal conditions as freshwater and seawater mixes in estuaries. If one should consider the rate of change of Al concentration at the specified salinity ranges, the maximum rapid variability is noted in the salinity range of 5 – 10 psu, followed by considerable variations in the range 25 – 30 psu. Thus it is inferred that the removal of dissolved Al due to induced ionic charges by flocculation is more pronounced in low saline waters. This mechanism slows down as the salinity of the water increases. Since the main mechanism of flocculation is a coagulation of negatively-charged colloidal humic substances (Eckert and Sholkovitz, 1976; Sholkovitz, 1976, 1978), river water containing more colloidal humic substances is susceptible to salt induced flocculation and dissolved Al is coagulated with these colloidal humic substances. The extent of the flocculation may also be controlled by the existence of colloidal forms of Al. If Al is associated with humic substances, it may exist as organic colloids, which may be easily removed once again by flocculation. It is also likely that the speciation of Al in river water could play an important factor in determining whether dissolved Al is removed by flocculation or not during estuarine mixing, more aspects related to phase affinity is dealt in the next chapter.

The findings are augmented by drawing two lines based on theoretical mixing and another by polynomial fit. The significance of these relates to results on simple mixing or any implicit trend in the behaviour of Al with change in salinity. In both cases, the actual values lie on either side of the postulated lines indicating equilibrium conditions (under laboratory control) to be attained under different ionic conditions – depletion as well as addition during estuarine mixing, often observed in reality.

Kinetics of Al under changing SPM content

The results of ad-/de-sorption experiments in filtered river water at salinity zero psu and Al concentration near detection limit is shown in fig.14 (along with an expanded version of x-axis [0-3 hours]). The water initially of very very low Al
exhibited concentration levels of the order of 0.01-0.28 μM on addition of SPM concentration of 300 mg/l and 0.04-0.65 μM for added SPM concentration of 150 mg/l respectively. After agitation, there is an initial rapid rise in Al concentration in the water column for about half an hour, suggesting desorption of Al from the added SPM, as part of a transient reaction under agitated conditions. After this initial increase, a rapid decrease was observed, which signifies adsorption back onto SPM and subsequent removal as particles settle. The reaction kinetics are very visible while accounting for the values (since initial settling) from first hour to twenty eighth hour which evidence methodical enhancement in dissolved Al concentration (at 17 hr 30 min) followed by a gradual fall. Notably, lower SPM support higher reaction kinetics and vice versa, prompting a suggestion (a) higher number of reaction sites necessarily need not involve larger exchanges (reaction proceeding in a subdued nature, as Al may be limited) or (b) Al fills up most of the available ligands, succeeding the scope for higher kinetics in exchange, in light of lower SPM content (competence of Al to liberally interact in solution and at de-sorption sites).

At higher SPM, the de-sorption proceeds at a moderate rate whereas, sorption and settling (along with aggregate formation) accelerates to limit the initial Al build up in solution; saturation is attained in solution at a lower concentration in this case. At lower SPM, the de-sorption kinetics permits Al to diffuse into solution as the counter process is limited by competing sites of adsorption as well as the particles may be slow in its settling features or has lower opportunity to form new masses.

Within 48 hours, noticeable and substantial removal of Al from solution occurs to attain near initial conditions. The increase/decrease in Al values indicated de-sorption/adsorption process to be more prominent at SPM 150 mg/l than for 300 mg/l. The magnitude of sorption is almost the same as that of de-sorption as noted in each individual case (fig.14). Thus it is concluded that in this experimental set up, adsorption and de-sorption processes largely influenced the Al values and the corresponding changes in SPM concentration (150 and 300 mg/l) well affect the trend in removal to varying degrees, in both cases.
Sediment - Water Interactions

Water samples selected:

<table>
<thead>
<tr>
<th>Water sample</th>
<th>salinity (psu)</th>
<th>Al concentration (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>0</td>
<td>near detection limit</td>
</tr>
<tr>
<td>Tap Water</td>
<td>0</td>
<td>2.04</td>
</tr>
<tr>
<td>River Water</td>
<td>3</td>
<td>3.56</td>
</tr>
<tr>
<td>Brackish Water</td>
<td>19</td>
<td>0.67</td>
</tr>
<tr>
<td>Sea Water</td>
<td>31</td>
<td>near detection limit</td>
</tr>
</tbody>
</table>

