

**THE PROBLEM OF WATER POLLUTION
DUE TO OIL REFINERY EFFLUENTS**

Dissertation submitted to the Jawaharlal Nehru
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PREFACE

Three interrelated parts of work have been compiled in this dissertation. The first part, the impact and characteristics of refinery effluents on water bodies reveals the pilot works carried out in the different parts of the world on refinery effluents pollution aspect. It is the guide lines for the developing country like India where little work has been done in this field. Similarly in the second part, a case study of Gauhati refinery views the effects of refinery pollutants on public health through water system which leads the enthusiasm to study the fate of inland water bodies by other refineries of India. Finally third part represents how to balance the aquatic ecosystem against the refinery effluents and control of pollution problem.

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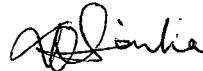
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CERTIFICATE

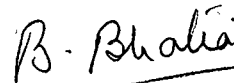
This dissertation entitled ~~THE~~ PROBLEM OF WATER POLLUTION DUE TO REFINERY EFFLUENTS has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi-67. The work is original and has not been submitted in part or in full for any degree or diploma of any University.



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PART - ONE

EFFLUENT CHARACTERISTICS AND
IMPACT ON WATER BODIES

(REVIEW PAPER)

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SUMMARY

This review paper gives the clear picture of pilot study carried out on the oil refinery effluents of the different parts of world. The major components of the refinery effluents, disposal of it on the water bodies resulting effect on aquatic eco-system through the biodegradation of hydrocarbons as well as inorganic compounds, bio-accumulation of it is represented to study the fate of environment. The joint effect of the pollutant toxicity on the system and the water management control of refinery effluents is an integral part of the impact on water system.

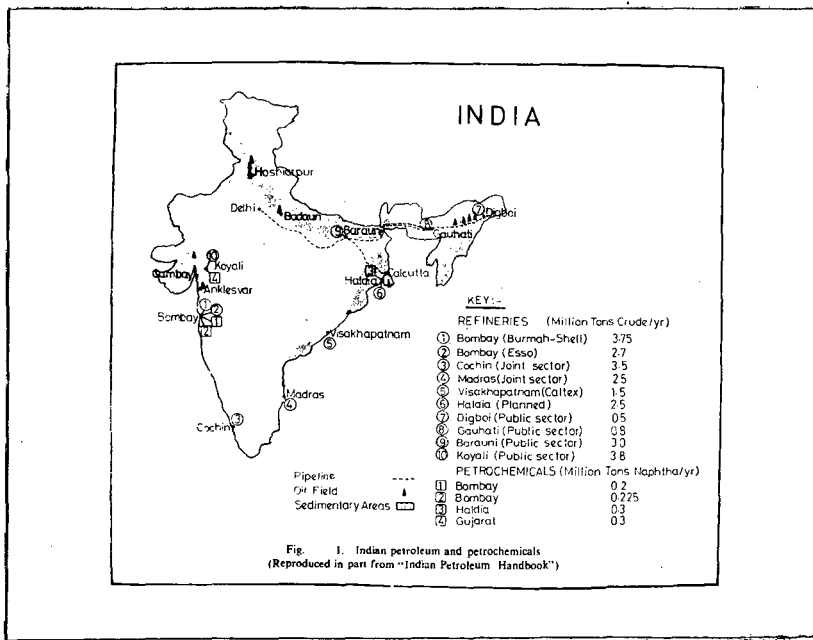


Fig. 1. Indian petroleum and petrochemicals
(Reproduced in part from "Indian Petroleum Handbook")

CHAPTER 1

INTRODUCTION

At present in our country the number of refineries are increasing day by day (Fig.1). It is necessary to view (the picture of) the effect on water bodies. The discharge of noxious or harmful substances in the refinery effluent has been substantially reduced during the past decades. Very often much reductions have been the result of industry's decisions rather than legislative pressure. Since the effluent quality cannot be expressed in a single measurement, for the purpose of this comparison two parameters were chosen, viz., oil content and biochemical oxygen demand (BOD 5), which are (the) represent(atives) for) other effluents.

Parameters of refinery wastes water and the potential for ecological damage in general:

OIL CONTENTS: The 1950's measurements showed average oil and grease content of 20 ppm with some measurements very significantly higher, this level continuously has been reduced, primarily as and when new refineries have been commissioned. It expressed in terms of gm^s of oil discharged per ton of oil processed the above reduction ratio of 10:1 could be easily represented a decrease from 19gm/ton to less than 0.2gm/ton.

BIOCHEMICAL OXYGEN DEMAND: Reduction of this parameter has been the same order of magnitude, while previous values of 100 mg. O₂/litre were considered average, modern refineries have proved to read much lower levels. Again the general reduction in the quantity of water used and discharged has a similar impact on the BOD 5 per crude-through out as in the case of the oil content.

The environmental protection Agency (EPA) has defined significant pollutants parameter for the petroleum refinery as a contrasting of BOD 5 COD, TOC, oil grease (O and G) NH₃-N, phenolic compounds, sulphides and chromium BOD 5 COD, NH₃-N, and provide a measure of oxygen-depleting stress placed on a refinery stream. The substances NH₃-N, chromium, phenolics, sulphides and the like provide measure of toxicity placed on indigenous biological species. Parameter which relate to taste, odour, and miscellaneous "nuisance" properties include phenolics, oil and grease, phosphates and NH₃-N (9).

Handling and disposing of the solid wastes can be major cost items in the refinery water management problem. One case study in U.S. conducted that the following guidelines would reduce wet sludge quantities by more than 50% and help^{to}(the) optimise the end of pipe sequence: (A) Removal of solids from making water (B) Removal of all oily solids from effluent prior to the secondary treatment (C) Use of the Biological (Activated

sludge) treatment element in the end of pipe sequence to remove stable contaminant.

To study the antagonistic and synergistic effect of the pollutants the Arbitrary Reference Mixture (ARM) can be introduced (Dr Lee's Ph.D. Thesis) (6).

Specific enzymes exists in micro-organisms such as bacteria, fungi, and yeasts and animals, to metabolize and catabolize hydrocarbons. Paraffinic hydrocarbons are most liable to microbial attack but olifins and napthenes are also biodegradable. Aromatic compounds with or without paraffinic side chains are readily metabolized by various bacteria, such as some strains of micrococcus, mycobacterium, pseudomonas vibrio, nocardio, Flavobacterium, and others. The available evidence suggests that a long term accumulation of hydrocarbons in marrine and esturine organisms is unlikely, while most of these organisms may temporarily, store all kinds of hydrocarbons as long as they are exposed. When they excrete them the source of pollution is removed.(5).

THE OVERALL REFINERY WASTE WATER TREATMENT SEQUENCE(9).

(1) Minimize removal of soluble contaminants contributing to BOD₅; (2) Minimize Ammonia removal; (3) Maximize removal of contaminants contributing to COD and (4) Maximize final effluent clarify (5) Effect the efficient removal of gross quantities of the solids and oil; (6) Provide for hydraulic and chemical equilization of refinery wastes (7) Minimize the generation of

excess of biological sludges; (8) Minimize any odour and bulking problem from biological sludges; (9) Minimize the immediate oxygen demand (IOD) of water entering secondary treatment; and (10) Minimize sulphide in the effluents and (11) discharge on effluent contaminating dissolved oxygen and a good threshold odour number.

CHAPTER 2

CHARACTERISTICS OF THE EFFLUENTS

The liquid effluents emitted from oil refinery has its own interesting characteristics to influence the water bodies. One aspect is not enough to study the entire characteristics. The following four parameters should be considered to the effluent study.

2.1 Principal sources and the types of pollutants(9).

The petroleum point source category, the environmental Protection Agency (EPA) has defined significant pollutant parameters for the petroleum. Refining industry as consisting of BOD₅, COD, TOC, oil and grease (O and G), NH₃-N, phenolic compounds, sulphides, and chromium. Typical refinery waste load concentrations in mg/l for each of the refinery subcategories are listed in Table (1). The oxygen-depleting parameters BOD₅, COD, NH₃-N, and TOC provide a measure of the oxygen-depleting stress placed on a receiving stream. The toxic substances NH₃-N, Chromium, phenolics, sulphides, and the like provide measures of toxicity placed on indigenous biological species. Parameters which relate to taste, odour, and miscellaneous "nuisance" properties include phenolics, oil and greases, phosphates, and NH₃-N.

The EPA has considered 65 potentially toxic compounds or classes. Until suitable analytical procedures are developed, it

remains unclear how many of these 65 compounds, if any, are present in refinery effluent in significant quantities.

2.2. Disposal Refinery Wastes (9).

Handling and disposing of solid wastes can be major cost items in a refinery water management problem. Much, however, can be done to alter the nature and quality of water-treating sludges. One case study in U.S. concluded that implementing the following guidelines would reduce wet sludge quantities by more than 50%, generate sludge that are easier to de-water, and help optimize the end-of-pipe treatment sequence:

- i. Remove all the solids from make up water. Combine these removed solids with lime-softening sludges for a syngegistic effect in dewatering properties and chemical usage. Dispose of these solids wastes independently of organically contaminated solid wastes.
- ii. Remove all oily solids from the effluents prior to the secondary treatment. Using very efficient filters, oily sludge of "primary" type, which is easiest type to dewater. This goal is achieved by removing essentially all dispersed phase oil and grease as well as suspended and colloidal solids, leaving only residual soluble contaminants for removal by biological processes.
- iii. Use the biological (activated sludge) treatment element in the end pipe treatment sequence to remove only soluble contaminants. This practice has a major impact on minimizing the quantities of waste-activated sludge requiring disposal. Two mechanisms are involved:

- (a) The quantity of BOD/COD available for conversion to cell material is minimized; and
- (b) The process can be operated in an unusual mode, that very high sludge age, which minimizes the net conversion of BOD/COD to cell material, thereby minimizing the quantity of waste-activated sludge.

2.3 Study the interaction of different pollutants and their effect on ecosystem (12).

Terminology: A simple approach for determining how to classify the interaction of two toxicants is to expose organism to half concentration of toxicant 'A' necessary to produce a given response and half the concentration of toxicant 'B' necessary for the same response. If this combination just causes the response the actions of A and B are exactly additive; if it causes more than given response they are more than additive. If it does not cause the response the toxicants are either less than-additive, show no interaction, or are antagonistic and further experimentation is necessary. This approach will now be decided in more detail with reference to figure 1a.

The diagram (Fig.1a) represents the combination of two toxicants. The axes represent concentrations. The concentration of 1.0 unit of toxicant 'A' produce the response (death in case) in absence of toxicant 'B' and 1.0 unit of B will do the same in absence of A. If the response is produced by combination of the two toxicants represented by points inside the square, the toxicants

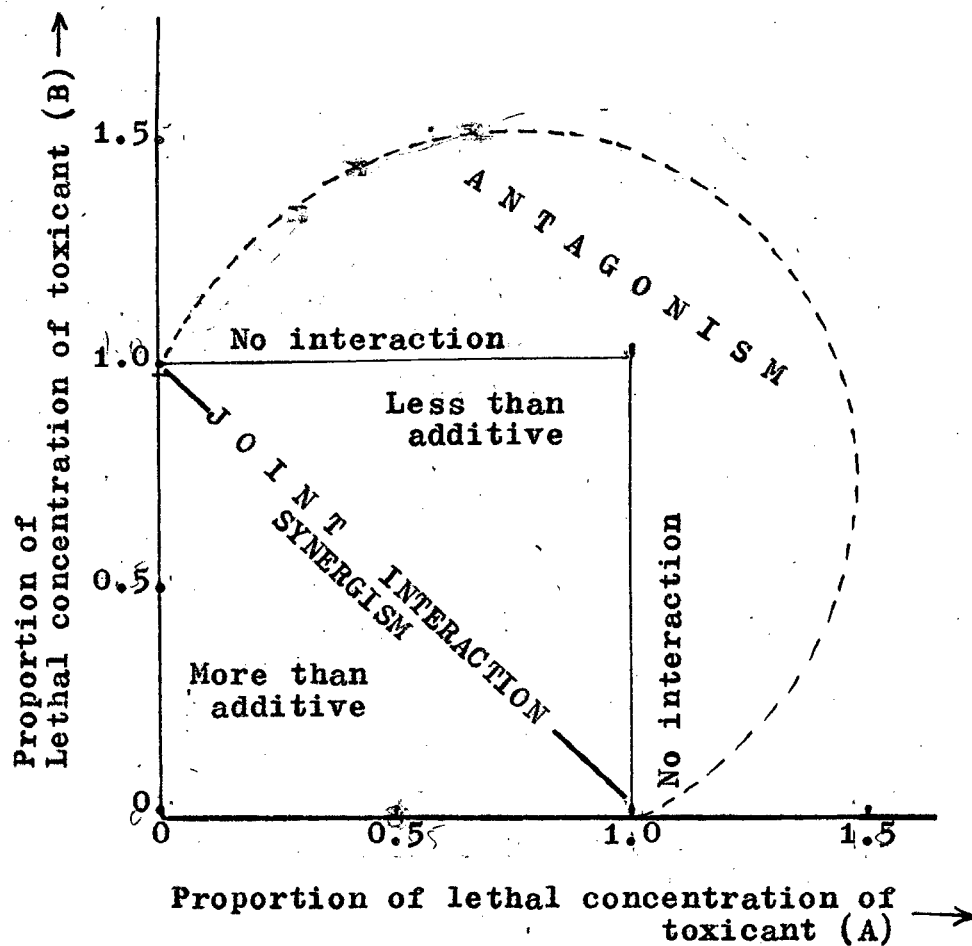


FIG 1a. Diagram showing the terms used to describe the combined effect of two pollutants (Modified from Gaddam, 1948; after Sprague 1970)

are helping one another, this is called joint action which may be further broken-down into 3 special cases, as follows. If the response is just produced by combinations falling in the lower left triangle (e.g. 0.5 A + 0.2 B), the effect is more than additive. The upper right angle (e.g. 0.8 A + 0.7 B) the toxicants are still working in joint act on but one less than additive. Those combination falling exactly on the upper and right boundaries of square show no interaction between the toxicants. For example, if 1.0 unit of 'A' is required to just produce the response, no matter what concentration of B, below 1.0 unit, is present, then 'A' is causing the response and B is neither helping nor hindering. If more than 1.0 unit of A is required to produce the effect, because of the presence of B, this is antagonism, with B antagonizing the effect of 'A'. That combination of concentrations which would fall outside the square would represent antagonism, and loosely represented by the broken curve line.

JOINT TOXICITY STUDY

The effects, if any, of contaminants present in refinery effluents on the aquatic environment can be determined by the bioassay technique (Dr Lee's Ph.D. dissertation).

Arbitrary Reference Mixture(6)

This study was carried out first in ^{??} useful ^e invertebrates and finally on fish. It was impossible to define an "average effluent" or a "Typical value" for each component of an effluent because of variability of refinery effluent.

Because chemical changes occur during storage of refinery effluents, an arbitrary reference mixture (ARM, Table 2) was formulated to approximately the same levels in the EPA guidelines for 1977. The ARM contained several components of refinery wastes. No. 2 fuel oil was used as the oil and grease component of the ARM, because treated refinery effluents were not expected to have significant amounts of hydrocarbons with relatively low boiling points. Zinc ion was not included in the ARM because of high concentration it forms an insoluble complex with sulphide. Additional chemicals would have made the ARM unnecessarily complex for the initial phases of bioassay development.

TABLE 2
ARBITRARY REFERENCE MIXTURE (ARM)

| Parameter | Concentration | ingredient |
|------------------------|---------------|---|
| NH ₃ (N) | 10 mg/l | NH ₄ cl |
| Cr (Total) | 0.25 mg/l | K ₂ Cr ₂ O ₄ |
| Oil and grease | 10 mg/l | No.2 fuel oil |
| Phenol | 0.1 mg/l | Phenol |
| Sulphide | 0.17 mg/l | H ₂ S, 9H ₂ O |
| Total suspended solids | 20 mg/l | Kaolinite |
| pH | 6.8-7.2 | NaOH/H ₂ SO ₄ |

2.4 The fate of effluents in environment (5).

The determining factor for the environmental impact and resulting ecotoxicological effects of any product is the ratio between quantity released and rate of removal, i.e., the concentration of a substance persisting for some length of time and in extended regions or even globally. The removal may be brought by two principal mechanisms. Firstly, the substance may undergo degradation or conversion within a relatively short period of time after their discharge. The degradation may take place under biotic conditions, i.e., the substances are metabolized or catabolized by Micro-organisms, plants or Animals.

Secondly, the substances may be physically transported away from this point of origin, the most important transport media being the running water (sewers, rivers, streams, sea etc.). The result is a dilution at local levels and a regional or global dispersion. The extent of dispersion is determined by the persistence of the chemical substance and the sinks available.

2.4a Biological degradation of aliphatic hydrocarbons:

Specific enzymes exist within micro-organisms, such as bacteria, fungi and yeasts and in animals, to metabolise hydrocarbons. Paraffinic hydrocarbons are most liable to microbial attack but difins and naphthenes are also biodegradable. In most cases, the first step is an oxidation of the terminal - CH₃, followed -in case of odd-numbered alkanes α -oxidation also takes place. While the hydrocarbon-oxidizing enzymes are not very specific, and an adaptation may occur to some extent, a correlation between

oxidizability and alkane structure still exists. A preference for n-alkanes is well established, branched alkanes are less easily (particularly the presence of a quaternary C-atom) reduces the biodegradability. Alternative pathways exist for the biodegradation of olefins: The primary attack may be oxidation of the double-bond or the oxidation of the saturated end of the molecular^e. The intermediates of all these oxidative reactions are alcohols, aldehydes and ketones, fatty acids and esters. Naphthenes are only slowly oxidized by microbial enzymes.

