## Geochemistry of Different Aquatic Systems in Thiruvananthapuram, Southern Kerala

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Abstract— Aquatic systems of Thiruvananthapuram receiving waste water from various anthropogenic activities. The study reveals that the chemical and heavy metal concentration of almost all station selected from the present study area was high. The present investigation mainly concentrates on the physical and chemical properties of the sediments like pH, Conductivity, Organic carbon, nutrients and heavy metals. Moreover other anthropogenic activities affect the soil texture of these aquatic systems.

*Index Terms*— Nutrients, Heavy metals, Pollutants, trace metals, Aquatic system.

#### I. INTRODUCTION

Sedimentation is an important natural process that operates through a chain of actions that involve erosion, transportation and finally deposition sediments consists of soil and minerals particles washed by storms/flood water from crop lands, barren land and over grazed pastures (Sharma and Kaur, 1997). The sediments are both carriers and potential sources of natural geochemical constituents derived principally from rock weathering. The sediments mostly govern the nutrient economy of an aquatic system and knowledge on the role of sediment nutrient is especially useful in determining the sediments- water interaction, which eventually affects the productivity (Balakrishnan et al (1984). The sediment acts as a sink for they play a vital role in changing the quality of the overlying water column. The geochemical characteristics of aquatic sediments in different parts of the world have been worked out in detail (Jitts, 1959; Aston and Hewitt, 1977). The fate of heavy metals in estuaries has been extensively studied by Bloom and Ayling (1977). Sedimentological studies have been conducted in velar estuary (Chandran et al., 1982).

The sediment texture and organic matter of Vembanad Lake and near shore sediments has been done (Murthy and Veerayya, 1972; Seralathan and Padamala, 1994). The present study mainly deals with the variation of texture, pH, conductivity, total nitrogen, total phosphorous, organic carbon, sodium, potassium and some heavy metals. The texture of sediment is one of the important physical parameters of an aquatic environment, which influence the physico chemical and biological characteristics of the system (Hakanson and Janson, 1983). The textural characteristic of sediments plays a significant role in the distribution and concentration of carbon, nitrogen and phosphorous, both in the bottom sediments and in the overlying water column.

#### II. MATERIAL AND METHODS

The sediment samples were collected from the six stations within the study area (Fig.1) during Nov. 2003 (Post monsoon) and March 2004 (Premonsoon) using a Van Veen Grab. A representative portion of the sample was scooped into polythene bags and preserved till analysis. A part of the air-dry samples are used for textural analysis by the pipette analysis methods suggested by Lewis (1984). The organic carbon of the sediment samples was analysed by an oxidation method as adopted by EI Wakeel and Veerayya (1957). Total phosphorous content of sediment sample was measured by the modified method of Murphy and Riley (1962) and total nitrogen is measured by Kjeldahl method described by Barnes (1959). The major ions like Na, K, Li and Ca were determined using the flame photometer based on the procedure described in APHA (1995). Heavy metals such as Fe, Cu, Zn, Pb, Cr, Li, Cd and Mg were determined using a double beam Atomic absorption Spectrophotometer following the method of Rantala and Loring (1975).

#### III. RESULTS AND DISCUSSION

The percentage of various size classes, concentrations of nutrients and heavy metals of sediments from the six different stations are given in table 1 and 2. The percentage of sand fraction varied considerably for different station. The sand fraction varied from 9.58 (S1) to 92.89% (S<sub>1</sub>) during post monsoon and 8.16 (S1) to 90.83 %(S<sub>6</sub>) during premonsoon season. The maximum value of 92.89% was reported in station 6 (Post monsoon) and minimum of 8.16 was noticed in station 2 (Premonsoon). The season-wise analysis shows that maximum sand deposition was noticed at station S<sub>6</sub> during post monsoon and minimum during Premonsoon season. Considerable variation in the silt percentage was also noticed. It varied from 5.61 (S1) to 57.71 %( S<sub>2</sub>)) during post monsoon and 7.63 to 55.70 % (S2) during the Premonsoon season. The highest value of 57.71% was reported at station S<sub>2</sub> (Post monsoon) and lowest of 5.61% was noticed at station  $S_6$  (Post monsoon). The results show that station  $S_2$  is silty in nature. This may due to the settling of the particles from the overlying water. The allochthonous material reaching from Milma dairy was

