4.1 STUDY AREA

Tamirabarani river estuary is located in the South East Coast of India, Tuticorin District, Tamilnadu. The Tamirabarani River originates from Western Ghats and reaches in Gulf of Mannar (Punnaikayal Mouth and Palayakayal Mouth). It travel 120 km and crosses two districts Tirunelveli and Tuticorin. This river is the major drinking water resource for four districts like Tirunelveli, Tuticorin, Kanyakumari and Viruthunagar. This river travel beyond some major and minor towns namely Papanasam, Ambasamuthiram, Chernmagadevi, Tirunelveli, Srivaikundam, Eral and Authoor. Industrial wastes, agricultural wastes and sewage were dumped in to Tamirabarani river.

The north border of Tamirabarani Estuary is surrounded by a number of major and minor industries namely Tuticorin Houbor (TPT), Tuticorin Thermal Power Station (TTPS), SPIC Industry, TAC, Heavy water plant (HWP), Zirconium atomic complex are present. The Darangadara Chemical Factory (DCW) and V.V Minerals Company and many salt pans are in southern side.
The present investigation is carried out in five different stations in the different zone of Tamirabarani River Estuary. The study areas are tabulated in table.

Table 1 Study area

<table>
<thead>
<tr>
<th>S. No</th>
<th>Station Name</th>
<th>Place</th>
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<tr>
<td>1</td>
<td>Station I</td>
<td>Punnaikayal Mouth</td>
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<tr>
<td>2</td>
<td>Station II</td>
<td>Palayakayal Mouth</td>
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<td>3</td>
<td>Station III</td>
<td>Sernthalappoomangalam Bridge</td>
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<tr>
<td>4</td>
<td>Station IV</td>
<td>Mukkani Bridge</td>
</tr>
<tr>
<td>5</td>
<td>Station V</td>
<td>Eral Bridge</td>
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</tbody>
</table>

4.1.1 Station I

Punnaikayal Mouth is located at Punnaikayal Village, Tuticorin District. The latitude and longitude level is 8.6322° N and 78.1119° E. In Northern and Southern of this area, many salt pans are present, In Eastern side the sea source and in Western side boatyard or jetty. During the monsoon time, this area receive high level of fresh water. Some time mouth is closed with effect of tidal power, wind velocity and sand deposition. Immediately local people come and open this mouth because local area peoples mainly utilize this mouth for fish capturing purpose and other transport from boatyard to Gulf of Mannar sea source and vice versa.

In this area, a large level of mangrove plants are present especially Avicenna species. These plants are the major nourishment for aquatic organism and this area play livelihood for all aquatic plants and animals.
4.1.2 Station II

Palayakayal Mouth is another part of Tamirabarani River. This study area is located at Palayakayal village, Tuticorin district of Tamilnadu. It is the oldest and historical mouth region in past centuries. The latitude and longitude level is 82°39'08"N and 78°27'20" E. In Northern and Southern side of this area high level of mangrove plants are present. In Eastern side Gulf of Mannar sea source and In Western side high number of saltpans are present. This area mainly receive high level of saltpan's effluents. This study area is one of the spiritual area in Tuticorin District. Lord Pillayar Temple is present in nearby this study area. Some religious peoples come and take water for celebrating holy festival and some people come and give offerings for their previous generation.

4.1.3 Station III

This study area is 2 km from Punnaikayal Mouth. This area is located at Sernthapoomangalam village. In Southern side agricultural field, in northern side many number of saltpans, In Eastern side a large checkdam is present which is made up of sand. The river water is present in both Eastern and Western side. This area is mainly used by peoples for domestic purpose. Saltpan's wastes and agricultural wastes are the major effluents in this area. This check dam is prevent the entry of sea water into river.

4.1.4 Station IV

This study area Mukkani Bridge is 2 km from station III and it's located at Mukkani village near by Authoor. This area's latitude and longitude level is
This study area is fresh water area. In Southern side Authoor town, in Northern side Mukkani village, in Eastern and Western side river water are present. In Eastern and Western side two pumping stations are present. These pumping stations are build by two major factory of this nearby area namely DCW and VV Mineral companies. These companies take fresh water from this area through pumping for all their purposes. This area is mainly surrounded by agriculture field. The sewage waste of Authoor merge near this area. This area people mainly use this water for their various purposes like bathing, vehicle cleaning and agricultural field.

