Chapter V
A model approach towards evaluating fate of Aluminium in Cochin Estuary

5.1 Introduction

This chapter deals with a model approach for understanding the cycling of Aluminium in Cochin Estuary. Temporal changes of Aluminium and suspended solids in water column and benthic sediment are simulated along with transport mechanism using the Water Quality Analysis Simulation Program (WASP, US EPA), which was developed as part of water quality analysis (Wool et al., 1996). WASP is a dynamic compartment model applicable to all kinds of aquatic systems and has a sub model, which is called TOXI, for simulating the fate and transport of organic chemicals or metals. A detailed description of WASP 6.0 and the TOXI model is provided in WASP 6.0 manual, which is available on the web (Wool et al., 1996).

The element aluminium (Al) is included under lithophiles (mostly terrestrial-those that bond to silicates) because their mass transport to the ocean occurs primarily through streams. Al cycling in aquatic systems is a complex problem and aquatic sediments often act as a sink for Al. This element can accumulate in the sediments depending on a number of environmental processes governed by chemical, physical, biological, geological and anthropogenic processes. Mostly, heavy metals have a strong affinity for sorption onto particulate matter given the Eh and pH conditions found in most aquatic environments (Morel & Hering, 1993). Several contaminated river systems convey roughly 90% of their total heavy metal load via sediment transport (Hurley et al., 1995; Meade et al., 1995).

5.2 Study Site

The upstream portion of the northern and southern arms of the Cochin estuary was selected for modeling the fate of Al (fig.17).

Northern arm characteristics:
- Irregularities in bottom topography are marginally less and the system is comparatively simple.
Fig. 17. Cochin Estuary with study area as shaded region
- Witness large inputs from industrial effluents.
- Low pH conditions prevail at times in this particular portion leading to increased content of dissolved Al.

The selected field has an area of 34.057 km², a volume of 1.107 x 10⁸ m³, a length of 8.14 km and mean depth of 3.25 m. Flow is primarily from river Periyar, which exhibits large flow rates during monsoon season. This region is seasonally contaminated because of the presence of large number of industrial establishments on the banks of river Periyar.

Southern arm characteristics:
- Presence of a pool riffle system at the river mouth.
- Partial impact of effluents from the Velloor News Print Factory (K N L) situated on the banks of Muvattupuzha river.

The study region has an area of 97.91606 km², a volume of 7.6662 x 10⁸ m³, a length of 16.28 km and mean depth of 7.83 m. Flow is from river Muvattupuzha, which branches out into Ithipuzha and Murinjupuzha before debouching into the estuary. Four more river catchment systems, Pamba, Meenachil, Achankovil and Manimala also contribute to the inflow to the southern parts of the estuary.

5.3 Modeling approach and procedure

WASP 6 traces each water quality constituent from the point of spatial and temporal input to its final point of export, conserving mass in space and time.

The mass balance equation around an infinitesimally small fluid volume is

**Equation-1: General mass balance equation**

\[
\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(U_x C) - \frac{\partial}{\partial y}(U_y C) - \frac{\partial}{\partial z}(U_z C) + \frac{\partial}{\partial x}(E_x \frac{\partial C}{\partial x}) + \frac{\partial}{\partial y}(E_y \frac{\partial C}{\partial y}) + \frac{\partial}{\partial z}(E_z \frac{\partial C}{\partial z}) + S_L + S_B + S_K
\]

where:
- \( C \) = concentration of the water quality constituent, mg/L or g/m³
- \( t \) = time, days
- \( U_x, U_y, U_z \) = longitudinal, lateral, and vertical advective velocities, m/day
E_x, E_y, E_z = longitudinal, lateral, and vertical diffusion coefficients, m^2/day
S_L = direct and diffuse loading rate, g/m^3-day
S_B = boundary loading rate (including upstream, downstream, benthic, and atmospheric), g/m^3-day
S_K = total kinetic transformation rate; positive is source, negative is sink, g/m^3-day

By expanding the infinitesimally small control volumes into larger adjoining segments and by specifying proper transport, loading and transformation parameters, WASP implements a finite-difference form of the Equation-1. For brevity and clarity, however, the derivation of the finite-difference form of the mass balance equation will be for a one-dimensional reach. Assuming vertical and lateral homogeneity, we can integrate over y and z to obtain Equation-2.

Equation-2: WASP implementation of the finite difference form of mass balance equation:

$$\frac{\partial}{\partial t} (AC) = \frac{\partial}{\partial x} \left( -U_x AC + E_x A \frac{\partial C}{\partial x} \right) + A(S_L + S_B) + A S_K$$

where A = cross-sectional area, m^2.

This equation represents the three major classes of water quality processes — transport (term 1), loading (term 2), and transformation (term 3).

Modeling parameters such as physicochemical and hydro geological data were either collected from literature that dealt with Cochin backwaters or computed employing spatial and temporal data sets. Al concentration was determined from analysis of samples collected during seasonal surveys. The WASP 6.0’s TOXI model is used for simulating a 9-month period, from August 1998 to May 1999, a period when field measurements were available. In this model, WASP 6.0 is set to calculate net flow transport across a segment interface, sediment bed volume statically and modeling time step automatically.