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subjected to bio degradation, which results in the high percentage of silt apart from the death and decaying of vegetation (Prasanthan, 1999). The clay content of present investigation also shows wide fluctuations. The value ranged from 1.5 ( $S_6$ ) to 47.5 % ( $S_1$ ) during the post monsoon and 1.54  $(S_6)$  to 51.81 5%  $(S_1)$  during Premonsoon. The maximum clay content of 51.81 % was found at station S<sub>1</sub> (Premonsoon) and least value of 1.5 % at station  $S_6$  (Post monsoon). The high content of Clay indicates the comparatively low energy conditions prevailing at the station  $S_1$ . Besides this stations, selected from Parvathy Puthen Ar receive maximum amount of organic and domestic waste from the city. This will also facilitate the high content of clay. The transport of sediment occurs across the sediment-water interface both upwards and downwards affecting the quality and composition of water.

The result of the various geochemical parameters and heavy metals analysed in the sediment are furnished in Table 2. Hydrogen ion concentration of the aquatic sediment varies considerably. It ranged from 4.61  $(S_4)$ -9.23  $(S_5)$ during the post monsoon and 5. 63 ( $S_6$ ) to 8.13 ( $S_4$ ) during the Premonsoon. The maximum pH of 9.23 (Alkaline) and the lowest of 4.62 (Acidic) were reported at station  $S_5$  and Station S<sub>4</sub> respectively during the post monsoon season. The major factors governing the pH of the soil include the concentration of reduced iron, manganese, hydroxides, Carbonates, carbonic acid, and humic acid (Patric and Mikkelson, 1971). The acidic pH reported at stations S<sub>4</sub> may due to the substantial quantity of urban waste discharged into the water. Conductivity values ranged from 0.106 (S<sub>4</sub>) to 0.592 ms/cm ( $S_5$ ) during post monsoon and 0.094 ( $S_4$ ) to 0.831 ms/cm (S<sub>3</sub>) during Premonsoon. The highest value of 0.831 ms/cm was obtained at station S<sub>3</sub> during Premonsoon and the lowest of 0.094 ms/cm was reported at station-S<sub>4</sub> during Premonsoon. The high value of conductivity of the present investigation as reported at station S<sub>3</sub> during Premonsoon was contributed by influence of city sewage. Consequently station S<sub>4</sub> shows minimum conductivity during the overall study. These may be due to the effects of freshwater from Karamana and Killi Ar.

Sediment is the major source of nitrates. Nitrogen is an important nutrient element in the sediment that controls the quantity of overlaying waters in an aquatic system. Nitrogen sources are mainly the oxidation of nitrogenous organic matter. Nitrogen content in the sediment is depending upon local condition of rainfall, quantities of freshwater inflows, turbulence and biological activities (Kemp, 1971). Total nitrogen content varied from 0.896 (S<sub>6</sub>) to 13.44 mg/g (S<sub>3</sub>) during post monsoon and 0.448 ( $S_6$ ) to 19.712 mg/g ( $S_1$ ) during Premonsoon. The station S<sub>1</sub> recorded maximum total nitrogen content (19.712 mg/g) and minimum of 0.448 mg/g at station S<sub>6</sub> during Premonsoon. The higher concentration of total nitrogen at station S<sub>1</sub> during Premonsoon may be attributed to the disposal of effluent from Milma dairy and also it was promoted by anthropogenic influence. The comparatively low concentration of nitrogen in the estuarine region may be attributed to the denitrification process that takes place in the overlying water due to the anoxic condition that prevails in the region (Santhosh, 1999)

