CHAPTER IV

DISCUSSION OF RESULTS

As in previous chapters, to maintain continuity, the results are discussed in three separate sections, viz., (1) Uranium, (2) Silicon and (3) particulate trace metals.

IV.1 Uranium:

The geochemical behaviour of uranium isotopes in the Narbada and Tapti rivers, in the estuaries of Narbada, Tapti, Godavari and Mahanadi and in the Arabian sea sediments are discussed sequentially.

IV.1. (a) Distribution of uranium in the Narbada river-tributary system:

The Narbada river and its major tributaries were sampled for uranium, major cations and \( \text{HCO}_3^- \) during May 1978. The samples were collected from selected sites along the 1300 km stretch of the Narbada river. The uranium concentration (dpm/l) and \( ^{234}\text{U} / ^{238}\text{U} \) activity ratio (designated henceforth as A.R., Table III.7) are shown in Fig. IV.1. At Amarkantak, the region of inception of Narbada, the \(^{238}\text{U} \) concentration is very low, 0.031 dpm/l and it gradually increased to 0.82 dpm/l near Broach. The uranium content of the four tributaries analysed ranged between 0.031 to 3.2 dpm/l. The concentrations in Hiran and Orsang (Fig. IV.1) tributaries are 0.96 and 3.17 dpm/l respectively,
Fig. IV.1. $^{238}\text{U}$ concentration (given in units of dpm/l in parenthesis) and $^{234}\text{U}/^{238}\text{U}$ A.R. along the course of the Narbada river and its tributaries.
Fig. IV.1
significantly higher than that in the Narbada river. The A.R. in the main river and tributarine waters ranged between 1.12 to 1.67. At Broach, beyond which the estuarine region begins the non-monsoonal average A.R. is 1.40±0.02 and the uranium concentration is 0.77 dpm/l. The U concentration and the activity ratios in the Narbada river appears to arise because of simple mixing between the water in the main river and that from the tributaries. Though our results permit calculation of mixing volumes, these computations have not been carried out due to the paucity of data on the water discharge of tributaries and Narbada, an essential information to check the validity of the mixing model. Quantitatively, the Hiran tributary seems to be a major source of water to Narbada, at the time of sampling i.e. May 1978.

IV.1.(b) Relationship between $^{238}$U, major cations and HCO$_3^-$ :

In the Narbada and Tapti rivers and their tributaries the uranium concentration is strongly correlated with that of the total major cations (Fig.IV.2). The total major cation content of the water is a measure of the intensity of the weathering of the terrain over which the river flows. It thus appears that the release of uranium isotopes to Narbada and Tapti and their tributaries is controlled by the intensity of weathering of rocks present in their drainage basin. Similar trend for several Indian and American rivers have been reported earlier (Bhat and Krishnaswami, 1969; Turekian and Chan, 1971 cited in Turekian and
Fig. IV.2. $^{238}\text{U}$ concentration (dpm/l) versus Na + K + Ca + Mg concentration (mg/l) in Narbada river and its tributaries. The three measurements of Tapti and its tributary are also shown. For 14 Narbada samples, the correlation coefficient is 0.95 (see also Table IV.1).
Fig. IV.2
The abundance ratio of uranium to the sum of major cations (U/E (Na + K + Ca + Mg)) in the soluble phases of Narbada river and its tributaries is 2.6x10^-2. A similar ratio for 47 samples from selected rivers (Table IV.1) so far studied is found to be 1.3x10^-2. This ratio in rivers and streams is nearly two orders of magnitude higher than that in shales and crustal rocks. This high abundance of uranium relative to major cations could arise either because of preferential leaching of uranium from the rock matrix or because of its availability in regions which are more susceptible for enhanced weathering, such as cracks, cleavages and crystal dislocations. Uranium being a large ion lithophile element, the latter alternative seems more likely to be the cause of its relatively higher abundances in river waters. The $^{238}$U concentration is also strongly correlated with the HCO$_3^-$ content of the waters of Narbada and its tributaries (Fig. IV.3). Similar inferences were made by BROECKER (1974); MANGINI et al. (1979) for lakes, rivers and ground waters. This correlation is attributable to the formation of uranium carbonate complexes during weathering.

In order to plot all the existing data on U and total dissolved salts (TDS) of various world rivers and streams available in literature, the present data on total major cations (in Narbada and Tapti and their tributaries) had to be converted to TDS. This was done by multiplying the major cation data with
Fig. IV.3. $^{238}\text{U}$ concentration (dpm/l) versus $\text{HCO}_3^-$ content (mg/l) for Narbada river and its tributaries. Three measurements of Tapti and its tributaries are also shown. The correlation coefficient for all the samples is 0.884.
Fig. IV.3
the conversion factor 4.43 (TDS/ Σ (Na+K+Ca+Mg)) computed from data available in literature (LIVINGSTONE, 1963; MEYBECK, 1979).

The plot of $^{238}\text{U}$ versus TDS for world rivers and streams is shown in Fig. IV.4. It is gratifying to note that the slopes of $U$-TDS best fit lines for different sets of data (such as Indian, American, etc. see Table IV.1) representing different geological and climatic conditions is in good agreement within about a factor of two. The relation between uranium and TDS for 47 observations is found to be: $^{238}\text{U} (\mu g/l) = 0.03 \text{TDS (mg/l)} - 0.053$. This observation namely the $U$/TDS ratio is nearly constant in river waters flowing through different climatic regimes and geological terrains, if not a coincidence, provides a very quantitative and reliable method to compute the annual flux of uranium into the oceans. Based on the slope of the best fit line (for all the data) $2.96 \times 10^{-3} \text{mg U/g TDS}$, and an annual TDS flux $4.0 \times 10^{15} \text{g/yr}$, the uranium flux to the ocean is calculated to be $1.19 \times 10^{10} \text{g/yr}$.

Based on this dissolved uranium flux to the ocean and taking average uranium concentration $3.3 \mu g/l$ in sea water the residence time of uranium in the ocean is calculated to be $3.8 \times 10^5 \text{yrs}$.

IV.1.(c) Uranium isotopes in the estuaries of Narbada, Tapti, Godavari and Mahanadi:

The measured uranium concentrations and the A.R. in these four rivers and their estuarine regions are given in Tables III.2 to III.5. There is a marked seasonal variation in the uranium
Fig. IV.4. $^{238}$U concentration (μg/l) versus Total Dissolved Solids (mg/l) for world rivers and streams. See Table IV.1 for correlation coefficients and for slope of the best fit lines drawn through various sets of this data.
TOTAL DISSOLVED SOLIDS (mg/l) vs. 238U CONCENTRATION (µg/µL)

- Present Study
- Turekian and Chan (1971)
- Bhat (1970)
- Lewis (1976)
- Martin et al. (1978)

Fig. IV.4
Table IV.1:
Correlation coefficients and slopes of best fit lines for $^{238}\text{U}$-TDS plots

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample details</th>
<th>No. of samples</th>
<th>Correlation coefficient</th>
<th>Slope of the best-fit-line (mg U/g TDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Narbada and its a) tributaries</td>
<td>14</td>
<td>0.951</td>
<td>5.89x10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>Narbada, Tapti and b) tributaries and Mahanadi</td>
<td>26</td>
<td>0.826</td>
<td>3.24x10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>American Rivers*</td>
<td>11</td>
<td>0.898</td>
<td>4.56x10^{-3}</td>
</tr>
<tr>
<td>4</td>
<td>Selected data existing in literature**</td>
<td>47</td>
<td>0.823</td>
<td>2.96x10^{-3}</td>
</tr>
</tbody>
</table>

a) Data of NE-6 set
b) Data includes all fresh water-end-member measurements of NE-1 through NE-6, TP-1 through TP-5 and MN-1.

