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FLUORIDE CONCENTRATION IN THE SURFACE WATERS OF PULICAT LAKE, SOUTH EAST COAST OF INDIA

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***Abstract*– Recent days, lakes are facing pollution threats due to of various domestic and industrial waste. Contamination due to excess fluoride to industrial and domestic source is one such. Naturally fluoride of <1.5mgl^{-1} is present in waters. Fluoride is needed for humans and animals. Living beings including humans need certain fluoride concentration. Pulicat Lake was determined with Zirconyl-SPADNS method by analysing 20 water samples and was compared with other physico chemical parameters such as pH, salinity and nutrients like Orthophosphate-P, Nitrate-N, Nitrite-N and Ammoniacal-N etc. Statistical analysis of the physico chemical parameters with fluoride was carried out using IBM SPSS-20, shows strong positive correlation of fluoride concentration with chloride (r=0.75), Mg (r=0.48) and nitrate-N(r=0.59). This correlations, indirectly suggests the probable water contamination of the lake with domestic discharges from the nearby main land. Though the Flouride source can be from marine source especially in the case of a negative estuary like Pulicat the strong correlation indicate its riverine source.**

Keywords*– *Fluoride, Pulicat, Pollution, Negative Estuary, Earth, Chloride, Nutrients, Main Land, Rivers.

INTRODUCTION

Earth crust contains about 0.06-0.09% as different fluoride compounds(1) in rocks, soils, plants, salt, sea water and also present in rivers, lakes and almost all fresh ground water at varying concentrations. Fluorspar is found in sedimentary rocks and as cryolite in igneous rocks. Fluoride minerals are mostly insoluble in water, so they come in water when conditions favor their dissolution or due to fluoride containing agrochemicals or industrial effluents (2). The concentration of fluoride found varies from rock to rock , basalt, 360 µg/g; granites, 810 µg/g; limestone, 220 µg/g; sandstone and greywacke, 180 µg/g; shale, 800 µg/g; oceanic sediments, 730 µg/g; and soils, 285 µg/g(3). It is an essential constituent in minerals such as fluorite, apatite, cryolite, and topaz. Whereas, minerals such as biotite, muscovite and hornblende contain large per cent of fluoride (4) and therefore, would o be the main source of F in surface waters (5).

Major reason for increased fluoride concentration in water bodies in the present days is excessive usage of fluoride containing agrofertilizers and industries. Approximately 20 to 400 g fluoride per hectare is annually leached from soils, about the same amount that is added to the soil from the atmosphere, but fertilizing adds another 5 to 30 kg F per hectare per annum (6). This fluoride accumulates in the soils and directly or indirectly reaches water bodies. Major part of fluoride in rainwater originates in sea aerosols: K_2SiF_6 (hieratite) and Na_2SiF_6 (malladrite), where tiny droplets of foam are caught up by the wind(7) and which is carried far from the ocean to continental areas. The F content of various continental precipitations shows a range of 4–89 ppb and in the vicinity of urban and industrial areas, a mean of 290 ppb can be found (8). Major industrial source of fluoride is manufacture of aluminium, combustion of coal and other manufacturing processes of steel, copper, nickel, glass, brick, ceramic, glues and adhesives(9).

Generally, in the surface water concentration of fluoride ranges from 0.01 to 0.3 mgl^{-1}. However, seawater contains more fluoride than fresh water, with concentrations ranging from 1.2 to 1.5 mgl^{-1}. Fluoride is found in seawater in the forms of MgF^+ (46%), CaF^+ (2%) and F^- (51%) with a concentration of 1.3 mgl^{-1}(10). Higher levels of fluoride occur in areas where the natural rock is rich in fluoride, and elevated inorganic fluoride levels are often seen in regions where there is geothermal or volcanic activity. In hot springs, fluoride concentration as high as 25–50 mgl^{-1} are found, also in geysers as much as 2800 mgl^{-1} is found as in East African Rift Valley lakes(11). To a certain extent fluoride is beneficial for skeletal growth, and WHO recommended that drinking water should contain 0.5-1.0 mgl^{-1} fluoride, as it helps to prevent dental caries and specially effective on children with developing teeth. However more than 1.5 mgl^{-1}, fluoride is harmful as per WHO and Australian recommended limit (12). It results in skeletal flourosis, and also causes severe adverse impact on the health of human and animals (Table.1). When human beings ingest

fluoride, with an acidic stomach, it is converted in to HF and out of the 75-90% part of it, about 40% of it is absorbed by the intestine [13]. It readily gets distributed in various organs but more than 90% will be deposited in the calcium rich bones and teeth [14].

