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Toxicity of Pulp and Paper Mill Effluent

A Literature Review

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TOXICITY OF PULP AND PAPER MILL EFFLUENT

A Literature Review

by

Floyd E. Hutchins
Western Fish Toxicology Station
Corvallis Environmental Research Laboratory
Corvallis, OR 97330

CORVALLIS ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OR 97330

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FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its 15 major field installations, one of which is the Corvallis Environmental Research Laboratory.

The primary mission of the Corvallis Laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects and control of pollutants in lake systems; and the development of predictive models on the movement of pollutants in the biosphere.

This report reviews the current knowledge of acute and sublethal effects of pulp and paper mill effluents on aquatic organisms. Toxic effects of treated and untreated effluents as well as the primary toxic components from kraft, sulfite, and groundwood effluents are covered. This review was conducted to ascertain the need for further laboratory studies to provide toxicity data for effective regulation of these effluents.

James C. McCarty
Acting Director, CERL

ABSTRACT

This review of pulp and paper mill effluents considers the need for additional toxicity data to insure effective effluent regulation. Effluent characteristics and problems of toxicity testing particular to pulp and paper mill effluents are discussed; however, the emphasis is on toxic effects of these effluents to aquatic life.

Untreated pulp and paper mill effluents are very toxic to most aquatic life. Concentrations as low as two percent can be acutely toxic to fish. Sufficient treatment can render the effluent essentially nontoxic much of the time; however, treatment processes used by most mills reduce toxicity but do not eliminate it. Even effluents receiving "good" treatment may exhibit sporadic and dynamic increases in toxicity (due in part to spills or dumping of spent pulping chemicals). Sublethal exposures to aquatic organisms to pulp effluent may affect a number of their physiological and behavioral functions. The more sensitive functions, growth rate, coughing reflex, and temperature tolerance, are affected at concentrations less than 1/10th of the 96-hr LC50. Many other systems such as respiration and circulation may be affected at concentrations near 1/10th of 96-hr LC50. The principal toxic components in pulp and paper mill effluents are resin acids and fatty acids naturally occurring in the wood pulp and, in effluents from bleaching processes, toxic chlorinated compounds predominate. Untreated effluents have caused considerable environmental damage, but well-treated effluents have had minimal effects on fish production, although shifts in biological diversity have occurred.

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INTRODUCTION

The impact of pulp and paper mill discharges on receiving waters results from the integrated action of oxygen demand, suspended and dissolved solids, pH, color, and toxicity. This review of the literature emphasizes effects due to toxicity. Because of the rapid progress in recent years in effluent treatment and recovery of spent chemicals, the review concentrates on data published since 1960. For information on earlier publications, one should see the reviews by Van Horn (1961 and 1971). More recent reviews have been published by Marier (1973) and Walden and Howard (1971). Davis (1976) has reviewed the progress in sublethal effects studies with kraft pulpmill effluents. The latest review by Walden (1976) covers many publications and progress reports from Canada that have not been included in other reviews. However, the majority of the Canadian publications and progress reports, plus reports not covered by Walden (1976) were obtained and cited in this review.

Most of the information on the impact of pulp and paper wastes on the aquatic environment comes from laboratory studies under controlled conditions, with limited data available concerning impacts of effluents in natural ecosystems. However, sufficient studies have been conducted under natural conditions to demonstrate that the effluent can be quite harmful if not properly treated (Filimonova 1968; Washington, State of, 1967; Gregory and Loch 1973a,b; Stone et al. 1974; Dickman 1973; Leppäkoski 1968). Adverse effects on the environment have not been demonstrated with secondary-treated effluents other than as a result of spills or other malfunctions, even though many of these effluents are still acutely toxic at full strength to trout and salmon. Dilution is the primary reason many effluents are apparently not causing major adverse environmental effects, but failure to detect more subtle and longer term effects may also contribute to the apparent lack of adverse impacts.

CONCLUSIONS

1. Large quantities (tons) of toxic and nontoxic materials are released into receiving waters daily by each pulp mill.

2. Untreated pulp and paper mill effluent can be acutely toxic to fish at concentrations as low as 2% by volume. Sufficient treatment can render the effluent virtually nontoxic much of the time; however, treatment processes used by most mills reduce toxicity but do not eliminate it.

3. Toxicity of the effluent to aquatic organisms other than fish is not adequately known.

4. Toxicity of pulp and paper mill effluents is highly variable and treatment reduces this variability but does not eliminate it.

5. Predictive value of the bioassay of pulp and paper mill effluents is considerably reduced by the variable nature of these effluents.

6. Sublethal effects of pulp and paper mill effluents are varied. The threshold concentration for sublethal effects appears to be near 1/10 of the 96-hr LC50 concentration.

7. Except for bleaching effluents which contain several types of chlorinated compounds, natural resin and fatty acids from wood are the principal toxic components of pulp and paper mill effluents.

8. Other chemicals, especially fungicides, can add to the toxicity of the effluents.

9. Untreated effluents have been shown to cause considerable environmental damage, but well-treated effluents have had minimal effects on fish production, although shifts in biological diversity indices have occurred. The apparent lack of adverse effects may be due, in part, to the masking effect of nutrient addition or the inability to detect subtle adverse effects.

10. In artificial stream studies, kraft mill effluents have been shown to increase production of fish and some fish food organisms at low effluent concentrations, presumably through organic enrichment. At higher concentrations of effluent, production of fish and some fish food organisms can be reduced.

RECOMMENDATIONS

1. The toxicity of whole pulp and paper mill effluents to fish has been adquately demonstrated and further bioassays do not appear to be needed except in support of other studies or for effluent management.

2. Further research may be conducted to identify those aquatic organisms more sensitive than fish to pulp and paper mill effluent.

3. The sporadic and dramatic increase in the toxicity of even "well-treated" effluents appears to justify monitoring the toxicity of pulp and paper mill effluents for proper management.

4. The effects of short-term, near-lethal exposures of pulp and paper mill effluents to aquatic life are not known and should be determined.

5. Currently, bioassays are the only reliable method of assessing the effluent's toxicity. However, certain sublethal tests such as the "cough reflex" in fish appear to have some merit as a monitoring tool. Chemical assay of principal toxic components may soon serve to monitor toxicity of the effluent.

6. Toxicity studies necessary to establish water quality criteria or effluent guidelines should be conducted for the principal toxic components in pulp and paper mill effluents. (These compounds include the natural resin acids and fatty acids, the insect juvenile hormone analogs and, in effluents from mills using chlorine bleach, the chlorinated alcohols, chlorinated lignins and chlorinated resin acids and fatty acids.) The effects of the insect hormone analogs on aquatic insects should be determined.

7. The increase in the toxicity of pulp and paper mill effluents following chlorination should be further investigated before requiring chlorination of treated pulp and paper mill effluents.

8. To identify pollution problems, a toxicity survey of pulp mill effluents may be necessary.

LITERATURE REVIEW

PULPING METHODS

The toxicity and other characteristics of pulp mill effluents are largely influenced by the pulping process and its efficiency, the type of wood pulped, and the frequency of malfunctions or spills. Three methods of pulping, or combinations and/or modification of these, are generally used. These are: alkaline digestion, known as the kraft process; acid digestion, known as the sulfite process; and the mechanical or groundwood process. A simplified schematic description of these processes and their effluents is given in Figure 1.

Kraft

Kraft pulp is produced by digestion of wood chips under heat and pressure in a highly alkaline sodium sulfide solution. Digestion results in the formation of black liquor, containing the wood extractives and solubilized lignin, which is separated from the fiber. Weak black liquor is produced in successive washing stages, and only the most dilute wash waters are discharged to sewers. The combined black liquors are concentrated in multi-effect evaporators and the residue is burned in a chemical recovery furnace to retrieve pulping chemicals. The furnace smelt is redissolved, adjusted to strength with fresh chemicals and reused. Approximately 95% of the chemicals are recycled and most soluble organics are burned in the recovery furnace. Condensates from the evaporators are recycled within the pulping process to minimize water use and heat loss.

To produce a white paper the pulp must be bleached with a series of bleaching and extraction steps. Acid bleaching solutions are generally chlorine dioxide or aqueous chlorine, and extraction is with caustic sodium hydroxide. Bleaching is followed by washing and drying to produce a finished pulp. Some mills in Europe use ozone for bleaching which essentially eliminates the toxicity associated with chlorinated compounds in bleaching waste.

This brief description does not reflect the complexity of the kraft process. The design and location of the mill, the type of wood pulped, the additives used and the plant operation influence the toxicity of the effluents.

Sulfite

The sulfite pulp is produced by acid digestion of woodchips in sulfite of ammonia, sodium, calcium, or magnesium. The only other major difference from the kraft process is that the digestion chemicals are not generally recovered, but instead are dumped as sulfite waste liquor (SWL). Rosehart *et al*. (1974)

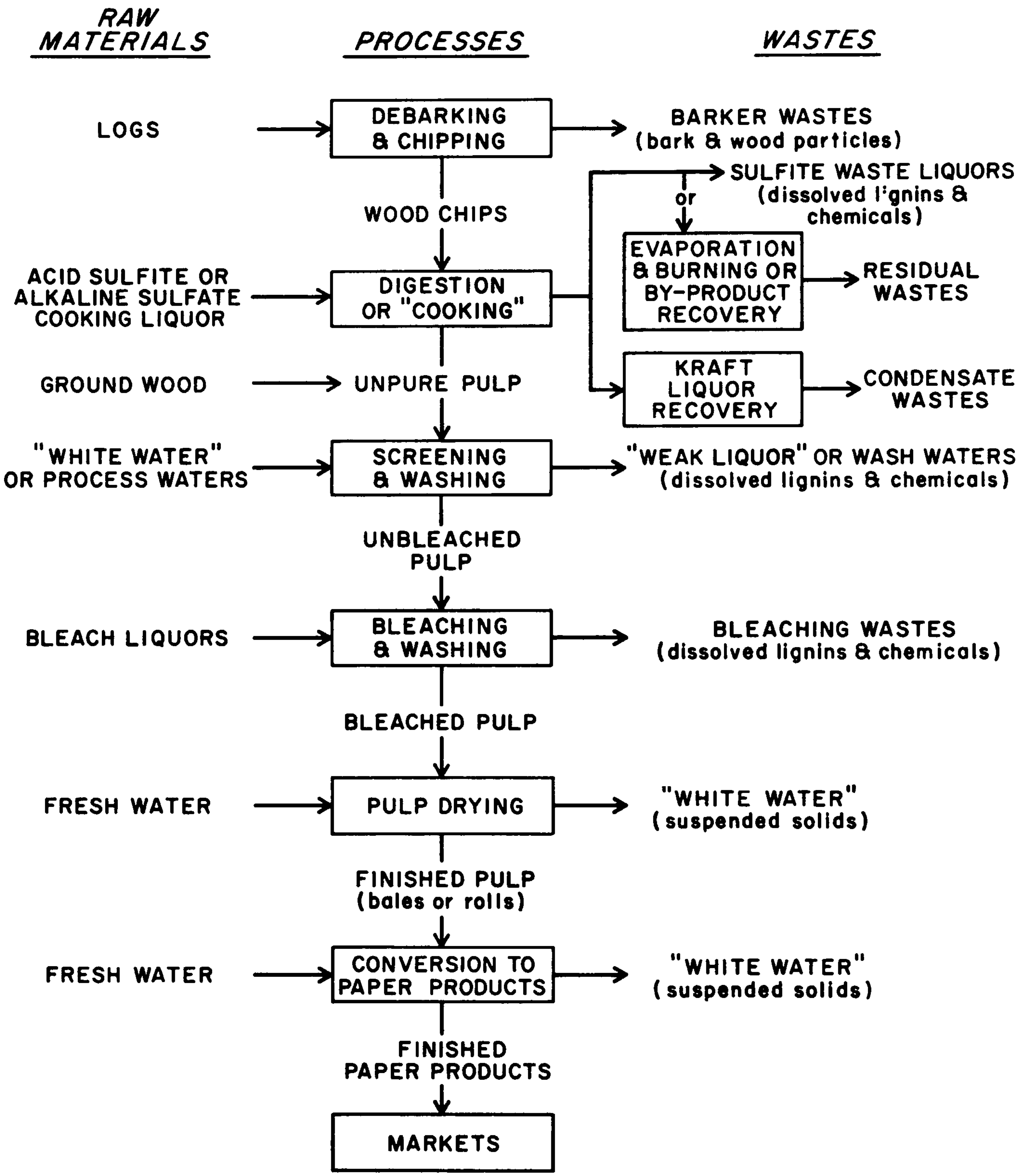

Figure 1. Simplified schematic of pulp and paper processing.

have reported on a sulfite process with good chemical recovery, relatively low toxicity, and apparent operating economy. If this proves successful, the sulfite process may regain some of its previous popularity.

