Synergic Reactions in the Estuarine Environment leading to Modulation of Aluminium metal during Transport Processes (in Cochin Estuary)

THESIS SUBMITTED
TO THE

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Doctor of Philosophy
in
Oceanography

UNDER FACULTY OF MARINE SCIENCES

By

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April 2005

to my beloved parents

DECLARATION

I hereby declare that the thesis entitled, "**Synergic Reactions in the Estuarine Environment leading to Modulation of Aluminium metal during Transport Processes (in Cochin Estuary)**" is an authentic record of research work carried out by me under the supervision and guidance of Dr. A. N. Balchand, Professor, Department of Physical Oceanography in partial fulfilment of the requirements for the Ph. D. degree of Cochin University of Science and Technology and that no part thereof has been presented for the award of any other degree in any University.

Sanjana M. C.

Cochin-16
11/04/2005

CERTIFICATE

This is to certify that this thesis entitled, "**Synergic Reactions in the Estuarine Environment leading to Modulation of Aluminium metal during Transport Processes (in Cochin Estuary)**" is an authentic record of the research work carried out by Smt. Sanjana M. C., under my supervision and guidance at the Department of Physical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the Ph. D. degree of Cochin University of Science and Technology under the Faculty of Marine Sciences and no part thereof has been presented for the award of any degree in any University.

Cochin-16
11/04/2005

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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Dr A. N. Balchand, Professor, Department of Physical Oceanography, for his supervision, invaluable insights and patient hearings throughout the course of this thesis.

I am also grateful to Dr R. Sajeev, Head, Department of Physical Oceanography, for providing me the necessary facilities for the smooth conduct of research. I also thank Sri P. K. Saji, Lecturer, Department of Physical Oceanography for his valued suggestions.

Dr S. Muraleedharan Nair, Department of Chemical Oceanography has played a decisive role in the moulding of this thesis; sincere thanks are credited. I also thank Dr A. C. Narayana, Department of Marine Geology and Geophysics, for his timely guidance.

I would like to acknowledge Dr Babu Philip, erstwhile Head, Department of Marine Biology, Micro Biology & Biochemistry, for making available the fluorescence spectrophotometer used in the analysis. I also thank Dr N. Nandini Menon for the assistance rendered in sample analysis.

Financial support from Cochin University of Science & Technology and Council of Scientific & Industrial Research, India is thankfully acknowledged. Central Water Commission, Cauvery & Southern Rivers Circle, had been kind enough to provide valuable data; my acknowledgments are recorded here.

I am thankful to Smt. R. Rethnambal, Retd. Professor & Dy. Director, Maharajas College, Ernakulam, for her valued comments, which helped me, clear doubts relating to the topic.

I am indebted to Dr K. Ajith Joseph for his suggestions and timely help and to Dr K. Rasheed for his cooperation in the thorough scrutiny of this work, which greatly improved the manuscript. Their perceptive comments and criticisms were helpful in progressing with this work. The assistance rendered by Mr Venu G. Nair, Department of Atmospheric Sciences is greatly acknowledged.

My special thanks are due to Dr Geetha Bhaskar & Mrs B. V. Charlotte for the moral support and encouragement during the crucial stages of my work. Smt. N. Lalithambal, former Section Officer, of this department and currently Assistant Registrar, was always around giving me full support and encouragement. The office staffs of Department of Physical Oceanography were willingly helpful to me and I thank them too. I record my sincere thanks to Smt. M. G. Sreedevi from the Department of Atmospheric Sciences for all the help rendered.

The wholehearted cooperation rendered by Dr M. S. Madhusoodanan & Mr T. Chandramohan is thanked; my colleagues, Ms C. P. Neema, Ms K. Jossia Joseph, Mr Mohammed Asharaf, Ms B. R. Smitha, Ms T. R. Resmi, Mr E. Harikrishnan and Mr P. Anand have supported me during the entire course of this work which is greatly acknowledged. I am also pleased to acknowledge the cooperation by Ms Jiji Paulose and Ms N. K. Sreedevi during the course of this work.

My family was always with me during the trying times, always urging me to go on and on. Without their care and consideration, this work would likely not have matured. I express my solemn indebtness to my beloved and revered parents for their perseverance and wholehearted support during the tenure of this doctoral work.

At this point of time, I am also blessed by the great fortune in having beside me, my most trusted and ardent life partner, bestowing his kind and selfless encouragement and relentless support. I greatly appreciate the wits in having silently consented to my plea to run this show.

Above all, I thank God for His grace and mercy.

And also to anyone, I missed, who deserves a mention.

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CHAPTER I
Global Aluminium – A Perspective

1.1 Introduction

On the planet earth, where the river and the sea intertwine the line dividing the ocean and continent blurs; a rather complex buffer zone called estuaries that is dynamic, diverse and highly productive comes into existence. From estuaries, freshwater amassed over vast regions of the land pours into the ocean and on the reverse, tides move salt water upstream, far inward of the river mouth. Estuaries are not always associated with drainage from land; but our understanding of estuarine dynamics was developed upon pioneering research efforts in the lower reaches of rivers. A definition on the term estuary is still often based on the assumption that the water of estuaries has to be diluted by freshwater. This is of course, an over qualification. A classical definition of an estuary, still quoted frequently in the literature but based on the above assumption is,

"An estuary is a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage."

(Cameron & Pritchard, 1963). Estuaries described by this definition are known as positive estuaries. In recent years the definition has been modified (as stated below), to include all other types of estuaries by applying three changes (Tomczak & Godfrey, 1994). The first change allows intermittent closure of the estuary to the sea. This situation is common with gently sloping, sandy coasts in regions with strong seasonal or irregular fluctuations of rainfall; reduced river runoff during the dry periods allows the establishment of a sand bar, turning the estuary temporarily into a brackish lake. The second change addresses the situation where evaporation exceeds the fresh water supply from the rivers and from local rain, and as a consequence the water in the estuary is more saline than in the open ocean; such estuaries are known as negative or inverse estuaries. The third change, which specifies that estuaries are narrow, is required to specify estuaries from seas of Mediterranean type.

Thus the following definition was introduced:

"An estuary is a narrow, semi-enclosed coastal body of water which has a free connection with the open sea, intermittently and within which the salinity of the water is measurably different from the salinity of the open ocean."

The driving force in an estuary is the gravity driven fresh water vs. tidal currents generating varied circulation patterns. However, the circulation in an estuary is also influenced by the large density differences produced by the salinity contrast between freshwater and oceanic water (or, in the case of the inverse estuary, by the salinity contrast between the hyper saline estuary and the open ocean). The wind may modify the circulation and could become a dominant force, but it is not responsible for the mean circulation over extended periods of time.

Estuaries may be narrow, semi-enclosed bodies of water, but their entrance to the sea is wide enough to allow deep penetration of the tidal wave into their lower reaches. It is a mixing zone of riverine and oceanic waters with widely varying composition where end members interact both physically and chemically. The importance of estuaries lies in the fact that they act as a mediator (filter) in the transfer of substances from continents to oceans. Estuaries thus act either as a source or sink for different substances.

These complex systems receive chemical inputs from a variety of sources. Materials are continuously supplied from marine, riverine, atmospheric and local sources and lost by seaward transport as well as permanent or semi-permanent sediment action. River runoff contributes dissolved species derived from chemical weathering of rocks, suspended material from mechanical weathering of terrigenous matter, and dissolved and particulate organic matter of biogenic origin. Superimposed on these natural sources are inputs resulting from anthropogenic activities. Biogeochemical characteristics of each element determine the type of behaviour exhibited during its passage through the estuarine system. The balance between the input and output of these elements, together with physical flow regime determine the specific physico-chemical characteristics of the estuary.

The study of chemical and physical aspects of this near shore environment provides the necessary background for understanding the coastal oceanographic processes. The structure of physical and chemical environment is commonly expressed in terms of water quality parameters such as temperature, salinity, suspended particulate matter, dissolved oxygen, nutrients, metal concentration and pigments.

A complete understanding of the estuarine chemistry of any component and of its ecological significance requires not only an assessment of concentrations and speciation in each phase, but also knowledge of fluxes between phases. Although chemical and biological transformation processes are common to all estuaries, the distribution of reactants and the rate of reactivity vary greatly between estuaries, under the influence of varying combinations of environmental factors such as hydrodynamic residence times, the nature of inputs, internal mixing, transport processes etc. Many hazardous substances discharged into the aquatic environment are known to accumulate in rivers and estuaries. Among them trace metals have been recognised as toxic to aquatic organisms depending on their concentration and chemical speciation.

1.2 Trace metals

Persistent chemicals that do not breakdown stand to pose serious environmental problems. Trace metals because of their relatively long half-life and biological significance, constitute one such class among non-degradable contaminants causing great concern.

The term "trace element" is used in current literature to designate those elements, which occur in small concentrations in natural systems. For all practical purposes, the terms such as "trace metals", "trace inorganics", "heavy metals", "micro elements" and "micro nutrients" are treated as synonymous with the term trace elements (Forstner & Wittmann, 1983).

Chemical reactions with trace metals are much more difficult to predict than those involving macro elements and thus concentration levels often show large temporal and spatial variations even within specific aquatic systems. Understanding the sources, fate and cycling of trace metals in estuaries has been modified by the need to understand the impact of anthropogenic inputs of toxic or polluting metals into rivers and estuaries and also by increasing realisation of the importance of the estuarine interphase in global geochemical cycling of the elements.

Sources of trace metals

The various anthropogenic activities by which trace metals are introduced into the aquatic system include smelting, mining, shipping, industrial effluent discharge, urbanisation, automobile exhaust, application of fertilisers, algaecides, fungicides etc. Secondly, the natural processes that contribute metals to the aquatic environment include weathering of rocks, leaching of ore deposits, natural fires in the forests, terrestrial and marine volcanism etc. The above sources directly regulate the net flux of trace metals that interplay with natural/artificial systems and pose relevant questions on their cycling, transport and ultimate removal.

In general, it is possible to distinguish between seven different sources from which metal pollution of the environment originates (Unnikrishnan, 2000):

1. Geological weathering
2. Industrial processing of ores and metals
3. The use of metal and metal components
4. Burning of fossil fuels, production of cement and bricks
5. Leaching of metals from garbage and solid waste dumps
6. Animal and human excretions that contain heavy metals
7. Non-point sources

Upon locating the source of metal input of receiving water bodies, a distinction is often made between non-point and point sources. Essentially, rural areas and agricultural land are regarded as non-point source, since the metal supply originates from large regional areas.

Estuarine behaviour of trace metals

Once introduced in the aquatic system, trace metals undergo transformation - physical, chemical, biological and geological - processes such as sorption at solid water interface, diffusive fluxes across the sediment water interface, uptake by planktonic organisms, sedimentation etc, that bring about their degeneration and sometimes ultimate removal. As a result of these reactions a large fraction of the trace metals introduced into the aquatic environment is normally found associated with bottom sediments. Typically, sedimentary metal concentrations are three to four orders of magnitude higher than in the dissolved phase.

The chemical behaviour of trace metal during its transport within the estuary is determined to a large extent by the chemical form, prevalent in the river, as given below,

- In solution as inorganic ion and both inorganic and organic complexes
- Adsorbed onto surfaces
- In solid organic particles
- In coatings on detrital particles after co-precipitation with and sorption into mainly iron and manganese oxides
- In lattice positions of detrital crystalline material and
- Precipitated as pure phase, possibly on detrital particles

Estuaries are characterised by strong hydrodynamic and physico-chemical gradients and these two are responsible for modifications of the distribution of trace elements between various dissolved and particulate species. These modifications combined with fluctuations in river discharge and total particle discharge, may affect significantly the fluxes of heavy metals of the estuarine region. Aluminium (atomic number 13) and the metalloids arsenic and selenium (atomic number 33 and 34) often are included in the broad class of pollutants. In this study the objective was to gain a better understanding of cycling and fate of the trace metal aluminium (Al) in the estuarine environment, focusing on its role as a terrigenous borne tracer.

1.3 Aluminium (Al)

Al is the third most abundant element in the Earth's crust, after oxygen and silicon. It makes up about 8% by weight of the Earth's solid surface. The "metal of clay" as it was known in ancient times, remained locked in the rudiments of the earth for thousands of years. Not until the mid 18th century did chemists begin to unlock its secret. It never occurs naturally in pure metal form, but it's found in most rocks, clay, soil and vegetation, in combination with other elements.

While Al is abundant in the environment, the naturally occurring forms are usually stable and do not interact with living organisms. Under acidic conditions, however, Al may be released from rocks and soils in soluble form, which can be absorbed, by plants and animals. It is widely used by geochemists as a tracer for detecting aluminosilicate material in atmospheric, oceanic and sedimentary particulate matter. Recent field and laboratory experiments have indicated that the marine geochemistry of Al is regulated by the removal onto particles throughout the water column, which induces a typical residence time of 1-100 years for this element in the ocean (Orians & Bruland, 1985, 1986; Measures et al., 1986; Maring & Duce, 1987; Measures & Edmond, 1988; Buat-Menard et al., 1989). Although Al in drinking water has been suggested as a cause of some neurological diseases, scientific research has not been able to support this.

Chemistry of Aluminium in water

The ability of Al compounds to dissolve in water is affected by the chemical composition of water. The pH of water is the main factor in determining how well Al compounds will dissolve (May et al., 1979). Unless conditions are highly acidic or basic, little Al will remain in solution. Rather, it will precipitate out of the water column as a white or off-white floc. The same conditions that affect the physical characteristics of Al compounds, also affect the size and appearance of the floc.

When Al precipitates out of water, it takes other substances with it. This is known as coagulation. If conditions are conducive, the coagulated material (floc) forms large, heavy particles, which quickly settle out of the water column. However, some residual Al is always left in solution.

Al reactions in water are complex, as reactions differ depending upon pH levels. Al levels are usually measured as total Al, which is the sum of all dissolved and particulate Al forms. Dissolved Al occurs as compounds that range from being fairly reactive (bound to inorganic complexes) to fairly non-reactive (bound to organic complexes). As pH of most marine waters are >7, dissolved Al is in anionic form $[Al(OH)_4]^-$. Thus, the chemistry of Al in water is essentially the chemistry of aluminium hydroxide, which differs from the hydroxides of other non-transition metals in the following, three important respects (Burrows, 1977):

- It is readily amphoteric.
- It forms complex ions with other substances present in the water, and
- It tends to polymerise.

Thus, the form and concentration of Al in water depends to a lesser extent, on the temperature and duration of exposure to the water apart from pH and nature of substances dissolved in the receiving waters. The following exposition, which is adopted from the work of Brossett (1952), Brossett et al., (1954), Turner (1969) and Hem and colleagues (Hem & Roberson, 1967; Hem, 1968, Roberson & Hem, 1969; Smith & Hem, 1972; Hem et al., 1973;) is applicable to dilute solutions of the type most common in natural environments.

Monomeric Aluminium Hydrates: When an Al salt of a noncomplexing acid (such as aluminium perchlorate) is dissolved in pure water, it dissociates to form an aluminium ion generally considered to be six-coordinated with water molecules, $[Al(H_2O)_6]^{3+}$. Solutions of the aluminium ions are acidic because of the hydrolysis equilibrium.

$$[Al(H_2O)_6]^{3+} + H_2O = [Al(H_2O)_5\ OH]^{2+} + H_3O^+$$

Thus, a solution of 10^{-3} M aluminium per-chlorate in pure water will have an initial pH value close to 4. This is important when evaluating the toxicity of Al compounds, because the lethal limit for many aquatic organisms occurs at $pH \geq 4$.

Progressive hydrolysis of the aluminium ion leads to the univalent ion and, finally, colloidal aluminium hydroxide, as follows

$$AlOH^{2+} + H_2O = [Al(OH)_2]^+ + H^+$$

$$[Al(OH)_2]^+ + H_2O = Al(OH)_3 + H^+$$

In basic solutions, aluminium hydroxide exhibits its amphoteric nature by conversion to the aluminate ion

$$Al(OH)_3 + H_2O = [Al(OH)_4]^- + H^+$$

Aluminate ion represents the apparent limit for hydrolysis of Al^{3+}.

Polymeric Aluminium Hydrates: There is a strong tendency for dissolved Al to form dimeric, oligomeric and polymeric species. This tendency is enhanced as the ratio of Al-bound hydroxide to Al increases from 0 to 3. Removal of a proton from the hexacoordinate aluminium cation $[Al(H_2O)_6]^{3+}$ gives the bivalent cation $[Al(H_2O)_5OH]^{2+}$, for which the OH:Al ratio is 1. Dimerization of this cation proceeds with loss of two molecules of water to give $Al_2(OH)_2 \ x \ (H_2O)_8^{4+}$, a pair of octahedrons with a shared edge. Three dimers may now combine in ring formation as follows

$$3[Al_2(OH)_2(H_2O)_8]^{4+} \rightarrow [Al_6(OH)_{12}(H_2O)_{12}]^{6+} + 6H_3O^+$$

For this hexomer the OH:Al ratio is 2. Combination of many such hexomers in parallel sheets results in construction of mineral gibbsite, which has an OH:Al ratio of 3, corresponding to electrical neutrality. It is important to recognise that the dimers and higher oligomers are kinetic, rather than thermodynamic, species.

Complex ions: Al is capable of forming strong coordinate bonds with substances other than water and hydroxide. Al^{3+} forms six different complexes with fluoride ion. If one considers only the first equilibrium, for which $K_1 \approx 10^7$, it is readily shown that a solution containing 10^{-4} M aluminium (2.70 mg/l) and 10^{-4} M fluoride (1.90 mg/l) would contain only 3×10^{-6} M (0.08 mg/l) uncomplexed Al. The stability constants for aluminium sulphate complexes are much smaller than those for fluoride complexes, because sulphate is a much more important constituent of most natural waters, sulphate complexes may be as prevalent as fluoride complexes. In a solution containing 10^{-4} M aluminium (2.70 mg/l) and 10^{-3} M sulphate (96 mg/l), the concentration of uncomplexed Al would be approximately 0.038×10^{-3} M (1.0 mg/l). When several different ligands compete for Al, the distribution of Al species will depend on the concentration of each ligand and on the pH.

In so far as complexing ligands such as fluoride and sulphate are present in water, they will increase the amount of dissolved Al in equilibrium with solid aluminium hydroxide. In most natural waters with pH 6.5-8.5, neither fluoride nor sulphate will be present in significant concentration to enhance the solubility of aluminium hydroxide.

Dissolved silica is also in competition for Al in natural water. Hem et al. (1973) have examined the synthesis of halloysite, $Al_2Si_2O_5\ (OH)_4\ (H_2O)_x$, from solutions containing Al and silicic acid at various pH levels. Silicic acid has the curious property of inhibiting crystallization of aluminium hydroxide, further illustrating the fact that the chemical form of Al is affected in many subtle ways by the properties of the receiving water.

The solubility of Al in water is enhanced manifold by synthetic chelating agents such as ethylenediamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and sodium tripolyphosphate (STPP). The presence of these agents in wastewater effluents could greatly elevate the concentrations of soluble aluminium in receiving waters. This effect would usually be limited to the region of discharge, as EDTA, NTA and STPP are all biodegradable to some extent.

The physical chemistry of turbidity reduction using Al compounds is a highly complex subject involving the interrelation of temperature, turbulence, particle size, pH and concentrations of ions present including sulphate and orthophosphate. The forms of Al present in turbid waters may be quite different from those present in clear waters.

Natural organic complexes: Many organic materials of natural origin are capable of mobilizing Al from the soil. These include humic and fulvic acids from decay of the litter matter and a mixture of polyphenols, reducing sugars and organic acids present in forest canopy drip (Malcolm & McCracken, 1968). The role of organics in mobilising polyvalent metals in some coastal plain rivers of the south-eastern United States has been discussed by Beck and Reuter (1974), who gave evidence on significant enhancement of Al levels in waters of high organic content. They noted that humic substances probably occur in solution as micro colloids, which are subject to aggregation, flocculation and precipitation. Thus, the concentration of organoaluminium complexes in a sample of natural water may diminish with time, whether or not the organic moiety is biodegraded.

Reactions in aqueous media

Reaction of aluminium with halogens

Al metal reacts vigorously with the halogens to form aluminium halides. So, it reacts with Chlorine, (Cl_2), Bromine, (Br_2), and Iodine, (I_2), to form respectively aluminium(III) chloride, $AlCl_3$, aluminium(III) bromide, $AlBr_3$, and aluminium(III) iodide, AlI_3.

Reaction of aluminium with acids

Al metal dissolves readily in dilute sulphuric acid to form solutions containing the aquated Al(III) ion together with hydrogen gas, H_2. The corresponding reactions with dilute hydrochloric acid also give the aquated Al(III) ion. Concentrated nitric acid passivates Al metal. Dissolving Al compounds with sulphuric acid will produce aluminium sulphate, otherwise known as alum. Alum is used in a wide range of water treatment applications ranging from large, municipal water plants to on-farm dugout coagulation practices.

Reaction of aluminium with bases

Al dissolves in sodium hydroxide with the evolution of hydrogen gas, H_2, and the formation of aluminates of the type $[Al(OH)_4]^-$.

Environmental prevalence of aquatic Aluminium

It has been seen that there is no clear distinction between dissolved and suspended Al. Some filters pass microcrystalline or colloidal aluminium hydroxide, while others absorb much of the soluble Al. Many investigators now (arbitrarily) use a 0.45 µm Millipore filter to distinguish between dissolved and particulate Al. From the data collected all over the world, the following information has been extracted (Burrows, 1977):

- Acid waters consistently contain much more soluble Al than neutral or alkaline waters.
- Highly saline waters contain higher levels of Al than fresh waters.
- Hot waters tend to contain more Al than cold waters.
- Moving waters give higher Al analysis than quiescent waters.

One would anticipate that alkaline waters with pH levels greater than 9 would also contain more Al; that they do not is a further demonstration of the limited solubility of aged aluminium-bearing formations as compared to freshly precipitated aluminium hydroxide. Hem (1970) has discussed the sources of Al in natural waters.

The increased solubility of Al in salt wells and springs may be due to complexing of the aluminium cations by anions such as sulphate; it may also be due in part, to the strongly depressing effect the solutions of high ionic strength have on the activity coefficients of polyvalent ions (Burrows, 1977). Because solubility equilibria are based on activities rather than concentrations, a brine solution can accommodate more Al at equilibrium than fresh water. This raises the question why soluble Al is apparently less prevalent in seawater than in fresh water. One possible answer is that colloidal Al particles are consolidated in seawater, so that materials too fine to be removed by filtration are greatly reduced in the oceans.

The higher apparent solubility of Al in moving waters than in quiescent waters suggest that much of what is alleged to be soluble Al is suspended material; however the higher levels may also be due to Al complexing organics present in many rivers and streams (Burrows, 1977).

Thus far, only chemical equilibria have been considered, but equilibria involving bioaccumulation of Al may also influence levels of dissolved Al in water. Although Al is one of the most abundant elements on earth, its biogeochemical behaviour in natural waters is not well understood. Studies on Al in oceans have revealed that the entire oceanic system is in a steady state and estuarine cycling of Al is a complex phenomenon (Hydes and Liss, 1977; Orians and Bruland, 1985; Chou and Wollast, 1997; Zhang et al., 1999). The marine geochemical cycling of Al is relevant to such oceanographic processes as the diagenesis of aluminosilicate material (Mackin & Aller, 1984b) and tracing atmospheric dust inputs to oceanic surface waters (Hydes, 1979; Measures et al., 1984, 1986). Al has also been used as a non-transient water mass tracer (Measures & Edmond, 1988). It is evident that Al is very reactive in the marine environment and has a relatively short residence time, ranging from 35 days in upwelling regions to 50-150 years in deep waters (Orians & Bruland, 1985; 1986).

Three main potential sources of dissolved Al for marine systems may be considered.

- River input: The concentration of Al is much higher in river water than in seawater. Stoffyn & Mackenzie (1982) have given an estimate of (4-29) x 10^{11} gm/year of dissolved Al being added to the oceans from stream discharges and a value of 15 x 10^{14} gm/year as river borne sediments.

- Atmospheric input: Measurements of the solubility of Al in rain water and on marine eolian dust suggest that 5-10% of Al present in the aluminosilicates could be released in the surface water and the water column during settling (Maring & Duce, 1987; Prospero et al., 1987; Losno et al., 1993; Lim et al., 1994). It has been suggested by several authors that eolian dust is the primary source of dissolved Al in the open ocean (Hydes, 1979, 1983; Measures et al., 1984,1986; Orians & Bruland, 1985, 1986; Measures & Edmond, 1990).

- Sediment-Water interface: There are only limited data available on the concentration of dissolved Al in pore waters (Caschetto & Wollast, 1979b; Stoffyn-Egli, 1982; Mackin & Aller, 1984b; Hydes et al., 1988). The concentration gradient near the interface suggests that pore waters could be either a source or a sink for dissolved Al for the overlying water. Hydrothermal vents also could act as a potential source for this element.

The principal inputs of Al to the oceans are from the atmosphere and rivers and have been reasonably well quantified. In order to make budget calculations for dissolved Al, it is needed to identify and quantify the various sources of input and output of this element.

1.4 Aluminium in water bodies

In common with silicate, dissolved Al in fresh water originates mainly from the natural weathering of alumino-silicate minerals (Krauskopf, 1956). The low solubility of Al has led to its traditionally being considered immobile during weathering processes. Water will however transport Al in some form, from all areas of active weathering as the products of both chemical and mechanical attack as simple Al species in solution, as polymeric material, and in small particles of the parent rock. The most common monomeric Al species in natural water are Al^{3+}, $[Al(OH)_2]^+$, $[Al(OH)_4]^-$ and aluminium fluoride complexes (Hem, 1968). The solubility data and calculations of Hem and co-workers (Hem et al., 1973) show that only concentrations of the order of micrograms per litre of dissolved aluminium ions can be expected in the usual pH range of natural waters. Because Al occurs in a wide range of forms and also due to the slow reaction rate of many Al species in water, clear-cut speciation into dissolved and particulate categories is not possible.

Despite its crustal abundance, the concentration of Al in natural waters is very low, with typical values of <10 μg/l in seawater and 10-80 μg/l in river water (Stoffyn & Mackenzie, 1982). This difference in concentration levels arises from the tendency of Al^{3+} to hydrolyse into polymeric colloidal forms (Stumm & Morgan, 1970), which are easily destabilized in saline solution by the presence of electrolytes (Eckert & Scholkovitz, 1976). Elevated levels of Al in acidic surface waters have been attributed to the dissolution of soil minerals by acidic atmospheric deposition (Dickson, 1978; Johnson et al., 1981).

Aluminium in estuaries

Estuaries are aquatic ecosystems of a dynamic nature, and are potential reaction sites for chemical processes and geo-chemical alterations affecting the flux of elements from rivers into the oceans (Boyle et al., 1974; Turekian, 1977; Officer, 1979). When river water mixes with seawater, the chemical species carried into the estuarine mixing zone by the river experiences a rapid change in their chemical environment. For some elements this change may be sufficient to bring about chemical reactions and in such cases their concentration in estuarine waters will be controlled by chemical reactivity as well as simple physical mixing. This would imply that Al derived from weathering of continental rocks and transported through rivers may not find its way uninterrupted into the oceans via estuaries and shelf seas.

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 (Hozakawa 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. It has been shown that river borne clay particles are irreversibly coagulated on entering an estuary and that this coagulation process starts at low salinities (Wollast, 1973; Edzwald et al., 1974). Colloidal Al has indeed been observed in the Conway River (Hydes & Liss, 1977) and in the Zaire River (Van Bennekom & Jager, 1978). In estuaries with low dissolved iron (Fe) and organic matter, Mackin & Aller (1984a) and Mackin (1986, 1989) have demonstrated that authigenic aluminosilicate formation is the major mechanism, which control the concentration of dissolved Al. Their authigenic aluminosilicate equilibrium model can explain the removal of dissolved Al at low salinities as well as on addition of dissolved Al at high salinities. In contrast, Morris et al., (1986) 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 in return, Al flux is expected from mid-estuarine sediments to the dissolved phase.

It has also been shown that estuarine bottom sediments are very reactive toward dissolved Al due to rapid adsorption, dissolution and precipitation reactions (Mackin & Aller, 1984c). Laboratory experiments by several researchers (Hem et al., 1973; Willey, 1975) strongly suggest that removal of dissolved Al within many estuaries may be at least partially due to reaction with Si and cations in solution. Also, Upadhyay & Sen Gupta (1995) have shown that sorption exchange processes dominate the geochemical interaction of Al in estuarine sediments. Their data indicate that the removal of dissolved Al onto riverine sediments tends to occur during the initial stages of estuarine mixing but with little or no permanent loss, as the sediments on resuspension release sorbed Al into solution.

On the other hand, Chou & Wollast (1997) have reported a conservative behavior of dissolved Al in three different seasons in the Rhone River plume in the Mediterranean Sea, where the fresh-water residence time is only of the order of a few days.

Takayanagi & Gobeil (2000) have studied the distribution of dissolved Al in the St. Lawrence Estuary, one of the world's largest estuaries, and also conducted laboratory experiments simulating estuarine processes, in order to further elucidate the geochemical cycling of Al in the coastal marine environment. An almost complete removal of dissolved Al was observed in the low salinity area upto 10 psu with an intense removal in the turbidity maximum zone. Principal mechanisms responsible for Al removal inferred from laboratory experiments were flocculation and adsorption onto suspended particulate matter (SPM).

Aluminium in seas

The most abundant metallic element of the earth's crust i.e., Al, remains in very low concentrations in ocean of the order of ~2 nmol/kg with a residence time of <200 years (Orians & Bruland, 1985). The source of dissolved Al in the ocean include transport via various pathways, such as river runoff, deposition of atmospheric aerosols and coastal dumping of Al wastes as well as diffusion of dissolved Al from sediment pore waters (Hydes, 1983). As is the case with other metals, river water is believed to be one of the major sources of Al in seawater. But the impact of river inputs on the oceanic concentration and budget of Al is uncertain, because the processes operating in estuaries and shelf seas are not well understood (Hydes & Kremling, 1993). All previous observations indicate that Al occurs in lower concentration in seawater than it does in river waters. This implies that there must be some mechanism by which the seawater concentration of Al is limited.

The entire oceanic system is in steady state with respect to dissolved Al (Stoffyn & Mackenzie, 1982). It is evident that Al has a unique oceanic chemistry relative to that of other metals. External sources and rapid particle scavenging throughout the water column are the major controls on dissolved Al distributions in the oceans. Consequently, the distribution is strongly influenced by local sources and sinks. Vertical profiles obtained from various parts of the world ocean (Mackenzie et al., 1978; Hydes, 1979, 1983; Caschetto & Wollast, 1979a; Moore, 1981; Measures, et al., 1984; Orians & Bruland, 1985, 1986) have sometimes shown non-nutrient type behaviour; also it is established that the inter-ocean variability of this element is the largest found so far. The vertical profiles of dissolved Al in the North Atlantic (Hydes, 1979, 1983; Measures et al., 1986) and the Pacific Oceans (Orians & Bruland, 1985, 1986) are found to exhibit surface enrichment, a mid-depth minimum and a gentle rise in concentrations near the bottom. This suggests two sources of dissolved Al, one to the surface waters and the other to the deep waters. Eolian input has been proposed as the dominant source of dissolved Al to the surface waters of the open ocean. Concentrations decrease with depth as a result of absorptive scavenging, but increase towards the sea floor, indicating a flux of dissolved Al from underlying sediments, in combination with advection of other water masses or remineralisation processes (Measures et al., 1986). Deep water concentration decrease with the age of deep water, from about 25 nmol/kg in the North Atlantic Ocean (Hydes, 1979;

Measures et al., 1986) to about 1-2 nmol/kg in the northeast Pacific Ocean (Orians & Bruland, 1986). Many studies have shown that there is an increase in dissolved Al concentration with increasing pressure. Laboratory experiments conducted by Moore & Millward (1984) showed that at 1000 atm. pressure the dissolved Al concentration increased by about 30% in two days. It was also observed that when the pressure was released the excess dissolved Al was rapidly removed from solution onto the clays. Observations that dissolved Al levels increase with increasing salinity towards open-ocean gyres are consistent with the significant atmospheric contribution of Al (Hydes, 1979; Measures et al., 1984, 1986; Orians & Bruland, 1986) coupled with low biological productivity characteristic of open-ocean regions (Parsons et al., 1977). In contrast, Al in the Mediterranean co-varies with silicate exhibiting nutrient type surface depletion and enrichment at depth (Caschetto & Wollast, 1979a; Stoffyn & Mackenzie, 1982). However, the reason for this contrasting behaviour and the factors controlling the Al distribution in seawaters are not well known.

Stoffyn (1975) proposed a model on the cycling behaviour of dissolved Al (Al_{aq}) in the oceans. The cycle was constructed on the assumption that the mass balance of Al_{aq} in the oceans is controlled solely by the uptake of Al_{aq} in siliceous organisms. Sedimentation of the frustules of dead organisms constituted the only output of Al_{aq} from the oceanic reservoir in this cycle. This model was later substantiated by observations on the concentrations and distributions of Al_{aq} in the hydrographic profile of the Mediterranean (Mackenzie et al., 1978). Perhaps the major importance of the latter work is that it established the role of biological activity in the cycling behaviour of Al_{aq} in the marine environment and it has become apparent that Al_{aq} does not behave simply as a nutrient in the oceans. Hydes (1979) found that Al_{aq} may be controlled by inorganic processes in the Atlantic Ocean. Moreover, it has been shown that concentrations in marine sediment pore waters may be considerably higher than those in the oceanic water column (Caschetto & Wollast, 1979b; Stoffyn-Egli, 1982). Therefore, it is possible that there is a flux of Al_{aq} into the oceans associated with diffusional transport of Al_{aq} from sediment pore waters into overlying waters. Stoffyn & Mackenzie (1982) have considered all the known fluxes of Al_{aq} within the oceanic system and made quantitative estimates of the magnitude of the Al_{aq} fluxes from river discharge, biological processes, diffusive processes and authigenic mineral formation. He has summarized that the fluxes of dissolved Al through the ocean system from land runoff, biological activity, upwelling and eddy diffusion and biogenic deposition maintain the concentration of Al in the surface waters of the oceans at steady state. The small portion of Al lost from the surface waters by sedimentation of dead organisms is balanced by the land runoff and by eddy diffusion and upwelling. Deep waters of the oceans cannot be maintained at steady state unless a removal process other than biogenic sedimentation is invoked. The conclusion that deep waters are not maintained at steady state unless a removal of Al occurs in deep waters is supported by the observed vertical concentration profiles of Al_{aq}, which imply a removal of Al_{aq} at depth in the oceans. The magnitude of this removal has been estimated by assuming a steady state condition for deep waters. Finally, the amount of Al incorporated in sediments because of the formation of authigenic minerals necessary to balance the influx of Al to the sediments (minus the amount which diffuses back into deep waters) is of the same order of magnitude as the stream input of Al into the oceans. Thus, the cycle maintains the oceanic system at steady state with respect to dissolved Al.

Particulate Al (Al_p) in seawater is associated almost exclusively with crust derived aluminosilicates (Sackett & Arrhenius, 1962), which are among the most popular weathering products to reach deep-sea areas. Because the Al_p in oceanic surface waters is derived from crustal weathering, its concentration is related to the transport of particulate material from the continents. Krishnaswami & Sarin (1976) were able to demonstrate that the distribution of Al_p in Atlantic surface waters is related to the transport of aluminosilicates from the surrounding landmasses with the highest concentrations being found in equatorial latitudes (arising from transport in the northeast trade winds) and in the southern polar regions (where glacial weathering is important). The Al_p in surface waters eventually combines with that transported to deep seas by other processes, such as bottom and intermediate water movement from the shelf and slope regions, to be incorporated into oceanic sediments. The particulate elemental oceanic fluxes have a predominant atmospheric source but this does not apply to all oceanic regions; in coastal environments rivers will be the dominant Al_p source and in bottom waters the resuspension of sediments will be important.

Aluminium in ocean sediments

The Al concentration in the marine sediments has long been considered as an indicator of terrigenous abundance and dominated by lithogenous phase. Murray et al., (1993) and Murray & Leinen (1996) suggested that Al/Ti values in the biogenic sediment dominated by Calcium carbonate ($CaCO_3$ >90%) in the equatorial Pacific reflect particle flux and by extension, therefore, the ocean productivity. Dymond et al., (1997) confirmed these observations of excess Al (non-detrital) source, but instead considered the Al/Ti ratio to reflect opal rain to seafloor, based on the studies of settling particles collected by sediment traps. Recently, Timothy & Calvert (1998) speculated that high Al/Ti could be due to the presence of authigenic clay minerals. Variation of Al/Ti in the sediment cores from Oman Margin and Owen Ridge in Northwest Arabian Sea was attributed to variation of dust transport (Shimmield et al., 1990). In the surface sediments of Central Indian Basin (CIB), Banakar et al., (1998) suggested that the presence of higher Al excess in both siliceous (where carbonate is absent) and carbonate (where opal is absent) sediments is attributed to the surface water productivity. Earlier, Al and titanium concentration profiles in a few sediment cores from the CIB were studied and the reasons for the elevated Al/Ti values above the potential crustal sources were not considered (Mudholkar et al., 1993). Al/Ti values in the CIB subsurface sediment reached 48.5, up to three times higher than the average shale and crustal potential sources. Pattan & Shane (1999) studied factors controlling excess Al in sediments of CIB and found that volcanic glass contributes significantly to the elevated Al/Ti ratio in the sediments where ash is present.

1.5 Aluminium in air

It has recently become apparent that transport via atmosphere is an important route by which some trace metals are delivered to the sea surface (Chester, 1990). The concentrations of trace metals in aerosols are now known over a number of marine environments and the principal trend to emerge from this data is that, in general, there is a decrease in the trace metal concentrations towards the more pristine oceanic regions. Further, there are differences in the concentrations of some trace metals in coastal environments in which the aerosols are influenced most strongly by either pollutant or crustal sources.

The impact of atmospheric aerosols on the chemistry of Al in surface seawater is known, the concentrations increase in the presence of landmasses due to the importance of atmospheric Al fluxes (Maring & Duce, 1987). The concentration and geographic distributions of trace metals in aerosols from the Atlantic and Pacific Oceans are now known in detail. Few data are available on the concentrations and distributions of trace metals over the Indian Ocean, particularly for the remote southern regions of this major marine environment. Chester et al., (1991) had undertaken a study to provide preliminary data on the trace metal chemistry of the Indian Ocean aerosol. The data indicate that the input of crustal materials to the Arabian Sea gives rise to an average Al concentration of about 1000 ngm^{-3} of air in the northeast monsoon regime. Al can be used as an indicator of the amount of crustal material in the atmosphere, and for the northeast trades population, Murphy (1985) reported Al concentrations in the range 1,060-57,000 ngm^{-3} of air.

1.6 Aluminium in Indian Ocean

A review of literature on Al from the Indian Ocean sector has provided the following information. The Arabian Sea is surrounded by land on three sides; Al can be transported to the sea via various pathways, such as river runoff, deposition of atmospheric aerosols and coastal dumping of Al wastes. The northern Arabian Sea is more vulnerable to these processes than the southern part because of the closer proximity of the former to land. Data from the eastern Arabian Sea reveal high and variable concentrations of dissolved Al in the surface micro-layer and surface waters (Narvekar & Singbal, 1993). The concentration of Al (~37-52 nM)) in the open surface waters of the Arabian Sea is higher than in the Atlantic (16-33 nM, Hydes, 1983; 29-43 nM, Measures et al., 1984) and the Pacific (0.3-6 nM, Orians & Bruland, 1985, 1986). Atmospheric Al concentrations over the northern Arabian Sea averaged 1227 ng m^{-3} and are among the highest recorded for the marine environment (Chester et al., 1985, 1991). Hence, atmospherically transported land derived material might have contributed to such a high concentration of Al in the Arabian Sea. Winds from the northeast blowing directly across the arid lands during the northeast monsoon were expected to cause a high input of mineral aerosols to the northern Arabian Sea.

The coastal waters of the Arabian Sea are relatively enriched in Al (~55-74 nM) over the offshore waters (~37-52 nM) (Upadhyay & Sen Gupta, 1994). The estuaries along the Arabian Sea coast exhibit higher values when compared to coastal waters. The concentration of dissolved Al in the freshwater (~0.8-0.23 μM) and sea water (≤0.07 μM) end members of the Mandovi estuary indicated Al removal from solution in the low salinity regions (Upadhyay & Sen Gupta, 1995). Studies in the high energic Tapi estuary has shown the release of dissolved Al from suspended particulate matter, dispersed by strong tidal currents (Sharma & Zingde, 1995). In Vembanad estuary Al is derived principally from aluminosilicate minerals of detrital origin and clay minerals though some of them could be from authigenic processes (Cronan, 1980). The Al profiles in sediments and interstitial waters of Cochin estuary do not show any remarkable variation between environments and also with depth (Bava, 1996). Alumino-silicate and clay minerals were the controlling factors of sediment Al distribution and the interstitial Al were mainly due to dissolution of detrital feldspars. Specific studies on dissolved Al in Cochin backwaters have not been attempted earlier.

1.7 Processes affecting the behaviour of Aluminium in natural waters

The annual stream discharge from the land to the oceans is $0.36\text{x}10^{20}$ g/year (Meybeck, 1977) at average dissolved Al concentration, 10-80 μg/l; $4\text{-}29 \text{ x } 10^{11}$ g/year of dissolved Al are added to the ocean reservoir (Stoffyn & Mackenzie, 1982). Estuaries, the meeting place of river and sea water where a large variation in salinity is noticed as a result of dilution of sea water with river water, serves as a favourable medium for various reactions to take place. Reactions occur within estuaries to alter the flux of dissolved Al from rivers into the oceans. Various studies have shown that the dissolved Al exhibits non-conservative behaviour in estuaries.

Various factors causing the non-conservative behaviour of dissolved Al in estuaries can be summarised as:

Tidal sediment disturbance

Dissolved Al is a highly reactive constituent, undergoing net removal in the very low salinity region and net input to the mid-estuary (Morris et al., 1986; Upadhyay & Sen Gupta, 1995). The extent of both the depletion and the augmentation varies systematically with tidal energy input, indicating tidal sediment disturbance as the principal controlling agency. The influence of sediment water interactions, on the distribution of dissolved Al was studied by Mackin & Aller (1984a). 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 sediments will cause a release of dissolved Al into relatively Si-depleted estuarine waters.

Particle solution reaction - Flocculation

Rivers carry mainly unflocculated clay mineral, but that in saline water leads to flocculation; clay particles by themselves do not settle as single solid grains or in irreversible solid states of aggregation; according to Postma (1967) clay particles of colloidal and sub colloidal dimensions have a charge which is usually negative. A double layer of hydrated cations balances this charge. The thickness of this layer depends on various factors, including the total ionic concentration of the surrounding liquid phase. An increase in total ionic concentration of the surrounding solution decreases the thickness of the double layer. If the thickness decreases below a critical value flocculation occurs and small particles conglomerate into larger units and tend to settle. This occurs at fresh water-saline water boundaries and causes unflocculated river borne clay mineral to flocculate as it enters the marine environment. Flocculation of colloidal material may cause a net consumption of dissolved aluminium in estuaries. The amount of flocculated constituents increase as salinity increases from 0.0 to 5.0 psu; above which, little additional removal occurs.

Sorption/De-sorption processes

Sorption of elements or compounds can be a physical process by Van der Waals forces or ion-dipole or dipole-dipole interactions. This can occur on the outer surface of the particles as well as the inner surface of the pores of a porous particle. Sorption occurs as a chemical process by ion-exchange through which positive or negative charges on the mineral lattice of the particle are compensated by ions of opposite charge, which are exchangeable with ions in solution. Scavenging process, as sometimes named, is dominated by small particles of 10 μm or less. Resuspension or increased turbidity, gives enhanced scavenging, which is probably the cause to bring about concentration changes in Al in the turbidity maximum, present in many tidally mixed estuaries. The small particles themselves can be scavenged by the larger ones, resulting in a relatively quick removal of particles as well as the adsorbed elements. Morris et al., (1986) with the help of field data and laboratory simulations, has shown that the removal of Al in the Tamar estuary is due to sorption onto resuspended particles. In the St. Lawrence estuary (Takayanagi & Gobeil, 2000), the intense removal in the turbidity maximum zone was attributed to adsorption onto SPM.

Diagenesis

The sedimentary geochemistry of dissolved Al is complicated by a number of different reactions. Complexation by organic matter, adsorption onto Fe-oxyhydroxides and reaction with Si in solution has important effects on the distribution of dissolved Al in sediments. In the absence of physical resuspension of sediment into overlying waters, dissolved Al is rapidly consumed at the sediment-water interface and is subsequently released upon reduction of Fe-oxyhydroxides (Mackin & Aller, 1984b). This release does not cause noticeable perturbations in dissolved Al concentrations in sediments because of rapid consumption reactions which mask the true mobility of Al. Results suggest that one of the consumption reactions may be due to formation of an Fe-Al-silicate. The amount of authigenic aluminosilicate formed in estuarine sediments must be very small relative to the detrital component (Mackin & Aller, 1984b).