2.4b Biodegradation of aromatics and polynuclear aromatics:

Aromatic compounds with or without paraffinic side chain are readily metabolized by various bacteria such as some strains of micrococcus, pseudomonas vibrio, nocardia, flavobacterium and others. The first step in benzene degradation is an oxygenase-induced 1,2-addition of molecular oxygen, the resulting cyclohexadiene-diol is then dehydrogenated to form catechol. Catechol is an intermediate in the degradation of many aromatic compounds, including naphthalene, anthracene and odd-numbered alkylbenzenes. Catechol is further metabolized to either acetic acid and pyruvic acid or to 3-oxoadipic acid, all of which may eventually, enter the tricarboxylic acid cycle.

Several of these degradation mechanisms are possible not only in bacteria but in higher animals, including mammals. (Diamond and Clark, 1970; Daly, Jerina and Witkop, 1972).

The microorganisms effecting the biochemical degradation of aliphatic and aromatic hydrocarbons are found in the hydrosphere while it is known that pelagic and benthic organisms utilise hydrocarbons, the authors point out the complexity of the problem of biodegradation of hydrocarbons in the marine environments, which make it difficult to arrive at a quantitative statement as to the rate of biodegradation by marine (and estuarine) organisms. One may safely assume that the oxygen content is always sufficient to allow oxidation of hydrocarbons. Other mechanisms are also at work. Several organisms e.g. some kinds of plankton and barnacle larvae ingest large quantities of oil droplets, but the oil passes unchanged through the guts and is excreted in the form of faecal pellets. For instance, copepods may encapsulate up to 1.5×10^{-4} g of oil per day per individual. A population of 2000 individuals/m³ covering an area of 1km² to a depth of 10 m could remove 3 tons of oil per day if the concentration was 1.5 ppm or greater. The oil precipitated in faecal matter may serve as nutrient for other marine organisms and either be metabolized by them or accumulated.

2.4c Bioaccumulation

The available evidence suggests that a long-term accumulation of hydrocarbons in marine and estuarine organisms is unlikely while most of these organisms may temporarily store all kinds of hydrocarbons as long as they are exposed to them- they excrete them once the source of pollution is removed. For instance, upto

95% of the amount of hydrocarbon retained in mussels are excreted within two weeks. Molluscs which excrete aliphatic faster than aromatics, discharge the latter to levels below 0.1 ppm within 2-7 weeks. However, some bivalve molluscs appear to retain a small proportion of aromatic hydrocarbons for at least periods of months.

National Academy of Sciences, Washington, D.C. 1975 indicates hydrocarbon stored in marine macroorganisms. It has to be borne in mind that long-chain paraffinic hydrocarbons ($C_{12}-C_{30}$) are common constituents of marine organisms, also in particular, di and triolefins. These biogenic hydrocarbons are, in many cases, clearly distinguishable from petroleum hydrocarbons. (For methods of distinguishing petroleum hydrocarbons from native biogenic hydrocarbons), While hydrocarbons, on account of this store in marine organisms, may enter the food chain, it is suggested (Burns and Teal, 1973) that there is no relation between the total amount of pollutant hydrocarbons stored and the animals position in the food chain. This is explained with the fact that the most important route of hydrocarbon uptake for most aquatic animals is probably through direct adsorption from the water passing over the gills rather than through ingestion of other organisms. Therefore, a magnification along the food chain is not to be expected.

The available evidence does not appear to support the assumption of actual bio-accumulation of hydrocarbons in marine and estuarine animals and neither are data available with respect to bioaccumulation in terrestrial animals.

CHAPTER 3

THE ENVIRONMENTAL IMPACT OF REFINERY EFFLUENTS(7)

A petroleum refinery is a complex combination of independent operations engaged in the separation of crude molecular fractions, molecular cracking and rebuilding, and solvent finishing to produce a variety of products.

These refineries require large amounts of water, mainly for heat removal and in various process operations. Each process operation has different water usages associated with it, and the characteristics of the waste-waters produced differ considerably.

The most significant pollutants present in these various waste-waters are oil and grease, phenols, ammonia, suspended and dissolved solids, sulphides, and chromium. In addition, some waste-waters are highly alkaline while others are acidic. As a result of widely differing water usages and process in refineries, the quantity and quality of waste-waters varies considerably from refinery to refinery. These wastes, however, readily treatable with a combination of in-plant controls and treatment techniques and end-of-pipe treatment. The last consists mainly of primary separation of oil and solids and neutralization, followed by biological treatment using activated sludge systems, aerated lagoons, or oxidation ponds. The

pollutants named above are largely removed; the effluents discharged from most refineries contain them in only low concentrations.

Toxicity of Major Contaminants in Refinery Effluents

The toxicity of individual contaminants present in these effluents, however, is fairly well documented.

Ammonia: The toxicity of aqueous solutions of Ammonia is attributed to the NH_3 species. Because of the equilibrium relationship among NH_3 , NH_4^+ , and OH^- , the toxicity of Ammonia is very dependent upon PH as well as the concentration of total ammonia. The concentration of NH_3 increases with increasing temperature and decrease with increasing ionic strength. NH_3 concentration decreases with increasing salinity.

Fromm⁷ found that at total Ammonia ($\text{NH}_3 + \text{NH}_4$) concentration of 3mg/l ammonia nitrogen, rainbow trout became hyperexcitable. At 5 mg/l ammonia, excretion was inhibited; and at 8 mg/l, 50 per cent died in 24 Hrs. Anderson⁷ reported that the threshold concentration of NH_4OH for mobilization of D. magna was less than 8.75 mg/l.

Chromium: Fish appears to be relatively tolerant to chromium.

But some aquatic invertebrates are quite sensitive. Toxicity varies with species, chromium oxidation state, and pH. Pickering and Henderson⁹ conducted static bioassays

With warm water fish species. They obtain ^dsoft water 96-hours LC_{50} values for hexavalent chromium ranging from 17.6 mg/l for fathead minnows to 118 mg/l for blue-gill. The hard water 96 Hrs LC_{50} value for hexavalent chromium was 27.3 mg/l for fathead minnows. Trivalent chromium values ranged from 3.33 mg/l for guppies to 7.46 mg/l for blue gill in soft-water. The LC_{50} for fathead minnows exposed to potassium chromate in soft water was 45.6 mg/l.

Raymont and Shields¹⁰ reported chromium threshold toxicity levels of 5 mg/l for small prawns, Hender squills, 20 mg/l (as $Na_2 CrO_4$) for the shore crab, Carcinas maenus and 1 mg/l for polychaetes, Nereis-nirens. Dendenning and North³ showed that 5.0 mg/l hexavalent chromium reduced photosynthesis by 50% in the giant kelp, Macrocystis pyrifera, during four days of exposure.

Oil: One of the assumed effects of oil on aquatic organisms is the coating of the respiratory surface, thereby inhibiting gaseous exchange (Wilber)¹⁴, Tarwell¹³ summarized some of the early literature on the toxicity of oil on aquatic life. He reported that oils and its components adversely affected the ciliary activity of the molluse gills and the chaemo-tactic reaction of the invertebrates.

Phenol: Phenolic compounds can affect fresh water fishes adversely by direct toxicity to fish and fish pond organisms, by lowering the amount for available oxygen because of the high

oxygen demand of the compounds, and by fainting of fish flesh. Various environmental conditions increase the toxicity of phenol-lower dissolved oxygen concentrations, increased salinity, and decreased temperature all enhance the toxicity of phenol.

McKee and Wolff⁸ following a review of world literature, concluded that phenol in a concentration of 1 mg/l would not interfere with irrigation, and 1,000 mg/l would not interfere with stock watering.

Chlorinated phenols present problems in drinking water supplies because phenol is not removed efficiently by conventional water treatment and can be chlorinated during the final water treatment process to form persistent odour-producing compounds.

Sulphides: The degrees of hazard exhibited by sulphides to aquatic animal life is dependent upon the temperature, pH and D.O. At lower pH values, a greater portion is in the form of the toxic undissociated H_2S . In winter, when the pH is neutral or below or when D.O. levels are low but not lethal to fish, the hazard from sulphides is exacerbated. Fish exhibit a strong avoidance reaction to sulphides. If they encounter a lethal concentration of sulphides, there is a reasonable chance they will be repelled by it before they are harmed.

Adelman and Smith¹ found that the maximum safe level of H₂S for eggs of northern pike was 0.014 to 0.018 mg/l and for Sac fry at the same species, the maximum safe level was 0.004 to .006 mg/l for 96 Hrs exposure. Smith¹⁷, working on the walleys and fathead minnows, found the safe levels varied from 0.0029 to 0.012 mg/l, with eggs being the least sensitive and juveniles being the most sensitive in 96 Hrs tests.

Total Suspended Solids: Fish and other aquatic life requirements concerning suspended solids can be divided into those whose effect occurs in the water column and those effect occur following sedimentation to the bottom of the water body. Noted effects are similar for both fresh and marine water.

The effects of suspended solids on fish have been reviewed by the European Inland Fisheries Advisory Commission (1965). This reviewed identified four effects on the fish and fish food populations. (1) By acting directly on fish swimming in water in which solid are suspended, and either killing them or reducing their growth rate, resistances to diseases, and the like; (2) By preventing successful development of fish eggs and larvae; (3) By modifying natural movements and migration of fish; and (4) By reducing the abundance that some species of salmonids will not spawn in such areas.

pH: pH is an important factor in the chemical and biological systems of natural waters. The degree of dissociation of

weak acids or bases is effected by pH. This effect is important because the toxicity of many compounds is effected by the degree of dissociation. One such example is hydrogen cyanide. Cyanide toxicity to fish increases as the pH is lowered, because the chemical equilibrium is shifted toward an increased concentration of HCN. Similar results have been shown for hydrogen sulphide.

Present evidence indicates that a pH range of 6.5 to 9.0 provides adequate protection for the life of freshwater fish and bottom dwelling invertebrate fish food organisms. Outside this range, fish suffer adversely physiological effects, increasing in severity as the degree of deviation increases until lethal levels are reached.

Some marine communities are more sensitive to pH change than others. Normal pH values in sea are 8.0 to 8.2 at the surface, decreasing to 7.7 to 7.8 with increasing depth. Plankton and benthic invertebrates are probably more sensitive to pH change than fish, and mature forms and larvae of oysters are adversely affected at extremes of the pH range of 6.5 to 9.0.

CHAPTER 4
WATER MANAGEMENT CONTROL
OF REFINARY EFFLUENT

Refinery water uses can be categorized as (1) cooling, (2) boiler feed, (3) direct processing, (4) Sanitary and miscellaneous utility uses, and (5) fire protection.

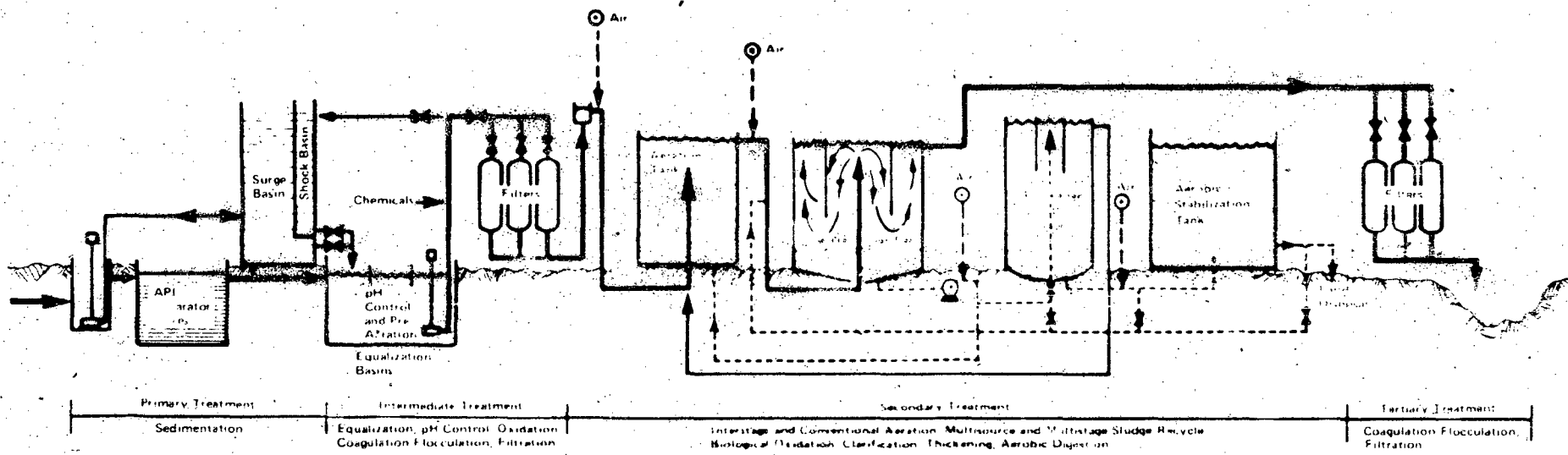
Water management of cooling towers is one of the most important means of controlling effluent volume. In general refinery, about 650,000,000 gal/D of cooling water recirculate through towers, the waste heat being dissipated by the evaporation of some 13,000,000 gal/D of water. The cycles of concentration achieved in the recirculating cooling water relate directly to the volume of slow down in the refinery effluent and the consumptive use of water, as shown in Table 4.

Recirculating cooling water may contain fixed concentrations of such materials as metallic corrosion inhibitors, biocides, slimicides, dispersants, and crystal modifiers. Direct reduction of the amount of these materials lost to the effluent is achieved at higher cycles of concentration. Chemical costs and the impact of the added chemicals on effluent treatment, particularly biological, are reduced.

Optimizing the overall refinery waste treatment sequence (9).

When designing an end-of-pipe treatment sequence for maximum contaminant removal efficiency (Fig.2), the objective are

FIGURE 2 WASTEWATER END-OF-PIPE TREATMENT SEQUENCE*



* Proprietary Design, Standard Oil (Indiana).

usually to:

1. Maximize removal of soluble contaminants contributing to biochemical oxygen demand (BOD);
2. Maximize ammonia removal;
3. Maximize removal of contaminants contributing to chemical oxygen demand (COD); and
4. Maximize final effluent clarify.

Achieving the foregoing objectives give rise to secondary design objectives, namely, to

5. Effect the efficient removal of gross quantities of solids and oil;
6. Provides for the hydraulic and chemical equalization of refinery wastes;
7. Minimize the generation of excess biological sludges;
8. Minimize any odour and bulking problems from the biological sludges;
9. Minimize immediate oxygen demand (IOD) of water entering secondary treatment;
11. Minimize sulphides in the effluent and
12. Discharges an effluent containing dissolved oxygen and a good threshold odour number.

Raw effluent waste contains high amount of toxicants. The end-of-pipe sequence treatment for removal of pollutants indicates the outline of pollutants removal and amount required to be reduced as indicated in Table (5). In API separator step,

TH-246



90 P.C. to 98 P.C. of oil and grease would be removed and in Dissolved Air Flotation method 70 P.C. and in Filtration step 80%. Similarly activated sludge and final filtration steps the removal amount range should be 80 P.C. and 20 P.C. respectively. Thus the range of the amount of the oil and grease present in discharging liquid effluents is 1 mg/l to 4 mg/l. No removal of phenolics in API separator step. But should be highly removed (i.e. 95 P.C. to 99 P.C.) in the activated sludge step. $\text{NH}_3\text{-N}$ must be reduced to 0-99 P.C. in the activated sludge process. The maximum BOD removal should be done in steps activated sludge and filtration by the percentage amount 90P.C. to 95 P.C. and 50 P.C. respectively.

