FOREWORD

In the present scenario, due to Industrialization & Urbanization have mainly contributed to the economic growth of the developing nations like India to cater the needs of the population. Production and productivity has been given importance for economic growth of the nation which has exerted tremendous pressure on the environment, on all its wings - air, water, and land. But the pressure should not be so high that it will break the resilience capacity of the environment. Water environment is the most affected and exploited among all the environments.

While granting environmental clearance keeping above reasons in mind & to regulate the load & keep the resilience capacity under control Union Government has framed some environmental Acts & Rules. Ministry of Environment & Forests lays down certain conditions for compliance at the time of granting the environmental clearances for the projects. Ministry of Environment & Forest vide their environmental clearance no 11011/ 17/ 86- IA- II dt. 23.7.1990 for Phase – II expansion has directed PPL to comply to 22 no's of specific conditions incorporated in the environmental Clearance and out of 22 nos. of specific conditions **"Routine toxicity bio -assay based on the effluent with fish and fish food organisms must be carried out at least once in a year".**

As a renowned & responsible corporate house M/s PPL knowhow to execute their responsibility towards the society & environment. In order to fulfill the commitment towards the conservation of environment & aquatic resources, M/s PPL have decided to carry out the Bio-Assay Toxicity Study. Accordingly M/s PPL entrusted M/s SIMA LABS PVT. LTD., NEW DELHI A NABL accredited lab an empanelled from MoEF to carry out the test. M/s SIMA Labs Pvt. Ltd. have deputed their technical & scientific team for conducting the study from 26th December to 28th December 2017. The study was carried out as per standard methods and practices and we are sure, the findings of the study incorporated in this report will undoubtedly help PPL in augmenting their planning for treatment of effluent, its monitoring, disposal and its management.

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PROJECT PERSONNEL

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SAMPLING TEAM
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1. Introduction:

Paradeep Phosphates Limited an OHSAS:18001, ISO 14001:2004 and ISO 9001:2008 certified company, situated at Paradeep in Jagatsingpur District of Odisha and was established in 1982 to manufacture 2400 TPD Di-ammonium Phosphate (DAP) consisting of four streams each of 600 TPD capacity under phase-I programme. The commercial production started in the year 1986. The fertilizer complex is using imported Sulphur and Rock phosphate to produce Phosphoric acid. The captive production of Phosphoric acid partly caters the requirement for production of DAP through 4 streams of DAP/ NPK. Remaining requirement of Phosphoric acid is met through imports. The requirement of Ammonia is through imports. Phase II plants comprising of a 750 TPD Phosphoric Acid Plant (PAP), 2 x 1000 MTPD Sulfuric Acid Plant (SAP) and a 2 x 16 MW Captive Power Plant (CPP) were commissioned in 1992. Subsequently in the year 2010 the capacity of DAP plant, SAP and PAP was enhanced to 5000TPD,2400TPD and 1400TPD respectively after getting the environmental clearance from MoEF, New Delhi. In January,2016 SAP-C stream of capacity 2000MTPD and byproduct power generation of 23 MW was commissioned. Besides, M/s PPL has developed a product Zypmite which is a mixture of Phospho gypsum and basic slag byproduct of steel industry. The project was set up during the year 2010 with a capacity of 240TPD and commissioned in the year 2012.The basic raw materials are Rock Phosphates, Sulphur and Ammonia are imported and Phosphoric acid & Sulphuric Acid are manufactured indigenously.

Although, the entire DAP manufacturing plant along with SAP and PAP has been conceived on zero effluent concept; occasional overflows, leakages and floor washings come out of the plant battery limits as effluent that needs proper treatment before its final discharge. The plant to its credit has a well built modern Effluent Treatment Plant (ETP) in which the effluent is being treated and then recycled to ball mill in PAP or released out in the event of stoppage of PAP and conforming to the prescribed norms of Odisha State Pollution Control Board. At the behest of PPL, M/s SIMA Labs, New Delhi carried out in-situ toxicity tests at various points of the water streams. The Bio-assay test was carried out in December, 2017 with fresh water fishes locally available and with fishes from the Atharbanki river and local pond. Range finding Bio-assay (RFB), Static Bio-assay and In-situ Bio-assay was carried out at guard pond. In-situ Bio-assay study was not covered the storm water drains as both storm drains (1. storm water drain near zero point 2. storm water drain near Time office) are having zero discharge.