Active biological uptake

Living cells are able to take up elements from solution against a concentration gradient. Many marine organisms contain trace elements at concentrations as high as 10^6 times their seawater concentrations. When the organisms die, bacterial attack return trace elements to the water, perhaps initially in the form of organic complexes. Further decomposition of these complexes liberates ionic or colloidal species of the elements. Stoffyn (1979) obtained experimental evidence that dissolved Al can be incorporated into the opal skeleton of diatoms. Marine planktons can take up a significant amount of Al probably by surface adsorption mechanism or active incorporation into cell tissue. Also, Mackenzie et al., (1978) has shown that the nutrient-like distribution of dissolved Al in the Mediterranean can be attributed to control by biological activity because of the observed good correlation of this element with dissolved Si. Moran & Moore (1988) found that rapid removal of dissolved Al occurs by a surface adsorption mechanism and/or incorporation into soft tissues of diatoms. These observations represent the first direct demonstration of the influence and mechanism of biogenic particle removal of Al. Residence time of Al in the upwelling regions was found to be very short of the order of 35 days (Orians & Bruland, 1985; 1986).

Thus, scavenging of Al in estuaries may be presumably a result of biological uptake, adsorption, flocculation or reverse weathering, or both (Lin et al., 1985; Moran & Moore, 1988, Benoit et al., 1994). Scavenging is rather inferred by the inter-relations between dissolved Al and conservative indices (e.g. salinity and chlorinity), sedimentary dynamics (e.g. coagulation of suspended particles) and thermodynamic estimates (e.g. reverse weathering) occurring in the mixing zone (Li et al., 1993). In the case of reverse weathering reactions in an estuary, a stoichiometric relationship (i.e. removal) can be expected between Al and other mineral forming elements (e.g. Si), which apparently happens in an area with progressive weakening of hydrodynamic conditions (e.g. lower estuary) (Mackin & Aller, 1984c).

Various factors causing the non-conservative behaviour of dissolved Al in estuaries may be summarized as

- Complex and rapidly changing speciation.
- Non-specific/passive sorption/desorption processes associated with particulate matter of either riverine or estuarine or oceanic origin.
- Cationic complexing capacity of seawater.
- Flocculation of colloidal material.
- Formation of mineral phases (stable as well as reversible) of aluminosilicates and its diagenesis.
- Dissolved and particulate organic matter easily complexing free aluminium.
- Diffusion processes at sediment-water interface.
- Biogenic and microbial transformations.

Thus the behaviour of dissolved Al may be dominated by relative influence of each of the above factors or a combination; not excluding the superimposed physical processes in estuaries from tidal incursions and resultant resuspension and transport of particulate matter interacting with varying riverine inputs.

1.8 Objectives of the thesis

- To determine the spatial/temporal variation of Al in Cochin estuary. Surveys of selected locations along the coast of Kerala for content of dissolved Al.
- To understand the behaviour of Al vis-a-vis dissolved Si, SPM salinity and pH.
- To comment on salinity intrusion and turbidity maxima which are important concepts as far as terrigenous borne trace metal cycling is concerned.
- To gain insight into the geochemical processes operating in estuaries through laboratory simulation experiments.
- Interpretation and prediction of Al concentration in response to estuarine forcing as assessed by Water Quality Analysis Simulation Program (WASP).

1.9 Scheme of the thesis

Chapter I is a general introduction of the topic of study, including a survey on literature in the relevant fields and an account on the possible mechanisms operating in estuaries bring about the non-conservative behaviour of metal, Al. Description of the study area referring to its geological, hydrological and climatological setup along with the methods of data collection and adopted analytical techniques has been presented in chapter II.

The distribution of Al and its variation, in respect to dissolved Si, SPM, salinity and pH are detailed in chapter III. The influence of each parameter in regulating Al levels in the study region and their inter relationship are studied in detail.

The kinetics of dissolved Al in estuarine waters, figure in the next chapter. Laboratory simulation experiments were conducted to estimate the level of interaction of Al under riverine, brackish and marine conditions. Based on the above results, an attempt has been made to delineate the behaviour of Al under different estuarine conditions and the possible mechanisms operating in tropical estuaries; the above are detailed in chapter IV.

Chapter V discusses the application of Water Quality Analysis Simulation Program (WASP) model for understanding the fate of Al in Cochin estuary. The result also throws light on the extent of cycling of the metal between the water column and benthic sediment. Predictive analysis by the model for different estuarine conditions is also attempted. The salient features emanating from the foregoing discussions are summarised in chapter VI.

(Baseline) data on dissolved Al concentration along selected locations of Kerala coast is given under Appendix A.

CHAPTER II

Environmental Setting and Analytical Techniques

2.1 Description of the study area

The Cochin estuary together with the Vembanad lake on its southern parts forms the largest backwater on the west coast of India (9°30'-10°10'N; 76°10'-76°30'E), with its northern boundary at Azheekode and southern boundary at Alleppey (fig.1). It covers an area of almost 235 km^2 with one permanent bar-mouth maintained at 13 m depth at Cochin and two seasonal openings during the peak monsoon period located at Andhakaranazhi and North Paravoor. This tropical positive estuary has two main rivers flowing into it, the Periyar from the north and the Muvattupuzha from the south, thus transporting alluvial laterite particulates. Water and sediments to this estuarine system also comes from four other river catchment systems: Pamba, Meeenachil, Achankovil and Manimala rivers, emptying through the Kuttanad paddy fields on south.

This water body is characterised by its long axes running parallel to the coast and is separated from the sea by barrier spits interrupted by tidal passes. The water body has a length of 75 km and the width varies between 500 m and 4000 m. Severe floods repeatedly affect the cultivable land of Kuttanad (on the southernmost region of Vembanad lake) during the southwest monsoon season. On the other hand, tidal intrusions of saline water from Cochin estuary were predominant before the construction of a bund. The Thannirmukham bund was constructed in Vembanad Lake at a narrow constriction near Vaikom to regulate and prevent saline water intrusion from Cochin estuary into the Kuttanad region. The 1402 m long regulator was commissioned in 1974. During the months December to June the gates are lowered preventing the saline waters (5-15 psu) from entering the Kuttanad paddy fields. During other months, the regulator allows the passage of floodwaters from paddy fields into Cochin estuary which is derived from four rivers named above. Thottapally spillway was constructed to channel water from the low-lying areas connected to the Vemband lake to the nearby Arabian Sea, at a point 20 km south of Alleppey in order to drain monsoon floodwaters. It was observed that during floods,

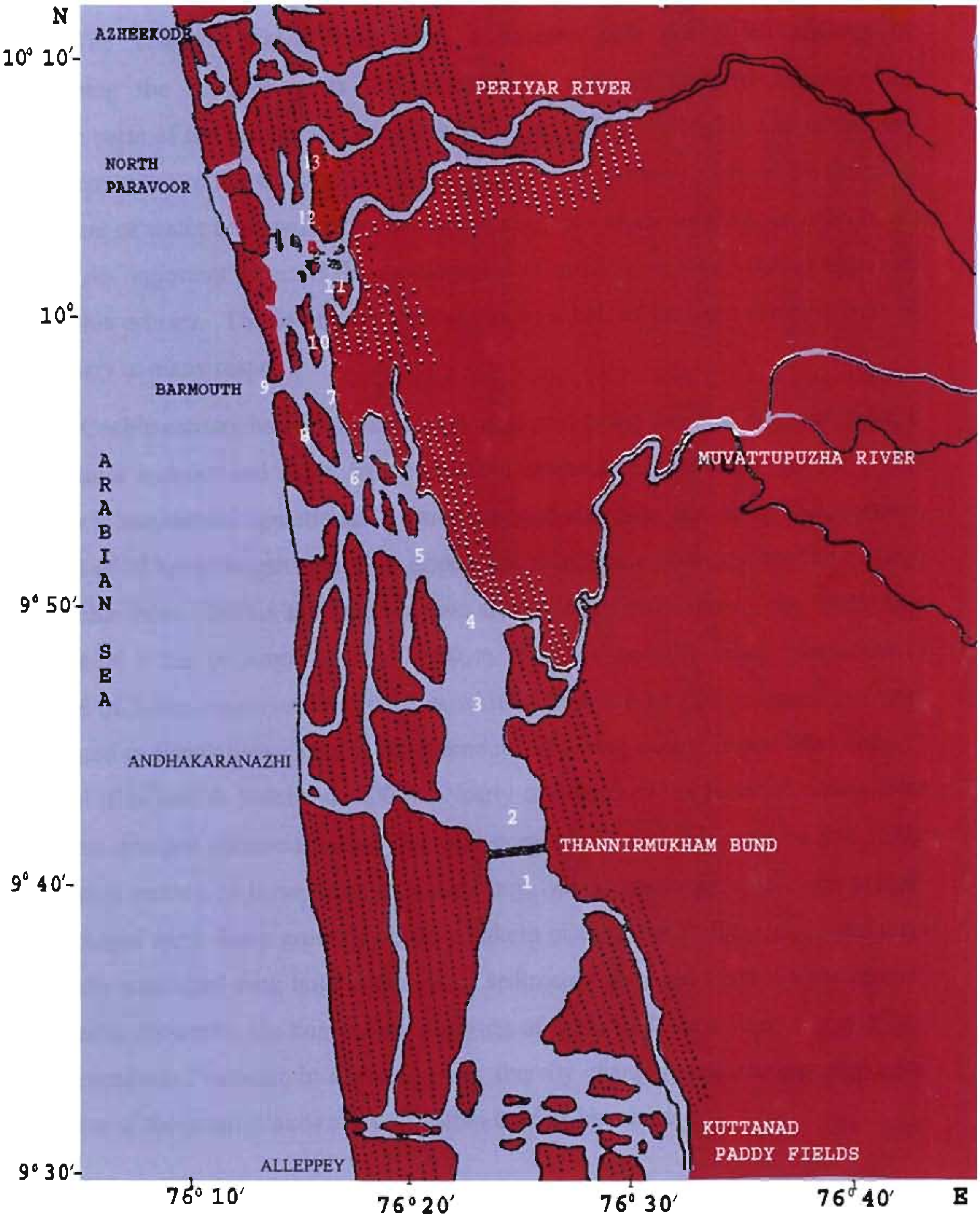


Fig.1.Map of Cochin Estuary and Vembanad Lake

nutrient rich alluvial sediments are also transported by rivers from the western mountain ranges which settle down in the low lying paddy fields.

The Thannirmukham bund plays a decisive role during all seasons by maintaining the southern parts well-mixed with uniform seasonal salinity. The northern parts of the estuary are subjected to higher salinity wedging and oscillatory movement with vertical temperature exchange than the southern parts where the mass movement of water body with considerable mixing was observed (Lakshmanan et al., 1982). An important aspect is the development of turbidity maxima during high tide within this estuary. The bar mouth region acts as a barrier between the two arms of the estuary in many respects.

Cochin estuary houses the second largest port along the west coast of India. It is a natural harbour and has a free permanent connection with the open sea. This harbour is maintained operational by three dredged channels, one being the approach channel of 10 km in length having an orientation along the east-west direction through the Cochin inlet. Within the harbour, two channels are maintained - the Ernakulam channel of 5 km in length and 250-500 m in width and the other, Mattancherry channel of 3 km length and 170-250 m width which are navigable round the year. Compared to Ernakulam channel, more amount of silting occurs in the Mattancherry channel (Rasheed & Balchand, 2000). Nearly one-third of the reported silting from the three dredged channels during the year occurs here and this may be due to the circulation pattern in these parts of the estuary, where weak currents often prevail. The dredged spoil dump grounds on the southern parts of the Willingdon Island were gradually nourished with huge amounts of sediments, dredged from the above sited channel(s). However, the continuous dredging of material from a fixed site will lead to unprecedented increase in channel depth, thereby changing the geo-morphological character of the small islands situated within the Cochin estuary.

Barmouth, the permanent connection to the Arabian Sea, about 450 m wide, forms the main entrance to the Cochin port. This region is subject to tidal influence. Studies on tidal characteristics at barmouth and within the estuary by several investigators have explained that the tides are mixed with predominantly semidiurnal character having a maximum range of 1 m whose influence is felt approximately 25 km upstream (Qasim & Gopinathan, 1969; Varma et al., 1981, Joseph & Kurup, 1987

& 1989, Ajith & Balchand, 1994). During flood tide, the seawater enters the estuary via Cochin bar mouth (12 m deep) and the flow reverses during the ebb tide. The magnitude of influence of the tide progressively decreases with increasing distance from the bar mouth.

In recent years, great concern has been expressed with regard to environmental deterioration of Cochin backwaters and consequent loss of supportive functions of this wetland system, especially due to urbanisation, industrialisation and agricultural activities in the downstream zones of the rivers. The 16 major and several minor industries situated in the upstream region of the backwaters discharge nearly 0.104 Mm^3d^{-1} of effluents (Anon, 1996), causing large-scale environmental pollution. Backwaters also receive organic wastes (~260 td^{-1}, Anon 1998) from domestic sewage, coconut husk retting yards, fish processing plants etc. The main functions affecting the coastal waters apart from sewage are effluents from fish processing plants, industrial wastes, navigational dredging and dumping of dredge spoil and sand mining for filling and construction. The annual dredge spoil from the harbour area alone comes to the tune of 10^7 m^3, which are dumped in the near coastal seas. The influence of industries and sewage make the northern parts of the backwaters moderately polluted (Remani et al., 1983).

Cochin being the second largest city along the west coast, the coastal circulation of this region is critical, because as compared to the Mumbai coast where the mean tidal height is >3 m, this southwest coast location experience only one metre range. Because of the low tidal amplitudes, the coastal regions have small inter-tidal expanses, perhaps the smallest among the Indian coasts. This results in incomplete flushing, leaving behind parcels of perennially undulating water. Any substance released in such a water body will always have a fraction of it left behind; however small that might be, residence time will continuously increase with increasing number of oscillations. Therefore to estimate the carrying capacity of any coastal waters, it is imperative to critically examine the residual tidal effect of any eventual pollutant in these waters (Sen Gupta & Geetanjali, 2000). One of the noticeable changes that had occurred to this estuary is that there has been a considerable reduction in the exchange volume of estuarine waters with coastal water. The tidal transport which was between 80 and 125 Mm^3 /tidal cycles during 1960's has been reduced to about 35 Mm^3 /tidal cycle in 1980's of the last century and no further reduction has been reported since then. The decrease in transport volume has reduced the flushing characteristics of the backwaters. Studies on the propagation of tides in the Cochin estuarine system by Srinivas et al., (2003) reveal that during spring tide, one can expect stronger circulation, mixing and flushing because of the higher tidal ranges and more frequent flood and ebb phases as compared to neap tides.

Considerable shrinkage of the Cochin backwaters has reduced the tidal response of the system (Gopalan et al., 1983). The response of such events is complex, as the suspended sediments and estuarine waters, instead of flushing out into the sea, is pushed inward and ultimately is retained within the lower estuary itself favouring accumulation.

2.2 Station network fixing and sampling strategies

A network of 13 stations was fixed spanning the entire estuary and lake, covering the northern and southern arms (fig.1). Seasonal surveying was conducted during the period of August 1998 to May 1999 covering the three seasons (monsoon: June to September, postmonsoon: October to January and premonsoon: February to May), to study the distribution of Aluminium (Al) and the associated estuarine parameters. For the laboratory mixing experiments, water and sediment samples were collected from the riverine, mid-estuarine and seaward locations.

The depth range of the estuary and lake is 2 m to 13 m. At each station, water samples were collected from surface and bottom (0.5 m above estuarine bed) using a Hytech sampler.

2.3 Determination of Aluminium in water

Two types of procedures are usually adopted for Al analysis. One measures all the Al in a particular sample, while the other measures only the Al in a certain chemical form (such as the monomeric ion). Many instrumental procedures, such as emission spectroscopy and neutron activation, lie in the first category; colorimetric methods and polarography fall into the second.

Colorimetric methods

Colorimetric procedures exploit the property of Al salts long known in the dyeing industry: the ability to form brightly coloured, insoluble lakes with certain dyestuffs. Colorimetric methods for determining Al have been reviewed by Sandell (1959) and in part by Packham (1958), Giebler (1961), and Dougan & Wilson (1974). A method in common use is based on the ammonium salt of aurintricarboxylic acid, a triphenylmethane dye known as aluminon, which combines with the aluminium ion to give a deep red colour. The test is carried out at pH 4 and is specific for monomeric Al ions; however, low-molecular-weight oligomers of aluminium hydroxide, which are readily converted to monomeric ions, will also be detected. The detection limit is approximately 0.02 mg/l. Substances which react with aluminium (such as fluoride and polyphosphate) and substances which react with aluminon (such as iron) interfere with the test. A modified procedure by Shull (1960), later incorporated into the 12th edition of Standard Methods (APHA, 1965), uses thioglycolic acid to eliminate iron interference.

Because the aluminon procedure is complicated and time consuming, the 13th edition of Standard Methods (APHA, 1971) tentatively specified the Eriochrome® cyanine R method adopted by Shull & Guthan (1967) from the procedure of Knight (1960). Eriochrome® cyanine R, a triphenylmethane dye also known as Solochrome® cyanine R, produces a red aluminium complex with an absorption maximum at 535 nm and is more sensitive than aluminon. The interference of iron and manganese is eliminated by addition of ascorbic acid.

For determination of total Al and Al ion in water, the American Society for Testing and Materials (ASTM, 1955) specifies the hematoxylin method, adopted from the procedure of Strafford and Wyatt (1943). Hematoxylin (a natural dyestuff derived from heartwood) produces a blue lake with Al.

Alizarin red S, an anthroquinone dye, has been used for determination of Al in organic materials, but it is also acceptable for analysing water samples. It forms a deep red lake at λ_{max} 480 nm (Packham, 1958).

Ferron, an 8-hydroxyquinoline derivative, reacts with Al to give a complex which adsorbs at 370 nm (Rainwater & Thatcher, 1960). Dougan & Wilson (1974) have developed a method using (pyro)catechol violet which they have found to be superior to methods based on Eriochrome® cyanine R or Stilbazo. Panovsky (1974) has described a fluorimetric procedure based on the complex of aluminium with morin (a natural flavone) as well as two colorimetric procedures suitable for determination of low levels of Al in treated drinking water and boiler feed-water. For very low concentrations of Al, procedures have been devised to extract the Al as the 8-hydroxyquinoline complex with chloroform and determine the quinolinate in chloroform solution either spectrophotometrically (Goto, 1957; Motojima & Ishiwatari, 1965) or fluorimetrically (Noll & Stefanelli, 1963; Nagy & Polyik, 1962).

The traditional fluorimetric determination of Al by the complex with lumogallion (LMG) is based on the exhibition of Al-LMG compound (Al-LMG) at an excitation wavelength of 465nm and an emission wavelength of 555nm. The method was first proposed by Nishikawa et al., (1967 & 1968) and modified by Hydes & Liss in 1976. This method has been widely accepted for the determination of dissolved Al in aquatic environments during the last three decades (Hydes, 1983; Morris et al, 1986; Upadhyay & Sen Gupta, 1995). However, the traditional LMG method exhibits two important shortcomings. Firstly, the determination is biased by ionic interference like F^- and Fe^{3+}; hence for the application to natural water samples (e.g. estuarine water), an increment calibration procedure has to be used recognising that the standard addition procedure may not eliminate the spectrum interference (Chou & Wollast, 1990). Secondly, though the detection limit of Al by the LMG method was reported to be as low as nano-molar level (e.g. 3 nM), based on the standard deviation of repeated determinations, the analysis of real samples is deteriorated by the reagent blanks and a reduction in the signal to noise (background) ratio of the instrument, which leads to the lowest concentration reached being often at tens of nano-molar level for routine analysis (Xu, 1995; Ren, 1998). This detection level is much higher than those reported by other techniques, for examples, liquid-liquid extraction and electrothermal atomic absorption spectrometry (ETAAS) in combination (0.09 nmol kg^{-1}) (Orians & Bruland, 1986).

Resing & Measures (1994) recently improved the fluorimetric method by employing the flow injection analysis (FIA technique) in combination with inline pre-concentration of Al onto a column of resin-immobilised 8-hydroxyuinoline. Extraction of Al in estuarine and seawater samples indicates, however, a rather low recovery compared to standard addition, which is probably due to the fact that 8-hydroxyquinoline may not be able to release Al^{3+} combined with F^{-}, e.g.$[AlF_x]^{-(x-3)}$ (x:1-6) (Xu, 1995). A sensitive and selective extraction fluorimetric method for the determination of trace amount of dissolved Al in natural waters was developed by Zhang et al., (2000). Al-LMG complex is extracted into n-hexanol, and the fluorescence can be extracted upto 20-fold. Compared to other publications in the literature, the method reported here is free from matrix effects, and the interference from iron and fluoride has been minimised successfully by Be^{2+} and o-phenanthroline respectively. The detection limit of dissolved Al is 0.25 nM, which is one order of magnitude lower than the traditional fluorescence techniques, with a precision of 5% at an Al level of 40 nM and 6.7% at an Al level of 1.0 nM in routine analysis.

Instrumental methods

The 13th edition of Standard Methods (APHA, 1971) specifies the atomic absorption procedure for determination of Al in water. The three spectro-chemical approaches to the quantitative analysis of Al and other minor elements in natural waters (Silvey, 1961) are:

1. Direct sparking of a water sample or partially evaporated water sample.
2. Direct arcing of the residue obtained by evaporating the sample to dryness.
3. Separation of the minor elements by chemical precipitation and subsequent arcing of the ash precipitate.

In the first procedure, a water sample is concentrated 10 to 100 fold by evaporation. After addition of an internal standard, the concentrate may be sparked in a porous cup electrode with the spectrum recorded on photographic film (Wilska, 1951). In the second method, the dry residue is mixed with one or more times its weight of powdered graphite and either put into an open cup electrode (Haffty, 1960) or compressed under ultra high pressure into a briquette (Hitchcock & Starr, 1954). In the third method, trace metals are precipitated from the water sample by 8-

hydroxyquinoline aided by tannic acid and thionalide at pH 5 2, as described by Silvey (1961) and Silvey & Brennan(1962).

Several studies (Hodgson & Glover, 1951; Maienthal & Taylor, 1967) have suggested that polarography may provide a sensitive tool for water analysis. Spark source mass spectrometry is a promising tool for trace metal analysis (Wahlgren et al., 1972). Neutron activation is also a sensitive method for analysis of many trace metals (Fujinaga et al., 1973).

Miscellaneous methods

Chromatographic techniques have found limited application to analysis of Al in water. Quentin (1953) has analysed mineral waters of high Al content using paper chromatography. Yamane et al., (1968) have derived a procedure for determination of Al by thin-layer chromatography (TLC). A procedure employing gas-liquid chromatography has been devised by Lee & Burrell (1973). Several workers (Budevski & Simova, 1962; Solomin & Fesenko, 1963 and Maksimova, 1973) describe compleximetric procedures for Al without reporting sensitivities.

2.4 Recommended methodology for Aluminium analysis

Al was determined using the fluorimetric method initially proposed by Nishikawa et al., (1967) and later modified method by Hydes & Liss (1976). This method is sufficiently sensitive to investigate changes in dissolved Al concentrations during the mixing of river and sea waters in estuaries. The reagent Lumogallion, employed in the fluorimetric method was found to have a detection limit of 0.05 µg/l of Al and a coefficient of variation of 5% at the 1.0 µg/l level and 2.7 % at the 22 µg/l level. The samples were analysed applying standard addition technique. The only interference likely to be important in most natural waters is that from fluoride, and this interference can be dealt with by using an incremental calibration procedure. For acidic waters, iron is a potential interfere but has no significant effect at concentrations of less than 100 µg/l. In water abnormally rich in dissolved organic material there may be competition for the dissolved Al between the natural organic ligands and the lumogallion. The analysis detects all forms of Al in filtered natural water samples except when the Al occurs in stable mineral structures, e.g., clay particles small enough to pass through the filter. Al adsorbed on the surface of such particulate material appears to be accounted during the determination.

The samples were also subjected to analysis based on the selective extraction-fluorimetric method developed by Zhang et al., (2000). It was observed that the results obtained by the recent method of Zhang et al., and the traditional method of Hydes & Liss (1976) are identical. Hence for all further analysis, the traditional method of Hydes & Liss was adopted.

Sample pre-treatment

When natural water samples are routinely filtered and acidified before analysis, the measured soluble Al concentration may depend on the type of filter used and the length of time the sample is allowed to stand after acidification. Kennedy et al., (1974), who have reviewed earlier work, have studied the effect of filter pore size on the analysis of Al in water. They report that sufficient fine-grained material can pass 0.45 and 0.22 μm membrane filters to introduce large positive errors and recommend the use of 0.1 μm filters. Wagemann & Brunskill (1975) have presented evidence that a silver membrane filter gives more complete removal of particulate matter than a cellulose acetate membrane filter of the same pore size. Materials, which adsorb Al ions, can introduce negative errors; Shull & Guthan (1967) have found that glass wool, absorbent cotton, and most paper filter papers remove much of the soluble Al in water samples.

In this investigation, the water samples were filtered immediately after collection. The filtered (through 0.45μm Whatman's filters) sample, transferred into pre-cleaned plastic bottles, was stored in an icebox in the field and thereafter in the laboratory in the refrigerator (~4°C). Water samples were analysed for dissolved Al, and dissolved Si. All experiments were performed with high purity analytical grade reagents and solvents. Double distilled and Milli-Q waters were used in the experiments. All plastic-ware used was made of polypropylene.

Reagents

Lumogallion solution. 0.02% in distilled water. The lumogallion reagent was used within one month of preparation in order to avoid reddening of the solution after one month, which produced erratic results.

Buffer solution. Re-crystallised sodium acetate plus acetic acid (4 M with respect to acetate) adjusted to give a pH of 5.0 in the water type being analysed.

Standard aluminium solution. Dissolve 1.758 g of analytical-reagent grade aluminium potassium sulphate in 100 ml of distilled water. A 0.5 ml volume of this solution diluted 1+999 and added to 50 ml of sample increases the Al concentration of the sample by 10 µg/l.

Experimental

Dissolved Al was detected by employing fluorimetry (Hitachi-Model F-3010 Fluorescence spectrophotometer). 50 ml portions of well shaken samples were dispensed into reaction bottles, 0.5 ml of the buffer solution is added bringing the sample to a pH of 5.0, followed by further addition of lumogallion reagent and allowing to react with the dissolved Al to form a complex. The samples were allowed to stand for 10 -12 hours at room temperature (25 – 30°C) in subdued light after the addition of the reagents; the fluorescence is measured using an excitation wavelength of 465 nm and an emission wavelength of 555 nm.

2.5 Determination of associated parameters

Salinity: Salinity values were obtained by using an inductively coupled salinometer (EMCON make). Accuracy of measurement was ± 0.05.

Suspended Particulate Matter: Suspended particulate matter concentration (in JTU units) was determined in the field by making use of an in-situ turbidity meter which makes use of the optical scattering principle (in range of 0 to 1000 JTU, ±2%) (EMCON make). Linear calibration was achieved by means of the following method. Water samples collected in a Hytech water sampler of 1.2 litre capacity from surface and bottom were filtered at 0.45µm (using Whatman's filter cum Millipore unit) and dry weight of filtrate was determined and instrumental readings calibrated to report values in mg/l.

pH: pH of the water samples were measured by a portable pH scanner on board, in-situ. The precision was ±0.05 pH units.

Dissolved Si: Dissolved Si was determined with a precision of ≤ 5% by the ammonium molybdate-ascorbic acid method (Grasshoff et al., 1983).

The details of laboratory experiments pertaining to kinetics of dissolved aluminium are incorporated within chapter IV.

CHAPTER III

Aluminium Behaviour in Cochin Estuary

3.1 Introduction

Trace metals are transported into the marine environment by rivers (via estuaries), atmospheric deposition (via particulates and rain) and direct land runoff. During these transport processes, metals react with dissolved constituents, suspended particles and biota as they move from one environment to another. The filtering role of estuaries makes them crucial transitional areas, trapping significant quantities of particulate and dissolved matter (including metals) through a wide range of physical and biogeochemical processes. Trace metals enter the estuary in particulate and dissolved forms and during estuarine mixing they behave either conservatively or non-conservatively, depending on various physico-chemical factors such as pH, Eh, surface characteristics and content of suspended solids, ionic strength and the extent of solid-solution exchange.

Aluminium (Al), the world's most common metallic element, constitutes about 8% of the earth's crust. As is the case with many other trace metals, river water is believed to be one of the major sources of Al in seawater. Estuaries being part of the aquatic ecosystem of a dynamic nature, these regions are potential reaction sites for chemical processes; geochemical alterations often affect the flux of elements from rivers to the oceans (Boyle et al., 1974; Turekian, 1977; Officer, 1979). This would imply that Al derived from weathering of continental rocks and transported through rivers may not find its way uninterrupted into the oceans via estuaries and shelf seas.

This chapter deals with the distribution of dissolved Al in the tropical Cochin estuary, providing an insight into the geochemical factors, which influence the behaviour of dissolved Al in estuarine waters. Behaviour of Al with respect to changing patterns of dissolved Si, suspended particulate matter (SPM), salinity and pH are discussed in detail.

3.2 Results and Discussion

Cochin estuary exhibits tropical characteristics of a region that is dominated by transport and settling of voluminous amounts of suspended material of terrestrial origin (Balchand & Nambisan, 1988; Ajith & Balchand, 1994). The Periyar and Muvattupuzha rivers originate on the Western Ghats, flow west and empty into the Cochin estuary on the northern and southern parts, respectively. The drainage basin of Periyar consists of rocks such as cordierite gneisses, horne-blende biotite gneisses, charnockites, pyroxinites, laterites and alluvium (Padmalal, 1992). Laterites and alluvium are observed only in the lower reaches. Muvattupuzha drainage basin consists of cordierite gnesisses, horne-blende biotite gneisses, calc-granulites, granites and laterites. Laterites are also found in the low-lying reaches of this river. Thus, alluvial laterite particles are the major component species of particulates entering this estuary.

Riverine fluxes

The influx of dissolved and particulate matter into Cochin estuary depends largely on the freshet discharge, which in turn depends on the cycle of seasons. The type of material too entering the estuary is mainly determined by the geochemical characteristics of the drainage basin. The overall content of dissolved Al and Si along with SPM concentrations are stated below, pertaining mainly to the concentrations in the freshwater sector or lower river reaches.

Dissolved Aluminium

The monsoon months, August and September exhibit high river inputs of dissolved Al. During August 1998 the river influx of dissolved Al into the northern and southern arms of the estuary was 1.14 µM and 1.22 µM respectively. By September 1998 the influx of Al into the estuary decreased, 0.79 µM into the southern arm and 0.97 µM into the northern arm of the estuary. The monsoon months exhibit very high input of dissolved Al into the estuary compared to the non-monsoon (pre- and post-monsoon) months. During January 1999, input at the southern side of the estuary amounted to 0.18 µM. On the northern side, the input was comparatively low, indicating Al concentration of 0.09 µM. By March 1999, the input to the estuary at the southern side further decreased, showing a concentration of 0.09 µM whereas for the northern side the values increased indicating upto 0.48 µM. For April 1999, the values were 0.19 μM into the southern arm and (abnormally) high values of 3.55 μM into the northern arm (discussed later). During May 1999, the values were 0.16 μM in the southern arm and for the northern arm very low inputs of 0.003 μM were noted.

Hence the riverine input of dissolved Al into Cochin estuary during the period of observation fell in the range of (~ 0.006 – 4.38 μM), which is relatively very high and variable when compared to the dissolved Al concentration in the Mandovi river (~ 0.08-0.23 μM) (Upadhyay & Sen Gupta, 1995), the Niger river (~ 0.11-0.22 μM) (Van Bennekom & Jager, 1978), the Chiang Jiang river (~ 0.10-0.25 μM) (Mackin & Aller, 1984a) and the Amazon river (~ 0.11 μM) (Mackin & Aller, 1986).

Dissolved Silicon

Dissolved Si in an estuary is mainly terrigenous in origin. During August 1998 the riverine input of dissolved Si was 114.22 μM into the southern arm and 232.64 μM into the northern arm. By September 1998, the riverine input decreased to 71.95 μM into the southern arm and 131.61 μM in the northern arm respectively. Thus the northern arm showed very high input of dissolved Si during this season. January 1999 showed a further decrease in dissolved Si values at the riverine end to 57.5 μM in the southern arm and 158 μM in the northern arm respectively. During March 1999 the values decreased further, showing 33.44 μM in the southern arm and 53.6 μM in the northern arm respectively. And in April 1999, dissolved Si values were 47.47 μM in the southern arm and 98.68 μM in the northern arm of the estuary. The dissolved Si input in May 1999 amounted to 52.92 μM in the southern arm and 104.60 μM in the northern arm of the estuary. Thus we observe that dissolved Si inputs into this estuary decreases as the season progresses from monsoon to premonsoon, through post monsoon.

Dissolved Si input into the estuary during the monsoon period was high in the fresh water, ranging from ~ 64.03-372.44 μM, coincident with high dissolved Al concentration, probably due to heavy input from rivers and land runoff owing to monsoonal precipitation. During non-monsoon months, dissolved Si varied within the range of 30.12 – 158.34 μM, much lower than the monsoon values when dissolved Al also exhibits a similar trend. Thus we infer that the variation of dissolved Al and Si may follow the same trend, both being mainly terrigenous in origin.

Suspended Particulate Matter (SPM)

The SPM in the river water was generally low; but often increases in the high salinity waters. August 1998, recorded the lowest SPM values of 3 mg/l in the southern arm; the northern arm showing value of 23 mg/l. During September 1998, the SPM values were 28.75 mg/l in the southern arm and 50 mg/l in the northern arm. The SPM value had increased possibly due to high river influx as the monsoon progresses. By January 1999, the SPM values decreased considerably to 5 mg/l at south but the northern arm showed moderate SPM values of 25 mg/l. During March 1999, the values in the southern arm increased slightly to 8.50 mg/l but for northern arm the values decrease to 13 mg/l. The values in the southern arm further increased to 10.50 mg/l during April 1999; the northern arm showed 18.25 mg/l. During May 1999, further increase in SPM values to 17.25 mg/l are observed in the southern arm. Northern arm also shows increased values of 19.75 mg/l.

Thus, as the season progresses from monsoon to premonsoon, the riverine input of SPM into the southern arm of the estuary increases but in the northern arm, a decrease is noted. The bottom values in the estuary, which show higher concentrations, compared to surface may be due to the resuspension of bottom sediments.

Distribution of dissolved Al, dissolved Si, SPM and salinity in Cochin Estuary

The distribution of dissolved Al, dissolved Si, SPM and salinity recorded during the observation period at all stations in the northern and southern arm of Cochin estuary are provided in figs.2a-f.

August 1998

This month is characterised by considerable quantities of Al being present throughout all the stations (fig.2a). Since Al in freshwater originates mainly from the natural weathering of alumino-silicate clay minerals, during monsoon season there is high influx of Al into the estuary either by direct river input or by land run-off. Surface and bottom waters of the southern arm of the estuary indicate a strong removal in the upper estuary followed by regeneration in the mid-estuarine regions and then continuous decrease in concentration further downstream. The surface concentration values (0.38-1.2 μM) are lower than the bottom values (0.19-1.79 μM). For the

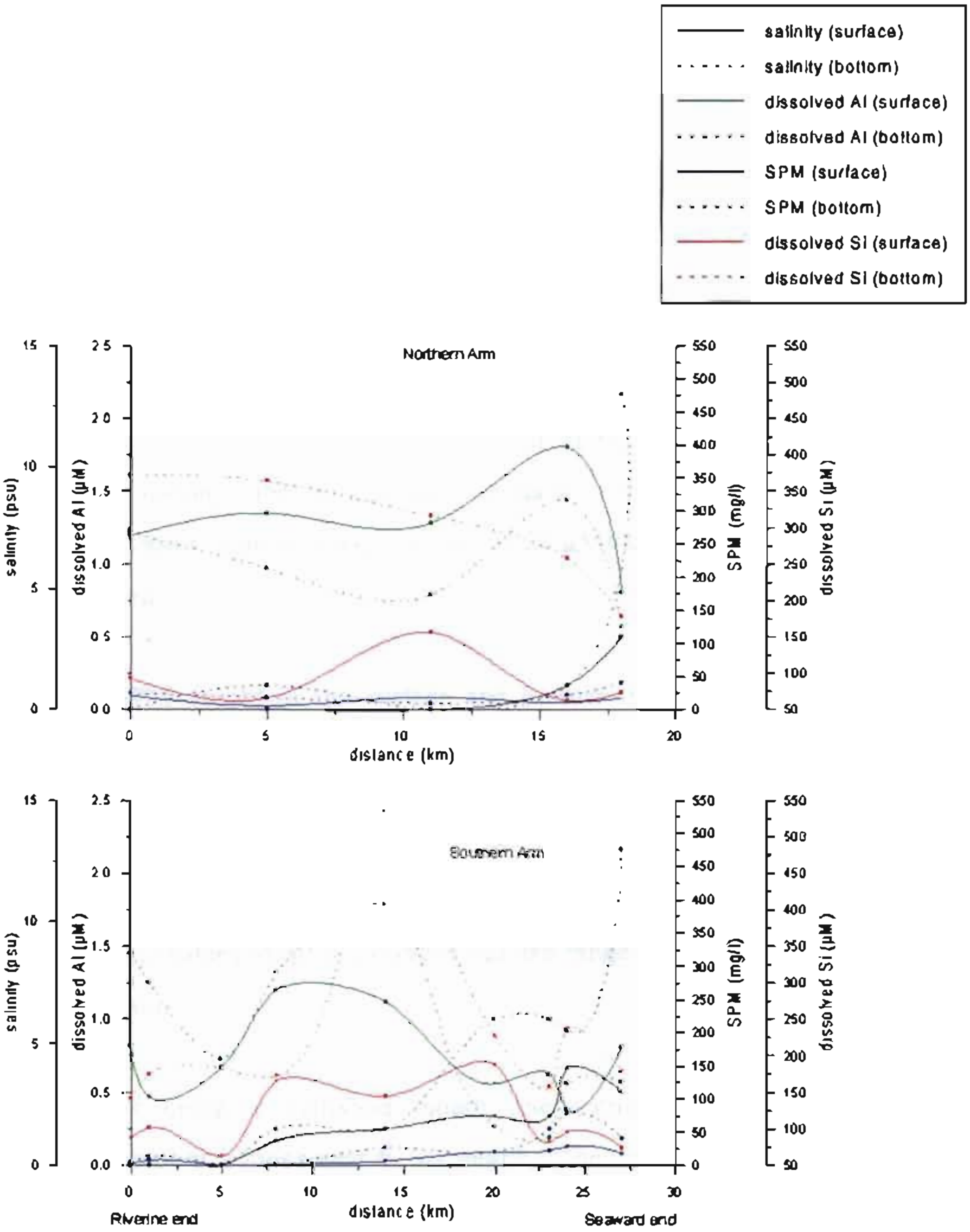


Fig.2a. Distribution of dissolved. Al & Si, SPM and salinity in the southern and northern arms during August 1998

northern arm, bottom waters exhibit removal of Al in the upper and mid estuarine regions followed by regeneration in the lower estuary. Surface waters indicate almost steady values in the upper and mid estuarine regions followed by a slight increase and further decrease in the lower estuary. Contrary to what was observed on the southern arm, the surface water concentration (0.81-1.85 μM) in the northern arm exhibits higher values than the bottom waters (0.57-1.44 μM).

Dissolved Si in the mid estuarine regions exhibits high values for both surface and bottom waters in the southern arm (fig.2a). This trend is more prominent in the bottom waters. The surface water values range from 61.91-187.32 μM. For bottom waters, the entire estuary shows high values (~141.37-534.90 μM), with a peak in the mid estuary. For the northern arm, high values are noted for the bottom waters (178.20-372.44 μM), showing a decreasing trend towards downstream in the estuary. Dissolved Si in surface waters is much lower (62.30-156.28 μM) showing a mild peak in the mid estuarine region.

The SPM values in the surface and bottom of the southern arm shows an increasing trend as studied for waters downstream in the estuary. The values in the surface and bottom range from 1-28 mg/l and 1-73 mg/l respectively. Surface and bottom values are almost coincident in the upper and mid estuary but the lower estuary shows considerable variation. For the northern arm, the entire part of this water body shows moderate values of SPM, falling within the range of 6-21 mg/l at surface and 10-40 mg/l at bottom.

August being a monsoon month, the entire estuary exhibits freshwater conditions except at stations near to bar mouth. The surface salinity values vary from 0-4 psu in the southern arm and 0-3 psu in the northern arm respectively (fig.2a). For bottom waters, the bar mouth region alone shows salinity of 13 psu while rest of the estuary comes within the salinity value of 0-6 psu. The bottom values are higher when compared to surface values, ranging from 2-13 psu in the southern and northern arm, indicating intrusion of high saline water. Thus it is clear that concurrent with the large volume of freshwater discharged into Cochin estuary during monsoon season, a mild incursion of denser saline waters from Arabian Sea is observed in the lower most reaches of this estuary. The general trend in salinity variation is thus an increase from the riverine end/mid estuary to the seaward end.

September 1998

The entire estuary exhibits presence of considerable quantities of dissolved Al as was seen during August 1998 (fig.2b). For the southern arm the surface water concentration values range from 0.27-1.77 μM and for the bottom waters the values range from 0.16 to 2.25 μM. A prominent feature noticed is the enhancement of dissolved Al in the mid estuarine region. For the northern arm, enrichment of dissolved Al is seen in the lower estuary too, both at the surface and bottom. The upper and mid estuary shows almost constant values without much variation.

Dissolved Si shows a similar trend in surface and bottom waters of the southern arm as was seen during August 1998 with mid estuarine region showing high values. The surface values range from 58.72-164.12 μM and the bottom values range from 64.56-346.09μM. The mid-estuarine enhancement of dissolved Si observed in the southern arm is not noticed in the northern arm. Surface value falls within the range of 68.46-98.64 μM and bottom values fall within 86.72-206.78 μM. The bottom values are higher and variable than the surface values.

In the southern arm, the upper and mid estuary is depleted as far as SPM values are concerned, the seaward end showing large values. The SPM concentration in the surface waters (1.0-27.5 mg/l) of the southern arm exhibit low values throughout the estuary but the bottom waters (10-270 mg/l) show significant amount of SPM mainly at seaward locations (fig.2b). The northern arm exhibits SPM values of 11-40 mg/l and 22-75 mg/l for the surface and bottom waters respectively. The surface waters show a gradual decrease in concentration as we proceed from riverine to seaward end, without much variability. Extremely high values of SPM are not noticed here as was seen for the downstream regions in the southern arm.

The salinity values in the southern arm range from 0-4 psu at surface and 0-5 psu in the bottom and in the northern arm the values vary from 0-2 psu and 0-3 psu at surface and bottom respectively (fig.2b). Here, it is seen that the salinity values decrease as the monsoon progresses, in view of enhanced fresh water runoff during this

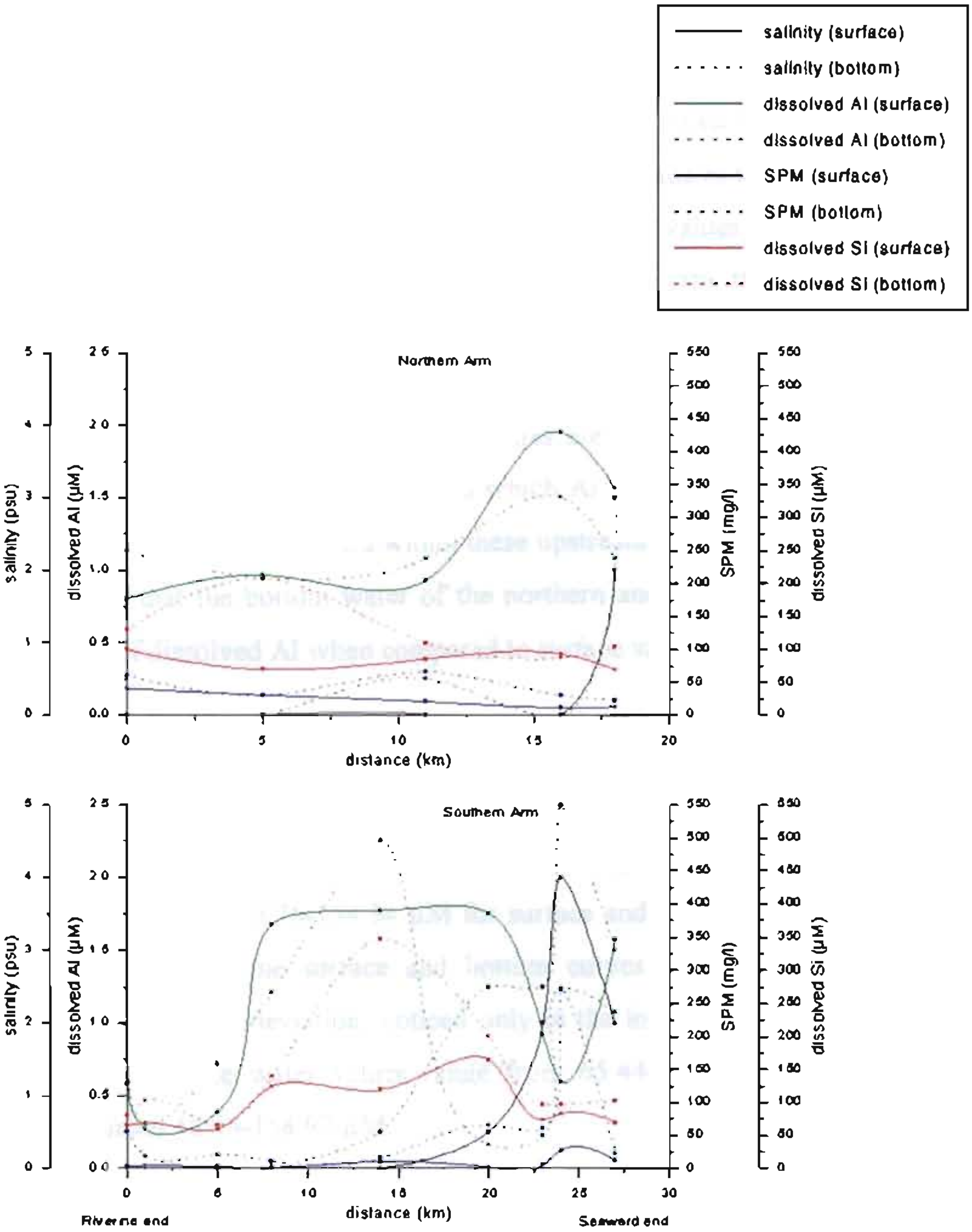


Fig.2b. Distribution of dissolved Al & Si, SPM and salinity in the southern and northern arms during September 1998

month. The mid and lower estuary of the southern arm shows large variations between the surface and bottom values, indicating stratification.