Groundwood

Groundwood pulp is produced by mechanical grinding to separate the fibers in lieu of chemical digestion. This process is generally used for low quality paper such as newsprint or used in combination with other pulp to form products of intermediate quality. Groundwood pulp is not usually bleached.

EFFLUENT CHARACTERISTICS

Kraft

The kraft process uses tremendous volumes of water: older mills use 20,000 gal/ton of air-dried pulp in the pulping process plus 30,000 gal/ton in the bleach plant; newer mills may use 30,000 gal/ton in the overall process. Additional water is used in the paper-making process. Typical mills produce 200-600 tons of pulp per day, so the volume of effluent can be great; 20 million gallons of effluent per day (24 hr) are common. The average 5-day BOD (biological oxygen demand) of kraft pulping effluent is in the range of 200-300 mg/l plus another 15-30 mg/l from bleaching wastes. The combined effluents could contribute 20-40 tons of BOD per day if not treated. Many tons of materials that do not exhibit a significant BOD are also dumped. Considering the volume of effluent, it is obvious that large quantities of dissolved and suspended materials are released into the aquatic environment. The pH of kraft effluent is high, but is normally neutralized before discharge. Color and foam can also cause water quality problems. In addition, fish below the outfall may have an objectionable flavor and odor (Cook et al. 1971).

The principal factors affecting toxicity of unbleached kraft effluent are efficiency of pulp washing and frequency of spills or other malfunctions. Improper washing and improper treatment of wash waters lead to high concentrations of naturally occurring resin acids and fatty acids. Bleaching of pulp usually reduces the concentration of resin acids but toxicity is usually not reduced because some phenolic and other compounds are chlorinated that contribute significantly to toxicity. The nature and toxicity of pulp effluent constituents will be discussed later. The species of wood pulped also influences the characteristic of the effluent.

Sulfite

The sulfite process also requires large volumes of water and the BOD per ton of pulp can be more than ten times that of the kraft process. It is common to find the BOD of raw sulfite effluent near 2,000 mg/l and that of treated (lagooned) effluents near 1,000 mg/l. In fact, the BOD of sulfite waste liquor (SWL) is so high (20,000-30,000 mg/l) that early investigators attributed the principal toxicity of the liquor to BOD depleting the oxygen levels in the test chambers. Generally the toxicity is less than that of kraft waste on a volume basis, because fewer of the naturally occurring resin acids survive the acid digestion process (Walden 1976). If the ammonia base sulfite pulp is subsequently bleached with chlorine, highly toxic chloramines can be formed. Color and foam are not the problem that they are in kraft effluent but some taste and odor problems have been attributed to sulfite effluents. The pH of the untreated effluent has been reported occasionally to fall below 2 and even after treatment in lagoons, a pH of 4 is common.

Groundwood

Mechanical pulping requires about one-third the water used in chemical pulping. The fiber size is usually larger and less fiber is lost in the effluent. As a result, the BOD of the effluent is quite low, 70-80 lb/ton pulp or 500-1500 mg/l for untreated effluent (Howard and Leach 1973b; Leach and Thakore 1974c). Groundwood effluents which have received primary treatment have a BOD of about 125 mg/l. The effluent is slightly acid with a pH of 5 to 6. The toxicity of groundwood mill effluent (GME) is due primarily to natural resin and fatty acids.

TOXICITY TESTING

It will be worthwhile to examine some of the difficulties in assessing the toxicity of pulp and paper mill effluents so that toxicity values presented later may be placed in perspective. One of the problems with bioassays of pulp mill effluent is the variability of effluents, both within a given plant and among plants (Howard and Walden 1971; Walden and Howard 1971; Walden et al. 1971). Howard and Walden (1971) reported the mean survival time (MST) of salmonids varied from 485 to 1298 minutes in full strength bleached kraft mill effluents from seven British Columbia mills during a 40-day period. Depending upon the mill, 21-82% of the samples were not acutely toxic. Gordon and Servizi (1974) monitored the toxicity of a British Columbia bleached kraft pulp mill effluent to sockeye and pink salmon through a year-long series of consecutive 4-day bioassays. They found 94% of the samples were toxic at 90% (v/v) concentration, 76% were toxic at 65% concentration, and 60% were toxic at a 25% concentration. Treated effluents retained some of this variability. With 29-hour aerobic fermentation 29, 15, and 8% of the samples were still toxic at 90, 65, and 25% concentrations. Even with 99-hour treatment 7% of the samples were toxic at 90% concentration. Bruynesteyn and Walden (1971) found considerable variation in the toxicity of samples collected at intervals as short as 15 minutes. Therefore, statements concerning toxicity of an effluent must be made with caution if based on only a few samples. When only a few samples are available one should ascertain that the mill was operating "normally" with no shut downs or spills.

Another variable feature of pulp mill effluents is the toxicity added by many chemicals used in addition to actual pulping chemicals. These chemicals include anti-foam agents, anti-pitch agents, sizings, biostatic agents, etc. A review by Conkey (1968) listed over 100 biostatic agents in use in 1968. The groundwood process is defined as "non-chemical," but 21 chemical additives were used in one mill (Gordon and Servizi 1974). The use of additives fluctuates as need, price availability, and formulations change.

Another feature of pulp mill effluents which tends to make the reported toxicity values less useful is the change in quantity and quality of the effluent in a relatively short period of time through mill expansion, change of process or chemical recovery systems, or improved treatment. The pulping industry in the United States generally has had considerable success in reducing toxicity of their effluents. Therefore, this literature review has concentrated on data published since 1960. Even toxicity data presented early in this period may not be applicable to the current situation. For example, one mill has expanded, and has added terpene recovery systems, secondary aeration lagoon treatment and a polishing basin since initiation of Warren's studies in 1960 (Warren et al. 1974). It appears that, with the variability within a mill and among mills of the same type, meaningful comparisons of toxicity values reported in the literature are difficult to make.

Chemical assays are not yet feasible as a technique for assessing toxicity of pulp and paper mill effluents. Some toxicants have not been identified and consequently can not be determined chemically; moreover, chemical assays of toxicants are toxicologically useful only when related to biological responses. This "dose-response" relationship has not been adequately established for chemicals in pulp mill effluents; therefore bioassays are currently the only method of assessing toxicity of effluents (Betts 1976).

The bioassay of pulp and paper mill effluents poses special problems because of low concentrations of toxicants, high BOD, and chemical instability. Recently, Walden and McLeay (1974) and Walden et al. (1975) have undertaken a detailed study of the problems specific to the bioassay of pulp mill effluents. Walden et al. (1975) suggested that the standard acute toxicity test for pulp mill effluent should be a 96-hr exposure with solution replacement every 24 hr and a fish loading density of less than 0.5 g/l. Sprague (1969) has shown that 96-hr exposure to pulp mill effluents will adequately assess acute toxicity. Minimum exposure time should be 24 hr if a good correlation with 96-hr LC50 is to be maintained.

Solution replacement is necessary during the 96-hr exposure because of loss of toxicants through degradation or uptake by the fish. The required frequency of replacement depends on stability of the toxicants and fish density. Raw effluent requires more frequent replacement than do treated effluents. In a series of tests by Walden et al. (1975), depletion of toxicants by the fish was slight at fish densities of 0.5 g/l in static 96-hr tests with primary treated effluent, however, fish densities of 2 g/l required solution replacement every 24 hr.

Solution replacement can be achieved either by static replacement of the solution or by flow-through replacement. Static replacement simply entails periodically placing the fish into a new solution of the desired concentration. The flow-through system provides a more constant exposure but requires larger volumes of effluent. Betts et al. (1967) devised a flow-through apparatus for replenishing test solutions which requires only a small volume of effluent. However, the replacement rate was no greater than achieved by direct transfer of the fish into a new solution every 12 hr. This flow-through system required 10 times more effluent than simple static replacement.

Walden et al. (1975) reported very little difference in 96-hour LC50 values between flow-through bioassays and those with static replacement of the test solutions. Handling of the fish during transfer into new solutions every 12 hr did not appear to cause undue stress. In comparative tests, Walden and McLeay (1974) reported that 96-hr LC50 values for 12-hr and 24-hr solution replacement were similar, however, 96-hr LC50 values were considerably higher with 48-hr replacement of test solutions.

Walden (1976) has classified various acute toxicity tests as to their sensitivity in terms of toxic units. He assigned unity to the concentration killing 50% of the fish in 96 hr with static replacement every 24 hr and a fish density of 2 g/l. This sensitivity data may make it possible to compare toxicity tests of varying duration, replacement rates, fish density, and percent mortality.

The majority of acute toxicity tests reported do not conform to the standard test proposed by Walden et al. 1975. For practical reasons 24-hr exposures are often used. In the interest of conserving time and effluent, mean survival time (MST) in full strength effluent is often given as the end point—a procedure recommended by Walden and McLeay (1974) for rapid effluent monitoring since death is usually quite rapid and solution change is unnecessary.

The dissolved oxygen concentration in test solutions should be maintained near 9.0 mg/l at 15 C to avoid influences of reduced oxygen concentration on toxicity of the effluent to salmonids (Ozburn et al. 1973, 1974; Hicks and DeWitt 1971). These high oxygen levels cannot be maintained with static replacement of test solutions because of the high BOD and, therefore, oxygen must be added. Procedures for adding oxygen can lead to depletion of unstable toxic materials through volatilization and oxidation. Direct addition of minimal amounts of oxygen through small tubes appears to be the best way to maintain oxygen levels without considerable reduction in toxicity, although some reduction is unavoidable (Walden and McLeay 1974; Blosser and Owens 1970).

Little information is available on the influence of pH on the toxicity of pulp mill effluent. Ladd (1969) reported coho salmon (Oncorhynchus kisutch) survived longer in bleached kraft mill effluent (BKME) when pH was between 8 and 9. Leach and Thakore (1974a) have shown that pH values just below 7 increased the toxicity of the resin acids in the effluent. High pH values in ammonia-base sulfite wastes can cause toxicity due to un-ionized NH_3 (Tabata 1965).

Most acute bioassays with salmonids have been conducted at temperatures between 10 and 15 C. Walden et al. (1975) proposed 15 C as a standard. High test temperatures can increase the toxicity of the waste (Loch and MacLeod 1974). Solution replacement rate may have to be increased at higher temperatures because of the increased rate of breakdown of toxic substances.

Effects of storage of the effluent prior to an assay must not be overlooked. Davis and Mason (1973) have cited instances where toxicity declined, remained the same or increased with storage. Degradation of toxic constituents can occur during storage even at temperatures near 0°C (Howard and Walden 1965; Servizi et al. 1966; Webb and Brett 1972). This is particularly true of untreated effluent. If the effluent has received adequate secondary treatment, storage at very low temperature is not necessary if oxygen can be kept from the effluent (Walden and McLeay 1974). For example, samples can be held at temperatures up to 25 C for four days prior to the test with virtually no loss of toxicity. Storage at elevated temperature under anaerobic conditions can lead to the formation of hydrogen sulfide. The odor is evidence of the problem and the sample should be discarded.

Low temperature during the treatment process can lead to inadequate secondary treatment and increased toxicity. This is a particular problem in most northern mills (Howard and Leach 1973b) although Seim et al. (1977) reported this may happen even in Oregon's temperate Willamette Valley.

Rainbow trout (Salmo gairdneri) have been suggested as the standard test species on the basis of availability and ease of maintenance under laboratory conditions. Considerable evidence shows that the rainbow is at least as sensitive as any salmon. Warren and Doudoroff (1958) have suggested the guppy (Poecila reticulata) be used for routine bioassays of pulp effluent because of the difficulty in maintaining adequate oxygen concentration for salmonids without undue oxidation of the sample and because much less effluent is needed for the guppy bioassay. Numerous other fish species have been used as test animals and may have advantages in specific locations. Salmon between ages of 50 and 450 days appear to have similar sensitivities to bleached kraft effluent, however, salmon embryos are more resistant (Holland et al. 1960). Based on the reaction of salmonids to some chemicals, ages between 20-40 days (post-hatch) may be the most sensitive (Larson et al. 1977).

Other problems associated with acute bioassays of pulp effluent include slime growth on flow-through dilution apparatus and the color of kraft effluent. Vigorous treatment of kraft effluent reduces its toxicity considerably but not its color. The high concentrations of treated effluent necessary to kill fish are often so colored that the fish are difficult to observe.