The organic carbon content in the sediment is derived from the primary production with in the water body and also

from terrigenous runoff. The reduced organic carbon provides the main energy source for heterotrophic organisms in the aquatic sediments (Hakanson and Jannson, 1983). An understanding of the distribution of organic carbon and its impacts on other physicochemical and biological parameters is a prerequisite for nutrient input and biological transformation of major and minor element of the system. The organic carbon % varied from. 0.315 (S<sub>2</sub>) to 6.5 % (S<sub>3</sub>) during post monsoon and 0.29 ( $S_6$ ) to 3.968 % ( $S_3$ ) during Premonsoon. The maximum organic carbon content of 6.5 5 was reported at station S3 during post monsoon and minimum of 0.29 % was found at station S<sub>6</sub> during Premonsoon. The high organic carbon contents observed at station S<sub>3</sub> may due to the deposition of terrestrial organic matter from the excessive land runoff, settling of material and decay of vegetation which is in agreement with value obtained for Paravur-Kappil backwater (Santhosh, 2002). In present work the organic matter content varied between 0.29 % and maximum 6.5 %, which is less than the value obtained in Karamana River (Krishnakumar, 2002).

Phosphorous is one among the chief nutrients in an aquatic environment. The increased phosphorous loading in aquatic systems from cultivated lands, domestic and industrial sewages have created the eutrophication problems (Parry, 1998). The phosphorus ranged from 0.012 (S<sub>5</sub>) to  $0.096 \ \mu g/g$  (S<sub>2</sub>) during post monsoon and 0.012 (S<sub>6</sub>) to 0.097 $\mu g/g$  (S<sub>1</sub>) during Premonsoon. The highest of 0.097  $\mu g/g$ was reported at station S1 during Premonsoon and lowest of  $0.012\ \mu\text{g/g}$  was reported at station  $S_5$  during post monsoon and at station  $S_6$  during Premonsoon. At station  $S_1$ , maximum value of 0.097 µg/g was obtained during Premonsoon, may be due to pollution by anthropogenic activities, disposal of wastes and decay of vegetation. Besides this Milma dairy effluent also enriched the phosphorous concentration in the station Nair et al, 1987 also observed similar increase in phosphorous level in the polluted zone.

Sodium is an important constituent in sediment. The carbonates, sulphate, nitrate and chlorides of sodium are found abundantly in nature. The season wise analysis of sodium shows that it value ranged from 1.38 (S<sub>2</sub>) to 8.02 $\mu g/g$  (S<sub>1</sub>) during post monsoon and 0.26 g (S<sub>4</sub>) to 1.9  $\mu g/g$  $(S_1)$  during Premonsoon. The maximum value of 8.02  $\mu$ g/g was observed at station S<sub>1</sub> (Post monsoon) and minimum of 0.26  $\mu$ g/g was reported at station S<sub>4</sub> (Premonsoon). The maximum concentration of 8.02  $\mu$ g/g was reported at station  $S_1$  (Post monsoon) indicating high degree of pollution due to the intervenes of human activities and the application of fertilizers in the adjacent areas. Similarly many industrial wastes and domestic sewage are rich in sodium and increase in its concentration in the natural water after disposal of wastes and anthropogenic activities (Trivedi and Goel, 1986). Like sodium, potassium is also a naturally occurring constituent in sediment. The major source in freshwater is weathering of rocks. But the quantity increases in the polluted water due to the disposal of domestic wastes. The potassium content in the sediment sample ranged from 0.88  $(S_2)$  to 5.32 µg/g  $(S_4)$  during post monsoon and 0.32  $(S_4)$  to 4.34  $\mu$ g/g (S<sub>6</sub>) during Premonsoon. The maximum of 5.32  $\mu g/g$  was found at station S<sub>4</sub> (Post monsoon) and least of  $0.32 \ \mu g/g$  at Station S<sub>4</sub> during Premonsoon. The increased Proceedings of the World Congress on Engineering 2009 Vol I WCE 2009, July 1 - 3, 2009, London, U.K.