1.2Project Setting

Paradeep Phosphates Limited is located in Kujang Tehsil of Jagatsingpur District. The project site is situated at 200 16’ 45.54” North latitude and 860 38’ 43.7” East longitude and about 50 km from the Jagatsingpur town. On the East of PPL, Paradeep port is situated.

This site is situated in a remote area on the coast of Bay of Bengal and is mainly low lying area with a few creeks, sand dunes subjected to submersion of high tides. Paradeep Phosphates Limited is spreaded over on an area of about 915 hectares with Phosphatic fertilizer complex, township and gypsum storage ponds. It is one of the largest complex fertilizer plants in the country and produces Di-Ammonium Phosphate, NPK fertilizers as its final product with intermediate products like Sulfuric acid and Phosphoric acid. Mahanadi River is flowing at a distance of about 5 km from the project site and meets Bay of Bengal which is about 3 km away from the site. Atharbanki River is flowing along the boundary wall of the site and is between Paradeep port and plant site. Study area of the project site is shown in **Fig. 1.1**. The mean sea level of the site is 0.6m to 3 m. Paradeep area is very much prone to frequent and severe cyclonic storms and very windy during most of the times of the year. The average annual rainfall is 1500 mm most of which falls during June to September. Paradeep weather is highly humid due to the influence of the sea. The mean relative humidity varies from 75% to 85% and the average wind speed varies from 12 to 70 Kmph. The maximum temperature goes upto 40^0C in summer while the minimum temperature is around 12^0C in winter season. Seismically Paradeep lies in Zone III with an expected seismic intensity of VII on the modified Mercalle scale 1931, corresponding to horizontal seismic ground acceleration range of 18-140 cm/sec depending upon the ground conditions.

ETP PLANT

Study Area - Fig 1.1

Plant at Glance

1.3 Utilities

The other offsite and support facilities include 5 x 10,000 MT atmospheric Ammonia storage tanks, 6 x 10,000 MT Phosphoric acid storage tank, 3 x 10,000 and 6000 MT Sulphuric acid storage tank as well as 2 x 1500 MT fuel oil tanks, bagging facilities and silos. The imported Ammonia and Phosphoric acid are pumped through pipeline from fertilizer berth of Paradeep port to storage tank. The water requirement for entire plant and colony are met from Taldanda canal, which runs from the Mahanadi barrage from Jobra of Cuttack city. The canal is situated at a distance of 4km from PPL.

The existing 3 x 120 MT/hr demineralization plant (DM plant) is sufficient to meet requirement of CPP and Sulphuric acid plant. Out of total demand of 25.5 MW power, 13.5 MW is supplied by Odisha State Electricity Board (OSEB) and remaining 12 MW is from captive generation from the by-product steam available from Sulphuric acid plant. In case of total power failure, the backup HT power is supplied through 5 MVA DGset and LT power through two numbers of 1 KVA DG sets.