ACUTE TOXICITY OF PULP AND PAPER MILL EFFLUENTS

Much data are available concerning acute toxicity of pulp and paper mill effluents to fish, particularly salmonids, but information concerning the effect of pulp effluents on invertebrates and algae is limited. Much of the more recent toxicity data has come from private research groups sponsored by the pulp and paper industry. In the United States, the National Council for Air and Stream Improvement (NCASI) located at several universities throughout the country, is responsible for the bulk of the toxicity information available. In Canada considerable work is being done on all phases of effluent toxicity. B.C. Research personnel (Walden, Leach, McLeay, Thakore, and Howard) at Vancouver, British Columbia are responsible for a considerable portion of our knowledge concerning the factors affecting the toxicity of kraft and groundwood pulp mill effluents, including analyses of toxic constituents. Wilson and Chappel of Bio-Research Laboratories, Ltd., Quebec, have done similar work for sulfite mills. Much of the Canadian work has been published in progress reports of the CPAR (Committee for Pollution Abatement Research), a cooperative effort of the Canadian Department of Environment and the pulp and paper industry. Portions of these studies have been published. More information will be forthcoming from NCASI and CPAR, as their programs continue.

Table 1 summarizes some of the 96-hr LC50 data available on whole unbleached and bleached kraft-, groundwood-, and sulfite-mill effluents. Also included in this table are toxicity data for some of the major process streams. Bark and woodroom leachates are included because they contain most of toxic components found in unbleached kraft and groundwood effluents, however, these components are more concentrated in the leachates than in whole effluents. Sulfite waste liquor (SWL) data are included because they likewise contain most of the toxic constituents present in whole effluent. However, the SWL stream is many times more toxic than the whole sulfite mill effluent (SME).

The 96-hr LC50 concentrations given in Table 1 are expressed as percent by volume. The concentration of toxic materials in the effluent is usually not known, therefore, the concentrations in the dilutions are also unknown. Water use in relation to the volume of wood pulped will, to a large extent, determine the concentration of toxic components. The concentration of sulfite mill effluent has sometimes been given as mg/l based on the Pearl Benson Index (PBI) which is an indication of the amount of lignin present. PBI is not currently used as an expression of concentration since it measures only one group of compounds that contributes little to the toxicity of the effluent (Walden and McLeay 1974). Expressing effluent concentrations in terms of total resin acids has failed to predict acute toxicity, even though their contribution to toxicity is quite high (60-80% for unbleached kraft), because the composition of the total resin acids is variable. In addition, resin acids are not the major toxicant in bleached pulp mill effluent (Leach and Thakore 1977). In a study by Wilson and Chappel (1973), the toxicity of sulfite wastes from several mills correlated well to the dissolved-solids concentration, but not to volume-to-volume dilutions. Considering the variable factors influencing the toxicity of pulp effluent and the variable assay procedures used, only very general conclusions can be made from a collection of LC50 values such as those listed in Table 1.

Kraft

Whole, unbleached kraft mill effluent can be quite toxic, with 96-hr LC50 values of only a few percent by volume for salmonids held in effluents receiving only suspended solids treatment. Conversely, well-treated effluent can be nontoxic even at full strength (Seim *et al*. 1977; Tokar and Owens 1968). In the only study reviewed here where salmonid and non-salmonid fishes were used to test with the same effluent, Tokar and Owens (1968) found young guppies were slightly more sensitive than were juvenile chinook (*O. tshawytscha*). However, the guppies were exposed at a higher temperature (25C) than the salmon (15C).

Kraft mill effluent (KME) can also be toxic to fish food organisms. Only a limited number of studies have been reported where the same effluents were used with both invertebrates and salmonids. Micro-crustaceans and insect larvae appear to be only slightly more resistant than salmonids (Van Horn *et al*. 1949, 1950; Dimick and Haydu 1952; Livintsev 1967). Fahmy and Lush (1974) showed a chironomid (*Chironomus tentans*) larva to be more sensitive

TABLE 1. CONCENTRATIONS OF PULP AND PAPER MILL EFFLUENTS LETHAL TO AQUATIC LIFE.

Effluent type	Species	96hrLC50 (% by volume)	Comments	Reference
Kraft (KME)	Rainbow trout	< 15	Integrated newsprint	Loch & MacLeod 1973
	" "	15-50	---	Loch & Bryant 1972
	"	755 mg/l (PBI)[a/]	---	Jacobs & Grant 1974
	"	26	Untreated newsprint	Wilson 1975
		> 100	Biotreated	Fahmy & Lush 1974
	"	< 15	---	Loch & MacLeod 1973
	Chinook salmon	4-24	Primary treatment	Seim et al. 1977
	" "	> 100	Secondary treatment and stabilized (SKME)	" "
	" "	7	Primary treatment Mill A	Tokar & Owens 1968
		40	" " Mill B	" " "
	Coho salmon	> 100	SKME non-chlorinated effluent	Stiles 1977
	" "	18-32	SKME chlorinated effluent	" "
	Perch	24	---	Cook et al. 1971
	Guppy	4.5	Primary treatment	Tokar & Owens 1968
	Oppossum shrimp	4.7	Untreated 17°C	Jacobs & Grant 1974
	" "	2.6	" 26°C	" " "
	Marine invertebrates	3.7 (ave.)	Clams, mussels, sea worms, zooplankton tested (abstracted article, details not available)	Donnier 1972
	Daphnia & insect larvae	"Toxic"	---	Van Horn et al. 1949
	Insects and trout	"	Sensitivity: Chironomus > trout > gammarus > mosquito	Fahmy & Lush 1974
	Micro-crustaceans	"Toxic"	Slightly more resistant than salmonids (Abstracted article—details not available)	Litintsev 1967
	Micro-crustaceans		Sensitivity: Gammarus > Daphnia > cyclops	Wilson 1975
	Stonefly	"Lethal"	Lethal conc. 0.1 × 24hr LC50 for guppy	DeWitt 1963
	Stonefly larvae	"Toxic"	Slightly more resistant than salmonids	Dimick & Haydu 1952
	Phytoplankton	2.5	Coccochloris sp. Untreated effluent	Rainville et al. 1975
	"	> 100	" Secondary treatment	" "
Kraft-bleached (BKME)	Rainbow trout	32	---	Loch & MacLeod 1973
	" "	4-10	Non-chlorinated effluent	Seppovaara 1973
		0.6	Chlorinated effluent	" "
	Chinook and Coho salmon	1.9-3.6	Untreated	Holland et al. 1960
	Chinook salmon	6.5	Secondary treatment	Loch & MacLeod 1973
	Sockeye salmon	34-64	Demonstrated acclimation to toxicant	Howard & Walden 1965
	" "	12-43	---	Servizi et al. 1966
		60% tests toxic @ 25% v/v	Biobasin treated	Gordon & Servizi 1974
	"	7% tests toxic @ 90% v/v	99 hr additional treatment	
		12-15	Untreated	Howard & Walden 1974
	Atlantic salmon	12-15	Untreated	Sprague & McLeese 1968
	" "	14	Untreated	Betts & Wilson 1966
	Guppy	34-36	---	Howard & Walden 1974
	Pontogammarus	12	A crustacean	Gazdziauskaite 1971a

TABLE 1. CONCENTRATIONS OF PULP AND PAPER MILL EFFLUENTS LETHAL TO AQUATIC LIFE. (continued)

Effluent type	Species	96hrLC50 (% by volume)	Comments	Reference
Sulfite (SME)	Pacific salmon	2	Untreated; Na and Ca base mills	Rosehart *et al.* 1974
	" "	3-45	Untreated Mg base	" "
	Atlantic salmon	25-60	Untreated, Na base, high yield	Wilson & Chappel 1973
	" "	11-24	Untreated, Na base, low yield	" " "
		15	NH_4 base including bleachery wastes	
Sulfite (SWL)	Pacific salmon	0.7-1.45	---	Rosehart *et al.* 1974
	" "	2,340 mg/l (PBI)	Neutral sulfite semi-chemical process	Kondo *et al.* 1973
	Rainbow trout	3,000 " "	Aged 5 days	Wilson 1972
	" "	0.18-0.29	Samples limited to red liquors, NH_4 base	Grande 1964
	" "	1.1-3.5	" " " " " Mg base	Wilson & Chappel 1973
	" "	8-12	Main sewer	" " "
	Atlantic salmon	2,500 mg/l (PBI)	---	Wilson 1972
Groundwood (GME)	Pacific salmon	1-2	Mixed hardwood and softwood—maritime mill	Leach & Thakore 1974c
	" "	Varied	Mixed wood species—many mills	Howard & Leach 1973b
	Rainbow trout	25	Groundwood and some BKME effluent	Wilson 1975
	Daphnia	14-18	" " " " "	" "
	Gammarus	18-32 (72 hr)		"
	Cyclops	> 100	" " "	
	Snail	> 100	"	
Wood and debarking leachates	Rainbow trout	0.2-4	Fir and spruce wood, nontoxic when bio-treated 3 days	Howard & Leach 1973a
	" "	0.2-2	Pine, fir, and spruce wood, nontoxic if treated > 5 days	"
	"	9-45	Dense hardwoods	
	"	~ 1	Estimated LC50 from % survival in 1% solution	McKague 1975
	"	1.5-6	Jackpine wood; > 5 day treatment required to detoxify	Howard & Leach 1973a
		0.2-10	Softwoods (bark leachates)	Leach *et al.* 1974

[a]/Concentration expressed as Pearl Benson Index, an index to the amount of lignin present.

than rainbow if the chironomid had no sediment in which to burrow. Juvenile amphipods (Gammarus pseudolimnaeus) were more sensitive than were adults, but there were no differences in sensitivity among instars of either chironomid or mosquito (Aedes aegyptii).

Rainville et al. (1975) reported that untreated KME was as toxic to algae as to salmon; however, secondary treatment rendered the effluent nontoxic to algae, but slight toxicity to salmon was retained. Wilson (1975) reported reduction of growth of green algae was a more sensitive test than was death of Daphnia magna, Gammarus fasciatus or rainbow trout, all of which were much more sensitive than the growth of bluegreen algae or death of Cyclops sp. Reduced algal growth may have been the result of increased death rate of cells.

Sulfite

Early investigators seldom demonstrated acute toxicity of sulfite effluents other than that caused by high oxygen demand. More recently, acute toxicity of whole sulfite effluent to juvenile Pacific salmon (Oncorhynchus spp.) and Atlantic salmon (Salmo salar) has been reported at concentrations as low as 2-3% v/v, indicating that untreated sulfite effluent can be as toxic as kraft effluent; however, many 96-hr LC50 values have been reported between 20 and 60%. Effluents from the NH_4-base mills are not appreciably more toxic than those from Na-, Ca-, or Mg-base mills (Rosehart et al. 1974). However, effluent from an NH_4-base mill utilizing bleach process was five times as toxic as unbleached NH_4-base sulfite effluent (Wilson and Chappel 1973). Lagoon treatment lowered the toxicity of whole effluent (including bleaching effluent) to near that of unbleached raw effluent.

Very little recent work has been reported on acute toxicity of sulfite wastes to invertebrates, particularly with whole effluent. Gazdziauskaite (1971a,b) reported sulfite mill whole effluent was "toxic" at 12.5% to the freshwater shrimp Pontogammarus. Numerous studies have been reported concerning the effect of sulfite wastes on bivalves, but the effect studied has been abnormal development, not death, although the abnormalities often resulted in death (Stein et al. 1959; Woelke 1960, 1965; Woelke et al. 1970).

Most studies with sulfite effluents have been conducted with spent sulfite waste liquor (SWL) stream rather than whole effluent. SWL constitutes the majority of the whole effluent and contains most of the toxic agents. With the exception of bleaching effluents which are uncommon in sulfite mills, inclusion of other process streams usually lowers the toxicity of SWL (Wilson and Chappel 1973).

Groundwood

Reports concerning the toxicity of mechanical pulping effluents are limited. This may be due to the belief that chemicals used in the other pulping processes are primarily responsible for the toxic effects. Relatively few chemicals are used in the groundwood process yet effluents of these mills can be as toxic as any chemically produced pulp effluent. The 96-hr LC50 for untreated groundwood effluent averages 5-10% (Howard and Leach 1973b), and values as low as 1-2% have been reported (Leach and Thakore 1974c). The toxicity is due to the natural resin acids and fatty acids (Row and Cook 1971). Leach and Thakore (1974c) surveyed a number of Canadian groundwood pulp mills and reported toxicity was a function of waste recycle and type of wood pulped. Pine effluents are considered most toxic, followed by fir and spruce. Hardwood effluents are the least toxic when groundwood pulped. The season the wood is cut also has some influence on the toxicity of the effluent (Howard and Leach 1973b).