January 1999

Fig.2c gives the distribution of dissolved Al & Si, SPM and salinity during January 1999. Considerable decrease in overall content of dissolved Al, compared to monsoonal values, is noted here due to decrease in river inputs as the season progresses. In the southern arm, the surface and bottom waters exhibit values in the range of 0.02-0.14 μM and 0.28-0.89 μM respectively. For the northern arm, the surface waters are depleted, with only trace amounts present in the upper estuary, but the upper and mid estuarine bottom waters shows the presence of Al (0.08-0.50 μM). Both for the northern and southern arms, dissolved Al values are detected only for a distance of about 15 km from the river mouth, beyond which Al is undetectable. It may be noted that complete removal of Al occurs within these upstream regions. A prominent feature noticed here is that the bottom water of the northern and southern arms exhibit high concentration of dissolved Al when compared to surface waters.

Dissolved Si values are observed to increase in the upper most portion of the estuary and then gradually decrease towards the lower estuary in the surface and bottom waters along the southern arm. At the seaward end, slight perturbations are noticeable. The values range from 46.76-154.34 μM for surface and 25.01-156.91 μM at bottom. For the northern arm, the surface and bottom curves of dissolved Si are almost coincident with a slight deviation, noticed only in the lower estuary as the Si content decreases. The surface water values range from 65.44-160.45 μM and the bottom values range from 46.94-158.97 μM.

The SPM values increase continuously from the riverine end to the seaward end, in both the surface and bottom waters on the southern arm. While the bottom waters exhibit high values throughout (5-175 mg/l), the surface values fall within a short range (3.5-53.0 mg/l). In the lower estuary, the high SPM values at the bottom indicate resuspension of bottom sediments due to tidal effects. On the northern arm, the surface and bottom curves follow the same trend except for a sudden increase in bottom values at the bar mouth region. The surface values range from 12-48 mg/l and the bottom values range from 22-175 mg/l.

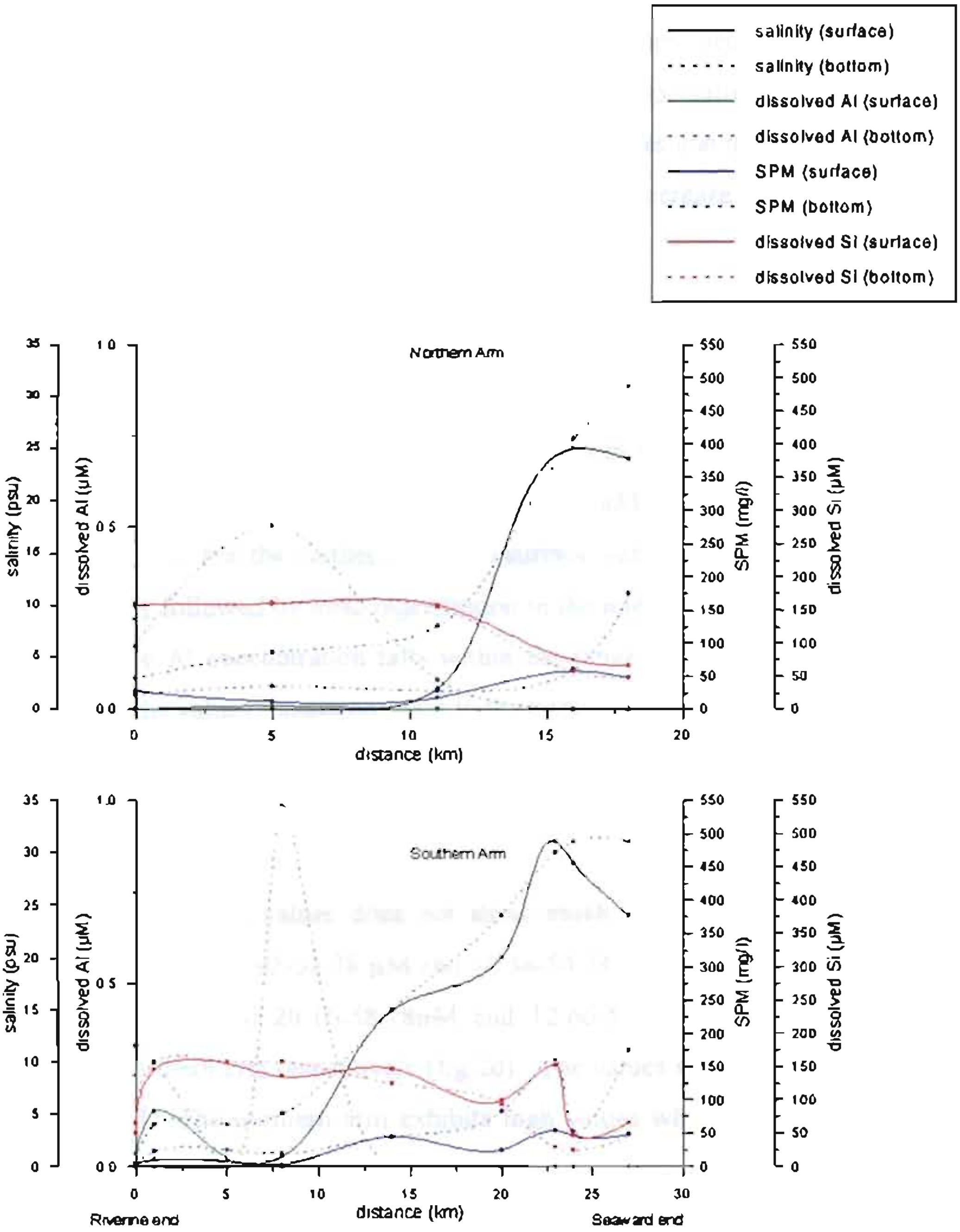


Fig.2c. Distribution of dissolved Al & Si, SPM and salinity in the southern and northern arms during January 1999

The salinity values show steady increase as the season changes from monsoon to postmonsoon. They range from 0-31 psu at both the surface and bottom in the southern arm and 0-25 psu and 0-31 psu at the surface and bottom in the northern arm respectively (fig.2c). Following a reduction in runoff, increased intrusion of hyper saline water into the estuary leads to increase in salinity especially near the bar mouth and nearby regions. A sharp increase in salinity is noticed as one proceeds downstream from the southern arm but in the northern arm, this sharp increase is noticeable only in the lower estuary.

March 1999

The surface waters of the southern arm are deficient in dissolved Al concentration except at the riverine end, but the bottom waters of the upper and mid estuarine region show the presence of Al (0.16-0.42 μM); Al is not detected beyond mid estuary (fig.2d). For the northern arm, the surface waters exhibit a clear removal in the upper estuary followed by mild regeneration in the mid estuary and thereafter no Al is detected. The Al concentration falls within the range of 0.005-0.48 μM. For the bottom waters, the values remain constant in the upper and mid estuarine region, with a decreasing trend and further, near removal in the lower estuary. The values vary from 0.38-0.49 μM.

The dissolved Si values does not show much variation in the estuary, with values in the range of 18.92-52.78 μM and 10.36-54.74 μM for the surface and bottom in the southern arm and 20.16-58.78μM and 12.66-57.84 μM for the surface and bottom in the northern arm respectively (fig.2d). The values show a decreasing trend at the seaward end. The northern arm exhibits high values when compared to southern arm.

The SPM values moderately increase towards the lower estuary for both the southern and northern arms. For the southern arm there is not much variation between the surface and bottom waters (7-102.50 mg/l at surface and 10-87.50 mg/l at bottom); in fact, a slight variation is seen only at the seaward end. The bottom waters (20-58 mg/l) of the mid and lower estuarine region of the northern arm exhibits much higher concentration when compared to surface waters (2-58 mg/l).

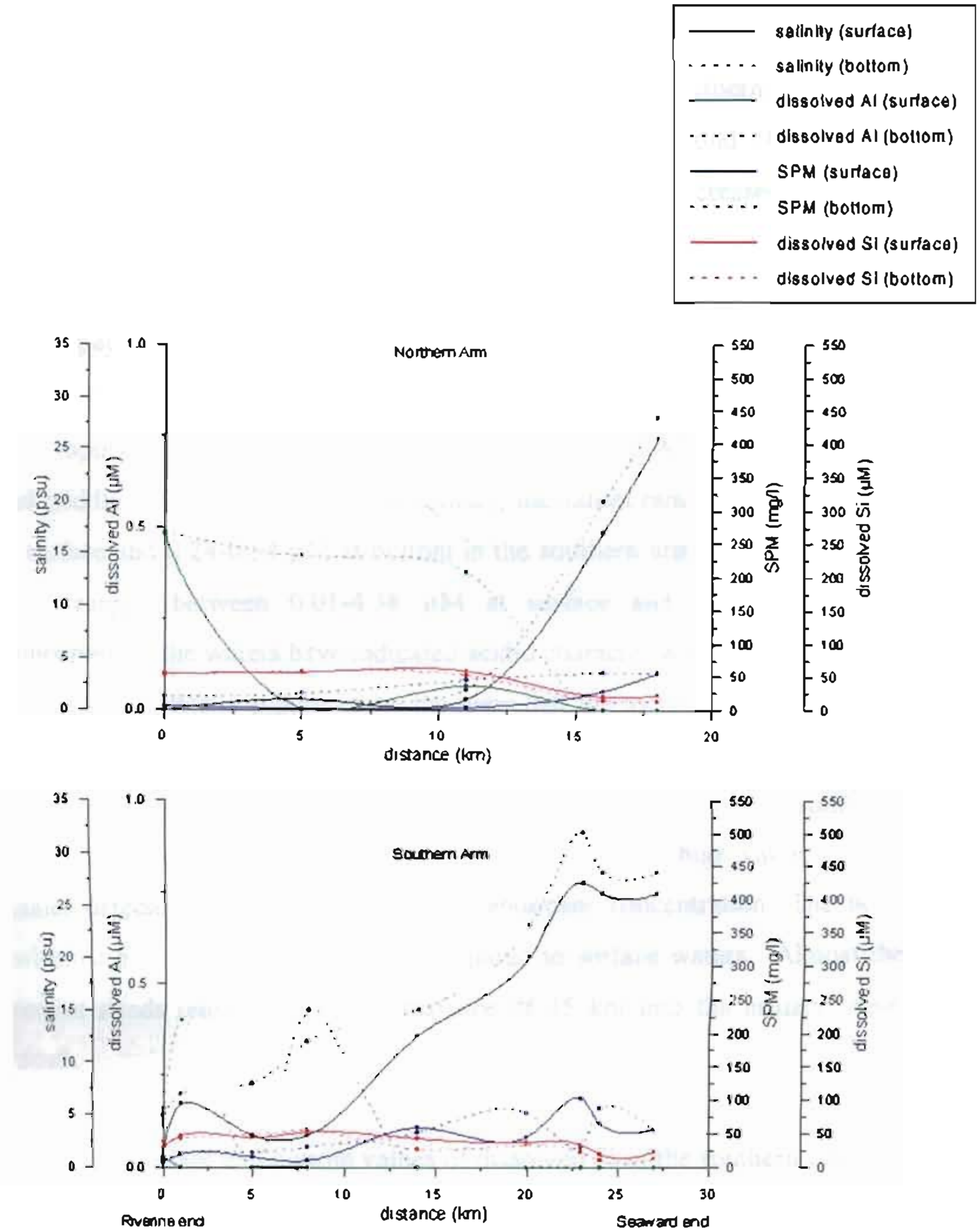


Fig.2d. Distribution of dissolved Al & Si, SPM and salinity in the southern and northern arms during March 1999

Salinity values vary from 1-27 psu and 5-32 psu in the surface and bottom waters in the southern arm. In the northern arm, the values are 0-26 psu and 0-28 psu in the surface and bottom layers respectively (fig.2d). With markedly reduced precipitation and runoff during this month, the saline water further intrudes into the estuary, causing an increase in the salinity values. The southern arm exhibits a sharp increase in salinity values in the surface and bottom beyond 10 km from the river mouth where as for the northern arm the salinity steadily increases from the riverine to the seaward end.

April 1999

The dissolved Al values further decrease as the season progresses, as minute river inputs were observed during this month (fig.2e). Al is noticed only in the upper and middle estuarine reaches of the estuary, the values ranging between 0.004-0.07 µM at surface and 0.24-0.54 µM at bottom in the southern arm. For the northern arm, the value ranges between 0.01-4.38 µM at surface and 0.08-2.72 µM at bottom. Concurrently, the waters have indicated acidic character which is likely to influence the content of Al; this is supported by the view that the increasing trends in the dissolved Al content in rivers and lakes have been associated with acidification process (Johnson et al., 1981). It has been shown that acid waters contain much more soluble Al than the neutral or alkaline waters (Burrows, 1977). Except this high value, the dissolved Al values detected is within the normally abundant concentration. The bottom waters exhibited high concentration when compared to surface waters. Almost the entire Al content stands removed within a distance of 15 km into the estuary, from the river mouth.

The surface and bottom values of dissolved Si in the southern arm of the estuary fall between 31.01-143.75 µM and 31.82-57.11 µM, respectively. Surface and bottom curves follow the same trend with major departure at the upstream end. The surface and bottom values of dissolved Si throughout northern arm of the estuary are almost coincident, the values ranging from 45.57-96.72 µM at surface and 31.82-100.64 µM at bottom. For the northern arm, the mid and lower estuary shows a continuous decrease in dissolved Si values at both the surface and the bottom as observed, downstream.

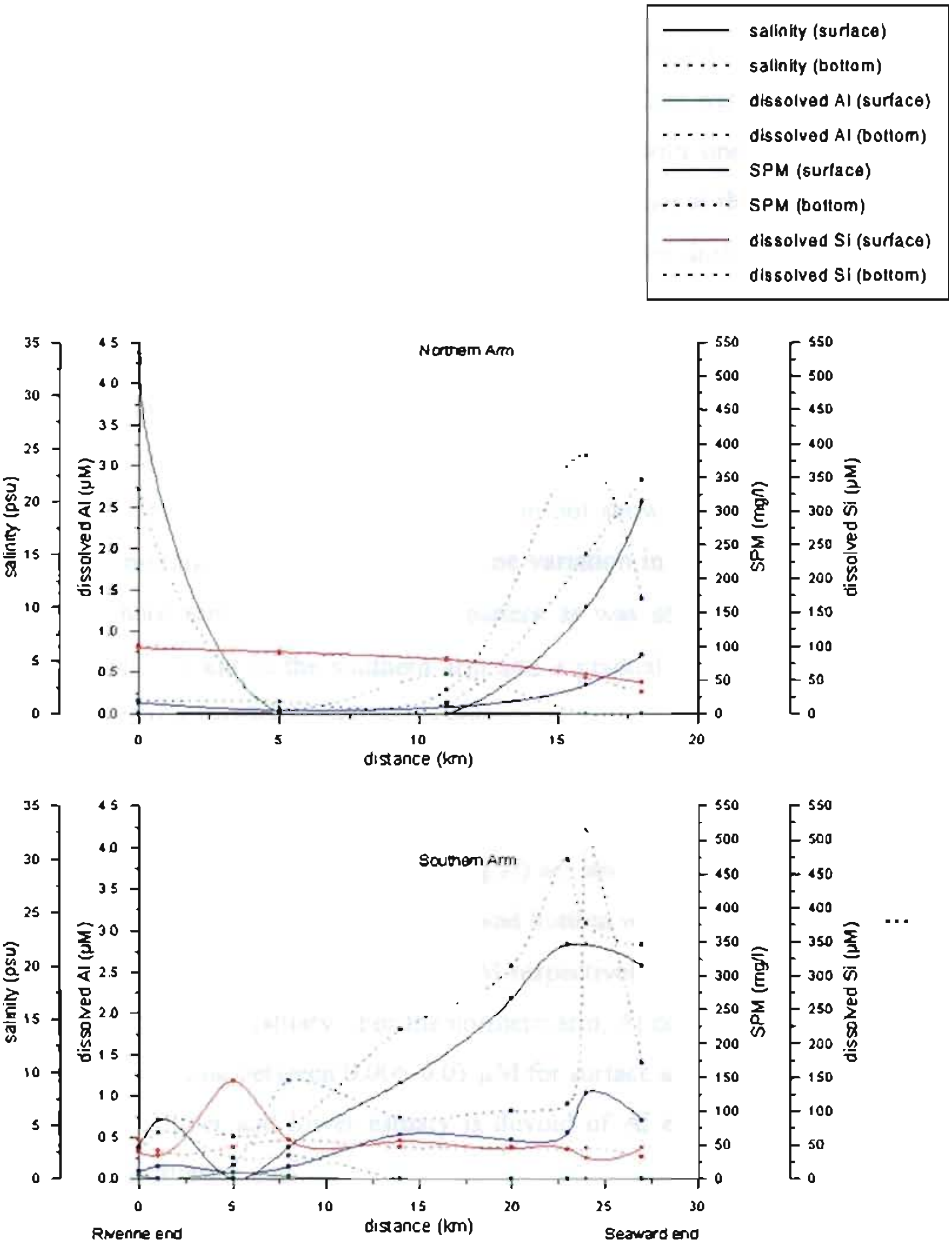


Fig.2e. Distribution of dissolved Al & Si, SPM and salinity in the southern and northern arms during April 1999

Southern arm also exhibits the same trend but with slight perturbations. The values noted for the northern arm are high compared to southern arm.

The SPM concentration increases continuously from the riverine to the seaward end in the southern arm at both surface (9.0-126.5 mg/l) and bottom (0.0-515.0 mg/l). The bottom waters show higher concentration than the surface waters. For northern arm also the values increase from riverine to seaward end with one or two exceptional observations. The SPM concentration ranges from 5-86 mg/l at the surface and 20-382 mg/l at the bottom. The SPM values are high and variable during this period for the entire estuary.

The salinity values range from 0-22 psu and 3-30 psu at the surface and bottom of the southern arm; and 0-20 psu and 0-22 psu at the surface and bottom in the northern arm. The surface and bottom waters do not show much variations indicating good vertical mixing in the water column. The variation in salinity along the northern arm and southern arm exhibits the same pattern as was seen during March; a sharp increase beyond 10 km in the southern arm and a gradual increase throughout in the northern arm of this estuary is well noticeable.

May 1999

Dissolved Al values in May 1999 (fig.2f) are lower than that was noticed during April 1999. In the southern arm, the surface and bottom waters exhibit Al concentration ranging from 0.11-0.13 µM and 0.04-0.20 µM respectively. Al was detected only in the upstream regions of this estuary. For the northern arm, Al concentration values are still lower, the range falling between 0.006-0.03 µM for surface and 0.0-0.08 µM for bottom in mid-estuary. Upper and lower estuary is devoid of Al except for trace amount of 0.006 µM at the riverine end.

The surface waters in the southern parts indicated dissolved Si concentration to increase towards the upper estuary, reaching a maximum of 138.20 µM and then decrease, continuously to the seaward end. The surface values range from 32.25-138.20 µM and the bottom values range from 33.13-69.50 µM. The northern arm exhibits

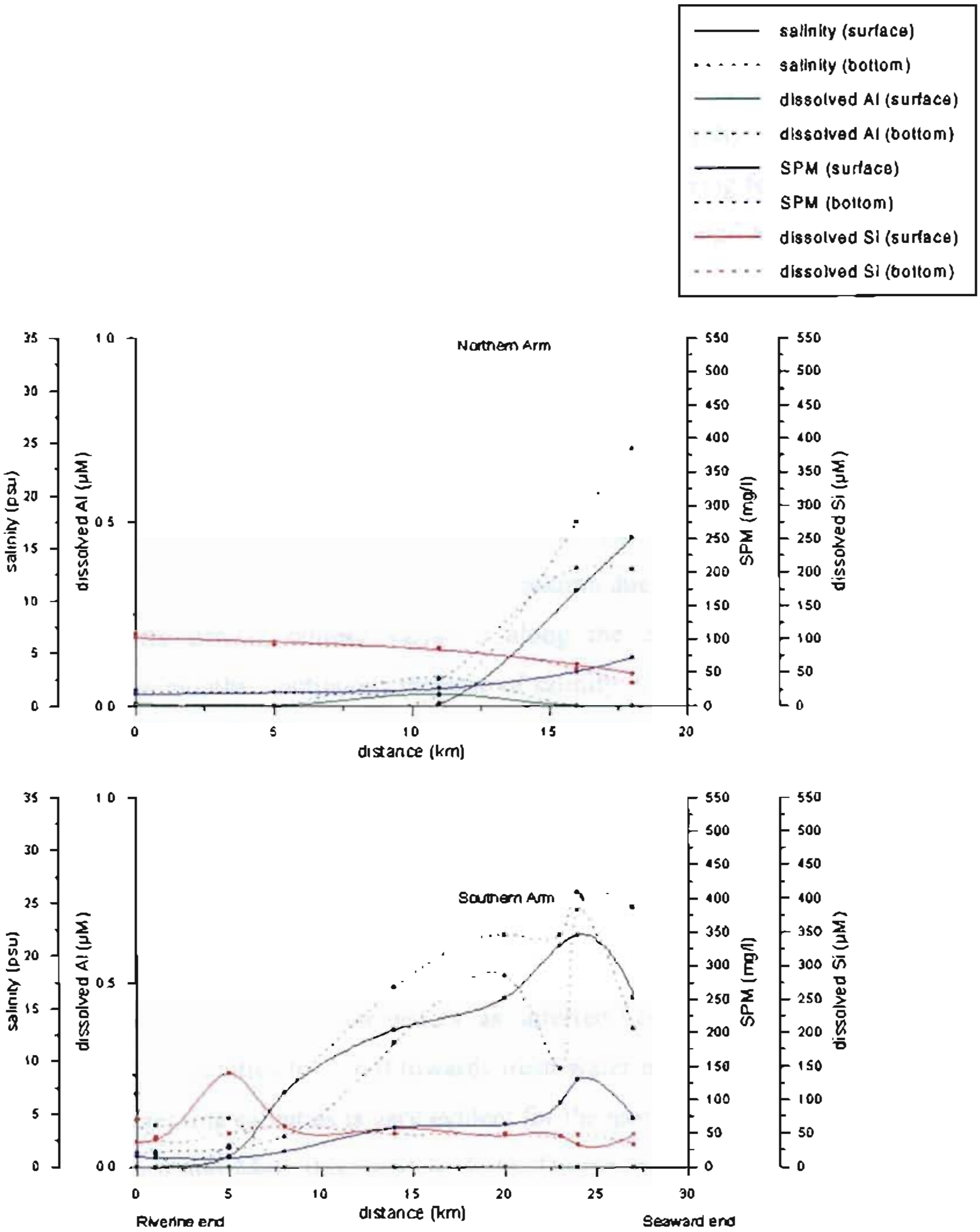


Fig.27. Distribution of dissolved Al & Si, SPM and salinity in the southern and northern arms during May 1999

continuous decrease from riverine to seaward end, the values occurring between 47.78-101.40 µM at surface and 33.13-107.80 µM at bottom.

The southern arm contained SPM, whose values remain constant in the upper estuary and then increases continuously towards the seaward end. The mid and lower estuary shows high values of SPM compared to upper estuary. The values fall within 13-130 mg/l at surface and 20-382 mg/l at bottom (fig.2f). A sudden dip in the distribution curve at the bar mouth is noticed when considering features on the southern arm. For the northern arm, the values range from 17.5–72 mg/l and 20–206 mg/l at the surface and bottom, respectively. The lower estuary shows the presence of considerable amounts of SPM.

During May 1999 the salinity in the southern arm varies from 0-22 psu at the surface and 0-26 psu at the bottom (fig.2f). For the northern arm, the surface values range from 0-16 psu at the surface and 0-24.5 psu at the bottom. The estuary is vertically well mixed throughout the water column due to tidal turbulence. This month also exhibits similar salinity variation along the estuary as was seen for other premonsoon months: continuous increase of salinity in the middle and lower estuary of the southern arm and sharp increase in the downstream parts of the estuary for the northern arm.

pH, SPM, dissolved Si & Al vs. salinity

pH vs. salinity

The pH of the estuarine waters as inferred from fig.3, decrease steadily from ~ 8.0 at high salinities to ~ 6.0 towards fresh water end. The decreasing trend in pH against decreasing salinities is very evident for the months, January and March. For the months April and May, this trend is slight. During monsoon season, no such trend is visible; the pH limits in a very short range from 6.6-7.6 and the salinity ranges from 0-6 psu. This can be attributed to the high influx of freshwater as a result of monsoonal precipitation and further dilution of estuarine waters.

Suspended Particulate Matter vs. salinity

The SPM in the fresh water is low (<60 mg/l) but increases in the high salinity waters, reaching upto 515 mg/l in certain cases as observed from fig.4. The high-suspended load in the lower stretch of the estuary is a result of resuspension due to churning action of bottom sediments, which decreases upstream as a function of distance from the inlet (mouth). During monsoon months, the variation of SPM with salinity does not show any particular trend (as expected) but as the season progresses, an increase in SPM value with increase in salinity is noticed. This increase is more prominent for the premonsoon months. Upstream data on northern and southern sides of the estuary indicate that there is comparatively lower suspended solid content (1-35 mg/l), than at locations near the estuarine bar-mouth that exhibited much higher values (50-515 mg/l). But, during monsoon months, the difference in values between the seaward and riverine end is much reduced, probably due to high river influx and subsequent addition of particulate material to upstream regions. Another observation relates to the features during the months of January and March when a clear correlation exists between the two estuarine parameters indicating vertical mixing with longitudinal heterogeneity.

Dissolved Si vs. salinity

Dissolved Si concentrations are plotted as a function of salinity in the estuarine transects in fig.5. High values of dissolved Si are noticed for monsoon months; the values go on decreasing as the season progresses. Dissolved Si shows initial rapid decrease at low salinity values during the postmonsoon and premonsoon months; a decrease with increase in salinity is deduced at values > 5 psu in April & May and >10 psu in January and March. However, it is closely observed that Si is substantially removed from solution in the high salinity waters; for monsoon months, no significant removal is noticed since the salinity falls within a low range of 0-6 psu. Thus Si removal is strongly salinity induced and can vary with fresh water inflow. Since the profiles show a distinct function with salinity, it indicates the dominance of simple dilution by Si poor seawater over other biological or non-biological removal and/or supply.

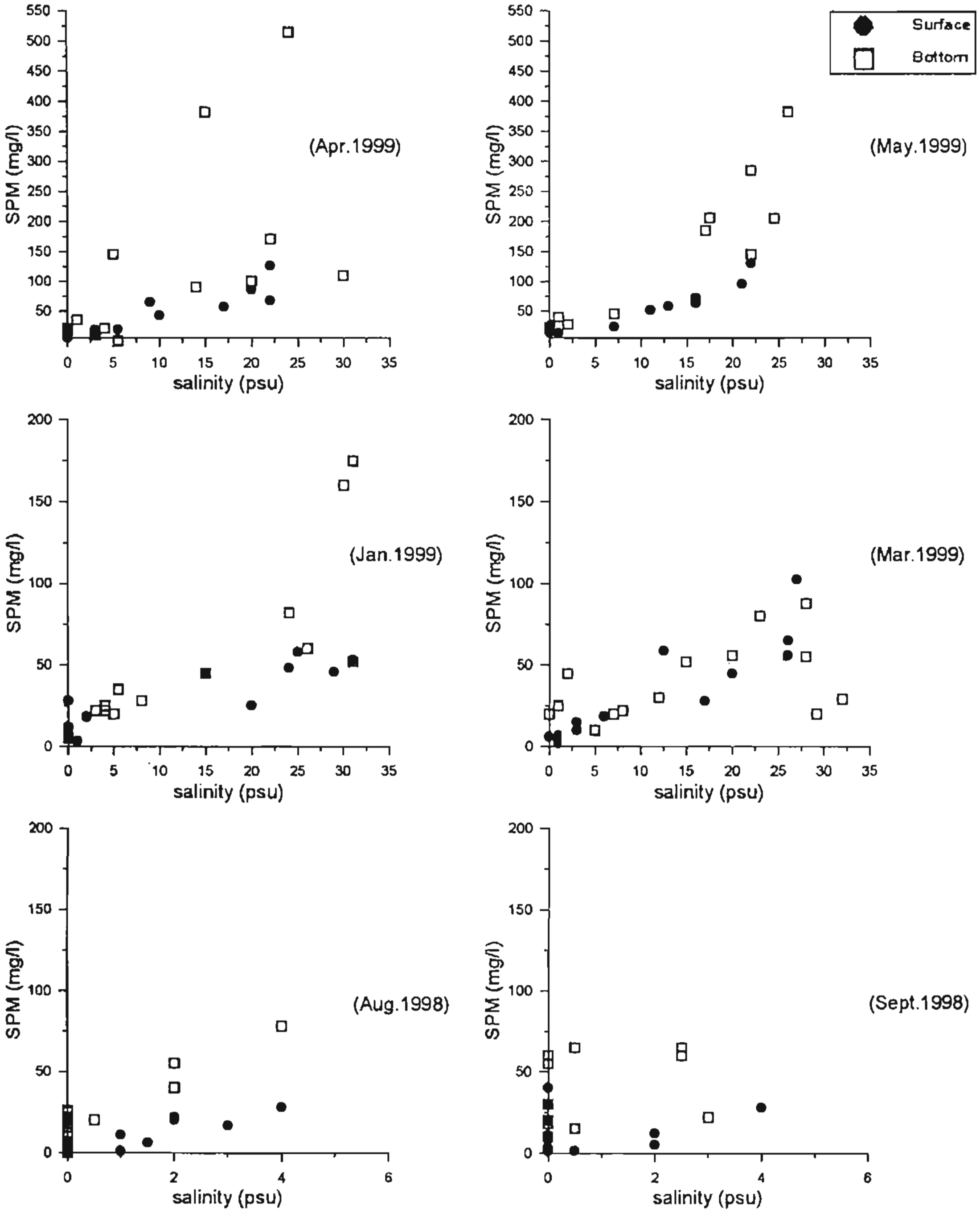


Fig.4.SPM as a function of salinity in estuarine waters during different months

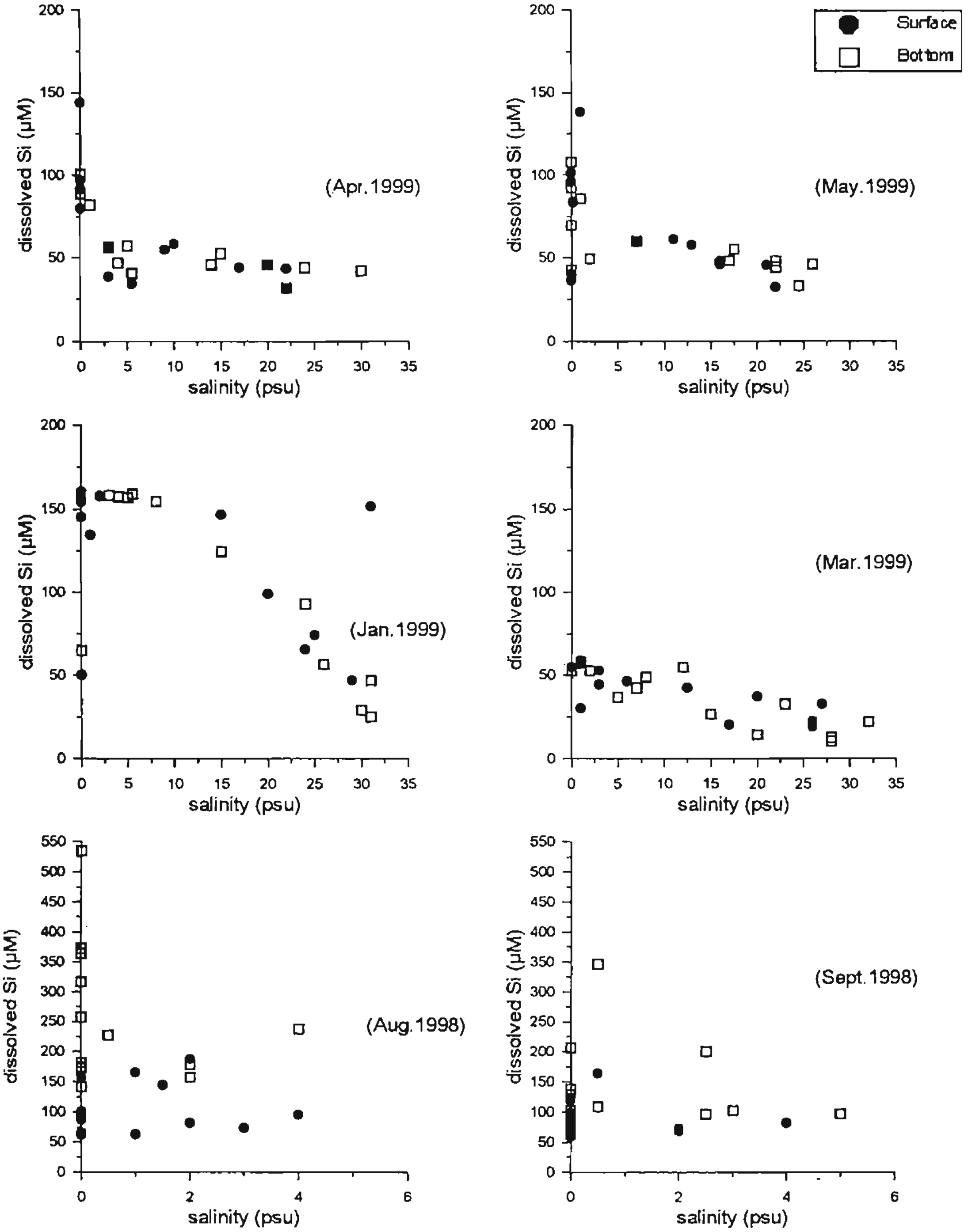


Fig.5. Dissolved Si as a function of salinity in estuarine waters during different months

Dissolved Al vs. salinity

The variability pattern of Al in the estuarine transects is shown as plots of dissolved Al vs. salinity (fig.6). The important feature noticed is that dissolved Al concentration is limited within a salinity value of < 10 psu, beyond which no Al is detectable. The monsoon month is characterised by considerable quantities of Al present throughout the estuary at salinities as low as 5 psu. Since Al in freshwater originates mainly from the natural weathering of alumino-silicate clay minerals (Edzwald et al., 1974) and since there is high influx of Al into the estuary either by direct river inputs or by land run-off during monsoon time, such a scatter diagram is presentable. The high influx of freshwater causes the salinity to decrease drastically and the estuary attains almost freshwater conditions with traces of salinity only near the bar mouth regions (Menon et al., 2000). There is initially slight decrease in dissolved Al concentration as the salinity increases. In monsoon, no rapid removal of Al is detected as was observed in contradiction to the features obtained during premonsoon and postmonsoon months.

In the months of January and March, dissolved Al shows a perceptible, initial decrease in concentration at very low salinities, followed by further decrease as salinity increases and most of the dissolved Al fraction stands removed from solution within the salinity range of 0.02 ~ 10 psu (fig.6). It is ascribed that Al concentrations decrease as the metal is adsorbed onto particulates and subsequently settles out of the water column as suggested elsewhere (Measures et al., 1984,1986; Orians & Bruland, 1986). Moreover, the input via rivers as well as land runoff is minimal during this season. The role of turbidity maxima is dealt separately.

The dissolved Al profile during the premonsoon months shows that Al is present only within low salinity regions, upto a salinity around 5 psu. Beyond that Al is not detectable, due to its removal from solution as a result of flocculation. The bottom concentrations are higher than the surface concentrations for the premonsoon months. The distribution is similar to those in previous months, with detectable Al only in the low salinity regions while complete removal occurs, downstream. The overall concentration of Al was less in April & May than in January & March.

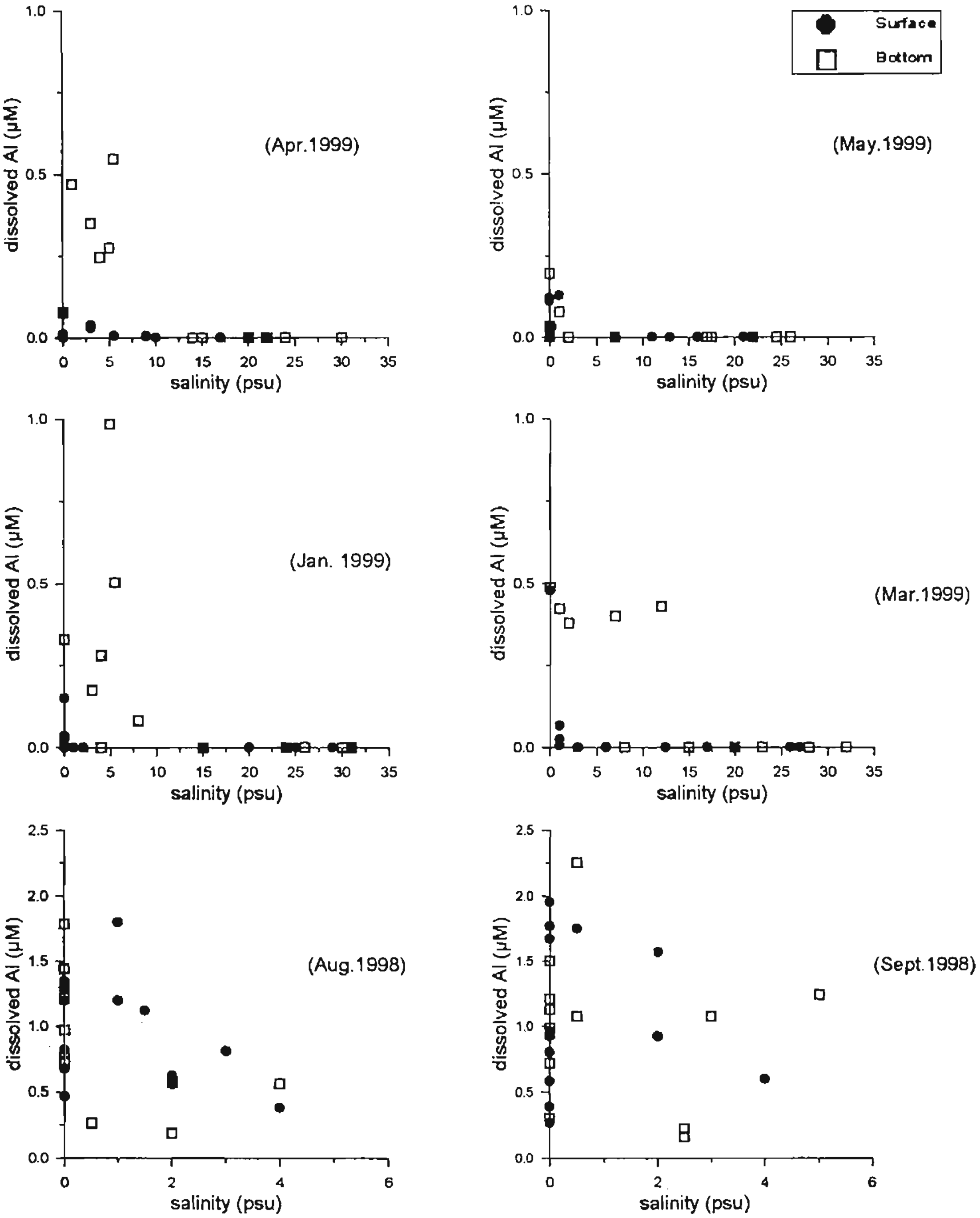


Fig.6. Dissolved Al as a function of salinity in estuarine waters during different months

The dissolved Al concentration range in waters of the Cochin estuary during the dry season (high salinity) was found to be 0.004 μM to 0.89 μM and during wet season (low salinity), the value ranged from 0.16 μM to 2.25 μM. This distribution appears to be a function of freshwater input. The abnormally high values of 4.38 μM and 2.72 μM in April is excluded while considering the range, because these values may be due to an increase in soluble Al as a result of the acidic character of the water, owing to effluent discharge in the upstream region of this estuary. Comparing salinity and Al, it is noticed that Al concentration decreases as salinity increases, the general trend indicating that Al is removed from solution at very low salinities itself.

The foregoing observations suggest that geochemical interactions as well as hydrological properties of the estuary are important in regulating the distribution of dissolved Al in Cochin backwaters whereas geochemical interactions alone account for the behaviour of dissolved Al in Mandovi estuary (Upadhyay & Sen Gupta, 1995).

Dissolved Al vs. dissolved Si, pH and SPM

Dissolved Al vs. dissolved Si

Dissolved Al vs. Si plots for all the three seasons are shown in fig.7. During the monsoon season, high levels of dissolved Al and Si are seen throughout the estuary and this point out to a positive correlation between the two species. During this season whole of the estuary attains fresh water conditions due to high river influx. Indeed, the occurrence of high levels of both dissolved Al and Si together in river water is common in many river estuaries (Hydes & Liss, 1977; Mackin & Aller, 1984a,c, 1986) in view of their common source, i.e. continental weathering. For the post monsoon season no signals are depicted in relationship between dissolved Al and Si and the scenario does not change during the premonsoon months.

Dissolved Al vs. pH

pH changes were observed over a range of 6.2-8.5. The acidic pH of 4.3 and 5.2 observed during April was at an effluent discharge spot in the upstream region; this is excluded while considering the range. It is noted that changes in pH over the above stated range is sufficient to cause major variations in the speciation of dissolved Al (discussed in a later chapter). Hence, due to the speciation of dissolved Al, the

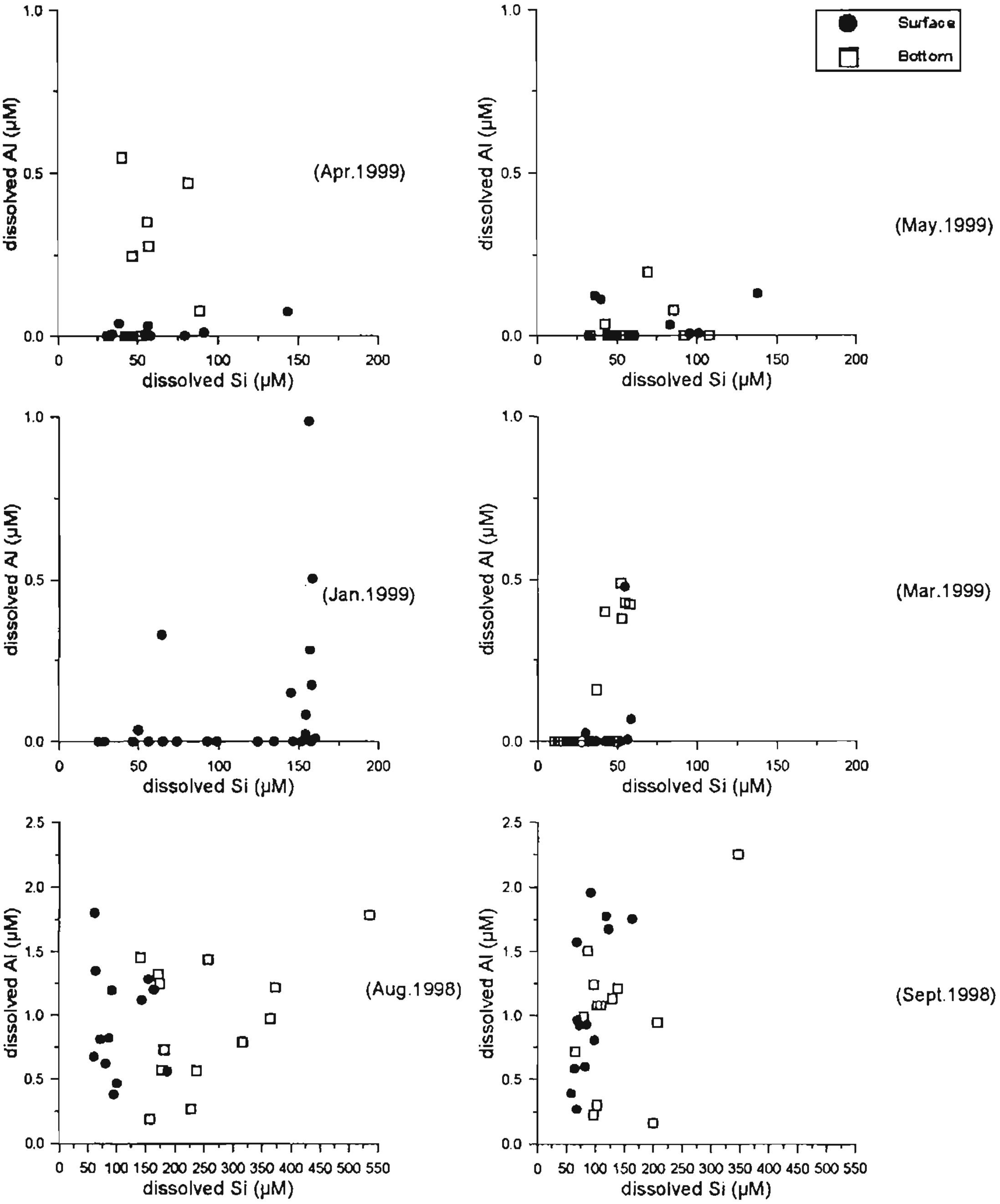


Fig.7.Dissolved Al as a function of dissolved Si in estuarine waters during different months

solubility of Al exhibits a minimum which is usually close to pH~6.0 (May et al., 1979); hence the removal of dissolved Al in the Cochin estuary may also be pH induced. With the rise in pH, uncomplexed Al^{3+} ions undergo rapid hydrolysis forming negatively charged $[Al(OH)_4]^-$ species (May et al., 1979). A fairly strong relation between pH and dissolved Al underlines the influence of pH on the speciation and hence, on the solubility of Al-bearing phases in the estuarine waters. The plots (fig.8) suggests that during monsoon, Al content in this estuary is rather not depended on pH variability as the values are fairly distributed across the pH range 6.5 – 8.5; but during other months, presence of Al in solution is recorded for pH values below 7.5.