Sediment samples selected:
- Riverine Sediment
- Brackish Sediment
- Marine Sediment

The results of sediment water interaction experiments indicated that bottom sediments may act either as a source or as a sink for dissolved Al, depending on the characteristics of the representative samples of sediment and water taken for the experiments (figs.15a-o). Generally, water with high Al concentration, when agitated with sediment and allowed to settle, exhibited Al removal from solution. On the other hand, water devoid of Al, showed considerable quantities of dissolved Al after agitation with sediments. In most of the cases, almost complete removal of dissolved Al from solution is noticed when allowed to stand for a day or more. Thus the distribution of dissolved Al in solution depends mainly on the salinity of the water column and the nature of suspended solids content, which in turn triggers the process of flocculation and adsorption/desorption processes. The concentration of Al found in the solution at any particular time must represent a complex balance between production from available sources, consumption by reaction with Si in solution and complexation of Al by organic matter. The results of different interaction experiments are given here under.

**Distilled Water & Riverine Sediment**

Distilled water is devoid of Al and salts. It was noticed that considerable release of Al from the sediment into the water column occurred on vigorous stirring (fig.15a). In the undisturbed state, the Al in the water column remains in increasing
Fig. 15. Dissolved Al as a function of time in mixing experiments.
concentrations for an hour, reaching a peak of 0.43 \( \mu \text{M} \), and after that removal of Al is observed from solution, reaching a minimum value (below detection limit) in a day. Thereafter the concentration continuously increases reaching 0.25 \( \mu \text{M} \) in 48 hours. This was interpreted as part of that Al released from the sediment returns back to the sediment within a day of settling; further settling leads to a continuous release of Al from sediments into the water column. The variation in concentration may be mainly due to the effects of adsorption onto suspended particulate matter and release from sediments.

**Tap Water & Riverine Sediment**

The concentration of Al in tap water is 2.04 \( \mu \text{M} \). During the initial stages the Al concentration in the water column is seen to decrease for a day (fig. 15b). Rapid decrease is noted for 3 hours after agitation (about 38\% of the total Al in the water column is lost during agitation and settling for half an hour), beyond that the decrease is gradual. This may be due to adsorption onto suspended particulates. Thereafter, very moderate release of Al into water is noticed. Al concentration reaches 1/4 of the initial value in a day but afterwards a slight increase is noticed.

We know that riverine sediment contains Al that is released by stirring (as seen from the previous experiment). But in this case, the released Al as well as some amount of Al present in the water column initially stands removed. This can be inferred to be due to adsorption mechanism.

**River Water & Riverine Sediment**

The concentration of Al in river water is 3.56 \( \mu \text{M} \). After agitation, dissolved Al concentration changed to near the detection limit of the analytical method (0.002 \( \mu \text{M} \)) for 24 hours (fig. 15c). Thus considerable amount of dissolved Al present in river water (of salinity 3 psu) is removed from solution on agitation and settling within half an hour itself. Here salinity plays an important role in the removal of Al from the water column. We have seen from flocculation experiments (fig.13) that removal of Al is very rapid within a salinity range of 3 to 10 psu. Release was noticed after a day and the concentration reached 0.98 \( \mu \text{M} \) by 48 hours possibly due to release of Al from sediments, as equilibrium conditions are being attained.
Brackish Water & Riverine Sediment

The concentration of Al in brackish water is 0.67 μM. After agitation with riverine sediments the water column exhibits the presence of higher concentration of Al than was originally present (fig. 15d). The increase is probably due to Al imparted into water column from sediments and salinity not being favourable for rapid flocculation to occur. Then it continuously decreases reaching a minimum value in a day and after that the concentration increases slightly, which may be due to release from sediment. The removal process and sorption mechanisms are gradual and slow as seen in figure.