Potential toxicity of groundwood effluent to invertebrate species was indicated in a study of newsprint operations which utilized groundwood pulp and purchased kraft pulp. This effluent at 20 C was nontoxic to Cyclops at 100% but toxic to Daphnia at 14-18% and Gammarus at 18-32% as compared to 25% for rainbow trout at 15 C. No deaths were observed with snails (Bithynia sp) but they showed a strong avoidance reaction by crawling out of the test chammers. Green and blue-green algae were also exposed to the effluent, and cell biomass was reduced in concentrations >50% (Wilson 1975).

Bark- and woodroom- leachates contain most of the toxic constituents found in groundwood effluent, show similar toxicities, and therefore are included in the groundwood section. These effluents can be a process stream in kraft and sulfite mills as well. Less water is used per ton of material during the debarking and chipping process than during mechanical pulping so the effluents from the woodroom and debarking plants are generally more toxic on a volume basis. Acute toxicity values (96-hr LC50) of 0.2 to 2% were reported for woodroom effluent when pine was processed and 9 to 45% when hardwood was processed (Howard and Leach 1973a,b; Leach and Thakore 1974c). Groundwood effluent and woodroom- and bark- leachates respond to biotreatment in a similar manner. These effluents from pine processing required more than 5 days biotreatment to render the effluent "nontoxic" during the 96-hr acute bioassay; effluents from fir, spruce, and hemlock required 3 to 5 days, and those from hardwoods 1 to 3 days. Such detoxification does not guarantee that the effluent will not have a long-term or sublethal effect on aquatic life.

SUBLETHAL EFFECTS

The objective of investigation of sublethal effects is to determine the nature of sublethal stress or effects due to pollutants, and then to measure the threshold levels below which no effect can be observed. Stresses are usually cumulative; one stress may ultimately reduce an organism's capability to meet other stresses and, therefore, can influence the organism's survival. Not all sublethal effects of pollutants are necessarily detrimental. Sprague (1971) reviewed general procedures for sublethal effects measurements and discussed the problem of ascertaining "safe" levels for pollutants.

Known sublethal effects of pulp and paper effluents are attributed to conifer fibers, volatile reduced-sulfur compounds, and nonvolatile soluble toxic components. Table 2 lists much of the recent data on sublethal effects of whole pulp mill effluent on aquatic organisms. Most of the work has been with salmonids, with only a few observations on invertebrates and algae. The table is arranged by system affected. Because of the large variation in toxicity of pulp mill effluents, sublethal effects are expressed as a fraction

TABLE 2. SUBLETHAL EFFECTS OF PULP AND PAPER MILL EFFLUENTS ON AQUATIC LIFE.

Effects	Species	Effluent type	Threshold concentration: fraction of 96-hr LC50	Threshold concentration: % volume	Comments	Reference
RESPIRATORY						
Coughing response elevated	Rainbow trout	KME	0.08-0.18	11	Immediate effect	Walden *et al.* 1970
" " "	" "	"	0.5[a]		Untreated; (treated no effect)	Schaumburg *et al.* 1967
"	Sockeye salmon	BKME	0.1-0.2		Possible adaptation	Davis 1973
Ventilation volume increased	" "	"	0.2		Immediate effect	" "
Oxygen uptake increased			0.33		" "	"
" " "	*Pontogammarus*	SME	---	12	LC50 independent of life stage	Gazdziauskaite 1971a,b
	Salmonids	SWL	> 1.0	100		Williams *et al.* 1953
CIRCULATORY						
Arterial oxygen tension reduced	Rainbow trout	BKME	0.47		No adaptation	Davis 1973
" " " "	Sockeye salmon	"	0.33		" "	" "
White blood cells reduced	Coho salmon	KME	0.1	2.4	21 day expos.	McLeay 1973
Blood neutrophil count elevated	" "	"	0.25		200 day expos.	Howard & McLeay 1972
Hematocrit reduced	Sockeye salmon	KME	---	1.5	8 week expos.	Webb & Brett 1972
Small lymphocytes decreased	Coho salmon	"	> 0.33		25 day expos.	McLeay 1973
Neutrophilis increased	" "		"		12 day expos. (returned to normal in 25 days)	" "
Hematocrit reduced	"		"		25 day expos.	Howard & Walden 1967
Blood values reduced	Rainbow trout	SME	---		Abstracted article	Seppovaara 1973
" " "	Carp	"			" "	" "
" " "	*Pontogammarus*		---	12-25	Increased respiratory quotient	Gazdziauskaite 1971b
METABOLISM						
Plasma glucose elevated	Coho salmon	BKME	0.8[a]	44	Fish also stressed by swimming	McLeay & Brown 1975
" "	"	KME	0.1		200 day expos.	Howard & McLeay 1972
" "	" "	"	0.0-0.3		Increased for 12 days; decreased in 25 days.	McLeay 1973
"	Rainbow trout	BKME	0.1-0.25		200 day expos.	McLeay & Brown 1974
Body protein decreased	" "	"	"		" " "	" " "
Muscle protein depressed	Coho salmon		0.1		"	Howard & McLeay 1972
Liver glycogen depressed	*Sparus macrocephalus*	KME	---	3.2-6.2	12-24 hr. expos. in river	Fujiya 1961
"	Coho salmon	BKME	0.1		" " " "	Howard & McLeay 1972
Liver RNA decreased	*S. macrocephalus*	KME	---		" " "	Fujiya 1961
Blood and muscle lactate increased	Coho salmon	BKME	0.25		200 day expos.	Howard & McLeay 1972
Swimming ability reduced	" "	KME	0.1-0.2	1.8-9.0		Howard 1975
" " "	*Pontogammarus*	SME		12-25	Abstracted article	Gazdziauskaite 1971a,b

TABLE 2. SUBLETHAL EFFECTS OF PULP AND PAPER MILL EFFLUENTS ON AQUATIC LIFE. (continued)

Effects	Species	Effluent type	Threshold concentration: fraction of 96-hr LC50	Threshold concentration: % volume	Comments	Reference
BEHAVIOR						
Avoidance	Sockeye salmon	BKME	0.8		Bleachery wastes—not whole effluent	Servizi *et al*. 1966
"	Atlantic salmon	KME	0.37	50	Strong response	Sprague & Drury 1969
	" "	"	0.0006		Vague response	" " " "
"	Chinook salmon	KME	---	5-10		Jones *et al*. 1956
"	" "	"	---	50	Variable results	Dimick *et al*. 1957
"	Lobster	BKME	---	> 20	Bleachery wastes	McLeese 1970
"	Snail	KME & GME	---	---	Lowest level tested	Wilson 1975
"	Salmonids	SWL	---	---	Avoid low but not high conc.	
No avoidance	Coho salmon & Steelhead	KME	---	100	Variable results	Dimick *et al*. 1957
Drift increased	*Gammarus*		---	> 1		Galtsoff *et al*. 1947
Orientation to current	Sockeye salmon	BKME	0.8	---	Bleachery wastes	Servizi *et al*. 1968
Alarm response slowed	" "	"	0.4	---	" "	"
Unresponsive	Coho salmon	KME	0.15	---		Davis 1973
Feeding reduced	" "	"	0.1-0.2	---	Response lasted 2 wks.	" "
" "	Chinook salmon	"	0.14-0.36	---	Long term study	Ellis 1967
" "	" "	"	0.1-0.3	---	2 week expos.	Tokar & Owens 1968
" "	*Pontogammarus*	SME		12-25	LC50 independent of life stage	Gazdziauskaite 1971a,b
" "	Lobster	BKME		> 10		McLeese 1970
No feeding	Salmonids	KME		100		Williams *et al*. 1953
MORPHOLOGY, HISTOLOGY						
Liver, kidney, intestine	*Sparus macrophalus*	KME	---	3.2-6.2	12-24 hr expos. in river	Fujiya 1961
Liver	Chinook salmon	KME	---	33[t]	"Synthesized wastes" 7 day expos.	Holland *et al*. 1960
Opaque eyes	" "	"	---		" "	"
" "	" "		---	6.6	"	" "
Abnormalities increased	Oyster	SWL	---	6-12 mg/l (PBI)[b/]	> 20% increase in abnormalities	Woelke 1960
" "	Clams	"	---	1-3 mg/l (PBI)	" " " "	Woelke *et al*. 1970
" "	Oyster		---	0.15-0.5	Mg base most toxic (untreated effluent)	1970, 1972
GROWTH						
Growth rate reduced	Sockeye salmon	KME	---	10-25	8 wk expos.	Webb & Brett 1972
" " "	" "	BKME	0.05-0.1	---	---	Servizi *et al*. 1966
" " "	Chinook salmon	KME	0.14-0.35	1.5	---	Ellis 1967
" " "	" "	"	0.1-0.3	---	---	Tokar & Owens 1968
" " "			---	6	---	Warren 1972

TABLE 2. SUBLETHAL EFFECTS OF PULP AND PAPER MILL EFFLUENTS ON AQUATIC LIFE. (continued)

Effects	Species	Effluent type	Threshold concentration: fraction of 96-hr LC50	Threshold concentration: % volume	Comments	Reference
GROWTH (cont)						
Growth rate reduced	Chinook salmon	KME	1 mg/l BOD[c]	4.5	30 day expos. treated effluent	Borton 1970
" "	Coho salmon	"	0.12-0.14	0.6	30 day expos.	Holland et al 1960
" "	Pontogammarus	"	---	12-25	---	Gazdziauskaite 1971a
" "	Oyster larvae		---	0.15-0.5	Untreated effluent	Woelke et al. 1972
" "	" "		---	1.3	Treated effluent	" "
" "	Coho salmon		0.1-0.2	---	Several wk. exp.	Davis 1973
" "	" "		0.1-0.25	---	70 day expos.	Howard & McLeay 1972
" "	"		> 0.25	---	---	McLeay & Brown 1974
" "	Green algae	SME	---	15	Abstracted article	Seppovaara & Hynninen 1970
" "	Selenastrum	KME & GME	---	25	(a green algae)	Wilson 1975
" "	Senedesmus	" "	---	50	(a green algae)	" "
" "	Anabaena		---	50	(a blue-green algae)	
" "	Selenastrum		---	50	(a green algae)	" "
" "	Senedesmus	" "	---	50	(a green algae)	" "
"	Anabaena	"	---	50	(a blue-green algae)	"
Growth efficiency reduced	Sockeye salmon		---	10-25	8 wk. expos.	Webb & Brett 1972
" " "	Chinook salmon	" "	0.06-0.12	0.4-0.9	12 day expos.	Tokar & Owens 1968
PRODUCTION-ABUNDANCE						
Production reduced	Chinook salmon	KME	0.19	1.5	Lab streams; winter, biotreated effluent	Seim et al. 1977
"			0.08	---	Lab streams (untreated effluent)	Ellis 1967
" "		" "	0.03 mg/l BOD	1.5	Lab streams (untreated effluent)	Lichatowich 1970
"	Caddis larvae	"	0.75 mg/l BOD	0.35	Stream channel (prim. treatment)	Warren et al. 1974
"	Amphipods		"		" " "	
" "	Fish food organisms		---[d]	---	Outfall area (Cladocera and rotifers absent)	Filimonova 1968
Production enhanced	Chinook salmon		0.2	1.4	Lab streams (stabilized effluent) Mill B	Lichatowich 1970
" "	"		1.5-3.0 mg/l BOD	0.7-1.5	Lab streams (prim. treated effluent) Mill B	"
"	"	"	1.5 BOD	7.5	Lab streams (stabilized effluent) Mill A	
" "	Amphipods	"	---	5	Stream channels (treated effluent)	Warren et al. 1974
" "	Snails	"		0.2-5	Stream channels (treated and untreated effluent)	
Diversity change	Insects	"	---[e]		Stream channels (untreated effluent)	Warren et al. 1974
"			---	100	Treated effluent channel	Shireman 1975

a/ tested concentration, not a threshold value
b/ Pearl Benson Index, an index to the amount of lignin present
c/ effluents were not acutely toxic, therefore effective concentrations were expressed as 5-day BOD.
d/ threshold concentration given as 0.5 of the 96-hr LC50 value for rainbow trout.
e/ " " " " 0.05 " " " " " " Chinook salmon.

of the LC50 value for that organism. If known, the percents by volume (% v/v) are included. In cases where 100% effluent was not acutely toxic the concentration has sometimes been expressed as mg/l BOD.

