

SOME OBSERVATIONS ON POLLUTANTS OF VELSÃO BAY (GOA)

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ABSTRACT

Analytical results have been reported on As, Cu and Zn in some of the dead fishes collected during the fish mortality at Velsão Bay where the effluents from a fertilizer factory were being discharged. The levels were compared with those from unpolluted localities. While the levels of copper and zinc are comparable, arsenic was higher in dead fishes. The observed concentrations, however, do not indicate acute toxicity. The environmental parameters indicate significant changes in the water quality of the Velsão Bay. Trace metals in the oysters of the Velsão Bay were monitored and the observed concentrations of Mn, Fe, Ni, Cu, Zn, As and Pb do not indicate any significant influence of the factory effluents.

INTRODUCTION

Continuous discharge of industrial waste into the aquatic environment endangers the safety of aquatic life and can reach the human body through the food chain. In this study, some environmental problems created by the discharge of a fertilizer factory situated at Velsão on the west coast of India have been reported.

The fertilizer factory with a production capacity of 2,20,000 tons of ammonia, 3,40,000 tons of urea and 1,50,000 tons of N.P.K. went into production in June 1973 and discharged about 500 m³/h of waste water into the nearby Velsão Bay which is an important fishing area. This bay was virtually uncontaminated prior to the commissioning of the factory.

A large number of substances in the form of chemicals, intermediates and final products were discharged in varying amounts with the effluents of the fertilizer factory. The major contaminants were found to be arsenic, ammonia and urea. To separate carbon dioxide after gasification of naphtha, the gas mixture is scrubbed with solutions containing arsenous oxide in the Vetrocoke process. It has been observed that although the absorption towers are operated in closed circuit in this process, leakage of some of the solution through the condensation of solvent vapours trapped in gas in the coolers, cannot be avoided. Ammonia obtained from the catalytic reaction of hydrogen and nitrogen is reacted with carbon dioxide in urea autoclave at high temperature and pressure to produce urea. It is well known that the loss of ammonia in the fertilizer factories can be as high as 13 kg ammonia-nitrogen and 22.60 kg urea-nitrogen per ton of the product (Mohanrao and Subrahmanyam, 1973).

Fish mortality for the first time was observed in September, 1973, which created an immediate reaction that arsenic was probably responsible for the

mortality. Some marine animals found dead on the beach, were collected and preserved in the laboratory for the analysis of arsenic, copper and zinc. Our objective was to determine levels of arsenic in these animals to ascertain whether arsenic was responsible for this mortality. The samples were preserved in formalin for subsequent analysis (Bertine and Goldberg, 1972). The analysis of the preservative did not show any detectable arsenic level thus ruling out the possibility of arsenic being present in the formalin.

In order to have an idea about the comparative degree of variability of metals from different regions, copper and zinc were estimated in the animals from other locations also along the Goa coast (Fig. 1).

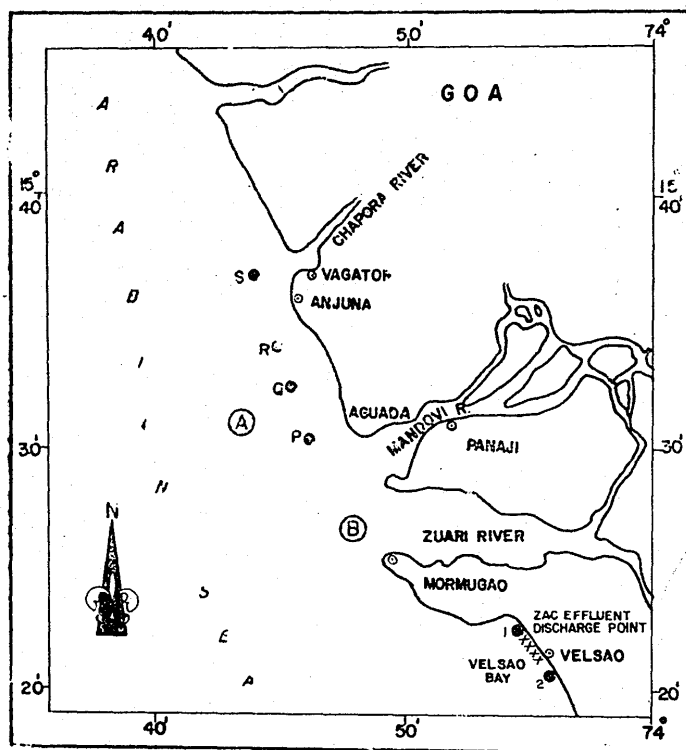


Fig. 1. Map showing the station positions.

