TOXIC EFFLUENTS FROM PULP AND PAPER MILLS

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INTRODUCTION

The fibrous raw material used in pulp and paper industry consists of less than 50 % cellulose and the remainder is mainly made up of lignin, hemicellulose, mineral fillers, extractives, organic acids and inorganic salts. Part of these substances as well as some of the process chemicals and the auxillary chemicals used in paper making cannot be entirely recycled or reclaimed and is therefore discharged into receiving waters. Thus the effluent from pulp and paper mills have a high pollution load and needs to be reduced before being discharged into receiving water so that the environment can be maintained safe and free from pollution hazards.

The effluent is characterized by suspended solids, BOD, COD and colour. The BOD value indicates the easily biodegradable compounds and the amount of slowly biodegradable compounds is indicated by (COD-BOD) value. The lower the BOD/COD ratio, the higher is the fraction of slowly biodegradable compounds. Such compounds are usually coloured and therefore reduce light penetration to water.

Large volumes of the effluents are generated by the pulp and paper mills. The volume of the effluents as well as the pollution load of the the various sections of the large paper mills in India are given[1] in Table No.1. The composition of effluent loads from large and small mills is shown[2] in Table No.2.

In order to reduce the pollution load of the effluent, Indian Paper Industry mainly use primary and secondary effluent treatment processes. In the primary stage, suspended solids as well as colloidal materials

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are removed where as in the secondary stage, most of the easily biodegradable compounds are removed. Thus the slowly biodegradable compounds persist in the treated effluent. The effluent coming from pulp and paper industry is highly coloured and has a high COD value. The discharge of such an effluent is highly deterimental to the growth of vegetation and aquatic floura as it contains many toxic chemicals.

During the last 10-15 years, the toxicity of the pulp and paper mill effluent have attracted increased attention and intense research effort have been directed to identify and study the toxicity of the various chemicals coming from various sections of pulp and paper industry.[3-20] Toxicity is a vague and variable parameter. Toxicity is difficult to quantity as the results are strongly influenced by the intricacies of test techniques. The various toxicity terms used are given in Appendix-I. Lethal concentration indicated usually as 96 h LC50 is generally used to express effluent toxicity.

Early investigators recognised that volatile constituents of kraft effluents i.e. hydrogen sulphide, methyl mercaptan and methyl sulphide, were toxic to fish. They may be rapidly removed by special treatments such as air stripping and oxidation prior to effluent discharge. Over the last 15 years most non-volatile toxicants of importance have been identified and their contribution to the acute toxicity has been assessed[5](Table - 3). A perusal of Table 3 shows that with the exception of lignin degradation products and chlorinated compounds which are formed during pulping and bleaching, all other compounds belong to the category of extractives and their concentrations in the effluent depends upon the extent of recovery in pulping and other processes. Thus toxicity of the whole mill effluent of a given mill will directly depend upon the total organically bound chlorine, the extractive content of the raw material being used and to what extent these extractives are removed during pulping and other processes. Thus higher the extractives and total organically bound chlorine, higher will be the toxicity. Table 4 shows the extractive content of common raw materials used in paper industry.[21]

Investigations on the toxicity of the unbleached sulphate (kraft mill) effluents showed that black liquor is the most toxic followed by the condensate. The compounds responsible for the dominating part of the toxicity are resin acids and to some extent unsaturated fatty acids.[3] Bleach plant (kraft) effluent contains neutral toxic compounds and chlorinated compounds in addition to the above listed compounds.[22] First chlorination step accounts for the greatest quantity of toxic compounds.[3] A significant fraction of the acute toxicity of caustic extraction stage (E-stage) is due to six compounds, mono and dichlorostearic acid, 3,4,5 trichloro and 3,4,5,6 tetrachloroguaiacol.[7,8]

Some studies indicate that the toxicity of whole sulphite mill effluent is similar to that of sulphate (kraft) mill effluents.[23,24] Resin acids such as abietic, dehydroabietic, isopimaric and palustric acids etc. formed the major contribution to the total toxicity of the mechanical pulping effluents. Neutral materials like diterpene alcohols and aldehydes, juvajones and related compounds contributed about 30 % to the tototal toxicity.[6,13] Soft-wood debarking waste water contains mainly resin acids which contribute about 90 % to the total toxicity.[6]

The toxic effluents have adverse influence. These are indicated subsequently. The toxic influence of liquid effluents is discussed under the following areas.