4.1.5 Station V

This study area Eral Bridge is located at Eral town panchyat, Tuticorin District of Tamilnadu. this area's latitude and longitude level is 8.6300° N and 78.0200° E. In Northern side of this area a famous Serman Arunachala Temple is present, in Southern side of this area number of brick industries are present. In Eastern and Western side of this area fresh water source. One more famous Kurankani Muthumalai Amman Temple is present at 2 km distance from Eastern side. These two temples are the major temples in Tuticorin districts. Many number of pilgrims come and pray and take bath regularly. Large number of agricultural field and number of brick work factories are present nearby this area.

In these five stations a large number of fish species, prawn, crap, birds and other aquatic organisms are present. Fishing is the main profession of the local peoples.
Figure 1: Station I (Punnalkayal Mouth part)

Figure 2: Station II (Pazhyakayal Mouth part)
Figure 3: Station III (Sernthapoomangalam Bridge)

Figure 4: Station IV (Mukkani Bridge)
Figure 5: Station V (Eral Bridge)
4.2 METHODOLOGY

Water samples were collected in glass bottles having well filtered stopper. Bottles holding capacity of about 1 liter of water is necessary for the chemical analyze.

Bottles were thoroughly cleaned filter twice with water and trice emptied before collecting the sample. For collecting the sample of water from the river the whole bottle with stopper closed was suspended well under the surface of water and then only stopper of bottle were removed by the means of clean piece of string and then bottles were filled. Thus the entries of floating materials were prevented in the bottle.

After collecting the sample the stopper of bottle was well secured and the bottle containing the sample of water labeled staring the source data and time of collection.

4.2.1 Physico chemical parameters of water

The physico chemical parameters were analyzed with the water in,

- Turbidity
- $p^H$
- Electrical Conductivity
- Total Dissolved Solids (TDS)
- Total Alkalinity
- Total Hardness
- Calcium
- Magnesium
- Chloride
- Ammonia
- Nitrate
- Nitrite
- Sulphate
- Phosphate
- Fluoride
- Iron
- Tidy’s
4.3.1 Turbidity

Procedure

Thoroughly shake the sample, wait for disappearance of the air bubbles.

Take turbidity free distilled water (blank), turbidity standard (100NTU/400NTU) and the sample (or diluted sample) and pour them into three different turbidity meter tubes. Ensure that no bubbles stick on the tubes.

Set the blank for ‘0’ value

Set the turbidity standard for 100 NTU value

Measuring the turbidity value of the sample

Calculation

1) Turbidity in NTU = measured NTU value X Dilution factor

   ( when 100NTU is set for 100)

2) Turbidity in NTU = measured NTU value X 4 X Dilution factor

   (when 400NTU is set for 100)

4.3.2 pH

Procedure

Take distilled H\textsubscript{2}O, 7.0 p\textsuperscript{H} buffer and 9.2 p\textsuperscript{H} buffer in separate 50ml beakers, mark the beakers.
Dip the $p^H$ electrode in distilled $H_2O$, blot dry; and then dip in 7.00 $p^H$. Adjust the meter knob to read 7.00 $p^H$. Dip in distilled $H_2O$, blot dry; the dip in 9.2 $p^H$ and note the reading. If the reading is 9.2+/- 0.1 the meter is functioning alright. Otherwise it may require slope necessary slope adjustment. For slope adjustment, follow the procedure in the instruction manual supplied with the meter.

Now take each sample in two beakers and mark them nA and nB of successive samples. Every time keep it dipped in nA for 1 minute.

Keep the electrode in the sample (nB) till the reading gets stabilized. Record the pH value of the sample. (Dipping in “nA is for rinsing the electrode).

(Note when the meter is not in use dip the electrode in a saturated KCL solution or as instructed in the instruction manual.)

