DETERMINATION OF THE TOXICITY OF PAPER MILL EFFLUENTS

by

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I. INTRODUCTION

Pulp and paper production is a major industry in India, with a total capacity of over 3 million tonnes per annum. (CPCB, 2001). Large mills, with a capacity of over 10,000 TPA, produce just over half of this amount. The rest is produced by smaller mills, of which there are some 300 around the country.

In the paper making process, raw materials such as wood, bamboo, reeds, grasses, straw and bagasse are mechanically and chemically pulped by cooking in a mixture of water, caustic soda, sodium sulphate and sodium carbonate. The pulp is then bleached using chlorine or similar oxidising agents. The bleached pulp is then blown on to rotary driers, after which the paper is rolled out and cut to size.

Wastewaters from the pulping process, known as "black liquors", will usually contain high concentrations of lignin, and sodium hydroxide. Most paper mills with large capacities will have facilities for collecting and recovering "black liquor"; however, leaks, spills and operational failures may occur and release the wastewaters into the effluent channel.

Wastewaters from the bleaching process will contain sodium hydroxides, lignin and chlorinated lignin, and other chlorinated compounds. The wastewaters are not recycled and are released as effluent.

From the point of view of toxicity towards living organisms, the following are of concern:

- Mercury
- Chlorinated lignins and their derivatives.
- Chlorides
- Suspended solids.

Mercury is used in the production of caustic soda, which is used heavily in the pulping and bleaching processes. Mercury concentrations in caustic soda can be as high as 22 grams per tonne of caustic soda produced, according to the CPCB's Comprehensive Industry Document; Chlor – Alkali Industry (1982). For a large paper mill, the concentration of mercury in the wastewater could theoretically be as high as 0.015 mg per litre. This is a level that has been quoted as being toxic to fish (Klein, 1957). Heavy metals such as mercury are toxic to fish because they cause a build up of mucous on the gills, preventing the uptake of oxygen.

Chlorinated organics are of concern: as they constitute a huge array of substances, little is known about their toxic effects. Lignins are natural polymers in plants and have various chemical structures. The breaking down and chlorination of lignin in the pulping and bleaching processes complicates matters further: the toxicity of different chlorinated lignins will vary.

The chlorinated organic substances released in effluents by paper mills can be separated by their size: large particles such as lignin with low toxicity, and smaller particles such as chlorinated phenols with higher toxicity. Studies have shown that fish can tolerate phenols up to

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1 or 2 mg/L, yet they are generally not found in waters containing over 0.2 mg/L of phenol (Klein, 1957). Phenols also have some inhibitive effects on the growth of rice seedlings: Ayyamperumal *et al* (1968) extracted phenolic substances from rice shoots that acted as natural growth inhibitors. Trace concentrations of highly toxic dioxins may also be present.

Inorganic chlorides are also present in paper mill effluents due to chlorination in the bleaching process: about 90% of the chlorine used is discharged as chlorides. (Nordic Council of Ministers, 1989). Chlorides can be fatal to fish in concentrations above 400 mg/L (Rao, C.S., 1991) and inhibit the growth of plants such as rice (Indian Council of Agricultural Research, 1985).

Suspended solids can have toxic effects by clogging the gills of fish (Klein, 1957). They may also silt up streams, destroying plant life and benthos.

Table 1. Standards for effluents from large pulp and paper mills.

Parameter	**Limit (if specified)**
BOD	30mg/L$^+$
COD	350 mg/L$^+$
pH	6.5 – 8.5$^+$
Chlorides	1000 mg/L - surface waters 600 mg/L – irrigation*
Phenol	1000 µg/L*
Mercury	0.01 mg/L*
Suspended solids	100mg/l$^+$

* General standard for discharge of environmental pollutants, Part A, Schedule 4, MOEF, 1993.
$^+$ Minimum National Standards (MINAS) for large pulp and paper mills with chemical recovery.

The objectives of the study are twofold:

- To determine the threshold level of toxicity of the paper mill effluent, and the level of toxicity ensuing in the receiving water body.
- To identify the physico – chemical parameters of the effluent that may be causing the observed toxicity.

The Star Paper Mill in Saharanpur was selected for the study. It is one of the oldest and largest paper mills in the country, and is equipped with a sulphate pulping process and a three stage bleaching process (Chlorination, alkali extraction and hypochloridation). A soda recovery plant within the mill processes about 1700 m^3/ day of black liquor from the pulping process (Star Sandesh – Star Paper Mill Quaterly Newsletter, 2003). All wastewater from the mill is channeled through a single drain to the effluent treatment plant, where it is treated by activated sludge. The effluent is then released into the River Hindon, which is a seasonal river and has very low flows for much of the year.