2. TOXIC EFFECTS OF EFFLUENTS:

The toxic influence of liquid effluents is discussed under the following areas:

i) Sub level effects on aquatic animals.
ii) Toxic effects on algae.
iii) Genotoxic properties.
iv) Growth simulating substances.

2.1. Sub Level Effects on Aquatic Animals:

The impact of industrial effluents on streams, lakes, estuaries or the sea is highly complex and dependent upon the characteristics of the effluent, the composition of the receiving water, relative flows and the dispersion of the wastes. Much research has been directed towards the development of rapid bioassays to measure the threshold at which sub-lethal effects occur.[6,25] In Table - 5 are summarized different sub-lethal effects on fish of pulp and paper mill effluents.[26]

Recent studies have even shown that the reproduction of fish is affected at concentrations of pulp mill effluents at which they are frequently discharged.

Subsequental evidence now exists from different sources, relating to different organisms, which shows a consistent pattern indicating threshold concentrations for various sublethal parameters to be approximately between 0.05 and 0.1 of the 96- hour LC 50 value. At concentrations of pulp mill effluents in or below this range, no sublethal stresses have been observed.[6,12]

Recently it has been demonstrated that chlorinated lignin degradation products could be accumulated in fish living in water areas,which receive bleach plant effluents. Samples of stationary fish species have been analyzed and found to contain small amounts of chlorinated phenols and guaiacoles in their extractable fat. The biological effects of these bioaccumulating compounds, originating from the bleachery effluents, are presently not well known. However, this group of chlorinated phenols is generally known to interfere with energy metabolism in higher animals[10,12]. It has also been observed that an increase in temperature generally increase the toxicity of effluent to some extent.

2.2. Toxic effects on algae:

Most of the current knowledge concerning effects of mill effluents on productivity and growth of aquatic plants comes from laboratory experiments. Both stimulation and inhibition of the growth of algae have been shown to occur in waters receiving mill effluents. The effects seem partly to be related to the concentration of effluents. Inhibition of photosynthesis can be caused by increased light absorption, altered pH or toxic properties of the effluents. The substances responsible for the latter effect have not yet been identified.

Occasional reduction of photosynthesis was observed at effluent concentrations as low as 0.01 % but at effluents concentrations of 1 % and higher, consistent reduction of photosynthesis of both periphyton and phytoplankton was noticed. At high concentrations, pH elevation accounted for a significant portion of the inhibiting effect. As the reduction in available light was insignificant the depression in photosynthetic rates could be attributed to effluent toxicity. Condensates and mixed effluents from bleaching have been found to be less inhibitory than effluent from barking and pulp washing.[27] Only black liquor was very inhibitory or toxic. The unidentified toxicants were found not to be removed by biotreatment.[28] Of six types of effluents tested, sulphate effluent was most inhibitory to growth, while combined sulphate and newsprint effluent passed through a resin column was least inhibitory. In another laboratory experiment on marine phytoplankton, it was suggested that it is possible for phytoplankton to adapt to relatively high effluent concentrations if pH remains normal.[11,29,30]

2.3. Genotoxic Properties:

Nearly all of the chlorination stage effluents from bleached softwood and hardwood sulphate and sulphite pulps were found to be mutagenic.[31,32] The other bleaching effluents were not mutagenic at normal process concentrations. The mutagenicity of the standard C-stage effluent decreased to zero when the effluent was treated for 48 hours with a microflora adapted to this substrate.

Addition of liver microsomes decreased the mutagenic activity of the chlorination stage effluents, indicating that the mutagenic compounds are partly degradable in the mammalian liver.

The structure of the compounds causing the mutagenicity is not yet known. However, they can be extracted with ether and are known to be of small molecular size (1000 MW).