Sea Water & Riverine Sediment

The concentration of Al in seawater is at detection limit. Hence, all the Al detected in the water column must have come from the sediment as a result of agitation. After agitation, the water column shows maximum 1.0 μM of Al. There is no particular trend in variation of concentration initially, but after 3 hours, a continuous decrease up to 24 hours is observed and thereafter an increase is noted (fig. 15e). The graph is similar to that of distilled water & riverine sediment, but the concentration values here are almost double. The salinity of seawater restricts removal to a certain extent and the main mechanism expected is adsorption onto suspended particulates. Thus the removal mechanism commences after a short period of initial perturbations observed only in this case; considerable decrease of dissolved Al occurs thereafter for a longer period, up to 24 hours, as is quite evident from the plot.

We note from the above results that riverine sediment imparts Al in dissolved phase to distilled water, brackish water and seawater, all of which represent Al deficient conditions. Initial immediate release and gradual removal is noticed in all these cases. In waters of initially high concentrations of Al (tap water and river water), significant removal is observed. Probably in tap water, sorption mechanisms led to incomplete removal of the metal, whereas in river water, the rapid removal of considerable amounts of Al from solution can be due to water properties (salinity) being favourable for combined removal mechanisms (flocculation and adsorption). In
all these cases, release of Al from undisturbed sediments into water column in varying degrees is noticed after a day (leading to an equilibrium condition).

**Distilled Water & Brackish Sediment**

Distilled water is devoid of Al and salts. Dissolved Al concentrations remained near the detection limit of the analytical method (0.002 μM) for 24 hours after agitation (fig. 15f) indicating negligible input of Al from the sediments to the water column. After 24 hours, the Al concentration rose gradually and attains a value of 0.38 μM. This process indicates the re-conditioning of sediments from brackish area in the distilled medium.

**Tap Water & Brackish Sediment**

The concentration of Al in tap water is 2.04 μM. Even though the initial concentration of Al in the water column is high, after agitation, no detectable form of Al is present for 24 hours (fig. 15g). Thereafter, the concentration increases, reaching 0.52 μM at 48 hours. The Al present initially in the water column was incorporated into sediment by adsorption. The holding capacity of sediments towards selectively removing Al from solution is pointed out here. The change in textural characteristics of the sediment from sand to clay may aid its removal by adsorption due to enhanced surface area found in fine clay particles. The release of settled Al from sediments was seen after a day as the concentration increased with time.

**River Water & Brackish Sediment**

The concentration of Al in river water is 3.56 μM. After agitation more than 50% of the Al is still retained in the water column initially and then the concentration decreases throughout the period of observation (fig. 15h). The removal takes time and Al is detected in the water column throughout the period of observation. The decrease is sharp for first 24 hours and after that a very gradual decrease in concentration is noted, the value reaching almost 1/16th of the initial value. Again, the sediments from brackish area are capable to incorporate soluble Al.

**Brackish Water & Brackish Sediment**

The concentration of Al in brackish water is 0.67 μM. After agitation with sediments and further settling, the water column shows a concentration of 0.22 μM,
which is 1/3rd of brackish water concentration (fig.15i). Thus agitation causes rapid loss in solution. The concentration decreases and reaches near detection limit by 2 hours. Hence forth, release is seen from sediments to water column - the concentration value reaching a maximum of 0.62 μM and further, it decreases continuously. In this case, no particular trend in concentration values is seen. Al is detected in the water column even after a day indicating initial perturbation due to agitation and later harmonised conditions prevail as the liquid and solids were collected from the same region.

**Sea Water & Brackish Sediment**

The concentration of Al in seawater remained near the detection limit. Al is observed to be imparted into the water column from brackish sediment after agitation with seawater. During agitation, release of Al into the water column is noted which increases for an hour reaching a value of 0.37 μM and then decreases steadily reaching near detection limit in 24 hours, then the value increases slowly to reach a value of 0.13 μM, which is almost the same concentration as noticed in the water column after agitation (fig.15j).

From the aforesaid, it is clear that brackish sediments willingly contribute to the build up of dissolved Al in saline waters (brackish and marine) whereas it is capable of adsorption from low saline water samples (river water).

**Distilled Water & Sea Sediment**

Agitation promotes negligible release of Al from the sediments to the water column for initial 24 hours and the concentration remained near detection limit; but on analysing the water after 48 hours, Al is observed to be present in significant amounts reaching a concentration of 0.71 μM (fig.15k). Notably in this case, Al behaviour in non-saline waters indicates the ability of the metal to remain in the soluble phase.