**Calculation**

\[
pH\ value = \text{observed pH value for sample} \times \text{slope}
\]

(Note when the meter indicates the correct value of pH for buffer 7.0 and 9.2, the slope =1)

Formula for pH calculation

\[
\text{If pH is } > 7.0, \text{ pH for sample } = 7.0 + \frac{\text{observed pH value of sample} - 7.0}{\text{observed pH value for 9.2 buffer} - 7.0} \times 2.2
\]

\[
\text{If pH is } < 7.0, \text{ pH for sample } = 7.0 - \frac{(7.0 - \text{observed pH value of sample})}{(7.0 - \text{observed pH value for 4.0 buffer})} \times 3.0
\]
**4.3.3 Electrical Conductivity**

**Procedure**

**I) Standardization of Meter**

Take distilled H\textsubscript{2}O in two 50 ml beakers (marked as D1 and D2). Take std KCL (1413) in two 50ml beakers (marked as 1413A and 1413B), dip the conductivity cell in D1, D2, 1413A and 1413B in that order. When the cell is dipped in 1413 B adjust the meter to read 1413 EC.

**II) Conductivity Measurement for Samples**

Each sample is taken in two 50 ml beakers (mark as nA and nB where n is the sample number.

Dip the conductivity cell first in nA and then nB. when it is dipped in nB observe the conductivity value of that sample.

**III) Measuring Conductivity of other Standard**

When any of the sample conductivity is higher than 2000 EC., take the other standard each in two 50 ml beakers (marked as SA and SB where S is the value of Standard.)

Dip the conductivity cell first in SA and then in SB. when it is dipped in SB, observe the conductivity value of that standard.

(Each time before measuring the conductivity of samples / standard dip the conductivity cell in D1 and D2 in that order)
4.3.4 Total Dissolved Solids (TDS)

Procedure

Take 100ml sample (if EC less than 2000 micromho/l) or lesser volume (if EC greater than 2000 micromho/l) in a preweighted evaporating dish and dry over a water bath. Keep it at 180°C +/- 20°C for one hour. Cool in desiccators. Take the final weight.

Calculation

\[
\frac{\text{Observed Conductivity}}{\text{Sample X Theoretical Conductivity}} = \frac{\text{Value For Std. KCL}}{\text{Observed Conductivity}} \times \frac{\text{Value for the same std. KCL}}{\text{Sample Conductivity mic. S/cm}}
\]

(Note: the std KCL chosen should have a conductivity nearest to that of sample.)

Verification of result

I) Measured TDS at 180°C / calculated TDS = 1.0 – 1.2.

Where calculated TDS = (0.6 Alkalinity +Na+ K + Ca+ Mg +Cl + SO\(_4\) + SiO\(_3\) + NO\(_3\) + F.)

II) Measured TDS at 180°C / EC = 0.55 – 0.70.
4.3.5 Total Alkalinity

Procedure

Take 50 ml sample in a Erlenmeyar flask. If \( p^H \) is 8.3 or above, add 2 drops of Meta cresol purple indicator. Titrate with N/50 \( \text{H}_2\text{SO}_4 \). At the end point the colour changes from pink to yellow. Note the titer volume \( V_2 \). \( V_1 \) is the initial reading of the burette.

Continue the titration after adding 2 drops of Brom Cresol green indicator. At the end point (Blue to Yellow), note the titer volume \( V_3 \).

If the \( p^H \) is less than 8.3, immediately after addition of meta cresol purple, end point is reached. Therefore \( V_1 \) will be equal to \( V_2 \). Immediately add Borm Cresol green indicator and continue the titration.

Calculation

\[
\text{Alkalinity, at 8.3 as CaCO}_3 \text{ mg/l} = \frac{(V_2 - V_1) \times 100C}{\text{ml Sample}}
\]

\[
\text{Alkalinity, at 4.5 (Total) as CaCO}_3 \text{mg/l} = \frac{(V_3 - V_1) \times 100C}{\text{ml Sample}}
\]

4.3.6 Total Hardness

Procedure

Take 25 ml sample or lesser volume of sample and diluted to 50 ml. Add 1 ml buffer. Add 1ml Na\(_2\)S inhibitor and 1 ml calmagite indicator. Titrate against standard EDTA. The end point is change of colour from pinkish red to blue.
Calculation

\[
\text{Total Hardness as CaCO}_3 \text{ mg/l} = \frac{(\text{ml EDTA} \times 1000)}{(\text{ml sample})} \times \text{C.F}
\]

(Where C.F = Correction Factor.)