Chlorination stage effluent has also been shown to be mutagenic to bacteria as well as hamster cells. The neutral fraction of the chlorination stage effluent shows the highest mutagenic activity. One of the key questions in studies of mutagenic substances in bleaching effluents, is whether they are persistent enough in receiving water to be accumulated in the food chain and thereby constitute a potential danger to man and higher animals.

2.4. **Growth Stimulating Substances:**

The discharge wa ter contain significant amounts of inorganic phosphorous and nitrogen. Investigations have shown that the population of all types of bacteria such as heterotropic, organic sulphur reducers and sulphur oxidisers and enterobactericaceae were found to be higher near the effluent out fall than in the regions of receiving waters.[33,34] Growth tests on algae have shown that mill effluents sometimes enhance growth depending on the amount and variety of the effluents. Biotreated effluents were more stimulatory than raw and lime treated effluents.[35]

The content of carbohydrates and organic acids in pulp and paper mill effluents may also act as growth stimulators to colony forming bacteria (Sphaerotilus) or fungi, which can be found as yellow or brownish grey slimy covers on suitable substrates or floating on the surface downstream from an effluent outlet. This often causes increased mortality of fish eggs, anaerobic conditions and difficulties in handling fishing gear.

3. **EVALUATION OF IMPACT OF PULP AND PAPER MILL DISCHARGE:**

It is a difficult task to make an evaluation of the overall impact in the aquatic environment caused by combined mill effluents. The final effect of a water pollutant in the aquatic environment is the result of many factors acting together and of the interactions between them. The nature of these complex interactions is not well understood today.

In order to predict the environmental impact of a pollutant it is necessary to know how the pollutants are distributed in the system, i.e. between water, aquatic organisms and bottom sediments over a period of time i.e. after a few days, a few weeks and a few years. It is also desirable to know the rate of matabolism of the pollutants by micro-organisms and higher aquatic animals.

The determintal effects of pulp and paper effluents are very diverse and affects all trophic levels in the aquatic ecosystem. In an order to arrive at a common basis for evaluation of different types of determental influences, the effects can be classified into two categories:

1. extension of effect in time.
2. extension of effect in space.

It should be remembered that an 'ecological effect' repersents the departure from an original equilibrium of the ecosystem, i.e. a disturbance of the equilibrium.

The 'seriousness' of an effect is judged by the time required from when the disturbance takes place until the original equilibrium is restored.

Effects, causing irreversible changes in the aquatic ecosystem should consequently be regarded as the most serious ones. Whereas reversible damages should be regarded as less serious. It is also important to know the total area affected. If vast area is affected environmental effects are considered to be more serious than affecting a small area. Based on these principles some environmental effects are grouped in Table No.6.

3.1. Polluting substances causing short term effects:

A number of short term effects are listed in Table-6, may not cause the most adverse ecological effects but are generally considered very drastic (e.g. fisn kills) and have therefore caused much public attention. It is for this reason that the pollution abatement work in the pulp and paper industry has been concentrated on the elimination of these short term, effects.

These effects are caused by

- substances with high acute toxicity
- light absorbing substances
- substances causing avoidance reactions
- pH - changing substances
- soluble, oxygen-consuming substances
- substances stimulating heterotrophic growth,

3.2. Polluting substances causing long term effects:

The long term effects, which cause irreversible disturbances in the ecosystem equilibria are the most adverse ecological effects. Pollution abatement work based on ecological principles should give priority to the reduction or elimination of substances causing this type of effect. Growing awareness for these principles and priorities has led to their being increasingly applied in pollution abatement technologies. High priority should be given to reduce or eliminate substances causing these long term effects. Among the substances which may cause long term effects are:

- fibres and other settleable solids
- substances which show a tendency to bioaccumulate in fish and other aquatic organisms
- substances which through their accumulation may cause chloronic toxicity or interfere with reproduction
- substances giving bad taste or odour to fish and shell-fish.
- substances stimulating algal growth and thereby cause eutrophication
- persistant substances which have genotoxic and/or other chronically toxic properties and thereby present risks to consumers of drinking water contaminated by these substances.