**Tap Water & Sea Sediment**

The concentration of Al in tap water is 2.04 μM. After agitation, the entire Al present in the water column stands removed. Al values remained near the detection limit in the water column for initial 24 hours but later, release of Al is noticed reaching a value of 0.43 μM in 48 hours (fig.15l). The wider capacity of marine
sediments to interact either by adsorption or through desorption mechanisms are demonstrated in this case. In the case of marine sediments, adsorption is favourable due to increased surface area exposed for reaction since the particles are very fine.

**River Water & Sea Sediment**

The concentration of Al in river water is 3.56 μM. After agitation, the entire Al present in the water column gets adsorbed to the sediments and thereafter, immediate release of Al from sediments is noted here as compared to the previous results. After 5 hours, the Al concentration continuously increases reaching a value of 1.35 μM in 48 hours (fig.15m). Thus it is inferred that the Al initially present in the water column and which was lost into the sediment after agitation and settling, was partly released into the water column within 48 hours. This is one experiment, which indicates clearly the process of phase reversion subsequent to mixing reactions of samples from different environments. Under non-saline conditions or at very low salinities, the already Al rich sediments have the tendency to input Al in dissolved form to overlying waters.

**Brackish Water & Sea Sediment**

The concentration of Al in brackish water is 0.67 μM. Even though the amount of Al present in the water column is less, agitation and further settling does not remove the entire Al present in the water media. No particular trend in concentration is seen for initial three hours but after that Al concentration decreases to near detection value within a day and then the concentration increases steadily reaching a value of 0.103 μM in 48 hours (fig.15n). Al observed in the water column is in low concentration during the entire period of observation. As in the case of previous experiment using brackish sediments, a tendency is exhibited for return of Al to dissolved medium after an incubation period of more than 24 hours.

**Sea Water & Sea Sediment**

The concentration of Al in seawater is at near detection limit. After agitation minor amounts of Al is imparted into the water column from the sediment. The amount of Al imparted into the marine water column is marginal, indicating sea sediments to desorb very gradually. The maximum concentration of 0.26 μM is noted at 3 hours (after agitation), later Al content decreases reaching near detection limit at
24 hours (fig. 15o). Then a continuous increase is observed as the value of 0.12 μM is attained in 48 hours.

The removal is very intense in the case of reaction with sea sediments; by 2 hours, Al values in all the water samples fall below detection limit and whatever amount released within 24 hours is also at a very slow pace; after 24 hours, significant release is noticed which is more prominent for low saline waters.

The above results derived from fig. 15a–o, imply that salinity plays an important role in the control of dissolved Al concentration. Marine sediments are generally noted for holding higher concentrations of Al, which thence can be released under specific conditions; either low saline waters (most preferred) or release after an incubation period (say 24 hours) favour phase changes and ultimately, Al appears in the water media as dissolved metal. This and other aspects are further discussed below.

**Interaction of distilled water with different types of sediments**

The kinetic experiments provide two types of results. In case of samples collected from the riverine end rapid release followed by adsorption and further partial de-sorption indicate Al mobility within sediment and dissolved phases. On the other hand, sediments collected from both the brackish and marine areas indicate similar behaviour, which necessitated 24 hours of conditioning, followed by gradual but steady release of Al into the dissolved phase. In the above case, reaction is mostly uni-directional but in the previous instant reverse reactions attempted to produce equilibrium.

**Interaction of tap water with different types of sediments**

The Al present in tap water appears to be completely lost when interacted with the sediments from brackish and marine regions. On the contrary, when the same water sample is mixed with riverine sediment, the removal is rapid at first and gradual later, 50% reduction in dissolved Al concentration is noticed within an hour. In the case of brackish and marine, as seen for distilled water, here also, nearly one day inhibition is observed before Al is released to solution.
Interaction of river water with different types of sediments

