Studies on Nutrients of Mandovi & Zuari River Systems

S N DE SOUSA, R SEN GUPTA, SUJATA SANZGIRI & M D RAJAGOPAL
National Institute of Oceanography, Dona Paula, Goa 403004

Seasonal cycle of nutrients was related to rainfall and application of agricultural fertilizers in the low lying areas. The stations at the marine-end showed 2 peaks in nitrate and phosphate corresponding to monsoon and postmonsoon seasons, while the stations at the river-end showed only monsoon peak. Silicate showed a well-defined pattern of distribution with only one peak during monsoon. Applying 'simple mixture' relations using salinity as indicator, it was observed that in premonsoon nitrate, phosphate and silicate were removed from the water but during monsoon only phosphate was removed while nitrate and silicate showed a near-conservative behaviour. In postmonsoon there was a net addition of nitrate and phosphate while silicate showed 50% loss.

Observations on the distribution of micronutrients in the open ocean facilitate understanding ocean circulation and plankton ecology. However, in the study of estuarine processes such as mixing, circulation and cycling of nutrients their usefulness has not been understood well because of the complex sources and sinks for these micronutrients which result in temporal and spatial variations.

Estuaries are complex systems which receive chemical inputs from a variety of sources. River runoff contributes dissolved species derived from chemical weathering of rocks in the watershed, suspended material from mechanical weathering of terrigenous matter and dissolved and particulate material of biogenic origin; while the influx of sea water provides a strong electrolyte solution of nearly constant composition with respect to major ions.

Earlier studies on physical, chemical and biological characteristics of Mandovi and Zuari, the 2 most important rivers in Goa, have been reviewed recently. The present investigation reports data on micronutrients and their distribution in the Mandovi and Zuari rivers, collected between Oct. 1977 and Sept. 1978. Data on physico-chemical, biological and a few major ions such as calcium, magnesium and sulphate, collected during this study have been reported.

Materials and Methods

Eight stations along each of the 2 rivers including 1 each at the uppermost reaches, were selected (Fig. 1) to measure 26 chemical parameters. The total distance covered was 66 km in Mandovi and 67 km in Zuari. The last stations were considered as reference or control stations in the evaluation of the data. In addition, 2 stations were worked in the Cumbarjua Canal. Also 3 stations were worked in the coastal stretch between Baga and Colva. Monthly collection of water samples was carried out from mid-depth every 3 hr for 12 hr. Sampling was done at the mid-channel and was adjusted in such a way as to cover the entire river on a single day during the same 12 hr tidal cycle. This helped in eliminating the fluctuations with tide and to have only the residual tidal effect, which is normally the case in all tide-dominated estuaries. Due to rough weather it was not possible to sample the 3 coastal stations and the 2 stations at the mouth of the 2 rivers during monsoon months, except in September.

Samples for phosphate were fixed on board immediately after collection and estimated by the method of Murphy and Riley. Samples for other parameters were however frozen and analysed later in the laboratory. Nitrate was estimated by the modified method of Morris and Riley (Grasshoff), while salinity was estimated from conductivity measurements carried out using Autosal Model 8400 salinometer. All samples with salinity < 5‰ were, however, analysed.
Results and Discussion

Temporal and spatial variations—In order to understand the temporal and spatial variations in the chemical parameters the calendar year is divided into 3 periods — premonsoon (February to May), monsoon (June to September) and post monsoon (October to January).

Salinity—The extent of salt intrusion into the estuaries varied seasonally in relation to the amount of freshwater discharge. During premonsoon the intrusion by salt water into the estuaries was deep and was maximal in May, the distances being 63 km in Zuari and 55 km in Mandovi (ref. 3, Fig. 2) from the mouth. During most part of the year, salinity of the water in the lower reaches of both the estuaries was equal to or almost equal to that of the coastal water. Lowest salinities occurred from June to September when the intensity of monsoonal runoff was highest. In Mandovi salinity was lower than in Zuari, due to its larger tributary system and greater catchment areas. In Mandovi salinity in May varied from 36.1%o at the mouth (st M1) to 0%o at st M9. In July, when the highest rainfall occurred, salinity varied from 7.42%o at st M2 to 0%o at st M9. Similarly, in Zuari the range was from 36.14%o at st Z1 to 0%o at st Z9 in May, and from 12.26 to 0%o in July. The widest range of salinity observed in Mandovi occurred at st M4, with values fluctuating from 0.17%o in July to 34.66%o in May. Similarly, in Zuari the widest range in salinity occurred at st Z5 where the values fluctuated from 0.03%o in June to 33.58%o in May.