Because the data in Table 2 were derived from many effluents and over a considerable period of time, meaningful comparisons between tests are difficult to make. However, one can see some general trends in threshold concentrations in terms of 96-hr LC50 values. If the same compounds causing acute toxicity also cause the sublethal effects, threshold concentrations expressed as a fraction of the LC50 values should compensate for the difference in the concentration of the toxic constituents among these effluents and, thus, make comparisons of sublethal tests among mills more meaningful. For example, the threshold of sublethal effects of kraft mill effluents frequently appears to be about 1/10 of the 96-hr LC50 (0.1 LC50) concentration but could be almost any v/v concentration depending upon the mill sampled. Several sublethal tests showed effects at concentrations below 0.1 LC50. These were: the cough response in rainbow trout at 0.08 LC50 (Walden *et al*. 1970); reduced salmon production in laboratory streams at 0.08 LC50 (Ellis 1967); reduced growth of sockeye salmon (*Oncorhynchus nerka*) at 0.05 LC50 (Servizi *et al*. 1966); and reduced temperature tolerance of Coho salmon at 0.06 LC50 (Howard and Walden 1974). These more sensitive tests should be considered when sublethal effects of pulp mill effluents are to be studied.

Kraft

The effects of kraft mill effluents on respiration are evidenced by increased coughing, ventilation volume and oxygen uptake rate (Walden *et al*. 1970; Schaumburg *et al*. 1967; Davis 1973). These effects are exhibited rather rapidly and can be used in short term tests. Davis (1973) has shown that respiration effects diminish with long exposures and that the usefulness of these effects in continuous monitoring as suggested by Schaumburg *et al*. (1967) may be lessened. The threshold of the respiration tests is somewhere near 0.1 LC50.

The circulatory system was affected by kraft effluent resulting in reduced arterial oxygen tension and white blood cell count, small lymphocyte count, low hematocrit level, and elevated blood neutrophil count (Davis 1973; Howard and McLeay 1972). McLeay (1976) has developed a sublethal test which uses a "chemical profile" of biochemical responses in fish exposed to low concentrations of kraft mill effluent. After a few hours exposure to sublethal concentrations, blood parameters are significantly altered as are the glycogen and lactic acid contents of several tissues. The biochemical techniques have advantages because they have been completely automated by medical science and only small blood samples are necessary. The effects of pulp mill effluents on some of these biochemical parameters have also been reported to show adaptation after several days of exposure and may indicate that no permanent harm has been done to the fish (Davis 1973; McLeay 1973).

The effect of kraft mill effluents on metabolism in fish was evidenced by elevation of plasma glucose and blood lactate levels and depression of body protein, muscle and liver glycogen, and swimming ability. The range of sensitivities of these tests was 0.1 to 0.3 LC50 concentration.

Avoidance behavior often protects an organism from exposure to potentially lethal toxic materials. Some salmonids appear to detect concentrations of KME as low as 5% v/v but most avoid only much higher concentrations. Well-defined avoidance occurred only at concentrations approaching lethal levels (Dimick et al. 1957; Jones et al. 1956; Servizi et al. 1968). The increased drift of amphipods in streams containing 10% KME may have been an avoidance reaction (Ellis 1967; Galtsoff et al. 1947). Lobsters (Homarus americanus) have been shown to avoid concentrations of 20% or more (McLeese 1973). Snails (Bithynia) avoided, by escaping from the test containers, all concentrations (unspecified) of KME and GME tested, but when escape was prevented they survived even at 100% concentrations (Wilson 1975).

Feeding behavior is also influenced by KME. Appetite of juvenile coho and chinook salmon was reduced at concentrations of 0.1 to 0.36 LC50 (Davis 1973; Ellis 1967; Tokar and Owens 1968). Loss of attraction to food was reported in lobster at concentrations greater than 10% v/v (McLeese 1973; Galtsoff et al. 1947).

Morphological and histological changes in fish following exposure to kraft mill effluents have been observed. Holland et al. (1960) exposed chinook to "synthetic" wastes (bench-produced pulp wastes) for seven days and observed opacity of their eyes, discolored liver, and hemorrhages. Fujiya (1961) held the fish, Sparus macrocephalus, in live-boxes below pulp mill outfall for 12-24 hr. He reported considerable damage to the liver, kidney and intestine, but these results could not be substantiated by McLeay (1973). However Fujiya (1964) was subsequently able to duplicate his results and concluded that either the mill's effluent was reacting with some unknown constituent in the river water to produce the drastic effect or the effluent was particularly toxic.

A stress imposed on an organism may lower its tolerance to other factors. Howard and Walden (1974) have shown that very low concentrations of BKME (0.06-0.23 LC50) reduced the upper temperature tolerance in coho salmon. Starvation time to death in coho salmon was reduced at 0.4 LC50 of untreated BKME but treated BKME showed no effect at 0.7 LC50 (Brown and McLeay 1975). The decreased starvation time would be indicative of increased metabolic rate.

Growth of fish is generally decreased by KME. Concentrations as low as 0.05 LC50 reduced growth in sockeye salmon (Servizi et al. 1966). Other authors have reported threshold values for reduced growth up to 0.35 LC50 for salmonids (Table 2). Davis (1973) and Howard and McLeay (1972) observed reduced growth in coho for several weeks, followed by growth enhancement. Apparently the coho salmon adapted to the effluent and eventually gained some benefit from it.

Warren et al. (1974) developed a growth test that appears to be very sensitive. They used natural and artificial foods that, when uneaten, could be recovered and the actual food consumption rate determined. Fish are fed a series of rations from near-maintenance to satiation at each effluent concentration and food consumption and growth are measured. Growth can be restricted by decreased food intake (loss of appetite) or by a decrease in the efficiency of food utilization for growth, or both. The decrease in food utilization can be due to increased maintenance costs or decreased digestive efficiency. Kraft effluent has been shown to reduce appetite at concentrations as low as 0.06 to 0.1 LC50 and to increase maintenance costs at 0.2 LC50 (Davis 1973; Borton 1970; Tokar and Owens 1968; Ellis 1967).

The growth of algae is typically increased by low concentrations of KME due to nutrients in the effluents; however, at higher concentrations toxic components counter the effect of the nutrients and even higher concentrations reduce growth below that of the controls. The maximum increase in green alga growth occurred at a 25% v/v concentration which is near the 96-hr LC50 concentration (26%) for rainbow trout. However, the growth of blue-green algae was increased by all concentrations of effluent tested (Wilson 1975). Seppovaara (1973) observed maximum increase in the growth of green algae with 15% concentration of KME.

Growth and development of oyster larvae (*Crassostrea gigas*) were impaired at concentrations of 0.15 to 0.5% untreated KME and 1.3% biotreated KME (Woelke *et al*. 1972). Development and growth of salmonid embryos were more resistant to KME than was growth of later life stages (Holland *et al*. 1960).

For a number of years, researchers at Oregon State University have conducted investigations on the effects of untreated and biotreated KME on the productivity of laboratory streams and of 100 m stream channels dug in a natural environment. These streams contained many of the algae and invertebrates found in small natural streams. Fish placed in these streams were not artificially fed and their production was used as a measure of the productivity of the stream ecosystem. Initially, tests were conducted using KME that received only primary treatment to remove solids; later KME receiving secondary treatment in aeration ponds was tested and finally KME receiving more extensive biotreatment in stabilization basins was studied.

In early studies, Ellis (1967) showed that production of chinook salmon was reduced in laboratory streams receiving primary-treated KME at a concentration of 0.14 LC50 (0.75% v/v) in winter and 0.36 LC50 (1.5%) during spring and summer. These effects were more pronounced at higher fish densities. The reduced fish production was attributed to toxic effects of the effluent on the fish because the food supply of the fish increased.

More recently Seim *et al*. (1977) reported that fish production was reduced in laboratory streams receiving 1.5% biotreated effluent during the winter but production increased during other seasons at levels up to 4%, with the greatest increase at 1%. Enhanced production during the summer was attributed to enrichment effects and diminished toxicity from better biotreatment.

In all the laboratory stream studies conducted at Oregon State University none of the reductions in total fish food organisms observed could be directly attributed to either untreated or treated KME, although the abundance of some organisms would sometimes change. Increases in fish food organisms could often be attributed to both untreated and treated KME. The reduction in fish production or biomass in these streams may be due to loss of appetite or reduced food conversion to growth (Tokar and Owens 1968).

Trout and salmon production in artificial stream channels was not influenced by any concentration of KME tested (Warren et al. 1974). Snail populations increased with all effluents tested. Density of "fish-food" organisms (collectively) was not affected, although some shifts in species abundance did occur. Caddis fly larvae (Hydrosyche) and amphipod (mostly Crangonyx) populations declined with primary treated effluent. Amphipod densities increased with better treated effluents (Botton 1974; Warren 1972). No effect of KME could be shown on the hatchability of salmon eggs in these channels (Mower 1974). Initially these channels contained concentrations of primary treated effluent of about 0.22%, (∿ 0.25 LC50 for salmonids). Subsequently, the streams were dosed with biotreated effluent to obtain a 0.74% (∿ 0.01 LC50) concentration. As the mill effluent was improved through internal modification and more extensive biotreatment, the dosing rates were increased to obtain concentrations as high as 5% (100% effluent was not toxic in 96-hr tests). The 5% rate is many times (25-50) the concentration likely to exist in the Willamette River near Albany, Ore. at low flow, provided the effluent is completely mixed.

Warren et al. (1974) stated that fish production was not reduced in either the laboratory streams or the artificial stream channels by any effluent concentration not also causing growth reduction in salmonids during simple laboratory growth studies. Growth in laboratory tests appears to be a more sensitive test than is fish production in artificial streams. Growth studies, however, would not have predicted the enhanced fish production in the streams. The enrichment and associated increased production observed in some tests may be undesirable in some watersheds where increased eutrophication would be a problem.

The National Council for Air and Stream Improvement (NCASI) is initiating studies in Georgia with outside artifical stream channels similar to those used by Warren. Warm-water species will be tested but no reports are currently available.

Sulfite

Sublethal effects of sulfite wastes have received much less attention than those for kraft wastes because not many sulfite mills are being constructed and the effluent is not very toxic after BOD-reduction treatment. Because of the low toxicity of sulfite mill effluent (SME) many studies have been conducted with the spent sulfite waste liquor (SWL) stream which contains most of the toxic components. Table 2 lists many of the reported sublethal effects of both SME and SWL on aquatic organisms. The sublethal concentrations of SME and SWL reported in the literature usually have not been related to lethal concentration as has been the case with KME. Therefore sublethal concentrations of SME and SWL listed in Table 2 are expressed as percent by volume or by the Pearl Benson Index (PBI) which is an index to the amount of lignin present. The table is organized by system affected, however, the text will be presented by author since a small number of investigators have done most of the work.

Williams et al. (1953) described the sequence of effects of acutely toxic concentrations of SWL on fish prior to death. Many of these syndromes have been observed by others during sublethal tests. In an abstracted article, Seppovaara (1973) reported that "blood values" of rainbow and carp were reduced by sublethal levels of SME. The concentrations tested were not given in the abstract. In another paper he reported the production of green algae was reduced by concentrations greater than 15% SME (Seppavaara and Hynninen 1970).

A Russian author, Gazdziauskaite (1971a,b) studied the effects of SME on freshwater shrimp (Pontogammarus). He observed reduced growth at 1.5%, reduced reproduction at 3-12%, and at 12-25%; increased respiration rate, reduced feeding behavior, reduced "blood values", and in some cases immobilization. It should be noted that in this series of tests, growth was the most sensitive index of effect.

The effect of sulfite waste liquor (SWL) on the oysters (Ostrea lurida) and Crassostrea gigas) and clams (Tresus nutalli and Protheca stamina) have received considerable study as these animals are quite sensitive to SWL compared to Salmonids (Stein et al. 1959; Woelke 1960, 1965, 1976; Woelke et al. 1970, 1972). Concentrations above 55 mg/l (PBI) inhibit spawning; however, lower concentrations can stimulate spawning, but the resulting spawn shows a higher percentage of abnormal larvae. Concentrations as low as 0.15-0.5% or 1-3 mg/l (PBI) increase the number of abnormalities. Magnesium-sulfite mill effluent was more toxic than ammonia-sulfite mill effluent at pH 7. At high pH (above 9) the ammonia-sulfite mill effluent was more toxic indicating that ammonia was causing the toxicity.

Groundwood

Few references are available regarding the sublethal effects of whole groundwood mill effluent. Woelke (1976) examined the effect of groundwood and debarker wastes on the development of embryonic oysters and reported that the no-effect concentration was near 1.3% v/v. Wilson (1975) presented some sublethal effects data on effluents from a newsprint plant that manufactured groundwood pulp and purchased some BKME. Snails avoided the lowest effluent concentration tested by crawling out of the test chamber, but were not killed by full strength effluent when escape was prevented. Algal growth was also influenced by this effluent. Maximum stimulation of growth in algae occurred at 25% concentration for untreated effluent and 75-100% for treated effluent.