Table 1. Classification of water based on fluoride hazard [15]

Fluoride concentration (mgl^{-1})	Effects on Human Health
0.1-0.6	Low limit (dental caries)
0.6-1.5	Safe limit (bone development and prevent dental caries)
1.5-3.0	Dental fluorosis (discoloration mottling and pitting teeth)
3.0-4.0	Stiffened and brittle bones and joints
>4.0	Crippling fluorosis (deformities in knee and hip bones and finally leads to paralysis)
>10	Crippling skeletal fluorosis, Cancer

Globally, 200 million people from 25 nations have health risks because of high fluoride in ground water[16&17]. About 66 million people in India, are at risk of developing fluorosis and high fluoride concentration in groundwater, in the arid to semi-arid western states of Rajasthan and Gujarat and in the southern states of Andhra Pradesh, Karnataka and Tamil Nadu[18-21]. About 17 states of India are affected by fluoride contamination such as Andhra Pradesh, Assam, Bihar, Delhi, Gujarat, Haryana, Jammu and Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh and West Bengal[2]. Fluoride is a bio accumulator and about 50% of the fluoride ingested is retained in the body of living beings. Fresh waters and coastal waters can contaminate estuarine waters with higher levels of fluoride, and hence a study was conducted in Pulicat Lake for the status for fluoride concentration. Major route of fluoride is through food and water, and there are lesser chances of intake is negligible by inhalation. However, the workers in the aluminium, iron ore or phosphate ore processing industry are exposed via inhalation or dermal contact[9].

MATERIALS AND METHODS

Pulicat lake (13^0 20'–13^0 40'N latitude and $80^0$14'–$80^0$15'E longitude), was he study area, which is India's second largest brackish water (Figure.1) lake after the Chilika Lake in Odisha. About 84% of the lake is in Andhra Pradesh and 16 % is in Tamil Nadu. Large spindle shaped barrier island named Sriharikota separates the lake from the Bay of Bengal. It is spreads over an area of about 620 km^2, out of which about 360 km^2 of the water body in the southern part is active, northern part is dry and the rest of the lake is now mudflat.

Ephemeral rivers, Kalangi and Arani are the fresh water sources to the lake. Pulicat lake connects Buckingham canal with its northern part in Andhra Pradesh and its southern part which is in Tamil Nadu. Buckingham canal is an artificial coast parallel, British-made navigational channel, which extends from Kakinada of East Godavari district of Andhra Pradesh to Marakkaanam of Tamil Nadu located in north of Pondicherry. The lake is connected to the sea through three tidal inlets, one each at Tupilipalem, Rayadoruvu and Pulicat villages, respectively, from north to south. But at present the inlet at south in Pulicat village is only active. It has an average depth of 1.5 m. The lake receives indirectly and directly, huge amount of industrial effluent and aquaculture effluents from the neighboring Chennai city through the Buckingham canal throughout the year and also from the industrial and agricultural sites of Tada districts. 20 surface water samples were collected from the lake during August 2013 (Figure.1), after fixing GPS locations. In situ monitoring of basic water quality parameters were done with Hanna probe. Water samples were collected in pre acid washed plastic bottles and preserved with mercuric chloride and kept in -4^0C till analysis. Physico chemical parameters like pH, salinity, water temperature, total dissolved solids, and turbidity were determined by in situ method (Hanna probe). Nutrients were analysed by spectrophotometric methods. The phosphorus was analysed by molybdenum blue method following standard manual for sea water analysis by Grasshoff et al 1999[22]. The nitrogenous nutrients were nitrate and nitrite was done by Di-azo method, where nitrate was first reduced to nitrite and both measured at 540 nm, and ammonia by phenate method at 640nm. The fluoride concentration was determined by Zirconyl-SPADNS method at a wavelength of 570 nm [23].chloride, hardness method