During the non-monsoon months when fresh water addition was insignificant, the salinity was homogeneous from surface to bottom. However, with the onset of monsoon addition of fresh water increased considerably resulting in stratification due to the formation of salt wedge up to a short distance from the mouth, 10 km in Mandovi and 12 km in Zuari.

Inorganic nutrients—Premonsoon — Phosphate concentration was low in this season ranging from 0.6 to 1 µg-at/litre, the concentration decreasing from the sea-ends of the estuaries towards their river ends (Figs 2a and b). Nitrate concentration in Zuari ranged between 1.3 and 7 µg-at/litre, while in Mandovi it was comparatively lower (1 to 2 µg-at/litre; Figs 3a and b). Nitrate concentration was higher at the river end than at the sea end. In both the estuaries there was an area of low nitrate concentration in the mid-estuarine region.

Silicate distribution showed a concentration gradient decreasing from the river end to the sea end. In Mandovi silicate varied between 10 and 70 µg-at/litre while in Zuari it ranged between 10 and 50 µg-at/litre (Figs 4a and b).

The low concentration of nutrients in the 2 estuaries during this season may be due to (i) utilization by primary producers which were maximal in number during this season9,10 and (ii) low concentration of these nutrients in the river water itself. Since silicon is supplied mainly by the river water its concentration showed a decreasing trend from the head to the mouth of the estuary due to the dilution with sea water having low silicon concentration and also due to utilization by plankton and possibly its non-biological removal by adsorption onto suspended particulates11.

Monsoon—Phosphate concentration was high in both the rivers almost through their entire length. The concentration in Mandovi varied between 1 and 2.8 µg-at/litre while in Zuari it varied between 1 and 2.4 µg-at/litre. The concentration decreased from the river end towards the sea end indicating that the river water is the source of phosphate. In both the estuaries there was a region in the middle having a slightly higher concentration of phosphate (Figs 2a and b). Nitrate
concentrations ranged between 4 and 20 µg-at/litre in Mandovi and from 3 to 13 µg-at/litre in Zuari (Figs 3a and b). The concentration increased from the mouth upstream. Like phosphate, nitrate also showed a somewhat higher concentration at the intermediate stations. Silicate concentration was very high during this season (Figs 4a and b). In Mandovi the concentration varied between 100 and 160 µg-at/litre while in Zuari it showed a much wider range (10 to 190 µg-at/litre). In both the rivers the concentration decreased downstream.

Comparing the data on nutrient concentration of the monsoon with the rainfall data for 1977-78 we found that highest concentration of nutrients occurred in June and July when rainfall and runoff were also highest. This indicated the source of enrichment to be chiefly land drainage. High nitrate and phosphate concentrations could also be related to the large amount of fertilizers used in agriculture during this season. Nitrites are not well retained by soil and if not utilized quickly by plants are lost to the drainage, while estuarine sediments act as trap for phosphate. Jitts has shown that estuarine sediments can trap 80 to 90% of phosphate when present in high levels during periods of excessive runoff.

Postmonsoon — Phosphate concentration in Mandovi ranged between 0.6 and 2.4 µg-at/litre with a decreasing trend towards upstream. Highest concentration was found towards the sea. Similarly, in Zuari phosphate concentration varied from 0.5 to 2 µg-at/litre. Here also a decreasing trend from the mouth to upstream (Figs 2a and b) was noted. Nitrate concentration ranged between 1.1 and 12.7 µg-at/litre in Mandovi and between 2.3 and 12.7 µg-at/litre in Zuari. In both the rivers there were high concentrations in mid-estuary while the concentration at the sea end as well as at the river end was relatively less (Figs 3a and b).

Silicate ranged from 10 to 80 µg-at/litre in Mandovi and from 10 to 60 µg-at/litre in Zuari. Unlike phosphate and nitrate, distribution of silicate in this season showed a regular pattern, i.e. high concentration at the river end which decreased gradually downstream.

The salt wedge formed in the 2 estuaries during the monsoon subsided to a greater extent during this season, leading to well mixed conditions. The presence of high concentrations of nitrate and phosphate downstream in comparison with those in the river water suggests that these nutrients are supplied to the
estuary by sea water. Since silicate is mainly supplied by the river water, its concentration showed a regular distribution. Comparatively higher concentration of silicate in Mandovi may be due to the larger number of streams draining freshwater into it as compared to Zuari.