TOXIC COMPONENTS

Toxic components of pulp and paper effluents are complex mixtures of organic and inorganic moieties (naturally occurring and added or formed during pulping processes). Only recently have specific components been isolated and identified, mostly through the work of the Canadians. Many of these components have been tested for toxicity. Several naturally occurring resin acids are responsible for the majority of toxicity in non-bleached pulp effluent. Chlorinated compounds contribute the majority of toxicity in bleached pulp effluent. Tables 3 through 7 list the principal toxic constituents, their toxicity to salmonids, relative contributions and approximate loading in untreated pulping effluents.

TABLE 3. PRINCIPAL TOXIC CONSTITUENTS IN PULPMILL WASTE STREAMS (from Leach and Thakore 1977)

Effluent and 96-hr LC50 range (%v/v)		Major Contributor and Loading (kg/ton)[a]		Other identified contributors
Debarking	(0.2-40)	Resin acids	(0.02-0.35)	Diterpene alcohols
Mechanical pulping	(2-10)	Resin acids	(0.02-1.1)	Diterpene alcohols Unsaturated fatty acids Juvabiones
Kraft pulping (unbleached white-water)	(2-40)	Resin acids	(0.5)	Unsaturated fatty acids
Sulfite waste liquor	(0.02-0.05)	Resin acids	(0.9)[b]	Juvabiones
Acid bleach (chlorination stage)	(10-80)	Chlorolignins	--	
Caustic extraction	(2-40)	Chlorinated phenols Chlorinated resin acids Chlorinated stearic acids	(0.02-0.91) (0.02-0.01) (0.08-0.37)	Pitch dispersants

[a] Weight of major contributor produced per ton of wood debarked

[b] Limited sample size, may not be representative

TABLE 4. CONCENTRATIONS AND ACUTE TOXICITIES OF RESIN ACIDS FOUND IN SOFTWOOD PULPING AND DEBARKING EFFLUENTS (from Leach and Thakore 1977)

Resin Acid	96-hr LC50 (mg/l)[a]	Concentration Ranges (mg/l) in Effluents			
		Debarking	Mechanical Pulping	Kraft Pulping	Sulfite[b] Waste Liquor
Abietic	0.41	2.0-22.1	2.6-16.0	0.7-19.9	67.4
Dehydroabietic	0.75	3.4-22.9[c]	2.6-15.7[c]	0.4-22.1	51.8
Isopimaric	0.22	2.4-33.4[d]	2.7-35.0[d]	0.6-17.2	8.7
Palustric	0.55	---	2.8-7.7	---	---
Pimaric	0.32	0.8-7.6	< 0.1-5.9	0.2-8.7	9.8
Sandaracopimaric	0.36				
Total	0.3-0.5	10.4-78	12.1-61.8	2.3-54.8	141.8
No. of Samples	---	88	24	21	1
No. of Mills	---	10	2	10	1

[a] Toxicant solutions renewed every 4-8 hr; test fish was coho salmon

[b] Value is for SWL; not whole SME. Wilson and Chappel (1973) found total resin acid concentrations were generally less than 10 mg/l for SME.

[c] Includes neoabietic acid

[d] No solution replacement; test fish was rainbow trout

TABLE 5. TOXICITY TO JUVENILE COHO SALMON OF LONG-CHAIN FATTY ACIDS PRESENT IN DEBARKING AND PULPING EFFLUENTS (from Leach and Thakore 1977)

Fatty Acid	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Palmitoleic
Carbon No.	C_{16}	C_{18}	C_{18}^{-}	$C_{18}^{=}$	$C_{18}^{\equiv}$	C_{16}^{-}
LT50 (min)[a] at 12 mg/l	> 96 h	> 96 h	2000	220	160	150

[a] time to death for 50% of the test fish

TABLE 6. TOXIC CONSTITUENTS IN KRAFT MILL CAUSTIC EXTRACTION EFFLUENTS[a/] (after Leach and Thakore 1977)

Compound	96-hr LC50[b/] (mg/l)	Concentration Range (mg/l)	Toxic Units (max)	Loading Range	
				kg/day	kg per ton pulp
Trichloroguaiacol	0.75	0.2-1.2	1.6	1-26	<0.01-0.06
Tetrachloroguaiacol	0.32	0.2-1.1	3.4	1-18	<0.01-0.04
Monochloro-dyhydroabietic acid	0.6	ND[c/]-4.3	7.2	<0.5-35	<0.01-0.07
Dichloro-deyhydoabietic acid	0.6	ND-2.5	4.2	<0.5-20	<0.01-0.04
Epoxystearic acid	1.5	1.5-17	11.3	8-136	0.03-0.18
Dichlorostearic acid	2.5	ND-13	5.2	27-113	0.05-0.19

[a/] 17 samples from 9 mills

[b/] Test fish juvenile rainbow trout (*S. gairdneri*). Bioassay with no solution replacement.

[c/] not detected

TABLE 7. TOXIC NEUTRAL EXTRACTIVES FOUND IN VARIOUS EFFLUENTS (from Leach and Thakore 1977)

Diterpene Alcohols		Insect Juvenile Hormone Analogs	
Compound	96-hr LC50[a/] (mg/l)	Compound	96-hr LC50[b/] (mg/l)
Pimarol	0.3	Juvabione	1.5
Isopimarol	0.3	Juvabiol	1.8
Dehydradrobietol	0.8	Δ4'-Dehydrojuvabione	0.8
Abietol	1.8	Duhydrojuvabione	2.0

[a/] Bioassays without solution replacement; test fish was juvenile rainbow trout

[b/] Bioassays with solution replacement every 4 hr; test fish was juvenile rainbor trout - Leach *et al*. (1975)

Kraft

Early work demonstrated that bivalent sulfur compounds were present in lethal quantities in kraft mill effluents (Van Horn 1961, 1971; Van Horn et al. 1949, 1950). These compounds include hydrogen sulfide and methyl mercaptan which are toxic at very low concentrations. The acute toxicity of hydrogen sulfide to goldfish (*Carassius auratus*) and salmonids is in the range of 0.036 to 0.087 mg/l (Adelman and Smith 1972; Smith and Oseid 1972). Methyl mercaptan toxicity is similar to that for hydrogen sulfide. Because of the volatile nature of these compounds, most are lost to the atmosphere during aeration treatment that the majority of pulp effluents in the U.S. now receive. Ng et al. (1974) have shown that the relative contribution of these volatile substances to acute toxicity was only 5.4% in samples which were not biologically treated; such treatment would reduce the contribution even further. Chevalier (1973) emphasized that LC50 values for hydrogen sulfide measured by flow-through bioassays are about one-half those measured by static bioassays because of the volatility of hydrogen sulfide.

The non-volatile fraction contains most of the toxic components in KME. Rogers (1973) and Leach and Thakore (1974a) documented the contribution of the majority of non-volatile compounds to the toxicity of KME. Bioassays were run at each stage of extraction to insure that all toxic materials were retained. Eighty percent of the toxicity was due to resin acids and three unsaturated fatty acids in KME from hemlock and fir pulping wastes.

The acute toxicity of the more common resin acids and fatty acids in KME is given in Tables 4 and 5. The toxicity of resin acids was greater at pH 6.4 than pH 7.5 (Leach and Thakore 1977). Straight-chain fatty acids contributed 18% of the non-volatile toxicity in KME from hemlock and fir wood (Leach and Thakore 1973). None of these fatty acids alone were found to be toxic at the concentrations present in the original sample.

Various other toxic components in KME have been reported, although their contribution to toxicity is usually not known. Banks (1969) isolated an extremely toxic diol (structure not determined); Marvell and Werner (1963) isolated 4 (p-Tolyl)-1-1 penantol from the condensate stream; and Werner (1963) isolated a toxic sulfur-containing compound from black liquor wastes.

In non-chlorinated KME, lignin and its degradation products show little or no toxicity (Brebion et al. 1957). Various simple phenolic compounds in KME are quite toxic to fish, but they do not appear to contribute to effluent toxicity at concentrations present in KME.

Chlorine is commonly used to bleach kraft pulp. The KME has a high chlorine demand. Much chlorine is reduced to chlorides and some binds with other compounds. Chlorination reduces toxicity of resin acids, presumably through oxidation (Wong 1976; Leach and Thakore 1975b). Only the more stable pimaric and dehydroabietic acids survive chlorination in significant amounts.

If kraft pulp is acid-chlorine bleached, lignin and related compounds can become quite toxic, and constitute a major portion of the toxicity of bleachery effluent (Walden 1976). The exact nature of chlorinated lignins are not known. Other toxic components that have been identified in bleaching wastes are: tetra-chloro-o-benzoquinone and trichloro-vertatole (Das et al. 1969; Rogers 1973) and two chlorinated catechols (Servizi et al. 1968). With caustic extraction, resin acids, ligins, phenols and stearic acid can be chlorinated (Leach and Thakore 1974b, 1975a). These compounds were generally toxic at less than 1 mg/l and accounted for 80% of the toxicity of the original sample of BKME (Table 6). When these compounds were combined in original concentrations they yielded a concentration-toxicity curve identical to that obtained for the original sample.

The neutral fraction of BKME contains some toxic components; however, their contribution to toxicity is small (Table 7). Alcohols and aldehydes related to the resin acids are present (Leach and Thakore 1975a,b). Rogers and Mahood (1974) have identified diterpene aldehydes and ketones in BKME in which resin acids were absent and they suggested that resin acids may be converted to these compounds during the bleaching process. Wilson and Rennerfelt (1971) implicated terpenes from BKME in fish tainting. Warren et al. (1974) showed that BKME with added terpene recovery system exhibited reduced toxicity and permitted increased fish biomass in artificial streams.

The toxic effect of components of KME on aquatic organisms other than fish have received little attention. Wilson (1975) reported the 96-hr LC50 for Daphnia exposed to linoleic and dehydroabietic acid in soft water was 3.2 and 4.2 mg/l and in hard water was 5.2 and 7.4 mg/l. These values are much higher than those for salmonids. He also studied the effect of these acids on the growth of algae (Scenedesmus) and reported stimulation at 5.6 mg/l and retardation at 10 mg/l. Researchers for the NCASI (1947) have also studied the effects of KME components on Daphnia. Daphnia are quite sensitive to methyl mercaptan (1.5 mg/l, 48 hr LC20), hydrogen sulfide (1.7 mg/l, 28 hr LC20), fatty acid fraction (6 mg/l, 48 hr LC20) and resin acid fraction (10 mg/l, 48 hr LC20). Several species of freshwater minnows were even more sensitive to these compounds.

No references were found concerning the effects of chlorinated components in BKME on non-fish species.

Sulfite

Only recently have attempts been made to ascertain the toxic moieties of sulfite waste effluents. Wilson and Chappel (1973) identified approximately half of the total toxicity from a high-yield sodium-sulfite mill effluent. The normal resin acids constitute about 26% of the total toxicity or one-half of the identified toxicity. Two phenolic type compounds, eugenol and trans-isoeugenol represent about 20% of the total toxicity; another unidentified phenolic compound was responsible for 8% of the total toxicity. Nelson and Hemingway (1971) also found appreciable quantities of resin acids in bisulfite waste liquors.

More resin acids appear to survive the pulping process in high-yield than in low-yield sulfite mills, and thus high-yield effluents are generally more toxic than low-yield effluents (Walden 1976). The differential survival of resin acids between the two pulping process may explain why Kvasnicka and

McLaughlin (1955) found no resin acids present in waste from low-yield sulfite pulping of spruce, but found a number of toxic phenolic compounds. The toxicities of these compounds were not reported, but the compounds include: cyeme; tetrahydrocadalane; 2-furoic acids; vanillin; vanillic acid; 2-conidendrin melene; vanilloyl acetyl; dehydroconferyl alcohol; 3,3' dimethoxy 4,4' dihydroxystilbene; and 25 other phenolic compounds.

Groundwood

Resin acids have been implicated as principal toxic constituents in groundwood effluents (Row and Cook 1971, Zitko and Carson 1971). Recent studies by B.C. Research (Vancouver, Canada) have identified a number of resin acids as major contributors to toxicity (Table 3 and 4). This acid fraction, which included abietic, dehydroabietic and palustric acids, contributed the major portion of the toxicity. Minor constituents included pimaric, sandaracopimaric, isopimaric and neoabietic acids and the unsaturated fatty acids—oleic, linoleic and linolenic. Up to 35% of the toxicity in some samples was from the neutral fraction (Leach and Thakore 1974c; Leach et al. 1975). These materials include the diterpene alcohols, pimarol and isopimarol, and several juvabione compounds. The juvabiones are juvenile-insect-hormone analogs and may be particularly toxic to aquatic insects, but such tests have not been conducted (Table 7).