When interacted with riverine sediment, complete removal of Al is noted, postulating the assumption that Al removal is evident at and around salinity of 3 psu. Whereas, when interacted with brackish sediment, initially only 60% of dissolved Al present in water is lost. Then it steadily decreases, with only 4% remaining after 24 hours. Afterwards, a very gradual decrease is noticed up to 48 hours. Thus the removal is a very slow process but proceeding uni-directionally. When river water interacts with marine sediment, initially Al remains at near detection limit in the water column, which is evidence for complete Al removal. But after 5 hours, the concentration in the water column increases steadily reaching maximum value of 1.35 μM in 48 hours, again the mechanism working linearly with time. The three cases related to river water exhibit widely differing results and the processes prompt to point out different operational mechanisms, which control Al distribution within an estuary. These kinetic experiments help to point out the metal cycling processes under changing estuarine conditions leading to phase transformations and subsequent transport which was one of the objectives of this study.

Interaction of brackish water with different types of sediments

Immediately on mixing with riverine sediment, the concentration of Al in water (0.67 μM) is observed to increase (0.85 μM), due to Al being readily imparted from sediments. When allowed to settle, the concentration steadily decreases, reaching a minimum in a day and later it increases. When reacted with brackish sediment, at first, Al is removed from solution but attains maximum concentration in about 3 hours and then it continuously decreases throughout the period of observation. When interacted with marine sediment the concentration noticed in the water column is seen to be lowered, maximum value of 0.27 μM occur in 1 hour, thereafter it gradually decreases and reaches near detection limit in a day. After that, again the value steadily increases. As regards this experiment using brackish water (salinity 19 psu), the behaviour of Al in solution for sediments collected from mid or lower estuary are the same in pattern but contrary to this, the riverine sediments have the capability to bring about forward and backward (reverse) reactions. The mixing of brackish water and marine sediments, of course, exhibits only a subdued reaction, due to pre-established conditions of Al present in either of the medium.
**Interaction of seawater with different types of sediments**

Al is imparted to the water column initially, the maximum concentration being imparted from riverine sediments, followed by brackish and then marine sediments. For all the above cases, after agitation, the concentration increases reaching maximum value by 2-3 hours and then decreases attaining minimum value in a day. Thenceforth, the concentration is observed to increase due to release from the sediment material. Brackish and marine waters indicate a similar pattern of release mechanism while riverine sediments are no exception to the experimental results of previous study applying brackish water. The net result in these three samples is that lower estuarine conditions afford passive and gentle reactions while end member samples provide better opportunities in reactivity for phase changes.

**Acetic acid leachable Aluminium**

The acetic acid (HAc) leachable form of the sedimented Al refers to the metal fraction dissolved in acetic acid. In Cochin estuary this concentration varied considerably from riverine to seaward end (fig 16 provides a representative figure prepared by plotting three values from three reaches of the estuary). Sedimented Al values were noted at detection limit in the riverine end. Mid-estuarine region exhibited considerable quantities of Al, which then greatly increased towards the seaward end. The deficiency of acetic acid leachable Al in the riverine sediments can be explained by the formation of authigenic alumino-silicates, which are not susceptible to acetic acid leaching.

It has already been shown that in the surface waters of the open oceans, the HAc-Al fraction is generally <5% of the dissolved Al fraction, leading to little difference between dissolved and dissolvable determinations; in the deep waters and in the high energy coastal regions the fraction can become as large as dissolved Al resulting in 100% difference between dissolved and dissolvable determinations (Orians & Bruland, 1986). The HAc fraction is argued to be an indicator of the exchangeable or reactive portion of the sedimented Al. The HAc-Al fraction can also be used to give an upper estimate of the authigenic portion of the particulate Al (Chester & Hughes, 1967 and Landing & Bruland, 1987).
Fig. 16. Variability of dissolved and sedimented Al through different reaches of Cochin estuary - representative figure.
As far as Cochin estuary is concerned, marine particulate sediments transport fairly large amounts of exchangeable Al, but for riverine sediments, exchangeable Al remained near the detection limit. Thus it is inferred that the reason for the very low concentrations of dissolved Al noticed in the mid and lower estuary is due to Al being present as exchangeable Al (mostly held in the sedimented layers). This exchangeable form is susceptible to release from the solid phase to dissolved media only during monsoon season when the estuary represents a high energetic environment, as per the experimental results.