Dissolved Al vs. SPM

The plots of dissolved Al as a function of SPM (fig.9) show a general, negative correlation between the parameters, thus suggesting that resuspended sediments are unlikely to act as a source of dissolved Al. From the figure it is clear that most of the dissolved Al is present only in the low SPM range, 0-50 mg/l. It is also proposed that resuspended sediments/flocculation will aid the removal of Al by acting as sites of adsorption as SPM concentration tends to increase which is often noted in the mid and lower estuary.

Al distribution vs. SPM dynamics vs. salinity intrusion

The study on the dissolved Al of the Cochin estuarine environment is of great importance while attempting to characterise the specific features, relative prevalence and estuarine modification, which occur during the transport of this element. The behavior of dissolved Al in Cochin Estuary may be governed by dynamic transport of water and sediment, while hydrophobic sorption could be the other important physicochemical process. Longitudinal sections showing the distribution of salinity, SPM and dissolved Al are given in figures 10-12 which aid the attempt to summarize the prevailing character of this dissolved constituent.

Sectional analyses point out to stratification features in this estuary based on seasonal variations of estuarine characteristics. There are three seasonal conditions prevailing in this estuary, i.e., monsoon (June-September), post monsoon (October-January) and pre monsoon (February-May), which is evident from the fig.10a & b. The

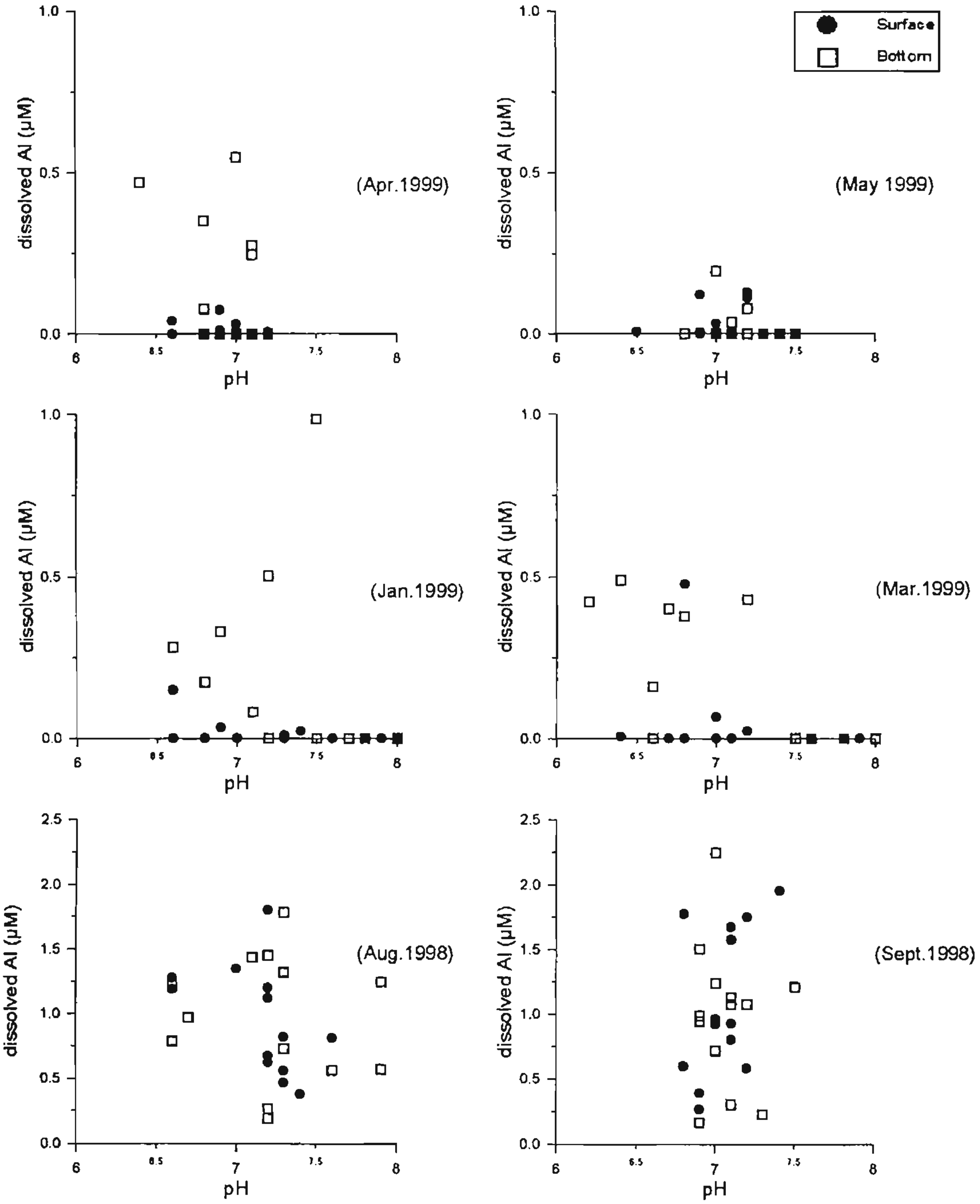


Fig.8.Dissolved Al as a function of pH in estuarine waters during different months

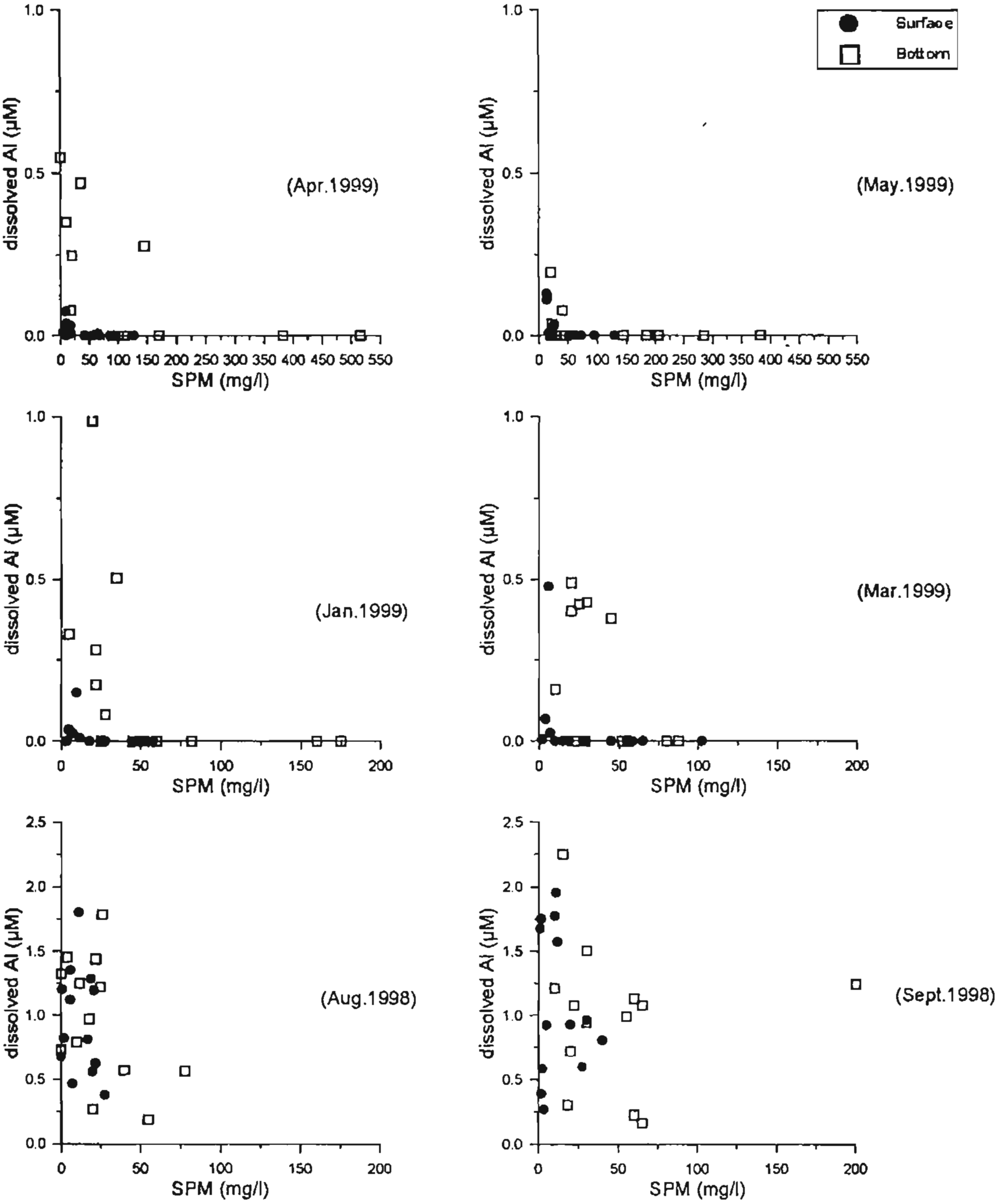


Fig.9.Dissolved Al as a function of SPM in estuarine waters during different seasons

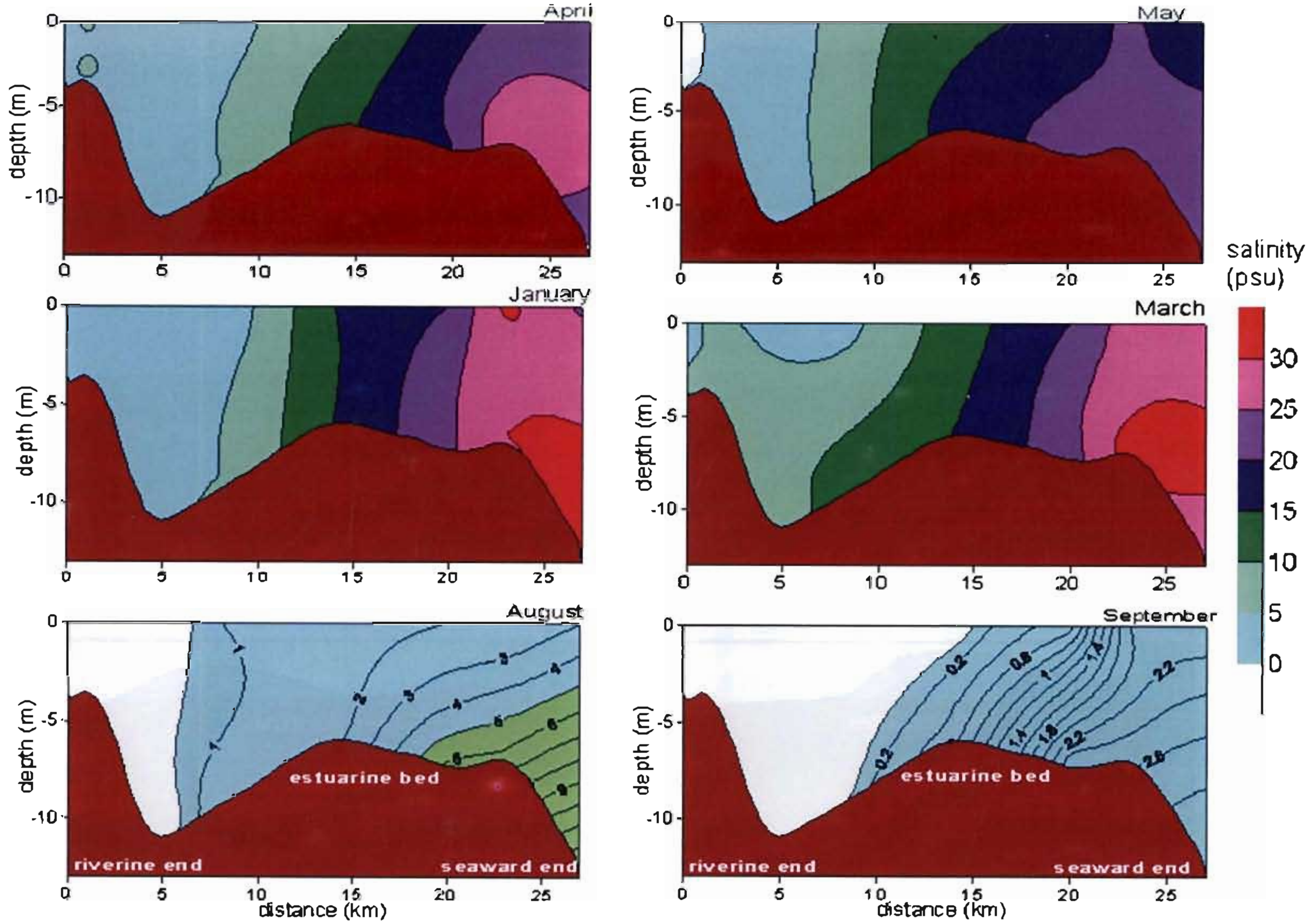


Fig.10a.Longitudinal sections of salinity during August 1998-May 1999 in Cochin estuary (southern arm)

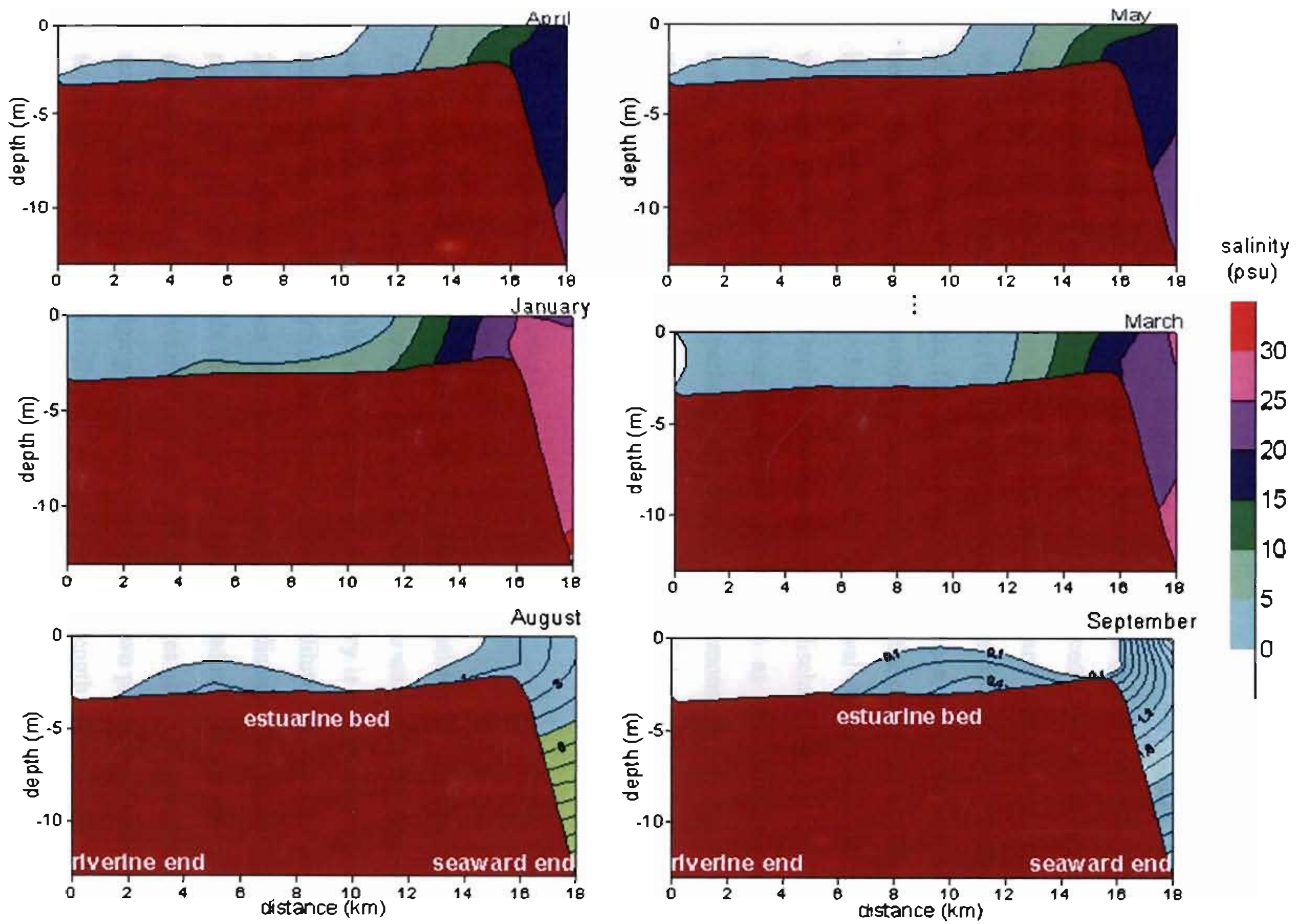


Fig.10b.Longitudinal sections of salinity during August 1998-May 1999 in Cochin estuary (northern arm)

estuarine features alter between a well-mixed type during premonsoon and a stratified type during monsoon as observed earlier (Qasim & Gopinathan, 1969; Wellershaus, 1971; Lakshmanan et al., 1987). During the monsoon season, the estuarine hydrography is mainly controlled by the interaction between the enhanced fresh water inflow from runoff due to heavy rains and consequently the high dense saline water which are restricted to the lower reaches (especially near and at the bar mouth). August and September represents active monsoon months and a large quantity of fresh water enters the estuary. By September, river discharge stands enhanced and stratification builds up, resulting in low saline water at the surface and denser and comparatively more saline waters to occupy the bottom (fig.10a & b). Salinity is near zero in the upstream portions of the southern arm, whereas, for the northern arm presence of freshwater extends well beyond the mid estuary towards the bar mouth. Taking the estuary as a whole, salinity is most often limited to <5 psu. With the withdrawal of monsoon, stratification weakens, proportionally. During postmonsoon, river discharge gradually diminishes and tidal influence progressively gains momentum as the estuarine condition commences to change to a partially mixed type. The premonsoon period indicates mild stratification in the upper and mid-estuarine regions of the northern arm alone. The northern part of the estuary is subjected to higher salinity wedging and oscillatory movement than the southern parts where mass movement within the water body with considerable mixing is observed.

A critical analysis of the section pertaining to salinity on the southern arm of Cochin estuary explicitly indicate presence of low saline waters during monsoon under which condition most of the upper portion of the estuary is engulfed with fresh water and the strong outflow through the rivers substantially dilute salt to values around 1.8-2.8 psu in the lower reaches. The bottom topography indicates a bed shape containing a pool riffle system towards the riverine end, which gradually builds up to shallower depths in the mid estuary and thereafter steeply wedges at the seaward end (due to maintenance form of dredging at port area). The next two preceding months permit us to witness near identical conditions emphasizing the strength of tidal incursions giving rise to vertically mixed water column with longitudinal extension – salinity is in the range of 5 to10 to 15 to 20 psu to occupy the mid estuarine portion (7.5 to 17.5 km) leading to further salinification during early premonsoon wherein upper estuarine region is also covered in the 5 to 10 to 15 psu salinity range (2.0-7.5 km). The impact of bottom topography is demonstrated by the vertical values at distances 7-9 km. Likewise at the lower estuary, dense waters occupy the wedge section over which slightly low saline waters exhibit mild stratification. On a general note, the southern estuary is mostly well mixed in the vertical but longitudinally heterogeneous.

The next set of figures (10b), demonstrates the spread of salt water towards the northern arm of Cochin estuary. The entire stretch is shallow with depths around 2.5-3.5 m except at the barmouth region where a deep wedge is facilitating the functions of a navigational channel. As expected, monsoon was the time when the entire northern arm is occupied by freshwater with the exception of very low saline waters in the wedge area. The next seasons (January – May) indicate presence of salt water >20 psu in the mid and lower estuarine region, 10-14 km. The remaining water body towards the fresh water side is either fresh water or of low salinity, 0-5 psu. Thence, the salt incursion into the northern arm is mostly restricted to around 6 km downstream with salt wedge phenomenon often occurring in the wedge zone; whereas, saline intrusion is often reflected in the upper and mid estuarine region. It is emphasized that the two arms of the estuary behave quite differently during the post and the premonsoon seasons – one in which salt wedge is often encountered towards the northern parts whereas on the other hand, good vertical mixing promotes longitudinal heterogeneity and thirdly, the entire estuary is turning into a fresh water "lake" with prevalence of non-saline waters in most places except around bar mouth region.

A significant indicator of the magnitude of sediment mobility within estuaries is the so-called turbidity maximum. This zone is characterised by an increased suspended solids concentration, which exceeds that of the river part or that of the estuary further seaward. It is generally located at the head of the salt intrusion. The turbidity maximum responds in a dynamic way to the varying river inflows and the state of the tide by changing its position and density. In estuaries, where tidal action is strong and influx of suspended sediment relatively large, the turbidity maximum is a permanent feature. Within the turbidity maximum, physicochemical and compositional properties of water change rapidly from those of fresh water to those of seawater, and it is a major site for chemical and biological reactions (Dyer, 1989). Also, flocculation and coagulation of clay-sized particles (< 2 μm) occur in this zone.

In Cochin estuary such a zone of high turbidity is clearly present and its location is confined to the mid and lower estuary during the non-monsoon months; but during monsoon season, the zone of high turbidity is less distinguishable (figs.11a & b). An important feature noticed is the location of turbidity maxima, which is further seaward in the northern arm. For mean flow conditions, this region is situated in the middle estuary, between 10 and 20 km from the river mouth in the southern arm, roughly corresponding to the transition zone from fresh water to brackish water. The turbidity maxima zone shifts upstream as the season progresses in both the arms. Hence, unlike the turbidity maximum observed in the low salinity regions of the Tamar estuary (Morris et al., 1986), the high salinity waters of the mid and lower stretches of the Cochin estuary are relatively high turbidity regions due to re-suspended sediments, with minor contribution from river-borne particulates as there is no continuous build up from the river end. The suspended matter is mainly composed of colloidal particles that flocculate easily such that pronounced deposition occurs as stated above. According to Wollast (1973), two-thirds of the fluvial sediments are deposited in this zone.

Figs.12a & b give the longitudinal sections showing the variation of dissolved Al in selected months. It is clear from the figures that high concentration is restricted to the monsoon months owing to considerable supply of this metal via river inflow and both, salinity and SPM acting favorably to sustain the metal in its dissolved form. The Al concentration diminishes as the season progresses, along with enhancement in values of salinity and SPM. Comparing the plots showing the distribution of dissolved Al, salinity and suspended solids, it is clear that in Cochin estuary dissolved Al maximizes in the fresh water zone upto the region where turbidity maxima occurs. During the period of observation, salinity of ≤10 psu and SPM values of ≤100 mg/l was limited up to the mid-estuary and within. This region coincides with Al presence as detected in Cochin estuary. Thus it is stated that these salinity values and SPM conditions favor the detection of dissolved Al as is evident from the figures 10-12. The above mentioned characteristics may be a limiting factor for sustaining Al in detectable dissolved forms.

In both the arms, from the figure, it is explicitly clear that diminishing conditions prevail, with respect to dissolved Al concentrations as investigated from the

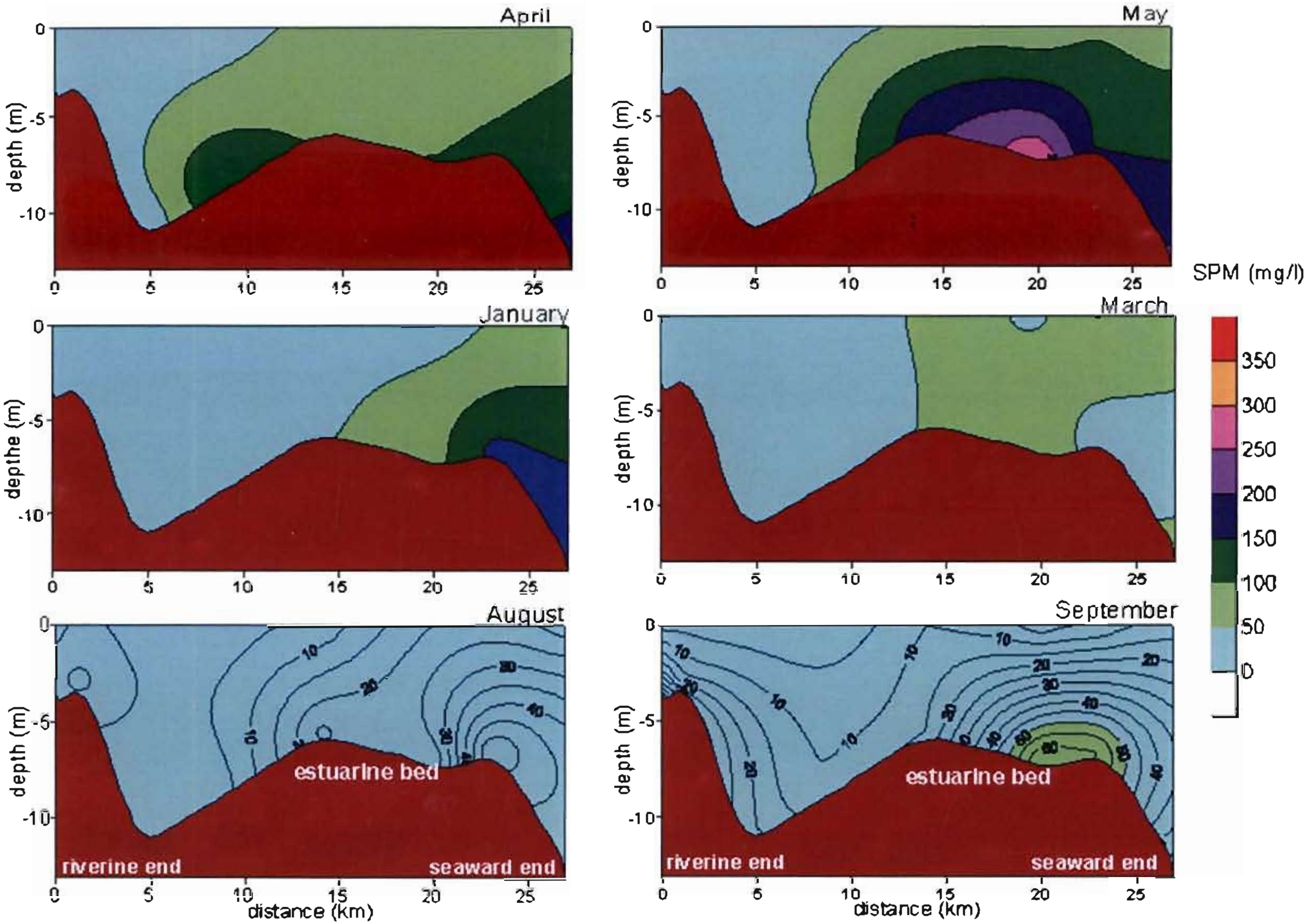


Fig.11a.Longitudinal sections of SPM during August 1998- May 1999 in Cochin estuary (southern arm)

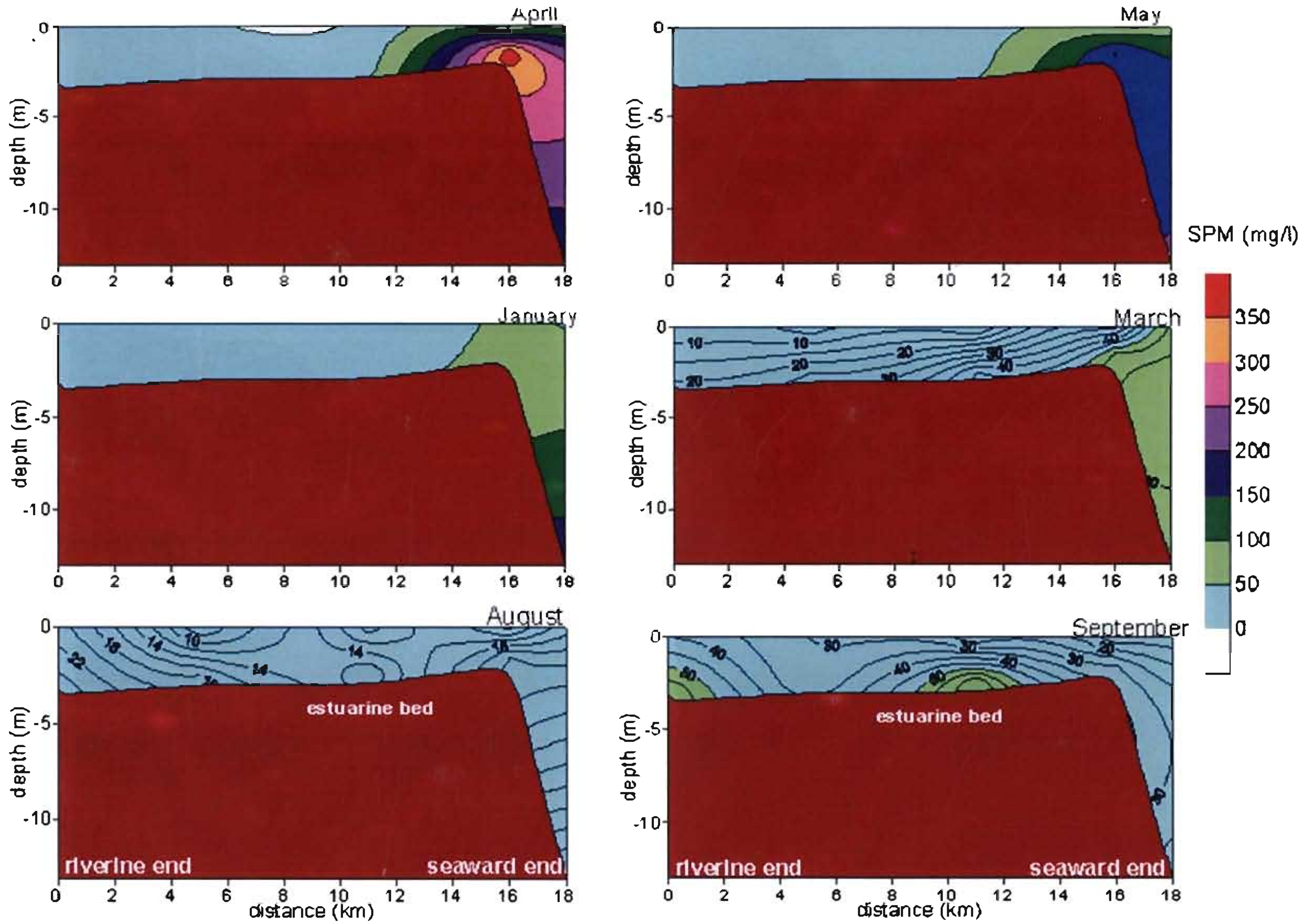
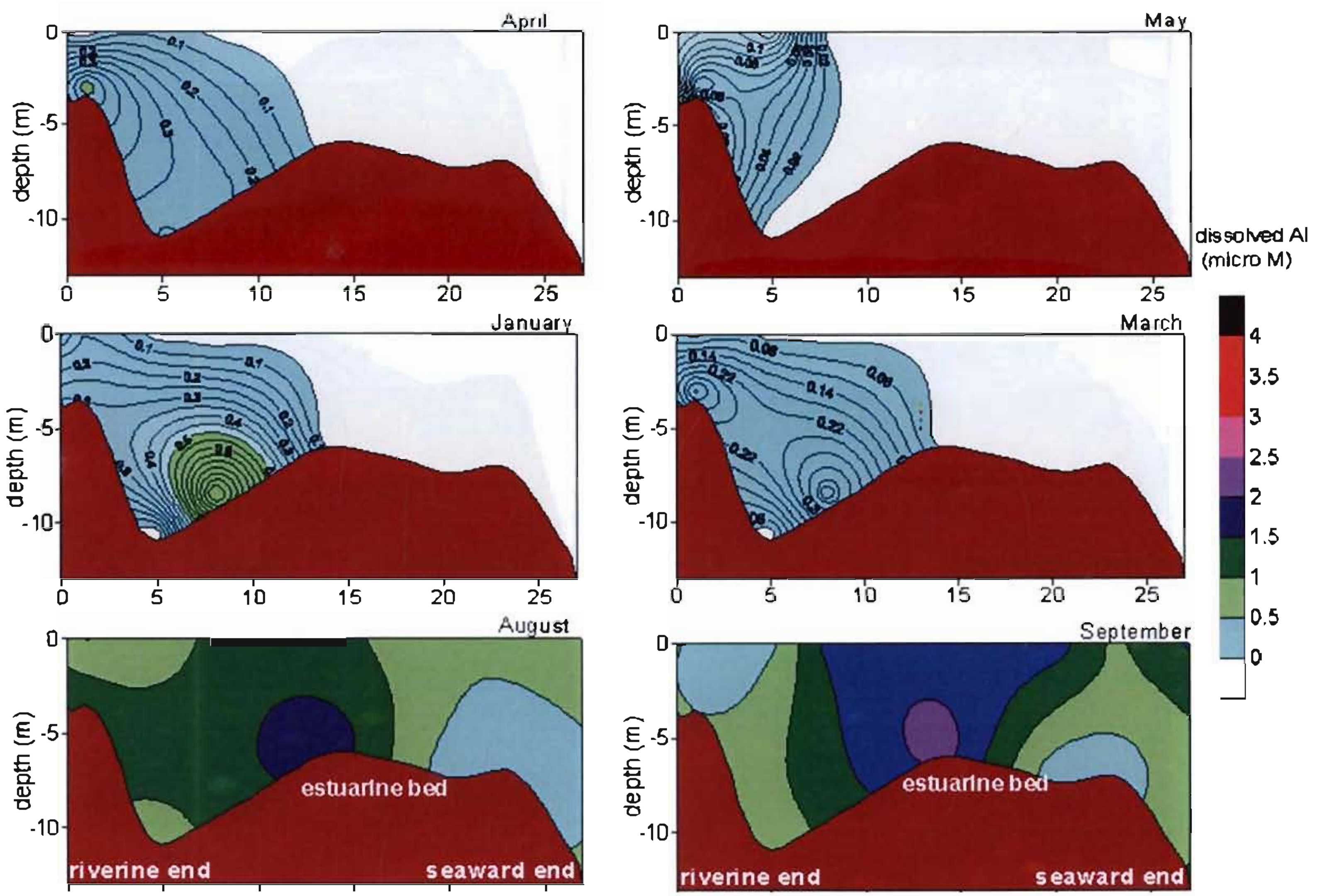


Fig.11b.Longitudinal sections of SPM during August 1998- May 1999 in Cochin estuary (northern arm)


April
May
January
March
August
September
depth (m)
0
-5
-10
0
5
10
15
20
25
dissolved Al
(micro M)
4
3.5
3
2.5
2
1.5
1
0.5
0
estuarine bed
riverine end
seaward end

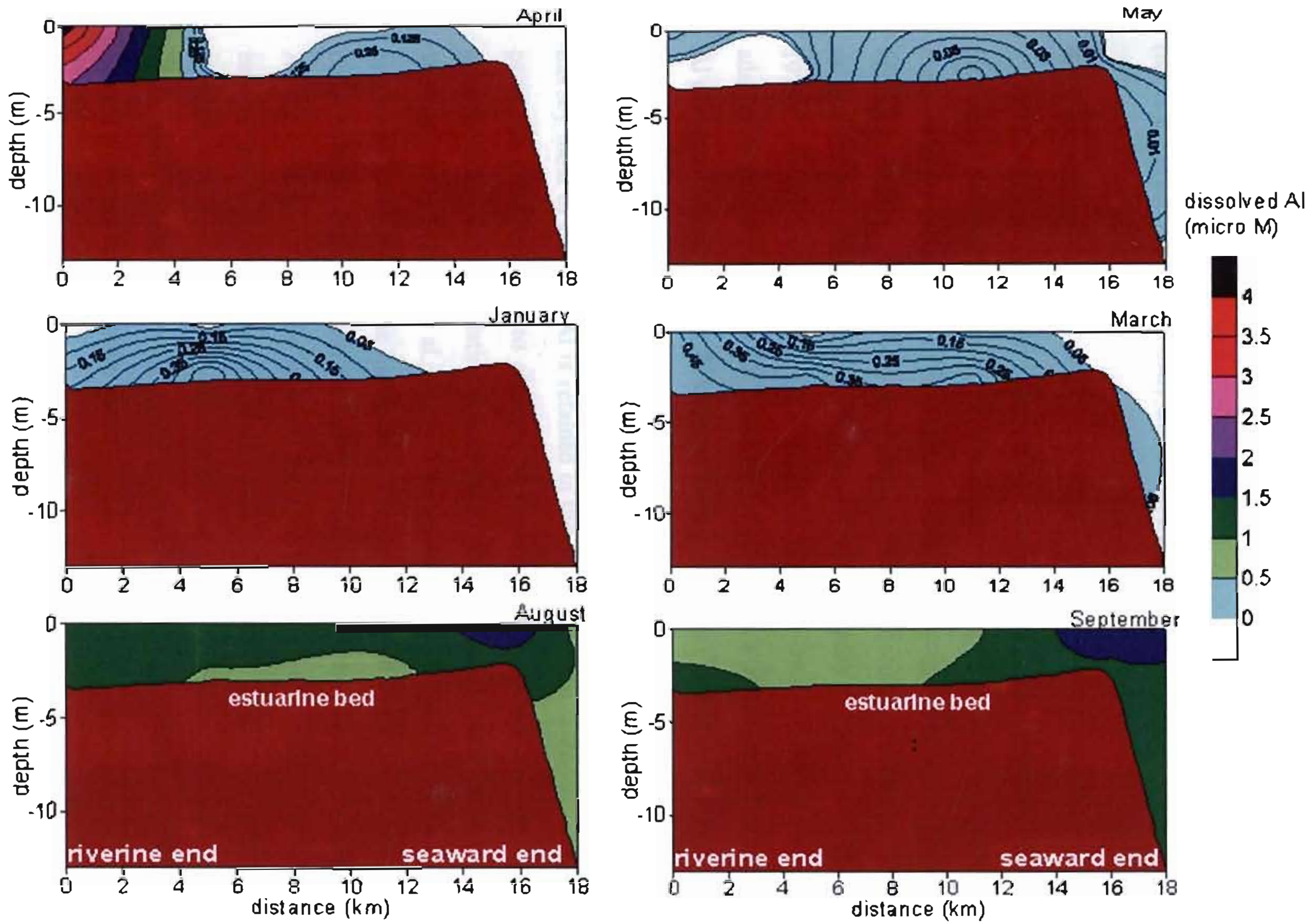


Fig.12b.Longitudinal sections of dissolved Al during August 1998- May 1999 in Cochin estuary (northern arm)

mid estuarine region to the lower estuarine region; a fact, concurrently observed with the increase in salinity towards the seaward end along with presence of higher suspended matter. This statement is also supported from parameter interrelation graphs figs. 6 & 9 (increasing SPM or increasing salinity bring about considerable diminishing in dissolved Al values). The only exceptional condition in monsoon (northern arm) relates to the estuary being mostly exhibiting freshwater conditions.

3.3 Discussion

The investigations on dissolved Al and associated parameters have led to the following. Substantial amount of aluminium entering this estuary appears to be removed in the early stages of freshwater - seawater mixing. A portion, at low salinities in Cochin estuary, could be lost on adsorption, due to flocculation (of colloidal species) as reported elsewhere (Eckert & Sholkovitz, 1976; Hydes & Liss, 1977; Sholkovitz, 1978). Rivers mainly carry un-flocculated clay minerals, whose surfaces acts as adsorption sites for aqueous Al^{3+} and $[Al(OH)_4]^-$ species with the formation of adsorbed Al clay complex controlling Al concentration in solution (Walker et al., 1988). A rapid decrease in salinity during the rainy season reduces flocculation of the suspended particles in the upstream regions. Further on, it's settling down stands diminished, thereby most of the total Al is retained in the dissolved form. Terrigenous river-borne particulates are sensitive to changes in estuarine environments and are irreversibly coagulated and this coagulation process starts at low salinities itself (Krauskopf, 1956; Wollast, 1973; Edzwald et al., 1974). This phenomenon appears to hold true in Cochin estuary as inferred from the longitudinal section on Al. On aggregation, these particles come onto the estuarine/riverine bed from the water column. Thus, it is proposed that Al adsorbed on the surface of very fine (clay) particles are trapped on entering the estuary and are coagulated on mixing with saline water. The hydrodynamic factors (Postma, 1967) might further augment the deposition of riverine suspended sediments at the convergence of the two opposing flows accelerating a net sedimentation in the upstream portion of the Cochin estuary.

As far as the dissolved Si is concerned, it may be irreversibly adsorbed onto the river-borne clay particles as well as freshly precipitated colloidal hydroxides of Al and Fe, which provide surfaces for adsorption and undergo sedimentation (Li, 1981). The adsorbed Si neither undergoes de-sorption nor dissolution on resuspension of the suspended particles in the lower reaches of the estuary. A decrease in dissolved Si values is noted for the northern arm as the season progresses from monsoon to premonsoon through postmonsoon. The reduction in the amount of dissolved Si during the premonsoon period could be a result of continuous removal processes due to the long residence time of water masses in the upper estuary arising out of low river runoff and dominating seawater influx. The continuous removal of Al and Si from solutions in the low ionic strength estuarine waters hints at incorporation of Al, Si (and cations) into authigenic mineral structures.

The suspended load in the uppermost region of Cochin estuary is due to riverine transport alone and there appears no contribution from resuspended estuarine bottom sediments. With the progressive weakening of the tidal energy spectrum, it is believed that the contribution of sediment from resuspension in the upper estuary is at a minimum. This is explicit from the SPM vs. salinity plot (fig.4). Hence, it appears that a major fraction of low-salinity removal of dissolved Al is due to adsorption onto riverine suspended particulates in contrast to the Al removal onto resuspended sediments in the Tamar estuary (Morris et al., 1986). However, it does not exclude the possibility of a fractional removal onto resuspended particles provided these particles are depleted with adsorbed Al content and/or possess unsaturated adsorption sites.

The main features observed in Cochin estuary are summarized as follows: dissolved Al in Cochin backwaters is mostly concentrated within the salinity range of 0-10 psu. Beyond this salinity value, Al is sparingly detected. The dissolved Al distribution within the salinity range 0–10 psu is due to combined removal and input processes taking place in the estuary. During monsoon time, whole of the estuary falls within salinities of 5 psu, owing to high river influx and further dilution and hence presence of Al is observed through out the estuary. Thus we can infer that the source of Al into this estuary is exclusively riverine and the removal of dissolved Al from solution is complete at very low salinity itself, often noted in premonsoon and post monsoon periods as of course reported elsewhere (referred to earlier) depending on the prevailing hydrographical conditions.

There must be some mechanism, as listed below, by which the seawater concentration of Al is limited. The low concentration of Al in seawater arises from the tendency for Al^{3+} to hydrolyse into polymeric colloidal forms (Stumm & Morgan, 1970), which are easily destabilised in saline solutions by the presence of electrolytes (Eckert & Sholkovitz, 1976). Hozakowa et al., (1970) and Hydes & Liss (1977) have detected significant removal of dissolved Al during estuarine mixing which is partially attributable to the preferential coagulation of Al polymers in the size range 0.10-0.45 µm. It is also suggested that the presence of suspended matter in low saline waters accelerate the process of dissolved Al removal from water, which is further substantiated by similar observations made in Mandovi estuary (Upadhyay & Sen Gupta, 1995) and Upper St. Lawrence estuary (Takayanagi & Gobeil, 2000). Thence, the dual control on estuarine Al behaviour is attributed to the ionic properties of seawater and the reactive behaviour of suspended particulate matter.