4.3.7 Calcium

Procedure

Take 50 ml or a portion of sample diluted to 50 ml. Add 1ml 1N HCL. Heat and Boil for 1 Minutes and Cool. Add 2-3 ml 1N NaOH mix. Add 0.25g Eriochrome Blue Black - R Indicator. Titrate against std. EDTA. The end point is change of colour from red to blue.

Calculation

\[
\text{Calculations as Ca mg/l} = \frac{\text{ml EDTA} \times 1000 \times 0.4 \times \text{C.F}}{\text{(ml sample)}}
\]

(Where C.F = Correction Factor.)

4.3.8 Magnesium

Calculation

Calculation of Magnesium mg/l = Total Hardness – Calcium
4.3.9 Chloride

Procedure

Take 100ml or a suitable portion diluted to 100ml. Add 1ml of K₂CrO₄ indicator. Titrate with std AgNO₃. End point is pinkish yellow.

Calculation

\[
\text{Chloride} \frac{\text{mg}}{\text{I}} = \frac{(A - B) \times 1000}{(2 \times V)} \times C.F
\]

Where \( A \) = ml titer volume for the sample

\( B \) = ml titer volume for blank

\( V \) = volume of sample

C.F = Correction Factor.

4.3.10 Ammonia

Procedure

Treatment

Take 100 ml sample. Add 1.0 ml ZnSO₄ solution. mix. Add 0.4 ml 6N NaOH, mix let stand for few minutes. Filter. Discard the first 25ml and collect the balance filtrate.
Nesslerization

The above filtrate take 50 ml or a portion diluted to 50ml. Add 2 drops of Rochelle Salt Solution. mix. Add 1 ml Nessler Reagent. mix. let stand for 10 minutes. Measure OD at 420mm.

Conduct a reagent blank by taking 100ml distilled H$_2$O and follow the procedures treatment and Nesslerization. Keep this for photometer setting.

Calculation

\[
\text{Ammonia as NH}_3 \text{ mg/l} = \frac{\text{O.D for Sample} \times \text{Slope} \times 50}{\text{mL Filtrate used for colour development}}
\]

4.3.11 Nitrate

Procedure

Take 10 ml or a portion diluted to 10 ml in a boiling tube. Place in a cool water bath. Add 2 ml NaCl solution and 10 ml H$_2$SO$_4$ solution. mix. Allow to cool.

Add 0.5 ml Brucine sulphanilic acid. Stir and mix. Keep in a water bath at 95$^\circ$ C for 2 minutes. Then immerse in a cool water bath. a yellow colour develops. Measure OD at 410 nm.

Carryout a reagent blank using distilled H$_2$O and use this for photometer setting.
Calculation

\[
\text{Nitrate as NO}_3 \text{ mg/l} = \frac{\text{OD for Sample} \times \text{Slope} \times 10}{\text{ml Sample}}
\]

Nitrate as NO\textsubscript{3} mg/l = OD for sample x slope x 10 / ml sample.

4.3.12 Nitrite

Procedure

Take 50 ml sample or a portion diluted to 50 ml add 2ml colour reagent. mix. Measure O.D at 540 nm after 10 minutes but before 2 hours.

Take 50 ml distilled H\textsubscript{2}O Add 2 ml colour reagent. Use this for photometer setting.

Calculation

\[
\text{Nitrite as NO}_2 \text{ mg/l} = \frac{\text{OD for Sample} \times \text{Slope} \times 50}{\text{ml Sample}}
\]

4.3.13 Sulphate

Procedure

Take 50 ml or a portion of sample diluted to 50 ml.(sample volume V ml) + 10 ml Buffer solution + a pinch of BaCl\textsubscript{2}. Mix and stir for 1 minute. Measure the Turbiditity (using Nephlometer). Note the NTU value (N\textsubscript{1}).