Proper treatment can greatly reduce the resin acid concentration. Activated sludge treatment of groundwood effluent reduced the average concentration of resin acids from 28 mg/l to 2.2 mg/l, whereas, aeration in a lagoon only reduced the resin acid concentration to 18.1 mg/l (Howard and Leach 1973b).

Process streams

Process streams other than the pulping effluent show toxicity. For some time it has been known that high levels of resin acids are present in barking effluent (Zitko and Carson 1971). More recently, McKague (1975) identified many of the toxic materials in softwood debarking effluents. The acid fraction containing the resin- and fatty-acids accounts for 90% of the toxicity. The neutral components showing some toxicity include a number of wood alcohols. Leach et al. (1974) have completed a definitive study on the toxic constituents in the effluents from woodrooms (debarking, grinding and storage) at several mills. Jackpine woodroom effluents had the highest resin acid concentration (35.7 mg/l) and were the most toxic. The lowest toxicity and the lowest resin acid level (5.4 mg/l) were in effluents from barking and storage of hardwoods. Hemlock, fir, and spruce effluents were intermediate.

Miscellaneous constituents

One component of all pulping processes which has caused major environmental damage in the past has been high suspended solids consisting mainly of wood fibers. Numerous references describing the extent and effect of fiber mats in receiving waters were cited by Springer and Atalla (1974). Even though fish can tolerate high levels of suspended solids, woody fibers can be acutely toxic to fish. Groundwood fibers are more toxic to fish than chemically produced fibers, but lethal doses of fibers are rarely released from the mills (Smith et al. 1965). MacLeod and Smith (1966), Kramer and Smith (1965, 1966), and Smith and Kramer (1964) reported 72-hr LC50 values between 738 and 2,000 mg/l for fathead minnows (Pimephales promelas). In addition, the high BOD of the fibers lowers the oxygen level which in turn lowers the 72-hr LC50 concentration of fibers to 272 and 738 mg/l at oxygen levels of 3 and 5 mg/l. Conifer fibers are more toxic than hardwood fibers to recently hatched fathead minnows (Smith and Kramer 1964). Wood fibers have no effect on the developing fish embryo if the ventilation of the eggs is not reduced (Kramer and Smith 1965, 1966).

Sublethal effects can occur at fiber concentrations present in some untreated effluents, but in well-treated effluents fibers are rarely a problem. At fiber concentrations as low as 100 mg/l a variety of sublethal effects have been reported: growth reduction, increased coughing, increased metabolic rate and increased numbers of mucous cells in the gill (Smith et al. 1965; Kramer and Smith 1965; MacLeod and Smith 1966). The cough response was more sensitive to fiber than were respiration, swimming performance and hematocrit level. The threshold concentration was 25 mg/l for the cough response and >100 mg/l for the other tests (MacLeod and Smith 1966). Brown trout and rainbow trout were more sensitive than were walleye (Stizostedion vitreum) and fathead minnows (Kramer and Smith 1965, 1966). Betts and Wilson (1966) recommended that total suspended solids should not exceed 36 mg/l for the protection of salmonids.

The discharge of fibrous materials has been greatly curtailed, but large quantities of other suspended and dissolved materials are still being released. These materials exert a significant BOD, even after treatment, and can contribute to low oxygen concentrations in lakes, bays, and slow-moving rivers. Even though these materials are not acutely toxic to fish, many will settle out, forming sludge beds, and may have deleterious effects on the bottom fauna (Washington, State of 1967). Definitive studies of these ecological effects are lacking. The dissolved solids are non-toxic per se, but can induce stress through alterations in osmoregulation (Tsai 1973).

Rosehart et al. (1974) warned that products such as dyes, coating lattices, alum, retention aids, beater aids, surface sizings and wet-strength resins can all contribute to the toxicity of effluents. Firipi and Scalata (1973) attributed a large portion of the toxicity to slimicides and fungicides. Pentachlorophenol has generally replaced mercury compounds as a fungicide thus increasing the effluent's acute toxicity to fish. Horning (1974) examined 29 dyes used in the pulp and paper industry and found 96-hr LC50's as low as 0.047 mg/l (for basic violet). Gordon and Servizi (1974) have bioassayed 22 chemical additives used in the kraft process and found seven to be toxic to salmonids at levels likely to be found in the effluent. Wilson (1972) concluded that metals normally do not contribute to the toxicity of effluents from sulfite mills.

Chlorination of the treated mill effluent has been suggested to control high coliform and Klebesiella pneumonia levels that develop during treatment. Such chlorination can increase effluent toxicity through the formation of more persistent chloramines in the presence of ammonia, especially in ammoniumsulfite plants. Seppovaara (1973) reported that chlorination of pine and beachwood pulp effluent increased the toxicity 10 to 20 times. A well-treated kraft mill effluent which was not acutely toxic at full strength to salmon, was acutely toxic at 18% v/v one hour after adding 1 mg/l chlorine even though no chlorine or chloramine could be detected (Stiles 1977). Chlorination of phenolic compounds was suspected.

Pulp mill effluents can cause a phenol-like flavor and odor in fish flesh. Shumway (1968) reported that the flavor of coho salmon was impaired by concentrations of untreated KME as low as 1.5% when the fish were exposed for 72 to 96 hr. In an extensive study by Domtar Fine Paper, Ltd, Cook et al. (1971) reported perch (Perca flavescens) flesh to be tainted by 10% but not by 0.3% effluent. The effluent came from an integrated mill producing both kraft and sulfite pulp. A study by NCASI (1973) demonstrated that, with heavy chlorine treatment, phenolic structures are ruptured and tainting qualities destroyed but, with smaller chlorine doses, some phenolic compounds were chlorinated although the flavor of fish flesh was not altered significantly from that of fish held in unchlorinated pulp effluent.

The color and foaming of pulp mill effluents, especially kraft mill effluent, are esthetically undesirable. Even at a 5% dilution of well-treated KME, a concentration that showed no adverse effects on fish production in artificial streams, the color was judged objectionable (personal communication).* Stone et al. (1974) reported that color could reduce photosynthesis below a pulp mill outfall. Parker and Sibert (1973) also reported that color from BKME restricted light to the halocline. Color can be removed with lime treatment (Spruil 1974), but the resulting effluent was more toxic to chironomids (Wilson 1975).

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* W. K. Seim, Dept. of Fish. and Wildl. Oregon State University, Corvallis.

CONCLUDING STATEMENTS

The toxicity of whole pulp and paper mill effluents has been adequately demonstrated. The variability in toxicity within and among mills severely limits the predictive value of these assays. Bioassays still have a place, however, in the management of these effluents. Because of the sporadic nature of effluent toxicity, frequent bioassays or other monitoring methods should be a condition of discharge permits. Certain sublethal tests, especially the "cough reflex," appear to have some merit as a monitoring tool. As techniques progress in the identification and quantification of the major toxic components in the effluents, it may be possible to reduce reliance on bioassays. As yet, bioassays appear to be the best way to assess toxicity of complex effluents. Research to find important species that are more sensitive to pulp effluents may be productive.

One of the major problems yet to be solved with pulp and paper mill effluent is the sporadic and dramatic increases in toxicity of "adequately" treated effluents. These sporadic toxic discharges have great potential to damage the aquatic environment. The effects of sporadic near-lethal doses are not known and should be studied.

The majority of pulp and paper mill effluent studies have been sponsored or co-sponsored by the industry. Many of these studies have been on newer mills in order to demonstrate the potential for low toxicity in their effluents. Effluents from older, more polluting mills may have been overlooked and a review of the literature may underestimate the potential environmental damage from these mills. A survey of these less frequently studied mills may be justified.

REFERENCES

Adelman, I. R. and Smith, L. L., Jr. (1972). Toxicity of hydrogen sulfide to goldfish (Carassius auratus) as influenced by temperature, oxygen and bioassay techniques. J. Fish. Res. Bd. Canada. 29:1309.

Banks, R. (1969). I. Isolation of certain toxic components of kraft mill waste and attempts to determine their structure. Ph.D. Thesis, Oregon State Univ., Corvallis.

Betts, J. L. (1976). Regulation and waste characterization. Proceedings of seminars on water pollution abatement technology in the pulp and paper industry. Environment Canada. EPS, Ottawa.

Betts, J. L., Beak, T. W., and Wilson, G. G. (1967). A procedure for small-scale laboratory bioassays. J. Water Pollut. Control Fed. 39:89.

Betts, J. L. and Wilson, G. G. (1966). New methods for reducing the toxicity of kraft mill bleachery wastes to young salmon. J. Fish. Res. Bd. Canada. 23:813.

Blosser, R. O. and Owens, E. L. (1970). A guide to the short-term bioassay of mill effluents. Tech. Bull. No. 233, NCASI, New York, N.Y.

Borton, D. C. (1970). Effects of biologically stabilized kraft mill effluents on juvenile coho salmonids growth. M. S. Thesis, Oregon State Univ., Corvallis.

Borton, D. C. (1974). Effects of primary treated and biologically stabilized kraft mill effluent on the production, biomass and growth rates of juvenile salmonids in three stream channels. Ph.D. dissertation, Oregon State Univ., Corvallis.

Brebion, B., Chopin, J., and Humbert, F. (1957). Toxicity to fish (minnows) of some phenolic derivatives formed by the decomposition of lignin in paper pulp factories. Chem. Ind. 77:1110.

Brown, D. A. and McLeay, D. J. (1975). Effects of bleached kraft mill effluent on the survival of starved juvenile coho salmon (Oncorhynchus kisutch). J. Fish. Res. Bd. Canada. 32:2528.

Bruynesteyn, A. and Walden, C. C. (1971). Origin of toxicity and biochemical oxygen demand (BOD) in the bleached kraft process. CPAR Report 10-1. Canadian Forestry Service, Ottawa, Ontario.

Chevalier, J. R. (1973). Toxicity of sodium sulfite to common shiners: Dynamic bioassay. TAPPI. 56(5):135.

Conkey, J. H. (1968). Relative toxicity of biostatic agents suggested for use in the pulp and paper industry. 1968 Review. American Paper Instititute, New York, #3170.

Cook, W. H., Farmer, F. A., Kristransen, O. E., Reid, K., Reid, J., Rowbottom, R., and Domtar Fine Paper Ltd. (1971). Effect of pulp and paper mill effluents on taste and odor of water and fish. Can. For. Ser., CPAR Project Final Rept. 12-2 CA.

Das, B. S., Reid, S. G., Betts, J. L., and Patrick, K. (1969). Tetrachlor-o-benzoquinone as a component in bleached kraft chlorination effluent toxic to young salmon. J. Fish. Res. Bd. Canada. 26:3055.

Davis, J. C. (1973). Sublethal effects of bleached kraft pulp mill effluent on respiration and circulation in sockeye salmon (Oncorhynchus nerka). J. Fish. Res. Bd. Canada. 30:369.

Davis, J.C. (1976). Progress in sublethal effects studies with kraft pulp-mill effluent and salmonids. J. Fish Res. Bd. Canada. 33:2031.

Davis, J. C. and Mason, B. J. (1973). Bioassay procedures to evaluate acute toxicity of neutralized bleached kraft pulp mill effluent to Pacific salmon. J. Fish. Res. Bd. Canada. 30:1565.

Dewitt, J. W., Jr. (1963). Effects of pollutional conditions on stream organisms with special emphasis on stonefly naiads. Dissertation Abstracts XXIV. 9:3507.

Dickman, M. S. (1973). Total dissolved electrolyte effects on periphyton. J. Water Pollut. Control Fed. 45:2211.

Dimick, R. E. and Haydu, E. P. (1952). The effect of kraft mill waste liquors and certain of their components on certain salmonid fishes of the Pacific Northwest. Tech. Bull. No. 51, NCSI, New York, N.Y.

Dimick. R. E., Warren, C. E., Jones, B. F., Doudoroff, P., and Amberg, H. R. (1957). Some preliminary observations on the avoidance reactions of salmonid fishes to pulp mill effluents. Tech. Bull NO. 93, NCASI, New York, NY.

Donnier, E. (1972). Toxicity of pulp and paper mill effluents on sea environments. Rev. Int. Oceangr. Medicale. 28:53. (ABIPC 44:6249).

Ellis, R. H. (1967). Effects of kraft pulp mill effluent on the production and food relationships of juvenile chinook salmon in laboratory streams. Tech. Bull. No. 210, NCASI, New York, NY.

Fahmy, F. K. and Lush, O. L. (1974). Sensitivity of major aquatic food chain organisms to treated kraft mill effluents. CPAR Rep. No. 356-1. Canadian Forestry Service, Ottawa, Ontario.