TABLE 1
 AN ESTIMATE OF RAW WASTE LOADS FOR
 EACH REFINERY SUBCATEGORY(9)
 (mg/l)

| Refinery Subcategory | BOD ₅ | | COD | | TOC | | O & G | | NH ₃ -N | | Phenolics | | Sulphides | | Total Chromium | |
|----------------------|------------------|---------|--------|----------|--------|---------|--------|--------|--------------------|-------|-----------|-------|-----------|-------|----------------|-------|
| | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range |
| Topping | 23.4 | 10-50 | 107 | 50-150 | 20 | 10-50 | 25 | 10-50 | 272 | 04-20 | 08 | 0-200 | 24 | 0.5 | 0 | 0-3 |
| Cracking | 169 | 30-600 | 468 | 150-1400 | 81 | 50-500 | 65 | 15-300 | 35 | 5-200 | 74 | 0-100 | 15 | 0-400 | 4 | 0-6 |
| Petro Chemical | 141 | 50-800 | 415 | 300-1400 | 135 | 100-250 | 45 | 20-250 | 41 | 4-300 | 10 | 5-50 | 1.7 | 0-200 | 46 | 0-5 |
| Lubes | 135 | 100-700 | 415 | 400-1400 | 115 | 100-400 | 128 | 40-400 | 19 | 1-120 | 5 | 1-25 | 06 | 0-40 | 13 | 0-2 |
| Integrated | 115 | 100-800 | 366 | 300-1400 | 52 | 50-500 | 44 | 20-500 | 14 | 1-250 | 2.28 | 5-50 | 125 | 0-60 | 28 | 0-2 |

TABLE 3

COMPARATIVE TOLERANCE OF SELECTED FRESH WATER
INVERTEBRATES AND FISH EXPOSED TO AN ARBITRARY
REFERENCE MIXTURE (ARM), THE LC₅₀ DATA EXPRESSED
AS MULTIPLES AND FRACTIONS OF THE ARM SHOWING (6)

| Organism | LC ₅₀ | | |
|-------------------------------|------------------|------------|-------------|
| | 24 Hr. | 48 Hr | 96 Hr |
| Gastropoda | | | |
| <u>Physa</u> sp. | 9.2 - 22.0 | 7.8 - 20.0 | 6.4 - 19.0 |
| <u>Helisoma</u> sp. | 7.4 | 7.4 | - |
| <u>Nitocris</u> sp | 3.7 | 1.4 | 1.8 |
| Goniobasis sp. | 4.6 - 7.4 | 4.5 - 4.9 | 0.37 - 3.3 |
| Amphipod | | | |
| Gammarus Sp. | 5.6 | 3.2 | 1.3 |
| Cladocera | | | |
| <u>Daphnia pulex</u> | 0.11 | 0.07 | 0.3 |
| <u>Daphnia magna</u> | 0.16 | 0.06 | - - |
| Oligochasta | | | |
| <u>Dero</u> sp | 5.6 | 5.6 | 5.6 |
| <u>Tubifex</u> sp. | 1.8 - 5.6 | 1.8 | 0.21 - 0.56 |
| <u>Stylaris</u> sp. | 6.0 | - - | 6.0 |
| Aeolosom ^u Wadleyi | 8.3 | - - | 6.0 |
| Planaria | | | |
| <u>Dugesia Tigrina</u> | 4.9 - 6.3 | 2.0 | 1.6 - 2.0 |
| Totifers* | | | |
| Philodina acuticornis | 1.0 or 6.0 | 1.0 or 6.0 | 1.0 or 6.0 |
| Insecta | | | |
| 3rd inster | 2.3 | -- | 1.8 |
| 1st inster | 0.5 - 0.8 | -- | -- |
| Osteichthyea | | | |
| <u>Salmo gairdneri</u> ** | 4.0 | 4.0 | -- |
| <u>Lepomis macrochirus</u> | 7.4 | -- | 5.6 |
| <u>Carassius auratus</u> | 7.8 | 7.0 | 6.4 |

* Two level of the effect

**Trout fingerlings

TABLE 4

CYCLES OF THE CONCENTRATION
AND VOLUME OF BLOWDOWN

| Cycles of Concentration | % blowdown | Gal/D blowdown |
|-------------------------|------------|----------------|
| 2 | 2 | 13,000,000 |
| 4 | .67 | 4,400,000 |
| 6 | .4 | 2,600,000 |

TABLE 5

TYPICAL REMOVAL EFFICIENCIES FROM END-OF-PIPE
TREATMENT ELEMENTS FOR A RANGE OF EXPECTED RAW
WASTE LOAD (RWL) (9)

| End Pipe Process Step | Parameter | % Reduction | Conc. range, mg/l |
|------------------------------|--------------------------|-------------|-------------------|
| 1. API Separator | BOD ₅ | - | 250-350 |
| | Total suspended solids | - | 50-200 |
| | Oil and grease (O and G) | 90-98 | 20-100 |
| | NH ₃ -N | 0 | 5-35 |
| | TOC | - | - |
| | Phenolics | - | - |
| 2(a) Dissolved Air Flotation | BOD ₅ | 40 | 150-210 |
| | Total suspended solids | 80 | 10-40 |
| | O & G | 70 | 6-30 |
| | NH ₃ -N | 0 | 5-35 |
| | TOC | - | 60-100 |
| | Phenolic | 10-30 | 2-13 |
| (b) Filtration | BOD ₅ | 50 | 125-175 |
| | Total suspended solids | 90 | 5-20 |
| | O & G | 80 | 4-20 |
| | NH ₃ -N | 0 | 5-35 |
| | TOC | - | 50-80 |
| | Phenolics | 10-30 | 2-13 |
| 3. Activated Sludge | BOD ₅ | 90-95 | 12 |
| | Total Suspended Solid | 0 | 6-40 |
| | O & G | 80 | 1-5 |
| | NH ₃ -N | 0-99 | 6-35 |
| | TOC | 60-80 | 10-40 |
| | Phenolics | 95-99 | .02-2 |

Cont'd..

Table 5 Cont'd.

| | | | | * |
|---------------|-------------------------------|-------|--------|---------------|
| 4. Filtration | BOD ₅ | 10-30 | 10 | 15 |
| | Total sus- pended solid | 65 | 2-15 | 10 |
| | O & G | 20 | 1-4 | 5 |
| | NH ₃ -N | 0 | 0-35 | 80% Reduction |
| | TOC | 10-25 | 8-30 | 2.2 |
| | Phenolics | 5 | .02-.2 | .1 |

*Attainable concentrations from the application of BPCTCA claimed by the EPA.

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PART - TWO

A CASE STUDY OF GAUHATI REFINERY, ASSAM

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CHAPTER 1

INTRODUCTION

In North-Eastern Region there are two operating refineries, one is at Digboi and the other is at Noonmati. The third refinery-cum-petrochemical complex is located at Bongaigaon. At present there are four operating refineries of Indian Oil Corporation Ltd., located at Noonmati, Barauni, Jawaharnagar (at Gujrat) and Haldia with a designed annual capacity of 0.75, 2.8, 4.5 and 2.5 million tons respectively. The fifth refinery which is under construction is located at Mathura and is of 6 million tonnes annual capacity (3).

The Gauhati Refinery was Commissioned on 1st January 1962, and it is using "once through system for industrial system". The refinery is situated very near to the Brahmaputra river just above the "Gauhati-city-water-supply-plant (GCWSP). The liquid effluents from refinery is discharged into ^{Brahmaputra} river at about 15 km away from the refinery to avoid the contamination of drinking water. The disposal of polluted water plan was approved by Prof. J.M. Dave (formerly, Chief Public Health Adviser, Government of India, year 1972). The most interesting point of ^Sview to be chosen ^o the Gauhati refinery as field study centre is that - previously polluted waste water directly discharged into Brahmaputra near Saraighat bridge through pumping main. But at that time "water pollution control Act" was not introduced in India. Yet, the refinery was possessing Aeration Basin Settling Basin to minimize the pollution load. Shri B.B.Rao

successor of Professor Dave, (the Chief Public Health Adviser Govt. of India, 1974) expressed that the effluent coming from the Aeration Basin would not exceed the Indian standard tolerance limits. But Gauhati refinery was built based on Romanian and Russian standards (4). Recently, modern design. Effluent treatment plant (ETP) has been come up and now its working efficiency test is going on. So Rao's statement is true or [^] false is a matter of research problem. At present expected non contaminated effluents are discharged into open channel which leads to the Brahmaputra via Bharalu nallah. General public and the official circles are ^{of the} ~~in~~ opinion that the refinery is solely responsible for the pollution and feeding of Bharalu.

The problem of inundation of low laying areas of basin, Bharalu nallah is the only channel of the city serving a major part inhabited area, carries all washing, effluent waste originating small industrial units. There is no treatment system in Gauhati city. The pollution load carried by this channel could thus influence the quality of water on in turn the biota including the fishes. It is felt that the present study may throw some light on this aspect also in addition to pollution levels at the different sites in the Bharulu proper.

CHAPTER 2

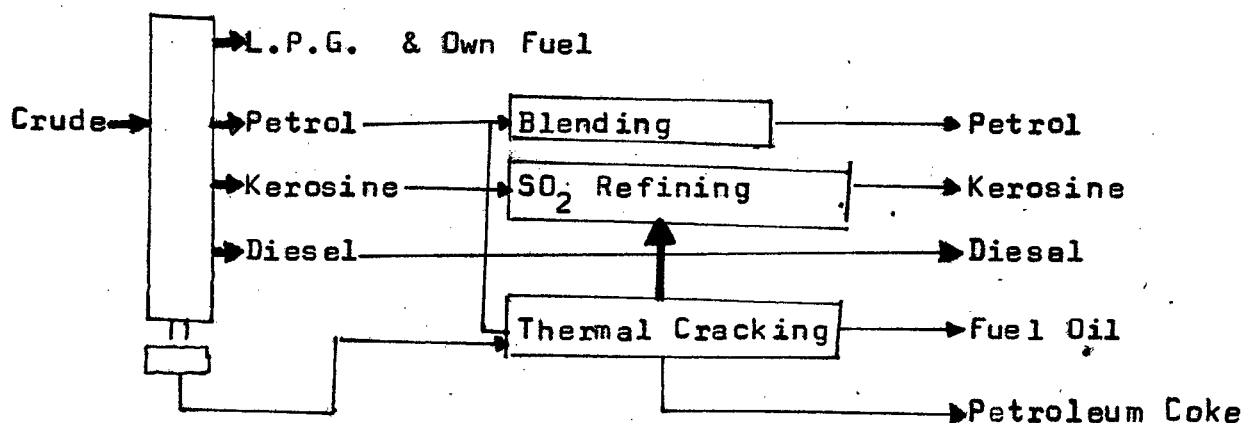
GENERAL DESCRIPTION OF GAUHATI REFINERY

2.1 Petroleum Processing Plant(5)

The petroleum processing plant is shown in the fig.(1). The processing of crude oil is same as other refineries of India. The following major steps are very essential to study the Gauhati Refinery.

1. Crude distillation: separation of different hydrocarbons (HC) by boiling point.
2. Kerosine treating unit: Removal of aromatic compounds by liquid SO_2 extraction for improving the burning property of kerosine.
3. Coking unit: Delayed thermal cracking of residue, under the high pressure and temperature, bigger molecules of HC crack into smaller molecule. Mixture of cracked products is again distilled to get higher products.

The simplified device of oil processing principle of Gauhati Refinery is shown below:



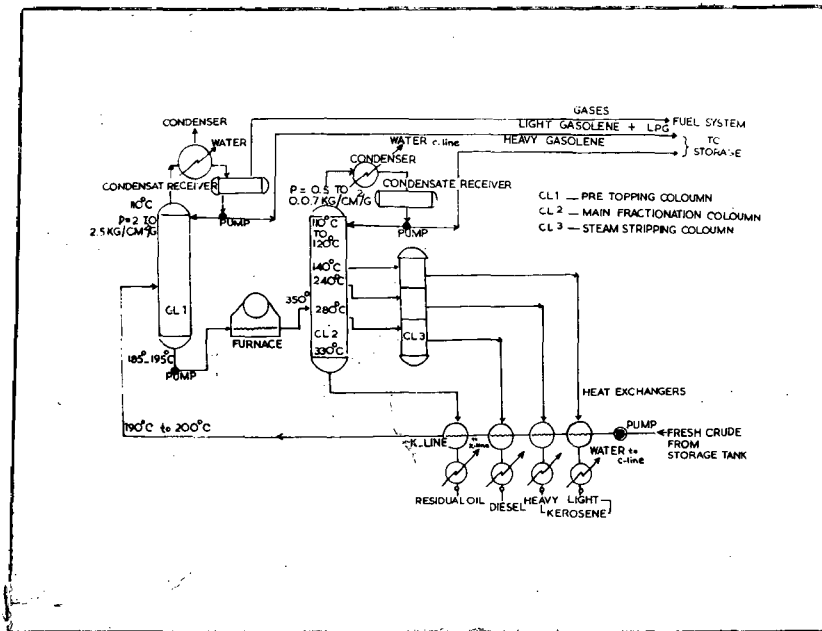


Fig.1 Graphical representation of petroleum processing plant of Gauhati Refinery.

The following products are producing^{ed} in refinery operations.

(A) Primary Products:

1. LPG (Liquified Petroleum Gas or Light Gasoline)
2. Motor Spirit (Petrol) → (Light gasoline)
3. Naphtha (to petrochemical/fertilizers) → (Heavy gasoline)
4. Superior Kerosine → (Light and Heavy Kerosine)
5. Aviation turbine oil → (light kerosine)
6. HSD (High speed diesel oil)

(B) Secondary Products

7. LDO (Low speed diesel oil)
8. FO (Furnace oil)
9. PC (Petroleum coke)
10. Aromatic extract as Comex
11. Low sulfure heavy stock → (residue)

2.2 Characteristics of Discharged Liquid Effluents

Gauhati Refinery is using once through system for industrial system (i.e. taking water from Brahmaputra using it once and allowing it go out at a temperature 40-45°C) The liquid effluents coming out is a combination of the following channels:

- i. CLEAN WATER SYSTEM (W-line)- When water has no chances to contact with contaminants (i.e. oil & grease). The waters is used on only cooling purpose of the heat exchangers. Only heat contamination i.e., the water temperature rises upto 45°C. Formerly negligible amount of metallic zinc was present. But recently all the zinc (Zn) containing pipes are replaced by steel pipe. Therefore, there is no chance for zinc contamination.

Treatment - Normally no treatment is applied.

ii. CONVENTIONALLY CLEAN LINE (C-line)- Effluent being contaminated with oil if any equipment fail. Normally free from oil.

Treatment- if oil is present in the water it is passed into the oil separator. Generally clean water is thrown directly to open channel.

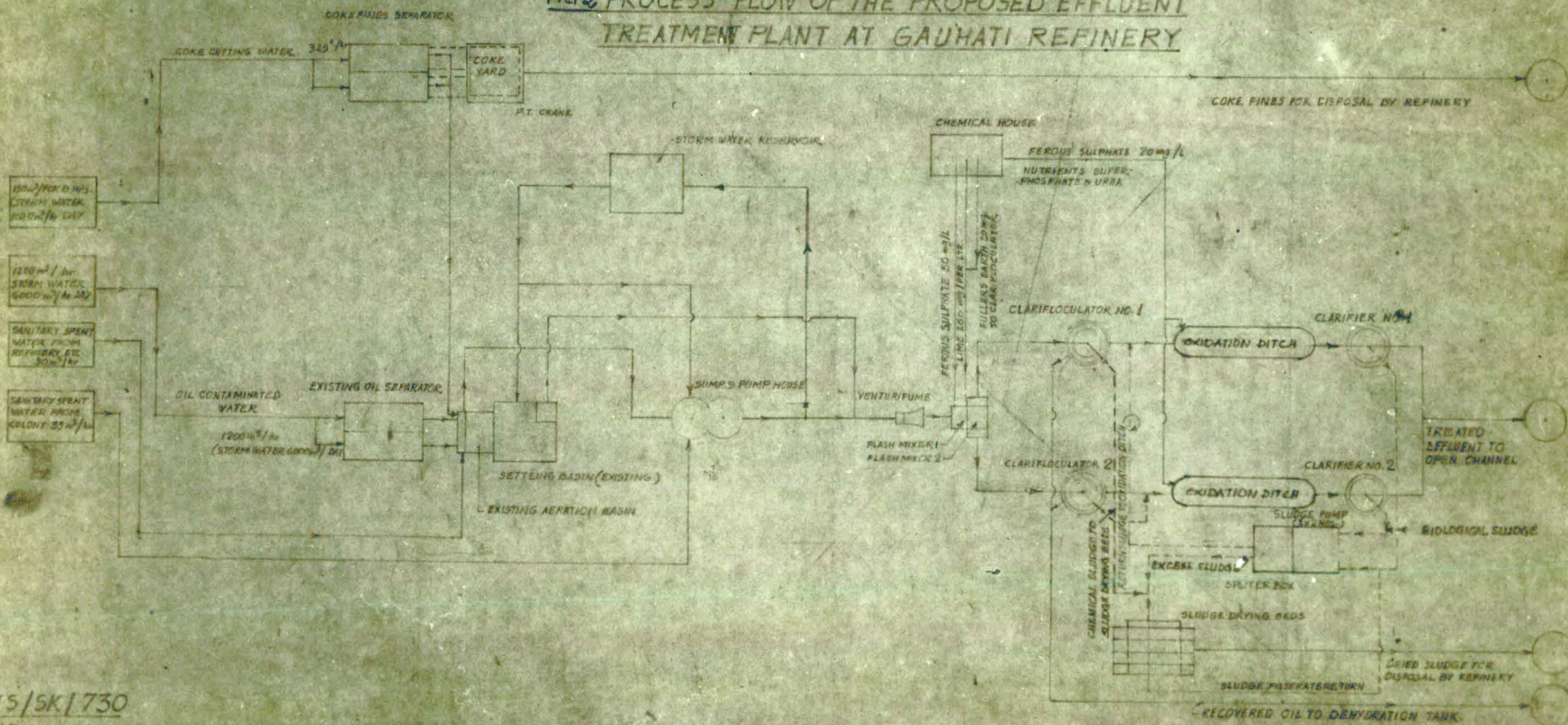
iii. CONTAMINATED EFFLUENT LINE (k-line)- The effluents contain all the contaminants such as spent caustic, acids and other chemical effluents from Refinery Laboratory; phen^oalic effluents from refinery system, coke cutting water; refinery and ^asanitary sewage.

Treatment— (1) Purification is done by removing oil. Before oil removing coke fines are separated by coke fine separator.

(2) Sanitary effluents join with K-line after oil separation. At present there is no design for outlet inlet. Other effluents are sent to new EPT for treatment.

iv. STORM WATER EFFLUENTS: It carries all waste water (surface run off water) from whole refinery area. It is collected by drainage systems. There are oil skimmers to remove the floating oil from open channel. After that a sets of hay screens are provided to absorb remaining traces of oil from this storm water effluent.

FIG. 2 PROCESS FLOW OF THE PROPOSED EFFLUENT TREATMENT PLANT AT GAUHATI REFINERY



T5/SK/730
D.H.D.

Treatment- Hay screens are replaced periodically after saturation of oil.

2.3 EFFLUENT TREATMENT PLANT (ETP)

- i. Unused Plant - In the original design of refinery the effluents from the oil separator was to pass through Aeration basin for supplying oxygen and then was allowed to settle down the sludge in settling basin. Biological treatment done automatically. From the settling basin the liquid effluents were discharged through under ground pipe line to KAMAKHYA (Near Saraighat Bridge) into Brahmaputra river at a distance of 15 km from the refinery proper (Fig. 2).
- ii. New ETP: The details of ETP is explained by fig.(2). The design capacity is $1600\text{m}^3/\text{hr}$. The flow of liquid effluent bifercates into two parallel structures of capacity of $800\text{m}^3/\text{hr}$. For emergency storage capacity (due to heavy rain etc.) provision is made $10,000\text{m}^3/\text{hr}$.