* Data from TUREKIAN and CHAN (1971).

** Only Godavari, Krishna and Cauvery data have been used from BHAT (1970). Her Ganges data as well as data for other small polluted rivers are not included. Similarly only RV-1, SR-11 and SR-15 samples which are upstream of the mine discharge in the Susquehanna river (LEWIS, 1976). Other data is from TUREKIAN and CHAN (1971) and MARTIN et al (1978b).
concentration as well as in the A.R. in the fresh water-end-member (0 to 0.10 g/l chlorosity region) of Narbada. Uranium concentration ranged between 0.18 to 0.87 dpm/l and the A.R. between 1.28±0.02 to 1.44±0.04; the lowest values in both parameters occurring during the monsoon (July to October). The non-monsoon (November to June) values occur for most part of the year. During this period the rivers could be receiving significant quantity of effluent seepage from subsurface waters, compared to that during the monsoon. For Tapti, we did not collect samples during the peak of the monsoon period (July to October) but collections were made just after the monsoon in November 1977 as well as in November 1978. All the four sets of samples yielded almost identical values for U and A.R. The uranium concentration ranged from 0.25 to 0.32 dpm/l and A.R. ranged from 1.22±0.02 to 1.26±0.04 in the fresh water region. In the case of Godavari and Mahanadi only one set of observations, during April and December 1976 were made. During the non-monsoon season the average uranium concentration and the A.R. for the four rivers are Narbada: 0.71 and 1.40±0.02, Tapti: 0.28 and 1.24±0.02, Godavari: 0.43 and 1.40±0.04 and for Mahanadi: 0.25 and 1.25±0.02.

Based on the study of several rivers in India BHAT (1970) obtained a range of concentrations for uranium (0.01-5.0 dpm/l) and for the A.R. (1.03-1.58). The present results fall within this range. BHAT (1970) based on her results observed that
the uranium concentration depends on the terrain through which the river flows. The lowest and highest concentrations were observed for rivers flowing through basaltic and sedimentary terrains respectively. A similar report was made by SACKETT et al (1973) showing that the primary factors determining the uranium concentration of a river are the relative amounts of different types of rocks in its drainage basin and the amount of precipitation. Thus both the previous investigators found that geology of the drainage basin plays an important role in deciding the dissolved uranium concentration of riverine waters.

In the present study Narbada and Tapti on the west coast essentially flow through the similar terrain whereas the east coast rivers Godavari and Mahanadidrain similar geological environments (Fig.11.2). Therefore one would expect that the U concentration and A.R. in Narbada and in Tapti as well as in Godavari and in Mahanadi to be similar. However, the uranium concentrations and the A.R. are distinctly different in both these cases.

It must be pointed out here that most of the measurements were made during the non-monsoon season. Only in Narbada there is extensive sampling during the monsoon where both the U and the A.R. are about the same as those Tapti (average U = 0.28 dpm/l and average A.R. = 1.24±0.02). These factor of two variations in the U concentration and significantly different A.R. during
the non-monsoon seasons could be natural or could be due to effluent seepage of ground waters. BOROLE et al (1979); HUSSAIN and KRISHNASWAMI (1980) and SOMAYAJULU et al (1980) have all found high U concentrations and high A.R. in ground waters from different regions of Gujarat. In fact ground waters were analysed from this general area for uranium isotopes by BOROLE et al (1979) and HUSSAIN and KRISHNASWAMI (1980) and their results indicate that U concentration varied from 0.03 to 8.3 dpm/l and the A.R. varied from 1.24 to 1.57.

Based on the average U concentration in the fresh water-end-members during the monsoon and non-monsoon seasons and the annual discharges of the rivers during the two seasons (for Narbada the annual monsoonal and non-monsoonal discharges are taken to be 94% and 6% of the total respectively whereas for Tapti the corresponding values are 77% and 23% respectively), the annual-weighted-mean-flux of uranium from Narbada and Tapti into the corresponding estuaries is calculated to be 20 to 4 ton respectively.

IV.1.(d) Distribution of dissolved U isotopes in estuarine waters:

The U concentration and the A.R. data of the four rivers Narbada, Tapti, Godavari and Mahanadi are given in Tables III.2 to III.5. The variation of uranium isotopes ($^{238}$U and $^{234}$U) concentration with chlorosity is shown in Fig.IV.5 to IV.7. In all the estuaries for all the periods sampled both $^{238}$U and $^{234}$U
Fig. IV.5. Variation of $^{234}\text{U}$ and $^{238}\text{U}$ concentration (dpm/l) with chlorosity in the Narbada estuary, during different seasons. For correlation coefficients and slopes of the best-fit-lines see Table IV.2.
Fig. IV. 5
Fig. IV.6. Variation of 234U and 238U concentration ($\text{dpm/l}$) with chlorosity in the Tapti estuary during different seasons. See Table IV.2 for correlation coefficient and slopes of the best-fit-lines.
Fig. IV. 6

CONCENTRATION (dpm/l)

CHLOROSITY (g/l)

$^{234}\text{U}$

$^{238}\text{U}$

○ TP 1
● TP 2
× TP 3
△ TP 4

Fig. IV. 6
Fig.IV.7. Variation of $^{234}$U and $^{238}$U concentration (dpm/l) with chlorosity in the Godavari and Mahanadi estuaries. See Table IV.2 for correlation coefficients and slopes of the best-fit-lines.
CONCENTRATION (dpm/l)

\[ \begin{align*}
\text{234}^\text{U} & \quad 2.4 \\
\text{238}^\text{U} &
\end{align*} \]

\[ \text{CHLOROSITY (g/l)} \]

Fig. IV. 7
Table IV.2

Correlation coefficients and slopes of uranium-chlorosity plots for different seasons in the estuaries

