In the Tamil Nadu state of India, three stations on the Ennore estuary and one station on the Kovalam estuary on the Bay of Bengal were studied for seasonal changes in water quality parameters for a period of two years from April 2005 to February 2007. It was confirmed that the values were significantly higher at Station III on the Ennore estuary when compared to Stations I and II and the Kovalam estuary station, which was used as the control site. The results suggest that an increased seasonal change in water quality parameters of the Ennore estuary may be due to high pollution caused by the surrounding industries. The seasonal variation of the parameters in the Ennore estuary appeared to be dependent on biological processes and the environment pollution status.
INTRODUCTION

The restricted exchange between estuaries and the open sea allows rapid changes in salinity, temperature, nutrients and sediment load, and this variability and low salinity have strong effects on both the composition and the dynamics of the biota. Runoff, enhanced by domestic inputs during rainfall, has become the main factor influencing water quality in the estuary today (Aslan-Yılmaz et al., 2004).

In an open estuarine ecosystem, the degradation and pollution will go on much longer before the size of the disturbance is noted. It has been reported that estuaries are often highly polluted brackish environments (Kautsky, 1998). The sources of pollution, such as industrial wastes, are recognized as long-term and widespread pollutant sources to aquatic systems.

Once chemical contamination reaches a concentration whereby it causes adverse effects to biota, then the estuary is considered polluted. One such contaminated estuary that is facing a great threat for the past few years due to indiscriminate disposal of waste from surrounding industries is the Ennore estuary situated on the east coast of the state of Tamil Nadu, India.

Physicochemical factors are also responsible for physical, and chemical partitioning behavior. Seasonal effects are critical in biomonitoring programs, especially when sampling is done at different times of the year. Currently little is known about the influence of seasonal changes on physicochemical characteristics in the Ennore estuary.

Padmini and Kavitha (2005a) have reported that the brain tissue of the grey mullet inhabiting the Ennore estuary is subjected to severe stress as it attempts to survive in the highly contaminated estuarine conditions.

The objectives of the current study were: (i) To study the short-term temporal and spatial distribution of the parameters in the Ennore estuary in order to evaluate the impact of increased pollution impact to the estuary, and (ii) to determine the influence of pollution on seasonal variation in the physicochemical parameters of the estuary by comparing it with the less polluted Kovalam estuary.

MATERIALS AND METHODS

Water samples for annual seasonal variation were collected during the period of April 2005 to February 2007. The study period was divided into four seasonal groups (based on the north east monsoon which brings the maximum amount of rainfall to the east coast of India); summer (April, May, June), pre-monsoon (July, August, September), monsoon (October, November, December), and post-monsoon (January, February, March).

To establish seasonal variation, two sites were included in the study; the Kovalam estuary, the less polluted control site, and three stations in the Ennore estuary. These are Station I (Bar mouth region), Station II (Ennore Creek region about 1.5 km from Station I) and Station III (left side of the railway bridge), which is the most polluted site. Two sites were selected in order to investigate whether the seasonal variations were dependent on the pollution in the environment. Water samples were taken every month for all the seasons for the water quality parameter analysis.

Water quality parameter analysis

Temperature of the water and atmosphere was recorded with a routine mercury thermometer and measurement of pH was made on a digital pH meter (ELICO model LI 120). Salinity of water
samples was estimated by the Skoog and West method (1976) a modified classical Mohr titration method, and dissolved oxygen by the Nowaczyk et al. (1993) method, Winkler’s method with some modifications.

For statistical analysis, the water quality parameters were analyzed using a 2-way ANOVA (Sokal and Rohlf, 1995) with seasons and stations as independent factors.

RESULTS

Results (Figures 1 and 2) showed that the Ennore estuary had significantly higher values of the water quality parameters. At Station III of the Ennore estuary, the range of parameters between summer and monsoon seasons was as follows: atmospheric temperature 34.57-32.54 °C (NS - non significant), water temperature 37.43–30.15 °C (p<0.01), pH 8.73-7.64 (p<0.005), and salinity 38.63–32.86 ppt (p<0.01). These values were highly significant compared to the control site which had parameter value ranges of 28.9–26.5 °C, 29.43–27.33 °C, 7.33–7.18, and 28.42-26.72 respectively, which showed no seasonal difference. The various characteristics (temperature, pH and salinity) of the Kovalam estuary were found to be around the normal range as prescribed by ISI. During both seasons, at Station III of the Ennore estuary, the values of the physicochemical parameters were significantly higher (p<0.01) when compared to the Kovalam estuary.