Fluctuations in nutrients followed a seasonal pattern (Fig. 5). While the stations at the marine end (M2 and M5; Z2 and Z6) showed 2 peaks in nitrate and phosphate, one corresponding to monsoon season and the other, comparatively smaller, corresponding to postmonsoon season, the stations at the river end (M8 and M9; Z8 and Z9) showed only 1 prominent peak in nitrate and phosphate concentrations corresponding to the monsoon season. Silicate distribution showed only 1 peak corresponding to the monsoon season. During post and premonsoon seasons, the range in silicate concentrations was narrow, though the stations at the river end had comparatively higher concentrations than the stations at the sea end.

Supply and removal of nutrients—In computing dilution, the salinities at sts M1 - M7 in Mandovi and Z1 - Z7 in Zuari were averaged for the 3 seasons separately. The salinity of the source water was calculated by averaging the salinities at st C2 for the premonsoon and postmonsoon months. However, the salinity of the source water during monsoon is represented by the average of 4 observations at C2 during September only as, due to rough weather conditions, it was not possible to make observations at this station from June to August.

In discussing the processes affecting nutrient concentrations we assumed that the nutrients behaved conservatively, i.e. the concentrations are changed only by physical processes of mixing and dilution and are unaffected by biogeochemical processes. This means

![Fig. 5—Variations in the concentration of nitrate, phosphate and silicate at selected stations in the rivers Mandovi and Zuari](image-url)
that if 2 water masses with differing but uniform nutrient concentrations and with different salinities are mixed, the resultant nutrient concentration of the mixture would be a simple linear function of salinity (chlorinity).

Then the fraction $F$ of freshwater in a sample of the mixture is given by the equation:

$$F = 1 - \frac{S_1}{S_2}$$
given by Ketchum\textsuperscript{14}

where $F$ is fraction of freshwater in the sample, $S_1$, salinity of the sample and $S_2$, salinity of the 'source water'.

Table 1 gives the fractions $F$ of freshwater and the percentage of sea water in Mandovi and Zuari estuaries during the seasons.

In order to compute concentrations of nitrate, phosphate and silicate in the 2 estuaries, as predicted by simple linear model, the observed concentrations of these nutrients at sts $M_1$ - $M_7$ and $Z_1$ - $Z_7$ were averaged for the seasons to give the observed average concentrations in the estuaries. The concentrations of nitrate, phosphate and silicate at sts $M_9$ and $Z_9$ were averaged for the seasons to give the average river water concentrations for the 2 rivers. Similarly the concentration of these nutrients at $C_2$ was averaged during premonsoon and postmonsoon to give the average concentration of the nutrients in adjoining sea water during these seasons. The average concentration of nutrients in sea water during the monsoon is represented only by the observation made in September at $C_2$.

Average concentrations of nutrients in sea water and river water along with the percentages of these 2 water masses present in the 2 estuaries were used to calculate the concentration of nutrients as expected from simple dilution of these 2 waters. The latter concentrations were also calculated using the mixing relation of Carpenter et al.\textsuperscript{15}.

\[ X_{\text{sample}} = X_{\text{river}} + \frac{(X_{\text{sw}} - X_{\text{r}})}{C_{\text{sw}}} \cdot C_{\text{sample}} \]

If the difference between the observed and the calculated concentrations is zero then it was assumed that the particular component follows the simple mixing relationship and is unaltered by biogeochemical processes. However, if the difference is positive then it shows that there is some process operating in the estuary by which the component is added to the estuary. Similarly, if the difference is negative then it shows that the component is removed from the estuarine system by some biogeochemical process.

Tables 2 to 4 give the average observed concentrations of nutrients in the 2 estuaries and their expected values calculated using dilution and mixing relations. The tables also give the percentage difference between the observed and calculated concentrations.

Nitrate—Nitrate was removed from the estuaries during premonsoon months while there was a net addition of nitrate during postmonsoon season (Table 2). During monsoon, however, the difference between the calculated and the observed values was very small suggesting a near-conservative behaviour during estuarine mixing.