FERRO BIOLOGICAL PROCESS

Step (1) - FeSO_4 - (chemical treatment)

Step (2) - Biological process - Activated sludge extended surface system.

(1) Chemical Treatment - It is done to reduce the remaining oil in the effluents coming from separator, to treat suspended solids; to reduce 50-60% BOD. Although BOD reduction is not done in this system but it is done naturally.

FeSO_4 provides $\text{Fe}(\text{OH})_3$ flocs on hydrolysis. Lime is used for increasing pH and providing OH group for hydrolysis. And Fuller's earth (clay) is used as the settling edges. $\text{Fe}(\text{OH})_3$ is a good co-agulent and absorb oil.

(2) Biological Process - Degradation of organic matters such as oil contents, phenols etc. Thus it is reducing the BOD load of system. This reduction of BOD is done by bacterial organisms. For the proper growth of bacteria the following chemicals are used as food of them.

i. Urea $\text{Co}(\text{NH}_2)_2$ provides nitrogen

ii. Superphosphate $\text{Ca}(\text{HPO}_4)_2$ provides phosphorus.

The significance of chemical added in the biological system are as follows:

| Species of chemical | Dose | Action |
|-----------------------------|--|---|
| 1. FeSO_4 | 50 ppm | Reduction for 150 ppm of oils and 200 ppm of T.S.S. |
| 2. Fuller's earth | 20 ppm | Corresponding to FeSO_4 . |
| 3. Lime | - | To increase the pH at a range 8.5-9 |
| 4. Urea and super phosphate | The dosing proportion required for a balance diet synthesis of cell is BOD:N:P=100:5:1 | Suppliment for nitrogen and phosphorus |

Lime, FeSO_4 and Fuller's earth are added into the effluents in chemical treatment process and pass through for the mixing and disposing the floc. Then it comes clariflocculator where inverted wire is provided at the out let of chemical flocculator to hold the floating oil inside. Oil is mechanically removed and recover.

8

From the clariflocculator it goes to oxydation tank. Nutrients are added before oxydation tank. The bacteria are living inside the basic sludge $[Fe(OH)_3]$. In oxidation tank air is mixed by cage rotars. It is found that oxygen is proportional to consumption of food. BOD increases in the case of disintegration of bacteria. It is supposed that the cause of disintegration of bacteria due to virus infection, more aeration, less food. Biological sludge is fed back to two oxydation ditches. Excess sludge is sent to drying beds.

CHAPTER 3

3. WATER POLLUTION FROM THE REFINERY

3.1 Sources and types of refinery pollutants:

The major pollutants released from refinery and its effect on the water system as well as public health are as follows:

| S.No. | Types of Pollutants | Sources | Effects |
|-------|---------------------|--|---|
| 1. | Oil and grease | Petroleum processing plant and storage tanks | It is the major pollutants. It keeps on floating very difficult to biological degradation. It may cause lot of fire hazards. There was a big fire in a Gauhati city because of high accumulation of it. Fish population vanished in Bharalu and decreases in Brahmaputra. The DO becomes less. The migratory fishes of Bharalu cannot be eaten because of kerosine smell. |
| 2. | Phenols | Condensate water from cracking, distillation product washing caustic treating operations Solvent production process using phenols. | It is water soluble and odour causing agent. It kills fishes. |
| 3. | Sulphides | Crude oil in the form of H_2S , RSH (Hs_2S) crude desalting gasoline condensate receivers at distillation unit and cracking units. | Bacterial oxidation causes the acidic condition of water body. |
| 4. | Spent caustic | Trace | - - - |

Cont'd..

| | | | |
|----|------------------|---|---|
| 5. | Zinc (Zn) | Brass equipments (condensers) | Highly toxic metal. New brass condensers are replaced by steel ones. At present there is no pollution effect. |
| 6. | BOD | Organic matter and sanitary sewage | Reduction in dissolved solids, fishkill. |
| 7. | suspended solids | sludge from tank bottom coke from equipment tubes, filter clays etc. | Fishkill |

3.2 Waste Water Treatment:

At the time of designing refinery at Noonmati and there was clear stipulations regarding the tolerance limits of the pollutants from the refinery effluents by the ISI as such the limits and adapted were those which were in vogue in the country where provided assistance for setting up these refineries. The Romanian and Russian standard was adopted at the refinery at Noonmati is given in Table (1).

ISI laid down the tolerance limits of the effluents discharged into inland surface water for the first time in 1963 vide 2496 -1963 and revised in 1974. It is given in the table II.

ASPECT OF TREATMENT (3)

The treatment process for refinery waste water can be classified broadly into :

- i. Physical Operation
- ii. Chemical Operation
- iii. Biological Operation

Physical methods: are adopted for primary removal of free oil and in almost all cases gravity differential separators are used for the purpose (API).

Chemical Co-agulation: Gravity oil separation (API) cannot be expected to remove the emulsified oil, phenols and other dissolved organic matters from the waste water — necessary oil separation effluent to chemical and/or biological treatment to render the effluent fit for discharge into a receiving water course.

Activated sludge process upset at an oil content of above 25 to 35 mg/l though trickling filter can tolerate upto 100 mg/l without effecting its BOD and phenol removal efficiency (Watson, Ray, 1952, and manual of Disposal of Refinery Waste).

Chemical treatment to remove emulsified oil and also to condition the waste for further biological treatment for removal of BOD and phenols. (Def: emulsion— mixture of two imiscible liquids one liquid being dispersed throughout the other in the shape of very fine droplets). Both the oil— in water and water in oil emulsion are present in refinery waste water.

The water emulsifying agent which are normally absorbed on the surface of the emulsified particles rendering the emulsion stable are soap, sulphate, sophonic and naphthenic acids, quaternary ammonium compounds, organic ethers, and esters.

The basic mechanism by which an oil in water is broken involved:
(a) Neutralization of the charge, carried by the oil droplets by forming a floc that is initially prediated with a charge opposite to that of on the oil.

(b) Absorption of the oil by floc which initially has a high absorptive capacity for the oil.

(c) Entrapment of the oil as floc forms and grows around the oil as the floc forms and grows around the oil droplets. The above objective can be achieved by adjusting the pH of the waste water between between 5 and 6 and subsequently precipitating the sulphonic and naphthenic acids as water insoluble calcium salts by addition of hydrated lime content of pH 7.5 to 8.5 is reached.

Co-agulating agent used — FeSO_4 and Fuller's earth (clay). The floc that are formed by such treatment absorbs most of the oil. depending on the initial oil concentration on effluent may be produced with an oil content of 10 mg/l or even less. Hydraulic decoking and delayed coker in the refinery produces an effluent containing between 1,500 to 15,000 mg/l coke fines and significant amount of oil and waxes. Plugging of drains and chokage of sewer in the refinery are often caused by this refinery.

BIOLOGICAL TREATMENT:

In the biological purification of sewage and organic waste waters in the presence of sufficient air, bacteria being about number of changes in the following order:

1. Coagulation stage, i.e. coagulation and flocculation of colloids and pseudo-colloids.
2. Oxidation stage, i.e. oxidation of carbonaceous matter to carbon dioxide.
3. Nitrification stage, i.e. Oxidation of ammonia, derived from the breakdown of nitrogenous organic matter, to nitrite and eventually nitrate.

In the activated-sludge plant it has, in the past, generally been considered uneconomic to nitrify the sewage (7).

Data are available on a number of biological treatment method for removing microorganisms from sewage. One of the greatest interest at the moments is activated sludge. Trickling filters and oxidation ponds appear erratic also, sometimes, removing large quantities of viruses from the waste-water, but often removing little or more (6).

The general treatment methods of waste water employed at Gauhati refinery are as follows:

| Pollutants | Treatment |
|-----------------------|---|
| 1. Oil and grease | API separator |
| 2. Coke fines | Hydrolic coke fine separator |
| 3. Phenol | Biologically |
| 4. Alkalinity/acidity | Neutralization |
| 5. BOD | Activated sludge process (Oxidation ditches) |
| 6. Domestic Sewage | Activated sludge process (Imhoff Tanks). |



FIG-3: MAP OF GAUHATI REFINERY WATER SYSTEM CARRYING EFFLUENT.

3.3 Disposal of Waste Water to Brahmaputra Through Bharalu.

The disposal of waste water from refinery is done in a sequence of channelized system such as drains — open channels — Bharalu Nallah — Brahmaputra river. Some other waste waters join to this channelized system from the different part of the city. A gross idea of it is given in the map of effluents carrying water system (Fig. 3).

(1) Refinery Waste Streams and their Disposal:

The main waste generated in the refinery operations are process waste waters, and more or less clean waters used as coolents. The refinery generate approximate $1200 \text{ m}^3/\text{Hr}$ oil contaminated waste water. The non contaminated waste waters of approximately $2000 \text{ m}^3/\text{Hr}$ are directly discharged into open drain running by the side of refinery plant, which finally joins Bharalu nallah near the Gauhati zoo.

(2) Open Channel Upto Zoo Road Confluence, and Flow:

(1) The major part of the existing open channel from the refinery plant upto the end of the boundary of the Bamunimaidan Railway colony was jointly constituted by the railways refinery during 1961-62 with the intention of effecting proper drainage of their area. The portion of the channel from the railway colony boundary upto the confluence with Bharalu near zoo, remain in original condition. The portion constructed by the railway and railway authorities is mostly lined and is maintained in good condition.

(ii) Though the refinery and railways had constructed a part of this channel, a natural drain existed originally to drain the run off from Noonmati-Bamunimaidan- Chandmari areas. The tributary area contributing to the run off to be carried by this drain.

(iii) The master plan prepared by Calcutta Metropolitan Planning Organization for water supply, sewage and drainage of "Gauhati Metropolitan District" has made the following observations on the Noonmati sub basin drainage system. There is already an existing channel constructed by Railways and refinery, passing through this area ultimately meeting the Bharalu at zoo-road point. Some part of the up stream part of this channel is fully lined and capacity of lined channel is 19300 L.P.S. This channel receives the waste waters discharges from the refinery and all other surfaces water run off from its tributary area which includes also the area occupied by railways at Bamunimaidan. Since it has not yet been found economically justified to increase the rate of protection in the area belonging to the upper reaches of the drain, which is situated at a higher altitude and no flooding problem exists, it has been proposed to keep the lined portion of the channel unchanged. Thus the refinery and railway have not only taken care of drainage problems of their own areas but also of the entire sub basin.

(3) The Bharalu Nallah; Its Origin and Course:

The Bharalu nallah into which the open channel from Noonmati sub basin discharges, is the natural surface drainage channel that serves the major part of the populated areas of the city and part of

its hilly environs. It originates from the Khasi Hills range and has a large tributary area measuring approximately 128.5 sq. kms. From its origin in the hills range it flows into the plains areas of Jawaharnagar, then crossing the Gauhati Shillong road, follows the road alignment till it meets the tributary stream from the Noonmati sub basin. From this point it takes a right angle turn and flows due west upto Bharalumukh area where again, taking right angle turn, it meets Brahmaputra river. Its entire course in the plain area, it may be seen, is through the developed areas of city.

(4) Bharalu Nallah- The Arterial Sullage Channel of Gauhati City.

It carries storm water run off of the entire Bharalu basin measuring about 123.5 sq. km in addition to all the sullage and effluent stream of the entire areas. Gauhati city does not get a process of sanitary sewer system as such all sanitary and other waste of the area is drained off into the nallah.

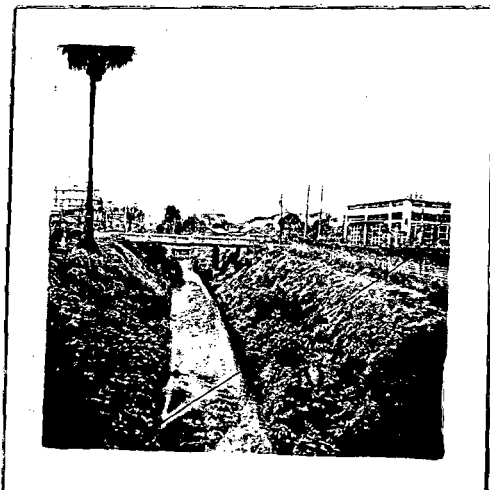
(5) Control and Presumptive Measure by Refinery:

(i) Conscious of its social responsibilities, the refinery has on its own along with railways continued and maintained a drain along the alignment of the original nature drainage stream draining this sector. This channel is capable of handling not only the flow from the refinery and railway areas but also the run off from the complete tributary areas without any flooding or even topping of the banks.

(ii) The refinery has also now completed the construction of Rs.80 lakhs effluent treatment plant for the comprehensive

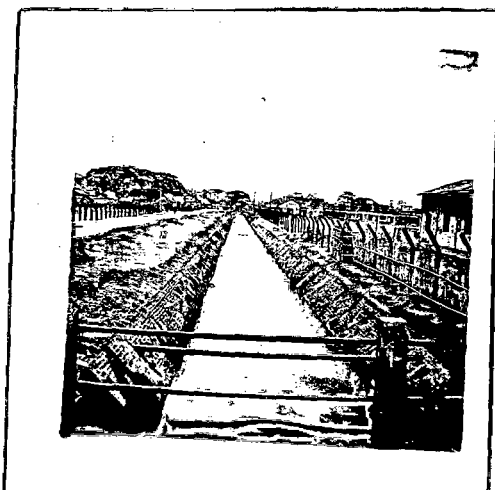
treatment of the contaminated effluent emanating from the refinery, its colonies and railway colony at Bamunimadan. The sanitary sewage of railway colony is treated by Imhoff Tank and finally it is taken to the refinery ETP. The treatment plant has facilities for treating all probable pollutants in the waste waters, viz., expected value of removal of oil upto 10 ppm, chemical treatment for breaking oil water emulsion and flocculation, sedimentation of suspended solids, secondary treatment for biological oxidation of organic matter to achieve reduction of BOD and phenols and final sedimentation before disposal. After the above treatment the water shall conform to the tolerance limit specified by ISI for oil refinery effluent. But it was observed that ETP does not follow the tolerance limit of ISI (Table VIII).

PLATE 1



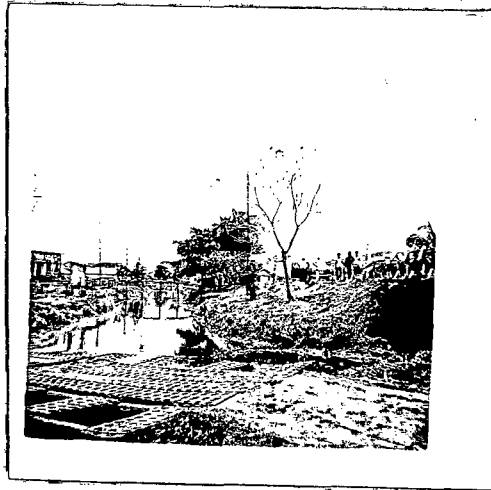
The photograph (1) shows the open channel at New Gauhati as it emerges from Gauhati Refinery battery area. It carries refinery waste and run off water wastes. On the bank beautiful vegetation growth.

PLATE 2



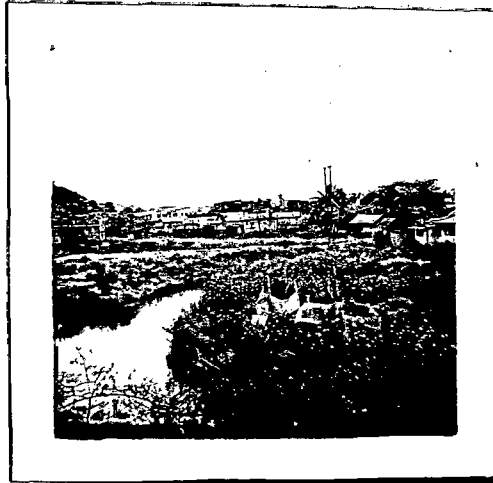
The channel as it flows through railway colony. It carries only washing water and refinery waste water. There is an Imhoff Tank in the Colony. The sewage is collected from it to the ETP of Gauhati refinery for further treatment. Zoo road sides are submerged during the monsoon - thus solid refuse are collected in the Bharalu.

PLATE 3



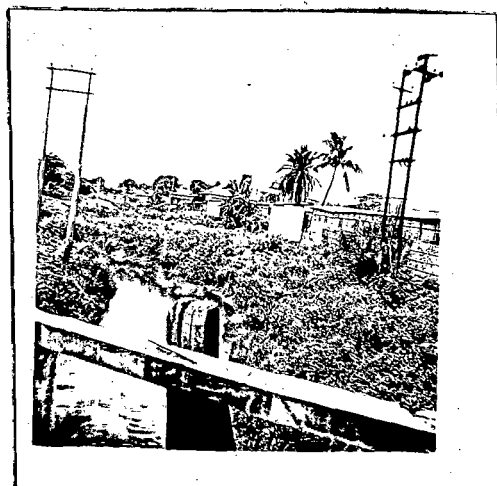
This view is of confluence of the open channel from refinery area and the Bharalu nallah from K.J. Hills. There is a well defined channel to contain the flow. A number of temporary cross built over the channel disturb the free flow of water. Effluents mixed from steel rerolling mills and Kamrup flower mills A.T. Road.

PLATE 4



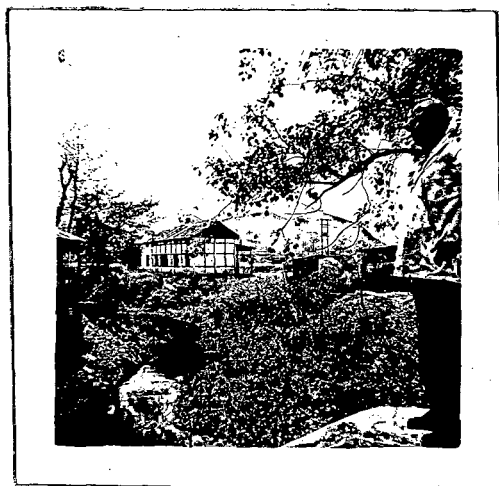
This is the Bharalu nallah as viewed from the cross of G.S. Road - it shows indiscriminate construction of toilets and hutments. Direct discharge of faecal matters and oil and greases from Assam Transport, garbage are the major pollutants. Besides these there is no proper garbage for solid refuses which are added into it during rainy season by submerged water.