Aluminium partitioning between solution-solid phases

The partitioning of a trace metal between solid and solution phases in natural waters can be described in terms of a partition coefficient, $K_p$:

$$K_p = \frac{C_p \times 10^6}{C_d \times S}$$

where $C_p$ is the particulate chemical concentration ($\mu$M), $C_d$ is the dissolved chemical concentration ($\mu$M), $S$ is the suspended solids concentration, mg/l.

The partition coefficient has been used in several studies to address the soluble particulate balance in the exchange of metal species in aqueous systems (Vuceta & Morgan, 1978; Balls, 1988; Honeyman & Santschi, 1988). The value of $K_p$ for Al in this study was estimated to be $0.241 \times 10^5$ ml/g in the upstream regions with low suspended particulate matter and $0.102 \times 10^5$ ml/g for the downstream regions. This value agrees well with other reported results ($10^5$ – Morris et al., 1986; 0.4-7.9 $\times 10^6$ – Moran & Moore, 1989; 10$^5$ – Hydes & Kremling, 1993, 0.26-7.92 $\times 10^5$ ml/g; Upadhyay & Sengupta, 1995).

4.4 Discussion

The study has demonstrated non-conservative behaviour of dissolved Al in the Cochin estuary. Net removal occurs in the low salinity, high turbidity region where as inputs into the upper estuary is exclusively of riverine origin. It has been established that the flocculation of riverine micro-colloids, destabilized by an increase in ionic strength, is the principal removal process for dissolved Al within the salinity range of
3 to 10 psu (fig.13). The results of field and laboratory experiments have shown that elevated SPM loads are essential for removal to occur and salinity increase alone is ineffectual. It has been noted in the previous chapter that the bottom waters upstream of the turbidity maximum show high concentrations of dissolved Al. This high concentration is depleted within the turbidity maximum zone, which leads to the conclusion that removal occurs through non-specific sorption uptake onto resuspending estuarine sediment particles. Continuous removal of dissolved Al by sorption can be maintained only if the particles accumulating Al to equilibrium or near equilibrium levels are continuously displaced from the site of removal by depleted particles. In this estuary, overturn of suspended particles at the site of removal occurs through continuous interchanges within the much larger total proportion of particles contributing intermittently to the turbidity maximum by resuspension and settling as it oscillated through the tidal excursion. The site of turbidity maxima nevertheless oscillates in the estuarine region largely depended on the marine and freshwater mixing patterns. The necessary condition for continuous removal is therefore that net depletion is maintained on this total population. The re-suspendable particle population contributing to the turbidity maxima is continuously being displaced by an influx of particles tidally pumped from lower estuary, since in Cochin estuary, turbidity maxima is of marine origin (Rasheed et al., 1995); Al replenishment in the re-suspended population within the turbidity maximum is controlled by net local sedimentation.

It is pointed out that re-cycling rather than net mobilization occurs in the other parts of the estuary. The suspendable particle population is mostly composed of particles which have for some time been in contact with the aqueous phase, alternating between suspension and settlement in the upper/mid (continuously) mobile sediment before final transit to the site of deposition. It is clear from this study that pronounced reactivity of dissolved Al in the Cochin estuary is a consequence of dynamic resuspendable particle behaviour augmented by a strong tidal (varying salinity) regime. High internal fluxes of particles vigorously promote both the removal of dissolved Al in the low salinity zone coupled with local deposition and a return flux from the mid-estuarine sediment. Pronounced removal and augmentation process similar to those encountered in the Cochin estuary cannot develop in less energetic systems where sediment mobility is more restricted and turbidity maximum
is not developed. It can be argued therefore that inter estuarine difference in Al behaviour reflect differing suspendable sediment dynamics. Thence the Al reactivity in this tropical estuary is more linked to controls by estuarine mixing and circulation.

During the high river discharge times, when the major form of dissolved Al in the river water was presumably colloidal, flocculation and adsorption onto SPM were two principal mechanisms controlling the Al distribution in the estuary, operating in the lower regions of this estuary. On the other hand, during the intermediate river-discharge periods, when dissolved Al presumably existed as inorganic forms, authigenic aluminosilicate formation and adsorption onto SPM become more prominent estuarine processes in deciding the fate of Al transport.