In the estuary nitrate is removed through biological productivity and denitrification, while it is added due to river run-off, land drainage and precipitation. Since the 2 estuaries are shallow and well oxygenated nitrate loss due to denitrification could be ruled out. Primary productivity in the 2 estuaries was reported to be maximal during premonsoon and postmonsoon seasons and minimal during monsoon months\textsuperscript{9,10,16,17}. Hence it could be inferred that biological productivity might be the chief process of nitrate removal in the 2 estuaries during the pre and postmonsoon periods. Thus the 14 and 32\% of nitrate loss in Mandovi and Zuari respectively during premonsoon (Table 2) can be attributed to the high productivity during this season. Since biological productivity in the 2 estuaries was minimum during

---

**Table 1—Fraction $F$ of Fresh Water and Percentage of Sea Water in the Estuaries**

<table>
<thead>
<tr>
<th>Sal. $\text{‰}$</th>
<th>Sea</th>
<th>Mandovi</th>
<th>Zuari</th>
<th>Mandovi</th>
<th>Zuari</th>
<th>Sea water $%$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mandovi</td>
</tr>
<tr>
<td>Premonsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>84</td>
</tr>
<tr>
<td>Monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>Postmonsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70</td>
</tr>
</tbody>
</table>

*Mean of 4 observations in September only*
monsoon months the nitrate removal due to biological utilization would also be minimum and in the absence of any addition of nitrate to the estuaries it might show a near-conservative behaviour leading to insignificant difference between the calculated and observed values.

During the postmonsoon, though productivity was high, its effect was neutralized by the intrusion of nutrient rich sea water into the 2 estuaries leading to high positive values of the difference between \((NO_3^{\text{obs}} - NO_3^{\text{cal}})\) which resulted in net addition of nitrate to the estuaries.

Phosphate—Observed phosphate values were smaller than the calculated values in the premonsoon and monsoon seasons while during the postmonsoon the trend was reversed (Table 3). This would mean that phosphate was removed from the estuaries during premonsoon and monsoon while it was added during postmonsoon. In river water phosphate is derived from natural weathering processes and breakdown of polyphosphates used in detergents. However, unlike nitrate, the contribution of phosphate by the atmospheric precipitation is negligible, for example nitrate concentrations ranging from 0.27 to 3.77 µg-at/litre were observed in monsoonal rain in 1975 while the phosphate content was negligible. Other sources of phosphate addition might be sea water and sediments. In addition biological productivity and suspended particulates also act as sources and sinks for phosphate. Possible loss of phosphate with calcium and magnesium in these 2 rivers during pre and postmonsoon has been reported by Sen Gupta and Naik.

Biological productivity in the 2 estuaries has been reported to reach a maximum during premonsoon. Hence loss of phosphate during premonsoon can be attributed to utilization by phytoplankton and removal by adsorption onto sediment and suspended particles. But during monsoon biological productivity was minimum. Hence the high suspended sediment load coupled with low salinity, low pH and highly oxygenated condition of the water might favour removal of phosphate. During postmonsoon enrichment of the estuary with phosphate by sea water was in excess of removal and hence there was a net addition.

Silicate—The negative values of the difference between \(Si_{\text{obs}}\) and \(Si_{\text{cal}}\) during the pre and postmonsoon

---

**Table 2—Average Observed Concentrations of Nitrate-N and the Expected Values**

<table>
<thead>
<tr>
<th>Season</th>
<th>NO(_3)-N µg-at/l (obs)</th>
<th>N(_{\text{cal}}) (µg-at/l)</th>
<th>N(<em>{\text{obs}})-N(</em>{\text{cal}})(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sea</td>
<td>Estuarine</td>
<td>Riverine</td>
</tr>
<tr>
<td>Mandovi</td>
<td></td>
<td>N(_{\text{obs}})</td>
<td>N(_{\text{obs}})</td>
</tr>
<tr>
<td>Premonsoon</td>
<td>3.7</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>Monsoon</td>
<td>11.9</td>
<td>5.9</td>
<td>7.7</td>
</tr>
<tr>
<td>Postmonsoon</td>
<td>3.9</td>
<td>5</td>
<td>2.8</td>
</tr>
<tr>
<td>Zuari</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Premonsoon</td>
<td>3.7</td>
<td>2.8</td>
<td>6.4</td>
</tr>
<tr>
<td>Monsoon</td>
<td>11.9</td>
<td>6.9</td>
<td>8.1</td>
</tr>
<tr>
<td>Postmonsoon</td>
<td>3.9</td>
<td>5.9</td>
<td>6.5</td>
</tr>
</tbody>
</table>

*Calculated from percentages of seawater and river water in the mixture using observed values.