II. METHODOLOGY

For the fish bioassays, Hamilton's Barilius (*Barilius Bendelisis*) were caught in local streams in the Dehra Doon area. Fish of the same size (2.5 cm – 4 cm in length) were selected from the catch and acclimatized in a laboratory tank for ten days. Samples of effluent from the paper mill were taken just before the confluence with the receiving water body (R. Hindon). The discharge rates of the effluent channel and the receiving river (after confluence) were measured. The bioassay tests were performed in 4L glass jars, containing 10 fish in each with concentrations of the effluent ranging from 100% to 30%. Atleast four concentrations of effluent were prepared for each test. Fish mortality was observed at 24, 48, 72 and 96 hours. A control containing only diluent water was included in the test.

Seed bioassays were performed using rice seeds collected from a Dehra Dun mill. The exact variety of the rice seed was unknown. The seeds were sorted with respect to size and inspected for damage. The bioassay was performed in petridishes containing 10 seeds and 30 ml of effluent/diluent water mixture in each. Parameters such as percentage germination, shoot length and root length were measured daily. The test solutions were renewed every two days to account for evaporative losses. A control containing only diluent water was included in the test. The test was conducted in quadruplicate.

Table 2. Protocol for fish (*Barilius Bendelisis*) bioassays.

Temperature:	Ambient Laboratory Temp
Light:	Ambient Laboratory Temp
Test Vessel:	4 litre glass jars
Fish / vessel:	10
Replicates:	1
Aeration:	Aerator for each test vessel
Control water:	Standard lab water (Dechlorinated).
Parameter:	Mortality
End point:	Over 50% mortality in highest test concentration.

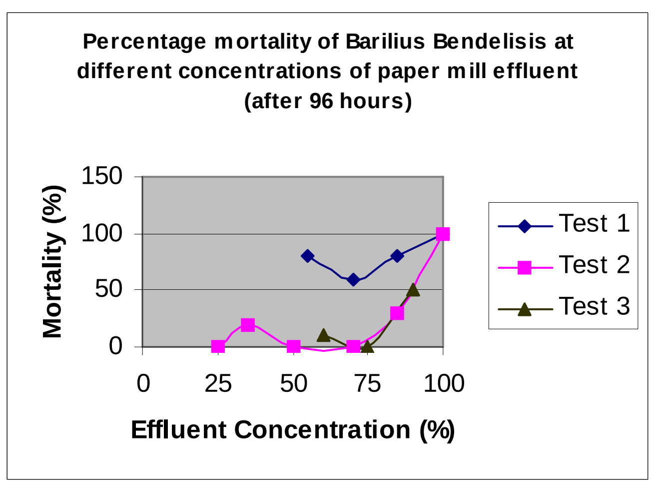
Table 3. Protocol for rice seed *(Oryza sativa)* bioassays.

Temperature:	30°C
Light:	Dark
Test Vessel:	Petridish (30 ml)
Seeds / vessel:	10
Replicates:	4
Aeration:	None
Control water:	Distilled water
Parameter:	Percentage germinations, Root and shoot length.
Endpoint:	Control mean shoot length in excess of 20 mm.

III. RESULTS AND DISCUSSION

The results of the three fish bioassays indicate that the toxicity of the paper mill effluent varies considerably (Figure 1). The results of tests 2 and 3 indicate high toxicity at effluent concentrations at and close to 100%, with the LC_{50} (after 96 hours) at 90% effluent concentration. The results of test 1 also indicates high toxicity at concentrations close to 100% effluent, but in this case remaining high as the effluent is diluted. The LC_{50} (after 96 hours) of the effluent sample used in test 1 can be estimated to be around 60% effluent (by extrapolation).

Fig. 1. Results of fish bioassays.



A comparison of the physico – chemical parameters of the effluent samples used in Test 1 with those measured in the samples of test 2 & 3 (**Table 4**) reveals a trend of increasing concentration, with the notable exception of mercury. Therefore, the high mercury concentrations found in the test 1 sample (12.2 µg/L – above permissible limits) may be responsible for the higher toxicity levels observed in this test.