4. CONTROL OF TOXIC EFFLUENTS DISCHARGE:

The minimum acceptable stadards for the quality of the effluent for the Indian paper Industry are

pH	5.5-9-0	
T.S.S.(Max)	100 mg/l	No value of COD has been prescribed for small paper mills.
BOD(Max)	30 mg/l	
COD(Max)	250 mg/l	

No value of the toxicity has been prescribed for the effluent in India. Thus toxicity has been neglected so far. Fedral Republic of Germany has also laid down values for toxicity towards fish i.e. 0.3 GF (GF is the dilution factor at which waste water is no longer lethal to fish).

In arriving at these values, paper industry mainly employ Primary and Secondary effluent treatment processes. In the primary treatment process, suspended solids are removed. The secondary effluent treatment processes are biological treatment methods like stabilization pond, serated lagoon, trickling filter and activated sludge. The comparasion of the various biological methods[36] is shown in Table 7.

The biological methods effectively reduce the BOD of the effluent, COD reduction is modest and colour reduction nil. Thus the effluent contains many toxic chemicals affecting the growth of vegetation and aquatic floura.

The pollution load of the effluent being discharged can be reduced by two approaches:

1. By suitably modifying the existing manufacturing processes viz, pulping and bleaching so that lesser amounts of the pollutions are generated.
2. By modifying the existing effluent treatment processes or developing new effluent treatment processes.

4.1. <u>MODIFICATION OF THE EXISTING MANUFACTURING PROCESS:</u>

Studies have shown that oxygen bleaching processes generate much less pollution load. These processes have been tried on a pilot plant scale but these processes are still not considered as commercially available technology due to high capital investment needed.

Studies have shown[37] that oxygen bleaching results in reduction of 65-77 % in BOD, 63-68 % in COD and 75-90 % in colour values of the effluent, being generated[38,39]. Partial substitution of chlorine by chlorine dioxide in C stage also results in a effluent with much lower toxicity.[40] The results are given in Table 8. Like wise replacement of chlorine by Hydrogen peroxide in C-stage results in the reduction of pollution load by 55-60 %[41,42]. Use of hydrogen peroxide in the extraction stage (E) also results in the reduction of the pollution load. Studies have also shown[43] that bleaching of acid pretreated hardwood and softwood pulps by hydrogen peroxide in place of chlorine in C stage results in the significant reduction in toxicity and corrosivity over

90 %, BOD 64 %, colour 40 %, DS and TOC 71 % in comparasion to the conventional CEDED sequence when the effluent from acid stage and peroxide stage is recycled to the recovery system of the kraft mill. The results are given in Table -9.

4.2. **Modification of the existing effluent treatment processes or developing new effluent treatment processes.**

A number of methods have been tried. These methods can be classified as chemical and physical treatment methods and are called advanced methods. Many of these methods have been used in full scale or large scale pilot plants but none of these methods can be considered as commercially available technology. These methods can be divided into:

a) adsorption and ion-exchange methods
b) flocculation and chemical precipitation methods
c) membrane methods
d) oxidation and other methods.

a) **Adsorption and ion-exchange methods:**

Two methods namely Billerud Uddeholms AB[44-46] and Rohm-Hass[47], employing ion-exchange resins have reached pilot plant scale or full scale application. The former is a Swedish development and makes use of a weak anionic resin (phenol formaldehyde type). This process has been applied to both chlorination and extraction stage (E_1) of the bleach plant effluents. It has also been reported that chlorinated phenols like 2,4,6 trichlorophenol, tri and tetrachloroguaiacol which are acutely toxic to fish are completely eliminated. The later method makes use of a highly crosslinked hydrophilic porous polymer containing no ion-exchange groups. This method has not been marketed. Feldmuhle's[48,49] method marketed by Dr. Otto and company (FRG) employs r-Al_2O_3 as adsorbent.