The riverine particulates on adsorbing Al from solution, settles down and are believed to be deposited at the sites of removal itself (low flow conditions), not exposing themselves to the outgoing tide to be carried to the lower estuary in the southern arm. This happens to be the reason why the resuspended sediments in the lower estuary do not act as a source of dissolved Al in the southern arm. Thus it is concluded that dissolved Al behaviour in Cochin estuary is governed by combined action of various factors; river influx, tidal sediment disturbance, flocculation, adsorption onto SPM and authigenic mineral formation. Flocculation process generally aids the removal of dissolved Al in the mid estuarine region on the southern arm, low salinity values being quite favourable. Removal by sorption process is also significant in turbid zones, in both the arms.

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 (eg. 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:

Salinity range (psu)	% Aluminium decrease (independent of initial value)	Slope (difference in concentration at lower and higher salinities vs. salinity variation)	Comments
3 – 5	6.14	4.4	Mild change
5 – 10	52.80	37.0	Very rapid variation
10 – 15	6.60	2.2	Mild change
15 – 20	4.50	1.6	Mild change
20 – 25	27.70	8.2	Moderate change
25 – 30	61.80	13.2	Considerable variation

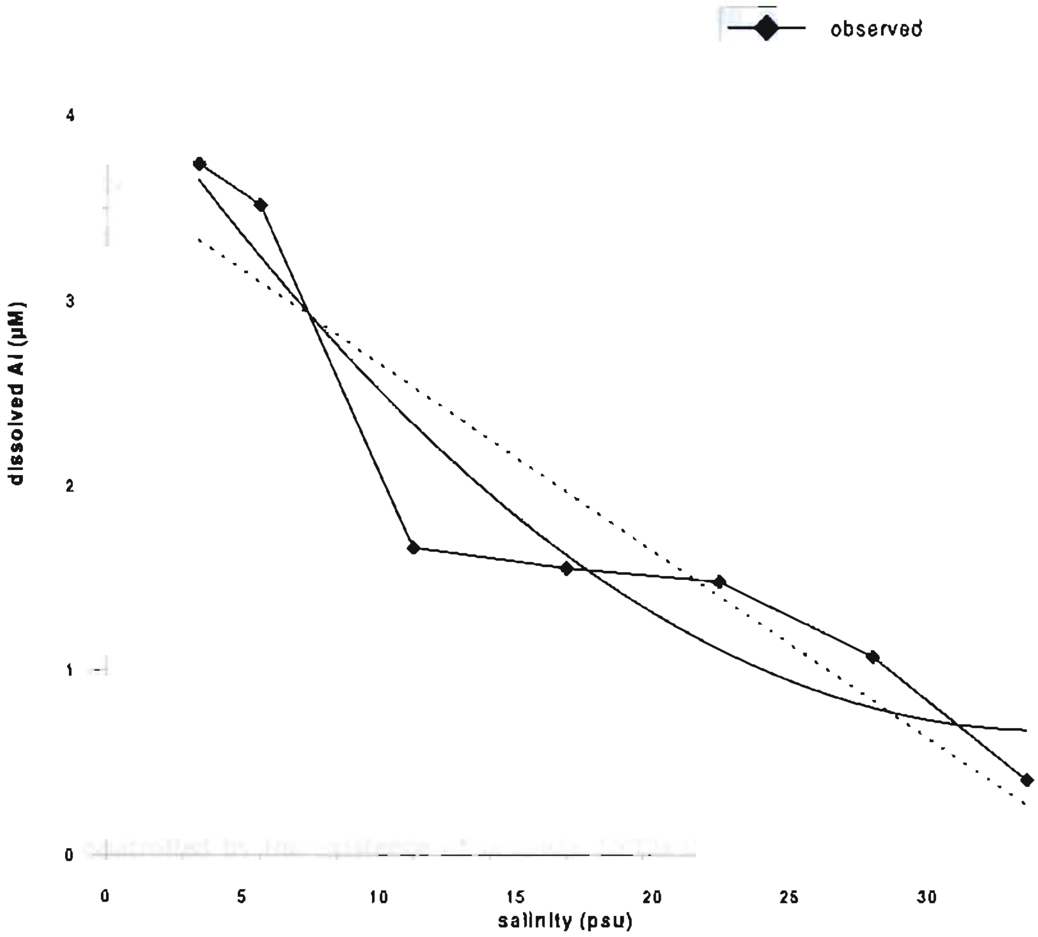
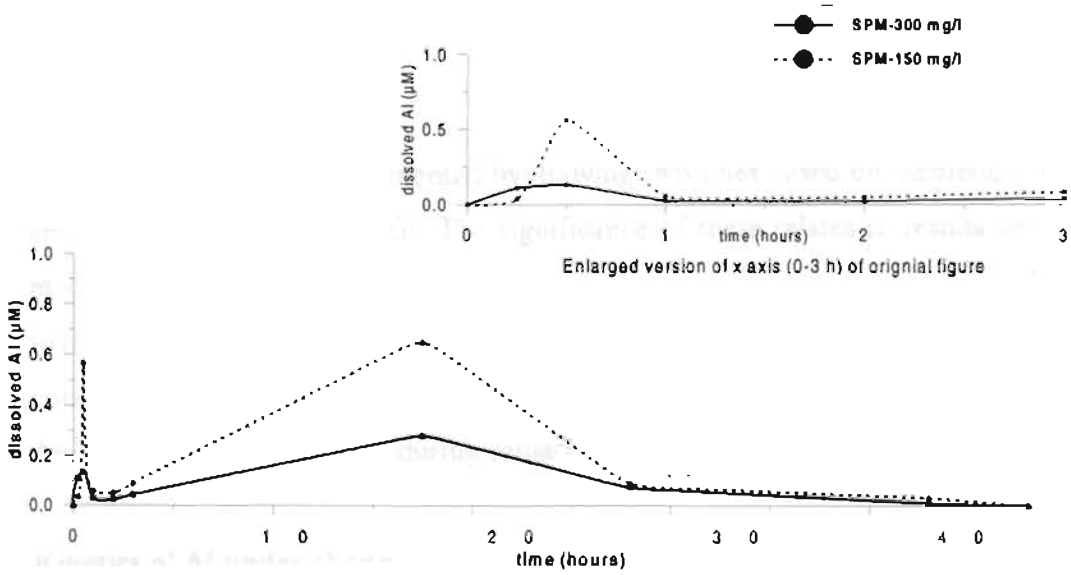


Fig.13.Mixing experiment: Dissolved Al vs. salinity. The broken line indicate theroretical dilution line between the two end members. The solid line is drawn by polynomial curve fit.



Enlarged version of x axis (0-3 h) of orignial figure

Fig.14.Dissolved Al vs. time for different conentrations 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:

Water sample	salinity (psu)	Al concentration (μM)
Distilled Water	0	near detection limit
Tap Water	0	2.04
River Water	3	3.56
Brackish Water	19	0.67
Sea Water	31	near detection limit

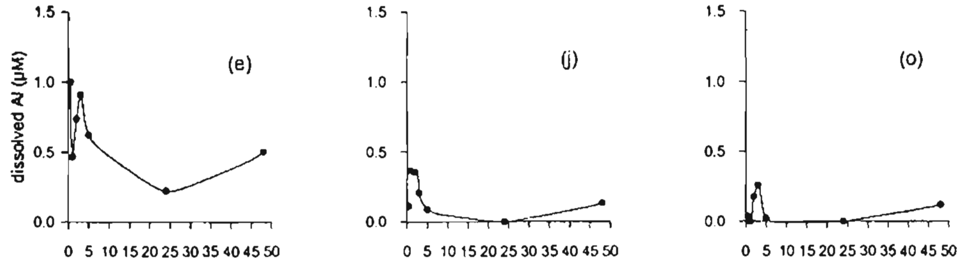
Sediment samples selected:

- 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



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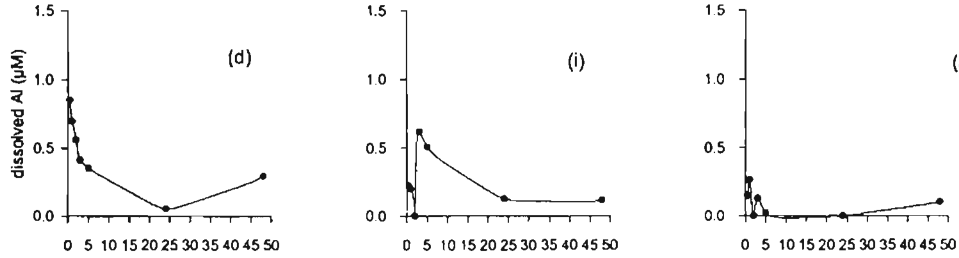

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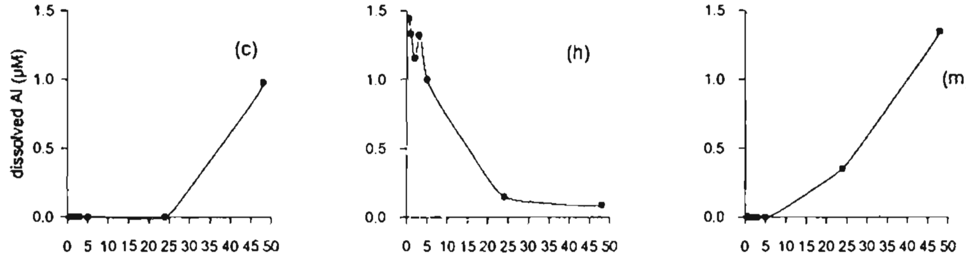

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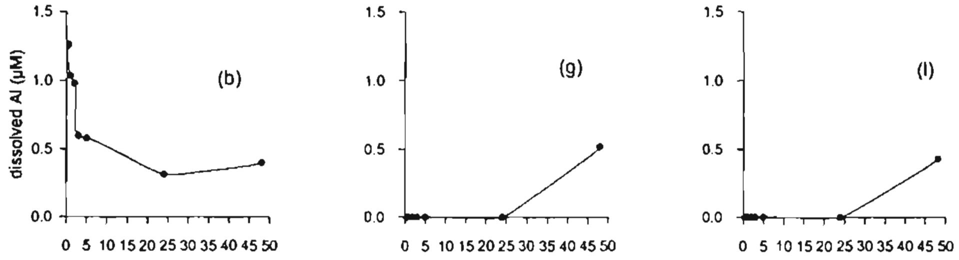
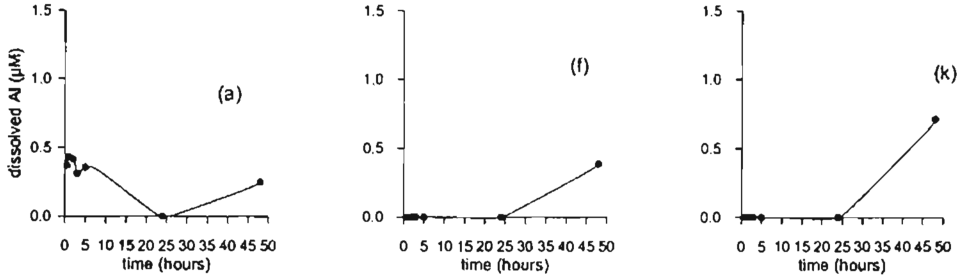


Tap Water & Riverine Sediment Tap Water & Brackish Sediment Tap Water & Sea Sediment



Distilled Water & Riverine Sediment Distilled Water & Brackish Sediment Distilled Water & Sea Sediment

Fig.15.Dissolved Al as a function of time in mixing experiments

concentrations for an hour, reaching a peak of 0.43 µM, 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 µM 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 µM. 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 µM. After agitation, dissolved Al concentration changed to near the detection limit of the analytical method (0.002 µM) 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 µM 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 (0.002μM) 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 upto 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 helps 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 (0.67µM) 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).

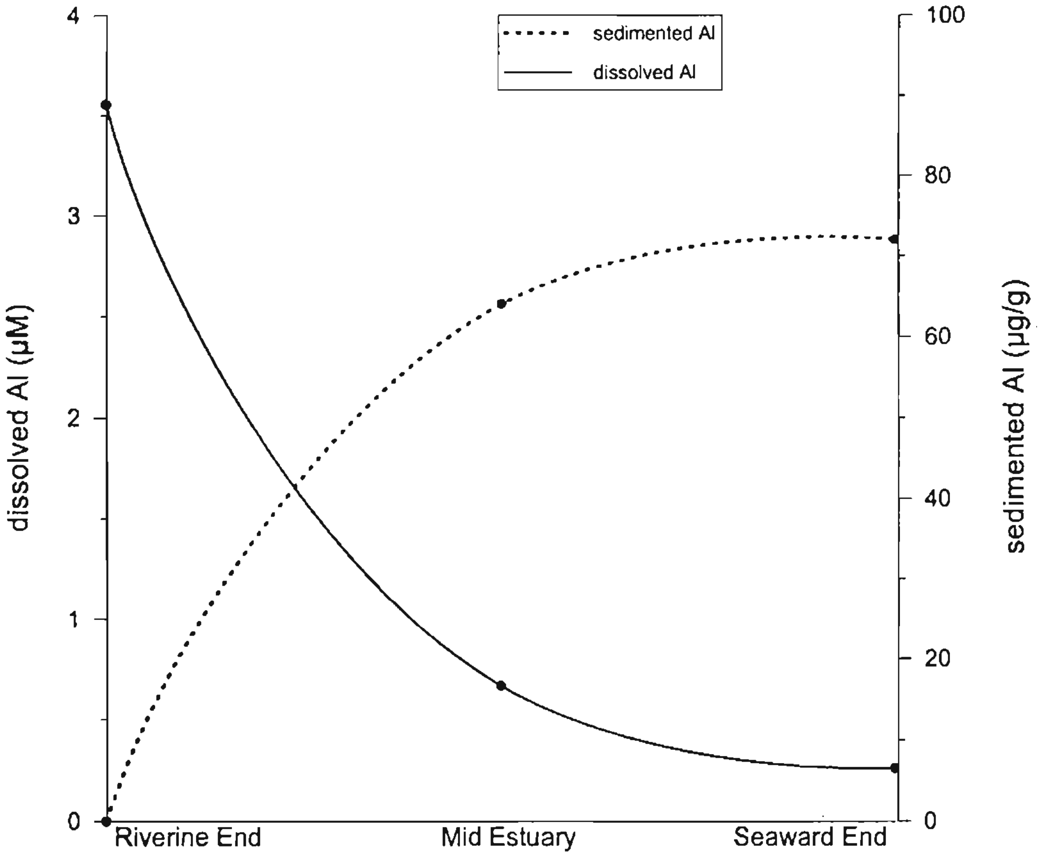


Fig.16.Variability of dissolved and sedimented Al through different reaches of Cochin estuary - representative figure

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 energic 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:

$$K_p = \frac{C_p \times 10^6}{C_d \times S} \tag{1}$$

where C_p is the particulate chemical concentration (μM), C_d is the dissolved chemical concentration (μM), 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 0.241x 10^5 ml/g in the upstream regions with low suspended particulate matter and 0.102 x 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 x 10^6 – Moran & Moore, 1989; 10^5 –Hydes & Kremling, 1993, 0.26-7.92 x 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.

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.

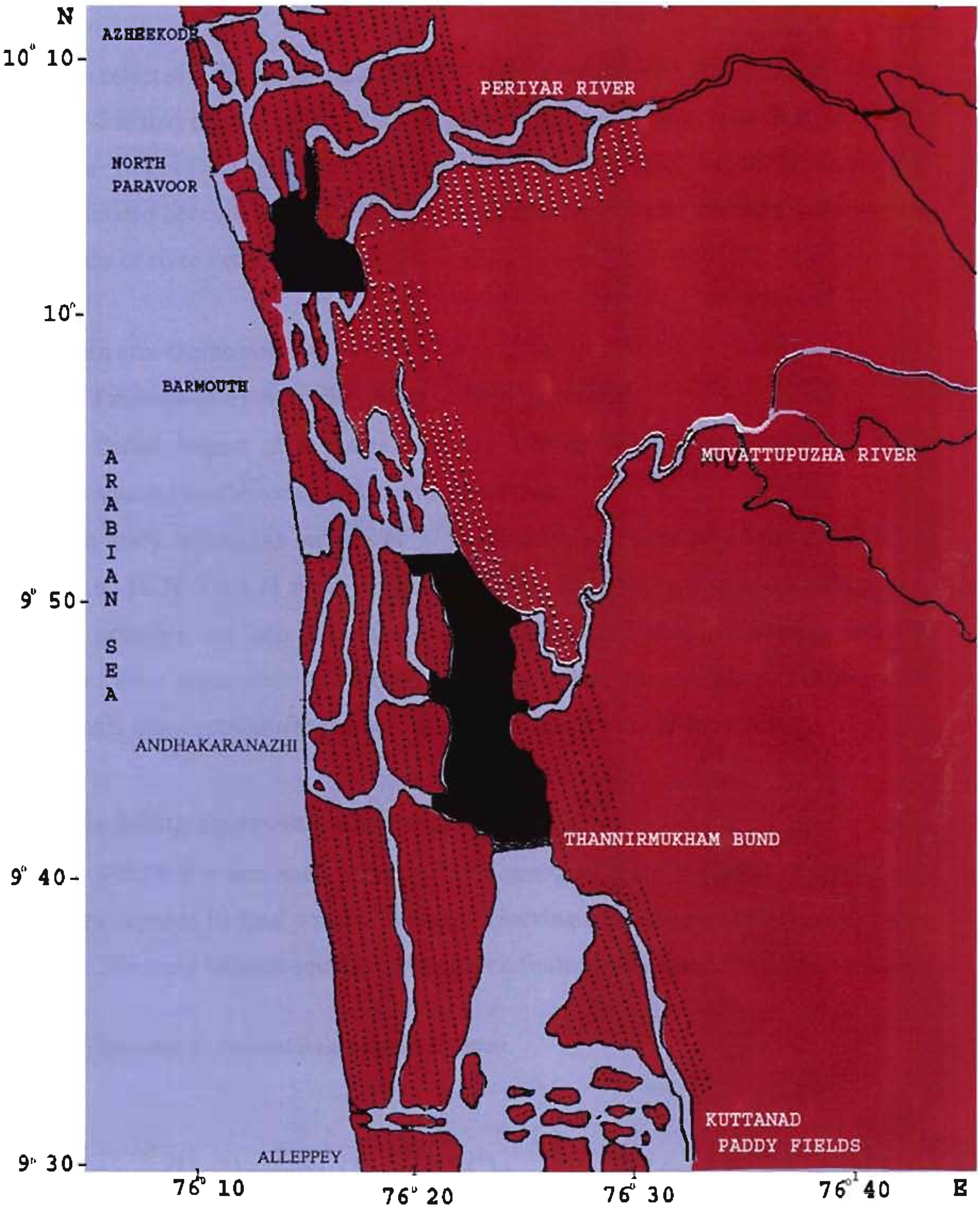


Fig.17. Cochin Estuary with study area as shaded region

- 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 km^2, a volume of 1.107 x 10^8 m^3, 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 km^2, a volume of 7.6668 x 10^8 m^3, 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

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(U_x C) - \frac{\partial}{\partial y}(U_y C) - \frac{\partial}{\partial y}(U_z C) + \frac{\partial}{\partial x}\left(E_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(E_z \frac{\partial C}{\partial z}\right)$$

$$+ S_L + S_B + S_K$$

where:

C = concentration of the water quality constituent, mg/L or g/m^3
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:

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

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

Parameter	Value	References
Geo hydrological parameters		
Water column		
Volume (m^3)	Northern arm-1.107x 10^8 Southern arm-7.6668 x 10^8	Calculated
Depth (m)	Northern arm-3.25 Southern arm-7.83m	Observed
Velocity (m/s)	Northern arm-0.1058 Southern arm-0.1422	Average flow for all months
Flow rate (m^3/s)	Variable	Central Water Commission data set (1998-99)
Benthic sediment		
Volume (m^3)	Northern arm-0.17028x10^8 Southern arm-0.48958x10^8	Calculated by using depth
Depth (m)	0.5	Assumed
Velocity (m/s)	0	Assumed
System parameter		
Water column		
Initial Al concentration (mg/l)	Northern arm-0.03190 Southern arm-0.02538	Observed
Solids concentration (mg/l)	Northern arm-17.5 Southern arm-3.33	Observed
Al loading (kg/day)	Time variable	Concentration data available calculated using average flow
Solids loading (kg/day)	Time variable	Central Water Commission data set (1998-99)
DOC (mg/l)	Northern arm-4.0 Southern arm-4.0	Approximated based on Rini, 2002
Temperature	Time variable	Observed
pH	Time variable	Observed
Benthic sediment		
Initial concentration (mg/l)	0	Assumed
Solid concentration (mg/l)	Northern arm-515480 Southern arm-558880	Calculated from density and moisture content (density- unpublished data, moisture content-Bava-1996)
DOC (mg/l)	Northern arm-4.0 Southern arm-4.0	Assumed
Temperature	Time variable	

pH	Time variable	Bava, 1996
Constant parameters		
Partition coefficient to solids (l/kg)	0.241×10^5	Calculated based on observed data
Partition coefficient to DOC (l/kg)	Northern arm-1.26×10^6 Southern arm-2.95×10^6	Calculated based on observed data
Log Acidity constant	-4.9	Stumm & Morgan, 1981
Activation energy of the dissociation reaction (kcal/mol)	11.49	Calculated
Exchange-Molecular diffusion coefficient (m^2/s)	1×10^{-10} m^2/s	WASP 6 Manual
Solid settling velocity (m/s)	0.02	Calculated using Stokes equation

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 0.241×10^5 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).

$$C_p = f_p\, C_T \qquad C_d^f = f_d^f\, C_T \qquad C_d^{DOC} = f_d^{DOC}\, C_T$$

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.

	DOC change (mg/l)-Northern arm				DOC change (mg/l)-Southern arm			
	3 to 4	4 to 5	20 to 40	40 to 60	3 to 4	4 to 5	20 to 40	40 to 60
Dissolved Al - Decrease ($x10^{-10}$ mg/l)	4.88	4.88	96.7	96.3	2.3	2.3	45.5	45.1
DOC sorbed Al – increase ($x10^{-5}$ mg/l)	0.95	0.95	18.9	18.9	0.52	0.52	10.1	10.1
Total sorbed Al – decrease ($x10^{-5}$ mg/l)	0.6	0.6	12	11.9	0.31	0.31	6.12	6.07

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 (H_2O) 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

ρ_s = density of sediment particle, 2-2.7 g cm^{-3}

ρ_w= density of water, 1 g cm^{-3}

g = gravitational constant, 981 cm s^{-2}

d_s = sediment particle diameter, mm

μ = 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 μm nominal diameter and 3-30 m/d for silts of 10-20 μm 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 1×10^{-10} m^2/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, $E_{(n)} = 89.381$ m^2/s

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

These values are applicable to the estuary in case the model is run for inter - connected 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

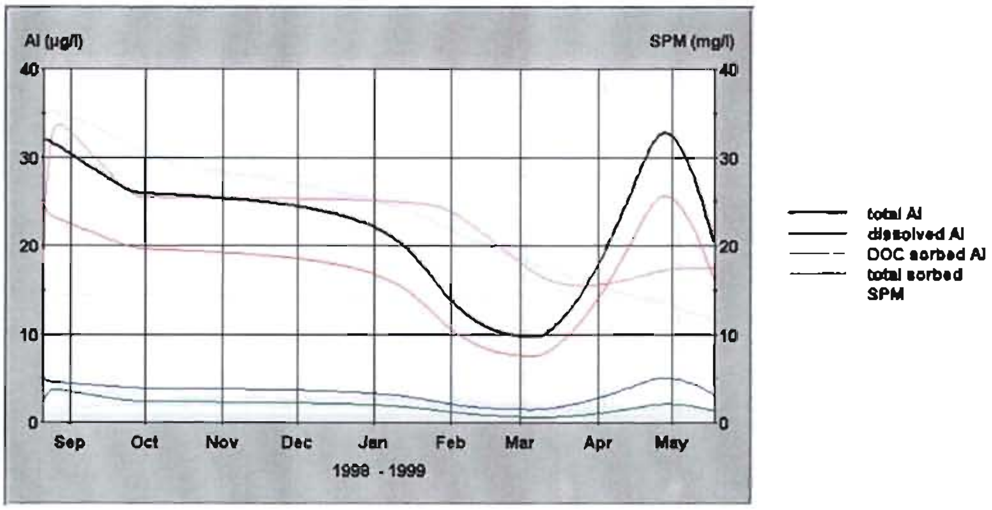
In the model (WASP 6.0), Al and SPM content were simulated to study the transport and transformation within the water column and bed sediment. Within the sub-model, TOXI, the simulated chemical 1 (Al) may occur in freely dissolved phase (dissolved Al), sorbed to DOC (DOC sorbed Al) and sorbed to solid 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 contributes 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.

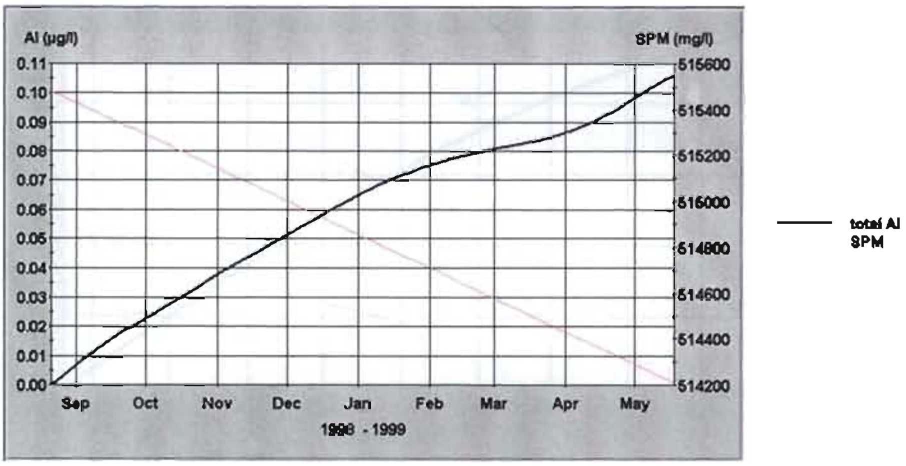
The dissolved organic substances play a vital role in biological (productivity), chemical (metal complexation, flocculation and absorption phenomena) and geological (sedimentation and early diagenesis) processes (Hayase & Shinozuka, 1995). Enrichment of DOC in the water column occurs through

Fig.18.Simulation results of Al and SPM-northern arm

Water column



Benthic segment



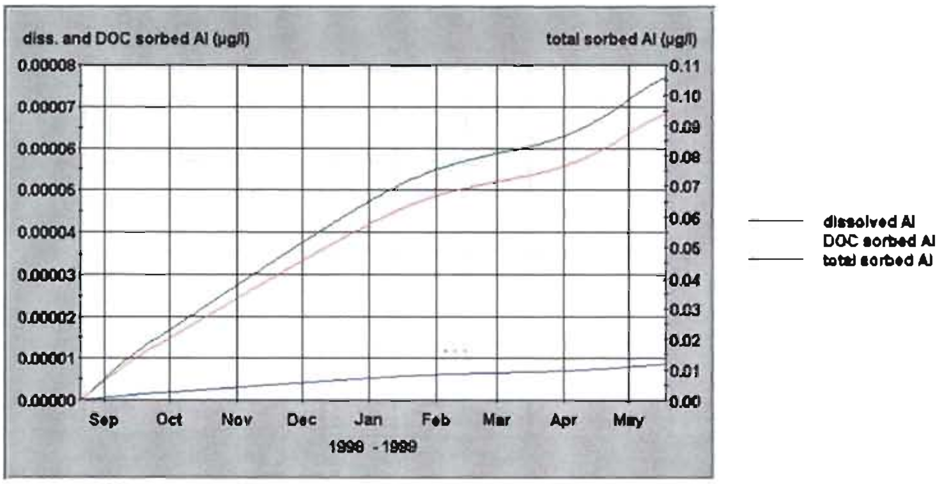
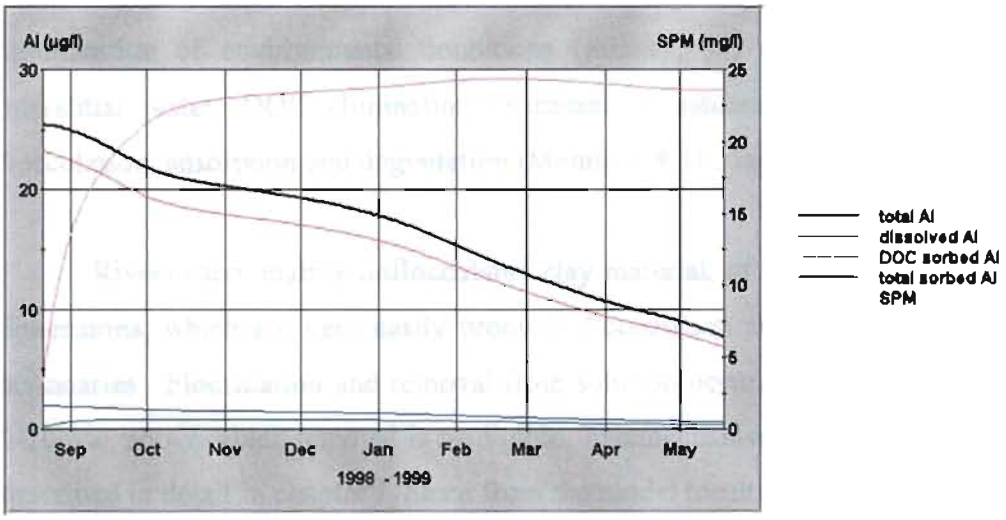
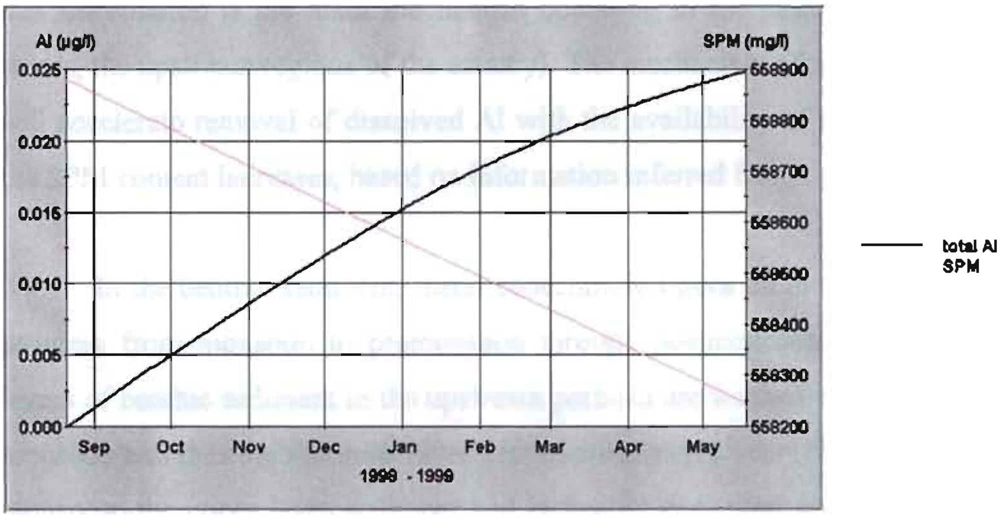


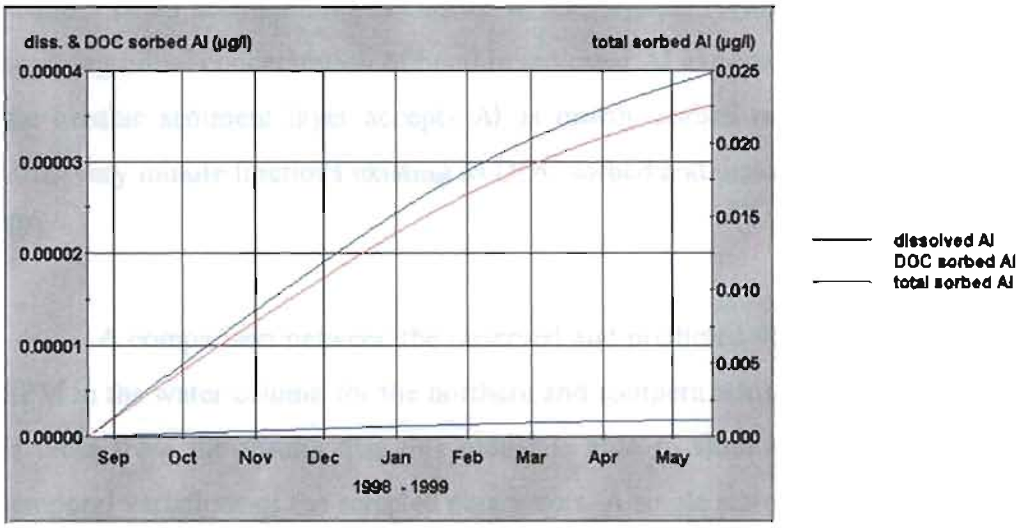
Fig.19.Simulation results for Al and SPM-southern arm

Water column



Benthic segment





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

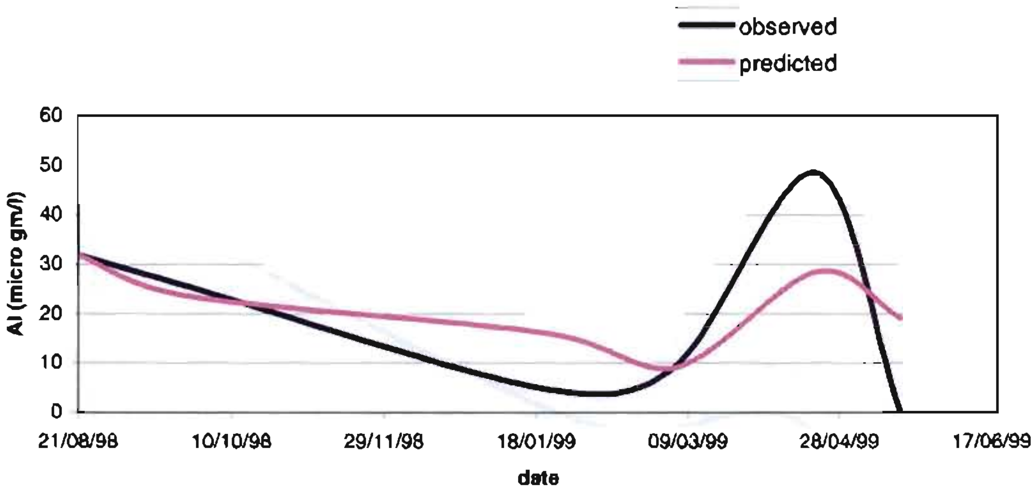


Fig.20b.Observed and predicted SPM in Cochin estuary-northern arm

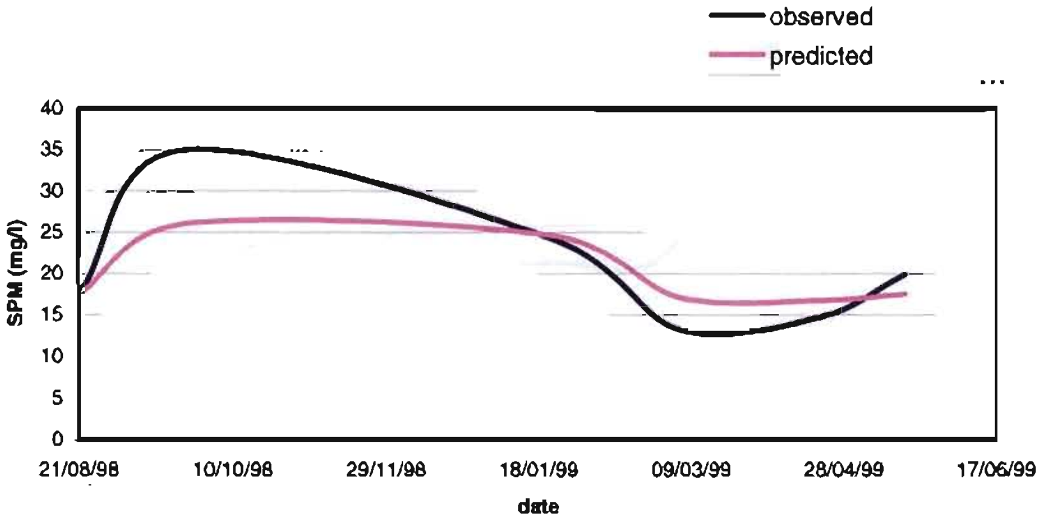


Fig.20c.Observed and predicted Al in Cochin estuary-southern arm

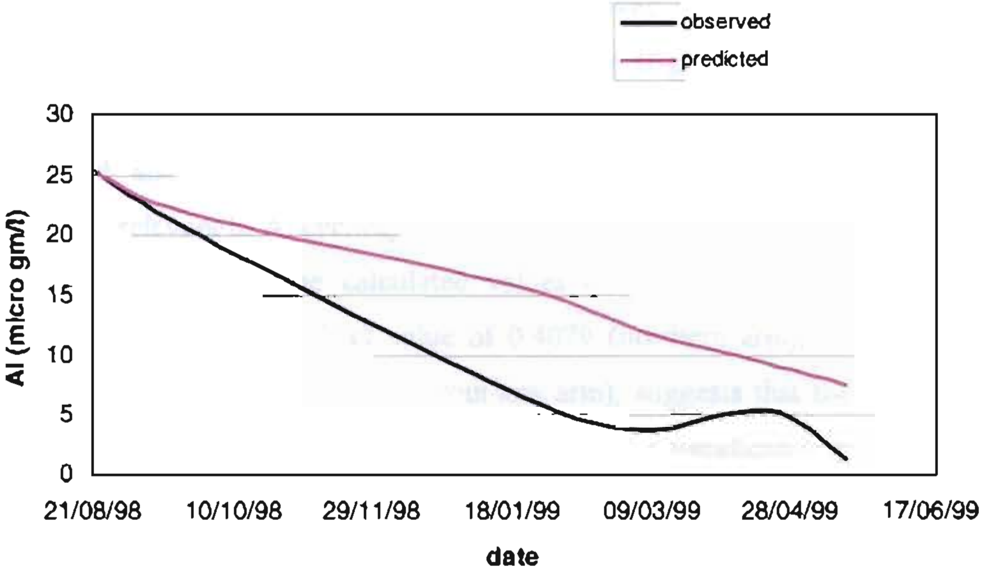
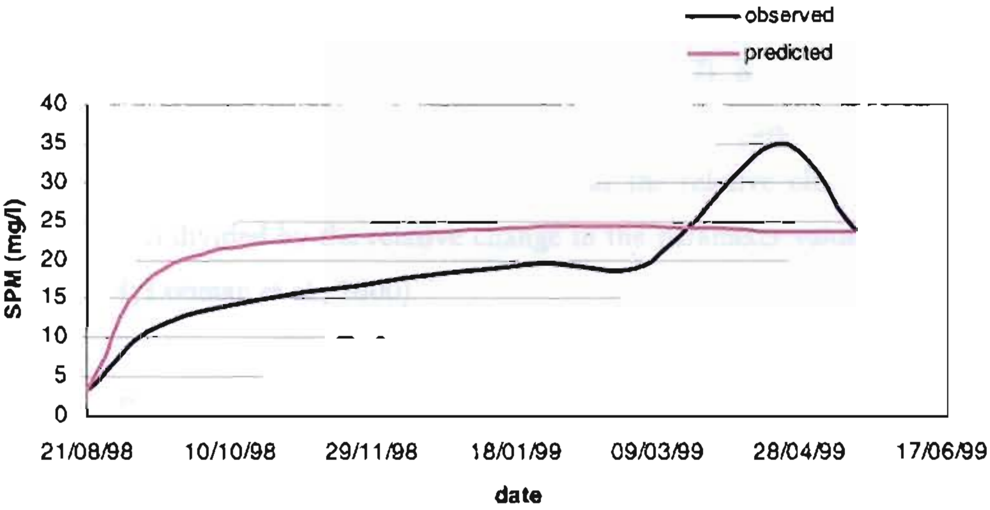


Fig.20d.Obseved and predicted SPM in Cochin estuary-southern arm



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).