A brief description of the individual model parameter incorporated in WASP 6.0 is as follows. A summary of the input parameters used in the model is also provided in Table 1. Input parameters required by WASP 6.0 include simulation and output control, model segmentation, advective and dispersive transport variables, boundary concentrations, point and diffuse source waste loads and finally, the initial conditions.
Segmentation

Each of the targeted regions was conceptually divided into two segments to represent the water column and the benthic sediment. The environmental conditions and Al transformation rates may differ in these two segments. The depth of the sediment segment was set to 0.5 m because contamination is generally limited to the upper 0.5 m of sediments with the majority of contamination localized in the upper 0.20 m.

System

Total Al and suspended particulate matter were specified as state variables in the model. Particulate matter whose diameter is larger than 0.45 μm was specified as Solids 1 and total Al specified as Chemical 1 in the model. Al concentrations and SPM values in the water column, which were observed during the start of simulation period, were averaged through the total volume of the study region and were used as input values for initial Chemical 1 and Solids 1 concentrations (Table 1). The initial concentration of Al in sediments is taken to be zero.

In the benthic sediment, solid concentration (515.48 g/l and 558.88 g/l in the northern and southern arm respectively) was estimated from the density (1.4 g/cm^3, unpublished data by A C Narayana, Department of Marine Geology and Geophysics, CUSAT) and moisture content (63.18% and 60.08% in the northern and southern arm respectively, Bava, 1996) of solids.

Modeling parameters

Sorption

Sorption is the bonding of dissolved chemicals onto solid phases, such as benthic and suspended sediment, biological material and sometimes dissolved or colloidal organic material. Sorption can be important in controlling both the environmental fate and the toxicity of chemicals. For certain chemicals in addition to partitioning to particulate organic carbon associated with sediment particles, there exists an additional partitioning by sorbing third phase which is not removed by conventional filtration (Di Toro et al., 1991). The third phase is identified as being
### Table 1. Input parameters for Aluminium modeling used in WASP 6

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td><strong>Geo hydrological parameters</strong></td>
<td></td>
<td></td>
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<tr>
<td><strong>Water column</strong></td>
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<tr>
<td>Volume (m³)</td>
<td>Northern arm-1.107 x 10⁸</td>
<td>Calculated</td>
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<tr>
<td></td>
<td>Southern arm-7.6668 x 10⁸</td>
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<tr>
<td>Depth (m)</td>
<td>Northern arm-3.25</td>
<td>Observed</td>
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<td></td>
<td>Southern arm-7.83m</td>
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<td>Velocity (m/s)</td>
<td>Northern arm-0.1058</td>
<td>Average flow for all months</td>
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<td></td>
<td>Southern arm-0.1422</td>
<td></td>
</tr>
<tr>
<td>Flow rate (m³/s)</td>
<td>Variable</td>
<td>Central Water Commission data set (1998-99)</td>
</tr>
<tr>
<td><strong>Benthic sediment</strong></td>
<td></td>
<td></td>
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<tr>
<td>Volume (m³)</td>
<td>Northern arm-0.17028 x 10⁸</td>
<td>Calculated by using depth</td>
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<td></td>
<td>Southern arm-0.48958 x 10⁸</td>
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<td>Depth (m)</td>
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<td><strong>Water column</strong></td>
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<td>Initial Al concentration (mg/l)</td>
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<td>Observed</td>
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<td>Southern arm-0.02538</td>
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<td>Southern arm-3.33</td>
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<td>Al loading (kg/day)</td>
<td>Time variable</td>
<td>Concentration data available calculated using average flow</td>
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<tr>
<td>Solids loading (kg/day)</td>
<td>Time variable</td>
<td>Central Water Commission data set (1998-99)</td>
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<td>DOC (mg/l)</td>
<td>Northern arm-4.0</td>
<td>Approximated based on Rini, 2002</td>
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<td></td>
<td>Southern arm-4.0</td>
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<td>Temperature</td>
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<tr>
<td>pH</td>
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<td><strong>Benthic sediment</strong></td>
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<tr>
<td>Initial concentration (mg/l)</td>
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<td>Assumed</td>
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<td>Calculated from density and moisture content (density- unpublished data, moisture content-Bava-1996)</td>
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<td>Southern arm-558880</td>
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<td>DOC (mg/l)</td>
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<tr>
<td>Temperature</td>
<td>Time variable</td>
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</tr>
<tr>
<td>pH</td>
<td>Time variable</td>
<td>Bava, 1996</td>
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<td><strong>Constant parameters</strong></td>
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<tr>
<td>Partition coefficient to solids (l/kg)</td>
<td>$0.241 \times 10^5$</td>
<td>Calculated based on observed data</td>
</tr>
<tr>
<td>Partition coefficient to DOC (l/kg)</td>
<td>Northern arm: $1.26 \times 10^5$, Southern arm: $2.95 \times 10^6$</td>
<td>Calculated based on observed data</td>
</tr>
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<td>Log Acidity constant</td>
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<td>Stumm &amp; Morgan, 1981</td>
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<td>Activation energy of the dissociation reaction (kcal/mol)</td>
<td>11.49</td>
<td>Calculated</td>
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<td>Exchange-Molecular diffusion coefficient (m$^2$/s)</td>
<td>$1 \times 10^{-10}$ m$^2$/s</td>
<td>WASP 6 Manual</td>
</tr>
<tr>
<td>Solid settling velocity (m/s)</td>
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<td>Calculated using Stokes equation</td>
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</table>
dissolved organic carbon (DOC), which is in colloidal sized particles that are too small to be removed by particle separation techniques. Dissolved chemicals in water column and benthic segments interact with sediment particles and dissolved organic carbon to form dissolved, DOC-sorbed, and sediment-sorbed phases.