Plant inside view

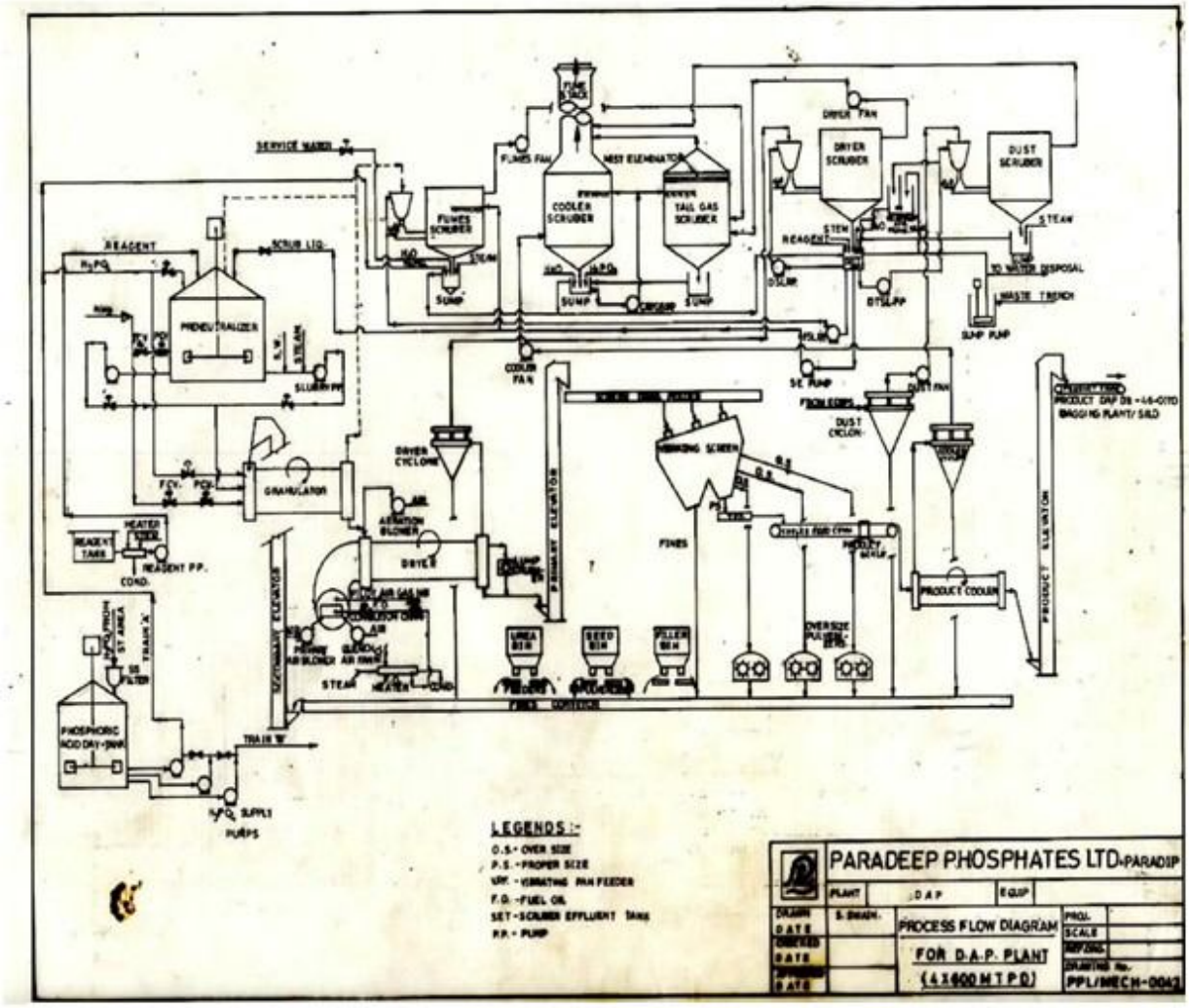
1.4 Brief Description of Manufacturing Process

1.4.1 Di-ammonium Phosphate Plant

The existing 5000 TPD DAP plant consist of four streams each of 1250 TPD capacity. The process is based on indigenous knowhow and M/s. Hindustan Dorr-Oliver Limited are the main engineering consultants for the DAP plant. The main raw materials used for production of DAP/NPK are Phosphoric acid, Ammonia, Sulphuric acid, MOP and filler. Phosphoric acid and Ammonia are pumped from storage tanks to preneutralizer where they react with each other to a mole ratio of 1.45 and a slurry of DAP and Mono ammonium Phosphate (MAP) are formed with about 80% solids. This slurry is again pumped to a rotary granulator where it is further ammoniated to convert MAP portion to DAP with a mole ratio of 1.7 to 1.8. Wet DAP granules are then dried up by a counter current stream of hot air in a rotary dryer. The dried up granules are screened for size separation in a double-deck vibrating screen. The fines and crushed over size fraction of DAP is recycled back to granulator and the proper size material is cooled in a product cooler. The cooled product is conveyed either to product silo (75000 MT capacity) for storage or to bagging plant for dispatch. The flow diagram of the process is shown in **Fig. 1.2**.