b) **Flocculation and Chemical precipitation methods:**

i) Stora lime method: This method can be characterized as a combination of sorption and precipitation methods, suitable for treating the caustic extraction effluent from bleach plant where lime mud is used as a cleaning mud.[44] The amount of produced lime is a limiting factor for this treatment.

ii) Precipitation with lime: Lime alone or in combination with magnesium or ferric chloride have been shown to precipitate a number of coloured and toxic pollutants. Based upon this property two methods viz., massive lime method[50,51] and minimum lime method[52-54] have been developed and tried for the caustic extraction bleach plant effluent.

iii) Precipitation with aluminium: Precipitation with aluminium of different effluents[44,45] have been tested. Results for E_1 stage of the bleach plant effluent are given in Table 10. In this process aluminium sulphate at pH 4 is used as a precipitating chemical and after flocculation with polyelectrolyte the floc is separated.

c) **Membrane methods**

Ultrafilteration and reverse osmosis methods are concentrating methods and all the polluting components will be present in the concentrate. A filteration method trade named ultra-sep (Sweden) has been applied to the caustic extraction stage effluent.[56] The main disadvantage of the ultrafilteration is that small molecules are transferred to the permeate resulting in the high BOD value in the effluent. A combination of Ultra-filteration technique with other methods such as ion-exchange or oxidation methods e.g. ozone treatment may be more suitable.

Table 10 summarises the results of the above methods.

d) **Oxidation and other methods:**

Ozone treatment has been shown to reduce the colour and highly toxic chlorinated phenols and guaiacols in the effluent.[56-61] However the COD reduction is much less.

Sulphur dioxide treatment[40] at pH 5 or above has been shown to reduce drammatically both toxicity and mutagencity of the kraft mill chlorination stage effluent when at least 0.02 % SO_2 (200 mg/l) is applied. The results are shown in Table 11 and 12.

Recently pilot plant studies[62-64] have shown that aerobic and anaerobic treatment of NSSC and CTMP effluent generates a non-lethal effluent. An over all reduction in BOD of over 80 %, COD 35 % and substantial reduction of toxicity (from 7 % 96 n LC 50 to non toxic) has been observed.[62]

CONCLUSIONS:

Greater social awareness to environmental pollution by paper industry and imposition of legal sanctions has made the industry to take necessary steps to reduce the effluents being discharged. Toxicity of the effluent and their related impact however has not received any major attention sofar. In order to control the toxic influence of the effluent there is a necessity to initate systematic studies on following areas:

i) Analysis of the toxic components generated during processing and eventually discharged to the surroundings. This called for advanced scientific and analytio procedures using techniques like GC-MS(Gas chromatography-mass spectrometry).

ii) Study of the impact of the toxic effluents (long and short range impacts) on the eco-system particularly on aquatic floura and fauna. This would indicate assessment of receiving water qualities, inplant process modifications, raw water quality, suspended and particulate matters in liquid effluents and gaseous emissions.

iii) Development of suitable alternative and economically viable process modifications for reducing toxic pollutant discharges. These will concentrate primarily in high yield pulping processes and modifications in bleaching and washing techniques.

iv) Development of new and cheap technologies for the external treatment of the effluent to reduce the toxic impact. These studies will simultaneously look into the demand for additional investment decisions and their influence on processing costs.

In view of the growing concern of toxic effluents and the present state of art in this vital area, a greater support is essential from all concerned in immediately initiating well identified R&D projects in the area of toxic effluents from paper industry and alternatives to control them.

TABLE- 1

CHARACTERISTICS UF WASTE WATER 'ROM DIFFERENT SECTIONS OF PULP & PAPER MILLS(ALL VALUES EXCEPT pH AND VOLUME ARE IN mg/l)