concentration in station  $S_4$  (5.32 µg/g) during post monsoon is due to the disposal of waste and also due to the after effects of monsoon. Nair *et al*, (1984) also observed a high concentration of potassium during post monsoon. Here it is found that the diary effluent release alone is not responsible for the increase in potassium level. The minimum of 0.88 µg/g at station  $S_2$  near to dairy effluent discharge point clearly shows that there is no interference between concentration of potassium and diary effluent.

Calcium is one of the most abundant elements existing from different forms in the natural water and soil. Being present in high concentration in the rock it is leached from there to contaminate the water. Disposal of sewage and industrial waste also contribute to the content of calcium and has a great affinity to absorb on the soil particle and in turn affects the soil texture. In the sediment samples the calcium value ranged from 0.08 ( $S_2$ ) to 0.76 mg/g ( $S_4$ ) during post monsoon and 0.08  $(S_4)$  to 0.68 mg/g  $(S_5)$  during premonsoon. At station S<sub>4</sub>, during the post monsoon, the maximum value was 0.76  $\mu$ g/g and the minimum value of 0.08  $\mu$ g/g was reported at station S<sub>2</sub> during post monsoon and station S<sub>4</sub> during Premonsoon. The maximum calcium content reported at station S<sub>4</sub> and S<sub>5</sub> may be due to the leaching of dead shelled organisms and some rock water and sediment interaction play an important role in the concentration of calcium irons in the water and soil. Similar finding were also reported by Santhosh (2002) at Paravur-Kappil backwater.

Sediment is the ultimate recipient of nearly all heavy metal pollutants in an aquatic ecosystem by various human activities. A large portion of metallic substances discharged in to the aquatic environment is ultimately incorporate into the sediment (Dursma and Gross, 1971). Heavy metals may associate with sediment particle either by adsorption or by complexation process. Iron is an essential element and most abundant metal found in Kerala Rivers. It is mainly derived from sources like industrial wastes, fertilizers and domestic waste. It is an important waste in sediment of estuaries (Nair et al., 1987). The concentration of iron in the sediment samples ranged from 8690.6 (S<sub>2</sub>) to 88741.2  $\mu$ g/g (S<sub>4</sub>) during post monsoon and the fluctuation is from 15855 (S<sub>2</sub>) to 17840.4  $\mu$ g/g (S<sub>5</sub>) in the Premonsoon season. The station  $S_4$  reported the maximum concentration of 88741.2 µg/g and station  $S_2$  reported the minimum of 8690.6-µg/g iron during the post monsoon season. The maximum content of iron among the six stations, both during the post monsoon and Premonsoon. The was found in station S<sub>4</sub> This station receives both the water from the Killi Ar and Karamana Ar and is purely riverine nature and it deposits maximum concentration of iron in this region. Studies shows that trace metal concentration are more in the riverine than the marine zone (Figures et al., 1985). This can also be explained on the basis of textural features of the sediment. The river has got finer particle like silt and clay where as the marine zone had finer and coarse sand as substratum. It is a well-known fact that finer particles contain more metal than the coarse particle (Fernandez and Jones, 1987).

