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Toxicity of Effluent from a Titanium Dioxide Factory on Some Marine Animals

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Received 9 *August* 1978; *revised received* 12 *October* 1978

Toxicity of effluent from a titanium dioxide factory containing sulphuric acid residue with soluble iron metallic salts and insoluble material such as silica, etc. on fishes, decapods and molluscs was studied. The effluent caused changes in *p*H and oxygen depletion of the sea water. Sublethal effects of the precipitate of ferrous salts were also studied. Dilutions of effluent up to 1:150 were LC_{100} for all organisms used while 1:200 dilution was LC_{50} for fishes at 36 hr and for other organisms at 48 hr. But death of organisms at this concentration was caused by *p*H changes and O_2 depletion and did not account for the effects of the precipitate. Below this level precipitation started soon after mixing with sea water causing death of organisms by choking their gills and siphons. Dilutions $\leqslant$ 1:1000 were 96 hr LC_0.

Pollution of natural environments from a wide range of sources and pollutants have become an inevitable feature of the present day living. This is particularly true of the areas situated near heavy industrialisation and urbanisation. While the influence of pollutants on marine ecosystems is known to some extent, information regarding their nature of action and physiological changes on marine organisms is meagre. Toxicity tests have become important tools in determining the permissible levels of these pollutants in the environment and thus in the ecological monitoring of systems. A titanium dioxide factory situated at Trivandrum, Kerala, discharges its effluents into Arabian Sea through the beach. The rate of effluent discharge is about 1600 m^3/day and the waste (temperature of effluent at discharge point – 45 to 50°C) having a pungent odour consists of a mixture of sulphuric acid (~3%) ferrous sulphate (10-40 g/litre) and insoluble materials such as silica and undissolved titanium dioxide. On mixing with the sea water, the ferrous sulphate gets oxidised to ferric form and precipitates as ferric hydroxide causing oxygen depletion and imparting a reddish brown colour to the sea water. The effluent spreads along the coastal waters as a patch and its direction depends on littoral drift. A survey conducted in 1976-77 has revealed[1] that there is a considerable depletion of the intertidal and benthic organisms in the area as a result of effluent discharge. Hence, it is felt necessary to conduct experimental studies to ascertain the levels of toxicity of the effluent.

A wide spectrum of animals were used for the studies consisting of fishes belonging to the genera [*Mugil, Salarias, Upenus, Chiloprion, Callydon, Chaetodon, Abudefduf, Pomocentrus* and *Chromis*], prawns [*Penaeus indicus* and *Metapenaeus dobsoni*], lamellibranch [*Donax* sp.], gastropod [*Terebra* sp.] and decapods [(Anomura) *Emerita* sp. and *Albunea* sp.].

Experiments were conducted after conditioning the animals in filtered sea water for 24 hr and introducing them into tanks (30 l) containing various concentrations of effluent diluted with filtered and aerated sea water. The effluent was collected freshly from the discharge point before dilution and was diluted for the experiment after cooling it to room temperature. Separate experiments were conducted with each group of animals using 10-15 for fishes and decapods and 25-30 for the molluscs. In experiments using molluscs and Anomurans bottom of the tank was filled with clean sand. Controls were set up with each experiment for comparison using the same filtered sea water. Measurements of *p*H were conducted with a *p*H meter and O_2 concentration by modified Winkler technique as described in Barnes[2]. During the experiments ambient temperature was maintained. Dilutions selected for the experiments (from 1:50 to 1:2000) covered a wide range of *p*H (2 to 7.5) to simulate the acid waste concentration and *p*H values observed in the actual area of effluent discharge. The area of effluent discharge was studied for 1 yr and it was observed that the *p*H of sea water at and near the point of mixing was as low as 2, although the *p*H rapidly increased in areas away from discharge point. Toxicity of the effluent was assessed from its lethality on the animals.