- Solid circles — stations monitored for environmental parameters.
- Dotted circles— trawling areas from where fishes were collected.
- Crosses — locations from where marine animals were collected.

The trace metals in animals (fish, mussels etc.) collected from the same area were determined using the methods described elsewhere (Zingde, Singbal, Moraes and Reddy, 1976).

MATERIAL AND METHODS

Sampling locations are shown in Fig. 1. Fortnightly or monthly observations on environmental parameters were made from 1973 to 1975, and the data are presented in Table I. The values were grouped into 3 seasons: pre-monsoon (February to May), monsoon (June to September) and post-monsoon (October to January), each group representing the average value for that period.

Salinity, dissolved oxygen, inorganic phosphate, nitrate, ammonia and urea in the waters were measured using standard laboratory techniques reported earlier (Singbal, Fondekar and Reddy, 1976). Urea was estimated by the method adopted by Newell, Margan and Cundy (1967). Arsenic in water was determined as described elsewhere (Fondekar and Reddy, 1974).

RESULTS AND DISCUSSION

The results of the analysis are presented in Table II along with the data from the animals collected from the trawling regions A and B shown in Fig. 1.

Table I. Chemical features of the effluent and of the waters of the different stations along Goa coast in different seasons.

| Period | Effluent | Velsao Bay | | Goa Coast | | | |
|------------------------------------|----------|------------|-----------|-----------|-----------|-----------|-----------|
| | | Station 1 | Station 2 | Station P | Station Q | Station R | Station S |
| SALINITY (%) | | | | | | | |
| Post-M 73 | — | 32.4 | 32.6 | — | — | — | — |
| Pre-M 74 | 0.3 | 33.0 | 32.9 | 32.9 | 32.9 | — | — |
| M 74 | 0.2 | 27.6 | 26.2 | 8.2 | 8.2 | — | — |
| Post-M 74 | 0.3 | 28.6 | 28.4 | 26.0 | 27.0 | 32.2 | 32.6 |
| Pre-M 75 | 0.1 | 32.8 | 33.1 | 33.2 | 33.1 | 33.1 | 33.3 |
| pH | | | | | | | |
| Post-M 73 | — | 8.4 | 8.3 | — | — | — | — |
| Pre-M 74 | — | 8.4 | 8.3 | 7.9 | 7.8 | — | — |
| M 74 | 7.9 | 7.8 | 8.1 | 8.0 | 8.2 | — | — |
| Post-M 74 | 7.8 | 8.2 | 8.2 | 7.9 | 8.0 | 8.0 | 8.0 |
| Pre-M 75 | 7.8 | 8.0 | 8.1 | 7.8 | 7.8 | 7.9 | 7.8 |
| OXYGEN (ml/l) | | | | | | | |
| Post-M 73 | — | 4.4 | 4.5 | — | — | — | — |
| Pre-M 74 | — | 4.6 | 5.9 | 4.7 | 4.7 | — | — |
| M 74 | 4.2 | 4.5 | 4.6 | 4.3 | 4.6 | — | — |
| Post-M 74 | 4.1 | 4.1 | 4.7 | 4.9 | 4.8 | 4.7 | 4.8 |
| Pre-M 75 | 4.1 | 4.1 | 4.8 | 5.2 | 4.8 | 4.8 | 5.0 |
| PHOSPHATE ($\mu\text{g-at P/l}$) | | | | | | | |
| Post-M 73 | — | 3.7 | 2.6 | — | — | — | — |
| Pre-M 74 | — | 3.0 | 3.0 | 1.2 | 1.0 | — | — |
| M 74 | — | 4.1 | 3.2 | 1.8 | 1.9 | — | — |
| Post-M 74 | 58.5 | 14.2 | 4.3 | 2.0 | 2.0 | 1.3 | 2.0 |
| Pre-M 75 | 53.0 | 4.0 | 3.8 | 1.0 | 0.9 | 0.5 | 0.7 |
| NITRATE ($\mu\text{g-at N/l}$) | | | | | | | |
| Post-M 73 | — | 26.4 | 12.4 | — | — | — | — |
| Pre-M 74 | — | 48.4 | 32.5 | 1.1 | 1.3 | — | — |
| M 74 | 120.7 | 98.3 | 27.3 | 3.0 | 2.9 | — | — |
| Post-M 74 | 343.6 | 80.2 | 26.6 | 1.8 | 2.0 | 2.2 | 6.0 |
| Pre-M 75 | 500.0 | 42.7 | 26.3 | 0.9 | 1.0 | 2.7 | 2.4 |
| NITRITE ($\mu\text{g-at N/l}$) | | | | | | | |
| Post-M 73 | — | — | — | — | — | — | — |
| Pre-M 74 | — | 12.3 | 10.9 | 1.0 | 0.6 | — | — |
| M 74 | 38.7 | 18.3 | 13.6 | 0.4 | 1.0 | — | — |
| Post-M 74 | 176.5 | 16.5 | 12.0 | 1.2 | 0.4 | 0.4 | 2.8 |
| Pre-M 75 | 362.6 | 42.8 | 16.2 | — | — | 1.0 | 0.8 |
| AMMONIA ($\mu\text{g-at N/l}$) | | | | | | | |
| Post-M 73 | — | 102.0 | 76.2 | — | — | — | — |
| Pre-M 74 | — | 24.1 | 20.7 | 0.5 | 0.7 | — | — |
| M 74 | 61.2 | 15.3 | 10.0 | 2.2 | 1.8 | — | — |
| Post-M 74 | 178.3 | 52.7 | 18.3 | 0.4 | 0.4 | 0.6 | 1.2 |
| Pre-M 75 | — | 17.6 | 4.8 | 0.9 | 1.0 | 0.4 | 0.8 |
| ARSENIC ($\mu\text{g/l}$) | | | | | | | |
| Post-M 73 | — | 275.8 | 201.8 | — | — | — | — |
| Pre-M 74 | — | 47.4 | 103.5 | — | — | — | — |
| M 74 | — | 37.0 | 34.8 | — | — | — | — |
| Post-M 74 | — | 43.6 | 61.0 | — | — | — | — |
| Pre-M 75 | — | — | — | — | — | — | — |