Nickel is an important heavy metal. The concentration of nickel ranged from 2.4 (S<sub>2</sub>) to 8.8  $\mu$ g/g (S<sub>4</sub>) during post monsoon and 0.4 (S<sub>6</sub>) to 4  $\mu$ g/g (S<sub>2</sub>) during Premonsoon. The highest concentration of 8.8  $\mu$ g/g was observed at S<sub>4</sub>

during post monsoon and the lowest of 0.4  $\mu$ g/g at station S<sub>6</sub> during premonsoon period. The concentrations of nickel in all the stations exist below the toxic limit (Saikia et al., 1987). Copper, despite its toxic effects is reckoned as an essential component of many enzymes. Copper reaches the aquatic environment chiefly from copper mine and a large number of industrial processes like agricultural chemicals paint etc. Sewage; industrial effluent and waste from electric generating plants also contain this metal. The limit of it in this standard is not due to its taste producing capacity. Variation in copper content is in such a way that, station  $S_1$ showing 335.2  $\mu$ g/g and station S<sub>3</sub> showing 47.2  $\mu$ g/g during post monsoon season. But during premonsoon station S<sub>1</sub> alone shows copper content (45.2 µg/g). In rest of the stations copper was found below detectable level. The high amount of copper content reported at station  $S_1$  may be due to the discharge of large amount of agricultural chemicals and sewage in to the water body. Generally in agricultural practice copper sulphate is widely used and it may be one of the reasons for higher concentration of copper.

Zinc is an essential element required in trace quantities to sustain biological life, but its large concentration is proved to be lethal. It is a common contaminant in industrial effluent (Dean et al; 1972). The concentration of zinc varied from 0.4 (S<sub>5</sub>) to 18.6  $\mu$ g/g (S<sub>3</sub>) during post monsoon. It shows a value ranging from 1 (S<sub>3</sub>) to 2.2  $\mu$ g/g (S<sub>5</sub>) during premonsoon. Station S<sub>3</sub> recorded the maximum zinc content of 18.6 µg/g during post monsoon and minimum value of  $0.4 \,\mu g/g$  was noticed in station S<sub>5</sub> during post monsoon. The result shows that zinc is presents only within the permissible level. The maximum value of zinc in the stations during the post monsoon may be due to the influence of chemical wastes disposed from different industries near the sampling sites which will generates zinc concentration in the sediment. The concentration of lead in the earth crust has been estimated as 12.5ppm ranking it as the 36<sup>th</sup> element in order of abundance (Abbasi et al., 1998). Major portion of lead in the surface water is from mining and smelting, refining etc. Lead reaches the aquatic sediment through precipitation; erosion and leaching of soil as well as municipal and industrial waste. Hydrogen ion concentration, hardness, and organic materials influence lead toxicity in sediment. In the present study the concentration of lead ranged from 21.2 (S<sub>2</sub>) to 99.4  $\mu$ g/g (S<sub>1</sub>) during post monsoon and 0.4 (S<sub>4</sub>) to 29.4  $\mu$ g/g (S<sub>1</sub>) during premonsoon. The high lead concentration of 99.4  $\mu$ g/g at station S<sub>1</sub> during the post monsoon season may be due to the anthropogenic activities and also due to the waste disposal from the adjacent automobile workshop.

Lithium is an important element present in the aquatic sediment. The concentration of lithium shows wide fluctuation during the two seasons. During post monsoon season it's varied from 6.6 (S<sub>1</sub>) to 41.2  $\mu$ g/g (S<sub>2</sub>) and ranges from 5.8 (S<sub>2</sub>) to 11.2  $\mu$ g/g (S<sub>5</sub>) during the premonsoon. The highest value of lithium during the overall studies 41.2  $\mu$ g/g at station S<sub>3</sub> during post monsoon and lowest of 5.8  $\mu$ g/g at station S<sub>2</sub> during the premonsoon season. Prasanthan (1999) also reported similar conditions in the Parvathy Puthen Ar. Only a few information is available on the distribution of lithium in the aquatic sediment. The important source of chromium includes wastes from electroplating, dyes,