A chemical is partitioned into a dissolved and particulate adsorbed phase based on its sediment-to-water partition coefficient \( K_p \). The dimensionless ratio of the dissolved to the particulate concentration is the product of the partition coefficient and the concentration of suspended solids, assuming local equilibrium. The partition coefficient for aluminium was calculated as \( 0.241 \times 10^5 \) ml/g.

Normalization of the partition coefficient by the organic-carbon content of the sediment has been shown to yield a coefficient, \( K_{oc} \) (the organic carbon partition coefficient) that is relatively independent of other sediment characteristics or geographic origin. Many organic pollutants of current interest are non-polar, hydrophobic compounds whose partition coefficients correlate quite well with the organic fraction of the sediment. Karickhoff et al., (1979) and Rao and Davidson (1980) have developed empirical expressions relating equilibrium coefficients to laboratory measurements leading to fairly reliable means of estimating appropriate values. The correlations used in TOXI are

\[
K_p = f_{oc} \times K_{oc}
\]

where \( f_{oc} \) denotes fractional organic carbon.

Contaminant transport model using the two partitioning coefficients in sediments addresses complex sorption/de-sorption phenomena between DOC-sorbed and particulate bound.

Total chemical concentration can be written as \( C_T = C_p + C_d \)

Where \( C_p \) = particulate chemical concentration and \( C_d = \) dissolved chemical concentration.

Dissolved chemical concentrations can be expressed as the sum of dissolved free chemical \( C_d^f \) and DOC complexed chemical, \( C_d^{DOC} \),

\[
C_d = C_d^f + C_d^{DOC}
\]
Particulate chemical concentration, $C_p$, can be related to free dissolved chemical concentration and sediment concentration $S$, using the partition coefficient as $C_p = S K_p C_d^f$

And the DOC bound chemical $C_d^{DOC}$, can be related to free dissolved chemical concentration and colloidal concentration $S_{DOC}$ using the partition coefficient $K_{DOC}$, as

$$C_d^{DOC} = S_{DOC} K_{DOC} C_d^f$$

Total chemical concentration can be written as

$$C_T = S K_p C_d^f + C_d^f + S_{DOC} K_{DOC} C_d^f$$

$$C_T = (S K_p + 1 + S_{DOC} K_{DOC}) C_d^f$$

The three forms of the chemical concentration can be formulated as the total chemical as follows (Hwang et. al., 1998).

$$C_p = f_p C_T$$

$$C_d^f = f_d^f C_T$$

$$C_d^{DOC} = f_d^{DOC} C_T$$

The fractions are given by

$$f_p = S K_p /(S K_p + 1 + S_{DOC} K_{DOC})$$

$$f_d^f = 1 / (S K_p + 1 + S_{DOC} K_{DOC})$$

$$f_d^{DOC} = S_{DOC} K_{DOC} / (S K_p + 1 + S_{DOC} K_{DOC})$$

Published data on benthic sediment DOC pertaining to Cochin estuary is not readily available from literature. It is usually noted that interstitial sediment water DOC concentrations are rather quite high, globally, ranging from 4-20 mg/l under aerobic conditions and 10-400 mg/l under anaerobic conditions (Leenheer et al., 1974). A trial run was attempted by applying the DOC values as 3 to 4 to 5 and 20 to 40 to 60 mg/l. The total Al and SPM concentration remained almost the same on varying DOC values, as selected above. The changes observed for dissolved, DOC sorbed and total sorbed Al are given below, tabulated. With increase in DOC values, dissolved Al and total sorbed Al is observed to decrease and DOC sorbed Al to increase.
The changes noticed in Al values with changes in DOC are very minute and hence it may be stated that changing DOC concentrations make little difference in final results. In this study, DOC in benthic sediment is accepted as 4 mg/l for both the northern and southern arms. The fractional organic carbon in benthic sediments was calculated to be 9830.20 mg/l and 4566.05 mg/l for the northern and southern arm, respectively.

**Ionization**

Ionization is the dissociation of a chemical into multiple charged species. In an aquatic environment some chemicals may occur only in their neutral form while others may react with water molecules to form positively (cationic) or negatively (anionic) charged ions. These reactions are rapid and are generally assumed to be at (local) equilibrium. At equilibrium, the distribution of chemicals between the neutral and the ionized species is controlled by the pH and temperature of the water and the ionization constants.

The maximum coordination number of Al is 6, and it coordinates six solvent molecules (H₂O) around it in solution. The log K value for Al was taken as -4.9 as given by Stumm & Morgan (1981). The activation energy of the dissociation reaction of Al was calculated from standard enthalpy values to be 11.49 kcal/mol.

**Transport**

*Settling and re-suspension of solids*

Suspended sediment load is conventionally classified as particles with a diameter smaller than 63 μm (in sedimentology). With regard to estuarine water quality, problems caused by suspended sediments arise from their ability to adsorb...
significant quantities of various pollutants. Therefore, prediction of transport, erosion, and deposition of estuarine particulates / sediment in itself forms a crucial subject.