	Chipper House	Digester House	Pulp Washing	Pulp bleaching	Paper Machine	Chemical recovery	Combined Waste water		
							Min.	Max.	Ave.
Volume of waste water m^3/tonne of Paper	20-60	5-10	20-40	140-180	40-90		240	360	305
Colour	Muddy	Dark Brown	Dark Brown	Brown	Whitish	Light brown	Brown	-	-
pH	6.4-8.0	9.0-10.0	8.5-9.6	6.0-9.0	5.3-8.1	7.0-9.0	6.5	8.2	-
Total solids	540-900	1000-2500	1400-2500	2100-2900	850-1250	1270-2800	1200	2000	1542
Suspended solids	240-520	140-190	350-1000	140-220	490-900	400-760	350	450	430
BOD_5	30-50	300-360	230-480	125-155	100-160	90-180	110	235	167
COD	175-450	1850-2200	900-1700	550-700	520-780	320-610	600	750	711

TABLE - 2

CHARACTERISTICS OF WASTE WATER FROM SULPHATE PULP & PAPER MILLS

1	2	3	4	5	6	7	8	9	Weighted Average 10
Installed capacity (TPD)	230	205	190	180	165	140	140	125	-
Raw Materials	Bamboo Wood	Bamboo Wood rags	Bamboo Wood rags	Bamboo Wood rags, Waste paper	Bamboo Wood	Bamboo Wood	Bamboo Wood	Pine, Educ-lyptus	-
Volume of waste water m^3/tonne paper	214	350	300	313	352	343	316	253	305
Colour	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown
pH	6.5-8.0	6.6-10.2	7.1-8.2	9.8	7.0-7.6	5.6-11.8	7.3-8.0	7.6	-
Total solids, mg/l	1770	1442	2014	1920	1186	1380	1210	1590	1542
Suspended solids, mg/l	410	386	503	600	290	400	423	380	430
BOD_5, mg/l	161	235	188	210	100	122	165	190	167
COD, mg/l	725	674	750	650	585	620	498	1270	711
Pollution load kg/toonne									
Suspendes solids	88	154	151	188	102	137	134	96	131
BOD	55	76	53	66	35	42	52	48	51
COD	155	238	213	234	206	213	158	321	217

TABLE - 3

COMPOUNDS TOXIC TO FISH IN PULP MILL EFFLUENTS

Chemical Compound(s)	Toxic contribution		
	Major	Intermediate	Minor
Resin acids			
Abietic, dehydroabietic, isopimaric, levopimaric, palustric, pimaric, sandaracopimaric, neoabietic	KP D M S		
Chlorinated resin acids			
Mono- and dichlorodehydroabietic		KC	
Unsaturated fatty acids			
Oleic, linoleic, linolenic, palmitoleic		KP	D M
Chlorinated phenolics			
Tri- and tetrachloroguaiacol		KC	
Diterpene alcohols			
Pimarol, isopimarol, dehydroabietal, abietal		M	D
Juvabiones			
Juvabiones, juvabiol, 1-dehydrojuvabione, 1-dehydrojuvabiol, dihydrojuvabione			M
Other acidics			
Epoxystearic acid, dichlorostearic acid, pitch dispersant		KC	
Other neutrals			
Abienol, 12E-abienol, 13-epimanool			D
Lignin degradation products			
Euganol, isoeugenol, 3,3' dimethoxy, 4,4' dihydroxy-stilbene		S	

Abbreviations: K=Kraft; P=Pulping; D=Debarking; M=Mechanical; S=Sulfite pulping; C=Caustic.

TABLE - 4

EXTRACTIVE CONTENT OF FIBROUS RAW MATERIALS EXPRESSED AS ALCOHOL BENZENE SOLUBILITY.

Raw Material	Alcohol-Benzene solubility %
Cotton Stalk	4-7
Jute	1-2
Rice Straw	1-7
Bagasse	3-11
Bamboo	3-6
Jack pine	3.3
Southern pine	2.5-3.6
Eucalyptus globulus	1.5
American aspen	2.9
European beach	1.8
Birch	2.8