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explosives, paints, ceramic and paper industries etc. The domestic input of chromium into the water bodies cause a sharp drops in the dissolved oxygen content with hydrogen iodide production (Mishra, 1990). In sediment the chromium concentration of 0.052  $\mu$ g/g was observed only in station S<sub>4</sub> during premonsoon season. In all other sample it was found below detectable level. According to Abbasi et al (1998) the concentration of unpolluted sediment in Kuthyadi reservoir was in the order of 12 µg/g. Comparing these value it is evident that the station  $S_4$  shows comparative low concentration of chromium. Cadmium is a hazardous heavy metal like mercury. Cadmium is not essential for plants and animals. So cadmium in the environment can cause only harm and no gain. The average concentration of cadmium in sediment is 0.2ppm (Abbassi et al., 1998). During the post monsoon season no cadmium was found to be reported. But it has got concentration of 39.4  $\mu$ g/g (S<sub>1</sub>), 40.2  $\mu$ g/g (S<sub>2</sub>) and 180  $\mu$ g/g at station S<sub>4</sub> during premonsoon season. The high value of cadmium at station  $S_4$  (180 mg/g) maybe due to the dumping of sewage effluent.

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Fig. 1 Map showing the study area

# Table.1.Variation in geochemical characteristics of sediments samples during post monsoon and premonsoon.

	Post monsoon							Post monsoon						
Sediment	Stations						Stations							
	1	2	3	4	5	6	1	2	3	4	5	6		
pH	6.42	6.93	6.63	4.62	9.23	5.44	7.68	7.05	6.52	8.13	6.72	5.63		
Conductivity (ms/cm)	156	34.6	248	106	59.2	28.5	0.283	0.138	0.831	0.094	0.384	0.699		
Total nitrogen (mg/g)	3.584	4.032	13.44	8.064	5.376	0.896	19.712	1.344	4.48	2.786	0.896	0.448		
Organic Carbon (mg/g)	3.82	0.315	6.54	3.82	2.678	0.984	1.911	0.97	3.968	0.382	0.44	0.29		
Total Phosphorus (mg/g)	0.075	0.095	0.039	0.024	0.012	0.021	0.097	0.084	0.044	0.017	0.023	0.012		
Sodium (mg/g)	8.02	55.338	1134.429	28133.839	379806.83	3342300.1	1.88	26.466	387.366	1474.757	180056.57	3608164.9		
Potassium (mg/g)	3.7	16.28	289.784	7708.2544	197331.31	1302386.7	1.58	3.108	85.53512	5585.7373	217972438	1.152E+14		
Calcium (mg/g)	0.46	0.184	0.423	1.608	2.573	6.947	0.16	0.119	0.018	0.0028	0.039	0.035		

### Table.2.Heavy metal contents of sediments samples during post monsoon and premonsoon.

Sediment (µg/l)	Post monsoon							Premonsoon						
	Stations							Stations						
	1	2	3	4	5	6	1	2	3	4	5	6		
Iron (µg/g)	85947.2	8690.6	85050	88741.2	17115	78654.6	16801.4	15855	17364	16099.4	17840.4	16098.8		
Nickel (µg/g)	6.6	2.4	7	8.8	3	2.9	2	4	1.8	0.8	1.2	0.4		
Copper (µg/g)	335.2	BDL	47.2	BDL	BDL	BDL	45.2	BDL	BDL	BDL	BDL	BDL		
Zinc (µg/g)	16.8	6.6	18.6	17.2	0.4	24	BDL	BDL	1	BDL	2.2	BDL		
Lead (µg/g)	99.4	21.2	49.8	52	33.6	47	29.4	2	10.2	0.4	BDL	BDL		
Chromium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	352	BDL	BDL		
(µg/g)														
Lithium	20.8	6.6	41.2	37.2	13	8.6	7.8	5.8	6.6	8	11.2	9.6		
(µg/g)														
Cadmium	BDL	BDL	BDL	BDL	BDL	BDL	39.4	40.2	BDL	180	BDL	BDL		
(µg/g)														
Magnesium	3844.6	1104	2946.6	3094.8	1567	2869.2	3108.8	1731.6	2242	2942.4	2658	1256.2		
(µg/g)														