Suspended sediment particles and adsorbed chemicals are transported downstream at nearly the mean current velocity. In addition, they are transported vertically downward by their mean sedimentation velocity. Generally, silt and clay size particles settle according to Stokes law, in proportion to the square of the particle diameter and the difference between sediment and water densities.

\[ W = 8.64 \left( \frac{g}{18\mu} \right) (\rho_s - \rho_w) d_s^2 \]

- \( W \): particle fall velocity, ft/s
- \( \rho_s \): density of sediment particle, 2-2.7 g cm\(^{-3}\)
- \( \rho_w \): density of water, 1 g cm\(^{-3}\)
- \( g \): gravitational constant, 981 cm s\(^{-2}\)
- \( d_s \): sediment particle diameter, mm
- \( \mu \): absolute viscosity of water, 0.01 poise (g cm\(^{-1}\) s\(^{-1}\))

(ft/s is the traditionally followed unit; retained for simplicity and clarity of the equation)

Generally, it is the wash load (fine silt and clay size particles) that carries most of the mass of the adsorbed chemical. These materials have very small fall velocities, on the order of 0.3-1.0 m/d for clays of 2-4 \( \mu \)m nominal diameter and 3-30 m/d for silts of 10-20 \( \mu \)m nominal diameter.

Sediment Transport Regimes (Graf, 1971) gives the relationship between stream velocity, particle size and the regimes of sediment erosion transport and deposition. For silt and sand sized particles, sedimentation occurs for low velocities 0.10 cm/s to 20 cm/sec. For higher velocities transportation occurs around 30 cm/s and chances of erosion is seen only for higher velocities than this value. For the specified study region the often observed current velocities, during the period of observation was limited to values < 30 cm/s; therefore re-suspension or erosion of bottom sediments can be taken as negligible.
*Exchanges*

Exchange fields may simulate all kinds of diffusion and dispersion within and between the water column and the benthic sediment. The interaction of turbulent diffusion with velocity gradients caused by shear forces causes a still greater degree of mixing due to dispersion. Transport of toxic substances in streams and rivers is predominantly by advection, but transport in lakes and estuaries are often dispersion-controlled. In this model, diffusion between the water column and benthic sediment was simulated by using $1 \times 10^{-10} \text{ m}^2/\text{s}$ as molecular diffusion coefficient, which was reported in WASP 6.0 manual (Wool et al., 1996). The longitudinal dispersion coefficient $E$, is estimated from salinity data and average fresh water velocity, $u$. A semi-log plot of salinity versus distance should have a slope of $u/E$. From the semi-log plot, the average longitudinal dispersion coefficient, $E$ is estimated.

Longitudinal dispersion coefficient-northern arm, $E_{(n)} = 89.381 \text{ m}^2/\text{s}$  
Longitudinal dispersion coefficient-southern arm, $E_{(s)} = 71.910 \text{ m}^2/\text{s}$

These values are applicable to the estuary in case the model is run for interconnected segments, spanning the entire water body.

*Loading*

River discharge in the study region varied throughout the year in response to inputs from precipitation events. Elevated concentrations of Al were typically associated with the leading edges of the runoff event hydrographs. Total Al concentrations varied over a wide range. Al loadings were simulated using boundary concentrations under the assumption that loading concentration is same as that of system concentration. Suspended sediment data at local gauging station is used to provide loading estimate for solids.

*Flow*

Flow rates of Periyar and Muvattupuzha were taken from the daily observed river discharge data reported by Central Water Commission (1998-1999). The flow into the southern arm contributed by Pamba, Meenachil, Achankovil and Manimala were calculated using velocity data and area of cross section at Thannirmukham Bund (Anon, 1998). The freshwater inflow to the estuary in the northern arm varies between 41.43 and 641.20 m$^3$/s and in the southern arm varies between 80.04 and 863.84 m$^3$/s.
5.4 Model Results

In the model (WASP 6.0), Al and SPM content were simulated to study the transport and transformation within the water column and bed sediment. Within the sub-model, TOXI, the simulated chemical 1 (Al) may occur in freely dissolved phase (dissolved Al), sorbed to DOC (DOC sorbed Al) and sorbed to solid phase (total sorbed Al). The total concentration of the particular chemical is the sum of the concentration of all these forms. Results of Al and SPM simulation in the northern and southern arm for the water column and benthic sediment are presented in figs. 18-19. The figure gives the profiles of total Al, dissolved Al, DOC sorbed and total sorbed Al, and total SPM. From the model results it is seen that the total Al is partitioned into dissolved, DOC sorbed and total sorbed Al. Dissolved and DOC sorbed fractions together contribute to the total dissolved fraction of the metal. In Cochin estuary, almost whole of the Al is present in DOC sorbed phase, i.e as colloidal and sub colloidal particles, with only minor contribution from freely dissolved and particulate sorbed species (figs.18-19). As the benthic segment volume is kept constant, the total Al and SPM indicate inverse variation, as expected.

From the model results, as stated above, it becomes evident that the major proportion of Al in Cochin estuary exists as DOC sorbed forms. DOC in marine and freshwater ecosystems is one of earth’s largest actively cycled reservoirs of organic matter (Burshaw et al., 1996). The ecological significance of DOC in aquatic ecosystems includes the following, like DOC affecting the acid-base chemistry and applying controls on the pH of many wetland waters (Mc Knight et al., 1985). Because natural dissolved organic matter is acidic and is a powerful agent for complexation of metals, it plays an important role in mineral weathering, metal toxicity and metal export (Mierle & Ingram, 1991), influencing the cycling of metals such as Cu, Hg and Al, which, in turn can affect the concentration of trace metals found in aquatic organisms.