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

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

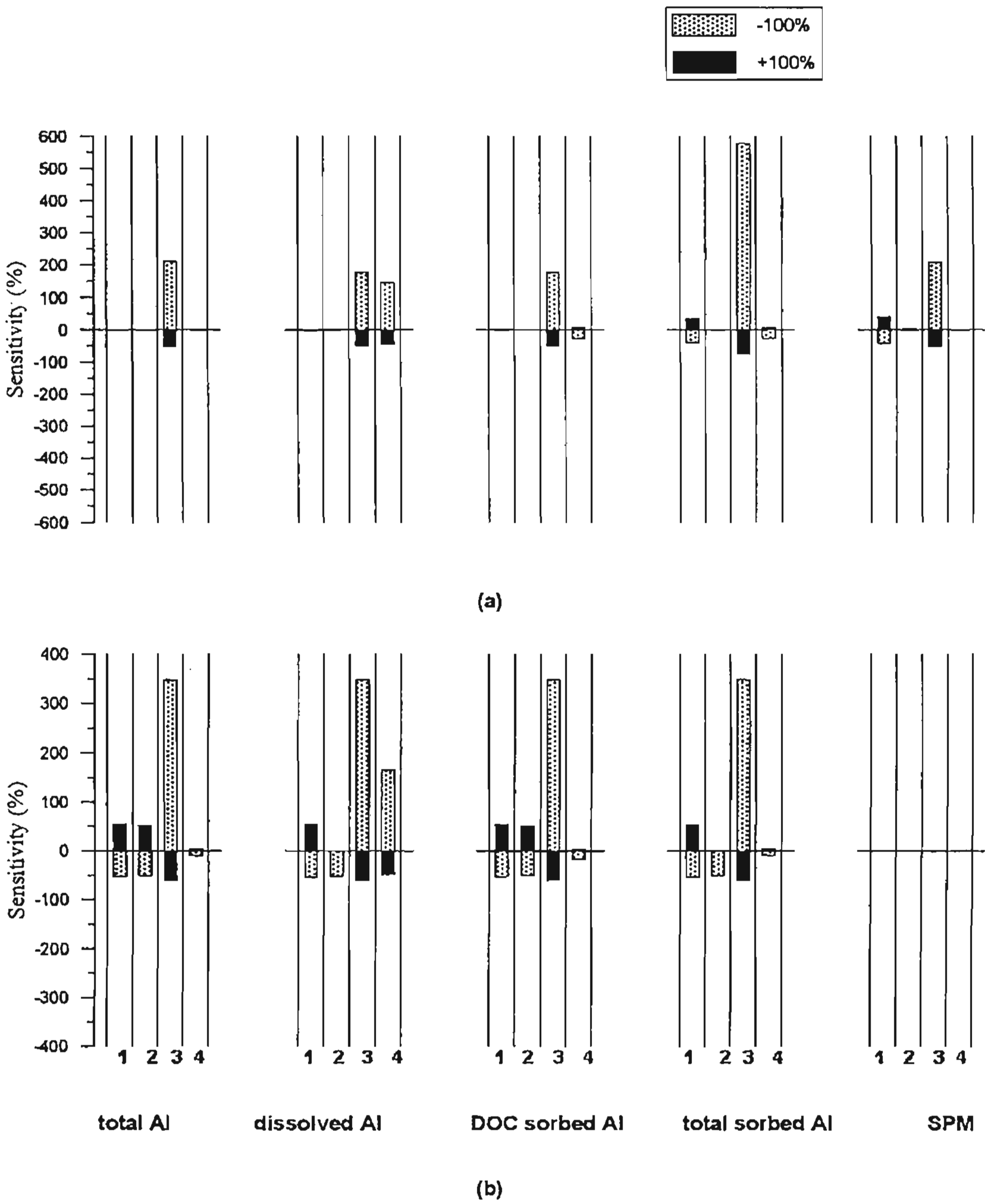


Fig.22a.Model sensitivity analysis in the (a)water column and (b)benthic segment for northern arm during 9 month simulation. 1-dispersion, 2-settling, 3-advection & 4-sorption

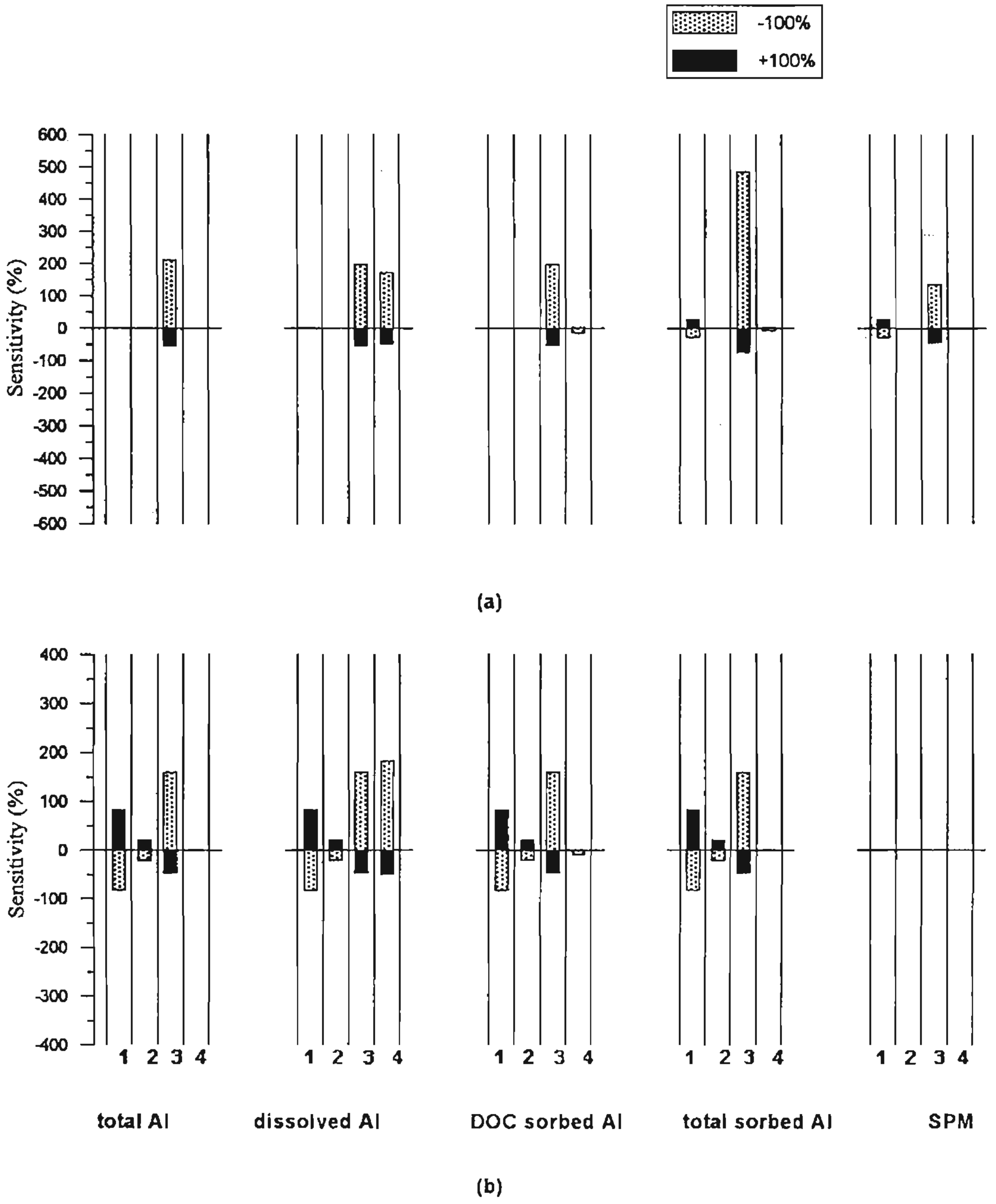


Fig.22b.Model sensitivity analysis in the (a)water column and (b)benthic segment for sourthern arm during 9 month simulation. 1-dispersion, 2-settling, 3-advection & 4-sorption

Table.2a. Sensitivity analysis results for northern arm

Parameter	% variation	Sensitivity (%)									
		Water column					Benthic sediment				
		tot Al	dis Al	DOC sorbed	tot sorbed	SPM	tot Al	dis Al	DOC sorbed	tot sorbed	SPM
diffusion	-100	0	2.98	2.97	-39.21	-41.16	-53.59	-53.88	-53.63	-53.59	0.12
	+100	0	-2.77	-2.77	36.41	41.06	53.52	53.72	53.41	53.32	-0.12
Settling	-100	0	0	0	0.02	0.02	-51.3	-51.48	-51.3	-51.3	0
	+100	0	0	0	-0.02	-0.02	51.49	51.49	51.29	51.29	0
advection	-100	211.04	178.22	178.22	579	209.84	347.49	348.79	347.49	347.49	0
	+100	-50.29	-48.14	-48.14	-74.14	-50.45	-61.03	-61.26	-61.03	-61.03	0
sorption	-100	0	189.1	-5.43	-5.44	0	-10.2	165.71	-17.09	-10.27	0
	+100	0	-49.3	1.41	1.40	0	4.13	-47.92	4.13	4.13	0

Table.2b. Sensitivity analysis results for southern arm

Parameter	% variation	Sensitivity (%)									
		Water column					Benthic sediment				
		tot Al	dis Al	DOC sorbed	tot sorbed	SPM	tot Al	dis Al	DOC sorbed	tot sorbed	SPM
diffusion	-100	0	1.06	1.06	-23.85	-24.73	-80.23	-80.57	-80.25	-80.23	0.06
	+100	0	-1.03	-1.03	23.33	24.71	80.16	80.56	80.19	80.16	-0.05
Settling	-100	0	0	0	0.01	0.01	-22.32	-22.40	-22.32	-22.32	0
	+100	0	0	0	-0.01	-0.01	22.32	22.40	22.32	22.32	0
advection	-100	236.22	221.16	221.16	578.15	163.45	214.05	214.85	214.05	214.05	0
	+100	-55.66	-54.8	-54.8	-75.86	-47.61	-52.08	-52.28	-52.08	-52.08	0
sorption	-100	0	171.56	-14.21	-7.28	0	-1.63	182.44	-8.76	-1.63	0
	+100	0	-48.05	3.89	3.9	0	0.88	-49.56	0.87	0.88	0

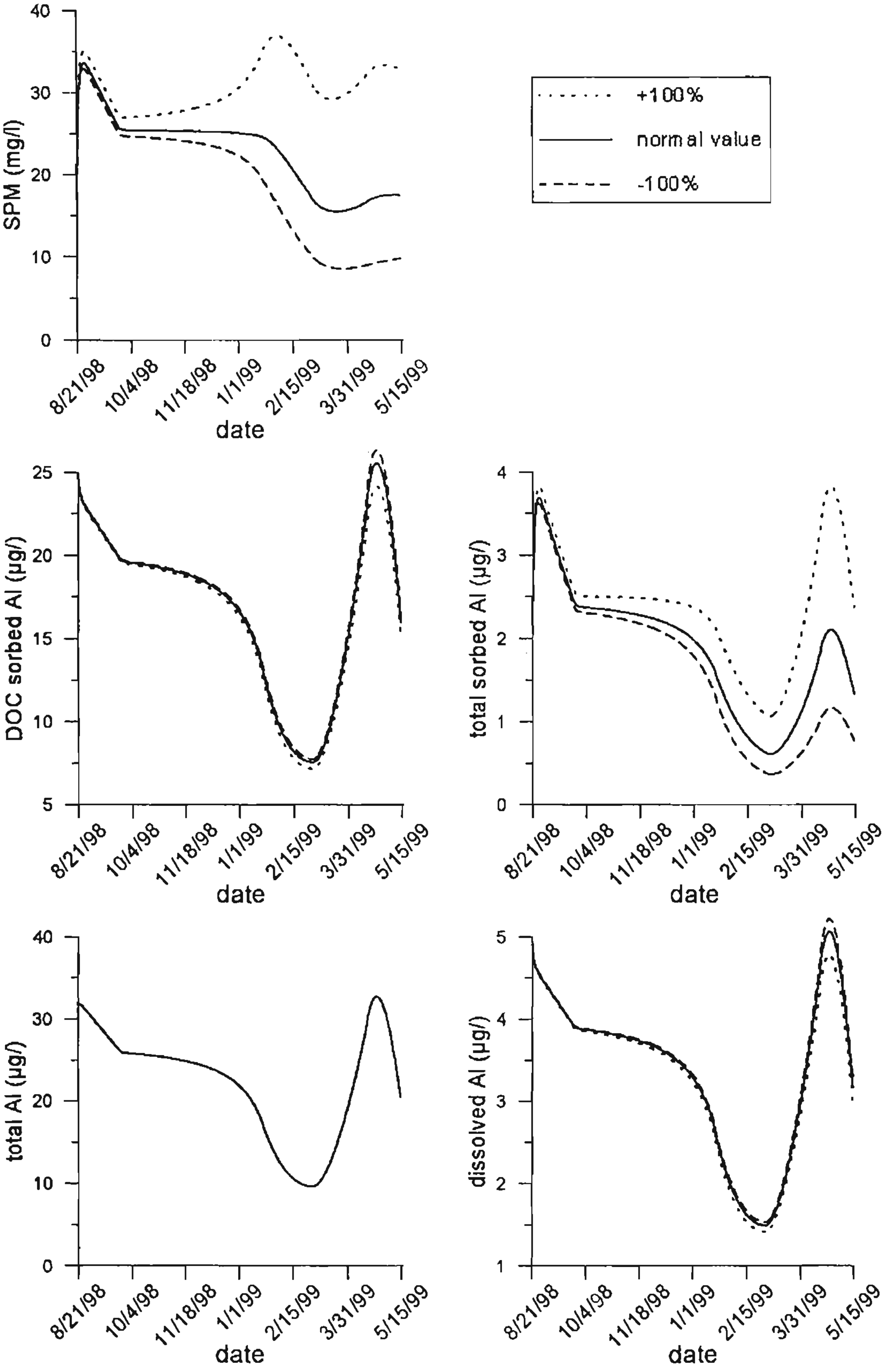


Fig.23a.Model sensitivity analysis for diffusion - northern arm - water column

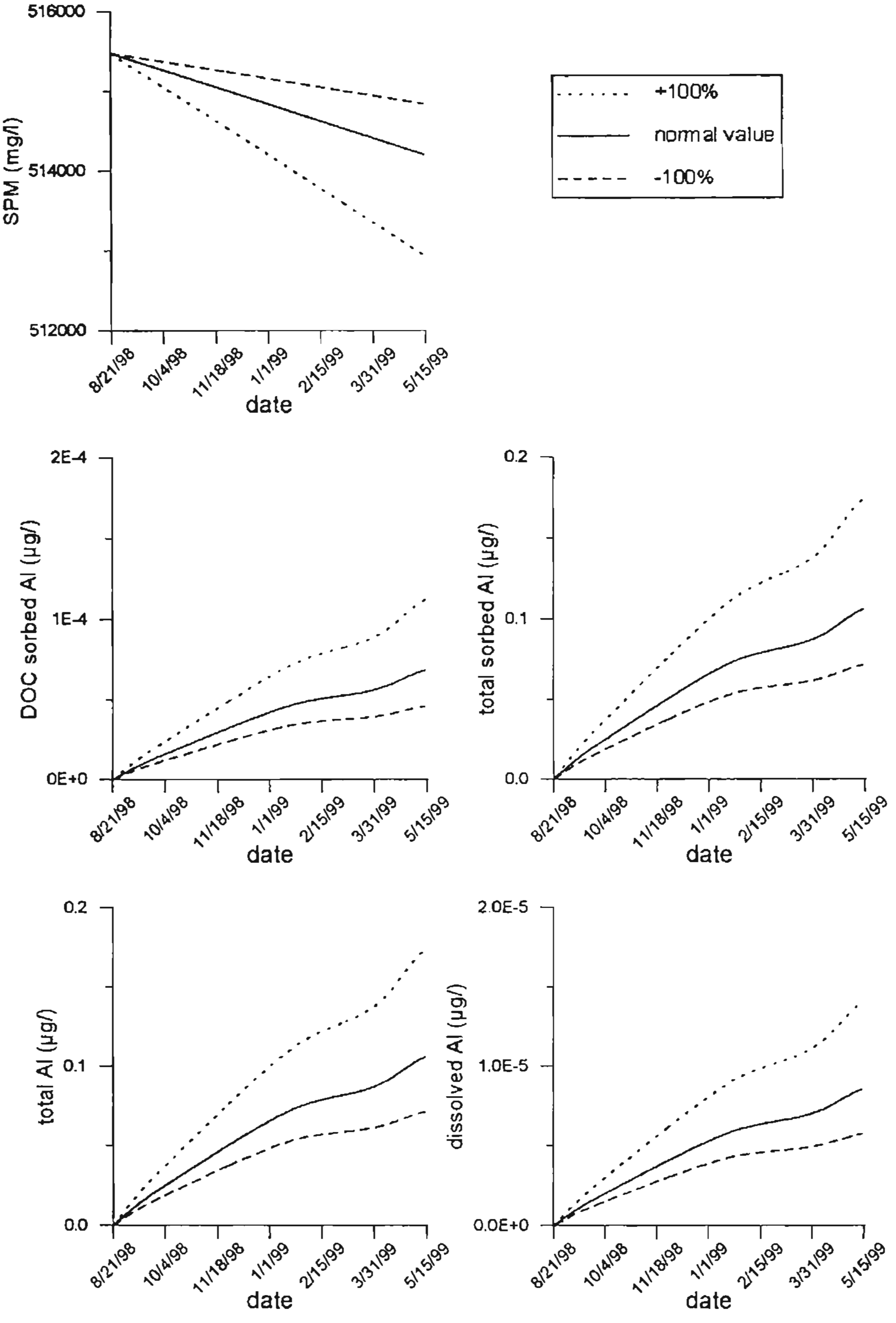


Fig.23b.Model sensitivity analysis for diffusion - northern arm - benthic segment

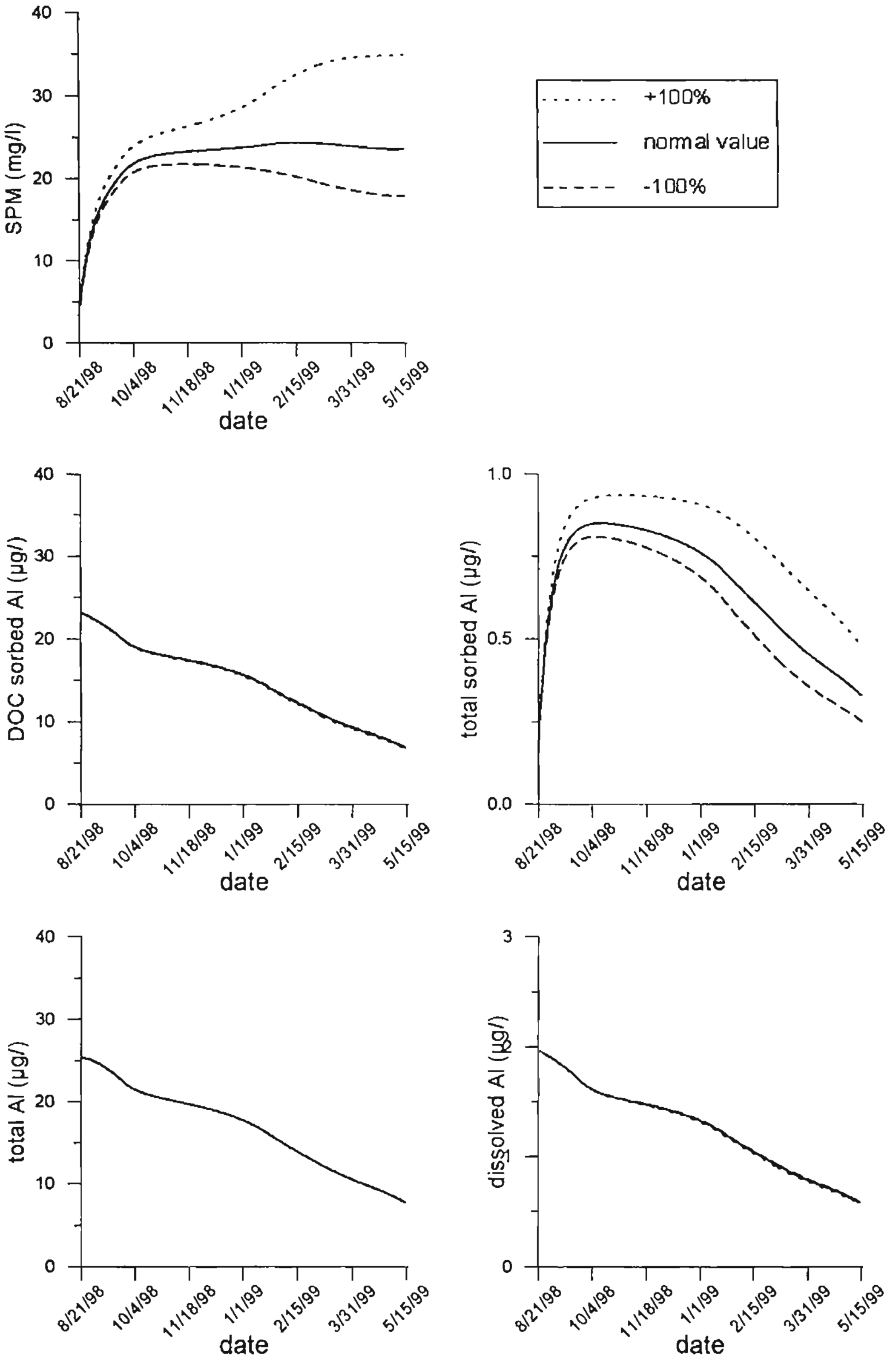


Fig.23c.Model sensitivity analysis for diffusion - sourthern arm - water column

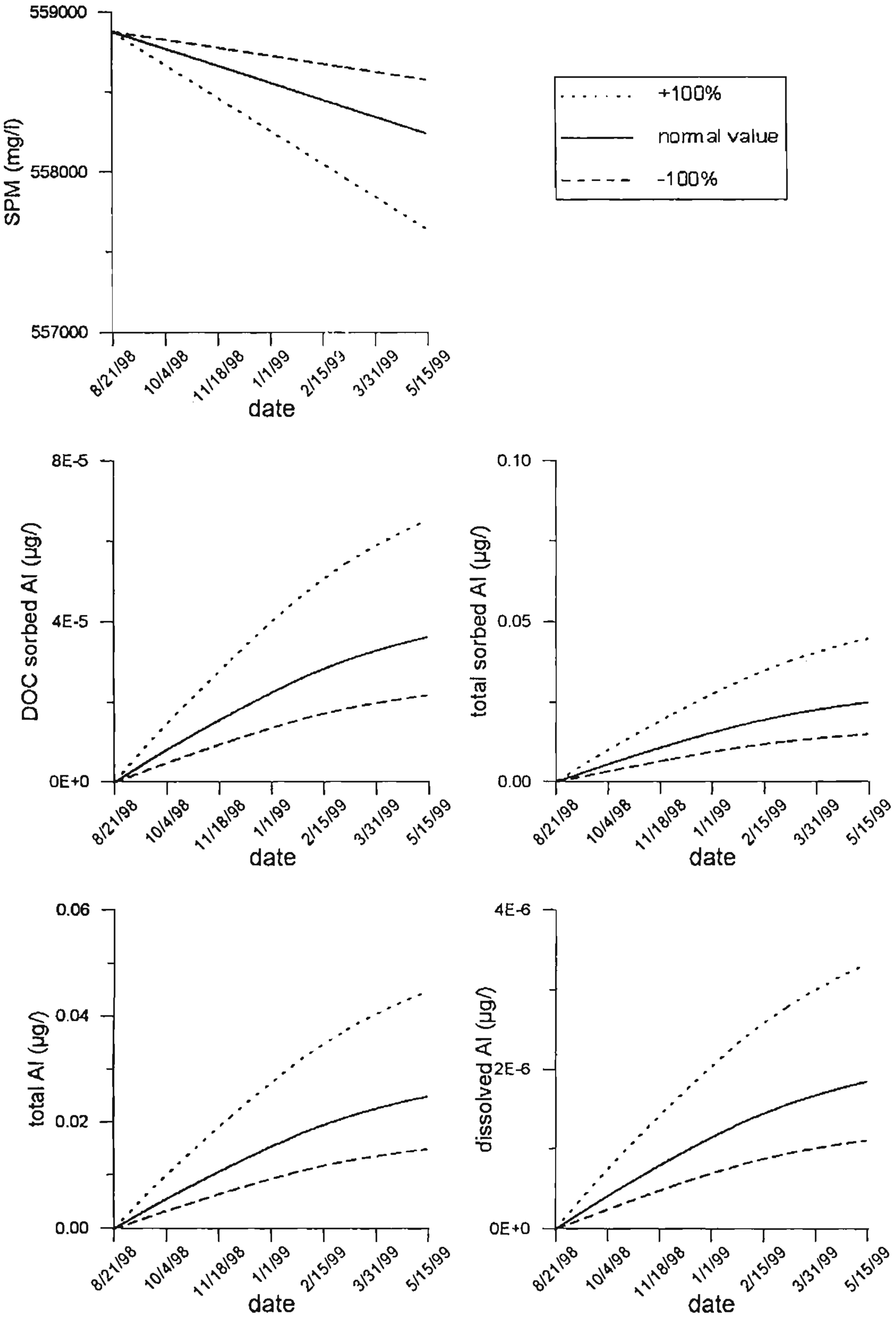


Fig.23d.Model sensitivity analysis for diffusion - sourthern arm - benthic segment

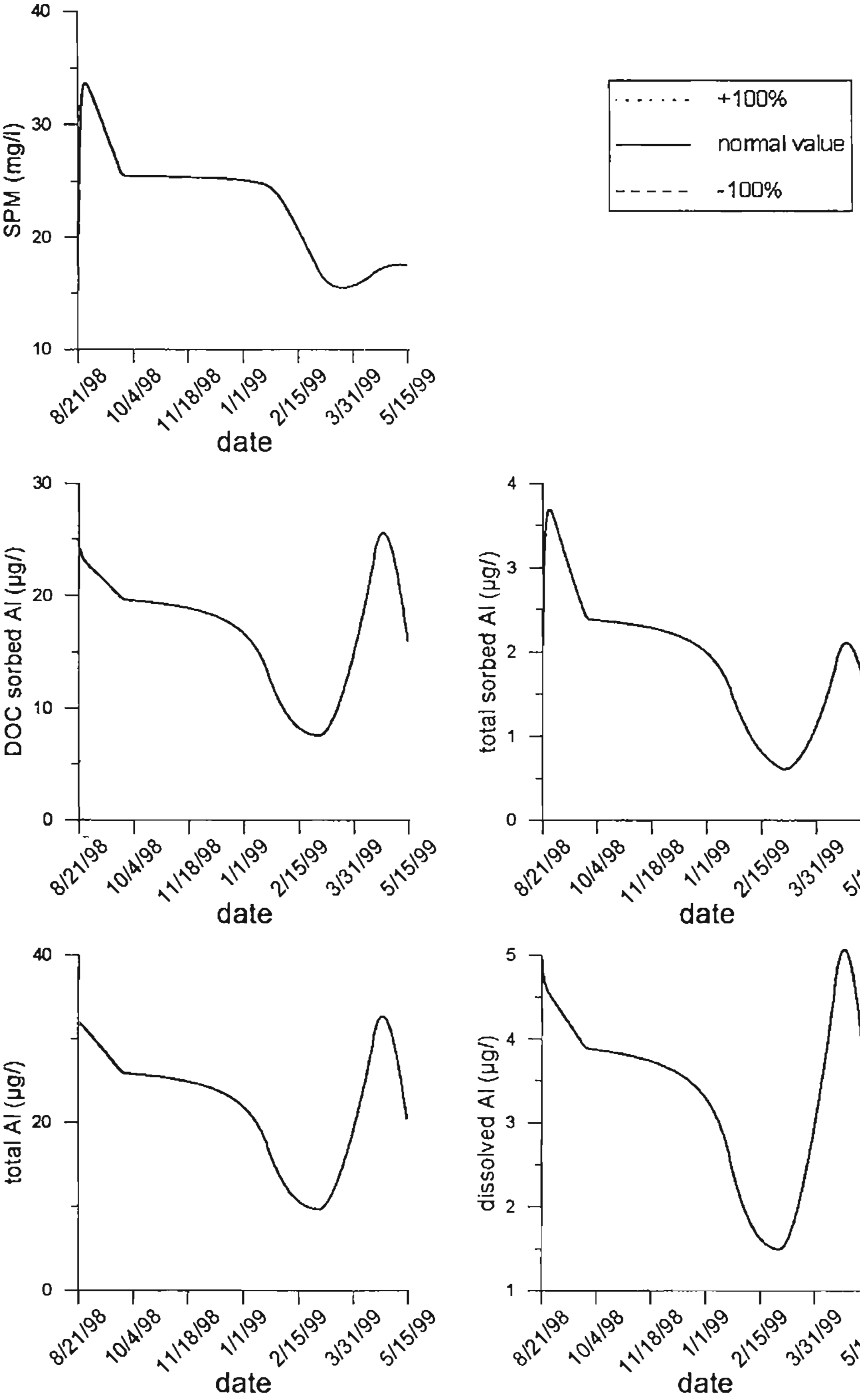


Fig.24a.Model sensitivity analysis for settling - northern arm - water column

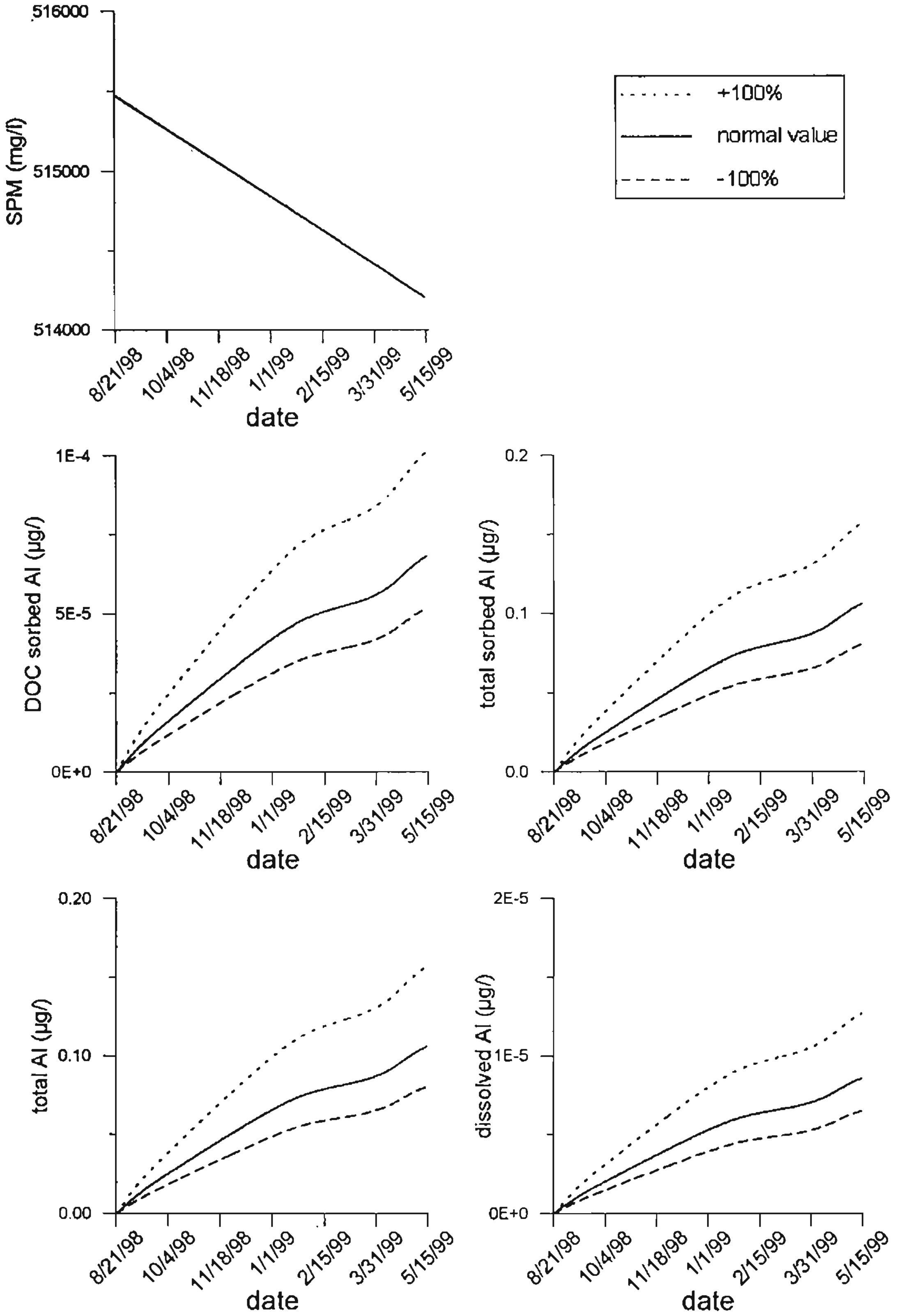


Fig.24b.Model sensitivity analysis for settling - northern arm - benthic segment

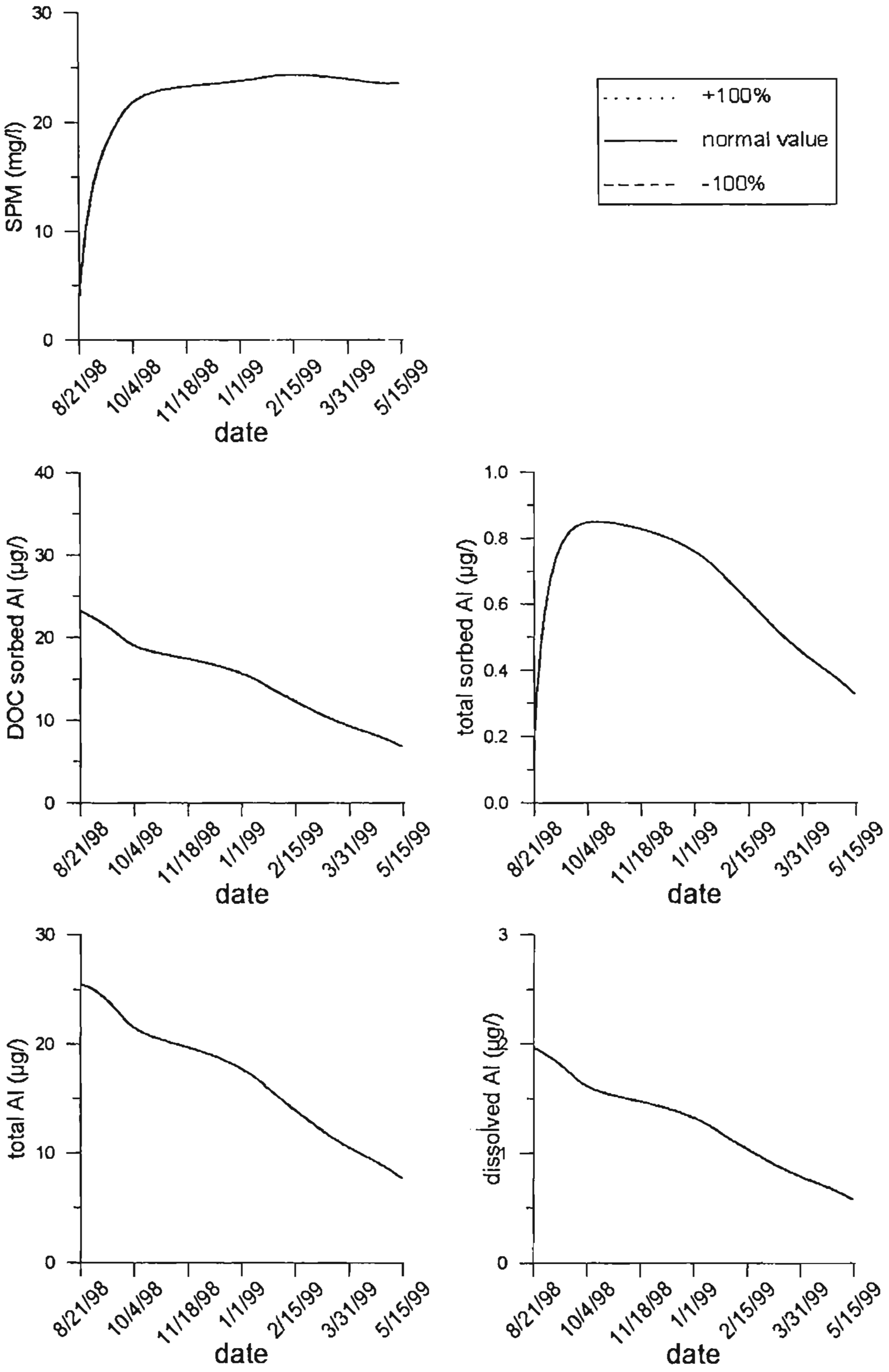


Fig.24c.Model sensitivity analysis for settling - southern arm - water column

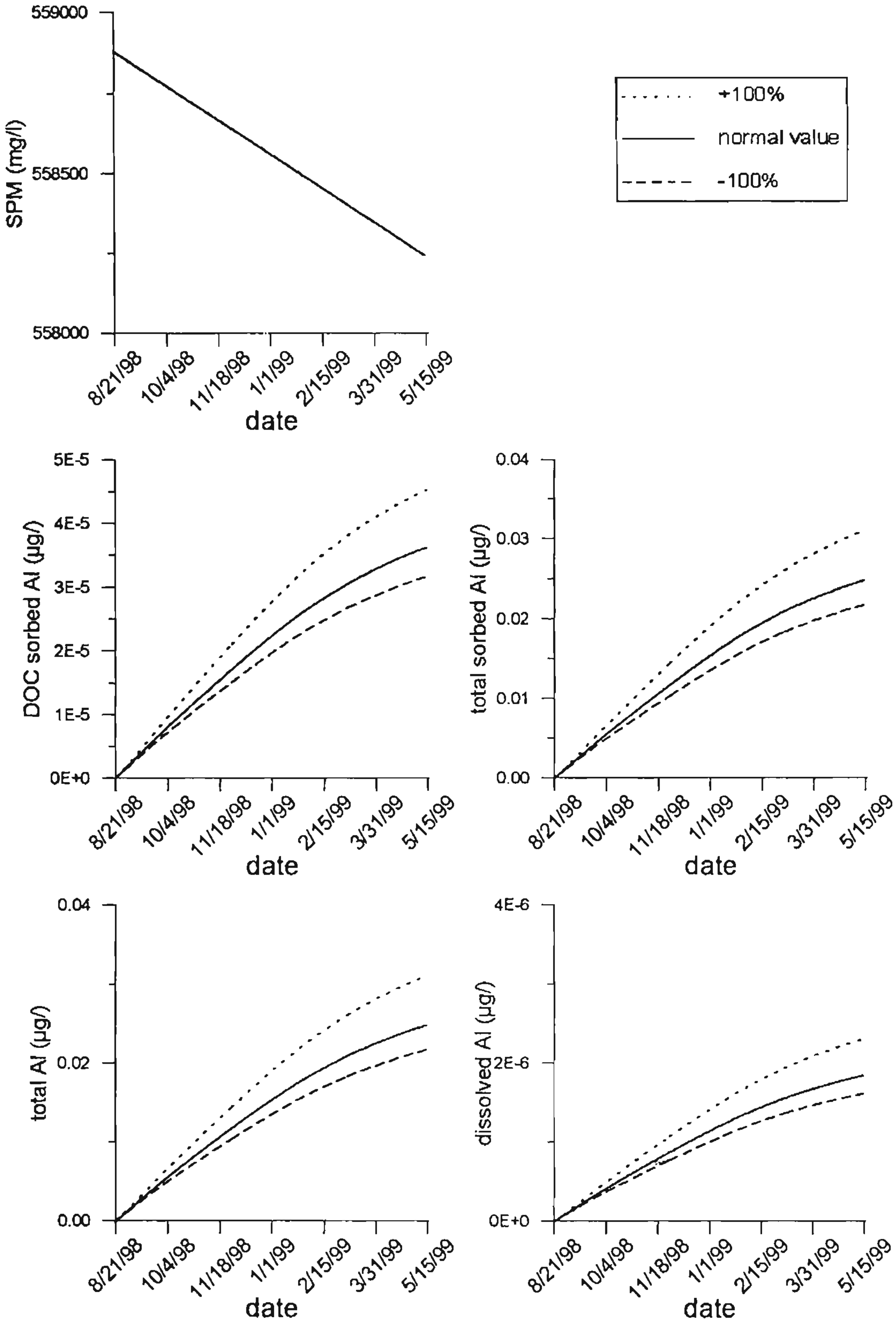


Fig.24d.Model sensitivity analysis for settling - southern arm - benthic segment

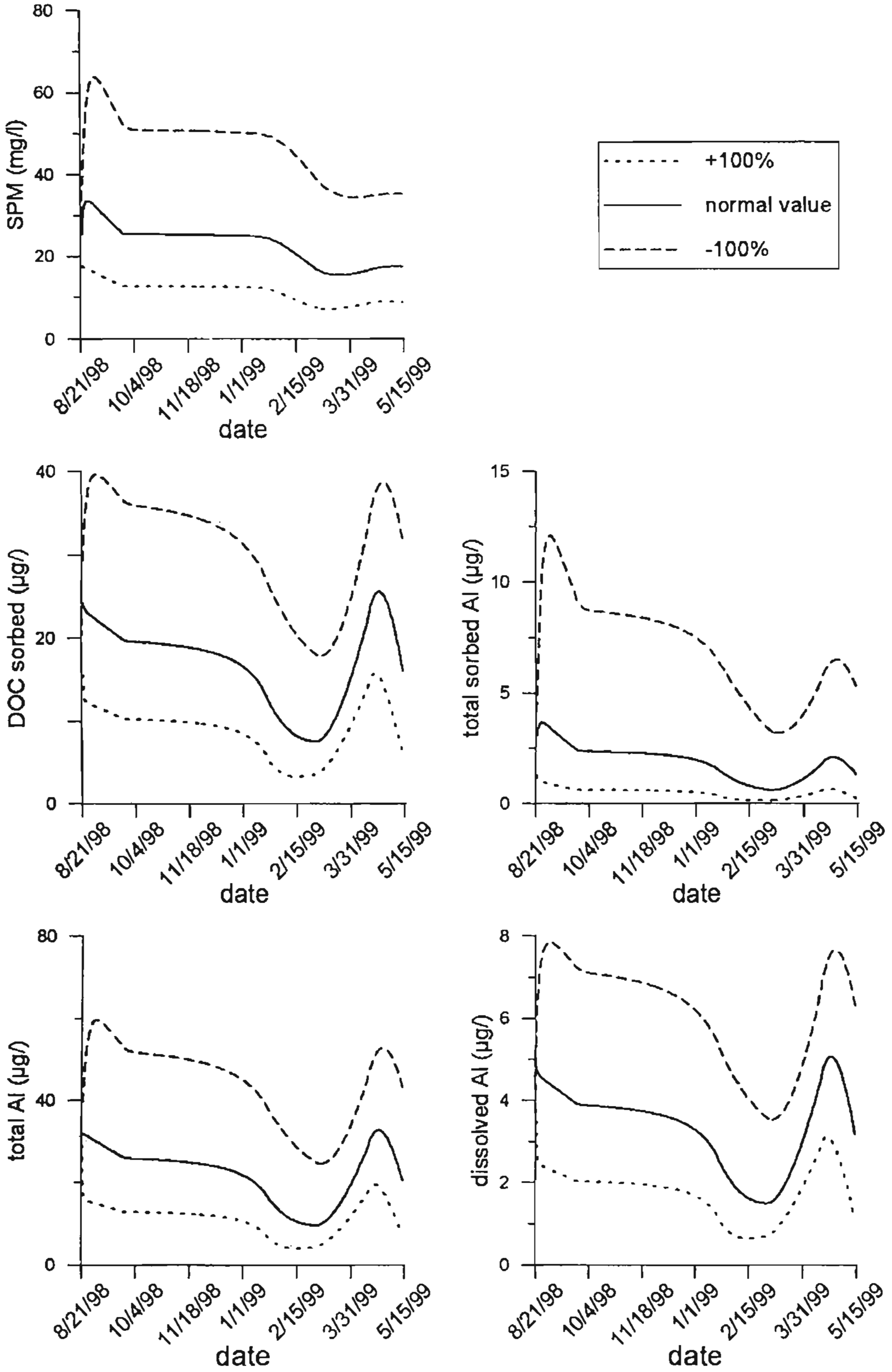


Fig.25a.Model sensitivity analysis for advection - northern arm - water column

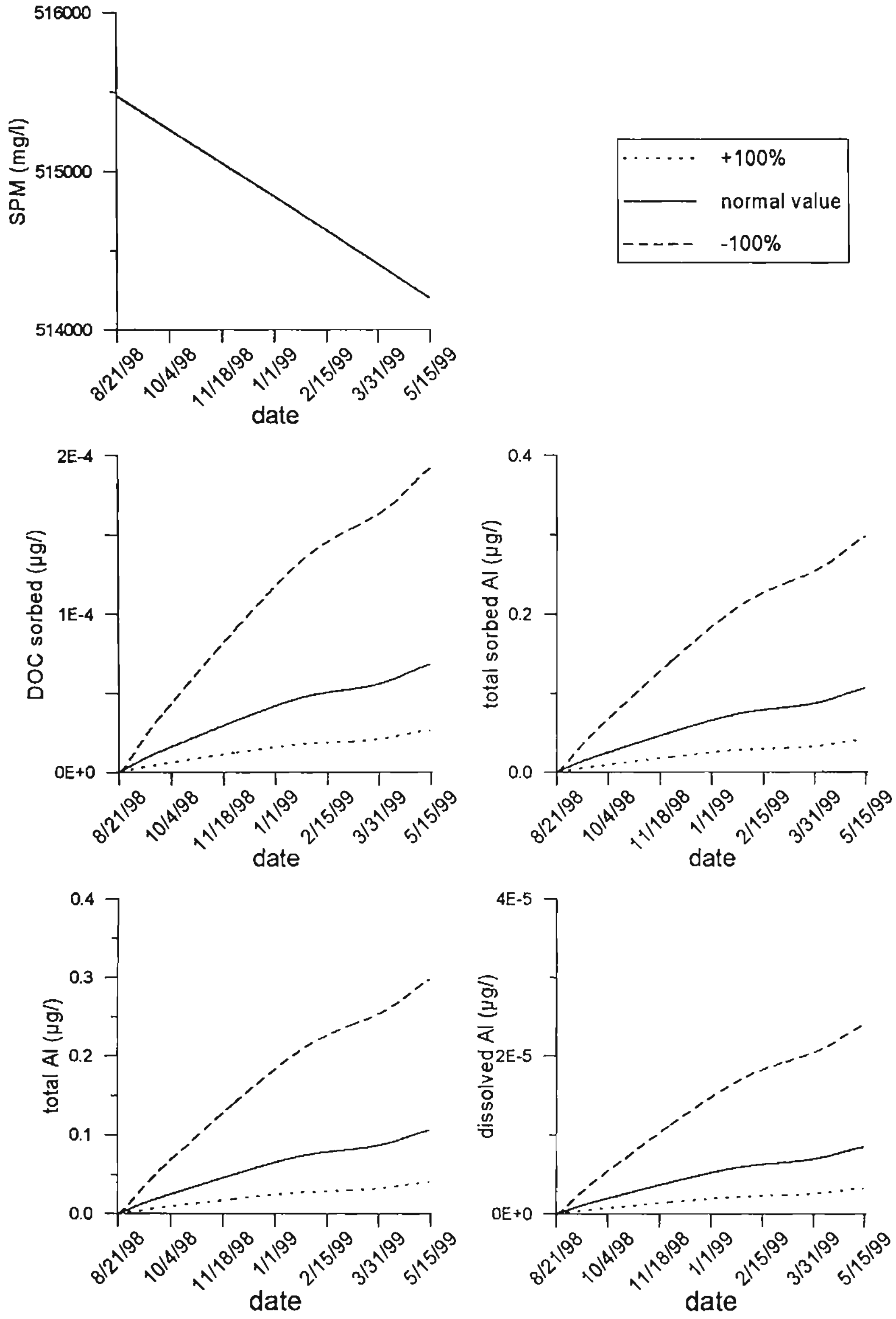


Fig.25b.Model sensitivity analysis for advection - northern arm - benthic segment