Plant inside view

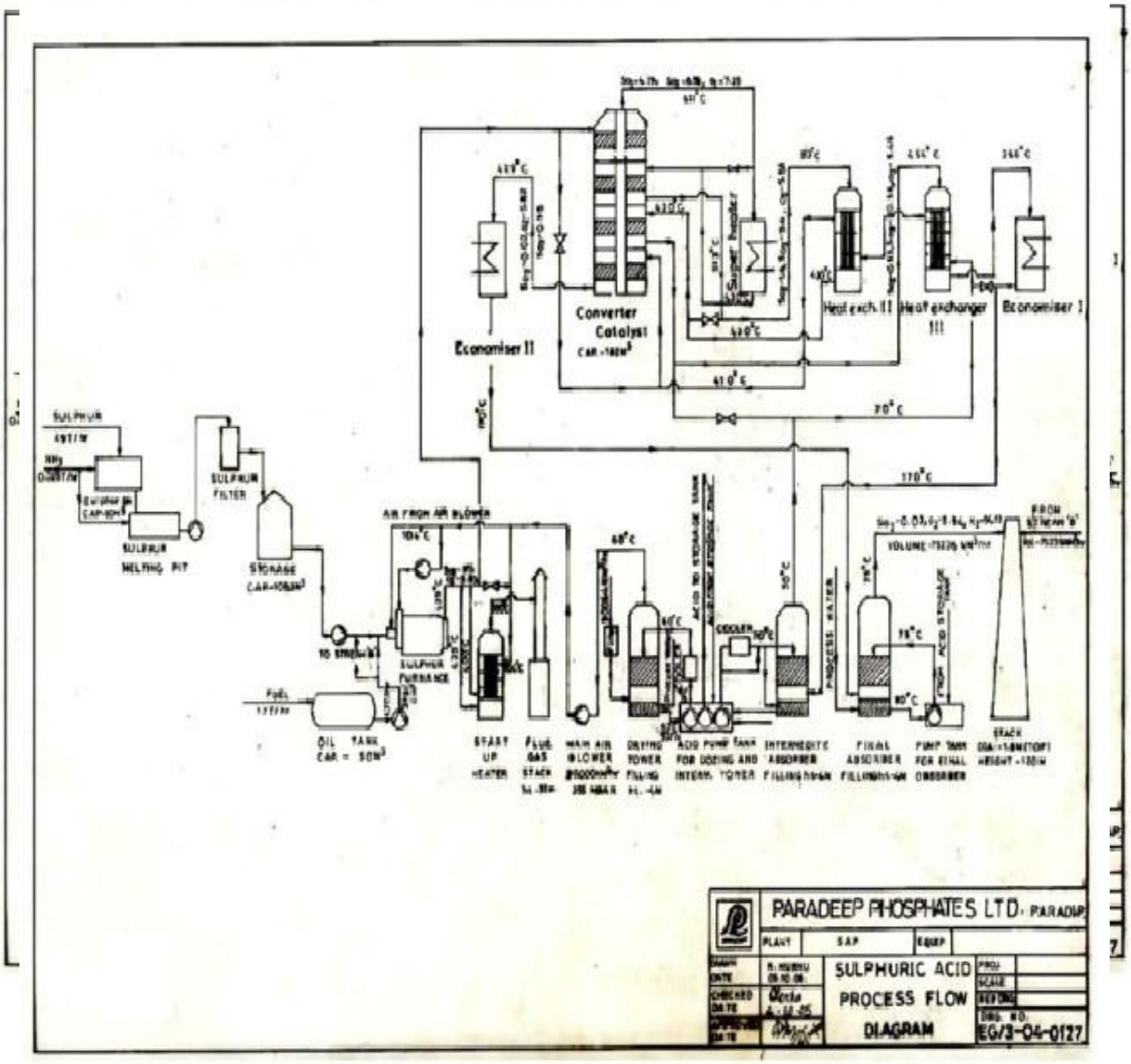
MANUFACTURING PROCESS FLOW DIAGRAM OF DAP PLANT