TABLE - 5
APPROXIMATE THRESHOLD FOR SUBLETHAL EFFECTS FOR SALMON FISH IN SULPHATE MILL EFFLUENTS

Function of System Affected	Effects of KME	Species	Size	Temp °C	CONC. TESTED	APPROX. THRESHOLD	COMMENTS
RESPIRATORY	"Coughing" response elevated	Rainbow	8 - 10 in.	11 ± 1	—	1.1% of full strength KME	
	" "	Sockeye	207 - 321 g	10.5 ± 0.5	—	0.1 - 0.2 LC50	Possible adaptation
	Ventilation Volume increased	"	" "	" "	—	0.2 LC50	" "
	Oxygen uptake increased	"	" "	" "	—	0.33 LC50	" "
CIRCULATORY	Arterial Oxygen Tension reduced	"	to 2 kg	" "	0.35 LC50	—	No adaptation
	" "	Rainbow	150 g	10	0.33 LC50	—	" "
	White Blood Cell, Thrombocyte Counts reduced	Coho	Juveniles	11 ± 1	—	0.1 TL_m96	after 21 days exposure
	Blood neutrophil count elevated	"	"	"	—	0.25 TL_m96	after 200 days exposure
METABOLISM	Plasma glucose elevated	"	"	"	—	0.10 TL_m96	after 200 days exposure
	Blood & muscle lactate elevated	"	"	"	—	0.25 TL_m96	" "
	Swimming ability reduced	"	"	13 ± 5	—	0.20 TL_m96	—
	Muscle glycogen depressed	"	"	11 ± 1	—	0.10 TL_m96	after 200 days exposure
GROWTH	Growth rate decreased	Sockeye	2.4 - 2.8 g	15	—	10-25% FULL strength KME	exoosed over about 8 weeks
	" "	"	Fingerlings	8	—	0.05 - 0.1 LC50	bleach waste
	" "	Chinook	Underyearlings	7 - 13	—	0.14 - 0.35 TL_m96	unbleached waste
	" "	"	Juveniles	—	—	0.1 - 0.3 TL_m96	unbleached waste
	" "				—	6% full strength KME=	
		Coho	Fingerlings	6	1:169 dilution	—	growth rate reduced after 30 days
	Food conversion efficiency reduced	Sockeye	2.4 - 2.8 g	15	—	10-25% full strength KME	8 week exposure
	Growth rate enhanced	Coho	4 - 10 g	10 - 13	—	0.1 - 0.2 LC50	several weeks exposure
	" "	"	Juveniles	11 ± 1	—	0.1 - 0.25 TL_m96	70 day exposure
BEHAVIOUR	Feed behaviour affected	Coho	4 - 10 g	10 - 13	—	0.1 - 0.2 LC50	response lasted for 2 weeks then disappeared
	Feeding behaviour affected	Chinook	Juveniles	—	—	0.14 - 0.36	long term study
	Fish sicw & "unreeponsive"	Coho	4 - 10 g	12 - 13	—	0.15 LC50	—
	"Alarm response" slowed	Sockeye	Fingerlings	8	—	0.4 LC50	Bleach waste
	Orientation to water current affected	Sockeye	Fingerlings	8	—	0.8 LC50	Bleach waste
	Fish avoid effluent	Sockeye	3 cm	10	—	0.2 LC50	within 1 hour
	Fish avoid effluent	Atlantic Salmon	7.7 - 14.8 cm	17 ± 0.2	—	10 mm (approx. 006 LC50)	"vague" response
	" "	"	"	"	—	3.77 × LC50	strong response
	" "	Chinook	Juveniles	—	—	5 - 10% full strength KME	—
MORPHOLOGY & PATHOLOGY	Opaque eye pupils, internal hemorrhages discolored livers	Chinooks	41.3 g	12	1:8.5 dilution	—	"synthesized waste"
	40% had opaque eye pupils after 7 days exposure	Chinooks	"	12	1:15 dilution	—	" "
HISTOLOGY	Histological & cytochemical change of liver, kidney, intestine	*Sparus macrocephalus*	25 CM	—	—	field exposure in cages off mill in seawater	12-24 Hr. Exposure (Sublethal)
ENDOCRINOLOGY	Plasma cortisol up	Sockeye	168 - 200 g	12.5	0.50 LC50	—	after 2 hr.
	Mucous Production increased	"Salmonids"	Juveniles	—	—	2-5% full strength KME	—
IMMUNOLOGICAL	Disease Resistance reduced	Coho	10 g	12.0	0.40 LC50	—	Methemoglobinemia Resistance