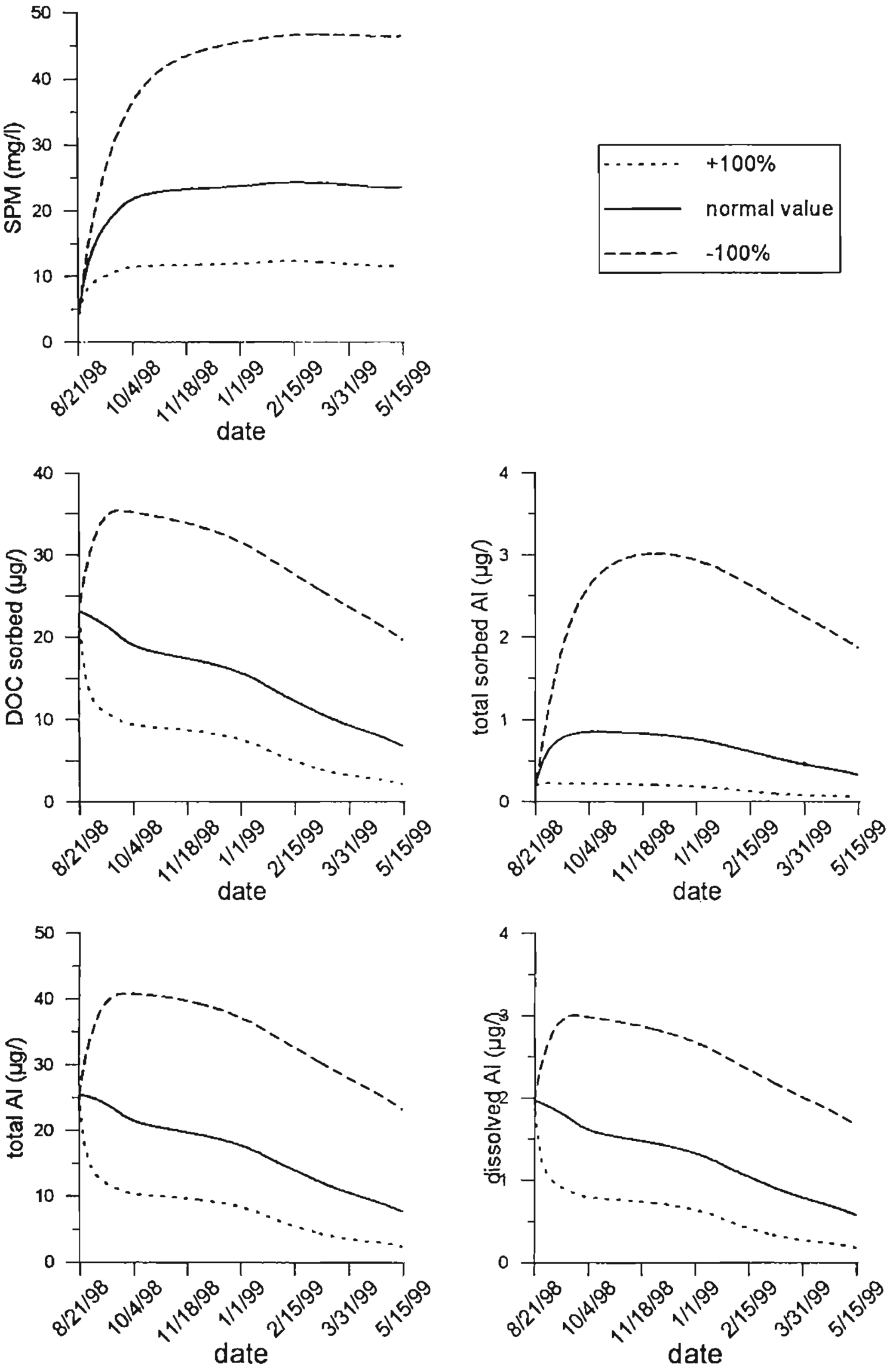


Fig.25c.Model sensitivity analysis for advection - southern arm - water column

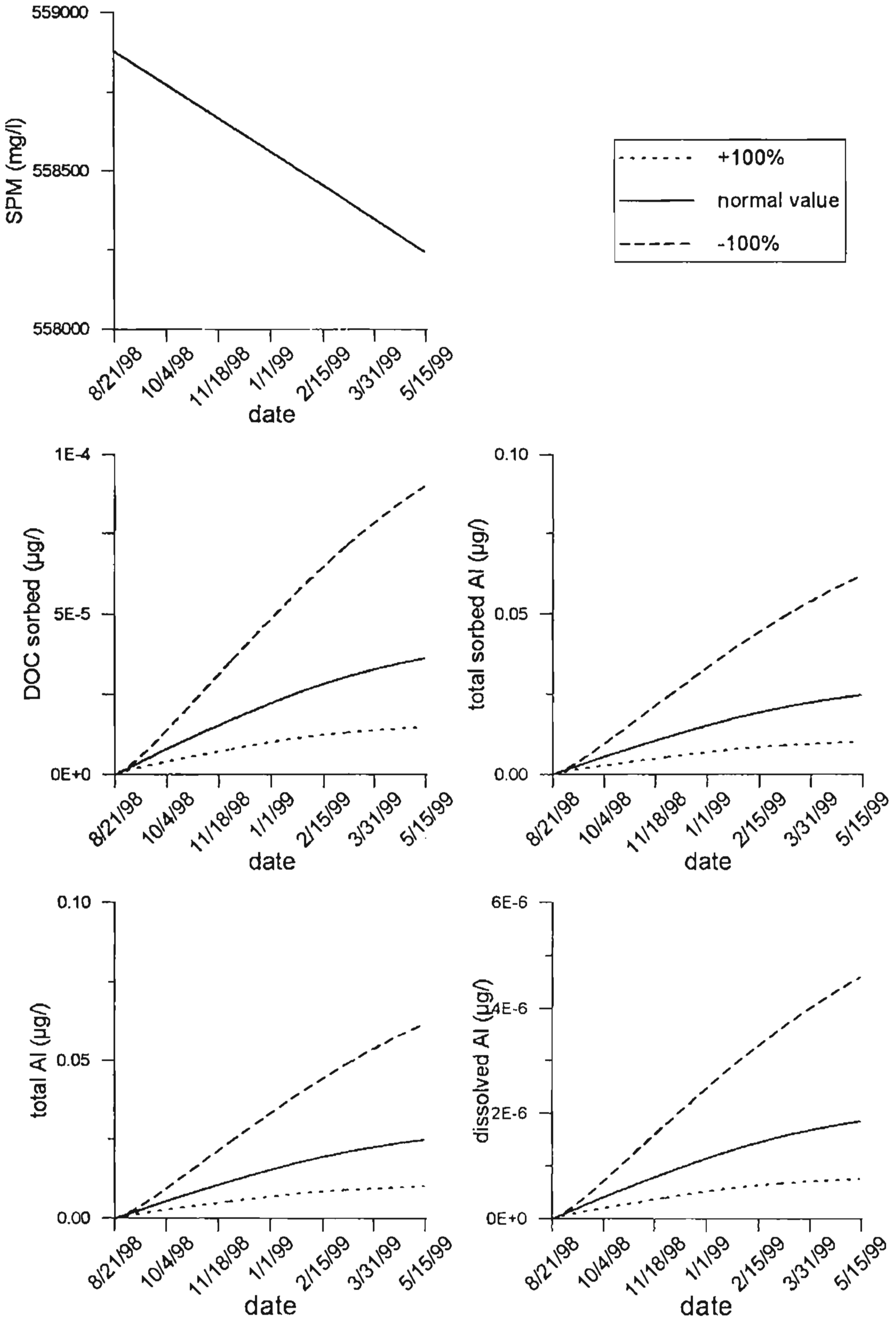


Fig.25d.Model sensitivity analysis for advection - southern arm - benthic segment

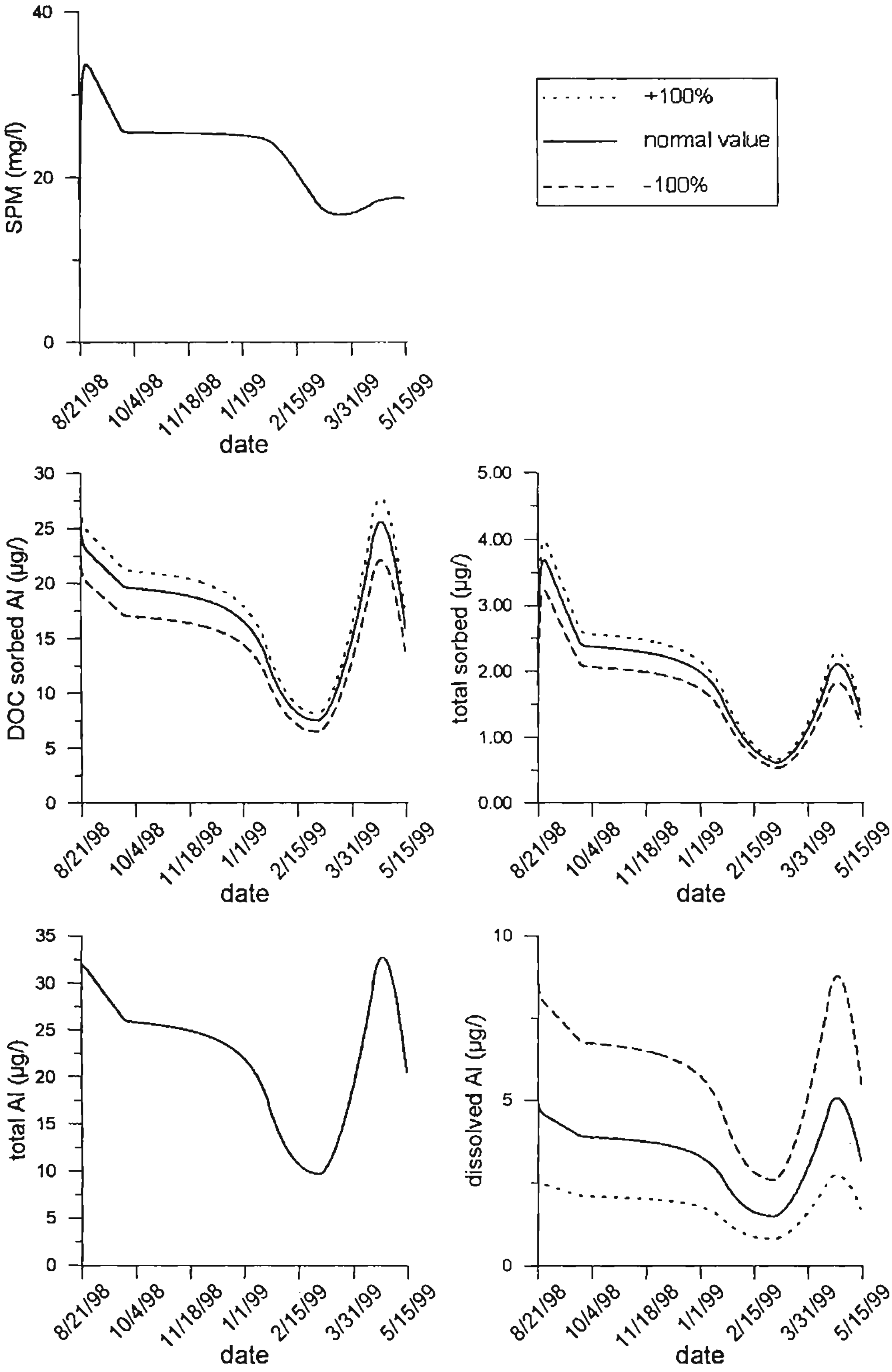


Fig.26a.Model sensitivity analysis for sorption - northern arm - water column

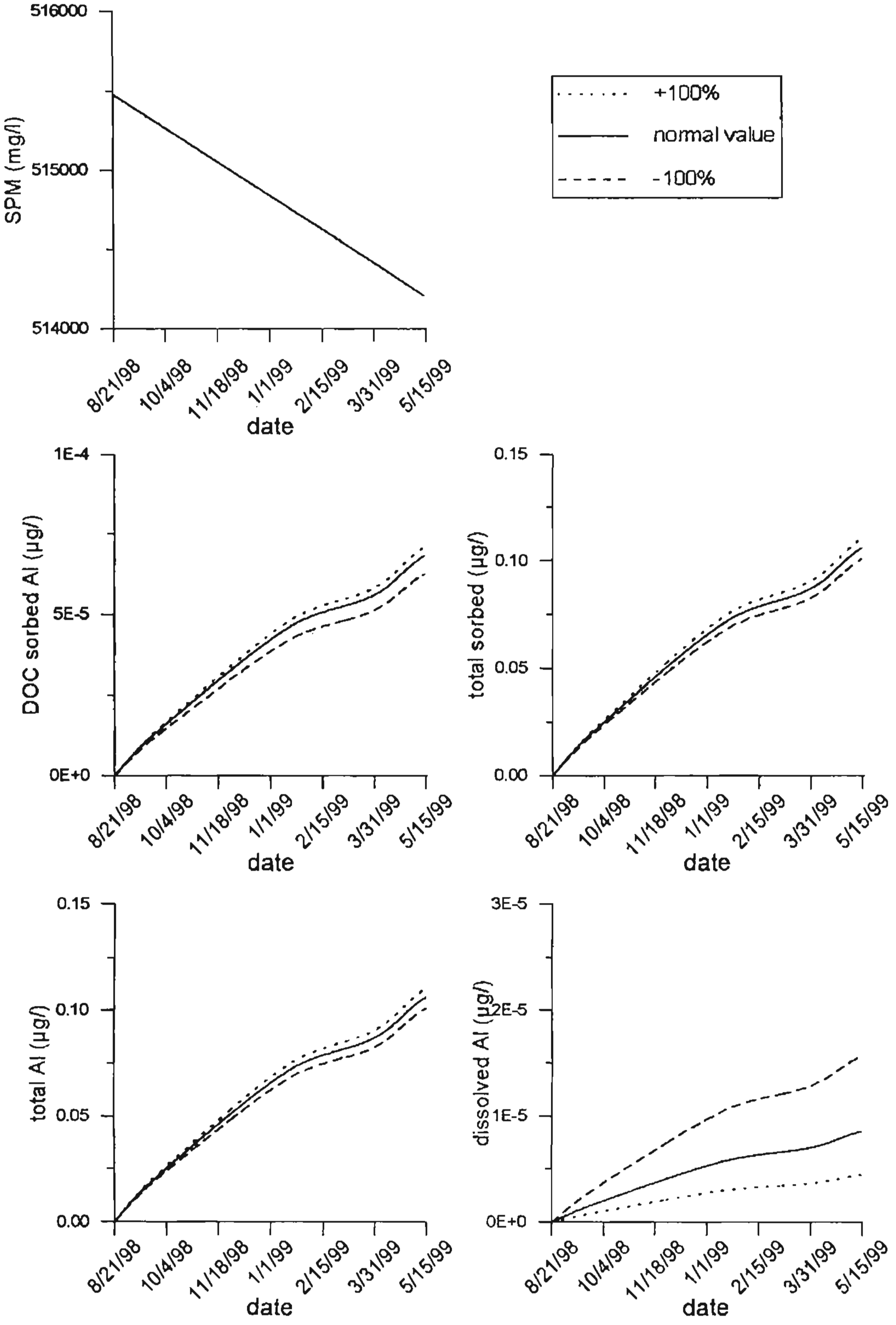


Fig.26b.Model sensitivity analysis for sorption - northern arm - benthic segment

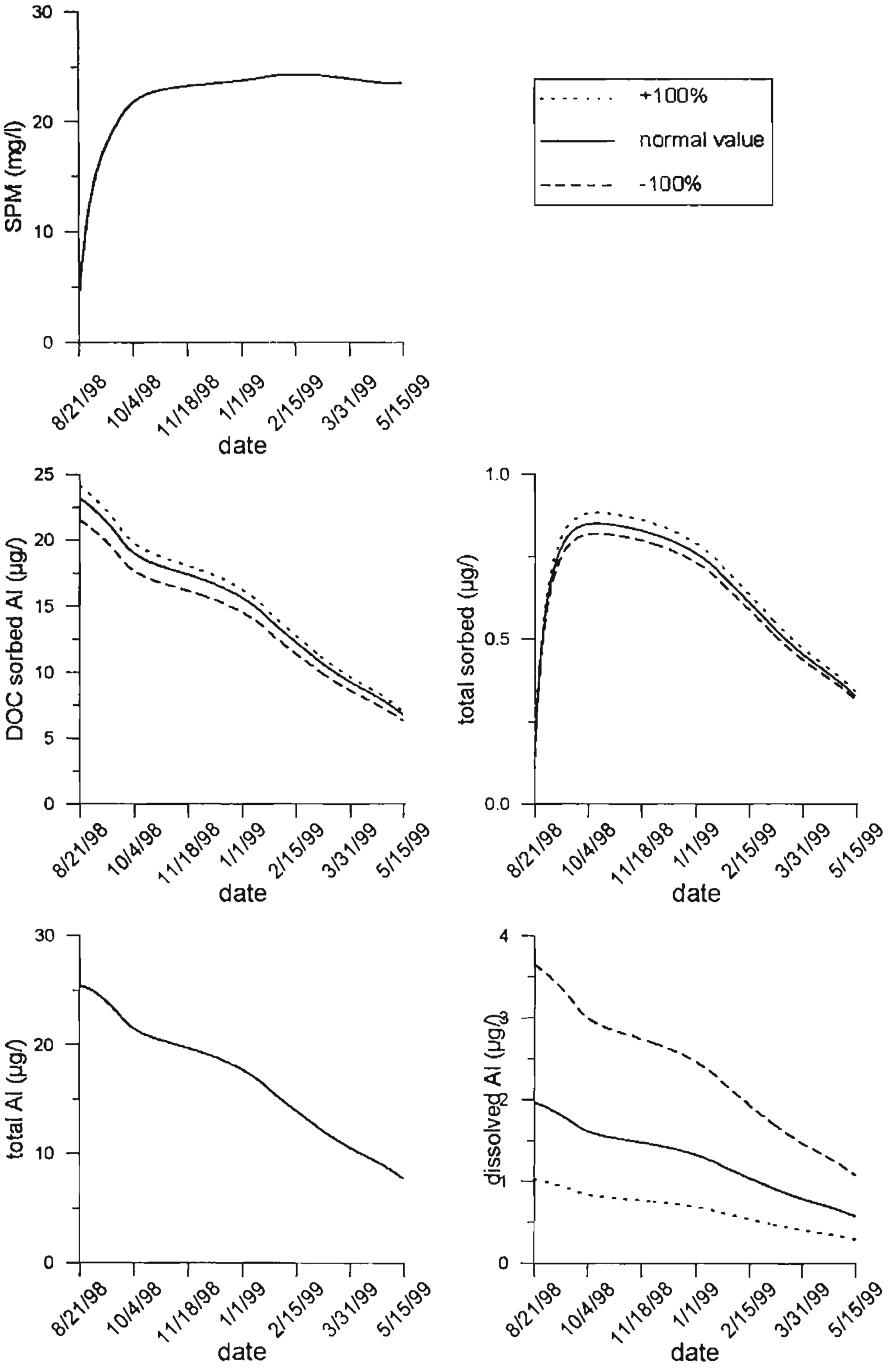


Fig.26c.Model sensitivity analysis for sorption - southern arm - water column

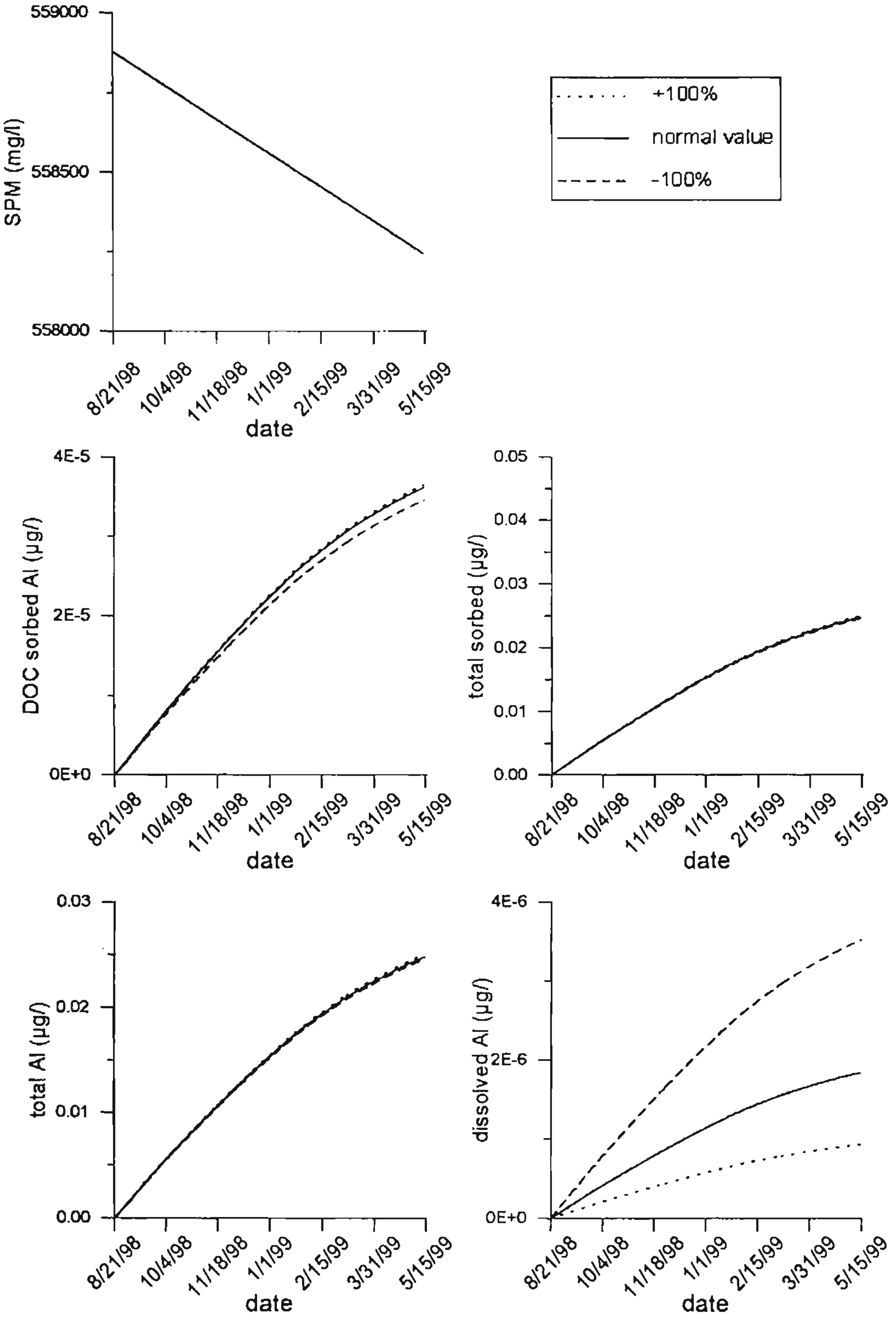


Fig.26d.Model sensitivity analysis for sorption - southern arm - benthic segment

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 other wise 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,i & l.

Fig.27.Predictive Analysis of the Model for different estuarine conditions-Northern arm

Al load 1- Al loading normal

Al load 2- Al loading doubled

SPM load 1-SPM loading normal

SPM load 2-SPM loading doubled

Flow 1- normal flow

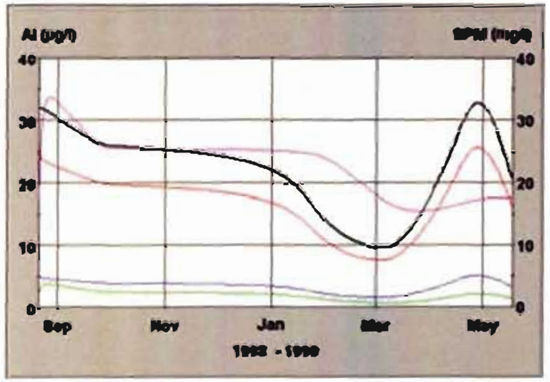
Flow 0.5- 1/2 the flow

Flow 0.1-1/10th of the flow

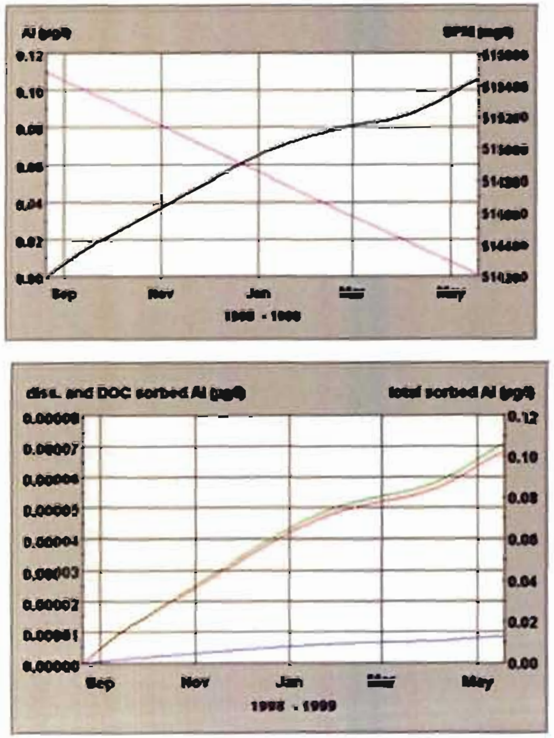
— total Al
— dissolved Al
— DOC sorbed Al
— total sorbed Al
— SPM

(a)Al load-1, SPM load 1, Flow-1

Water column

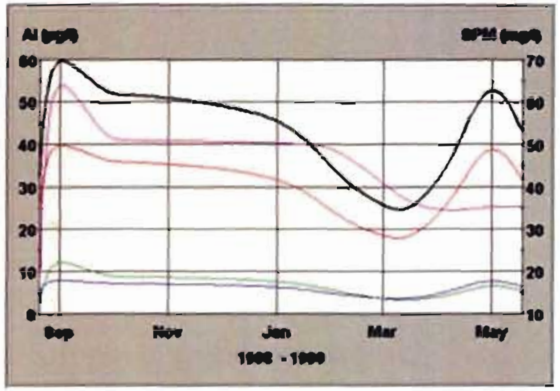


Benthic segment

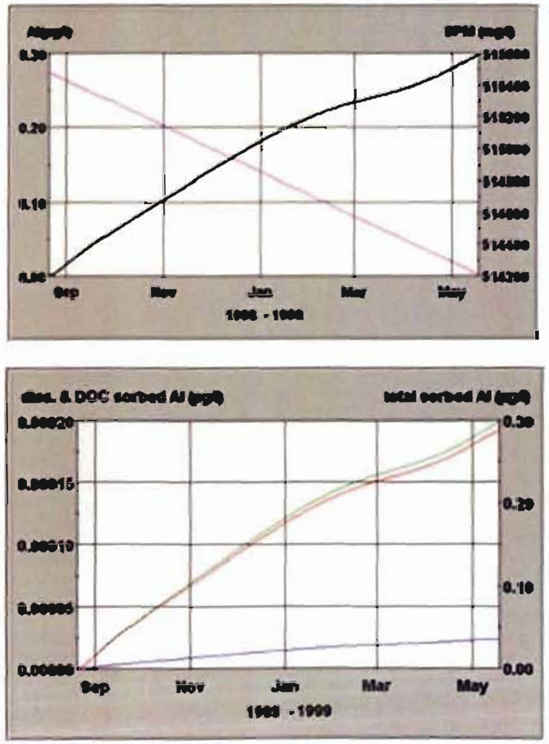


(b)Al load-1, SPM load-1, Flow-0.5

Water column

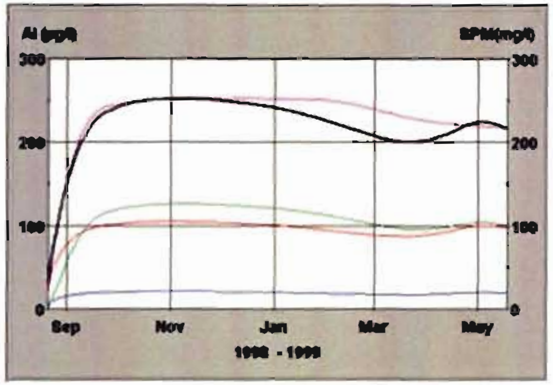


Benthic segment

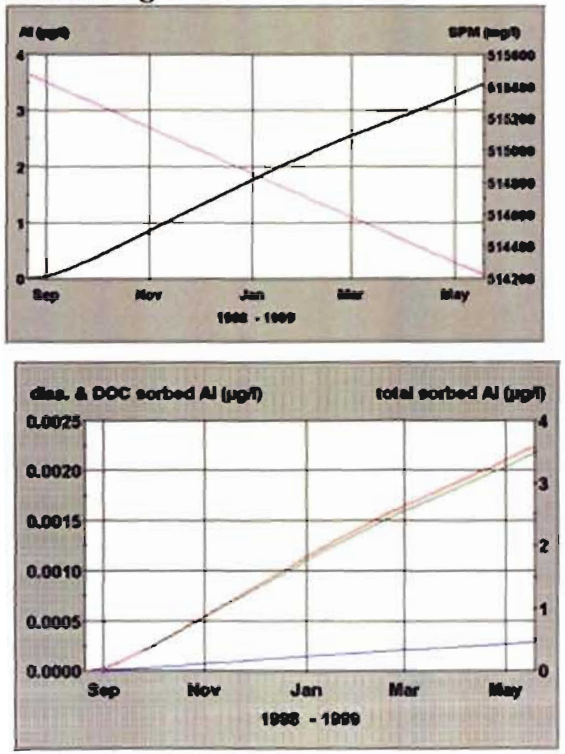


(c) Al load-1, SPM load-1, Flow-0.1

Water column

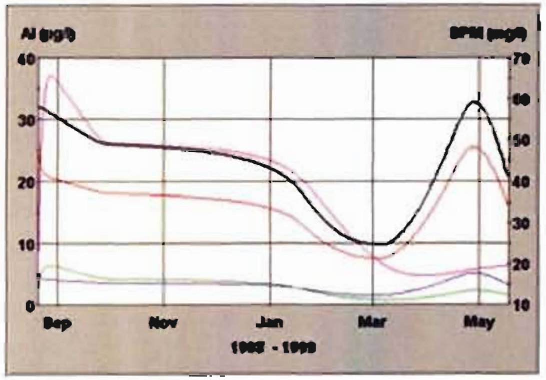


Benthic segment

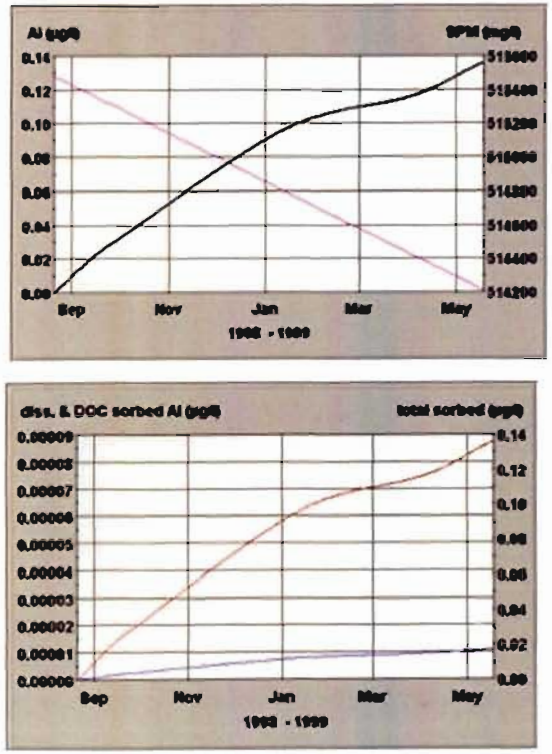


(d) Al load-1, SPM load-2, Flow-1

Water column

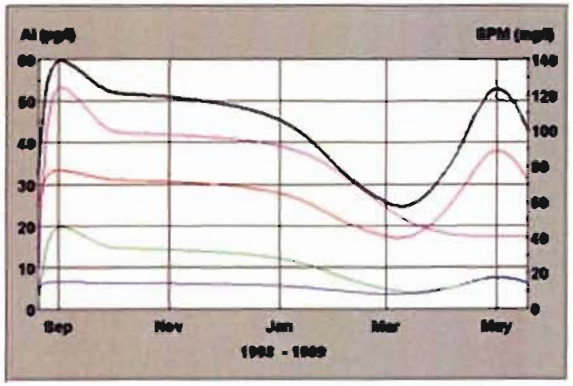


Benthic segment

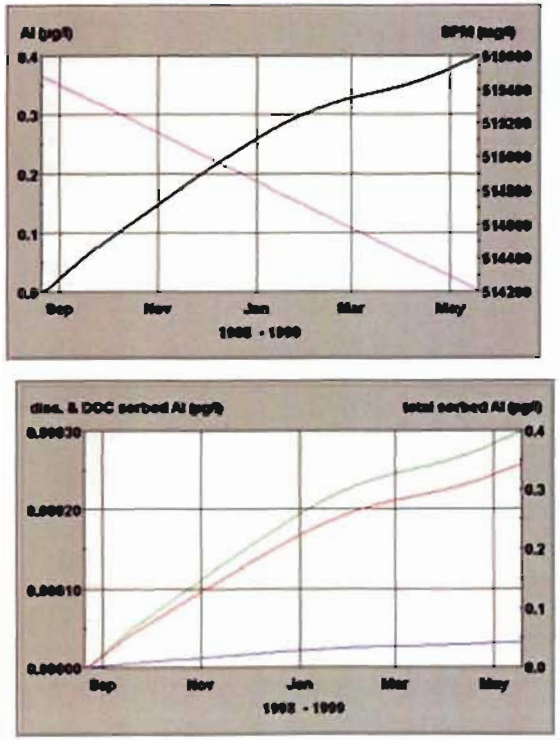


(e) Al load-1, SPM load-2, Flow-0.5

Water column

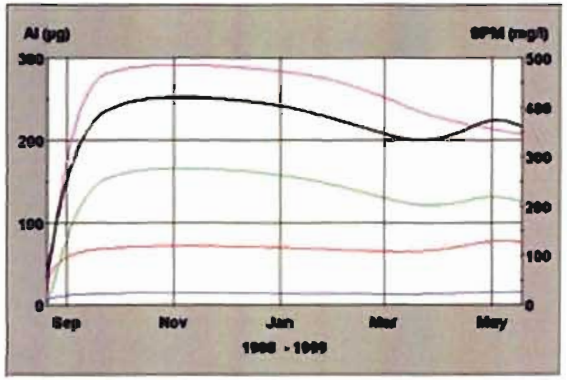


Benthic segment

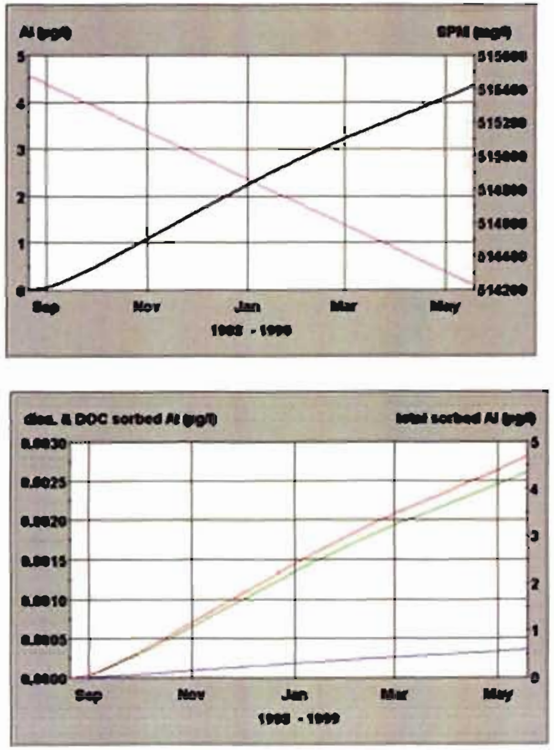


(f) Al load-1, SPM load-2, Flow-0.1

Water column

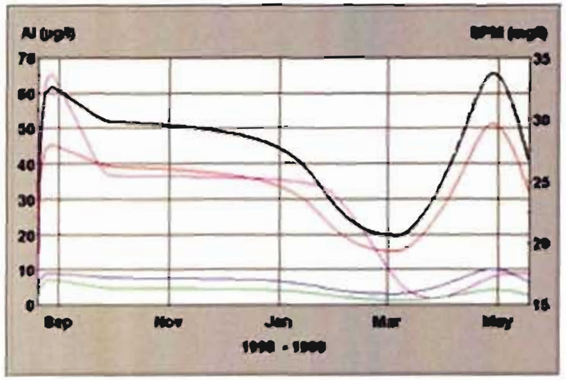


Benthic segment

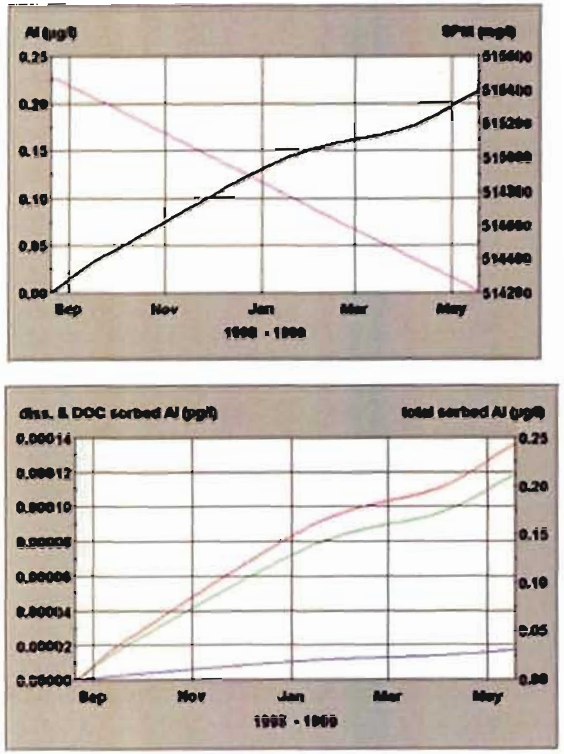


(g) Al load-2, SPM load-1, Flow-1

Water column

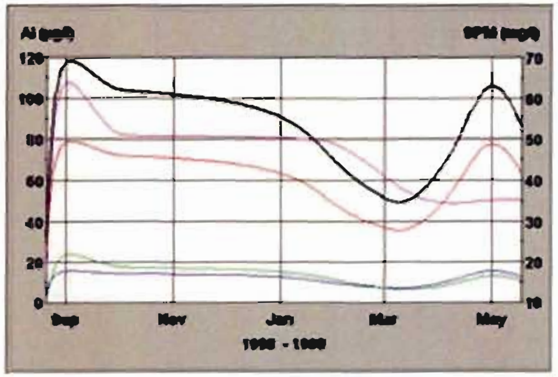


Benthic segment

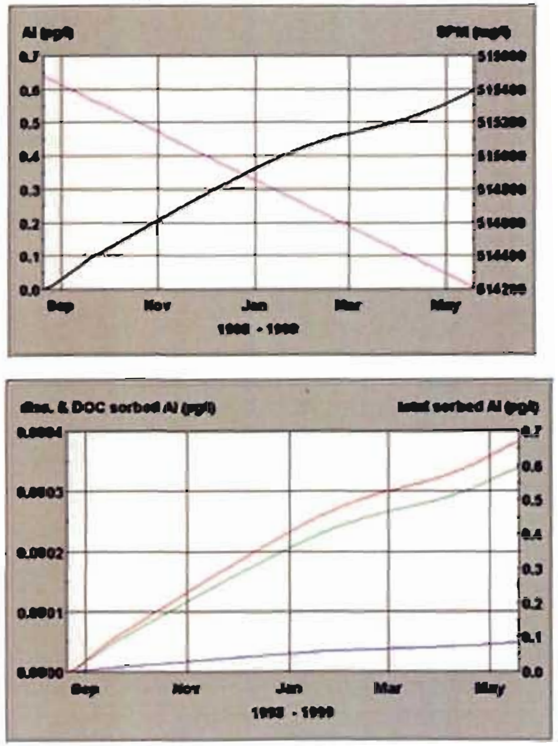


(h) Al load-2, SPM load-1, Flow-0.5

Water column

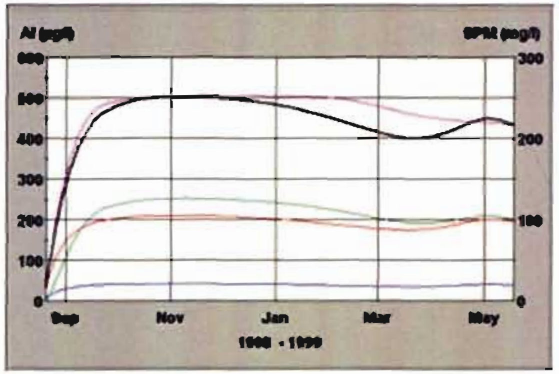


Benthic segment



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

Water column



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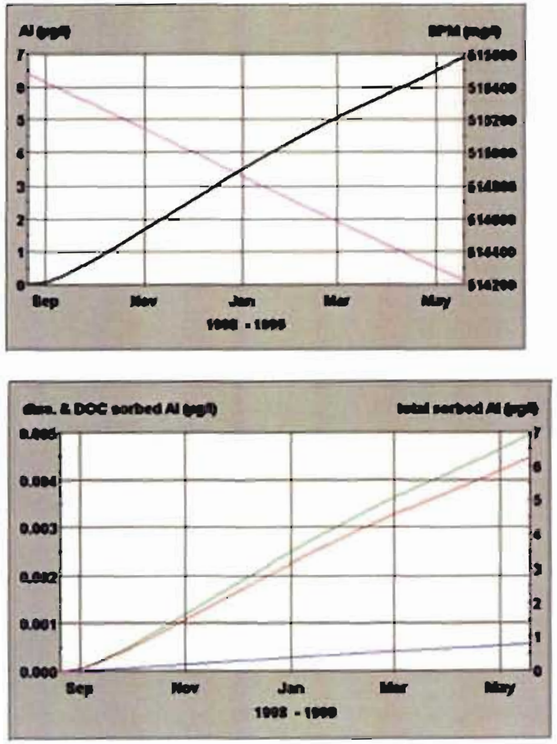
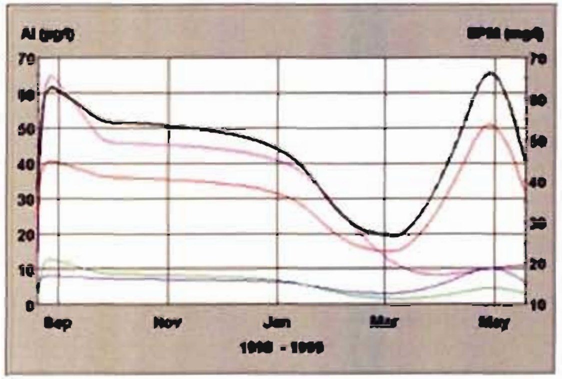


(j) Al load-2, SPM load-2, Flow-1

Water column



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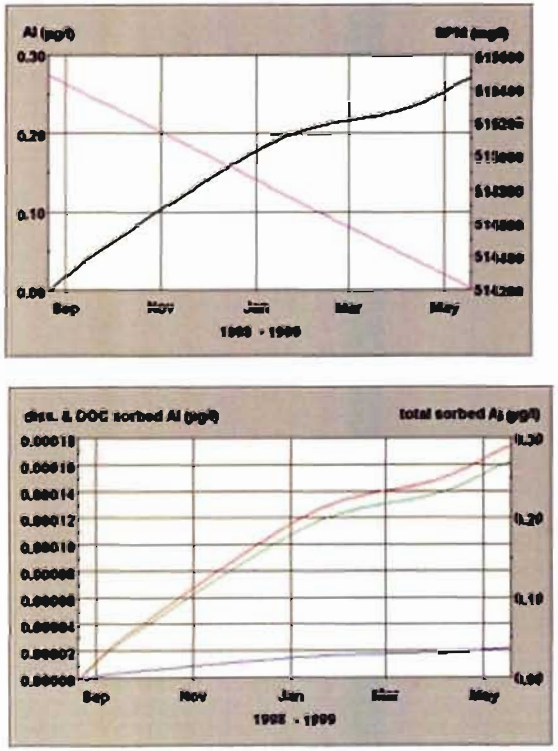
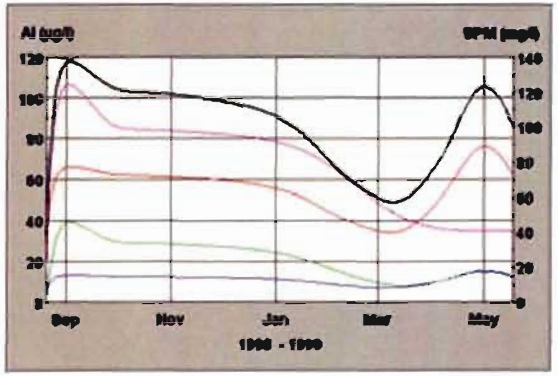


(k) Al load-2, SPM load-2, Flow-0.5

Water column



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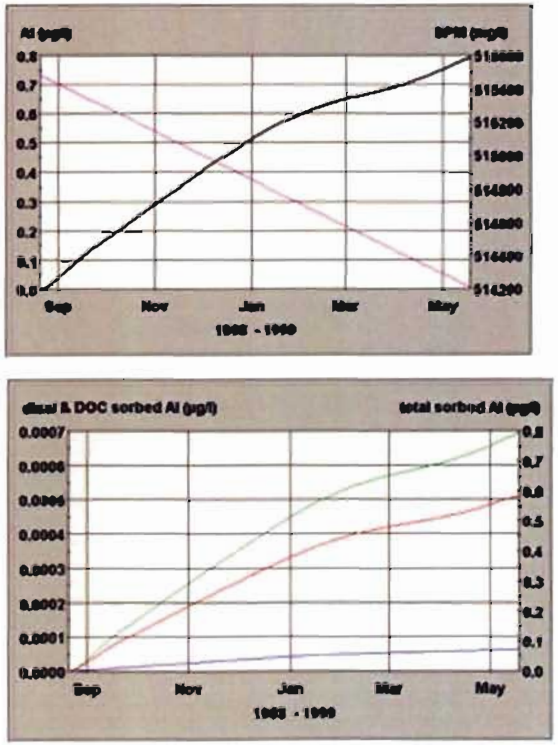
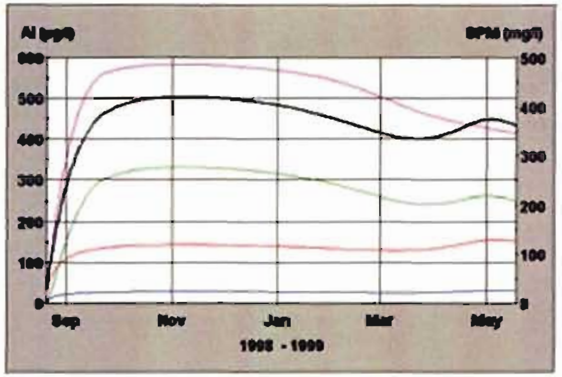