It can be seen from Table II that higher levels of arsenic were encountered in dead animals of the same species from other localities while copper and zinc concentrations were comparable. It is, therefore, evident that the effluents had indeed increased the arsenic levels in the marine animals. However, it is difficult to differentiate if the observed high levels were either due to normal bioaccumulation or due to bulk discharge of the effluents previously. Highest concentration (65.6 ppm) was observed in the crab while the butter fish exhibited the lowest concentration (6.8 ppm). The higher concentrations in the crab and also in the prawn were in accordance with the general observation that probably crustaceans are most susceptible to environmental conditions modified by human activities. Though arsenic concentrations were high in the dead animals they did not indicate severe arsenic poisoning. Arsenic in marine fishes generally ranges from 1 to 20 ppm (Leatherland and Burton, 1974). However, several cases of higher arsenic levels have been reported. Leblanc and Jackson (1976) found 37.8 ppm (wet weight) in the crab from the coast of British Columbia. In Greenland, arsenic in prawns ranged from 62 to 80 ppm (Bohn, 1975). As high as 540 ppm arsenic has been reported in samples of cod mussel (Robertson, Rancitelli, Langford and Perkins, 1972). These abnormal levels may be due to the natural bioaccumulation ability of these animals in the environment. There has been no earlier mention of any arsenic contamination from the Velsao Bay from where the data have been collected.

Ammonia is another dangerous toxicant which can cause mortality at higher concentrations. The data reveal abnormal concentrations of ammonia in the bay water (Table I). The concentration showed wide variation from one collection to another

Table II. Arsenic, copper and zinc in some marine animals collected from the Velsao Bay and localities A and B.

| Scientific Name | Common Name | Arsenic $\mu\text{g/g}$ (dry wt) | | | Copper $\mu\text{g/g}$ (dry wt) | | | Zinc $\mu\text{g/g}$ (dry wt) | | |
|--------------------------------|--------------------|----------------------------------|------------|------------|---------------------------------|------------|------------|-------------------------------|------------|------------|
| | | Dead animal | Locality A | Locality B | Dead animal | Locality A | Locality B | Dead animal | Locality A | Locality B |
| <i>Lactarius lactarius</i> | Butter fish | 6.8 | 0.8 | 1.8 | 4.1 | 3.5 | 4.8 | 15.1 | 8.6 | 12.0 |
| <i>Otolithus ruber</i> | Rosy Jew fish | 16.6 | 3.2 | 1.8 | 2.8 | 5.0 | 12.3 | 28.2 | 31.6 | 28.7 |
| <i>Trachysurus sp.</i> | Cat fish | 19.3 | 3.6 | 6.2 | 12.4 | 8.6 | 7.1 | 55.0 | 76.7 | 64.3 |
| <i>Epinaphelus malabaricus</i> | Rockcod | 18.2 | — | 3.4 | 8.2 | — | 2.6 | 35.5 | .. | 15.4 |
| <i>Penaeus indicus</i> | Jumbo prawn | 60.3 | 7.6 | 8.0 | 23.2 | 14.3 | 31.9 | 32.8 | 21.0 | 28.5 |
| <i>Leiognathus splendens</i> | Silver bellies | 12.0 | 0.7 | — | 3.9 | 1.7 | 4.2 | 8.6 | 30.0 | 22.6 |
| <i>Carcharias acudentis</i> | Shark | 56.3 | 8.3 | 11.5 | 10.3 | 15.6 | 8.1 | 22.6 | 25.8 | 36.9 |
| <i>Portunus pelagicus</i> | Blue swimming crab | 65.6 | 8.3 | 12.6 | 36.6 | 28.6 | 48.7 | 86.0 | 46.3 | 38.1 |