<table>
<thead>
<tr>
<th>Estuary</th>
<th>No. of observations</th>
<th>238U Slope (dpm/g.Cl)</th>
<th>Correlation coefficient</th>
<th>234U Slope (dpm/g.Cl)</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>NARB ADA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NB-1</td>
<td>7</td>
<td>0.098</td>
<td>0.985</td>
<td>0.109</td>
<td>0.980</td>
</tr>
<tr>
<td>NB-2</td>
<td>8</td>
<td>0.101</td>
<td>0.984</td>
<td>0.109</td>
<td>0.981</td>
</tr>
<tr>
<td>NB-3</td>
<td>14</td>
<td>0.093</td>
<td>0.987</td>
<td>0.099</td>
<td>0.988</td>
</tr>
<tr>
<td>NB-4</td>
<td>19</td>
<td>0.109</td>
<td>0.997</td>
<td>0.121</td>
<td>0.994</td>
</tr>
<tr>
<td>NB-5</td>
<td>6</td>
<td>0.096</td>
<td>0.996</td>
<td>0.110</td>
<td>0.997</td>
</tr>
<tr>
<td>TAPTI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP-1</td>
<td>4</td>
<td>0.118</td>
<td>0.999</td>
<td>0.137</td>
<td>0.999</td>
</tr>
<tr>
<td>TP-2</td>
<td>8</td>
<td>0.094</td>
<td>0.985</td>
<td>0.106</td>
<td>0.987</td>
</tr>
<tr>
<td>TP-3</td>
<td>6</td>
<td>0.144</td>
<td>0.995</td>
<td>0.164</td>
<td>0.997</td>
</tr>
<tr>
<td>TP-4</td>
<td>10</td>
<td>0.109</td>
<td>0.997</td>
<td>0.126</td>
<td>0.998</td>
</tr>
<tr>
<td>GODAVARI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GD-1</td>
<td>8</td>
<td>0.112</td>
<td>0.996</td>
<td>0.119</td>
<td>0.991</td>
</tr>
<tr>
<td>MAHANADI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MND-1</td>
<td>9</td>
<td>0.124</td>
<td>0.998</td>
<td>0.139</td>
<td>0.997</td>
</tr>
</tbody>
</table>
concentrations increase linearly with chlorosity, with high correlation coefficients (Table IV.2).

The slopes of the best-fit-lines for different seasons in a given estuary are consistent with each other. The extrapolated $^{238}\text{U}$, $^{234}\text{U}$ concentration as well as the A.R. (from the best fit lines) to sea water chlorosity yielded values that are in good agreement with the measurements (though few) made in the coastal Arabian sea waters (SARMA and KRISHNAMOORTY, 1968). All these observations strongly suggest that both the uranium isotopes behave conservatively in these estuaries. The results unequivocally suggest that the distribution of uranium isotopes (within the experimental uncertainties) in these estuaries is primarily governed by simple mixing between river water and surface sea water.

However, a very careful examination of the data for NB3 and NB4 profiles indicate that there is a minor, but measurable decrease in the U isotope abundance when the chlorosity increases from 0.02 to 0.13 g/l (Table III.2). It is uncertain as to whether this decrease is due to minor removal process at low chlorosities or whether it is due to scatter in the uranium isotope concentration in the freshwater-end-member. Many more samples in these chlorosity ranges are required to choose between these alternatives.

The investigations on the behaviour of uranium isotopes in
Two French estuaries and one African estuary have been made by Martin et al. (1978a & b). These investigators reported a conservative behaviour for $^{238}\text{U}$ in the two unpolluted estuaries Gironde and Zaire, whereas in the case of $^{234}\text{U}$ they have attributed a possible non-conservative behaviour. In the other highly polluted Charente estuary both $^{238}\text{U}$ and $^{234}\text{U}$ were reported to be non-conservative. I have tried to look at their data in Gironde and Zaire more critically by plotting separately $^{234}\text{U}$ and $^{238}\text{U}$ as a function of chlorosity. We have found that the A.R. is not as sensitive a parameter as the individual isotope concentrations. Such a plot for Gironde and Zaire is shown in Fig. IV.8. These plots have high correlation coefficients like the Narbada and Tapti plots and when U-Cl best-fit-lines are extrapolated to sea water chlorosity values, quite similar to the sea water concentrations of ($^{238}\text{U}$, $^{234}\text{U}$ and the A.R.) are obtained. Within the experimental uncertainties of their measurements it can be concluded that both $^{238}\text{U}$ and $^{234}\text{U}$ behave nearly conservatively in Gironde and Zaire estuaries. It thus appears that U isotopes behave conservatively in these estuarine environments.

Since there is no net loss or gain of U in the estuaries, the mean-annual dissolved U flux from Narbada and Tapti estuaries to the adjacent sea will be the same as its flux to the estuary viz., 20 ton and 4 ton respectively from Narbada and Tapti.
Fig. IV.8. Variation of $^{234}$U and $^{238}$U concentrations (dpm/l) with chlorosity in Gironde and Zaire estuaries. The correlation coefficients and slopes of the best-fit-lines respectively are:

0.999 and $8.4 \times 10^{-2}$ for $^{238}$U-Cl (Gironde),
0.997 and $9.2 \times 10^{-2}$ for $^{234}$U-Cl (Gironde),
0.994 and $13.7 \times 10^{-2}$ for $^{238}$U-Cl (Zaire),
and 0.995 and $15.2 \times 10^{-2}$ for $^{234}$U-Cl (Zaire See text for discussion).
Figure IV. 8
IV.1.(e) **Distribution of particulate uranium in estuarine waters:**

The particulate uranium concentration in the Narbada waters (chlorosity range: 0.34 to 19.5 g/l) ranged from 1.20 to 1.55 ppm with the A.R. ranging from $1.01 \pm 0.02$ to $1.06 \pm 0.02$ (Table III.6) during different seasons. The three Tapti values are also in the same range. The mean A.R. of all the measurements from Narbada and Tapti estuaries comes to $1.03 \pm 0.02$. Since the excess $^{234}\text{U}$ over the $^{238}\text{U}$ activity in the waters is due to the preferential leaching of the former from the solid material of the drainage basin (which includes the suspended material sampled for U work) one would expect a depletion in the A.R. from the equilibrium value of 1.0. Also the maximum in excess (6% see Table III.6) occurred when the particulate concentrations were high (860 to 6720 mg/l range) and mostly at chlorosities 5-8 g/l. Since the mean A.R. is only 3±2% in excess of 1.00, no serious attempts have been made to seek for an explanation as LEWIS (1976) did in the case of Susquehanna river suspended uranium data (A.R. = 1.21). Thus the uranium concentration, the A.R. as well as the U/Al ratio (Table III.6 and Fig. IV.9) in the Narbada particles (in all the season) have not shown any unambiguous variation with chlorosity in the estuarine region indicating that the adsorption-desorption effects, if any, are small (within the uncertainties of the measurements) in these estuaries. The three uranium and Al measurements made on Tapti suspended phases (Table III.6) are in
Fig. IV.9. (U/Al) ratio and A.R. in particles from different chlorosity zones of the Narbada estuary in the coastal and open shelf and slope sediments of the Arabian sea. Each point in the figure represents the average value of all the samples in that particular chlorosity zone.

The U/Al ratio as well as A.R. do not show any change from the fresh water-end-member to the sea water-end-member, as well as in the near-coastal sediments. An order of magnitude higher U/Al ratio and A.R. equalling that of sea water area seen for the open shelf and slope sediments.
good agreement with those of Narbada.

Taking an annual sediment flux of $5 \times 10^7$ tons and $1 \times 10^6$ tons respectively for Narbada and Tapti with a 1.33 ppm U content (same value is used for both rivers) the annual particulate U fluxes from Narbada and Tapti are calculated to be 65 tons and 1.3 tons respectively. For Narbada the dissolved U flux (20 tons/yr) is less than a third of its particulate flux whereas for Tapti the dissolved flux is about 3 times higher than the suspended flux.

IV.1.(f) Distribution of U in the sediments of the Arabian sea:

The uranium concentrations as well as A.R. for the near coastal surface sediments as well as in four cores from the open shelf and slope regions of the Arabian sea (Fig. II.8) are all given in Tables III.6 and III.7. The U/Al ratios are also given which normalises the U concentration to the clay content of the material. It is seen clearly (Fig. IV.7) that the U contents, the A.R. as well as the U/Al ratios in the sediments of the Gulf of Cambay and nearby near-coastal areas are about the same as those of the Narbada and Tapti suspended phases. This means that the suspended material from these two rivers deposits first in this area unchanged in the parameters studied.