PLATE 5



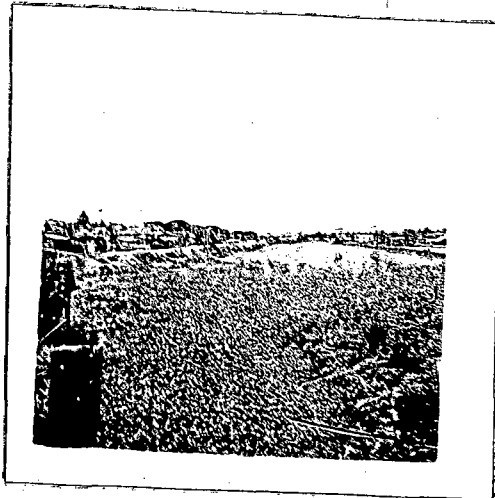
This is Bharalu nallah as viewed from the bridge of Rupnagar. Series of Latrines are discharging sewage directly into it. Besides these oil contaminants are added from state Electricity Board — results high BOD load.

PLATE 6



This is viewed from Phatasil market area. The Bharalu nallah carries the very dirty water from that area. The colour and odour of water is unpleasant. Solid waste and faecal matter are discharged on the both sides of bank, where new houses are coming up on the solid refuse. Some people are using this polluted water for domestic purposes.

PLATE 7



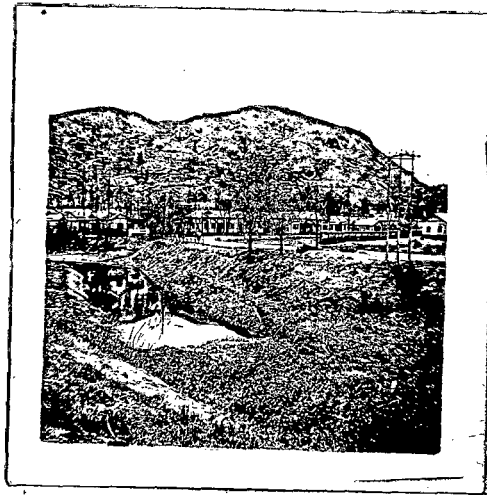
This is the view of polluted water body at phatasil market. The water surface is covered with water Hycinth. This polluted water body is connected with Bharalu nallah through a small passage. Glass factory is situated towards the up-stream side.

PLATE 8



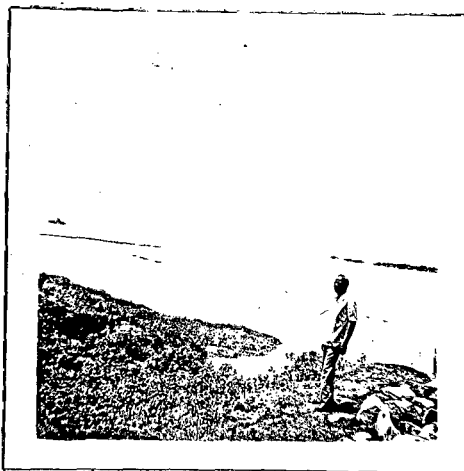
This is Bharalu nallah as viewed from Phatasil No.2. The source of pollutants is as same as Plate No.6. Building are still constructed over the bank. So also the toilet built over the nallah converting.

PLATE 9



This is Bharalu nallah as viewed above the sluicagate from Bharalumukh. Here the BOD load is very high. Besides the domestic refuses people are dumping the Dead Animal bodies.

PLATE 10



This is end point of Bharalu nallah opens at Brahmaputra river as viewed from Bharalumukh. The Saraighat bridge is seen 8 km from Bharalumukh, through the course of the river.

CHAPTER 4

A GENERAL SURVEY OF OTHER SOURCES CONTRIBUTING
TO THE POLLUTION OF BHARALU (4)

A survey of the course of Bharalu and its tributary nallah from Noonmati sector would reveal a large number of sources of pollution. The major industries which produce industrial waste of appreciable quantity are Gauhati Refinery, industrial gases, Indian carbon etc. located at Noonmati sector. The bicycle factory (producing Nitric acid effluent from pickling and electroplating) in Kalapahar area and some small industries like "Frutos" (a food processing industry) and some heavy and medium size motor garages (contributing oil and grease of appreciable quantity) and some heavy and medium size industries like steels worth, a few flour mills, biscuit manufacturing company located at Dispur area. These are the effluents that Bharalu carries today. None of the industries except the refinery have any treatment system.

(1) Gauhati city does not have a sanitary sewer system. It does not even have a proper surface drainage system. Large area of the city are served by dry latrine system with night soil being periodically collected by ^{the} municipality. Some of the better areas have individual septic tank for disposal of sanitary wastes. Most of the slum areas have periodically no facilities at all. House holds on both banks of the Bharalu nallah along its entire course, invariably have built lavatories directly

over this stream for direct disposal of the wastes into the stream bed.

(ii) There are also large number of small and medium industries and trade, discharging effluents and other wastes and washing into this stream without giving any prior treatment. These are partially enumerated under (Table VIa).

(iii) From the above it is to be noted that the entire city and its activities contributes a considerable degree of pollution of Bharalu and by allowing indiscriminate construction of toilets directly over the stream.

(iv) Additional waters discharged by the Refinery (from 1962 onwards) into the open drain and thence to Bharalu is so insignificant by small as to deserve any mention. The proposed design discharge of Bharalu of the sluiceway of Bharalumukh as computed by EMPD in their master plan proposals is 715001 l.p.s. The additional water discharged by refinery viz., about 2000 m³/Hr of clean water and about 1200 m³/Hr treated water. Gauhati Refinery reported open channel upto Zoo road has the requisite capacity to handle their flow without any adverse effects. But it should be noted that the sluiceway was made with a capacity to carry out the original water of Bharalu plus storm water run off and additional refinery water (2000+1200=3200 m³/Hr) may affect the sluiceway.

The section of tributary nallah between railway colony boundary and the zoo-road confluence is badly damaged by siltation, encroachment of water way, weed growth and construction of flow due to construction of a large number of crossings. The main reason

for siltation is the carry over of loose earth from the constructional activities in the tributary area through storm water run off. Because of this, there may be some influx heading inundation of low areas.

CHAPTER 5

RESULTS

TABLE 1

Romanian and Russian Standards

| Sl.No. | Nature of discharge | Conc. after treatment in mg/l | Conc. after discharge into river in mg/l |
|--------|------------------------------|-------------------------------|--|
| 1. | Petroleum Products | 50 - 100 | 0.02-0.04 |
| 2. | Phenol | 4 | 0.004 |
| 3. | Napthenic Acid | 3 | 0.003 |
| 4. | H ₂ S (Sulphides) | 3 | 0.003 |

TABLE II

ISI Tolerance Limit of Refinery Effluents

| Sl.No. | Characteristics | Tolerance Limit |
|--------|--------------------------------------|-----------------|
| 1. | Total suspended matter mg/l (max) | 100 |
| 2. | pH | 5.5 -9.0 |
| 3. | BOD for days at 20°C mg/l (Max) | 30.0 |
| 4. | Oil and grease mg/l (max) | 10.0 |
| 5. | Phenolic compounds mg/l (max) | 1.0 |
| 6. | Sulphides (as S) mg/l (max) | 2.0 |
| 7. | Ammonia cal Nitrogen mg/l (max) | 50.0 |
| 8. | COD mg/l (max) | 250.00 |

TABLE III

Typical Characteristics of treated effluent
from Gauhati
Refinery after treatment by the previous
facilities (1973)

| S.No. | Characteristics | Limit |
|-------|-------------------------|-------|
| 1. | T.S.S. mg/l | - |
| 2. | pH | 7.4 |
| 3. | BOD at 20°C mg/l | 30 |
| 4. | Oil and Grease mg/l | - |
| 5. | Phenolic Compounds mg/l | 5 |
| 6. | Sulphides (as S) mg/l | - |
| 7. | COD mg/l | - |

N.B. : Sulphides are generally not checked
as it is usually 2 mg/l.

TABLE IV

Arbitrary Reference Mixture derived from
the Gauhati Refinery ETP in year 1978.

| S.No. | Characteristics | Limits |
|-------|-------------------------|--------|
| 1. | T.S.S. mg/l | 361.05 |
| 2. | pH | 8.17 |
| 3. | Oil and Grease mg/l | 43.05 |
| 4. | Phenolic Contents mg/l | 2.41 |
| 5. | Sulphides (as S) mg/l | 4.40 |

5a SURVEY REPORT

TABLE VIa

(A) These sketches of open drain from Refinery upto Zoo-road

| | |
|---|--|
| 1. A number of motor garages | Oil and grease, acid and alkalis, dyes and chemicals, lubricating other organic and inorganic matters. |
| 2. Industrial units at Bāmunimaidan Industrial estate | |
| 3. Railway Marshalling yard washing | Suspended solids and other organic matter contributing BOD etc. |

(B) Stretch from Khanapara to Zoo-road

| <u>Industries/Trades</u> | <u>Main pollutants</u> |
|----------------------------------|--|
| 1. Cattle and poultry farm | Sanitary wastes contributing BOD etc. main pollutants. |
| 2. Milk Dairy Plant | Acids, volatile solids, suspended solids, oil and greases etc. and large BOD contribution. |
| 3. Frutos, Food processing plant | Solid wastes, large contribution of BOD |
| 4. A number of motor garages | Oil and grease |
| 5. Coffeine manufacturing plant | Benzene, solid waste BOD etc. |
| 6. Indian oxygen Ltd. | Alkali, Solid wastes |
| 7. Steel rerolling mills | Oil and grease, fine coke, Iron oxide |
| 8. Cattle feed mixing plant | High BOD |

(C) Stretch from Zoo Road to Outfall:

| | |
|---|------------------------|
| 1. A number of medium sized motor garages | Oil and grease |
| 2. Flour mills (3 in nos.) | Solid wastes and BOD |
| 3. Central Workshop of State road transport corporation | Oil and grease; solids |
| 4. A. S.E.B. Station, Ulubari | Lubricants |

5(b) ALGAL GROWTH IN GAUHATI REFINERY EFFLUENT CARRYING WATER BODIES.

A Survey was made on 22/04/78 to identify the algae (Phytoplankton) in open channel, Bharalu-nallah, Brahmaputra. The observations are given in the Table (VI)

TABLE VIb

| Sl.No. | Habitat | Types of Phytoplankton |
|--------|---|---|
| 1. | Open channel (Direct discharge of treated effluent water body) | 1. Fragelluria sps (diatom) 2. Euglena |
| 2. | Bharalu nallah (Diluted refinery effluents plus other pollutants from city) | 1. Diatom sps. 2. Microcystis sp.(maximum) 3. Cladophora sp. |
| 3. | Barahmaputra river (Highly diluted of refinery effluents at the mouth of Bharalu nallah) | 1. Microcystis sp. (Maximum) 2. Anabaena sp.(Minor) 3. Diatom sp. |

TABLE VII

Data of treated effluent before ETP*start. All the monthly data as produced, are derived from the average value of daily results in the year 1977

| MONTH | PARAMETERS | | | | | | |
|------------|--------------|--------|------|-----------|--------|-------|-------|
| | Oil & Grease | Phenol | pH | Sulphides | T.S.S. | BOD | COD |
| August '77 | 6 | 2.2 | 8.1 | - | - | 25 | - |
| Sept. '77 | 10.79 | 1.6 | 7.23 | - | - | 17.92 | 33.00 |
| Oct. '77 | 9.48 | 0.80 | 7.39 | - | - | 51.30 | 38.17 |
| Dec. '77 | 35 | 0.80 | 8.0 | - | - | - | - |

All the data except pH as expressed in ppm

TABLE VIII

Typical characteristics of effluent from Gauhati Refinery ETP after treatment for last four months (monthly value derived from the average daily value).

PARAMETERS

| Months | Oil and Grease | Phenol | pH | Sulphides | T.S.S. | BOD | COD |
|----------|----------------|--------|------|-----------|--------|-----|-----|
| Jan '78 | 61.15 | 1.06 | 7.53 | - | 693.33 | - | - |
| Feb. 78 | 42.11 | - | - | - | - | - | - |
| Mar. '78 | 30.79 | - | - | - | - | - | - |
| Apr. '78 | 38.14 | 3.75 | 8.8 | 4.40 | 28.77 | - | - |

All the values except pH are expressed in ppm.

Fig. 5. Comparison of Tolerance limits of liquid effluents with Gauhati Refinery effluents discharged into Brahmaputra surface water after ETP.

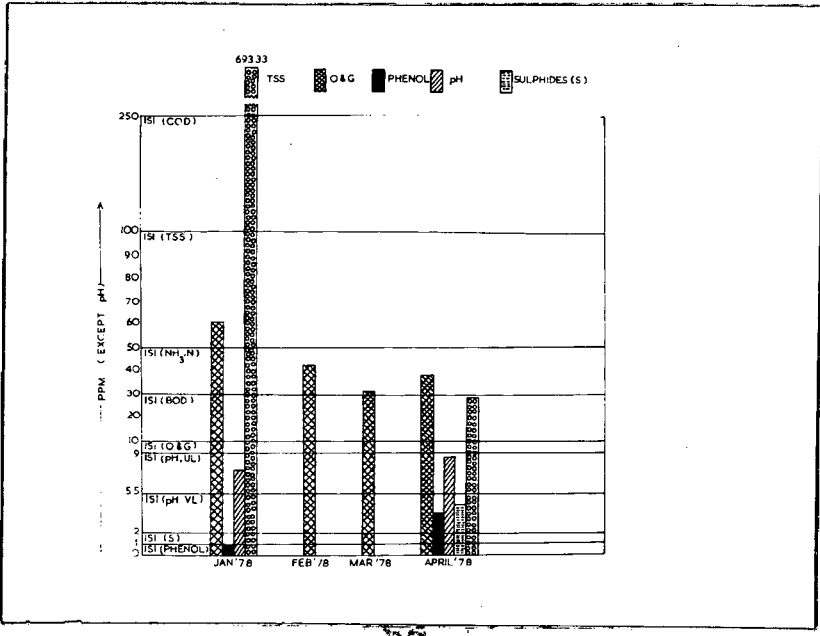
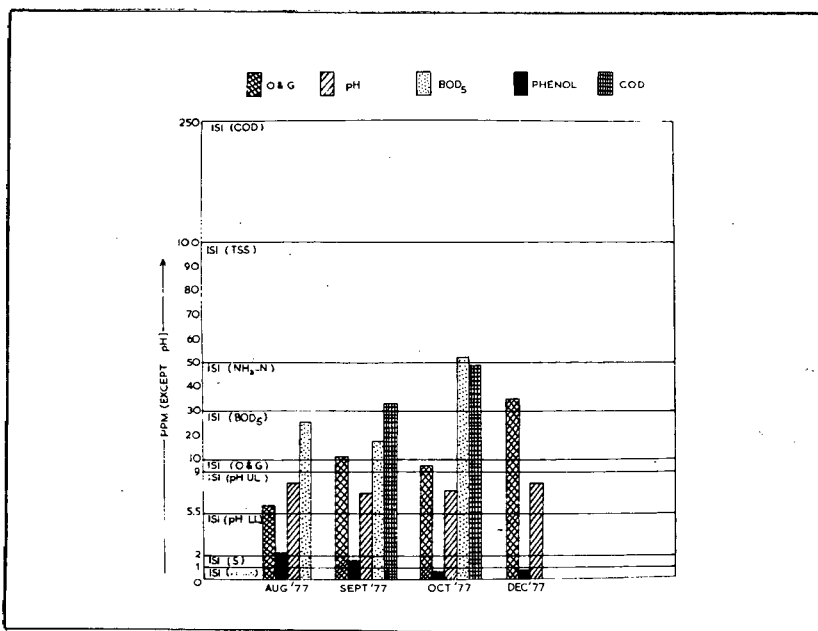


Fig. No. 4. Comparison of Tolerance Limits of liquid effluents (ISI) with Gauhati Refinery Effluents discharge into Brahmaputra surface water before ETP.



CHAPTER 6

DISCUSSION

The liquid effluent treatment Aeration basin of Gauhati Refinery was built based on Romanian and Russian standards(4). Rao (1974) reported that it would not exceed the ISI tolerance limit. But it was found that some parameters had exceeded the tolerance limit of ISI (Fig.4). The average data of last four months (August '77- Dec. '77) of Gauhati refinery indicated that the range of phenol was ^{2.2 to} 8 ppm; to ~~2.2 ppm~~ oil and grease was 6 ppm to 35 ppm; BOD₅ was 17.92 to 51.30 ppm whereas the ISI limit of these parameters are 1.0 ppm, 10 ppm and 30 ppm respectively. Most peculiar observation was that COD value was lesser than BOD in BOD₅ (17.92-51.30 ppm) COD (= 33 ppm to 38.11 ppm).