The dissolved organic substances play a vital role in biological (productivity), chemical (metal complexation, flocculation and absorption phenomena) and geological (sedimentation and early diagenesis) processes (Hayase & Shinozuka, 1995). Enrichment of DOC in the water column occurs through
Fig. 18. Simulation results of Al and SPM-northern arm

Water column

Benthic segment
Fig. 19. Simulation results for Al and SPM-southern arm

**Water column**

![Graph showing Al and SPM concentrations in the water column over time from September to May 1998-1999. The graph illustrates the variation of total Al, dissolved Al, DOC sorbed Al, and total sorbed Al with SPM.]

**Benthic segment**

![Graph showing Al and SPM concentrations in the benthic segment over time from September to May 1998-1999. The graph illustrates the variation of total Al, dissolved Al, DOC sorbed Al, and total sorbed Al with SPM.]

**Legend**
- total Al
- dissolved Al
- DOC sorbed Al
- total sorbed Al
- SPM
degradation/transformation of particulate organic carbon (POC) either in the water column or in bottom sediments by leaching processes, desorption of POC due to modification of environmental conditions (salinity, pH etc), and diffusion from interstitial water. DOC elimination processes in estuarine environments include flocculation, adsorption and degradation (Mannino & Harvey, 1999).

Rivers carry mainly unflocculated clay material, of colloidal and subcolloidal dimensions, which are very easily prone to flocculation at fresh water-saline water boundaries. Flocculation and removal from solution occurs as salinity increase from 0-10 psu, above which removal is negligible. The mechanism of flocculation has been described in detail in chapter I. Since from the model results it is now clear that major proportion of Al is in colloidal phase (expressed as DOC sorbed, above), it is stated that flocculation is the main mechanism operating in the targeted regions (in other words, the upstream regions of the estuary). The mechanism of sorption onto particles will accelerate removal of dissolved Al with the availability of more free surfaces as the SPM content increases, based on information inferred from figure 14.

In the benthic sediment, metal concentration goes on increasing as the season progress from monsoon to premonsoon through postmonsoon. The existing upper layers of benthic sediment in the upstream portions are washed off with the incoming monsoon and thus the sediment layer gets renewed every year (Nair, 1987). At start of monsoon, the upper layer sediment bed is freshly deposited sandy particles and the chances of Al accumulating are lesser in the targeted regions. This is the reason for applying initial concentration of benthic sediment Al as zero. As the seasons progress, the benthic sediment layer accepts Al as mostly sorbed onto sediment particulates with very minute fractions existing as DOC sorbed and dissolved forms too (figs. 18 - 19).

A comparison between the observed and predicted values of dissolved Al and SPM in the water column for the northern and southern arms is given in figs.20 a-d. It is clear from the results that this model is able to simulate to a large extent, the temporal variations of the selected parameters. A single state variable representing the total Al concentration is required as the input variable; the model simulates the
Fig. 20a. Observed and predicted Al in Cochin estuary-northern arm

Fig. 20b. Observed and predicted SPM in Cochin estuary-northern arm
Fig. 20c. Observed and predicted AI in Cochin estuary-southern arm

Fig. 20d. Observed and predicted SPM in Cochin estuary-southern arm
distribution of the chemical between the various phases based on the distribution of partition coefficients.

Model validity is checked using the statistical criteria of linear least-squares regression and paired t-test. The simulated dissolved Al showed good agreement with measured values as is clear from the trend line (figs. 21a & b). The coefficient of determination \( r^2 = 0.59 \) for northern arm and 0.92 for southern arm) between simulated and measured values indicates that the model captures most of the processes relevant to Al cycling. Observed and simulated values were compared using the paired t-test and the calculated values of (test statistic) \( t = 0.2456 \), with a corresponding \( p \) (probability) value of 0.4079 (northern arm), and \( t = 3.13 \) with a corresponding \( p \) value of 0.0130 (southern arm), suggests that the model results are found to be indistinguishable from the field data at a significance level of 59.21% and 98.7% for the northern and southern arm, respectively. From the results of the two statistical tests, it is clear that the model meets the validity criteria. Therefore, appropriately, this model enables to assess the sensitivity of Al to various estuarine forcing.

**Sensitivity analysis**

Sensitivity analyses of the model results were conducted for determining the impact of transport and speciation mechanism. This is one way to identify the importance of various model parameters (Chapra, 1997). Sensitivity can be analyzed by using specific perturbations in the input and output variables. Therefore, the model sensitivity to a parameter change is defined as the relative change in the variable concentration divided by the relative change in the parameter value, in this case (US EPA, 1997; Lohman et al., 2000).

\[
\text{Sensitivity(\%)} = \frac{C - C_B}{P - P_B} \times 100
\]

where \( C_B \) is the calculated value of model output in the base simulation, \( C \) is the calculated value of model output after a change in parameter, \( P_B \) is the model parameter value in the base simulation and \( P \) is the model parameter value in the sensitivity simulation.
Kinetic parameters, representing principal mechanisms for Al speciation and transport, were major targets for the sensitivity analysis. Diffusion, settling, advection and sorption were of great importance in this model. Sensitivity analysis was conducted by increasing or decreasing a single model parameter by 100% (Kim et al., 2004). The results are summarized in Tables 2a & b and figs. 22a & b. Model sensitivity analysis for each of the parameter, for both northern and southern arm segments is given in figs. 23a-d, 24a-d, 25a-d, and 26a-d. In the water column, Al concentration depended on advection, sorption and diffusion while settling had negligible influence. Also the magnitude of diffusion and sorption did not have any affect on the total Al level, though the partitioning between dissolved, DOC sorbed and total sorbed stands influenced. In the case of benthic sediment, the influencing parameters were diffusion, settling and advection while sorption influenced only the level of dissolved Al. The detailed results on analysis of sensitivity for the water column and benthic segment are given below.