The uranium concentrations in the four Arabian sea cores from the outer shelf and slope region (ARB 46, 52, 54 and 65 H - See Fig. II.8) ranged from 2 to 7.5 ppm (Table III.7) and all the surface sections of these cores have an A.R. of 1.14±0.02. These concentrations are quite high compared to the 1.3 ppm average
of the Narbada and Tapti particulates, the near-coastal sediments as well as the 1-2 ppm U values generally encountered in normal pelagic sediments (KU, 1965). The A.R. equalling the seawater value in these organically rich sediments (organic matter ranged from 5 to 18% see Table III.17) coupled with high U/Al ratios (see Fig. IV.9 which depicts the variation of U/Al and the A.R. in the suspended phases of the Narbada and Tapti estuarine regions, the near-coastal sediments and the shelf and slope sediments) suggest that this area is acting as a sink for uranium. This kind of a removal of dissolved uranium from seawater into the coastal sediments in other parts of the world oceans and in salt marshes have been reported in literature (STORM, 1948; HOLLAND and KULP, 1954; KOCHY, 1954; VEEH, 1967; SACKETT et al., 1972; MO et al., 1973, CHURCH et al., 1980). In reducing regions with high organic carbon uranium is known to be reduced from its +6 valence state in seawater to +4 in which state it gets quickly removed to sediments like for example Th (MCCLAIN et al., 1955; GOLEBERG and KOIDE, 1962). Oxygen deficient and H₂S bearing environments at depths greater than 1000 m in the Arabian sea were found by some Russian workers (DEUSER, 1975). The cores studied in this investigation were reported to be smelling of H₂S at the time of collection in 1967 (KAMESWARA RAO person, communication 1980). JOSHI and GANGULY, (1976) have also reported U enrichments in some of the samples.
collected from coastal environments of the Arabian sea.

IV. 1. (g) Dating of U rich sediments by the $^{234}\text{U}/^{238}\text{U}$ activity ratio method:

This method is based on the decay of the fourteen percent excess $^{234}\text{U}$ over its parent $^{238}\text{U}$ (in sediments where authigenic U precipitation takes place) with its half life of $2.48 \times 10^5$ yrs. Attempts so far made to use this technique on pelagic sediments (which contain 1-2 ppm U) proved unsuccessful since most of the uranium is detrital (KU, 1965) and since there is no proper way of separating the authigenic U from the total (KRISHNASWAMI, 1976).

Though all the four cores from the shelf and slope regions contain high U with the surface samples having an A.R. of 1.14, the seawater value, only one core ARB-52, from the deepest location (Table II.2) was long enough to observe a decrease in the A.R. (Table III.7). The technique, briefly is as follows:

\[
^{234}\text{U}_{\text{excess}} \times 100 = \left( \frac{^{234}\text{U}}{^{238}\text{U}} - 1 \right) \times 100 \quad .. \text{(1)}
\]

The $^{234}\text{U}_{\text{excess}}$ will decay according to the equation

\[
C_X = C_0 \exp (- \lambda_{234} \cdot t) \quad .. \text{(2)}
\]

where $C_X$ is the $^{234}\text{U}_{\text{excess}}$ at depth $X$ (cm) from the surface of the core and $t$ is the age of that layer which is $X/s$ where $s$ is the accumulation rate in cm/yr. Making the standard assumptions that the A.R. of sea water has not changed with time during the dating interval and that there had been no post depositional
migration of U in these reducing sediments one can plot \( C \) as a function of depth \( (X) \), from the slope of which 's' can be determined. Such a plot for core ARB-52 is shown in Fig. IV.10. The best-fit-line through the data yields an accumulation rate of 0.74 cm/10^3 yrs and the maximum rate (taking advantage of the statistical uncertainties on the measurements - Table III.7) can be as high as 2.3 cm/10^3 yrs. In order to make sure that the variation of detrital components (mainly clay) with varying U and A.R. are not responsible for the observed decrease in the A.R. with depth the following correction for detrital U was applied using two methods.

**Method 1:**

In each section of the core analysed the CaCO\(_3\) and organic matter contents have been determined. The remainder is assumed to be clay. Since the U as well as the A.R. of the Narbada and Tapti particles as well as the near-coastal sediments have been determined which are about the same, an average detrital value is calculated to be 0.98\(\pm\)0.01 dpm \(^{238}\)U/g with the A.R. 1.02\(\pm\)0.02. From the \(^{238}\)U and the A.R., the \(^{234}\)U can be calculated for the clay fraction of each section, these values are then subtracted from the corresponding total \(^{238}\)U and \(^{234}\)U contents to get the corrected value the division of which yields the corrected A.R. The corrected A.R. obtained by this method is given in Table IV.3.
Fig. IV.10. Plot of $^{234}\text{U}_{\text{excess}}$ (%) in Arabian sea core ARB-52 as a function of depth. The mean sedimentation rate for the core is deduced to be $7.4 \text{ mm/}10^3 \text{ yr}$ from the best line through the data. The maximum rate can be as much as $2.3 \text{ cm/}10^3 \text{ yr}$. 
Table IV.3

$^{234}\text{U}/^{238}\text{U}$ Activity ratio in core ARB-52 before and after corrections for detrital components

<table>
<thead>
<tr>
<th>Sample depth (cm)</th>
<th>Measured value</th>
<th>Corrected for detrital components*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Using Method 1</td>
</tr>
<tr>
<td>0-5</td>
<td>1.14±0.02</td>
<td>1.16±0.03</td>
</tr>
<tr>
<td>30-35</td>
<td>1.14±0.02</td>
<td>1.15±0.03</td>
</tr>
<tr>
<td>50-55</td>
<td>1.13±0.02</td>
<td>1.14±0.03</td>
</tr>
<tr>
<td>70-72</td>
<td>1.12±0.02</td>
<td>1.13±0.05</td>
</tr>
<tr>
<td>90-92</td>
<td>1.11±0.02</td>
<td>1.12±0.04</td>
</tr>
<tr>
<td>110-112</td>
<td>1.10±0.02</td>
<td>1.11±0.04</td>
</tr>
<tr>
<td>130-133</td>
<td>1.09±0.02</td>
<td>1.10±0.04</td>
</tr>
</tbody>
</table>

*See text for details of Methods 1 and 2.
Method 2:

This is based on the U/Al ratios. Multiplying the average U/Al ratio (of the estuarine suspended phases and that of the near-coastal sediments) with the Al content of each section the detrital $^{238}U$ is obtained. This is then multiplied with the average detrital A.R. (obtained in method 1) to get the detrital $^{234}U$. These values are then subtracted from the corresponding values of $^{238}U$ and $^{234}U$ of the total sediment to get corrected value which on division yeilds the corrected A.R. These values are also indicated in Table IV.3. It is clear that the original data and the corrected data by the two methods all show the same trend (Table IV.3) despite the fact that the corrected values have larger errors. The deduced accumulation rates from the corrected ratios also lie in the range of 0.74-2.3 cm/10$^3$ yrs.