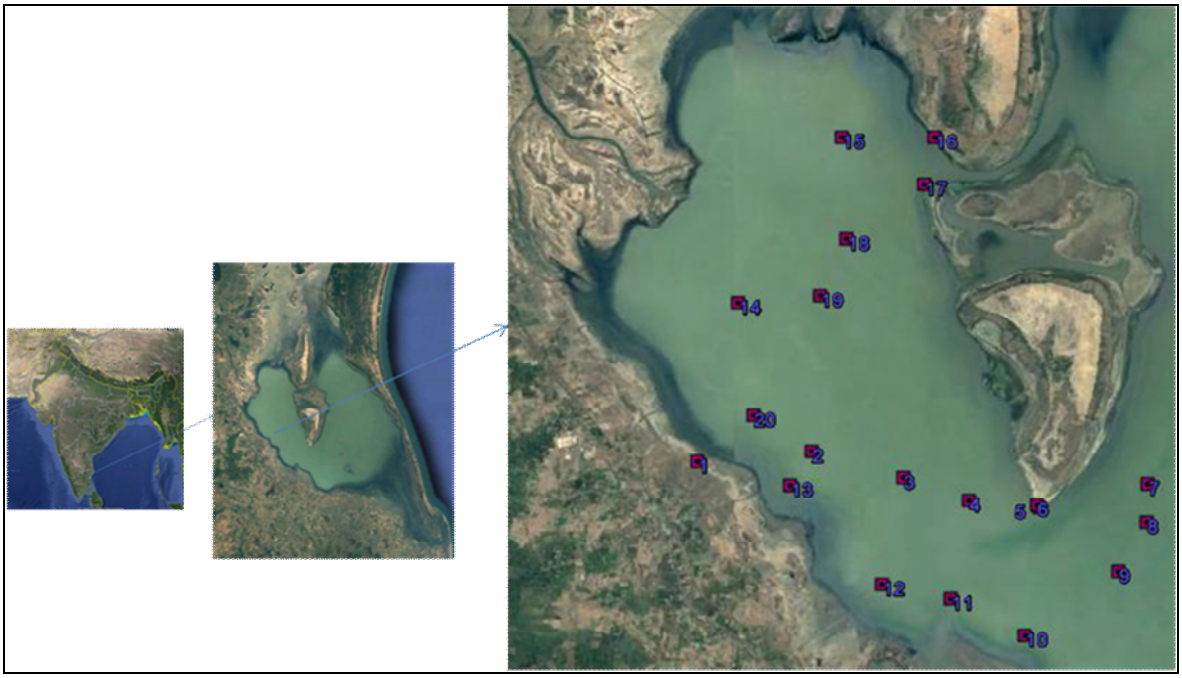

FIGURE 1. MAP SHOWING LOCATION OF PULICAT LAKE IN INDIA WITH SAMPLING STATIONS

RESULTS

The surface water temperature recorded an average of 31.6^{0}C, with a mean pH of 8.74. Average depth of the study region measures as 1 m. The total dissolved solids ranges from 0.6 to 54.60 gl^{-1}. Maximum salinity is 30.8psu and the average salinity is 17.31psu. Station 6, represent samples from a small fresh water source and hence all the physico chemical parameters were strikingly less. From this source, islanders were found collecting water for meeting their day to day domestic requirements.