By 2-way ANOVA, it was also shown that between the three stations of the polluted Ennore estuary, Station III had comparatively higher concentrations of the water quality parameters (p<0.05).

The seasonal variation of temperature showed more or less a decreasing trend from April to March with a maximum decrease in the month of October.

Unlike other parameters, higher values for dissolved oxygen were found during the monsoon compared to summer in both estuaries (Figure 3). In this figure, the concentration of dissolved oxygen (3.58±0.053 and 4.12±0.08 mg/L, p<0.01) at Station III of the Ennore estuary was significantly lower than the concentration in the Kovalam estuary (4.86±0.098 and 4.98±0.08 mg/L) respectively.

Though there were seasonal effects in the Ennore estuary, the changes were much greater than in the Kovalam estuary, which is likely to be due to contamination in the Ennore from surrounding industries.

DISCUSSION

Estuaries are among the most productive of marine environments, although food abundance does fluctuate greatly over space and time. The extraordinary productivity of estuaries is a product of the large amounts of nutrients that enter the estuary seasonally and of the extensive recycling of nutrients between the overlying water and the biologically active sediments. Few environments expose their inhabitants to such a variety of abiotic variables and of such large magnitude as does an estuary (Mees et al., 1995; Mees and Jones, 1997).

The annual average of water quality parameters agreed well with historical values for the Kovalam estuary and did not present any evidence of abnormality in their distributions.

The various water quality parameters were found to be high during summer and low during the monsoon in the Ennore estuary. The low values may be due to fresh water input, following rains.
as well as due to surplus water from Poondi reservoir discharged into the sea via the Ennore creek. Raised values may be due to summer evaporation (Murthy and Rao, 1987).

Sivasamy (1990) had reported that the concentration of organochlorine pesticides in water and sediment in the Ennore estuary had exceeded the safety limit which may be due to the influx of the industrial effluent from the surrounding industries.

Temperature plays many roles in the estuary. As water temperature increases, the capacity of water to hold dissolved oxygen increases. It also influences the rate of plant photosynthesis, the metabolic rates of aquatic organisms and the sensitivity of organisms to toxic waters, parasites and diseases. In the Cochin back water area, during monsoon months, a sharp decrease in ambient temperature is noted due to prevailing rain (Gopinathan, 1972; Ramamirtham and Jayaraman, 1963).

Under conditions of high energy demand such as during reproduction or summer heat stress, oysters may experience energy shortage due to the insufficient ability of their mitochondria to
produce ATP, which could threaten survival of populations chemically exposed to cadmium in polluted estuaries (Sokolova et al., 2005). Enhancement of cadmium effects by elevated temperature suggests that oyster populations subjected to elevated temperature due to seasonal warming or global climate change may become more susceptible to trace element pollution and vice versa (Sokolova et al., 2004).

Recent years have shown a rise in mean global temperatures and a shift in the geographical distribution of ectothermic animals. At high temperatures, excessive oxygen demand causes insufficient oxygen levels in the body fluids, whereas at low temperature, the aerobic capacity of mitochondria may become limiting for ventilation and circulation. This progressive increase in oxygen limitation at extreme temperature may even enhance oxidative and denaturation stress (Portner, 2001; Portner, 2002). Temperature in general had the most adverse effect on cellular energy allocation, an ecologically relevant biomarker of exposure to pollutants in estuaries (Verslycke and Jansson, 2002).

Figure 2. Seasonal variation of pH and salinity in the Ennore and Kovalam estuaries.
The intensive monitoring result demonstrated that the salinity regime of the estuary responds almost immediately to changes in discharge. Discharge tends to increase sharply at the beginning of a rain event. However, it falls off more gradually as the result of fresh water storage in the watershed. The discharge increase causes salinity in the estuary to fall quickly at the beginning and before the discharge had peaked (increase more slowly over the next few months). These results suggest that the salinity in Ennore Estuary will tend to decrease rapidly and increase more slowly in response to storm events. Roast et al. (2000) supported the fact that the temperature changes more slowly with a seasonal variability, where salinity and dissolved oxygen show high fluctuations linked to tidal influences in an estuary.

It has been observed that the seasonal changes in the temperature and salinity affect the solubility of carbon dioxide and the dissociation of carbonic acid in the estuarine water and is controlled by dilution of seawater by river water during the monsoon (Mukhopadhyay et al., 2002)

In winter, the intense rains cause an increase in the river flow, producing a dilution of the contaminants and a slight increase in pH (Olias et al., 2004). Alkalinity and pH showed clear seasonal variations in the values within the lower salinity region of the estuary and these could be related largely to changes in river flow and hence to variations in the ratios of the source waters (Howland et al., 2000).