depending upon the effluent discharge. Concentration as high as 100 μg at $\text{NH}_4^+-\text{N}/\text{l}$ was detected in the waters after the fish mortality had occurred.

The discharge of effluents with high urea content increased its concentration in the sea water to abnormal levels. While the natural background levels were in the range 0.9 to 4.9 μg at N/l , the concentrations in the bay were often 5 times greater (Table III). Urea in itself is non-toxic to marine life (D' Silva and Verlencar, 1974), but in the marine environment it hydrolyses to produce ammonia. However, hydrolysis is normally slow at normal temperature and pH of sea water (Stiff and Gardener, 1973).

Concentration of metals in marine organisms in Velsao Bay

Marine organisms have the ability to accumulate trace metals and therefore can be considered as supplementary evidence on the water quality. The levels of Mn, Fe, Ni, Cu, Zn, As and Pb in the oysters from the Velsao Bay were measured to serve as possible indicators for assessing the degree of pollution. Oysters were chosen for the study because they were plentiful, sessile in habit and have a tendency to accumulate several metals continuously from the environment. Specimens were collected every month from the rocky shores of the Velsao Bay from January 76 to April 76. The data collected are shown in Table IV. There were no regular variations from January to April. Comparison of levels (Table IV) in the bay

Table III. Concentration of urea in the effluent and at stations 1, 2, P, Q, R and S.

| Stations | Urea ($\mu\text{g-at N/l}$) | | |
|----------|-------------------------------|-----------|-----------|
| | October '74 | March '75 | April '75 |
| Effluent | 7000 | 7000 | 7000 |
| Stn. 1 | 102 | 84 | 52 |
| Stn. 2 | 24 | 32 | 18 |
| Stn. P | 3.3 | 2.7 | 2.8 |
| Stn. Q | 1.7 | 4.9 | 2.0 |
| Stn. R | 2.3 | 0.3 | 1.3 |
| Stn. S | 4.8 | 2.8 | 0.9 |

Table IV. Concentrations of Mn, Fe, Ni, Cu, Zn, Pb and As in oysters (*Crassostrea cucullata*) of Velsao Bay.

| Element | Oysters Conc. of metals in $\mu\text{g/g}$ | | Near the ZAC Discharge Point | Waters Conc. of metals in $\mu\text{g/l}$ | |
|-----------|---|---------|---------------------------------|--|--------|
| | Range | Average | | Area 1 | Area 2 |
| Manganese | 10-62 | 27 | 15.8 | 12.5 | 15.8 |
| Iron | 362-820 | 625 | 35.6 | 26.9 | 55.7 |
| Nickel | 0.5-4 | 1.8 | N.D. | N.D. | N.D. |
| Copper | 280-362 | 323 | 6.2 | 5.9 | 7.6 |
| Zinc | 1300-3000 | 2100 | 12.5 | 10.7 | 16.1 |
| Lead | 1.5-12 | 4 | N.D. | N.D. | N.D. |
| Arsenic | 5.8-2.11 | 3.95 | 100.64 | 16.11 | — |

water and those at locations A 1 and 2 (far from the discharge point) indicate that the factory effluents have not grossly modified the heavy metals load of the bay. The concentration of metals in the oysters when compared with those of the other animals from the polluted areas elsewhere indicates that the levels of metals in the oysters of Velsao Bay are not very high. They were similar to those recorded in the same species from other parts of Goa (Zingde, Singbal, Moraes and Reddy, 1976).

It may be mentioned here that the factory has now undertaken additional measures to avoid the contamination of Velsao Bay. The manufacturing process has also been changed from Vetrocoke to Benfield which eliminates the use of arsenic. The effluents are now being discharged far into the sea through a submarine pipeline. Further studies on the accumulation of metals in marine organisms will be taken up after the conditions in Velsao Bay are properly stabilized.

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