KME = Kraft Mill Effluent

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TABLE - 6

Area / Time	Short term, reversible effects	Intermediate effects	Long term, irreversible effects
Local	- Death(Fish,plankton) - Decreased light transmission(Plants) - Avoiding reactions (fish) - pH-change(fish) - Oxygen deficiency in mass(fish) - Growth stimulation (heterotrophic organisms)	-Accumulation of toxic substances(Fish,molluscs) -Bad taste(fish,molluscs) -pH-change(benethic animals) -Oxygen defi ciency in sediment-water-interface (benthic animals)	- Sedimentation of solids, i.e. fibres(benthic animals) - Formation of hydrogen sulphide(benthic animals) - Destruction of fish spawning grounds(Fish) -
Distant		- Decreased light transmission(Plants) -Hampering of photosynthesis (algae) - Avoiding reactions(fish)	- Accumulation of toxic substances(fish,molluscs). - Bad taste(fish,molluscs) - Growth stimulation(algae) - Persistant genotoxic substances in drinking water (higher animals)

TABLE -7

COMPARASION BETWEEN VARIOUS BIOLOGICAL TREATMENT METHODS

Parameter	Stabilization Pond	Aerated lagoon	Trickling filter	Activated sludge
Area requirement	V.large	large	small	small
Load range kg/m^3,d	0.055-0.01	0.04-0.2	2-5	1-4
BOD_5 reduction	50-80	50-90	40-75	70-95

TABLE -8

EFFECT OF CHLORINE DIOXIDE SUBSTITUTION ON COMBINED CEDED EFFLUENT TOXICITY

ClO_2 substitution in C stage	Toxicity 48 hLC 50 daphnia magna
0 %	70.6 %
10%	64.8 %
50%	56.5 %

TABLE - 9

PERCENT DISTRIBUTION WITHIN BLEACH SEQUENCE

	APPDED			CEDED			CEH			APP	
	A	PP	DED	C	E	DED	C	E	H	A	PP
DS	31	55	14	21	56	23	17	45	38	36	64
TOC	3	72	26	20	71	13	19	67	14	4	96
BOD	12	63	25	36	41	23	37	43	20	16	84
Colour	2	57	36	20	76	4	21	77	2	3	97

TABLE - 10

COMPARISION OF THE TREATMENT RESULTS OF VARIOUS METHODS FOR CAUSTIC EXTRACTION STAGE EFFLUENT(E)

	% Reduction						
	Billerud Uddeholm	Dr otto & comp.	Stora lime	pptn with aluminium	massive lime	minimum lime	ultra-filteration
Colour	90	95	90	90	90-97	85-95	60-68
BOD	20-50	35	20	50	20-40	45	23-41
COD	60-70	70	60	75	-	-	6-7
Organic chlorine	50-60	-	75	-	-	-	23-25

TABLE - 11

LABORATORY TREATMENT OF MILL ACID BLEACH PLANT EFFLUENT

Sample	pH*	48hLC 50 Daphnia magna**
Untreated	1.5	33.8 %(31.6-36.2 %)
Treated(0.025 % SO_2)	1.5	92 % (89.4-94.6 %)
Untreated	6.0	34.8 %(32.9-36.8 %)
Treated(0.025 %SO_2)	6.0	30 % mort at 100 %

* inital pH all bioassays run at pH 7.5

** 95 % confidence limits for LC50 in brackets.

TABLE - 12

LABORATORY TREATMENT OF COMBINED C_DEHED EFFLUENT

Sample	pH*	48hLC50 Daphnia magna**
Untreated	2.9	74.0 %(66.2-82.9 %)
Treated (0.025 % SO_2)	2.9	30 % mort at 100 %
Treated (0.025 % SO_2)	6.0	10 % mort at 100 %

*inital pH all bioassays run at pH 7.5

**95 % confidence limits for LC 50 in brackets.

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