The same core was also dated by the $^{14}C$ method (Fig. III.2) which yielded a sedimentation rate of 4.6 cm/10$^3$ yr. In view of the fact that the $^{234}U$ based maximum rate is only a factor of 2 lower than the $^{14}C$ based rate and considering the above, it gives confidence that $^{234}U$ may prove to be a potential dating technique in some areas of the Arabian Sea.

From a knowledge of the authigenic uranium content of the 0-5 cm section of ARB-52 core, its deposition rate (4.6 cm/10$^3$ yrs obtained by $^{14}C$ method) and assuming an in-situ density of 0.4 g/cm$^3$, the authigenic U deposition rate is calculated to be 6 µg/cm$^2$.10$^3$ yr. This rate has not varied by more than ±25%
during the past 30,000 years. This rate is 150 times faster compared to the authigenic U deposition rate (0.04 g/cm$^2$.10$^3$yr.) in the world ocean deduced by KRISHNASWAMI (1976). Such high U depositions have also been found in other coastal regions (VEEH, 1967; VEEH et al., 1974).

IV.2 Silicon and major cations:

IV.2. (a) Distribution of silicon in Narbada, Tapti, Godavari and Mahanadi estuaries:

In all the four estuaries studied, the silicon concentration in the fresh-water-end member (chlorosity < 0.1 g/l) varied from 200 to 470 μmoles/l. The Si concentrations for rivers flowing through the same terrain (Narbada, Tapti on the west coast and Godavari, Mahanadi on the east coast) are nearly the same (Tables III.10 to III.12). However, the west coast rivers have about a factor of two higher Si content compared to those on the east coast which can be attributed to the changes in the geology of the drainage basin and the high suspended matter content of the former (Table III.13 and III.15). The high suspended matter of the west coast rivers can in turn be related to the geology. Narbada and Tapti flow through the recent alluvial tracks in the last phase of their journey to the sea which is reflected in their high suspended matter contents.

In Narbada, where extensive sampling was done, the seasonal variations in the Si content is marginal; the monsoonal values are about 30% lower compared to the values measured
during the non-monsoon seasons. As in the case of uranium, the 30% high Si concentration during the non-monsoon seasons compared to the monsoonal values, is most likely to be due to subsurface waters. Whereas the U concentrations and A.R. of the sub-surface waters and river waters are distinctly different, the Si in these water types are in the same general range of 200-600 μmoles/l (subsurface waters in the Gujarat region have Si ranges from 400-600 μmoles/l (NIJAMPURKAR, 1974).

In the low chlorosity (0-1.0 g/l) region for all the four estuaries the Si concentrations vary significantly. MARTIN et al (1973) and NIJAMPURKAR et al (1980) have found similar Si variations in the low chlorosity regions of the French estuary, Gironde. It is likely that these variations are due to adsorption/desorption reactions involving the rather high suspended particulate matter (most of which is clay) and/or the influx of subsurface waters. To understand the first, some laboratory experiments were done using Narbada sediment from the fresh water end-member. This sediment was shaken with distilled water at room temperature for up to about 16 hours and small aliquots were taken out and analysed for Si every two hours. In about 8 hours the water reached a Si concentration of 250 μmoles/l which in another 8 hours shaking did not increase by more than ~30%. Though this experiment was carried out at suspended matter concentrations of about an order of magnitude higher than those existing in the river, it proves that leaching of
suspended matter for different periods of time can account for variations observed between 200-300 μ moles/l, the higher values can be attributed to subsurface waters. I now discuss the Si distributions in the west and east coast estuaries separately.

IV.2.(a). (i) Si distributions in Narbada and Tapti estuaries:

The Si variation as a function of chlorosity in the Narbada estuary, for all the seasons studied, is shown in Fig.IV.11 (data is given in Tables III.10 to III.12) and for Tapti the distribution is shown in Fig.IV.12. In both the estuaries there is a strong inverse correlation between Si and Cl with high correlation coefficients, -0.93-0.99. The strong inverse correlation for Si-Cl in all the seasons studied for both the estuaries (especially for Tapti) indicates that dilution of riverine Si by seawater is the major process that regulates the Si distribution in these estuaries. In Tapti, Si behaves conservatively within the errors on the measurements whereas in Narbada, there appears to be a slight deviation from the conservative behaviour. There appears to be some depletion (upto a maximum of 19%) in the Narbada estuary based on the departure of the data from the theoretical dilution curve. The processes responsible for Si depletion will be discussed in the next section.

IV.2.(a). (ii) Si distribution in Godavari and Mahanadi estuaries:

The Si distributions in Godavari and Mahanadi (only one
Fig. IV.11. Variation of silica concentration SiO$_2$ μ moles/l as a function of chlorosity in Narbada estuary, in different seasons. The strong inverse correlation (correlation coefficients -0.93 to -0.99) between silicon and chlorosity is evident. However, when compared to the theoretical dilution curve (not shown in the figure) there appears to be a net Si removal of < 20%. See text for discussion.
Fig. IV.12. Variation of silica concentration ($\text{SiO}_2$ $\mu$moles/l) as a function of chlorosity in Tapti estuary during 1976 to 1979. The strong inverse correlation (correlation coefficient -0.98 to -0.99) between silicon and chlorosity is evident. The results show that silicon behaves conservatively in this estuary.
season data have been collected, Table III.12) are shown in Fig.IV.13. Though the inverse trend between chlorosity and Si concentration is evident, there is no linear decrease of Si like, for example in the case of Tapti (Fig.IV.11 and Table III.11). In other words Si is not behaving conservatively in these estuaries - a significant amount of Si in the intermediate chlorosity regions is getting removed from water by processes other than mixing between the two end-members. Such non-conservative behaviour of Si has also been reported in several estuaries (BIEN et al., 1958; LISS and SPENCER, 1970; WOLLAST and DE BROEU, 1971; MILLIMAN and BOYLE, 1975; DEMASTER, 1979). Such a removal of Si can be due to adsorption on clays (BIEN et al., 1958; LISS and SPENCER, 1970) due to biological processes (WOLLAST and DE BROEU, 1971; MILLIMAN and BOYLE, 1975) or due to inputs of Si poor waters into the estuary at the appropriate chlorosities (presumably what PURUSHOTHAMAN and VENUGOPALAN, 1972 call as mixing). The adsorption/desorption processes may not be very significant as evident from the experiments carried out in the laboratory using sediment (mostly clayey) collected from the mouth of Godavari. It was added to several samples of the Godavari waters at different chlorosities ranging from 6.7 to 19.5 g/l and after periods of 7-30 days the supernate waters were analysed for Si. No loss of Si (from the previous measurements on the samples) was observed; if at all, there was a slight increase. Though not shown in the present investigation,
Fig. IV.13. Variation of silica concentration (SiO$_2$ µmoles/l) in Godavari and Mahanadi estuaries. There is no linear decrease of Si with increasing chlorosity like in the case of Tapti for example (Fig. IV.12). Using the theoretical dilution curve obtained by joining the mean Si concentration of the fresh water end-members and sea water values of Godavari, Si removal is estimated to be 30% in Godavari and 64% in Mahanadi.
it is known that all subsurface and stream waters have in general Si concentrations in the same range reported for subsurface waters and it is not unlikely (though I have no evidence at hand) that there had been some addition of Si poor waters to the estuary. To evaluate the biological process, waters from both Godavari and Mahanadi were filtered through 0.45 μm millipore filters and, these filters were studied under the scanning electron microscope. A large number of diatoms were observed which at least indicate that biological processes as one of the important ones for the nonconservative behaviour of Si in Godavari and Mahanadi estuaries. A similar study made on the Narbada and Tapti particulates using the SEM did not reveal such large abundances of diatoms (only very few numbers were seen). It is also likely that biological processes involving organisms are more common in waters with low suspended matter (Godavari and Mahanadi have a few mg/l compared to Narbada and Tapti which have 10-1000 mg/l - see Tables III.12, III.13 and III.15) compared to the ones with very high suspended matter. Thus it can be said that one of the important processes for Si removal in the east coast estuaries is biological growth of diatoms which convert Si from dissolved phases into suspended phases. It is estimated that the Si removal in Godavari is 30% whereas in Mahanadi it is 64% during the sampling periods (Table IV.4).
IV.2. (a). (iii) Fluxes of dissolved Si to estuaries and adjacent seas of Narbada, Tapti, Godavari and Mahanadi:

The dissolved flux of Si to the estuary is calculated from the annual mean concentration of Si in the water (from the fresh water end member) and the river discharge at that point or any other as close to it as possible. The discharge data is taken from RAO (1975) and the calculated fluxes are given in Table IV.4, these vary from $3.5 \times 10^5$ ton/yr for Tapti to $10.0 \times 10^5$ ton/yr for Godavari. Using these fluxes the corresponding dissolved fluxes of Si from the estuary to the adjacent sea can be obtained by taking into account the loss of Si in the estuary. The results are also summarised in Table IV.4, the fluxes range from $(2.2$ to $7.0) \times 10^5$ ton/yr.

IV.2. (b) Major cations:

The concentrations of major cations Na, K, Ca and Mg measured in the estuarine waters of Narbada (4 sets) and Tapti (3 sets) during different seasons are given in Tables III.10 and III.11 and their variation with chlorosity is shown in Figs. IV.14 and IV.15 respectively for Narbada and Tapti. But for a small scatter in the low chlorosity region ($< 0.5$ g/l) all the four major cations behave conservatively in both Narbada and Tapti within the uncertainties of the measurements ($\pm 5\%$). HASOKAWA (1970) and WARNER (1972) have also reported conservative behaviour for Na, K, Ca and Mg in other estuaries.
Table IV. 4

Fluxes of dissolved silicon to estuaries and to the adjacent seas

<table>
<thead>
<tr>
<th>River</th>
<th>Dissolved silicon flux to the estuary ($10^5$ ton SiO$_2$/yr)</th>
<th>Removal in the estuary (%)</th>
<th>Silicon flux to the adjacent sea ($10^5$ ton SiO$_2$/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narbada</td>
<td>7.7</td>
<td>19</td>
<td>6.2</td>
</tr>
<tr>
<td>Tapti</td>
<td>3.5</td>
<td>Negligible</td>
<td>3.5</td>
</tr>
<tr>
<td>Godavari</td>
<td>10.0</td>
<td>30</td>
<td>7.0</td>
</tr>
<tr>
<td>Mahanadi</td>
<td>6.4</td>
<td>64</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Monsoonal discharge for Narbada, Godavari and Mahanadi is taken to be 94% of the total whereas for Tapti it is taken to be 77% of the total.
Fig. IV.14. Variation of Na, K, Ca, and Mg concentrations (mg/l) with chlorosity in Narbada estuary during different seasons are shown (a), (b), (c) and (d) respectively.
Fig. IV.14
Fig. IV.15. Variation of Na, K, Ca and Mg concentration (mg/l) with chlorosity in Tapti estuary are shown in (a), (b), (c) and (d) respectively.
Regarding the seasonal variation in the fresh water-end-member (≤0.1 g/l chlorosity region) of Narbada Ca does not show any variation whereas the Na, K and Mg concentrations are a factor of 2-3 less during the monsoon season compared to the other seasons.

IV.2. (b). (i) Major cation fluxes to the ocean:

Since the behaviour is conservative the riverine flux of these elements to the estuary is the flux to the ocean. However, as the effect of sea salt spray via atmosphere to the fresh water end-member is not known, the estimates for Na and K may not be meaningful. I have therefore calculated the fluxes of Ca and Mg from Narbada and Tapti by multiplying their annual-mean-concentrations in the fresh water end-members with the annual river discharge. It is estimated that Narbada discharges 10^6 ton Ca/yr and 3x10^5 ton Mg/yr, whereas the corresponding Tapti fluxes are 4x10^5 ton Ca/yr and 2x10^5 ton Mg/yr.

IV.3 Distributions of suspended matter and particulate Al, Mn, Fe, Ni, Cu and Zn in Narbada and Tapti estuaries and in coastal Arabian sea sediments:

The results on the distribution of suspended matter in Narbada, Tapti, Godavari and Mahanadi, the composition of the Narbada and Tapti suspended phases in the estuarine waters of Narbada and Tapti measured during different seasons are reported. These are then compared with the composition of the near-coastal and open shelf and slope sediments of the Arabian sea. Finally
the transport rates of Al, Mn, Fe, Ni, Cu and Zn via suspended phases out of Narbada and Tapti rivers and their deposition rates in the Arabian sea are estimated.

IV.3. (a) Particulate matter concentrations in Narbada, Tapti, Godavari and Mahanadi estuaries:

The estuarine waters of Narbada have by far the highest concentrations of particulates (26 mg/l to 6.7 g/l, Table III.13) during all seasons compared to other three. Tapti has also high concentrations ranging from 20-440 mg/l (Table III.15), whereas in Godavari and Mahanadi the suspended matter content ranged from 2-8 mg/l and 4.0-40 mg/l (Table III.12) respectively. The higher concentrations of suspended matter in the estuarine waters of Narbada and Tapti compared to those of Godavari and Mahanadi can be attributed to the geology of the terrain of the west coast rivers (Fig. II.2). Narbada is a natural system since there is no dam on it whereas Tapti has (Godavari and Mahanadi have too) a dam near Ukai 200 km upstream of Surat (Fig. II.4) and this explains for the high particle concentrations of Narbada. It should also be pointed out that the highest concentration occurred in Narbada, where extensive sampling was done, during the monsoon seasons. In Tapti there is not that much change in these concentrations before and after monsoons, the dam presumably smoothen out the rather drastic changes that would have otherwise occurred. In the case of Godavari and Mahanadi only one set of data was collected. I now calculate the mean annual suspended flux from
Narbada and Tapti rivers to the Arabian sea. Taking a weighted average particle concentration in the fresh water end members (chlorosity < 0.1 g/l) of Narbada and Tapti as 1.17 g/l and 53.6 mg/l respectively and the river discharges from RAO (1976) (Table II.1) the suspended fluxes are estimated to be $5 \times 10^7$ ton/yr and $1 \times 10^6$ ton/yr respectively. The Narbada annual suspended flux obtained here is in good agreement with the average flux $6.8 \times 10^7$ ton/yr calculated by Central Power and Water Commission (CPWC) for the year 1973-1976.