Similarly four months (Jan. '78- April '78) average data after ETP indicated that it also does follow the ISI tolerance limit. (Fig.5). The range of T.S.S. was 28.77 ppm to 693.33 ppm, phenol was 1.06 ppm to 3.75 ppm, oil and grease was 30.79 ppm to 61.15 ppm. The removal of pollutants and efficiency of ETP was shown in the appendix I. The upper limit of removal of oil and grease is 98.18% yet it was observed that the oil and grease content in out-going water was very high. The phenol removal efficiency range was 32.50 % to 61.17% sulphide removal efficiency was 50% to 99%. It was known that the sulphide contents in the raw effluent is not so high. But the T.S.S. removal efficiency

is not sufficient. It was found that the highest value of T.S.S. was 693.33 ppm. According to NEERI report the higher value of T.S.S. perishes the fishes in aquatic ecosystem. Chakrabarty and Bhaskaran (1973) (3) stated that the destruction and other aquatic flora and fauna, to risk of the fire in rivers and other enclosed areas due to the high oil contents on water. Similarly sulphides, mercaptans, phenols are toxic and taste odour producing substances and destroy the fish and other aquatic organisms. They may also seriously affect the public water supply projects located down stream. Therefore it is necessary to reduce the concentration of pollutants since the ETP is on test.

The Bharalu will remain as the arterial drain channel of Gauhati city and it traverses the most polluted areas of Gauhati. It carries not only refinery effluents but also all sorts of pollutants from the Gauhati city (Table VIa). It was found that there is no fishes in the Bharalu due to pollution load. Besides these the problem of inundation of low ~~laying~~ areas of the city has always been there. The design of the present sluiceway is defective is the cause of major problem. Most of the time the outlet from the sluice gate is submerged and as such will not permit ~~to~~ escape into the river, further aggravating the situation, though the accumulation of weeds, water hyacinth etc. Any oil and grease particles which float over the surface of the stream water upstream of the sluiceway tends to accumulate over a period of time due to the construction of the sluiceway which prevent the floating matters from escaping.

Further the weeds and water hycinth which again accumulate and grow as it cannot escape into Brahmaputra along with the flow acts as a continuous filters for the oil and grease entrapping the same in its fold. It was known that Gauhati refinery had already contributed a sum of Rs.10 lakhs in 1974 to Government of Assam and that amount could be invested for the improvement of sluicgate and garbages along with stream course. Thus the pollution load of Bharalu could be reduced partially.

SINHA (1) reported that algal distribution in terms of diversity and density indicates the level of pollution load. In present study it was found that the diversity and density of the algae in the Bharalu nallah is very low. It was known that the N and P are poor and low in refinery effluents in connection with algal production (Kumar 1970) (3). The nitrogen fixing algae (i.e. cyanophyceae or Mixophyceae or blue green algae) was not found in the Bharalu nallah proper. Anabe^{ae}ana, pollution resistant blue green algae are present in the Eutrophic condition (1). The Anabeana sps. are predominant in the junction of Bharalu nallah and Brahmaputra, indicates the sufficient N and P. in that part of water body. It was supposed that the source of N and P are due to domestic sewage and detergents. Phenolic compounds, hydrocarbons or oil substances are utilized for the growth of algae(3). Frag^telleria, Euglena, Mi^{cy}rocystis and Gladophora are the dominant algal groups in Bharalu nallah carrying phenolic and oil components.

The fauna have not analysed in the Bharalu as well as Brahmaputra. It is reported that there are 126 existing sps of fishes ~~are~~ in Brahmaputra (Appendix II). But it is known that density of fish species is decreasing through the course of river from the junction of Bharalu nallah and Brahmaputra. It may be due to refinery and other industrial effluents and domestic sewage of city.

CHAPTER 7

SUMMARY

It is investigated that the effluent discharged from Aeration basin of Gauhati refinery did not follow *the stipulated* the ISI tolerance limit. Some case is observed new ETP. Besides the refinery effluents, Bharalu nallah carries the pollutants from the small industries garages and domestic sewage, are the causes of high BOD and COD. There is no nitrogen fixing algae (indicator of Eutrophic condition) in Bharalu proper. The density of 126 sps. of fishes of Brahmaputra decreases from the outfall of Bharalu nallah.

APPENDIX I

The efficiency of Effluent Treatment Plant of Gauhati Refinery, Assam.

- (1) Oil and Grease (2) Phenol
 (2) Acidity/Alkalinity (4) Sulphides
 (5) Total Suspended Solid (6) Biological Oxygen Demand

All Values except pH are expressed in ppm

| Date | INLETS OF ETP | | | | | | FINAL CLARIFIER | | | | | | REMOVAL OF POLLUTANT | | | | | | % REMOVAL OF POLLUTANTS | | | | | |
|---------|---------------|-------|-----|------|------|---|-----------------|------|-----|-------|------|---|----------------------|-------|---|-------|-------|---|-------------------------|-------|---|----|--------|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 |
| 7.4.78 | 645.0 | 5.0 | 7.3 | 0.4 | 136 | - | 26 | 2.5 | 8.5 | Trace | 14.0 | - | 619 | 2.5 | - | - | 116 | - | 95.97 | 50% | - | 94 | 85.29 | - |
| 8.4.78 | 625 | 5.6 | 6.8 | - | - | - | 46 | 2.8 | 7.8 | - | - | - | 580 | 2.80 | - | - | - | - | 92.80 | 50% | - | - | - | - |
| 9.4.78 | 148.6 | 5.64 | 7.5 | - | - | - | 21 | 2.19 | 8.7 | - | - | - | 127.60 | 3.45 | - | - | - | - | 85.87 | 61.17 | - | - | - | - |
| 10.4.78 | 32 | 4.07 | 7.6 | 0.48 | 62.4 | - | 15 | 2.5 | 8.8 | 0.24 | 20 | - | 17 | 1.57 | - | 24 | 42.40 | - | 53.13 | 38.57 | - | 50 | 67.95% | - |
| 11.4.78 | 170.8 | 4.0 | 7.5 | - | - | - | 24 | 2.7 | 9.3 | - | - | - | 146.80 | 1.3 | - | - | - | - | 85.95 | 32.50 | - | - | - | - |
| 12.4.78 | 1157.0 | 18.57 | 7.4 | - | 164 | - | 21.0 | 2.82 | 9.7 | - | 67.0 | - | 1136.00 | 17.22 | - | 97.00 | - | - | 98.18 | 35.49 | - | - | 59.15 | - |
| 13.4.78 | 144 | - | 7.4 | - | - | - | 12 | 10.9 | 9.4 | 0.16 | 26 | - | 132 | - | - | - | - | - | 91.67 | - | - | - | - | - |
| 14.4.78 | 76 | - | 7.8 | - | - | - | 18 | 3.13 | 8.6 | 6.24 | 4.8 | - | 58 | - | - | - | - | - | 76.32 | - | - | - | - | - |

APPENDIX (II)

The existing fishes of Brahmaputra river which are compitent of refinery and city producing pollutants (Recent survey report of Fishery Research Department of Assam Government).

LIST OF FISHES

Series ... Pisces

Class ... Teleostomi

Sub-Class..Actinopterygii

Order ... Clupeiformes

Sub-order..Clupeoidei

Family ... Clupeidae

1. Hilsa ilisha (Hamilton) ... Migratory

2. Gudusia chapra (Hamilton)

3. Gudusia Variegata (Day)

Family Engraulidae

4. Setipinna phase (Hamilton)

Sub-order Notopteroidei.

5. Notopterus chitala (Hamilton).

6. Notopterus Notopterus (pallas)

Order Cypriniiformes

Division Cyprini

Sub-order Cyprinoidei

Family Cyprinidae

7. Oxygaster bacaila (Hamilton)

8. Oxygaster gera (Hamilton)

9. Chela atper (Hamilton)

10. Chela laubuca (Hamilton)

11. Raiamas bola (Hamilton)

12. Barilius barila (Hamilton)

13. Barilius barna (Hamilton)

14. Barilius bendelisis var. chedra (Hamilton)

15. Barilius shacra (Hamilton)

16. Barilius vagra (Hamilton)

17. *Danio (Danio) aequipinnatus* (McClelland)
18. *Danio (Danio) dangila* (Hamilton)
19. *Danio (Danio) devario* (Hamilton)
20. *Danio (Brachydanio) rerio* (Hamilton).
21. *Esemus danricus* (Hamilton)
22. *Rasbora elanga* (Hamilton)
23. *Rasbora daniceni* (Hamilton)
24. *Rasbora rasbora* (Hamilton)
25. *Amblypharyngodon mola* (Hamilton)
26. *Aspidoparia jaya* (Hamilton)
27. *Aspidoparia morar* (Hamilton)
28. *Accrossocheilus hexagonolepis* (McClelland)
29. *Tor putitora* (Hamilton).
30. *Tor tor* (Hamilton)
31. *Tor progenius* (McClelland).
32. *Puntius chagunio* (Hamilton)
33. *Puntius chola* (Hamilton)
34. *Puntius conchenius* (Hamilton)
35. *Puntius phutunio* (Hamilton)
36. *Puntius sarana* (Hamilton)
37. *Puntius stigma* (Hamilton)
38. *Puntius tetrapagus* (McClelland)
39. *Puntius ticto ticto* (Hamilton)
40. *Catla catla* (Hamilton)
41. *Cirrhinus mrigala* (Hamilton)
42. *Cirrhinus reba* (Hamilton)
43. *Labeo bata* (Hamilton)
44. *Labeo calbasu* (Hamilton)
45. *Labeo dero* (Hamilton)
46. *Labeo dyocheilus* (McClelland)
47. *Labeo gonius* (Hamilton)
48. *Labeo nandina* (Hamilton).
49. *Labeo panguisa* (Hamilton)
50. *Labeo rohita* (Hamilton)
51. *Osteobrama cotio cotio* (Hamilton)
52. *Semiplotus semiplotus* (McClelland)
53. *Schizothorax progastus* (McClelland)
54. *Crossocheilus latius latius* (Hamilton).

Family Psilorhynchidae

55. *Psilorhynchus balitora* (Hamilton)
 56. *Psilorhynchus sucatio sucatio* (Hamilton)

Family Homalopteridae

57. *Balitora brucei brucei*, Gray

Family Cobitidae.

58. *Noemacheilus beavani*, Gunther
 59. *Noemacheilus botia* (Hamilton).
 60. *Noemacheilus corica* (Hamilton)
 61. *Noemacheilus savona* (Hamilton)
 62. *Noemacheilus scaturigina* (McClelland)
 63. *Noemacheilus sikmaiensis*, Hora
 64. *Noemacheilus zonatus* (McClelland)
 65. *Botia dario* (Hamilton)
 66. *Lepidocephalichthys annandalei* Chaudhuri
 67. *Lepidocephalichthys berdmorei* (Blyth)
 68. *Lepidocephalichthys guntea* (Hamilton)
 69. *Somileptes gongota* (Hamilton)

Division Siluri
 Sub-order Biluroidei

Family Siluridae

70. *Ompok bimaculatus* (Block)
 71. *Wallago attu* (Block & Schneider)

Family Bagridae

72. *Batasio batasio* (Hamilton)
 73. *Mystus (Mystus) bleekeri* (Day)
 74. *Mystus (mystus) cavasius* (Hamilton)
 75. *Mystus (mystus) menoda* (Hamilton)
 76. *Mystus (Mystus) montanus* var
dibrugarensis (Chaudhuri).
 77. *Mystus (Mystus) vittatus* (Bloch)
 78. *Mystus (Osteobagrus) aor* (Hamilton)
 79. *Mystus (Osteobagrus) seenghala* (Sykes)
 80. *Rita rita* (Hamilton)

Family Amblycipitidae

81. *Amblyceps mangois* (Hamilton)

Family Sisoridae

- 82. Bagarius bagarius (Hamilton)
- 83. Erethistes Pussilus (Muller and Troschel)
- 84. Erthistoides montana montana, Hora.
- 85. Gagata Cenia (Hamilton)
- 86. Gagata nangra (Hamilton)
- 87. Gagata viridescens (Hamilton)
- 88. Glyptothorax rabeiroi (Hora)
- 89. Glyptothorax striatus (McClelland)
- 90. Glyptothorax telchitta (Hamilton)
- 91. Sisor rhabdophorus (Hamilton)

Family Schilbeidae

- 92. Ailia coula (Hamilton)
- 93. Ailichthys punctatus, Day
- 94. Clupisoma garua (Hamilton)
- 95. Eutropiichthys vacha (Hamilton)
- 96. Eutropiichthys mirius (Hamilton).
- 97. Pangasius pangasius (Hamilton)
- 98. Pseudeutropius atherinoides (Bloch)
- 99. Silonia silondia (Hamilton)
- 100. Family Meteropneustidae
Heteropneustes fossilis (Bloch)

Family Clariidae

- 101. Clarias batrachus (Linnaeus)
Order Anguilliformes
Sub-order Anguilloidei
Family Ophichthyidae
- 102. Pisoodonophis boro (Hamilton)
Order Beloniformes
Sub-order Scomberesocoidei

Family Belonidae

- 103. Xenentoden cancila (Hamilton)
Order Mugiliformes
Sub-order Mugiloidei
Family Mugilidae
- 104. Mugil corsula (Hamilton)
- 105. Mugil cascasia (Hamilton)

Order Ophiocephaliformes

Family Channidae

- 106. Channa gachua (Hamilton)
- 107. Channa Marulius (Hamilton)
- 108. Channa punctatus (Bloch)
- 109. Channa Striatus (Bloch)

Order Symbranchiformes
Sub-order Symbranchoidei
Family Amphipnoidae

- 110. Amphipnous cuchia (Hamilton)

Order Perciformes
Sub-order Percoidei
Family Centropomidae

- 111. Chanda baculis (Hamilton),
- 112. Chanda nama (Hamilton)
- 113. Chanda ranga (Hamilton)

Family Sciaenidae

- 114. Sciaena coiter (Hamilton)
- 115. Pama pama (Hamilton)

Family Nandidae

- 116. Badis badis (Hamilton)
- 117. Nandus nandus

Sub-order Anabantoidei
Family Anabantidae

- 118. Anabas testudineus (Bloch)
- 119. Colisa chuna (Hamilton)
- 120. Colisa fasciata (Bloch)
- 121. Colisa lalius (Hamilton)

Sub-order Gobioidae

Family Gobiidae

- 122. Glossogobius giuris giuris (Hamilton)

Order Mastocembeliformes
Family Mastocembelidae.

- 123. Mastocembelus armatus armatus (Lacepede)

124. *Mastocembelus pancalus* (Hamilton)

125. *Macrognathus aculiatus* (Bloch)

Order Tetraodontiformes

Sub-order Tetraodontoidei

Family Tetraodontidae

126. *Tetraodon cutcutia* (Hamilton)

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PART THREE

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STUDY OF TL FOR INDEFINITE PERIOD OF TIME WITH REFERENCE TO GAUHATI REFINERY EFFLUENTS ON Puntius phutunie (Ham) AS a BIOLOGICAL INDICATOR

CHAPTER 1

INTRODUCTION

The increase in the use of automobile vehicles, industrial uses etc. the consumption demand of oil is increasing in a large scale. This has caused the establishment of more and more refineries in India. The liquid effluents of refineries being discharged into the inland water bodies after processing oil has a major toxic effects on public health through the water system. In India little work has been done in the field of composite refinery pollutants effects on aquatic organisms by bioassay techniques. The case study of Gauhati refinery (Part II of same thesis) reveals that there are no fish in the part of Bharalunallah where the refinery pollutants are present, whereas the upstream of Bharalunallah is having fishes. Since the inland fishes are important source of proteins in a nation's diet, the needs for understanding the toxicity of liquid effluents of Gauhati refinery on fish and evaluating circumstances when poisoning occurs is greater. The present investigation gives the information of the toxicity effect on physiological activities of puntius phutunie (fish species existing in Brahmaputra). Lee (1972) reported the effect of ARM derived from seven refineries of USA on Salmo gairderi (TL₅₀ for 24,48 Hrs was 4.0); Carassius auratus (24 Hrs-7.8;48Hrs-7.0; 96 Hrs 6.4). (5).

It was difficult to produce unique quantity of each component of refinery effluents in refinery laboratory, because complexity of chemicals and their concentration. The average value of liquid pollutants for 120 days (i.e. 4 months) was considered as ARM (Arbitrary Reference Mixture) Gauhati refinery for present study. Because the design capacity of ETP is $1600 \text{ m}^3/\text{h}$ and comprises two parallel structures of $800 \text{ m}^3/\text{h}$. In general the discharged polluted water load of Gauhati Refinery $1200 \text{ m}^3/\text{h}$ to $1400 \text{ m}^3/\text{h}$. The effluent is discharged directly into the common out let with treatment.

The grabs sampling method was employed for the collection of sample from Gauhati refinery outlet. Three days were required to bring the sample to JNU by train in closed condition where the temperature range was 29°C to 42°C . And it was kept for 5 days in cold room of laboratory at a temperature (25°C - 26°C).

The first experiment was done with original sample, which consisted of two sets of different dilutions— one with low concentration of pollutants (the range was 1 ml/10 litres to 2.5 ml/10 litres) another with high concentration of pollutants (the range was 3 ml/10 litres to 5.5/10 litres). The interval between dosages was 0.5 ml only. The observed negative result in this experiment due to the following defects: (i) store of sample for longer period of time; (ii) heat stroke, (iii) lack of acclimatization of fish at laboratory condition, (iv) high dilution of effluent concentration.

The second experiment was performed as same manner of first one to understand the effect of raw waste on experimental fish with

modified sample prepared based on ARM of Gauhati refinery as well as rectification of above mentioned defects.

The Arbitrary Reference Mixture (ARM) of Gauhati Refinery

| Parameter | Concentration |
|----------------------|---|
| Oil and grease (O&G) | 43.05 mg/l |
| Phenol | 2.41 mg/l |
| Sulphides | 4.46 mg/l |
| T.S.S. | 693.33 mg/l to 28.77 mg/l 361.3 mg/l* |
| pH | 8.17 |

*Mean of range

It is interesting to understand the acute and synergistic effect of ARM on experimental fish. In second experiment the volume of experimental water was 1,750 ml and the range of low concentration was (0.5 ml/l to 2.5 ml/l); the range of higher concentration 3ml/l to 5 ml/l. The positive i.e. decrease of concentration with increase of time was observed in this experiment.