1.4.2 Sulphuric Acid Plant

Sulphuric acid plant consists of two streams, each of 1200 TPD capacity and one stream of 2000 MTPD . The plant is based on most modern Double Contact Double Absorption (DCDA) process. The engineering consultants were M/s. Lurgi Gmbh of Germany along with M/s. FACT Engineering and Design Organization (FEDO) as Indian Associate. The raw material for the Sulphuric acid plant is elemental sulphur which is imported and is transported to the Sulphur Silo. Sulphur is melted in a melting pit by means of heating coils fed with steam. The molten Sulphur is fed to the Sulphur burner where complete combustion of Sulphur takes place giving rise to SO2 The heat of combustion is withdrawn by means of a waste heat boiler where saturated steam of approximately 46 bar is generated. The gas, cooled to a temperature of 4200C, is fed to a converter having 4 catalyst beds. The final gas of 4th catalyst bed, after getting cooled to a temperature of 1700C in an economizer, enters the final absorber where the SO3 is absorbed by 98.5% sulphuric acid. The remaining gas from the absorber passes through high efficiency filters located in the upper section of the absorber to eliminate spray acid mist. The acid concentration in both the intermediate and final absorber is maintained by the addition of process water. The flow diagram of sulphuric acid process is shown in **Fig. 1.3**.