IV.3. (b) Distribution of Al, Mn, Fe, Ni, Cu and Zn in the riverine particles (chlorosity 0.1 g/l):

There is no marked difference in the chemical composition of riverine particles of Narbada and Tapti which is expected due to the almost identical geology of their terrains. The concentration of all these elements are constant to within ±15% in the suspended phases (Table IV.5).

The elements Fe, Mn, Cu and Zn are enriched in the riverine particles of Narbada and Tapti by a factor of about 1.5 to 3 compared to average shale (TUREKIAN and WEDEPOHL, 1961) (Table IV.5), an observation similar to that reported for several north American and European rivers (TUREKIAN and SCOTT, 1967; MARTIN et al., 1979). The enrichment of these elements in the suspended phases of the Narbada and Tapti rivers could be either due to their adsorption on particle surfaces during weathering or due to the enrichment of these elements in the rocks and
Table IV.5
Average elemental concentration of estuarine particles and marine sediments

<table>
<thead>
<tr>
<th>Description</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narbada particles (Total)*</td>
<td>8.4</td>
<td>7.4</td>
<td>1182</td>
<td>72</td>
<td>133</td>
<td>143</td>
</tr>
<tr>
<td>(4.2x10(^{12}))</td>
<td></td>
<td></td>
<td>(5.9x10(^{-10}))</td>
<td></td>
<td></td>
<td>(7.2x10(^{-9}))</td>
</tr>
<tr>
<td>Narbada particles (&lt; 4 (\mu m))*</td>
<td>9.3</td>
<td>8.9</td>
<td>1077</td>
<td>81</td>
<td>136</td>
<td>140</td>
</tr>
<tr>
<td>Tapti particles (Total)*</td>
<td>7.4</td>
<td>7.8</td>
<td>1373</td>
<td>70</td>
<td>139</td>
<td>157</td>
</tr>
<tr>
<td>(7.4x10(^{10}))</td>
<td></td>
<td></td>
<td>(1.4x10(^{9}))</td>
<td></td>
<td></td>
<td>(1.6x10(^{8}))</td>
</tr>
<tr>
<td>Shales</td>
<td>8.0</td>
<td>4.7</td>
<td>850</td>
<td>68</td>
<td>45</td>
<td>95</td>
</tr>
<tr>
<td>Arabian sea coastal sediment (Grabs)</td>
<td>7.4</td>
<td>7.1</td>
<td>1075</td>
<td>73</td>
<td>121</td>
<td>113</td>
</tr>
<tr>
<td>Arabian sea cores (Surface sections)+</td>
<td>6.1</td>
<td>4.2</td>
<td>441</td>
<td>121</td>
<td>112</td>
<td>156</td>
</tr>
<tr>
<td>Equatorial Indian Ocean**</td>
<td>6.3</td>
<td>3.5</td>
<td>812</td>
<td>94</td>
<td>81</td>
<td>-</td>
</tr>
<tr>
<td>Deep Sea clay++</td>
<td>8.4</td>
<td>6.5</td>
<td>6700</td>
<td>225</td>
<td>250</td>
<td>165</td>
</tr>
</tbody>
</table>

Numbers in parenthesis indicate flux to the adjacent sea via suspended matter in ton/yr taking the suspended loads of Narbada and Tapti to be 5x10\(^{13}\) g/yr and 3.8x10\(^{12}\) g/yr respectively.

*Average of (0-0.1 g/l) chlororosity region in all seasons.
+On a CaCO\(_3\) free basis
++CHESTER and ASTON (1976).
soils of the drainage basin itself. However, in case of Narbada the concentration of elements in both total and <4 \mu m size particles (Table III.14) are almost identical which support that the concentration of the material of the drainage basin is reflected in the suspended matter.

IV.3. (c) Distribution of particulate Al, Mn, Fe, Ni, Cu and Zn in the estuarine regions of Narbada and Tapti:


Mixing of river water and sea water causes changes in the ionic strength and pH which can alter the partition of elements between soluble and suspended phases. Elements which are easily hydrolyzable and chemically reactive (e.g. Ti, Fe, Th) may get removed to sediments from solution by adsorption on particles or by flocculation and settling, whereas chemically passive elements may get solvated by desorption or exchange of the particles.
From the above mentioned studies on the distribution of dissolved and particulate elements in the estuaries it has been inferred that elements Mn, Co and Zn are desorbed from the particles (Detailed references are given at the beginning of this para).

The variation of elemental concentration with chlorosity (Tables III.13 and III.15) shows considerable scatter much above experimental uncertainties, but no systematic trend is observed, in all the seasons. The causes for the sporadic high values observed for Zn and Cu in the high chlorosity regions, of the Tapti estuary (Table III.15) and a few values in Narbada fresh water-end-member are not clear. Normalization of elemental abundance with Al (which can be used as an index for clays) reduces the scatter considerably. Figs. IV.16 and IV.17 show the variation of element/Al ratio with chlorosity for Narbada and Tapti (total) particulates. In the case of Narbada where the $<4\mu$m micron size studies were carried out (NB1, NB3 and NB4 - see Table III.14), the scatter in metal/Al ratio is further reduced to some extent. Since $<4\mu$m fraction is principally clay, it means that a significant part of the large scatter in the metal/Al ratios in the total particulates is due to the variation of the clay content in the suspended matter of the estuary.

YEATS et al (1979) inferred from our data on the Mn concentrations of total and $<4\mu$m particulates from the Narbada
Fig. IV.16. Scatter diagram of metal/Al ratios in total particulate versus chlorosity for the Narbada estuary.

(See Table III.13 for data). The mean metal/Al ratios together with the range (in parenthesis) are:

Fe/Al = 0.92 (0.79-1.07)
Mn/Al = 13.9 (10.5-19.4) x 10^{-3}
Cu/Al = 15.6 (13.7-18.1) x 10^{-4}
Zn/Al = 14.7 (12.9-25.0) x 10^{-4} and
Ni/Al = 9.0 (7.3-12.3) x 10^{-4}
Fig. IV.17. Scatter diagram of metal/Al concentration in the total particulate versus chlorosity for the Tapti estuary (See Table III.15 for data). The average metal/Al ratios together with the ranges (in parenthesis) are:

Fe/Al = 1.02 (0.9-1.24)
Mn/Al = 15.8 (13.3-22.9) x 10^{-3}
Cu/Al = 18.1 (15-29) x 10^{-4}
Zn/Al = 18.1 (10.7-40.3) x 10^{-4} and
Ni/Al = 9.7 (8-11.5) x 10^{-4}
Fig. IV. 17
estuary (only the first set - NB1 series - was published, BOROLE et al., 1977) that Mn is depleted in the <4 μm fraction compared to the total. I wish to add here that such an observation becomes less clear when one takes into account the data collected subsequently from NB3 and NB4 sets (Table III.14).

Despite the normalisation of the metal concentration to that of Al, there remains considerable scatter in the metal/Al ratios as a function of chlorosity, the scatter in the lower chlorosity regions (where larger number of measurements were made) is large (Figs. IV.16 and IV.17 give the mean concentrations as well as the ranges for Narbada and Tapti respectively). From Fig. IV.18, histogram of metal/Al ratios for Narbada and Tapti, it can be inferred that despite the scatter there is constancy in the ratios in the same estuaries during different seasons as well as between the two estuaries.