The aim of the present investigation is to evaluate the acute toxic ranges TL_m or TL_{50} for 3,24,48,72 and 96 hours intervals and the relative susceptibility of Puntius phutunie for ARM. The study will decidedly help in controlling the pollution problem caused by refinery effluent.

CHAPTER 2

MATERIALS AND METHOD

Reed and Muench Bioassay technique was used for present study. (1) (7). The grabs sampling method was employed for the collection of sample, because time was very short. The date of collection was 25/6/78, time 8 AM and seven minutes required for the same. The temperature of sample at Gauhati was 29°C. The Three days were required to bring the sample to JNU by train in closed condition where the temperature range was 29°C-42°C. And it was kept for 5 days in cold room of laboratory at a temperature (25°C-26°C). The equal size of eleven Aquariums were used the volume of each was 30x27x27 cu.cm. The first one was used for control experiment.

DESIGN OF EXPERIMENT

The first experiment was conducted with original effluent sample. The sample was diluted by adopting Reed and Muench method (1)(7). The interval between doses was 0.5 ml. The first set of experiment was done with low concentration (i.e. 1 ml/10 litres to 2.5 ml/10 litres) and the second set was performed with high concentration (i.e. 3 ml/10 litres to 3.5 ml/10 litres). But two sets of experiment were done in the same time using single control experiments. For easy calculation, the two sets of experiment were combined in the same table.

Chart Showing Dilution of Pollutants

| Aquarium No. | Volume of Expt. Water | Actual amount of original effluent sample added |
|----------------------|-----------------------|---|
| Control | 10 Litres | - |
| FIRST SET (low Conc) | " | 1 ml |
| 2 | " | 1.5 ml |
| 3 | " | 2.0 ml |
| 4 | " | 2.5 ml |
| 5 | " | 3.0 ml |
| 6 | " | |
| 2ND SET (high conc) | " | 3.5 ml |
| 7 | " | 4.0 ml |
| 8 | " | 4.5 ml |
| 9 | " | 5.0 ml |
| 10 | " | 5.5 ml |
| 11 | " | |

The oxygen was supplied 12 hrs/day in the first experimental period. Fifty milligrams of $Na_2 S_2 O_3 \cdot 5H_2O$ was added in per litre of tap water. to remove the chlorine. The physico chemical characteristics of chlorine free water as follows :

| Parameter | Initial | Final |
|-------------|---------|-------------------------------|
| Temperature | 42°C | 42°C |
| pH | 6.5 | - |
| D.O. | 8.6 ppm | Highly saturated with oxygen. |



Fig.1 Diagram showing the structure of Puntius
phutunie

Systematic position-

| | | |
|---------|---|-----------------|
| Class | - | Teleostomi |
| Order | - | Cypriniformes |
| Family | - | Cyprinidae |
| Genus | - | <u>Puntius</u> |
| Species | - | <u>phutunie</u> |

The D.O. was calculated with Winkler's method. The fishes were fed 3 hours before the experiments and only 24 hours acclimatization of fishes was done.

The fish Puntius phutuniae belongs to the order cypriniformes and family cyprinidae (fig. 1). Oxygen was passed continuously throughout the acclimatization period.

For assessing the toxicity of each concentration 10 fishes were used, which is homogenous as possible (same age, sex, recent history and genetic background etc. and the test fish should be healthy well fed before test). The test fish was transferred into aquarium one by one from storage tank. (The water should be same at the same temperature as that in the holding tank to avoid thermal shock). The experimental fishes were observed for any pathological symptoms before being transferred them into experimental containers. During the experiment no feeding to the fish was made because such feeding might increase the rate of metabolic activity and the excretory substances which may influence the toxicity of the test solutions. The reactions of fish towards the toxicants i.e. loss of equilibrium, operculum movement, swimming movement, breathing and mode of distress were observed throughout the experimental period. The fishes were considered dead when they gave no response to touch with a glass rod.

At the end of experiment (after 4 days) a fish from the store tank was transferred into one litre of 100% effluent sample. The fish showed erratic movement for five minutes and it was alive more than five days. From that observation it seemed that significant degradation of pollutants was occurred.

In the second experiment to rectify these errors and to understand the effect of raw waste on Puntius phutunie a modified sample was prepared based on the recommended ARM of Gauhati Refinery (Table IV, Part II). The following pollutants were added in original sample:

| Pollutants | Concentration | Ingredient |
|-----------------------------|---------------|---|
| Oil and Grease (O & G) | 43.05 mg/l | NO.2 fuel oil* |
| Phenol | 2.41 mg/l | Phenol (C ₆ H ₅ OH=94.11) |
| Sulphide | 4.40 | 2-Marcapto-benzothiozole** |
| pH | 8 | NaOH/H ₂ SO ₄ |

*Furnace oil from Indraprastha Power Station, New Delhi (India)

**Imported from England (Technical) BDH.
C₆H₄S. C(SH): N = 167.25.

The tap water used for dilutent for the present experiment. 5mg of Na₂S₂O₃, 5H₂O added per litre of tap water for chlorine removal. The experimental volume of water was 1,750 ml.

The modified sample was diluted in the following way:

| Aquarium No. | Actual Volume Expt. Water | Dose | Actual Amount of Modified Sample Added. |
|----------------------------------|---------------------------|----------|---|
| 1 Control | 1,750 ml | 0ml/l | - |
| FIRST SET OF EXPT. (Low Conc.) | | | |
| 2 | " | 2.5ml/l | 0.88 ml |
| 3 | " | 1.0ml/l | 1.75 ml |
| 4 | " | 1.5ml/l | 2.63 ml |
| 5 | " | 2.0ml/l | 3.50 ml |
| 6. | " | 2.5ml/l | 4.38 ml |
| SECOND SET OF EXPT. (High Conc.) | | | |
| 7 | " | 3.0ml/l | 5.25 ml |
| 8 | " | 3.5ml/l | 6.43 ml |
| 9 | " | 4.0 ml/l | 7.00 ml |
| 10. | " | 4.5 ml/l | 7.88 ml |
| 11 | " | 5 ml/l | 8.75 ml |

The physico-chemical characteristic of the experimental water as follows

| Parameter | Initial | Final |
|-------------|---------|---------|
| Temperature | 28.5°C | 28.5°C |
| pH | 8 | 8 |
| D.D. | 8.4 ppm | 6.4 ppm |

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Feeding of fish was stopped 2 days before the present experiment. The fish ranging in weight from 0.102 gm to 0.345 gm (2.1 cm to 3.2 cm in length). were used in all experiments. It was kept in the mind that test containers were to allow 0.5 litres of test volume per gram of Animal weight (5) $\sqrt{4}$ Hrs/day. Aeration was done with low speed to prevent effervescent loss of pollutants. Twenty five alive fishes were collected from the first experiment and acclimatized for 6 days with proper food and well aerated condition. These 25 fishes also were used in the 2nd experiment. Of these 10 fishes were dead in the control one.

To interpret the data in terms of survival over infinite period of time is ecologically more significant. Green's method (1)(7) was used in present experiment. The basic assumption is that survival varies inversely with time of exposure. As time approaches zero, the TL_m should approach infinity ^{Stated} (put) another way, any organism can survive on infinitely high amplitude for an infinitely short time. On the other hand, as the exposure becomes longer, the TL_m should approach some low asymptotic ^t value. This relationship can be expressed by the equation for a straight line written in the form

$$TL_m = a + b (t^{-1})$$

where "t" is the time exposure, If the reciprocal of time (t^{-1}) approximate zero (as "t" approaches infinity) then "a" approximate TL_m .

Experimentally determined TL_m versus the reciprocal of time were plotted on graph paper. The x-axis was used for the time (t^{-1}) Fitted a line to these points (by the best fit or least square method). The point at which the line would intersect the y axis would represent the TL_m for an infinite period.

PROCEDURE

The method was described by a reference ~~table~~ of sample data (shown Table 2.2). The data for first five columns are self-explanatory. Ten test animals were exposed to each concentration of pollutants (Ecological complitude), and the number dead and alive in each group at the end of test period were recorded. The accumulated death and survivals were calculated as follows:

1. Accumulated deaths were found by adding all the deaths in column 4 from the top of the column to the particular amplitude under consideration. Thus were added all animals that were killed by that amount a loss of the pollutants.
2. Accumulated survivals were found by adding all survivals in column 5 from the bottom of the column to the particular amplitude under consideration. Thus were added all animals that could survive that amount of pollutant or more.

The TL_m or TL_{50} was interpolated from the per cent mortalities bracketed it. In the example of 3 hours, 49 per cent and 65 per cent bracket the 10g TL_m which was - 0.4474 (Derived from the straight line of two points; details as shown in calculation example of 3 hour Table 2.2. The $\log TL_m$ was used for convenience in subsequent calculations.

Each group should be selected a different exposure time (if possible on the basis of data) and calculated the TL_m for the time. The calculation of the standard error and confidence limits as follows:

$$\begin{aligned} \text{Standard error of } \log TL_m &= \sqrt{\frac{0.79 h R}{n}} \\ &= \text{S.E. of } \log TL_m \end{aligned}$$

where n = number of animals per test group i.e. ten

h = log interval between the doses i.e.

log of 5ml = - 0.3010.

R = Interquartile range (i.e. the range of toxicant concentration between $\log TL_{25}$ and $\log TL_{75}$)

If the TL_{25} or TL_{75} is not available from the data, the interquartile range can be estimated by either $2(\log TL_{50} - \log TL_{25})$ or $2(\log TL_{75} - \log TL_{50})$

Then standard error can be calculated.

$$\text{S.E. of } TL_m = TL_m (\log e 10 \times \text{S.E. of } \log TL_m)$$

(conversion factor: $\log e 10 = 2.30$)

The confidence limits can be calculated. 95% confidence

$$\text{limits} = \log TL_m \pm \text{S.E. } \log TL_m$$

Example of standard error of TL_m and 95% confidence limit of 3 hours exposure time as follows:

| Ecological amplitude | Log amplitude | percent mortality |
|----------------------|---------------|-------------------|
| 1.5 ml/l | 0.1761 | 13 |
| 2.0 ml/l | 0.3010 | 33 |
| 2.5 ml/l | 0.3979 | 49 |
| 3.0 ml/l | 0.4771 | 65 |

From the above figure it was assumed that 25% would lie between 13 p.c. and 33 p.c. similarly. 50% would be in between 49 p.c. and 65 p.c.

Therefore TL_{25} or TL_{50} could be calculated from a straight line:

$$Y = m x + c$$

(a) TL_{25}

$$33 = 0.3010 m + c$$

$$13 = 0.1761 m + c$$

$$20 = .1249 m$$

$$m = 160.1281$$

$$13 = 0.1761 \times 160.1281 + c$$

$$c = 15.1985$$

$$25 = 160.1281 \times x - 15.1985$$

$$TL_{25} = 0.2510$$

(b) Similarly TL_{50}

$$65 = .4771 m + c$$

$$49 = .3979 m + c$$

$$16 = .0792 m$$

$$m = 202.0202$$

$$c = 48.6162$$

$$TL_{50} = .0068$$

$$\text{Antilog} = 1.014$$

$$R = 2 (\log 50 - \log 25)$$

$$= - .4884$$

$$\text{S.E. of } \log TL_m = \sqrt{\frac{0.79 \times h \times R}{n}}$$

$$\text{WHERE } h = \log .5 = - .3010$$

$$R = -0.4884$$

$$\sqrt{\frac{0.79 \times -0.3010 \times -0.4884}{10}} \quad n = 10$$

$$= 0.1078$$

$$\text{S.E. of } TL_m = TL_m (\log e \times \text{S.E. of } \log TL_m)$$

$$(\text{conversion factor: } \log e 10 = 2.30)$$

$$= 1.014 \times 2.30 \times 0.1078$$

$$= 0.2514$$

$$95\% \text{ confidence limits} = \log TL_m \pm 1.96 \text{ S.E. } \log TL_m$$

$$= .0086 \pm 0.2112$$

CHAPTER 3

RESULTS

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TABLE 1.1

OBSERVED MORTALITY RATIO OF *Puntius phutunie* (Ham) ON TL_m
WITH REFERENCE TO ORIGINAL GAUHATI REFINERY EFFLUENT
SAMPLE

| Aquarium No. | Actual amount added in 10 litres of water | 4/7/78 | | 5/7/78 | | 6/7/78 | | 7/7/78 | | 8/7/78 | |
|--------------|---|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|
| | | No. | Ratio | No. | Ratio | No. | Ratio | No. | Ratio | No. | Ratio |
| 1. | Control | - | - | 3 | 3/10 | 3+1=4 | 4/10 | 4+4=5 | 5/10 | - | - |
| 2. | 1.0ml | 2 | 2/10 | 2+2=4 | 4/10 | 4+1=5 | 5/10 | 5+1=6 | 6/10 | - | - |
| 3. | 1.5ml | 2 | 2/10 | 2+1=3 | 3/10 | 3+2=5 | 5/10 | - | - | 5+1=6 | 6/10 |
| 4. | 2.0ml | - | - | 5 | 5/10 | - | - | - | - | - | - |
| 5. | 2.5ml | 1 | 1/10 | - | - | 1+1=2 | 2/10 | - | - | - | - |
| 6. | 3.0ml | 1 | 1/10 | - | - | 1+1=2 | 2/10 | - | - | - | - |
| 7. | 3.5ml | - | - | 1 | 1/10 | - | - | - | - | - | - |
| 8. | 4.0ml | - | - | - | - | 1 | 1/10 | - | - | - | - |
| 9. | 4.5ml | - | - | 1 | 1/10 | - | - | - | - | - | - |
| 10. | 5.0ml | - | - | 2 | 2/10 | - | - | 2+1=3 | 3/10 | 3+1=4 | 4/10 |
| 11. | 5.5ml | 1 | 1/10 | 1+2=3 | 3/10 | 3+4=7 | 7/10 | 7+2=9 | 9/10 | - | - |

TABLE 1.2
 SAMPLE TOLERANCE DATA FOR 4 HRS - REED AND MUENCH METHOD

| Ecological amplitude | Observed mortality | Deaths | Survivals | Accumulated | | | Mortality ratio | Percent mortality |
|----------------------|--------------------|--------|-----------|-------------|-------|-------|-----------------|-------------------|
| | | | | Death | Surv. | Total | | |
| 0 ml/10 | - | - | 10 | - | 104 | 104 | - | - |
| 1.0ml/10 | 2/10 | 2 | 8 | 2 | 94 | 96 | 2/94 | 2 |
| 1.5ml/10 | 2/10 | 2 | 8 | 4 | 86 | 90 | 4/90 | 4 |
| 2.0ml/10 | - | - | 10 | 4 | 78 | 82 | 4/82 | 4 |
| 2.5ml/10 | 1/10 | 1 | 9 | 5 | 68 | 73 | 5/68 | 7 |
| 3.0ml/10 | 1/10 | 1 | 9 | 6 | 59 | 65 | 6/65 | 9 |
| 3.5ml/10 | - | - | 10 | 6 | 50 | 56 | 6/56 | 10 |
| 4.0ml/10 | - | - | 10 | 6 | 40 | 46 | 6/40 | 15 |
| 4.5ml/10 | - | - | 10 | 6 | 30 | 36 | 6/36 | 16 |
| 5.0ml/10 | - | - | 10 | 6 | 20 | 26 | 6/26 | 23 |
| 5.5ml/10 | 1/10 | 1 | 10 | 7 | 10 | 17 | 7/17 | 41 |

TABLE 1.3
 SAMPLE TOLERANCE DATA FOR 24 HOURS - REED AND MUENCH METHOD

| Ecological Amplitude | Observed mortality | Deaths | Survivals | Accumulated | | | Mortality Ratio | Percent mortality |
|----------------------|--------------------|--------|-----------|-------------|-------|-------|-----------------|-------------------|
| | | | | Death | Surv. | Total | | |
| 0ml/10 | 3/10 | 3 | 7 | 3 | 38 | 61 | 3/58 | 5 |
| 1.0ml/10 | 4/10 | 4 | 6 | 7 | 51 | 58 | 7/58 | 12 |
| 1.5ml/10 | 3/10 | 3 | 7 | 10 | 45 | 55 | 10/45 | 22 |
| 2.0ml/10 | 5/10 | 5 | 5 | 15 | 38 | 43 | 15/38 | 39 |
| 2.5ml/10 | - | - | - | 15 | 33 | 48 | 15/48 | 31 |
| 3.0ml/10 | - | - | - | 15 | 33 | 48 | 15/48 | 31 |
| 3.5ml/10 | 1/10 | 1 | 9 | 16 | 33 | 49 | 16/49 | 32 |
| 4.0ml/10 | - | - | - | 16 | 24 | 40 | 16/40 | 40 |
| 4.5ml/10 | 1/10 | 1 | 9 | 17 | 24 | 41 | 17/41 | 41 |
| 5.0ml/10 | 2/10 | 2 | 8 | 19 | 15 | 34 | 19/34 | 55 |
| 5.5ml/10 | 3/10 | 3 | 7 | 22 | 7 | 29 | 22/29 | 75 |