**Water column**

Diffusion is defined as the vertical exchange between pore water and the water column in this model. Diffusive water exchanges can significantly influence pollutant (or metal) concentrations depending on the dissolved concentration gradients in the two segments. Diffusion did not have any prominent effect on the total Al levels but the dissolved Al, DOC sorbed Al and total sorbed Al was affected in varying proportions. Among above, the dissolved and DOC sorbed Al was affected in minute amounts, the probable reason is that loading inputs were much higher than diffusion effects. The increased diffusion coefficient promotes diffusive flux transfer from the water column segment to the benthic segment resulting in variations in amount of dissolved and DOC sorbed Al in the water column to the extent predicted. Similarly, vice-versa, the decreased vertical coefficient could result in increased values of dissolved and DOC sorbed Al in the water column. The total sorbed Al will obviously increase/decrease with decrease/increase in the other forms of Al since the total Al is the sum of dissolved Al, DOC sorbed and total sorbed Al; in this case, the total Al remained a constant, the fractions being distributed accordingly. The magnitude of variation for the total sorbed Al is more than the other forms of Al (figs.23a & c). The reason being, total sorbed form is present in minute amounts in the water column
Fig. 22a. Model sensitivity analysis in the (a) water column and (b) benthic segment for northern arm during 9 month simulation. 1-dispersion, 2-settling, 3-advection & 4-sorption.
Fig. 22b. Model sensitivity analysis in the (a) water column and (b) benthic segment for southern arm during 9 month simulation. 1-dispersion, 2-settling, 3-advection & 4-sorption
Table 2a. Sensitivity analysis results for northern arm

<table>
<thead>
<tr>
<th>Parameter</th>
<th>% variation</th>
<th>Water column</th>
<th>Benthic sediment</th>
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<tr>
<td></td>
<td></td>
<td>Sensitivity (%)</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>+100</td>
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<td>-2.77</td>
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<td>0</td>
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<tr>
<td></td>
<td>+100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>advection</td>
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<td>178.22</td>
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<tr>
<td></td>
<td>+100</td>
<td>-50.29</td>
<td>-48.14</td>
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<tr>
<td>sorption</td>
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<tr>
<td></td>
<td>+100</td>
<td>0</td>
<td>-49.3</td>
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Table 2b. Sensitivity analysis results for southern arm

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<th>Parameter</th>
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<th>Water column</th>
<th>Sensitivity (%)</th>
<th>Benthic sediment</th>
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</thead>
<tbody>
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<tr>
<td></td>
<td></td>
<td>tot Al</td>
<td>dis Al</td>
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<td></td>
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<tr>
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<td>0</td>
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Fig. 23a. Model sensitivity analysis for diffusion - northern arm - water column
Fig. 23b. Model sensitivity analysis for diffusion - northern arm - benthic segment
Fig. 23c. Model sensitivity analysis for diffusion - southern arm - water column.
Fig. 23d. Model sensitivity analysis for diffusion - southern arm - benthic segment
Fig. 24a. Model sensitivity analysis for settling - northern arm - water column
Fig. 24b. Model sensitivity analysis for settling - northern arm - benthic segment
Fig. 24c. Model sensitivity analysis for settling - southern arm - water column
Fig. 24d. Model sensitivity analysis for settling - southern arm - benthic segment
Fig. 25a. Model sensitivity analysis for advection - northern arm - water column
Fig. 25b. Model sensitivity analysis for advection - northern arm - benthic segment
Fig. 25c. Model sensitivity analysis for advection - southern arm - water column
Fig. 25d. Model sensitivity analysis for advection - southern arm - benthic segment
Fig. 26a. Model sensitivity analysis for sorption - northern arm - water column
Fig. 26b. Model sensitivity analysis for sorption - northern arm - benthic segment
Fig. 26c. Model sensitivity analysis for sorption - southern arm - water column
Fig. 26d. Model sensitivity analysis for sorption - southern arm - benthic segment
whereas it is the major form of Al existing in benthic sediment and any increase/decrease in the diffusion coefficient will greatly enhance/deplete the Al influx from the benthic segment. The SPM concentration also showed similar pattern of enhancement and depletion as was seen in the case of total sorbed Al for both the northern and southern arms. It is also noted from figs.23a & c that the variation in constituent values from the normal values increases as the season progresses from monsoon to premonsoon.

Settling had no influence on any form of Al or SPM concentration in the water column for both the northern and southern arms except a very minute increase in the total sorbed and SPM values with decrease in settling velocity. Similarly, a very minute decrease was noted for increase in settling velocity for the total sorbed Al and SPM concentration. This minute increase/decrease can be accounted to be due to most of the Al in the water column being present as dissolved and colloidal forms. The deviation of the variables from the normal with changes in settling velocity is given in figs.24a & c.