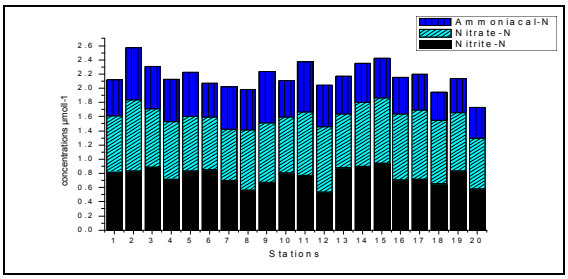

FIGURE. 2 CONCENTRATIONS OF NITROGENOUS NUTRIENTS IN SURFACE WATER

The dissolved oxygen in the surface water varies from 3.6 to 7.8 mgl^{-1} with a mean of 6.43 mgl^{-1}. The chloride has an average of 16.15 gl^{-1}. The average F/Cl ratio comes to 6.77x10^{-5} (5.01-9.01x10^{-5}). The nutrients phosphate shows a mean concentration of 3.82 µmoll^{-1}, nitrite-N denotes 0.76 µmoll^{-1}, average nitrate-N records as 0.84 µmoll^{-1}, the mean ammonia concentration is 0.56 µmoll^{-1}. Among the nitrogenous nutrients, nitrate-N dominated in concentration owing to sufficient amount of dissolved oxygen in the water (Figure 2). The inorganic phosphate concentration shows a higher side, for the salinity present in the water, which shows the presence of domestic sewage or chemical effluent in the lake water (Figure 3).

The fluoride concentration in the lake ranges from a minimum of 0.002 mgl^{-1} (station 6) to a maximum of 1.06 mgl^{-1} (station 2) with a mean of 0.88 mgl^{-1}. It is important to keep the level of fluoride in these waters as it is a bioaccumulator. Pulicat lake is hyper saline, and turns to negative estuary in summer and salinity of it is comparable with sea water in such occasions. As per experimental studies, sea water containing 1.5 mgl^{-1} of fluoride can result in accumulating 2.5gl^{-1} of

fluoride in tissues. During summer the water fluoride concentration increases in proportion to salinity. The crab muscle accumulates 5 times as much as fluoride, or 50 $mgkg^{-1}$, after 90 days exposure to 50 mgl^{-1} fluoride. On a wet weight basis this results in 5.7 $mgkg^{-1}$ pound or 12.5 $mgkg^{-1}$ in edible muscle tissue and increases to 150 $mgkg^{-1}$ when the water contains 400 mgl^{-1} fluoride. The average daily total fluoride dose from all sources for a 70 kg man is estimated to be 5.3 mg fluoride which is equivalent to 500g of crab meat for crabs grown in 50 mgl^{-1} fluoride seawater or 2 kg of crab meat for crabs raised in normal seawater. And also the parts of fish which are in contact with water such as its scales, fins and gills contains highest fluoride concentrations. Skin has highest percentage of fluoride and hence predators which consume the whole fish are subjected to very high fluoride concentrations [24]. The nitrate-N and fluoride shows positive trend, except (Figure.4) in station 6 fresh water source, here the fluoride is comparatively low while nitrate concentration shows no dip, indicating the domestic pollution in the region.

The datasets were introduced for Pearson correlation analysis by IBM SPSS, version-20. The salinity and TDS (r=0.95) showed strong positive correlation (Table.2) is obvious as salinity is the major factor part of total dissolved solids (TDS) in water. Similar is the positive trend in correlation showed by salinity and chloride too (r=0.52).The temperature and dissolved oxygen (r=0.55) showed slightly positive correlation which indicates the dissolved oxygen liberated when photosynthetic activity of phytoplanktons increase while the hours of solar radiation peaks during the day (Table.2).

Among the nutrients, nitrate-N showed a positive correlation with TDS (r=0.53). Nitrite-N showed a positive correlation with turbidity, might be indicating a domestic source of pollution in the lake. Similarly, the nitrate-N also shows a positive correlation with fluoride in the lake (r=0.59). The positive correlation of nitrate with fluoride indicates the probability of same anthropogenic origin where there is agricultural waste with excess fluoride and animal waste that increase nitrate-N concentration. The fluoride also shows a positive correlation with the chloride (r=0.75). The absence of any positive correlation with nitrogenous or phosphate nutrient with chloride and significantly positive correlation of chloride with fluoride indicate that one of the source of fluoride in Pulicat is the sea water enters through the Pulicat mouth. The fluoride also shows slight positive correlation (r=0.48) with Mg (Table.2), this further ascertains that major source of fluoride in this part of lake is the sea, and anthropogenic source is secondary. Similarly Ca, Mg and total hardness (TH) too shows positive correlation among each other.