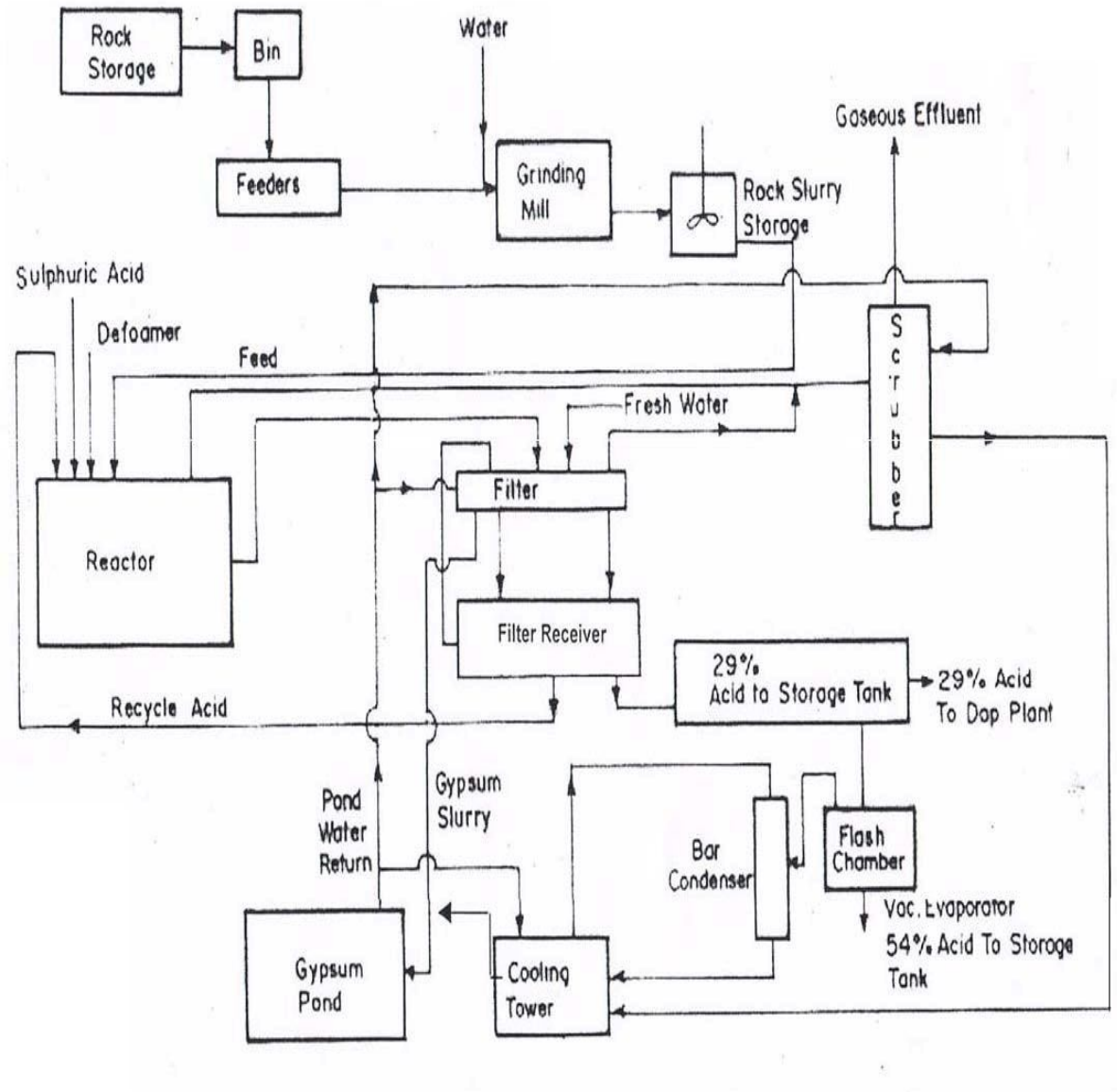
MANUFACTURING PROCESS FLOW DIAGRAM OF SULPHURIC ACID PLANT



1.4.3 Phosphoric Acid Plant

The 1400 TPD single stream Phosphoric acid plant is based on foreign knowhow. The engineering consultants are M/s. Jacobs International Inc. of Florida USA along with M/s. Hindustan Dorr- Oliver Ltd., Bombay as Indian counterpart. Rock phosphate is fed to a ball mill by an extractor weigher and wet grinding slurry of 65-75% solids is prepared. The slurry is fed to a reactor where Sulphuric acid with 70- 80% concentration and recycle Phosphoric acid is added. The reactor slurry proceeds through the reactor sections and under flows into the vacuum cooler feed compartment and from where the slurry is pumped to vacuum cooler where degassing takes place. Defoamer is added to the reactor to inhibit the formation of froth/foam. The slurry from vacuum cooler is pumped to a filter where Phosphoric acid is separated from gypsum. The cake in the filter is given four successive washings by filtrates of 12% P2O5, 5% P2O5, heated pond water and a final wash respectively. The dewatered cake is removed after final wash, then the cake is made slurry and pumped to the Gypsum pond. The Phosphoric acid plant has a provision of concentration unit of capacity 300 MT/day for concentrating 29% dilute acid to 52% with the use of evaporators. Normally 54% imported acid will be blended with 29% acid for direct use in DAP plant. The flow diagram of Phosphoric acid process is shown in **Fig1.5.**

FLOW DIAGRAM OF PHOSPHORIC ACID PLANT



The layout plan of the Phosphoric Fertilizer Complex is depicted in **Fig.1.5**.

2. SAMPLING POINTS

All the effluents from Sulphuric Acid Plant, Port Operation & Off-sites are diverted to ETP where the effluent is being treated scientifically as per the process requirement & to meet the prescribed standards. As the treated effluent passes through the guard pond, Bio-assay test was considered to be best suited in the **"Guard pond at the Discharge of ETP (Location 1, as L1)"**. The other two discharge points of the plant are "**Inside the Storm Water Drain at Near Time Office (Location 2, as L2)**" and "**Inside the Storm Water Drain at Near Zero Point (Location 3, as L3)**" running in front of ETP & Time office and the other running at the eastern side of the plant near Zero Point. These two points were found zero discharge. Samples were collected from the pre-determined points and analyzed for physico- chemical parameters in **SIMA Labs Pvt. Ltd.** to monitor the water quality during observation period. The analysis results are given in table – 2.

3. IMPACT OF STUDIES

Three types of investigations were made to evaluate the toxic conditions.

3.1 Range of Bioassay

To find out the concentration at which fish mortality occur, Range Finding Bio-assay (RFB) was carried out in the effluents samples supplied by PPL officials on **13.05.216** The Range finding Bioassay results are presented in **Table-I** for **guard pond (L1)** using fresh water fishes and estuarine fishes available in Atharbanki creek.

Cage for Bio-assay study

Status during study period

Table –1

Bioassay Test Result for Sample Location L1, L2 & L3.