The levels of Biological Oxygen Demand (BOD), Chemical Oxidation Demand (COD) and Total Suspended Solids (TSS) were close to or above the permissible limits in all samples taken. High TSS levels may be partly responsible for the toxicity observed at high concentrations of effluent, due to the fish gills being blocked by particulate matter.

At each time of sampling the dilution of the effluent by the River Hindon was minimal, due to very low flows in the river. The concentration of effluent in the river was estimated to be around 90% on each occasion. This concentration would lead to toxicity levels with respect to *Barilius Bendelisis* ranging from 50% to 85% mortality.

Table 4. Physico – chemical parameters of effluent samples for respective bioassay tests.

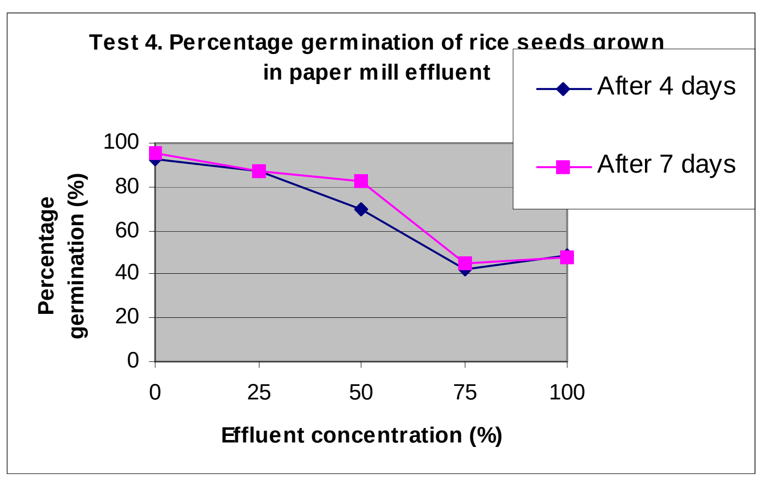
Parameter	Test 1 (4/6/2003)	Test 2 (13/06/2003)	Test 3 (06/08/03)	Test 4 (19/08/03)	Standard
Temp	35ºC	36ºC	35ºC	33ºC	-
pH	7.5	7.5	7.5	7.5	-
Discharge	0.113 m^3/s	0.278 m^3/s	0.203 m^3/s	0.255 m^3/s	-
B.O.D	**114 mg/L**	**156 mg/L**	**192 mg/L**	**96 mg/L**	**30 mg/L**
C.O.D	342 mg/L	**456 mg/L**	**402 mg/L**	**522 mg/L**	**250 mg/L**
TSS	**296 mg/L**	**212 mg/L**	**304 mg/L**	**132 mg/L**	**100 mg/L**
Chlorides	330 mg/L	395 mg/L	-	400 mg/L	**1000 mg/L**
Lignin	40 mg/L	100 mg/L	80 mg/L	100 mg/L	-
Phenol	70.91µg/L	179.71 µg/L	204 µg/L	625 µg/L	**1000 µg/L**
Mercury	**12.2 µg/L**	1.3 µg/L	2.7 µg/L	1.9 µg/L	**10 µg/L**
Effluent conc. in River Hindon	90 %	92.5 %	92 %	92.5 %	-

Values in bold are in excess of the standards listed in the last column of Table 4.

Threshold levels of toxicity can be estimated from the results of tests 2 & 3 at around 70% effluent concentration. The results of test 1 do not permit a threshold level of toxicity to be predicted.

The results of the rice seed bioassay show a 50% decrease in the germination percentage of rice seeds grown in effluent concentrations above 75%, when compared with seeds grown in the control. (**Fig. 2**). The most significant decreases in germination percentage occur after 25% effluent concentration.

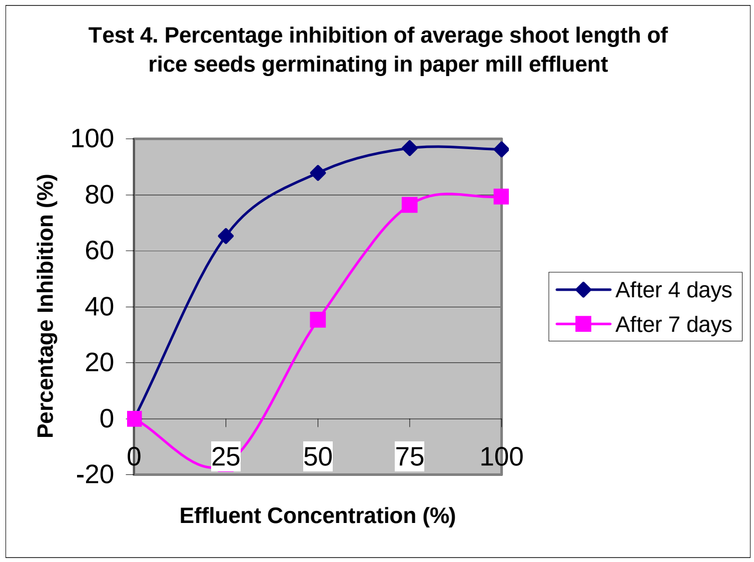
Fig. 2. Results of the rice seed bioassays.