The variables total Al, dissolved Al, DOC sorbed Al, total sorbed Al and SPM were fairly sensitive to advection in varying amounts, showing considerable increase on decreasing the advection rate. On decreasing the advection rate, total sorbed Al showed an enhancement of almost six fold and five fold for the northern and southern arm respectively while the rest of the Al forms showed almost two fold increases for both the northern and the southern arms (figs.25a &c). The advection related changes are functioned by the transport mechanism which is otherwise controlled by the residence time prevailing in that part of the estuary selected in this exercise. The SPM concentration in the northern arm also showed two fold increases but for the southern arm the enhancement was slightly less.

Dissolved Al, DOC sorbed Al and total sorbed Al too were affected by changes in sorption coefficients. Dissolved Al showed very large variation with changes in sorption coefficient, decreasing the sorption coefficient to half led to almost doubling of dissolved Al value while doubling the sorption coefficient led to reduction of dissolved Al to half the value. Total sorbed and DOC sorbed forms exhibited slight decrease with decrease in sorption coefficient and vice versa in both
the northern and southern arms (figs. 26a & c). The above deduced results are normally expected while dealing with estuarine conditions where sorption plays a major role in metal phase transformation.

The northern and southern arms of Cochin estuary reacted in a similar manner to sensitivity analysis. The constituents in both the targeted regions were highly sensitive to advection, followed by sorption (particularly dissolved form) and diffusion. Settling did not have large influence on any of the variables for both arms of this water way.

**Benthic segment**

Total Al, dissolved Al, DOC sorbed and total sorbed Al were the variables seen to respond against parameters in the sensitivity analysis. Suspended matter concentration remained unchanged during sensitivity analysis because about 60% of benthic segment consists of suspended particulates and any change brought about by changes in kinetic parameters remains ineffectual with respect to the total concentration.

On enhancing the diffusion coefficient, total Al, dissolved Al, DOC sorbed and total sorbed Al increased in both the northern and southern arms (figs. 23b & d). Similarly, on decreasing the diffusion coefficient the constituent concentrations decreased by the same amount for both the northern and southern arms. The main difference between water column and benthic sediment noted here is that in the water column total Al remained more or less the same, but in the benthic segment, total Al showed considerable increase/decrease with increase/decrease in diffusion coefficient. The reason for this is linked to loading factor being insignificant compared to diffusion effects and therefore the role of diffusion is visibly evident.

Total Al, dissolved Al, DOC sorbed and total sorbed Al decreased on decreasing the settling velocity for the northern and southern arms. An increase by the same amount is noted for northern and southern arms on doubling the settling velocity (figs. 24b & d). The settling particles adsorb Al onto its surfaces and thus this process serves in transporting of the metal between the two segments.
Advection strongly influenced total Al, dissolved Al, DOC sorbed and total sorbed Al concentrations in the benthic segment (figs. 25b & d). Decrease in advection by half led to a three and a half fold increase in constituent values for the northern arm and more than one and a half fold increase for the southern arm. Doubling advection led to considerable decrease in constituent values for the northern and southern arms respectively.

Changes in sorption coefficient on total Al was negligible, DOC sorbed and total sorbed Al influenced to a certain extent, but dissolved Al was highly sensitive to variations in sorption (figs. 26b & d). Decrease in sorption coefficient by half led to doubling of dissolved Al value and increase in sorption coefficient two fold led to decrease in dissolved Al values by half for both northern and southern arms. Dissolved Al concentration is very less in benthic segment compared to DOC sorbed and total sorbed and any small variation can make significant changes in the concentration value.

It is clear from the foregoing explanation that Al is sensitive to diffusion, all forms being affected to the same extent. Settling is another parameter bringing about alike changes in Al constituents. On the other hand, advection brings about reverse changes in all Al constituents and sorption also selectively influences the dissolved Al followed by sorbed phases.

**Predictive Analysis**

An attempt is also made on simulating Al levels in this estuary utilizing the predictive features of the WASP model. The results are presented in figs. 27 & 28. A composite analysis was performed by doubling the Al and SPM loads where as the flow was halved and lowered by one degree of order, both for the northern and southern arm. Though many options exist, the above inputs were made in reconciliation with the likely hood of such conditions, which may prevail in this water body. Fig. 27a is a repeat of original data. Figs. 27b & c indicate influence due to change in flow conditions, which is rather magnifying the processes that occur in the water column as well as benthic segment. The changes expected on reduction of flow will have to be carefully interpreted under very low flow conditions which is reflected in figs. 27f, j & l.
Fig. 27. Predictive Analysis of the Model for different estuarine conditions - Northern arm

AI load 1 - AI loading normal
AI load 2 - AI loading doubled

SPM load 1 - SPM loading normal
SPM load 2 - SPM loading doubled

Flow 1 - normal flow
Flow 0.5 - 1/2 the flow
Flow 0.1 - 1/10th of the flow

Legend:
- Total Al
- Dissolved Al
- DOC sorbed Al
- Total sorbed Al
- SPM
Fig. 28. Predictive Analysis of the Model for different estuarine conditions - Southern arm