The trend of chloride concentration and fluoride is positive. Research shows the influence of common ion effect when both are present varying proportions. This is proved by in situ experiments done by several researchers. By pretreating fish in high chloride solutions confers protection against subsequent high fluoride levels [25]. As per the condition here the both shows same trend, so such situation will result in accumulation of fluoride in living being.

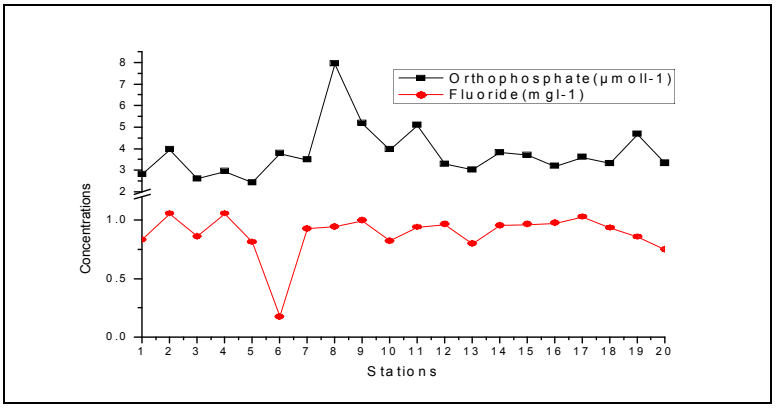

FIGURE.3: CONCENTRATION OF INORGANIC PHOSPHATE AND FLUORIDE

TABLE 2 PEARSON CORRELATION COEFFICIENT FOR SEDIMENT QUALITY PARAMETERS OF PULICAT LAKE (R>0.6 IS SIGNIFICANT AT 95 % CONFIDENCE LEVEL; N = 15)

	pH	Temp	TDS	Salinity	DO	Turbidity	Ortho-P	Nitirte-N	Nitrate-N	Ammoniacal-N	Flouride	Ca	Mg	TH	Cl
pH	1														
Temp	.030	1													
TDS	.016	-.092	1												
Salinity	-.101	.033	**.945****	1											
DO	.084	**.554***	.203	.275	1										
Turbidity	.256	.114	-.102	-.009	.411	1									
Ortho-P	.065	.081	.007	.038	.046	.075	1								
Nitirte-N	.152	-.032	-.265	-.221	-.063	**.491***	-.326	1							
Nitrate-N	.255	**.536***	-.063	.043	.146	.089	.164	-.005	1						
Amm-N	.234	-.350	.251	.203	-.244	-.054	.210	.102	.260	1					
Flouride	.280	.225	.377	.401	.188	.079	.105	-.220	**.586****	.387	1				
Ca	-.237	.259	-.033	.043	.280	.010	.003	.011	-.030	-.496*	-.265	1			
Mg	.338	-.133	.006	-.120	-.176	.178	.050	-.103	.241	**.458***	**.475***	**-.543***	1		
TH	.270	-.015	-.012	-.119	-.054	.216	.061	-.116	.269	.269	.416	-.090	**.885****	1	
Cl	.293	-.077	**.582****	**.527***	.091	.029	.052	-.184	.062	.311	**.747****	-.517*	.379	.163	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