Four days after the beginning of the test, the average shoot length of seeds grown in effluent are significantly inhibited when compared with seeds grown in the control water, even at low concentrations, and approach complete inhibition at 75% effluent concentration. However, after seven days, stimulatory effects can be observed below 30% effluent concentration, and the maximum inhibition is reduced to 80%.

Taken together, the results indicate that as the concentration of effluent increases, the percentage of rice seeds that germinate decreases, and the growth of the seeds that do germinate is inhibited. The results show a decrease in the degree of shoot growth inhibition over time, but no increase in the germination percentage over time. Therefore we can say that the paper mill effluent is toxic to rice seed germination, but that the effects on the seedling growth after germination may be inhibitory or stimulatory, and vary with the growth stage of the seedling. This has been reported before: (Murty, K.S, 1967) observed tolerance to salt in rice developing after three weeks of the seedlings growth.

Fig. 3. Results of the rice seed bioassays.



Therefore, in terms of measuring toxicity, the crucial parameter in this case is the percentage germination of the seeds. The threshold level of toxicity in this case is then 25% (see **fig. 3.**); the most significant reductions in germination percentage occur at concentrations higher than this. The IC_{50} (concentration at which 50% inhibition occurs) is at 75% effluent concentration. With a concentration of effluent in the River Hindon of 92.5% at the time of sampling, it can be seen that any river water used for irrigating germinating rice seeds will cause a 50% reduction in seed percentage germination.

The results of the tests for the physico – chemical parameters of the effluent used for the seed bioassay (Test 4) are shown in **fig. 3**. As the seeds bioassay has not been repeated with other samples of the effluent, it cannot be ascertained how changes in the physico – chemical parameters will affect the toxicity of the effluent towards rice seed germination. The concentration of chlorides (400 mg/L) is less than the maximum permissible limit but may be an important factor – chloride toxicity to rice seeds germination has been well documented (Indian Council of Agricultural Research, 1985) and is dependent on the variety of rice. The concentration of phenols will also be a factor; Ayyamperumal *et al* (1968) extracted phenolic substances from rice shoots that acted as natural growth inhibitors.

IV. CONCLUSIONS

- Undiluted effluent from the Star Paper Mill, Saharanpur, exerts 100% mortality to fish of the species *Barilius Bendelisis*. In two of the fish bioassays (Tests 2 & 3), the toxicity of the effluent rapidly decreases with effluent concentration. The LC_{50} of the effluent samples for these tests was estimated at 90% effluent concentration. The threshold level of toxicity of the effluent occurs at 70% effluent concentration.
- Results from one of the fish bioassays (Test 1) showed that toxicity decreased with effluent concentration at a lesser rate. The LC_{50} of the effluent sample for this test was estimated at 60% effluent concentration. The high toxicity observed in this test is lilely due to the higher levels of mercury in the sample, when compared with samples taken for Tests 2 and 3.
- The fish bioassays indicate that after confluence with the Star Paper Mill effluent channel, water in the River Hindon would cause a mortality rate of 50 – 85% mortality on *Barilius Bendelisis*.
- Bioassay tests on rice seeds show that the paper mill effluent is toxic to rice seed germination, but that the effects on the seedling growth after germination may be inhibitory or stimulatory, and vary with the growth stage of the seedling.
- The threshold level of toxicity with respect to rice seed germination is 25% effluent concentration. After confluence with the Star Paper Mill effluent channel, water in the River Hindon used for irrigating germinating rice seeds will cause a 50% reduction in seed percentage germination.
- The biochemical oxidation demand, chemical oxidation demand, and the concentrations of total suspended solids and mercury in effluents from the Star Paper Mill exceed the maximum permissible limits.

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