Time Period of Testing (Hrs)	Location Identification			
	L1		**L2**	**L3**
	Nos. Of Dead Fish	**%** of Dead Fish		
6	-	-	**These two points were found zero discharge.**	
12	-	-		
24	-	-		
48	-	-		
72	-	-		
96	6	6		

Table -2

Physico-chemical parameters of effluents taken for Bioassay:

Sl. No.	Parameters		Unit	Location Identification			Limits
				L1	**L2**	**L3**	
1	PHYSI	pH		8.42	**These two points were found zero discharge.**		6.5-8.5
		Conductivity	µS/cm	489			
		Total Dissolve Solids	mg/l	327			
		Total Suspended Solids	Mg/l	12			100
		Turbidity	NTU	7.8			
2	INOR	Total Hardness as $CaCO_3$	mg/l	151			
		Chloride as Cl	mg/l	24			
		Fluoride as F	mg/l	1.4			2.0
		Sulphate as SO_4	mg/l	87			
		Total Alkalinity as $CaCO_3$	mg/l	54			
3	NUTRIENT, DEMAND,	Ammoniacal Nitrogen as N	mg/l	2.1			50
		Nitrate as NO_3	mg/l	3.9			10
		Nitrite as NO_2	mg/l	1.3			
		Phosphate as P	mg/l	0.10			5
		Dissolve Oxygen	mg/l	5.6			
		Chemical Oxygen Demand	mg/l	18			250
		Biochemical Oxygen Demand	mg/l	<5			30
		Organic Matter	mg/l	36			
4	HEAVY-M	Iron as Fe	mg/l	Not Detectable			3.0
		Zinc as Zn	mg/l	0.3			
		Total Chromium as Cr	mg/l	Not Detectable			2.0

3.2 In-situ Bio-assay Toxicity Test

In-situ toxicity tests were carried out in pre-fabricated stainless steel cages (70 cm x 40 cm x 40 cm) provided with inside lining of 2 mm nylon mesh. The cages were allowed to dip into the channel by suspending them from the sides with the help of two nylon ropes. Three points of observations, First(L1) in the Guard pond at the discharge of ETP selected for detailed study from 26.12.2017 to 28.12.2017.

Cage for Bio-assay study

The tests were carried out at the above points with test species collected from Atharbanki Creek & Shyamkoti Creek and fresh water ponds. After proper conditioning observation on fish mortality were recorded at six hourly intervals with fresh water fishes and common fishes. The observations on fish mortality are presented below. 50 numbers of fresh water fish species and estuarine species were kept in the cages for observations on mortality. These tests were carried out on 3 species of freshwater fishes and 5 estuarine species and one prawn species. The test fishes were collected from local ponds (fresh water fish) and Atharbanki River (Estuarine fish). The following fish species were selected for the *in-situ* toxicity tests.

Table-3
Aquatic Species Distribution

Sl. No.	Species	L1	L2	L3
1	Kau	08	**These two points were found zero discharge.**	
2	Kerandi	15		
3	Balia	10		
4	Prawn	10		
5	Baliguri	12		
6	Bombite	08		
7	Khasuli	15		
8	Gong Tengra	08		
Total		86		

Table-4
LT50 / LT100

Sl. No.	Fish Species	L1		L2	L3
		LT50	**LT100**	**These two points were found zero discharge.**	
1	Bombite	90 hr	96 hr		
2	Kerandi	90 hr	96 hr		
3	Khasuli	96 hr	96 hr		
4	Prawn	90 hr	96 hr		
5	Baliguri	96 hr	96 hr		
6	Balia	96 hr	96 hr		
7	Gong-Tengra	96 hr	96 hr		
8	Kau	90 hr	96 hr		

Note: LT 50 & LT 100:- Time at which 50% and 100% mortality occurs.

The results suggest that the treated effluent in Guard pond and the untreated water in storm water drains do not show any perceptible toxic effect on fish species mentioned above available in the creek.

OXYGEN BALANCE IN THE EFFLUENT
Table – 5
DISSOLVE OXYGEN CONTENT IN WASTE WATER

Date	DO in mg / l			
	L1		L2	L3
	Day	Night		
13.05.2016	6.2	6.4	**These two points were found zero discharge.**	
14.05.2016	5.8	6.1		
15.05.2016	6.3	6.0		
16.05.2016	5.6	5.8		

The variations in the concentration of dissolved oxygen in the storm water drains and the guard pond during morning hours and evening hours do not indicate any anoxic conditions. Four days observations on dissolved oxygen at point L1 is given above.