IV.3. (d) Adsorption-desorption effects in the estuary:

We have only the suspended matter composition at hand, and in the absence of the corresponding composition in the dissolved phases, it would be difficult to understand quantitatively the sorption effects. The only way one can process data is to critically look at the data and set the most precise limits on the variation over the mean metal/Al ratio for each element. This was done for Narbada and Tapti particulates after discounting the extreme sporadic variations most of which occur in the TP2
Fig. IV.18. A histogram of metal/Al ratios for Narbada and Tapti particulates (total).
Fig. IV. 18
set (Table III.15). The percentage variation over the mean for Narbada and Tapti respectively are 9% and 8% for Fe/Al, 15% and 12% for Mn/Al, 17% and 12% for Nı/Al, 14% and 20% for Zn/Al and 8% and 17% for Cu/Al. This means that adsorption/desorption effects (if there are) are most probably in these ranges and these variations fall within the scatter itself and cannot be unequivocally estimated. In other words, it can be said that within ±20% the metal/Al ratios are constant in Narbada and Tapti. One of the reasons for not observing any large sorption effects could be due to the very high particulate concentrations and small residence times of water in these estuaries. In view of the low particulate contents, estuaries like Godavari should be more suitable for these studies. The concentrations of Mn, Ni, Cu and Zn in the suspended phases of European rivers, Rhine, Ems and Garonde (MARTIN et al., 1971, 1973) are much higher compared to those of Narbada and Tapti. As pointed out by the investigators the enhancement in the European river suspended phases is mainly due to pollution.

IV.3.(a) Al, Fe, Mn, Ni, Cu and Zn in the coastal, shelf and slope regions of Arabian sea:

The measured concentrations of Arabian sea sediments are given in Tables III.16 and III.17. The Al and Fe contents of Arabian sea sediments are in the range of 6.2 to 8.8% and 3.9 to 7.5% respectively. These are approximately similar to their concentrations in the Narbada and Tapti estuarine particles
which are 6.9 to 9.6% for Al and 6.9 to 9.3% for Fe. Such an observation is indicative of their association with highly resistant (to leaching) clays and that their distribution is controlled by the weathered terrigeneous products.

The Mn, Ni, Cu and Zn concentrations of the near-coastal Arabian sea sediments are almost identical to their concentrations in the Narbada and Tapti estuarine suspended phases.

In the open shelf and slope region cores CaCO₃ and organic matter contents have also been measured in addition to the elemental concentrations. It would be interesting to look into the inter elemental association in these sediments, which is done by calculating the correlation coefficients between the various measured parameters (Table IV.6). It is seen that all the metals measured in this study are inversely correlated to CaCO₃ indicating their detrital source. In the case of Fe and Mn this point is further proved by the high positive correlation 0.98 and 0.95 respectively with Al.

The other important correlation is between organic matter and Ni and Zn (correlation coefficients are 0.93 and 0.85 respectively for Ni and Zn), which indicate their association with the reducing environment. As has been pointed out in section IV.1.(f) of discussion, uranium is also enriched in these sediments. It is also known that these sediments, at the time of collection had H₂S which means that sulphate reduction has
Table IV.6

Correlation between CaCO$_3$, organic matter and elements in Arabian sea sediments

<table>
<thead>
<tr>
<th>Element</th>
<th>CaCO$_3$</th>
<th>Organic matter</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic matter</td>
<td>-0.07</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>-0.81</td>
<td>0.34</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>-0.82</td>
<td>0.37</td>
<td>0.98</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>-0.66</td>
<td>0.08</td>
<td>0.95</td>
<td>0.93</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>-0.68</td>
<td>0.93</td>
<td>0.43</td>
<td>0.44</td>
<td>0.18</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.77</td>
<td>0.82</td>
<td>0.59</td>
<td>0.56</td>
<td>0.36</td>
<td>0.91</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>-0.55</td>
<td>0.45</td>
<td>0.55</td>
<td>0.57</td>
<td>0.41</td>
<td>0.49</td>
<td>0.56</td>
<td>1.0</td>
</tr>
</tbody>
</table>

For 22 observations
been taking place. In such conditions one should find excess Ni and Zn concentrations compared to their detrital inputs. This is exactly what has been observed. In Fig. IV.19 are shown the metal concentrations and metal/Al ratios in the estuarine (Narbada and Tapti combined) particles at various chlorosity zones, in the near-coastal sediments and in the shelf and slope sediments. It is clearly seen that Ni and Zn (despite the rather large scatter) are enriched in the shelf-slope sediments and Mn is depleted by a factor of 0.2. The decrease in the Mn/Al ratio is due to Mn release (in +2 state) from the sediments. LYNN and BONATTI (1969); LI et al (1969); EVANS et al (1973) and SUNDBY (1977) have reported that under anaerobic conditions Mn forms soluble complexes and that it is released from sediments to overlying waters. Ni and Zn are probably enriched as sulphides. In the case of Cu, however, no significant change occurs between the estuary and the coastal Arabian sea (Fig. IV.19).

IV.3.(f) Elemental deposition rates in the coastal Arabian sea region:

The deposition rates of Al, Fe, Mn, Ni, Cu and Zn in the Gulf of Cambay and in the open slope region of the Arabian sea (core ARB-52) are calculated using their (total) concentrations, the deposition rates determined (1.9 cm/yr for Gulf of Cambay and 4.6 cm/10^3 yr for ARB-52 see Figs. III.1 and III.2) and an in-situ density of 0.4 g/cm^3 (KLESHA et al., 1980). Such
Fig. IV.19. Element/Al ratios of the Narbada and Tapti particulates in different chlorosity zones and in coastal and open shelf and slope sediments of the Arabian sea. Errors on the measurements are also indicated.
studies were made earlier by BENDER et al (1969) for Mn, SOMAYAJULU et al (1971) and KRISHNASWAMI and LAL (1972) for ascertaining the authigenic and detrital nature of elements in the marine environment. The average deposition rates for the past about sixteen years from the Gulf of Cambay (the core is only 32 cm long) and the past ∼1000 years (0-5 cm section) in the Arabian sea are given in Table IV.7 along with the rates calculated for deep sea clays (KALESHA et al., 1980). It is seen that the Ni and to some extent Zn are high in ARB-52 even compared to deep sea clays which is due to the special environmental conditions. Otherwise the accumulation rates of elements (corrected for differences in deposition rates) in the Gulf of Cambay and in the Arabian sea are same within a factor of 2-3 and that they represent detrital deposition when compared with the deep sea clay data. Data for more elements and from more areas of the anaerobic regions of the Arabian sea is needed to evaluate this region as a resource.
Table IV.7

Deposition rates of elements* in coastal Arabian sea in comparison with deep sea

<table>
<thead>
<tr>
<th>Location**</th>
<th>Time span (yrs)</th>
<th>Deposition rate (g.cm(^{-2}/10^6) yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Fe</td>
</tr>
<tr>
<td>Gulf of Cambay</td>
<td>16</td>
<td>58292</td>
</tr>
<tr>
<td>Arabian Sea (open shelf)</td>
<td>1000</td>
<td>164560</td>
</tr>
<tr>
<td>Deep sea clays+</td>
<td>67000</td>
<td>47000</td>
</tr>
</tbody>
</table>

*Corrected for differences in deposition rates of sediment (see text for discussion)

**See Fig. II.8 for locations

+KALESHA et al (1980)