†Mean of 4 observations during September only.

**Table 3—Average Observed Concentrations of Phosphate-P and the Expected Values**

<table>
<thead>
<tr>
<th>Season</th>
<th>PO(_4)-P (µg-at/l)</th>
<th>Dilution(%)</th>
<th>P(<em>{\text{obs}}),P(</em>{\text{cal}})(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mixing</td>
<td>Dilution</td>
</tr>
<tr>
<td></td>
<td>Sea</td>
<td>Riverine</td>
<td>Sea water</td>
</tr>
<tr>
<td>Mandovi</td>
<td></td>
<td>P(_{\text{obs}})</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(_{\text{obs}})</td>
<td>2.1*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(_{\text{obs}})</td>
<td>1.2</td>
</tr>
<tr>
<td>Zuari</td>
<td></td>
<td>P(_{\text{obs}})</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(_{\text{obs}})</td>
<td>2.1*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(_{\text{obs}})</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*Mean of 4 observations during September only
and the positive values of the same for the monsoon indicate that silicon was removed from water in the former, whereas it was added in the latter seasons (Table 4).

River discharge is the chief source of silicate to the estuary, whereas biological utilization and abiological removal of dissolved silicate by adsorption onto suspended sediments are the main processes of removal. High biological productivity together with high suspended sediment loads (Table 5) might be responsible for the removal of dissolved silicon from water during pre and postmonsoon. Burton while studying the behaviour of dissolved silicon in Vellar Estuary observed deviation of silicon values from the linear relationship with chlorosity. He attributed this deviation either partly or wholly to the dilution with freshwater from irrigation canals having low dissolved silicon. However, there was no such freshwater source discharging in Mandovi and Zuari estuaries, which could affect the silicon distribution. Since biological productivity was minimum during monsoon, removal of silicate might also be minimum. The small positive values observed for the difference (Si_{obs} - Si_{calc}) showed that during periods of high river discharge and low productivity, distribution of silicon behaves more or less conservatively, the deviations being due to additions of silicate by streams in small quantities.

Nitrogen-Phosphorus ratio—Redfield observed that in the sea water the ratios of change in carbon, nitrogen and phosphorus were similar to their ratios in phytoplankton. Redfield’s ratios after correction of salt-error in the analytical methods of nitrate and phosphate, finally gave the C:N:P ratio in the water as 106:16:1 by atoms. In the present study an attempt has been made to deduce the ratio of change between nitrate and phosphate in Mandovi and Zuari by applying the linear least-square regression method.

Utilizing all the values of nitrate-nitrogen and phosphate-phosphorus at the 18 stations in both the rivers (Fig. 1) Δ N: Δ P was 20.2:1 by atoms. Excluding the values at the far off stations in both the rivers, which do not have saline water influence, the Δ N: Δ P was 19.8:1 by atoms. In the main estuarine region which includes the first 5 stations in Mandovi and 3 in Zuari and 2 in the Cumbarjua Canal (Fig. 1) Δ N: Δ P remained as 19.4:1 by atoms. Thus the increase in ratio by the inclusion of far off stations was probably because of freshwater influence.

Ratio between nitrogen and phosphorus in the phytoplankton of the Goa coast was 15.4:1 by atoms. This is very close to oceanic ratio of 16:1. The general composition of phytoplankton in the main estuarine region largely included marine forms. Hence, the deviation in the nitrogen phosphorus ratio of the Mandovi-Zuari estuarine system from that of the open ocean is probably because of the addition of nitroenous material in the former from land and river runoff.

Acknowledgement
Grateful thanks are due to Dr S Z Qasim for going through the manuscript and for suggestions, to all colleagues who helped in observations in the field and in the laboratory, and to Mr C V Gangadhara Reddy.
DE SOUSA et al.: NUTRIENTS OF MANDOVI & ZUARI RIVER SYSTEMS

for all his help. This work was carried out under a project sponsored by the Central Board for the Prevention and Control of Water Pollution, New Delhi which generously provided the financial assistance, which is gratefully acknowledged.

References

7 Grasshoff K, Kieler Meeresforsch, 20 (1964) 5.

27 Redfield A C, in James Johnstone Memorial Vol, Univ of Liverpool, 1934, 176.