Take 20 ml of controll Standard. Make up to 50ml with double distrilled water + 10 ml Buffer solution + a pinch of BaCl\textsubscript{2}. Mix and stir for 1 minute. Measure the turbidity (using a Nephlometer) note the NTU value (N\textsubscript{2}).
**Calculation**

Sulphate as SO$_4$ mg/l = $N_1 \times Ps \times (50 / v)$

Where $Ps = (20 / N_2)$

**4.3.14 Phosphate**

**Procedure**

**Digestion**

Take 50 ml or a portion of sample diluted to 50 ml. Add 1 ml Con. H$_2$SO$_4$ and 5 ml Con. HNO$_3$. Digest to 1 ml and continue to heating until the solution becomes colourless so that HNO$_3$ is completely removed. Cool and add 10 ml d H$_2$O. Neutralize with 6N NaOH (to pale pink end point with phenolphthalein). Filter and make up to 50 ml.

**Colour development**

Add 2 ml molybdate reagent and 5 drops stannous chloride reagent. After 10 minutes but before 12 minutes measure O.D at 690nm.

**Blank**

Take 50 ml distilled H$_2$O and follow the procedure digestion and colour development. This is used as reagent blank for setting the photometer.
Calculation

\[
\text{Phosphate mg/l} = \frac{\text{O.D for Sample x Slope x 50}}{\text{Volume of Sample taken for digestion}}
\]

4.3.15 Fluoride

Procedure

Take 100ml sample or a portion of sample diluted to 100ml in a Nessler Cylinder. Add 5 ml. Acid – Zirconyl Alizarin reagent Mix and Keep it in the dark. Compare with colour standards after 1 hour note the volume of standard Fluoride with which it is compared.

Calculation

\[
\text{Fluoride mg/l} = \frac{(\text{ml Standard x 50 x1000})}{(\text{ml Sample})}
\]

4.3.16 Iron

Procedure

Sample

Take 50 ml or a portion of sample diluted to 50 ml \((V_1)\) in a 250 ml beaker. Add 2 ml H\(\text{NO}_3\) (1:1). Heat to boiling and reduce the volume to about 10 to 15 ml. Add N/8 KMnO\(_4\) and continue boiling till a permanent pink colour is obtained. Cool. Make up to 50 ml with double distilled H\(_2\)O in 50 ml Nessler tube. Add 1 ml
Ammonium thio Cyanate reagent. If iron is present, a red colour is developed. Stir and measure OD at 470nm (S).

**Control standard**

Take 5 ml control standard in a 250 ml beaker. Add 50 ml double distilled H$_2$O. Add 2 ml HNO$_3$ (1:1). heat to boiling and reduce the volume to about 10 to 15 ml. add N/8 KMno$_4$ and continue boiling till a permanent pink colour obtained. Cool. Make up to 50 ml with double distilled H$_2$O in 50 ml nessler tube. Add 1 ml Ammonium thio Cyanate reagent. a red colour is developed. Stir and measure OD at 470 nm(C).

**Blank**

Take 50 ml double distilled H$_2$O add 2ml HNO$_3$ (1:1). heat to boiling and reduce the volume to about 10 to 15 ml. add N/8 KMno$_4$ and continue boiling till a permanent pink colour is obtained allow to Cool. Make up to 50 ml with double distilled H$_2$O in 50 ml Nessler tube. Add 1 ml Ammonium thio Cyanate reagent. Use this as blank for 0 setting.

**Calculation**

\[
\text{IRON as Fe mg/l} = S \times Ps \times \left(\frac{50}{V_1}\right)
\]

(Where $Ps$ (present slope) = I/C)
4.3.17 TIDY’S Test

Procedure

Take 250 ml or a portion diluted to 250 ml of the sample in a wide mouth bottle. Add 10 ml 25% H$_2$SO$_4$ + 10 ml N/80 KMno$_4$. Allow to stand for 4 hours in a dark. If the pink colour fades or disappears in the middle, add additional 10 ml portion of N/80 KMno$_4$ added is noted (V ml). After 4 hours, add 2 ml 10% KI solution. Iodine liberated is titrated with N/80 thio using starch indicator. End point is disappearance of blue colour. Titer volume is noted as B ml.

Conduct a blank using 10 ml N/80 KMno$_4$ + 10 ml 25% H$_2$SO$_4$ and titrating after 4 hours with N/80 thio. Titer volume is noted as A ml.

Calculation

\[ \text{Tidy’s as 0 mg/l} = \frac{\{\left(A \times V\right) - B\} \times 4}{A} \]