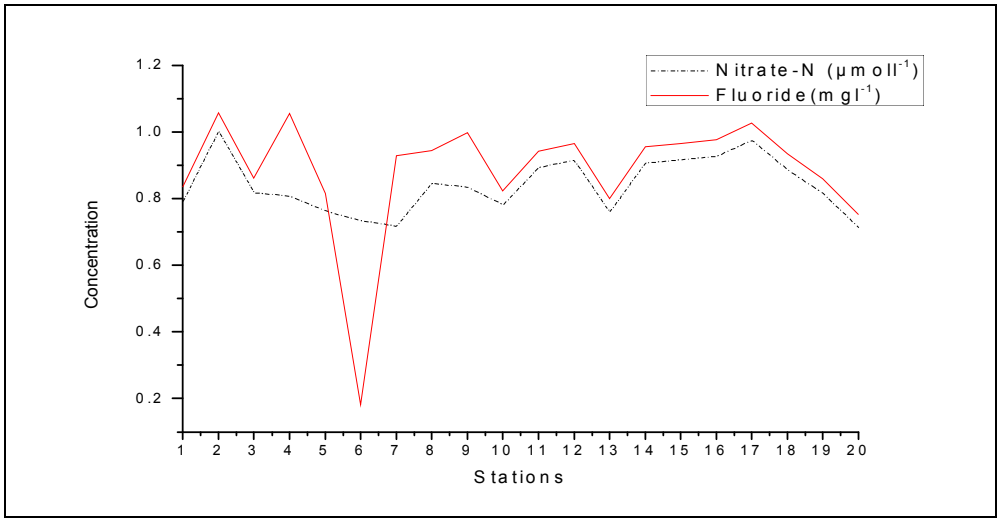

FIGURE.4 CONCENTRATION OF NITRATE AND FLUORIDE

Research carried out by Masoud et al 2006[26], on effect of various ions such as sulphate, calcium, magnesium, cadmium fluoride, Na, P, Fe, Zn, in red algae, sea grass, brown algae and green algae in the waters of Mediterranean Sea, Egypt reveals that in most of the cases the third most accumulating ion species is fluoride. Their study reveals both in sea weeds and sea grass there is high accumulation of fluoride, though fluoride did not show any significant correlation with other

parameters. Fluoride concentration is said to not affect the growth of higher plants like sea grass or sea weeds, but may act as a growth inhibitors for phytoplanktons. However nutrient rich environment can minimize the effect of toxic effect of higher fluoride condition. In summer however even the fluoride level raises up, the nutrient concentration will be able to reduce the effect of fluoride concentration on these micro algae. Similarly Nabipour & Dobaradaran 2013[27], in their study on Fluoride on the coastal waters of Persian Gulf mentions that consumption of fishes in this region can cause fluoride poisoning as the skin and muscle tissues of commercially important fish species shows high fluoride content. This is important in the case of Pulicat lake as the salinity of the lake increase during summer and reaches above sea water salinity, obviously the chlorides, fluoride must be also higher. Along with this comes the domestic and sewage pollution from Buckingham canal. Hence chances of bioaccumulation of fluoride in the fauna and flora of the lake and creating harmful effects on other predators including human being are higher.

CONCLUSION

Coastal waters are said to have higher fluoride concentration, compared to any other water bodies like wells, ponds, river, streams etc., unless there is fluoride mineral bearing rock in their vicinity or anthropogenic source for fluoride pollution. Pulicat lake is a negative estuary, with its salinity recorded as high sea water or more, in summer. The fluoride content can be expected to be high with increase in salinity. The study period was August and the maximum salinity recorded during the study was only 30.8 psu. The positive correlation of fluoride with nitrate shows a probable source of domestic pollution in the lake. At the same time it also shows a positive trend with chloride pointing fluoride from sea water. The fluoride concentration in the lake water is not high for the studied region and time of study. However the other regions of the lake and during the period of summer when the salinity peaks, fluoride concentration may be higher. The pH, temperature, salinity, Ca, Mg and phosphorus concentration plays major role in determining the complex formation, saturation, and precipitation etc. of fluoride in water. Detailed diurnal study can reveal more facts on fluoride status in the lake as it is a bio-accumulator and the lake is major source of fishery resource for large number of population. It is very interesting to take up further study on the fluoride concentration in the fauna and flora to find out the rate of bio accumulation of fluoride in different trophic levels. Studies show the organs of fishes, such as gills, fins etc. have varying capacity of concentrating fluoride. Also molluscans too accumulate fluorides. Pulicat lake being a major source of variety of resources, a study based on this is a requirement for this lake environment. The southern side of the lake receives large amount of industrial and domestic effluents from Chennai city and Ennore port through Buckingham Canal, hence a detailed study can be carried out in this region to find out the concentration of fluoride in this region. Also more detailed studies can be carried out in peak summer to find out the level of fluoride concentration in Pulicat lake.

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