TABLE 1.4
 SAMPLE TOLERANCE DATA FOR 48 HOURS - REED AND MUENCH METHOD

| Ecological amplitude | Observed mortality | Deaths | Survivals | Accumulated | | | Mortality Ratio | Percent mortality |
|----------------------|--------------------|--------|-----------|-------------|-------|-------|-----------------|-------------------|
| | | | | Death | Surv. | Total | | |
| 0ml/10 | 4/10 | 4 | 6 | 4 | 74 | 78 | 4/74 | 5 |
| 1.0ml/10 | 5/10 | 5 | 5 | 9 | 68 | 77 | 9/77 | 11 |
| 1.5ml/10 | 5/10 | 5 | 5 | 13 | 63 | 76 | 13/76 | 17 |
| 2.0ml/10 | - | - | - | 13 | 58 | 71 | 13/71 | 18 |
| 2.5ml/10 | 2/10 | 2 | 8 | 15 | 58 | 73 | 15/73 | 20 |
| 3.0ml/10 | 2/10 | 2 | 8 | 17 | 50 | 67 | 17/67 | 25 |
| 3.5ml/10 | - | - | 10 | 17 | 42 | 59 | 17/59 | 28 |
| 4.0ml/10 | 1/10 | 1 | 9 | 18 | 32 | 50 | 18/50 | 36 |
| 4.5ml/10 | - | - | 10 | 18 | 23 | 41 | 18/41 | 36 |
| 5.0ml/10 | - | - | 10 | 18 | 13 | 31 | 18/31 | 58 |
| 5.5ml/10 | 7/10 | 7 | 3 | 25 | 3 | 28 | 25/28 | 89 |

TABLE 1.5

SAMPLE TOLERANCE DATA FOR 72 HOURS- REED AND NUENCH METHOD

| Ecological amplitude | Observed mortality | Deaths | Survivals | Accumulated | | | Mortality Ratio | Percent mortality |
|-------------------------|-----------------------|--------|-----------|-------------|-------|-------|--------------------|----------------------|
| | | | | Death | Surv. | Total | | |
| 0ml/10 | 5/10 | 5 | 5 | 5 | 87 | 92 | 5/92 | 5 |
| 1.0ml/10 | 6/10 | 6 | 4 | 11 | 82 | 93 | 11/93 | 11 |
| 1.5ml/10 | - | - | 10 | 11 | 78 | 89 | 11/89 | 12 |
| 2.0ml/10 | - | - | 10 | 11 | 68 | 79 | 11/79 | 13 |
| 2.5ml/10 | - | - | 10 | 11 | 58 | 69 | 11/69 | 15 |
| 3.0ml/10 | - | - | 10 | 11 | 48 | 59 | 11/59 | 18 |
| 3.5ml/10 | - | - | 10 | 11 | 38 | 49 | 11/49 | 22 |
| 4.0ml/10 | - | - | 10 | 11 | 28 | 39 | 11/39 | 28 |
| 4.5ml/10 | - | - | 10 | 11 | 18 | 29 | 11/29 | 37 |
| 5.0ml/10 | 3/10 | 3 | 7 | 14 | 8 | 22 | 14/22 | 64 |
| 3.5ml/10 | 9/10 | 9 | 1 | 23 | 1 | 24 | 23/24 | 95 |

TABLE 1.6

SAMPLE TOLERANCE DATA FOR 96 HOURS - REED AND MUENCH METHOD

| Ecological amplitude | Observed mortality | deaths | Survivals | Accumulated | | | Mortality ratio | Percent mortality |
|----------------------|--------------------|--------|-----------|-------------|-------|-------|-----------------|-------------------|
| | | | | Deaths | Surv. | Total | | |
| 0ml/10 | - | - | 10 | - | 100 | 100 | - | - |
| 1.0ml/10 | - | - | 10 | - | 90 | 90 | - | - |
| 1.5ml/10 | 6/10 | 6 | 4 | 6 | 80 | 86 | 6/86 | 6 |
| 2.0ml/10 | - | - | 10 | 6 | 76 | 82 | 6/82 | 7 |
| 2.5ml/10 | - | - | 10 | 6 | 66 | 72 | 6/72 | 8 |
| 3.0ml/10 | - | - | 10 | 6 | 56 | 62 | 6/62 | 9 |
| 3.5ml/10 | - | - | 10 | 6 | 46 | 52 | 6/52 | 11 |
| 4.0ml/10 | - | - | 10 | 6 | 36 | 42 | 6/36 | 16 |
| 4.5ml/10 | - | - | 10 | 6 | 26 | 32 | 6/32 | 18 |
| 5.0ml/10 | 4/10 | 4 | 6 | 10 | 16 | 26 | 10/26 | 38 |
| 5.5ml/10 | - | - | 10 | 10 | 10 | 20 | 14/20 | 70 |

TABLE 2.2

SAMPLE TOLERANCE DATA FOR 3HRS- REED AND MUENCH METHOD

| Ecological amplitude | Log amplitude | Observed mortali- ty | Deaths | Survivals | Accumulated | | | Mortality ratio | Percent mortality |
|-------------------------|------------------|----------------------------|--------|-----------|-------------|-------|-------|--------------------|----------------------|
| | | | | | Death | Surv. | Total | | |
| 0ml/l | - | 0/10 | 0 | 10 | 0 | 58 | 58 | - | - |
| 0.5ml/l | -0.3010 | 0/10 | 0 | 10 | 0 | 48 | 48 | - | - |
| 1.0ml/l | 0 | 0/10 | 0 | 10 | 0 | 38 | 38 | - | - |
| 1.5ml/l | 0.1761 | 4/10 | 4 | 6 | 4 | 28 | 32 | 4/32 | 13 |
| 2.0ml/l | 0.3010 | 5/10 | 5 | 5 | 11 | 22 | 33 | 11/33 | 33 |
| 2.5ml/l | 0.3979 | 5/10 | 5 | 5 | 16 | 17 | 33 | 16/33 | 49 |
| 3.0ml/l | 0.4771 | 6/10 | 6 | 4 | 22 | 12 | 34 | 22/34 | 65 |
| 3.5ml/l | 0.5441 | 6/10 | 6 | 4 | 28 | 8 | 36 | 28/36 | 77 |
| 4.0ml/l | 0.6021 | 7/10 | 7 | 3 | 35 | 4 | 39 | 35/39 | 90 |
| 4.5ml/l | 0.6532 | 9/10 | 9 | 1 | 44 | 1 | 45 | 44/45 | 98 |
| 5.0ml/l | 0.6990 | 10/10 | 10 | 0 | 54 | 0 | 54 | 54/54 | 100 |

TABLE 2.3

SAMPLE TOLERANCE DATA FOR 24 HOURS - REED AND MUNCH METHOD

| Ecological amplitude | Log amplitude | Observed mortality | Deaths | Survivals | Accumulated | | | Mortality ratio | Percent mortality |
|-------------------------|------------------|-----------------------|--------|-----------|-------------|-------|-------|--------------------|----------------------|
| | | | | | Death | Surv. | Total | | |
| 0ml/l | - | 0/10 | 0 | 10 | 0 | 43 | 43 | - | - |
| 0.5ml/l | -0.3010 | 0/10 | 0 | 10 | 0 | 33 | 33 | - | - |
| 1.0ml/l | 0 | 1/10 | 1 | 9 | 1 | 23 | 24 | 1/4 | 4 |
| 1.5ml/l | 0.1761 | 5/10 | 5 | 5 | 6 | 14 | 20 | 6/20 | 30 |
| 2.0ml/l | 0.3010 | 6/10 | 6 | 4 | 12 | 9 | 21 | 12/21 | 57 |
| 2.5ml/l | 0.3979 | 7/10 | 7 | 3 | 19 | 5 | 24 | 19/24 | 71 |
| 3.0ml/l | 0.4771 | 9/10 | 9 | 1 | 28 | 2 | 30 | 28/30 | 93 |
| 3.5ml/l | 0.5441 | 9/10 | 9 | 1 | 37 | 1 | 38 | 37/38 | 98 |
| 4.0ml/l | 0.6021 | 10/10 | 10 | 0 | 47 | 0 | 47 | 47/47 | 100 |
| 4.5ml/l | 0.6532 | 10/10 | 10 | 0 | 57 | 0 | 57 | 57/57 | 100 |
| 5.0ml/l | 0.6990 | 10/10 | 10 | 0 | 67 | 0 | 67 | 67/67 | 100 |

TABLE 3

TOLERANCE LIMIT OF SELECTED FISH EXPOSED TO ORIGINAL EFFLUENT SAMPLE OF GAUHATI REFINERY THE TL₅₀ EXPRESS AS MULTIPLES AND FRACTIONS OF THE ORIGINAL EFFLUENT SAMPLE*

| Organism | TL ₅₀ values and acute toxicity range** | | | | |
|--------------------|--|---------|---------|---------|---------|
| | 4 Hrs | 24 Hrs | 48 Hrs | 72 Hrs | 96 Hrs |
| Puntius phutunie - | | 4.5-5.0 | 4.5-5.0 | 4.5-5.0 | 5.0-5.5 |

* The values were derived from the Table 1.1 to 1.6

** Values shown are the acute toxicity ranges
 TL = concentration in ml/l of original effluent sample at which 50% mortality occur.

TABLE 4

TOLERANCE LIMIT OF SELECTED FISH EXPOSED TO
 MODIFIED EFFLUENT SAMPLE (MES) OF GAUHATI
 REFINERY THE TL₅₀ DATA EXPRESSED AS MULTIPLES
 AND FRACTIONS OF MES SHOWN IN TABLE I*.

| Organism | TL 50 values and acute toxicity range ** | | | | |
|---------------------|--|----------|----------|----------|---------|
| | 3Hrs | 24 Hrs | 48Hrs | 72 Hrs | 96 Hrs |
| Puntius phutunie | 2.5-3.0 | 1.5-2.0 | 1.0-1.5 | 1.0-1.5 | 0.5-1.0 |
| | | 1.852*** | 1.304*** | 1.031*** | 0.6805 |

* Values were derived from the table 2.1 to 2.6

** Values shown are the acute toxicity range

TL = concentration in ml/l of MES at 50%
 mortality occurs.

***Actual value of TL₅₀ calculated by Reed and Muehch Method

RESULT

OBSERVED PHYSIOLOGICAL BEHAVIOUR:

When groups of ten fishes were transferred into different containers having different modified effluent sample concentrations, the fish showed remarkable changes in their ^{er} behaviour. The effects were counted by erratic swimming, difficulty in respiration and convulsions of the test fish prior to death. The rapid jerking movement of the body and ^f fins were easily observable. Disorder of central nervous system was observed when the fishes in the lethal concentrations (3.0 ml to 5.0 ml) lost the sense of equilibrium and turned with the belly upward and finally falling to the bottom and dying. Excessive secretion of the mucus by the fishes was also observed when they were introduced in the test solution. The fishes repeatedly came to the surface to avoid the toxic environment and for gulping the atmospheric air directly. The air ^{??} bubbles were visible to come from the mouth of the fishes. ^{= d} Shedding of the scales was also observed.

In ~~lower~~ concentrations (i.e. original effluent sample-OES) all the above mentioned effects were visible but to a lesser extent. Increase opercular movements were observed in the lower concentrations of pollutant mixture (i.e. OES).

However in the control experiments mortality of fishes was observed (i.e. in the first expt.=50% and in the second expt.=10%) the rest of the fishes showed normal behaviour in respiration and in opercular movement throughout.

TL₅₀ and acute toxic range:

In the present work the acute toxic range of *puntius phutunie* for each of original effluent sample and modified effluent sample at different concentration and different time intervals had been worked out and the value so obtained were shown in table 3 and table 4. The harmless concentration (i.e. 26ml/l of MES) was calculated from Fig. 2 which was drawn from table 5.

TABLE 5

DATA ESTIMATED FOR TL FOR INDEFINITE PERIOD OF TIME WITH MODIFIED EFFLUENT SAMPLE

| Exposure Period | Inversion of time (t^{-1}) | 95% Confidence Limits = $\text{Log TL}_m \pm 1.96 \text{ S.E. of } \text{Log TL}_m$ | Actual TL_m ml/l | Standard error |
|-----------------|--------------------------------|---|---------------------------|----------------|
| 24 Hrs | 0.0416 | 0.2678 ₊ -0.2632 | 1.852 | -1.3447 |
| 48 Hrs | 0.0208 | 0.1152 ₊ -0.2032 | 1.304 | -3.1037 |
| 72 Hrs | 0.0138 | 0.0135 ₊ -0.2303 | 1.031 | -0.2786 |
| 96 Hrs | 0.0104 | -0.1672 ₊ -0.0545 | 0.6805 | -1.8436 |

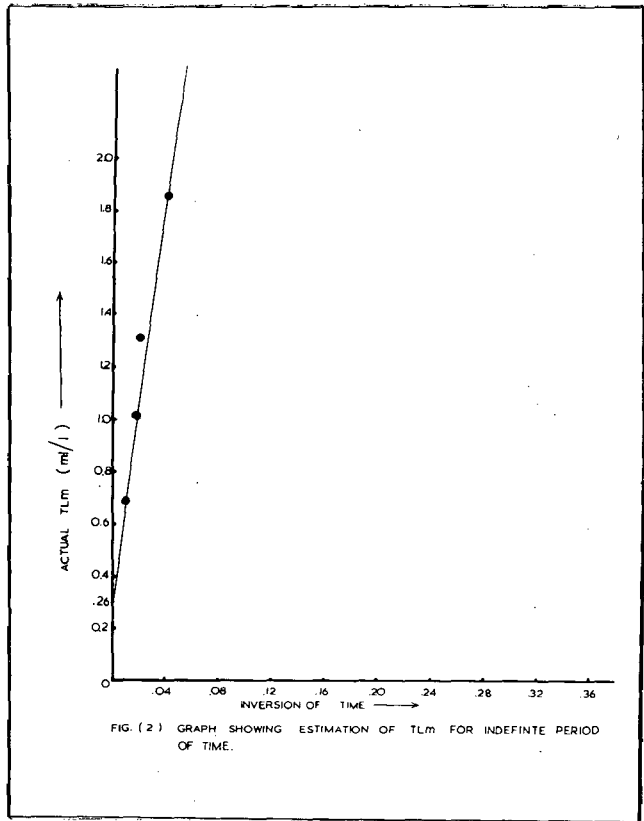


FIG. (2) GRAPH SHOWING ESTIMATION OF TLM FOR INDEFINITE PERIOD OF TIME.

CHAPTER 4
DISCUSSION

In ^{the} present work an attempt has been made to determine the TL_m and harmless concentration of Gauhati Refinery effluent and for a fish species existing Brahmaputra river, Puntius phutunie (Ham) using Reed-Muench Bioassay method. The time interval selected for this study was 3 to 4 hours, 24 hrs., 48 hrs., 72 hrs, 96 hrs. Several changes in the physical behaviour if the fish were observed during experimental period, such as fast jerky movements, increased opercular movement, erratic swimming and difficulty in respiration. Similar changes in behaviour were observed by Verma et al (4) in Labeo rohita both at lethal and sub-lethal aqueous concentrations of a few biocides (viz., chlorodane, Ekalau, Ekatin, Sumithion). Aderson (1968) (4) reported similar behaviour in brook trout, Salvelinus fontinalis due to the influence of sub-lethal concentrations of DDT on lateral line.

From the experimental observation of original effluent sample, the range of TL_{50} for 24 hours, 48 hours and 72 hours were same i.e., 4.5 ml to 5.0 ml and whose dilution factor was 1:2222 to 1:2000, similarly for 96 hours was 5.0 ml to 5.5 ml and its dilution factor 1:2000 to 1:1811. The observed negative result in the first expt. may be due to (1) chemical changes occurred in the sample for 5 days storage period; (2) dilution of original effluent sample; (3) non-acclimatization of experimental fish; (4) high temperature shock

(5) excess of $\text{Na}_2\text{S}_2\text{O}_3$, $5\text{H}_2\text{O}$ addition for chlorine removal;

(6) High saturation of oxygen in experimental water. It was supposed that these were the causes of failure of first experiment. But positive result was observed with modified effluent sample (being prepared for the study of the effect raw effluent) i.e. the TL_m concentration $(c) \propto \frac{1}{\text{Time}(t)}$. The range of TL_m of modified effluent sample (MES) for 3 hrs., 24 hrs., 48 hrs., 72 hrs., 96 hrs. were 2.5 ml/l to 3.0ml/l, 1.5ml/l to 2.0ml/l; 1.0ml/l to 1.5ml/l, 1.0ml/l to 1.5ml/l; 0.5ml/l to 1.0ml/l, and whose dilution factors were 1:400 to 1:333.3; 1:666.2 to 1:500; 1:1000 to 1:666.6, 1:1000 to 1:666.6; 1:5000 to 1:1000 respectively. It may be because of nondegradation of freshly prepared modified effluent sample (when oxygen supply was 4 hrs/day). The range of lethal dose was 3.0 ml/l to above and the range of sublethal dose 0.5 ml/l to 3.0ml/l. All these effects were observed after addition of phenols, oil and grease and sulphide (organic) into degraded original samples. Thus it can be said that phenol, oil and grease and sulphide are toxic to the fish groups. The harmless concentration was 0.26 ml/l (i.e. dilution factor 1:38462). It was clear from the Table 5 that the harmless concentration or safe concentration was a fraction of TL_m values. If, however, ecologists are willing to assume, that such a fraction of the TL_m would provide an adequate production for this species or other species in nature the value worked out in the present investigation as permissible harmless concentration for the Gauhati refinery effluent, is of great practical utility for regulating and controlling the pollution in the water body by this effluent.

CHAPTER 5

SUMMARY

Reed and Muench Bioassay method was employed to study the synergistic effect of Gauhati Refinery original effluent taking *Puntius phutunie* as test fish. The failure of the first experiment was due to high temperature, storing of sample, and dilution of it, non-acclimatization of fish. Second experiment has proved that phenols, organic sulphides, oil and grease are toxic to fish. The TL_m of modified effluent sample for 3 hrs. 24 hrs, 48 hrs. , 72 hrs and 96 hrs. were 1.014ml/l, 1.852 ml/l 1.304ml/l, 1.031ml/l and 0.6805ml/l respectively. Similarly the harmless concentration is 0.26ml/l estimated by adopting Green method.

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