Death of organisms from the effluent can be due to severe changes in *p*H of water, asphyxiation owing to oxygen depletion and prolonged sublethal effects of the precipitate suspension in the water column. Sulphuric acid is known to be harmful to marine organisms even at very low concentrations[3]. Oxygen concentration and *p*H of the sea water were drastically affected by the effluent (Fig. 1). Experiments showed that dilutions of the effluent up to 1:150 (*p*H 4.1, oxygen concentration (29.5%) were lethal within 2 to 10 min. Below this, varying degrees of stress conditions were observed

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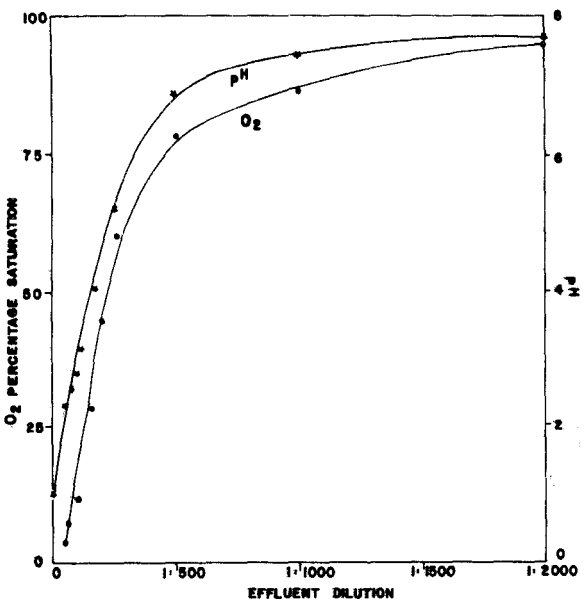

Fig. 1—Changes in *p*H and oxygen percentage saturation at different dilutions of the effluent

depending on the organism and concentration of the effluent; effluent affected the organisms in 2 ways—(i) due to lowering of *p*H and (ii) due to formation of precipitate. Dilution of 1:200 although observed not to cause immediate death of organisms caused stress. Many of the fishes tried to jump out on introducing them to the experimental tank. Later they became sluggish and soon moribund. Death of fishes introduced into this medium occurred in about 36 hr.

Dilution 1:200 was LC_{50} for fishes at 36 hr and for decapods and molluscs at 48 hr. The lamellibranchs which initially burrowed into the sand and had their siphons out, came out of the sand after sometime and closed their shells. Later the shells opened probably owing to the inactivation of the adductor muscles and the animals died. But these reactions did not include the reaction of the organisms to precipitate and its effects since precipitation at this concentration started only after 30 to 35 hr when the *p*H increased to 5.6 after 30 hr.

At 1:250 dilution, precipitation started after about 2 hr and death of organisms occurred within 5 to 8 hr. The gills of the fishes and decapods and siphons of molluscs were heavily deposited with the precipitate. The shells were also stained with it. It has been shown[4] that metals act on gill surfaces causing thickening of the epethelial walls resulting in death by asphyxiation. Even otherwise sufficient quantities of precipitate gathered in the gills and siphons would impair the respiratory and feeding mechanisms of these organisms. At 1:500 dilution precipitation started immediately but organisms survived 20 to 40 hr owing to the lower concentration of the precipitate.

Experiments were conducted by adding sulphuric acid to sea water to bring the acid content to levels imparted by various concentrations of the effluent. It was found that at 1:150 dilution (as of the effluent) the animals although survived a little longer than those at the same concentration of the effluent, died within 30 min to 1 hr confirming that the severe *p*H changes affect the organisms. Experiments conducted after bringing the effluent concentration to 1:250 and neutralising it to raise the *p*H to 7.1 showed immediate precipitation and the animals displayed stress conditions and were moribund within 5 to 6 hr. The precipitate after settling to the bottom was not seen to be avoided by fishes or prawns although the molluscs which are sedentary clustered in the places without precipitate.

It has been observed[5] that in spite of considerable accumulation of Fe-oxide-hydrate flakes directly above the sediment, settlement of new species or larvae of polychaetes were not hindered. But long term experimental studies[6] on mussels fed with ferric hydroxide flakes showed loss of body weight and high mortality rate among them. Substantial mortality of adult copepods in laboratory experiments to study effects of acid-iron wastes were observed[7] at *p*H 6.5 and less. Acute toxicity tests using different metals[8] had shown iron to be less toxic than other metals like mercury, copper or chromium with 48 hr LC_{50} for brown shrimp *Crangon* to be between 33 and 100 ppm and for European cockle *Cardium edule* between 100 and 330 ppm.

Dilutions of 1:1000 and 1:2000 over a period of 96 hr were safe for all types of organisms used, in spite of constant mixing of the water to keep the precipitate in suspension. Survival rate of 100% was observed in all controls used.

The authors thank Dr S.Z. Qasim, Director, for facilities and encouragement and Dr T.S.S. Rao, for his interest and suggestions.

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