(l) Al load-2, SPM load-2, Flow-0.1

Water column



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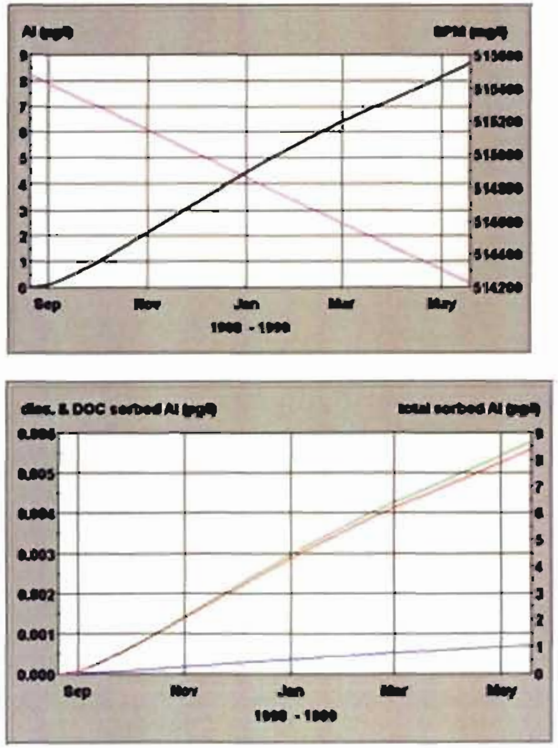


Fig.28.Predictive Analysis of the Model for different estuarine conditions -Southern arm

Al load 1- Al loading normal

Al load 2- Al loading doubled

SPM load 1-SPM loading normal

SPM load 2-SPM loading doubled

Flow 1- normal flow

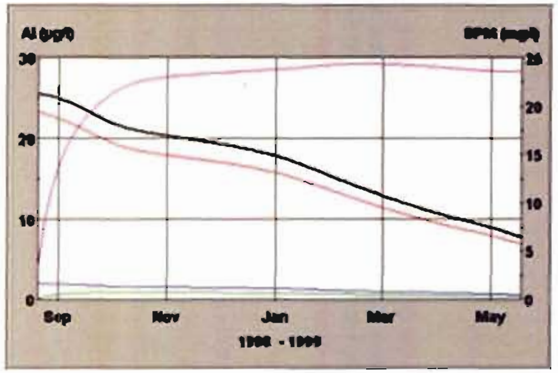
Flow 0.5- 1/2 the flow

Flow 0.1-1/10th of the flow

— total Al
— dissolved Al
— DOC sorbed Al
— total sorbed Al
— SPM

(a) Al load-1, SPM load-1, Flow-1

Water column



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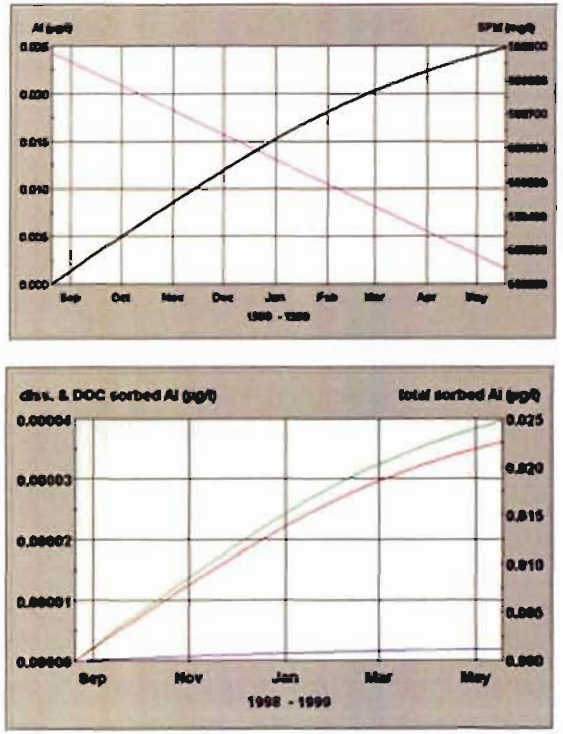
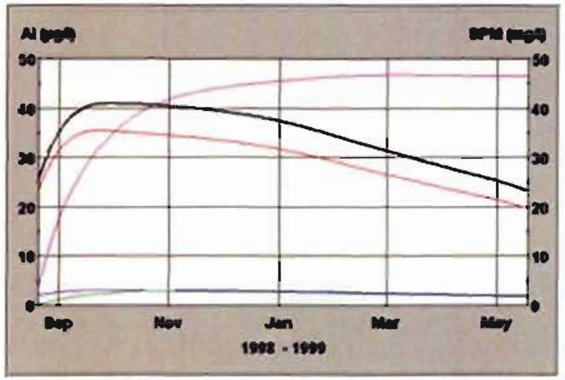
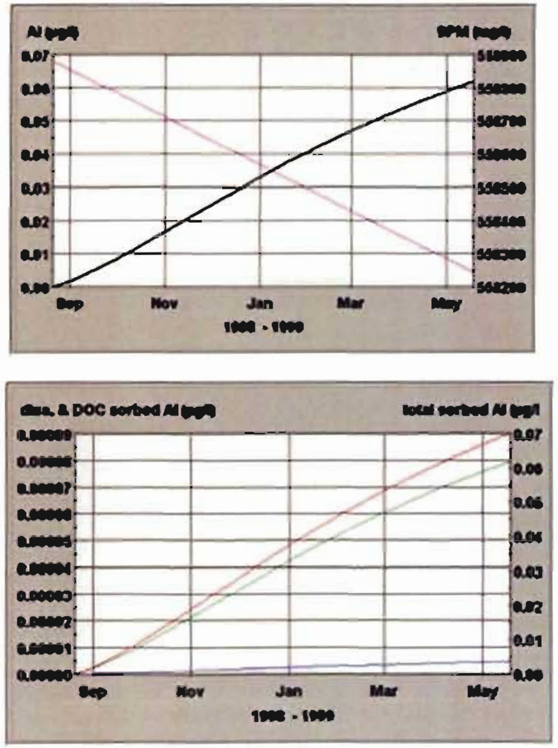


(b) Al load-1, SPM load-1, Flow-0.5

Water column

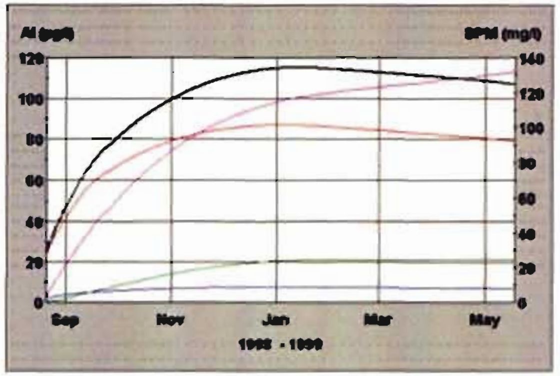


Benthic segment



(c) Al load-1, SPM load-1, Flow-0.1

Water column



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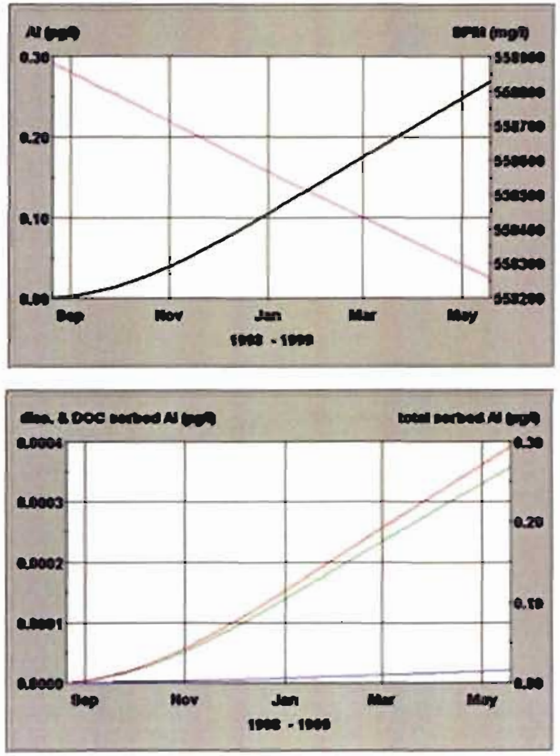
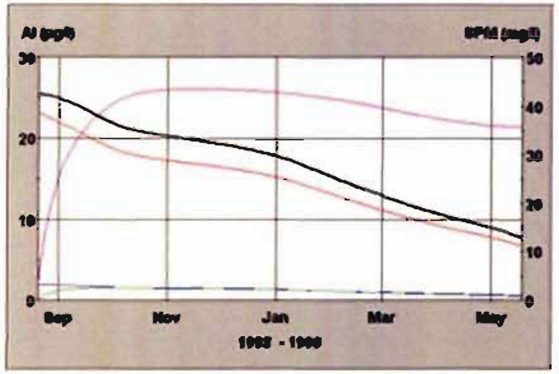
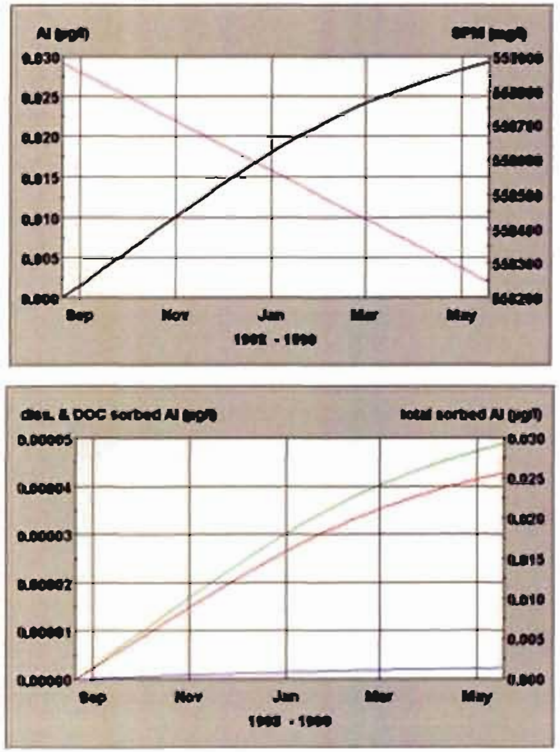


(d) Al load-1, SPM load-2, Flow-1
Water column

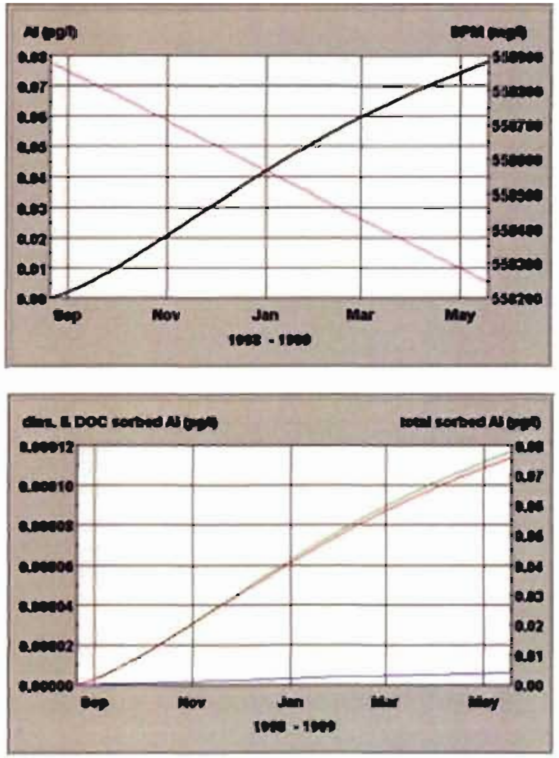


Benthic segment

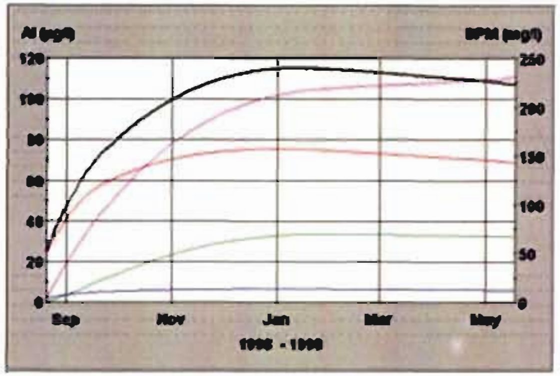


(e) Al load-1, SPM load-2, Flow-0.5
Water column

Benthic segment



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



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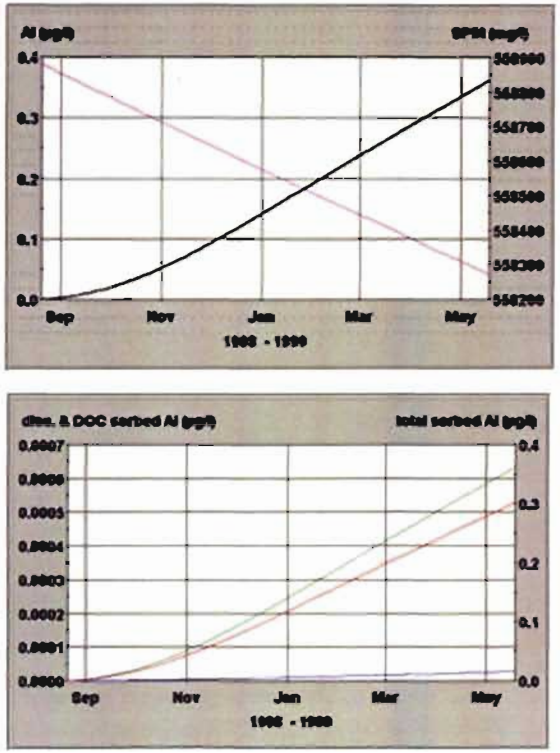
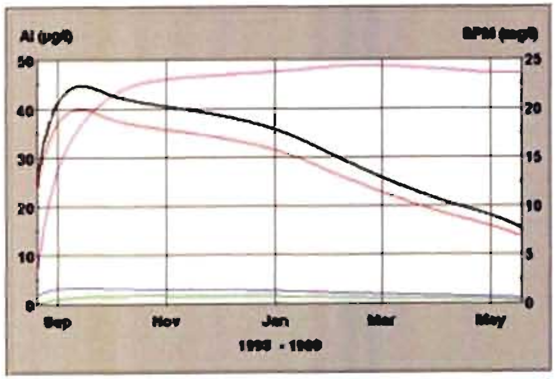


(g) Al load-2, SPM load-1, Flow-1

Water column



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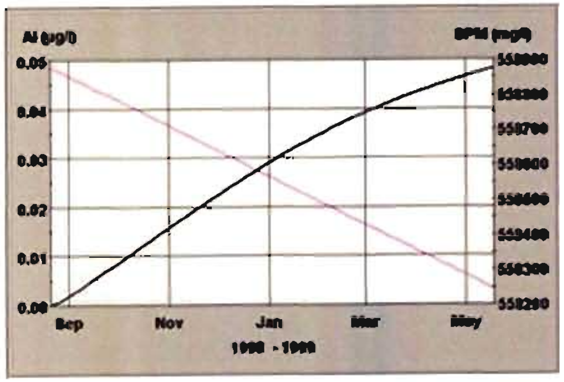
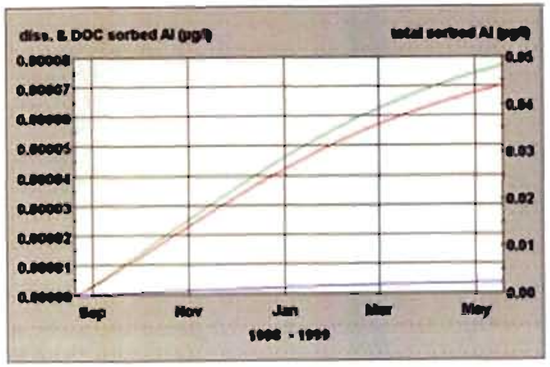
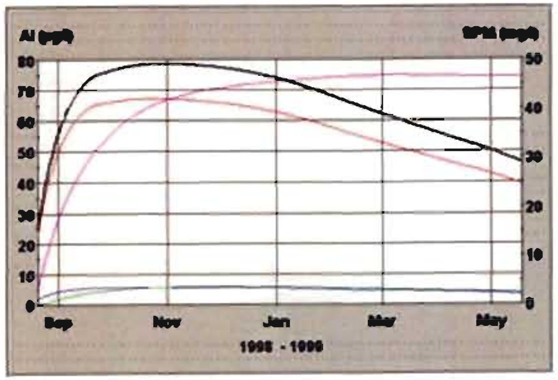


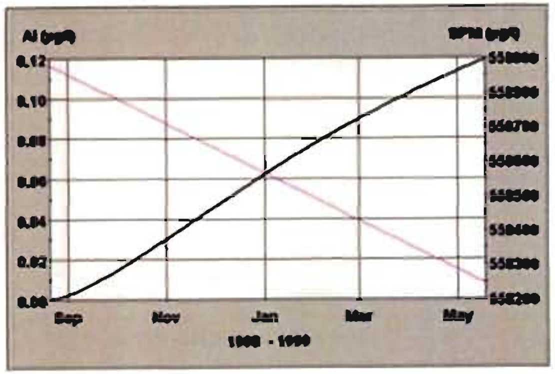


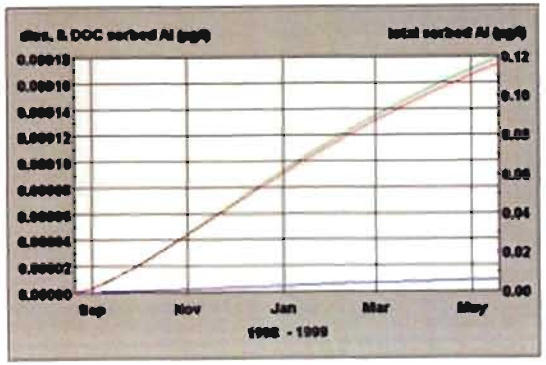
(h) Al load-2, SPM load-1, Flow-0.5

Water column



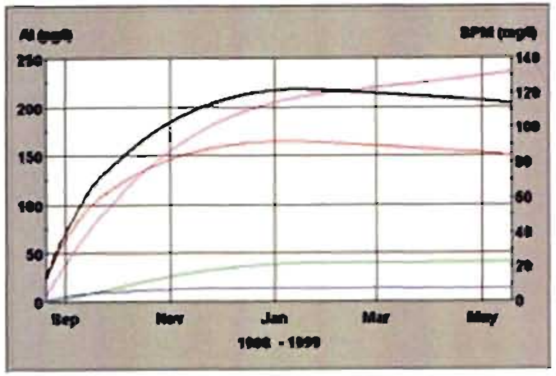
Benthic segment





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

Water column



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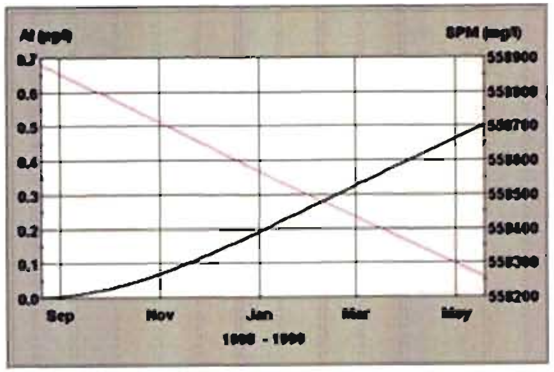
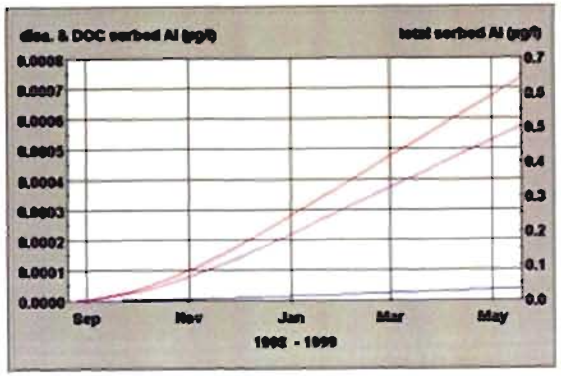
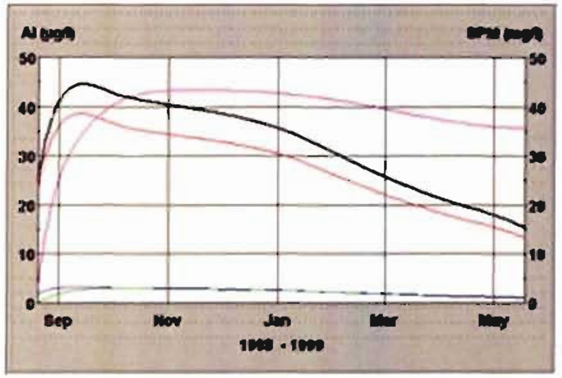




(j) Al load-2, SPM load-2, Flow-1

Water column



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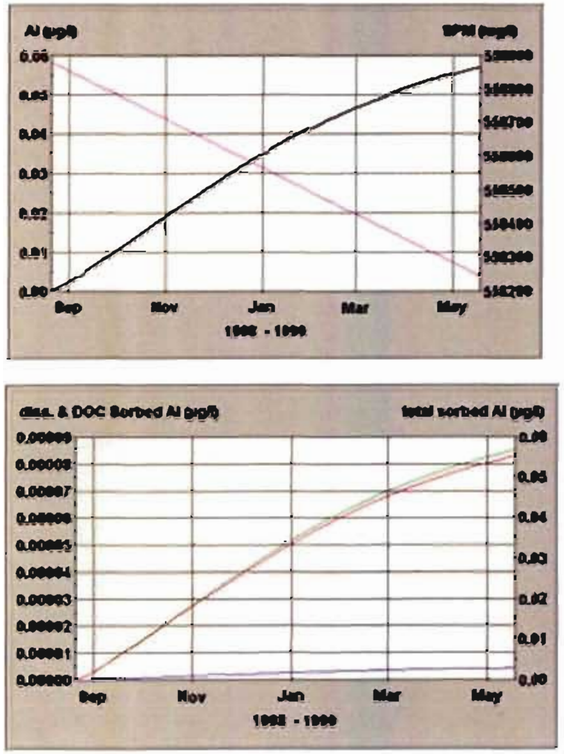
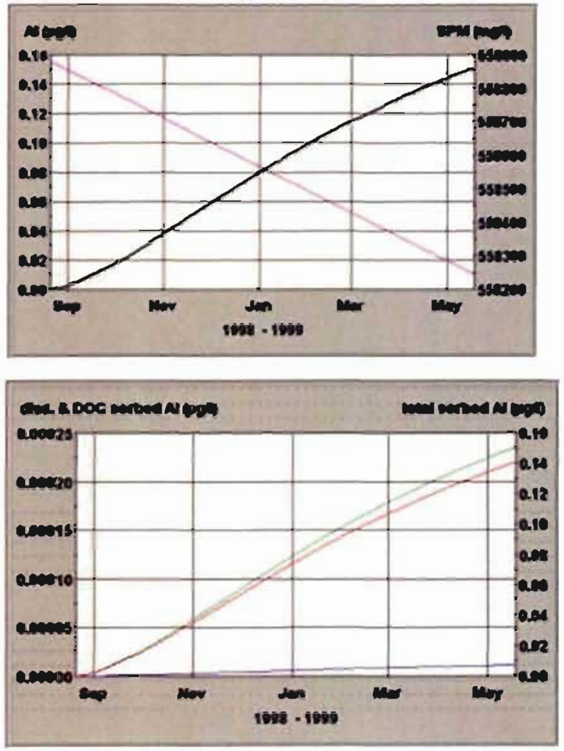


(k) Al load-2, SPM load-2, Flow-0.5

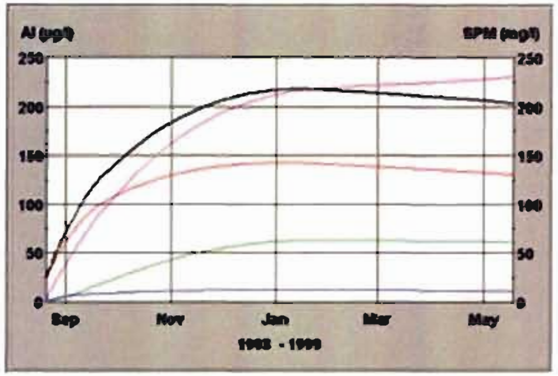
Water column

Benthic segment



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

Water column



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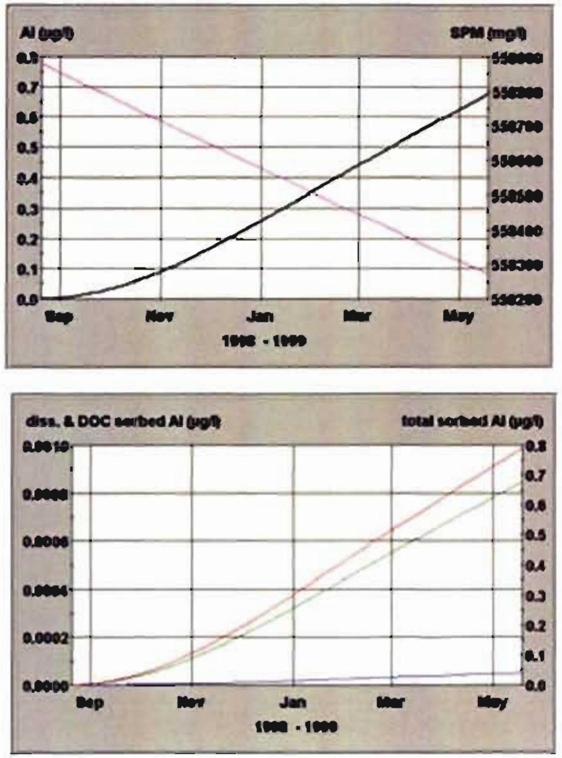

On altering the inputs of Al and SPM loads (figs.27d & g), the total SPM and total sorbed Al stands enhanced. In case both Al and SPM loads are doubled, the enhancement is proportionally predicted. This exercise viewed through fig.27k (flow halved) permits segregation of five different variables to indicate 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 1/10th, 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.

Chapter VI

Summary

Estuaries are considered as sink or source for terrestrial and various anthropogenically generated materials. These include naturally occurring elements Al, Si, Fe or trace inorganics or industrial pollutants of different types. There have been reports on both positive and negative impacts by the introduction of above materials into the ecosystem. By and large, in estuarine processes, both the physical and chemical regimes play an important role in the upkeep and modification of the ecosystem. It is essential to understand, quantify, categorise and formulate the ongoing processes, mainly the physical aspects supported by the chemical processes within estuaries, so as to elucidate information of this fragile environment. Tropical estuaries have a more significant role in modifying the coastal environments due to the prevalence of higher bio-diversity in changing climatic regimes, while critically acting to components of the hydrologic cycle and associated factors, which render our special attention. It is essential to know the aspects of river inputs, flux rates, chemical reactions on selected species of elements in light of (tropical) estuarine reactivity.

This thesis deals with the trace metal Aluminium (Al) whose average concentration (about 8%) in the earths crust is surpassed only by that of Oxygen and Silicon. There can be no doubt that most of the land derived materials reaches the ocean through rivers via estuaries. An important aspect noticed here is that the concentration of dissolved Al is much lower in sea water than in river water. In this connection, the entire coast of Kerala was surveyed for Al content. Appendix A gives the baseline data on dissolved Al along the entire coast of Kerala, on samples collected during March and June 2004. The concentration during the premonsoon period varies from near detection limit to 5.5 μM; maximum concentration was noticed in the central parts of Kerala coast. During the monsoon season, the values range from near detection limit to 1.2 μM. These values are in agreement with the dissolved Al values at Cochin bar mouth (near detection limit to 0.81μM). From the foregoing, it is clear that sea water concentration is generally lower than that of river water. The question becomes more intriguing when we consider the process in detail. What happens to the metal in estuaries? In this work an examination is held on the (probable) mechanisms operating in estuaries, especially the physical processes that go into the transformation of the metal, through field surveys, laboratory simulations and modelling.

On critically analysing Cochin estuary, for the entire cycles, covering monsoon, postmonsoon and premonsoon, the following salient features are documented as hereunder. Dissolved Al exhibits high and variable trends in Cochin estuary, the influencing parameters being salinity, SPM, pH and dissolved Si. A general profile showed removal in upper/mid estuary followed by regeneration in the mid/lower estuary and further decrease seawards in the southern/northern arms. Distribution appears to be a function of freshwater input, the monsoon season exhibiting very high concentrations throughout the estuary. As the river discharge decreased with the progress of seasons, dissolved Al concentration also decreased, the metal limiting itself to the upper and mid estuary. By premonsoon, Al concentration was very negligible, as trace amounts were noticed only in the upstream portions. Metal concentration was limited within a salinity value of 10 psu and SPM value of 100 mg/l on many occasions. Salinity intrusion and turbidity maxima played significant roles in metal removal from the dissolved state. During monsoon, the entire estuary exhibited near fresh water conditions; during the non-monsoon months, southern arm was characterised by well-mixed conditions in the vertical but longitudinally heterogeneous and the northern arm showed the existence of a salt wedge. Zone of turbidity maxima was confined to mid and lower estuary during non-monsoon months; during monsoon, this zone of high turbidity was clearly distinguishable. An accumulation of suspended matter close to the estuarine floor in the mid estuary was noticed in Cochin estuary, where the salinity ranged between 5 – 15 psu. This marine induced turbidity maxima robed off dissolved Al at the fresh water/salt water boundary, aiding metal removal from the water column. Dissolved Si showed a positive correlation with dissolved Al, both values decreasing as traversing downstream and as the seasons progressed. On inspecting the behaviour of Al with different estuarine parameters, the major mechanisms operating in Cochin estuary, influencing dissolved Al characteristics can be listed out as river influx, tidal sediment disturbance, flocculation, adsorption onto SPM and authigenic mineral formation.

In order to assess the above mentioned processes, laboratory simulation experiments were attempted Dissolved Al removal due to induced ionic charges by flocculation was more pronounced in low saline waters. Desorption under agitated condition and adsorption with the availability of free surfaces was a possible mechanism of addition/removal as demonstrated by sorption experiments. Riverine sediment imparted more Al to the water column than the brackish and sea sediment on agitation. The Al thus released was the loosely held fraction present in the interstitial water portion of the sediment. As far as particulate Al was concerned, the concentration in the sediments progressively increased downstream, maximum being noted in the sea sediments. For the release of particulate Al, an incubation period of 24 hours was necessary. In the upstream regions, flocculation aided the metal removal whereas in the downstream parts, adsorption dominated.

From acetic acid leaching experiments, it was noted that the reactive portion of particulate Al was more in sea sediments followed by brackish and then riverine. Riverine sediments can be considered to be composed of authigenic aluminosilicates which are not susceptible to acetic acid leaching. The reactive portion of Al in the marine sediments will be released to the dissolved media only during monsoon when the estuary represents a high energised environment.

The Cochin estuarine environment assessed in terms of the laboratory simulation experiments are as follows:

- In the upper estuary, where salinity around 3-10 psu prevails, flocculation was the dominant removal process.
- Sorption process activates with increase in SPM values and also where the sediment was very fine, owing to the prevalence of large surface areas available for binding. Thus, in mid and lower estuaries, sorption was the dominant removal process.
- Release on mechanical agitation was seen more prominent for the riverine sediment sample. Thus, the release due to tidal sediment disturbance in the mid and lower estuary was negligible; however, some release may be possible under high energic monsoon conditions.

- Reason for the decreasing trend in Al concentration in the mid and lower estuary was due to Al being present as exchangeable Al held in particulate sedimented layers.

Mathematical modelling employing WASP 6 along with the kinetic sub model TOXI was used to study the fate and transport of metal aluminium and associated parameter, SPM. The water volume and quality being studied are tracked and accounted for over time using a series of mass balance equations. Model was successful in simulating the Al and SPM concentration for a nine month period. Model simulation results lead to the following conclusions:

- Almost all the Al entering into the Cochin estuary is of colloidal or semi colloidal dimensions, thus existing as DOC sorbed phases with minor fractions as dissolved followed by total sorbed in the upper estuary. Thus flocculation will be the main process occurring in the upstream regions.
- Al content varies proportionally to river influx, high during high river discharge and decreases as the discharge wanes down, removal process acting, simultaneously.
- Model was successful in partitioning total Al into dissolved, DOC sorbed and particulate phases depending on the partition coefficients.
- It was possible to generate sediment Al concentration for the simulation period.
- From the results of sensitivity analysis, it was clear that in the water column advection, sorption and diffusion influenced the constituent concentrations to a large extent while settling had negligible influence.
- In the benthic sediment, the influencing parameters were diffusion, settling and advection while sorption influenced only the level of dissolved Al.

The purpose of the mathematical model was to determine the fate and transport of Al by quantifying their reactions, speciation and movement. Regardless of volumes of monitoring data that are available, it will always be desirable to have an estimate on chemical concentrations under different conditions, a figure or estimate on future waste load scenarios, a predicted hind cast or reconstructed history, or even make estimates at an alternate site where actual field data do not exist. The capability of the model to predict future scenarios appears strong. Given the prevailing processes operative in Cochin estuary the model predicts proportional changes in predicted variables subjected by enhancements in Al and SPM loads; a more realistic scenario could be the reduction in flow volume anticipated in future years. The gravity of such a situation imposing influences on Al chemistry and associated processes controlled by physical regimes present consequential implications in this estuary as postulated by the predictive mechanisms in WASP model. Based on these predictions, moderate to radical changes in surface water resources or variations in Al inputs or transformations in catchments practices leading to enhanced suspended loads – all of these could pave a possible scenario to reckon this abundant element, presently at negligible to very low toxic levels to generate alarming conditions, leading to apprehensions in environmental quality.

Drinking water quality level for Al as per Indian Standards is 30(µg/l), other established guidelines are 200 µg/l (WHO), 200 µg/l (EU) and 50-200 µg/l (US-Federal Standard) (Abhishek et al., 2003). In certain cases, the level of aluminium during monsoon months were above the water quality standards set by the Indian standards; also pH of less than 5.5 (acidic) leads to considerable increase in dissolved Al values during the non-monsoon months, when normally very low concentration of Al should have been noted. The acidification of estuarine waters is an issue that needs to be mitigated since northern arm is often prone to pollution and is susceptible to continued acidification. The only sure way to prevent further acidification is to control the emissions of acid pollutants.

On a general note, acidification of waters lead to striping toxic metals from solid phases, when metals like aluminium, manganese, iron, zinc, copper, nickel, vanadium, lead, and mercury (Skeffington, 1989) turn out to be very toxic to fish as well as humans (Wu et al., 2005). Aluminium concentrations as low as 0.05 mg/l can kill fish and macro invertebrate fauna; lower levels of aluminium may not kill but can severely impair growth and reproductive ability and hinder respiratory ability of fishes (Buchdahl, 1998; Alstad et al., 2005). Aluminium has been shown to cause Alzheimer's in humans (McDermott, 1991, Aremu & Meshitsuka, 2005). As the acidity of the water increases, aluminium is turns to be more soluble and the likely hood of release from soil stands enhanced. At pH 5.0, aluminium is at its most poisonous nature, being precipitated onto the gills of the fishes in the form of aluminium hydroxide. The end result is that the fish's metabolism is adversely affected (Muniz, 1987). Thus, in order to safeguard the biodiversity of Cochin estuary, certain criteria will have to be maintained as far as effluent discharge and sewage disposal is concerned, enabling to restrict the building up of toxic metals, which could be harmful to aquatic organisms.

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Appendix-A

Baseline data on Dissolved Aluminium along Kerala coast

Sl. No.	Station Name	Latitude	Longitude	Al concentration (µM)	
				premonsoon	monsoon
1	Pozhiyoor Pozhi	08° 18′ 11"	77° 05′ 05"	1	0
2	Poovar Beach	08° 18′ 50"	77° 04′ 14"	1.11	0
3	Puthiyathura	08° 20′ 02"	77° 02′ 05"	1.48	0
4	Vizhinjam north	08° 22′ 34"	76° 59′ 11"	-	-
5	Kovalam	08° 23′ 18"	76° 58′ 37"	1.04	0
6	Shunmugham Beach	08° 28′ 46"	76° 54′ 52"	0	0.52
7	Veli South	08° 30′ 22"	76° 53′ 20"	0	0.04
8	Anguthengu	08° 39′ 47"	76° 45′ 50"	1.04	0
9	Varkala	08° 44′ 38"	76° 41′ 54"	1	0.22
10	Kappil Beach	08° 45′ 59"	76° 41′ 04"	0.81	0
11	Kappil Approach	08° 47′ 04"	76° 40′ 16"	1.19	-
12	Paravoor Poozhikkara	08° 48′ 43"	76° 38′ 56"	-	-
13	Kollom beach	08° 52′ 35"	76° 35′ 25"	0.89	0
14	Thangasseri	08° 53′ 02"	76° 34′ 11"	-	-
15	Neendakara south break water tip	08° 56′ 00"	76° 32′ 08"	0.85	0.07
16	Puthanthura	08° 57′ 39"	76° 31′ 52"	-	-
17	Vallanathurutu	09° 01′ 21"	76° 30′ 57"	1.15	0
18	Alappat	09° 03′ 19"	76° 30′ 04"	0.70	0
19	Kuzhithara	09° 04′ 25"	76° 29′ 33"	-	0.19
20	Azhikkal south	09° 06′ 33"	76° 28′ 33"	1.19	0.22
21	Valiya Azhikal south	09° 08′ 07"	76° 27′ 50"	2.74	0.15
22	Enroute Valiya Azhikal	09° 09′ 21"	76° 27′ 17"	0.63	0
23	Arattupuzha	09° 13′ 07"	76° 25′ 33"	0.81	-
24	Trikkunnapuzha	09° 15′ 29"	76° 24′ 27"	0.89	0
25	Pallana Thotappally	09° 18′ 18"	76° 23′ 11"	0.6	0.07
26	Purakkad	09° 20′ 31"	76° 22′ 12"	0.96	0
27	Ambalapuzha	09° 23′ 12"	76° 20′ 56"	1.22	0
28	Punnapara	09° 26′ 24"	76° 19′ 56"	1.07	0
29	Alleppey	09° 29′ 35"	76° 19′ 07"	1.33	0
30	Thumboli	09° 31′ 12"	76° 18′ 44"	0	0
31	Marari south (College Jn)	09° 33′ 15"	76° 18′ 23"	0	0.07
32	Marari south (Fisheries harbour)	09° 34′ 38"	76° 18′ 10"	-	-
33	Marari beach	09° 36′ 05"	76° 17′ 56"	0	0
34	Arthungal	09° 39′ 40"	76° 17′ 35"	0	0
35	Thykkal	09° 41′ 09"	76° 17′ 26"	0.93	0
36	andhakaranzhi	09° 44′ 54"	76° 17′ 05"	0.78	0.52
37	Pallithodu	09° 46′ 38"	76° 16′ 49"	1.04	0

40	Fort Cochin	09° 57′ 50"	76° 14′ 18"	0.93	0
41	Puthuvypeen	09° 59′ 53"	76° 13′ 08"	1.3	0
42	Njarakal	10° 02′ 12"	76° 12′ 31"	1.04	-
43	Edavanakkad north	10° 05′ 31"	76° 11′ 29"	1.22	0.22
44	Kuzhipilli	10° 06′ 35"	76° 11′ 16"	1.19	0.04
45	Cherai Beach	10° 08′ 23"	76° 10′ 45"	1.15	0
46	Munambam inlet	10° 10′ 41"	76° 09′ 59"	0.81	0
47	Kara	10° 14′ 01"	76° 08′ 45"	1.22	0.15
48	Koolimattom	10° 16′ 49"	76° 07′ 56"	-	-
49	Kaipamangalam beach	10° 18′ 45"	76° 07′ 25"	1	0.48
50	Kazhibram	10° 22′ 10"	76° 06′ 12"	1.04	0.07
51	Valappad	10° 23′ 47"	76° 05′ 33"	1.04	0.59
52	Vatanapally	10° 27′ 40"	76° 03′ 51"	0.63	0.93
53	Chettuva Azhimukham	10° 30′ 42"	76° 02′ 10"	1.3	-
54	Chettuva Kadapuram	10° 32′ 04"	76° 01′ 31"	-	-
55	Blapangadu (Methala) beach- Chavakad	10° 34′ 18"	76° 00′ 31"	1.41	0.70
56	Puthan Kadapuram	10° 35′ 30"	75° 59′ 54"	1.3	0.52
57	Andhathodu	10° 40′ 14"	75° 57′ 50"	5.44	0.70
58	Puthuponnani Inlet	10° 47′ 11"	75° 54′ 47"	2.15	0.48
59	South of Kuttazhi	10° 51′ 27"	75° 53′ 48"	0.41	0.89
60	North of Kuttazhi (Unniyel)	10° 56′ 06"	75° 52′ 43"	0	0
61	Parapanagadi	11° 03′ 12"	75° 50′ 57"	0.07	0.96
62	Kadalundi	11° 07′ 20"	75° 49′ 37"	1.6	0.3
63	Beypore	11° 09′ 47"	75° 48′ 09"	5.52	0.85
64	Paiyanakkal (Kappakkal)	11° 13′ 04"	75° 46′ 57"	0.52	0.67
65	Calicut beach	11° 15′ 15"	75° 46′ 13"	1.04	0.56
66	Puthiyapa Harbour south	11° 18′ 43"	75° 45′ 00"	0	0.67
67	Azhikal Paravalapu	11° 21′ 33"	75° 43′ 57"	0.3	0.74
68	Kappad beach	11° 23′ 40"	75° 42′ 49"	0.19	0.33
69	Koilandi beach	11° 26′ 27"	75° 41′ 17"	0.04	0.78
70	Palithaye	11° 27′ 45"	75° 38′ 06"	0	-
71	Nandi Beach	11° 27′ 58"	75° 38′ 21"	-	0.3
72	Koodikal beach	11° 29′ 40"	75° 36′ 58"	0	0.70
73	Payyoli beach	11° 30′ 42"	75° 36′ 34"	0	0.19
74	Irigal – Khovayi beach	11° 32′ 53"	75° 35′ 43"	1.44	0.70
75	Vadakara	11° 36′ 05"	75° 34′ 39"	0.3	0.59
76	Chombal (fishing harbour)	11° 39′ 40"	75° 33′ 08"	0	0.85
77	Thalayi	11° 43′ 21"	75° 30′ 52"	-	-
78	Tellicherry inlet	11° 45′ 02"	75° 29′ 04"	0.3	0.37
79	Koduvalli –Tellicherry co-operative hospital	11° 45′ 52"	75° 28′ 47"	-	-
80	Dharmadom thuruthu	11° 46′ 24"	75° 27′ 20"	0	0.70
81	Muzhipilangadi beach	11° 47′ 47"	75° 26′ 32"	0	0.67

86	Muttom – Palakode bridge	12° 01′ 57"	75° 13′ 57"	0.33	-
87	Ettikulam beach	12° 00′ 38"	75° 12′ 49"	0.15	0.74
88	Thykadapuram inlet	12° 12′ 21"	75° 07′ 17"	0	0
89	Thykadapuram beach	12° 14′ 31"	75° 06′ 17"	0	1.11
90	Khanzhagat west	12° 18′ 00"	75° 04′ 52"	0.07	0.56
91	Bekal Fort Beach	12° 23′ 29"	75° 02′ 18"	0.22	0.11
92	Bekal bridge	12° 24′ 06"	75° 01′ 45"	-	-
93	Chadragiri Inlet	12° 28′ 37"	74° 59′ 39"	-	0.15
94	South CPCRI	12° 31′ 47"	74° 58′ 11"	-	-
95	Nellikkunu Kadapuram (CPCRI - west)	12° 31′ 04"	74° 58′ 02"	0.04	0.85
96	Kumbla bridge	12° 35′ 40"	74° 56′ 33"	-	-
97	Muttom – Swarnagiri bridge	12° 38′ 13"	74° 55′ 17"	0	1.11
98	Manjeswhar	12° 42′ 34"	74° 53′ 07"	0.85	1
99	Thalappadi (Kanvathrithum)	12° 44′ 34"	74° 52′ 16"	0.15	0.41