3.3 Static Bio-assay

Static Bio-assay tests were carried out with the water from the guard pond; storm water drains in three nos. of Aquarium of 20 liters capacity. Local fish species were taken for the test. Samples were collected from the three points L1 mentioned above and 10 nos. of each species were kept. The studies reveal that under static conditions the water does not have any effect on fresh water fishes as shown in the **Table – 6**

Table-6
LT50 / LT100

Sl.No.	Fish Species	L1		L2	L3
		LT50	LT100		
1	Kau	90 hr	96 hr	These two points were found zero discharge.	
2	Kerandi	96 hr	90 hr		
3	Balia	96 hr	96 hr		
4	Prawn	96 hr	90 hr		
5	Baliguri	96 hr	96 hr		
6	Bombite	96 hr	96 hr		
7	Khasuli	96 hr	96 hr		
8	Gong Tengra	96 hr	96 hr		

Cage for Bio-assay study

Table-7

Analysis of waste water sample collected on 28.12.2017

Sl. No.	Parameters		Unit	Location Identification			Limits
				L1	L2	L3	
1	PHYS	Ph		8.3	These two points were found zero discharge.		6.5-8.5
		Conductivity	µS/cm	511			
		Total Dissolve Solids	mg/l	346			
		Total Suspended Solids	Mg/l	14			100
		Turbidity	NTU	7.9			
2	INOR	Total Hardness as $CaCO_3$	mg/l	157			
		Chloride as Cl	mg/l	26			
		Fluoride as F	mg/l	1.9			2.0
		Sulphate as SO_4	mg/l	91			
		Total Alkalinity as $CaCO_3$	mg/l	63			
3	NUTRIENT, DEMAND,	Ammoniacal Nitrogen as N	mg/l	3.6			50
		Nitrate as NO_2	mg/l	4.6			10
		Nitrite as NO_3	mg/l	1.1			
		Phosphate as P	mg/l	0.07			5
		Dissolve Oxygen	mg/l	5.6			
		Chemical Oxygen Demand	mg/l	13			250
		Biochemical Oxygen Demand	mg/l	<5			30
		Organic Matter	mg/l	27			
4	HEAVY, M	Iron as Fe	mg/l	Not Detectable			3.0
		Zinc as Zn	mg/l	0.2			
		Total Chromium as Cr	mg/l	Not Detectable			2.0

4.0 FISH FAUNA IN ATHARBANKI & SHYAMAKOTI CREEK

Fishing is generally carried out in the adjoining Atharbanki & Shyamkoti Creek during the morning and evening hours. The species encountered in the creek, as ascertained from the local fisherman are given in Table – 8.

Table-8
Mass Distribution amongst the Available Species
Estuarine Fish / Saline
Fish

Local Name	Scientific Name	Approx. Size Of Catch
Bombite	*Cristis pectinata*	30-50gm
Kau	*Anabas festitues*	50-100 gm
Gong Tengra	*Gogata sp*	20-30gm
Kerandi	*Puntius conctonius*	05-10gm
Baliguri	*Glossogobious giuris*	10-30gm
Balia	*Wallago attu*	20-50gm
Bagda Chingudi	*Panaeus monodon*	05-10gm
Khasuli	*Colisa fasciata*	20-30gm

5.0 INFERENCE

The Bio-assay study carried out in the Guard pond reflects that the different parameters of treated effluent were within the prescribed limits and have no toxic effect on the fish. The surrounding low lying area to which the treated effluent is discharged in the event of stoppage of Phosphoric Acid Plant has a flush green area with presence of a variety of birds species indicates the state of environment itself. Bio-assay study is not carried out in both the storm water drains as both are found zero discharge.

6.0 ACKNOWLEDGEMENT

M/s SIMA Labs Pvt. Ltd., New Delhi express its deep gratitude to M/s. Paradeep Phosphates Limited for keeping faith on us & again entrusting the assignment for carrying out the Bio-Assay Toxicity Study. We thank Shri Pranab Bhattacharyya, Factory Manager; Mr. Ambikesh Kumar Mishra DGM(Env Mgt) Dr. Kedarnath Patnaik, Manger (Env. Mgt.) and Mr. Narayan Sahoo, Deputy Manager (Env. Mgt) for their wholehearted cooperation during the Study Period. The cooperation and hospitality extended by the other officials and staff of Paradeep Phosphates Limited is also gratefully acknowledged.