Ali load 1 - Al loading normal

Ali load 2 - Al loading doubled

SPM load 1 - SPM loading normal

SPM load 2 - SPM loading doubled

Flow 1 - normal flow

Flow 0.5 - 1/2 the flow

Flow 0.1 - 1/10th of the flow
(g) Al load-2, SPM load-1, Flow-1
Water column

(h) Al load-2, SPM load-1, Flow-0.5
Water column

(i) Al load-2, SPM load-1, Flow-0.1
Water column

Benthic segment
(j) Al load-2, SPM load-2, Flow-1
Water column

(k) Al load-2, SPM load-2, Flow-0.5
Water column

(l) Al load-2, SPM load-2, Flow-0.1
Water column

Benthic segment
On altering the inputs of Al and SPM loads (figs. 27d & g), the total SPM and total sorbed Al stands enhanced. In case both Al and SPM loads are doubled, the enhancement is proportionally predicted. This exercise viewed through fig.27k (flow halved) permits segregation of five different variables to indicate similar patterns of changes through period of observation in the water column. A similar instance is also supported in fig.27l. Again fig.27e & f bring out comparable patterns in variables, though the order of magnitude is less than those in fig.27k & l. It is concluded that the Al load changes promotes dissimilar enhancements in different variables but SPM loading offers systematic segregation within variables subject to enhancements governed by flow reduction.

Analysis of figs. 28a-l related to southern arm indicates alterations in the profiles proportional to loading factors in comparison to the northern arm. However, within variables, the segregation is not evident. As in the case of northern arm, when the flow is reduced by $1/10^6$, the prediction vastly changes the trends in profiles in the water column.

The simulation exercise utilizing the benthic segment promote proportional increase in Al load upon two cases of flow reduction, so is the case on doubling SPM and Al load; as compared to the water column, the benthic segment does not support alterations in pattern of variability. This is of course related to passive but important roles played by the boundary layer in most estuaries.

5.5 Discussion

The main processes that govern the transport and behaviour of Al in the estuary were studied applying the WASP model. A thorough understanding of the estuarine physics in terms of hydrodynamic, dispersive and means of sediment transport is a necessity when modelling transport of micro-pollutants is conducted. For Al in particular, hydrophobic sorption is also an important process, which distributes Al between sediment and water. The model was successful in partitioning the total Al into dissolved Al, DOC sorbed Al and total sorbed Al depending on the estuarine conditions. The results from the simulations performed using WASP suggest
that the model is capable of satisfactorily simulating evolution profiles of total Al, dissolved Al, DOC sorbed Al, total sorbed Al and SPM concentrations.

Aluminium and SPM concentrations in the study region were predicted quite well by WASP 6.0 model in comparison with the observed field data (figs.20-21). Northern arm may pose serious environmental problems as far as aluminium is concerned, owing to the discharge of effluents from the industrial establishments on the banks, which can alter the estuarine conditions leading to unprecedented increase in dissolved values of this metal which may prove hazardous to the ecosystem. Discharge of effluents can lead to acidification of the water body, a decrease in pH below 5.5 is seen to elevate dissolved Al values considerably. For the southern arm, the pH falls within the permissible limits, no drastic variations are noticed and hence the dissolved Al shows a gradual decreasing trend with the progress of seasons.

Advection, dispersion, sorption and settling were important mechanisms influencing Al transport in the water column. To the benthic sediment, settling and diffusion of Al from the water column were the most important input source of Al. Generally, exchange across the sediment–water interface serves as an important process in regulating water column concentration of metals in natural waters and the sediments act as a major sink for Al.

The results indicate that the Al input into Cochin estuary is particularly riverine and Al exists in the water column as DOC sorbed phase with minor fractions of freely dissolved and particulate sorbed phases. Al values decrease continuously as the season progresses, reaching minimum by the end of premonsoon but the estuary is replenished with the onset of monsoon. As far as benthic sediment is concerned, Al concentration gradually increases as the season progresses, from monsoon to premonsoon but this increase is restricted by the washing off the top layers during the succeeding monsoon (Nair, 1987), when the estuary represents a very dynamic environment. Thus it is unlikely that the benthic sediment may act as a sink for Al, than rather a major portion of the sediment Al will be transposed to the coastal ocean.

Considering the complexity of Al speciation and transport, this model simulation might have some limitations in the prediction of Al cycling, in full. The
WASP 6.0 model as implemented here does not fully accommodate the ecological variability in the estuary due to constraints on the specification of rate constants. Hence, it may not be appropriate for operational models to detail the spatial extent of the entire estuary. The focus of this study which deals with the temporal variability of Al / SPM constituents, the model was successful in revealing several issues explained in the context of water quality dynamics. As a research tool then, the model is quite versatile and aid in understanding the metal modulation, where knowledge is lacking in terms of water quality or on the study of specific locations of interest.

The predictive analysis has helped to identify the likely changes, which will be reflected in the various constituents – in terms of their absolute values and pattern of changes. As expected, enhancement in Al inputs or suspended loads, either singularly or in combination will proportionally generate enhancements in water column and benthic segment of variables. The alterations on reducing the flow to half are comprehensibly understood whereas further lowering of flow conditions is likely to bring about predominant changes in variable behaviour and distribution. A futuristic picture likely to develop within the predicted framework generates apprehensions on Al prevalence, absolute concentrations in the water media, coupled with augmentation from the benthic segment levels so as to rate this element to be of environmental concern.

This model can thus be used to predict future conditions under various loading scenarios provided the alterations in model parameters and coefficients pertaining to the study region can be well quantified. The chemical exposure concentrations to aquatic organisms and/or humans in the past, present or future can also be assessed.