The Swan Canning Estuary, in southwestern Australia, undergoes distinct seasonal changes, with freshwater discharge predominant in the winter season and low flow with high salinity predominant in the dry summer season (Webb et al., 2005).

Ammonia is toxic to aquatic life, and toxicity is affected by pond pH. Ammonia toxicity increases as pH increases. In the aquatic environment, the events like respiration and photosynthesis that affect carbon dioxide concentration also affect pH.
Our previous study reported that the ammonia becomes more toxic as pH increases. Higher concentrations of the toxic form of ammonia are formed in basic waters while the less toxic form, ammonium ion, is more prevalent in acidic waters. Since alkalinity increases pH, ammonia will be more toxic in waters with high total alkalinity (Padmini and Kavitha, 2003). The pH of natural waters is mainly controlled by the buffering action of calcium carbonate. Ennore estuarine water has a greater proportion of alkaline metals like Na, K, Mg, and Ca as observed from the results and is therefore bicarbonate rich. This may be the cause of raised pH in the Ennore estuary. However, the pH of water falls after heavy rain as the bicarbonate leached from the soil becomes diluted.

High pH of water can be fatal to fish as the pH of water is the main driving force in controlling the relative proportion of the different forms of chemicals present. Ammonia is present in water as the non-ionized toxic form and the ionized nontoxic form. The proportion of toxic form increases as the water becomes more alkaline. A pH rise above 10 can be lethal to fish (Wright et al., 1986).

All chemicals are harmful if they are present in high concentrations. Even sodium chloride is toxic to fish if found in the levels found in sea water because water may be drawn out of the body by osmosis and may lead to dehydration. Suspended solids are found to be present at higher concentration in the Ennore estuary, which may be due to anthropogenic inputs. Occurrence of low oxygen values at the estuary may be attributed to increased rate of decomposition of organic wastes/effluents and eutrophication which involves the utilization of oxygen and ultimately its depletion (Venugopalan et al., 1998).

The situation may be exacerbated during summer due to increase in water temperature as the solubility of oxygen in water decreases with increase in temperature. The rate of bacterial decomposition of organic matter increases with temperature and also the rate of bacterial decomposition of organic matter increases in warmer water leading to low dissolved oxygen content. In addition, increase in temperature is accompanied with increased metabolic rate of fish required to meet the oxygen demand (Lloyd, 1992). Water may be pumped through the gills at a faster rate to supply the fish with oxygen. As a result, toxic chemicals may come in to contact with the gills at an increased rate, so that greater amounts enter the body within a given period of time. Increased concentrations of toxic chemicals damage the delicate cells of the gill secondary lamellae and thus adversely affect the vital function of respiration and salt regulation. Our previous studies reported that there was gill mitochondrial damage in the fishes living in the polluted water, which leads to the oxidative stress. This oxidative stress in fishes may lead to decreased reproduction, susceptibility to quick infection and sudden death of fishes in large numbers (Padmini et al., 2004; Padmini and Sudha, 2004). It was already reported that the grey mullet surviving in the polluted Ennore estuary is subject to severe oxidative stress causing considerable DNA fragmentation, which may lead to cellular death (Padmini and Kavitha, 2005b).

Therefore, a small drop in dissolved oxygen has a greater proportional effect in warm water than when it is cold. It may be the reason for why fish kills are reported to occur more during summer and autumn.

**CONCLUSION**

The changes observed in the current study in the various environmental factors between Station III of the Ennore estuary and the Kovalam estuary are highly significant (p< 0.01) and will have a major impact on that ecosystem. Our studies clearly demonstrate that water quality in the Ennore
estuary is poor due to effluent discharge and anthropogenic activities. Though there is a significant seasonal variation in water temperature, pH, salinity and dissolved oxygen in the three stations of the Ennore estuary, between the three stations there is no significant variation in water quality, indicating that the entire estuary is uniformly polluted. This study of water quality will be useful for biomonitoring programs. Further, our previous work reports the fact that the fishes surviving in the polluted estuary are subjected to severe oxidative stress. This confirms that the Ennore estuary is highly contaminated. Hence it is critical at this point to take immediate appropriate management measures towards the rational exploitation of the valuable aquatic resource.

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