Filimonova, Z. I. (1968). Effects of effluents from pulp and paper mills on zooplankton in natural waters. Sanit. Gidrobiol. Vodn. Toksikol. 2:197. (Ab. Bull. Inst. Paper Chem. 40:3059u).

Firipi, M. and Scarlata, V. (1973). Study on fish, toxicity and biodegradability of paper mill wastes in relation to biocides used. Proc. EVCEPA Conf. Rome. 15:449.

Fujiya, M. (1961). Effect of kraft pulp mill wastes on fish. J. Water Pollut. Control Fed. 33:968.

Fujiya, M. (1964). Physiological estimation of the effects of pollutants upon aquatic organisms. Advances Water Pollution Research Vol. 3. pp. 315. Pergamon Press, Oxford.

Galtsoff, P. S., Chipman, W. A., Engle, J. G., and Calderwood, H. N. (1947). Ecological and physiological studies of the effect of sulfate pulp mill wastes on oysters in York River, Virginia. Fish. Bull. No. 43, U.S. Fish and Wildlife Service, Washington, D.C.

Gazdziauskaite, I. B. (1971a). Effects of effluents from the Sovetsk and Neman mills on the biology of <u>Pontogammarus robustoides</u>. (1) Vitality. (2) Respiration intensity. Liet. TSR Mokslu. Adad. Darbai Ser. C No. 2:93. (Ab. Bull. Paper Chem. 43:10694).

Gazdziauskaite, I. B. (1971b). Effect of effluents from the Sovetsk and Neman sulfite pulp and paper mills on the fertility of <u>Pontogammarus robustoides</u> (Grimm) sars. Rybokhoz. Isuch. Vnutr. Vodoemov No. 6:29-31. (Ab. Bull. Inst. Paper Chem. 43:3026).

Gordon, R. W. and Servizi, J. A. (1974). Acute toxicity and detoxification of kraft pulp mill effluent. International Pacific Salmon Fisheries Comm. Progress Report 31, New Westminster, B.C., Canada, #4380.

Grande, M. (1964). Water pollution studies in the river Otra, Norway—effects of pulp and paper mill wastes on fish. Int. J. Air Wat. Pollut. 8:77.

Gregory, L. A. and Loch, J. S. (1973a). Benthos survey in the North Saskatchewan River in the vicinity of the Prince Albert Pulp Company, Prince Albert, Saskatchewan. Can. Dept. Environ. Fish and Marine Serv. Tech. Report No. CEN T-72-2.

Gregory, L. A. and Loch, J. S. (1973b). Benthos studies on the Winnipeg River in the vicinity of the Abitilic Manitoba Paper Company, Pine Falls, Manitoba. Can. Dept. Environ. Can. Fish and Marine Ser. Tech. Report No. CEN T-73-3.

Hicks, D. G. and DeWitt, J. W. (1971). Effects of dissolved oxygen on kraft pulp mill effluent toxicity. Water Res. 5:593.

Holland, G. A., Lasater, J. E., Neumann, E. D., and Eldridge, W. E. (1960). Toxic effects of organic and inorganic pollutants on young salmon and trout. Res. Bull. No. 5. State of Washington Dept. of Fish, Olympia, WA.

Horning, R. A. (1974). The effect of selected dyes in the environment. TAPPI. 57:135.

Howard, T. E. (1975). Stamina of juvenile coho salmon in pulp mill effluent and in water after effluent exposure. J. Fish Res. Bd. Canada. 32:789.

Howard, T. E. and Leach, J. M. (1973a). Identification and treatment of the toxic materials in pulp and paper woodroom effluents. CPAR Rep. No. 148-1, Canadian Forestry Service, Ottawa, Ontario.

Howard, T. E., and Leach, J. M. (1973b). Identification and treatment of the toxic materials in mechanical pulping effluents. CPAR Rep. No. 149-1. Canadian Forestry Service, Ottawa, Ontario.

Howard, T. E., and McLeay, D. J. (1972). Sublethal effects of bleached kraft mill effluents to fish. CPAR Report No. 9-2. Canadian Forestry Service, Ottawa, Ont.

Howard, T. E. and Walden, C. C. (1965). Pollution and toxicity characteristics of pulp mill effluents. TAPPI. 48:135.

Howard, T. E. and Walden, C. C. (1967). Hematocrit variation at sublethal concentrations of kraft mill wastes. Presented at the 97th Ann. Conf. Am. Fish Soc., Toronto, Ontario.

Howard, T. E. and Walden, C. C. (1971). Effluent characteristics of bleached kraft pulp mills. Pulp Paper Mag. Canada. 72:T3.

Howard, T. E. and Walden, C. C. (1974). Measuring stress in fish exposed to pulp mill effluents. TAPPI. 57(2):133.

Jacobs, F. and Grant, G. C. (1974). Acute toxicity of unbleached kraft mill effluent to the opossum shrimp, Neomysis americana. Water Res. 8(7):439.

Jones, B. J., Warren, C. E., Bond, C. E., and Doudoroff, P. (1956). Avoidance reactions of salmonid fishes to pulp mill effluents. Sewage Ind. Wastes. 28:1403.

Kondo, R., Sameshima, K. and Kondo, T. (1973). Spent semichemical pulping liquor (3). Toxicity characteristics of SCP spent liquor and reduction of its toxicity. Japan TAPPI. 10:476. (ABIPC 44:12026).

Kramer, R. H. and Smith, L. L. (1965). Effects of suspended wood fiber on brown and rainbow trout eggs and alevins. Trans. Am. Fish. Soc. 94:252.

Kramer, R. H. and Smith, L. L. (1966). Survival of walleye eggs in suspended wood fibers. Prog. Fish-Culturist. 28:79.

Kvasnicka, E. A. and McLaughlin, R. R. (1955). Identification of spruce sulphite liquor components. Can. J. Chem. 33:637.

Ladd, J. M. (1969). Effects of pH on the acute toxicity of kraft pulp mill effluent to juvenile coho calmon, Oncorhychus kisutch. M.S. Thesis, Humboldt State Coll., Arcata, CA.

Larson, G. L., Hutchins, F. E. and Lamperti, L. P. (1977). Laboratory determination of acute and sublethal toxicities of inorganic chloramines to early life stages of coho salmon Oncorhynchus kisutch. Trans. Am. Fish. Soc. 106(3):268.

Leach, J. M., Gietz, W. C., and Thakore, A. N. (1974). Identification and treatment of the toxic materials in pulp and paper woodroom effluents. CPAR Rep. No. 148-2, Canadian Forestry Service, Ontowa, Ontario.

Leach, J. M. and Thakore, A. N. (1973). Isolation of the toxic constituents of kraft pulp mill effluents. CPAR Rep. No. 11-3, Canadian Forestry Service, Ottawa, Ontario.

Leach, J. M. and Thakore, A. N. (1974a). Isolation of the toxic constituents of kraft pulp mill effluents. CPAR Rep. No. 11-4, Canadian Forestry Service, Ottawa, Ontario.

Leach, J. M. and Thakore, A. N. (1974b). Identification fo the toxic constituents in kraft mill bleach plant effluents. CPAR Report No. 245-1, Canadian Forestry Service, Ottawa, Ontario.

Leach, J. M. and Thakore, A. N. (1974c). Identification and treatment of the toxic materials in mechanical pulping effluents. CPAR Rep. No. 149-2, Canadian Forestry Service, Ottawa, Ontario.

Leach, J. M. and Thakore, A. N. (1975a). Isolation and identification of constituents toxic to juvenile rainbow trout (Salmo gairdneri) in caustic extraction effluents from kraft pulp mill bleach plants. J. Fish. Res. Bd. Canada. 32:1249.

Leach, J. M. and Thakore, A. N. (1975b). Identification of the toxic constituents in kraft mill bleach plant effluents. CPAR Rep. No. 245-2, Canadian Forestry Service, Ottawa, Ontario.

Leach, J. M. and Thakore, A. N. (1977). Compounds toxic to fish in pulp mill waste streams. Prog. Water Tech. Vol. 9, 787.

Leach, J. M. Thakore, A. N. and Manville, J. F. (1975). Acute toxicity to juvenile rainbow trout (Salmo gairdneri) or naturally occurring insect juvenile hormone analogs. J. Fish. Res. Bd. Can. 32:2556.

Leppäkoski, E. (1968). Some effects of pollution (pulp and paper) on the benthic environment of Gullmarsfjord. Helohländer Wiss. Meeresunters (17) 291, Water Poll. Abs. (46) 576.

Lichatowich, J. A. (1970). Influences of kraft mill effluents on the production of salmon in laboratory stream communities. M.S. Thesis, Oregon State Univ., Corvallis.

Livintsev, A. N. (1967). Effect of waste waters from a wood hydrolyzing factory on aquatic organisms. Biol. Nauk. 10(3):2022. (Water Pollut. Abstr. 42:1710).

Loch, J. S. and Bryant, W. J. (1972). Toxicity and other pollution characteristics of unbleached kraft mill effluents. Report No. TR72-3 Res. Div. Br., Fish. Service. Environ. Can., Winnipeg, Man.

Loch, J. S. and MacLeod, J. C. (1973). Fish toxicity survey of four prairie province pulp mill effluents. Tech. Report No. CEN T-73-4. Fish and Marine Service, Environmental Canada, Ottawa, Ontario.

Loch, J. S. and MacLeod, J. C. (1974). Factors affecting acute toxicity bioassays with pulp mill effluents. Can. Dept. Environ. Fish and Marine Service, Tech. Rept. No. CEN T-74-2.

MacLeod, J. C. and Smith, L. L. (1966). Effect of pulpwood fiber on oxygen consumption and swimming endurances of the fathead minnow (Pimephales promelas). Trans. Am. Fish. Soc. 95:71.

McKague, A. B. (1975). Identification and treatment of the toxic materials in pulp and paper woodroom effluents. CPAR Report No. 148-3. Canadian Forestry Service, Ottawa, Ontario.

McLeay, D. J. (1973). Effects of 12-h and 25-day exposure to kraft pulp mill effluent on the blood and tissues of juvenile coho salmon (Oncorhynchus kisutch). J. Fish. Res. Bd. Canada. 30:395.

McLeay, D. J. (1976) A rapid method for measuring the acute toxicity of pulp mill effluents and other toxicants to salmonid fish at ambient room temperature. J. Fish. Res. Bd. Canada. 33:1303.

McLeay, D. J. and Brown, D. A. (1974). Growth stimulation and biochemical changes in juvenile coho salmon (Oncorhynchus kisutch) exposed to bleached kraft pulp mill effluent for 200 days. J. Fish. Res. Bd. Canada. 31:1043.

McLeay, D. J. and Brown, D. A. (1975). Effects of acute exposure to bleach kraft pulp mill effluent on carbohydrate metabolism of juvenile coho salmon (Oncorhynchus kisutch) during rest and exercise. J. Fish. Res. Bd. Canada. 32:753.

McLeese, D. W. (1970). Behavior of lobsters exposed to bleached kraft mill effluent. J. Fish. Res. Bd. Canada. 27:731.

McLeese, D. W. (1973). Response of lobsters (Homarus americanus) to odor solution in the presence of bleached kraft mill effluent. J. Fish. Res. Bd. Canada. 30:279.

Marier, J. (1973). The effects of pulp and paper wastes, with particular attention to fish and bioassay procedures for assessment of harmful effects. NRCC No. 13501. Nat. Res. Council of Canada, Ottawa, Ontario.

Marvell, E. N. and Werner, R. (1963). 4-(p-tolyl)-pentanol in Douglas fir pulping products. J. Org. Chem. 28:1542.

Mower, B. F. (1974). Growth and production of salmonids exposed to a stabilized kraft mill effluent in experimental stream channels. M.S. Thesis, Oregon State Univ., Corvallis, OR.

NCASI. (1947). The toxicity of kraft mill wastes to typical fish food organisms. National Council for Air and Stream Improvement. Tech. Bull. No. 10.

NCASI. (1973). The measurement of phenolic substances and the significance of their presence in pulp mill effluents on taste and odor in receiving waters. Tech. Bull. NCSAI No. 268.

Nelson, P. J. and Hemingway, R. W. (1971). Resin in bisulfite pulp from Pinus radiata wood and its relationship to pitch troubles. TAPPI. 54: 968.

Ng, K. S., Mueller, J. C., and Walden, C. C. (1974). Study of foam separation as a means of detoxifying bleached kraft mill effluents, removing suspended solids and enhancing biotreatability. CPAR Rep. No. 233-1 (part I), Canadian Forestry Service, Ottawa, Ontario.

Ozburn, G., Kraft, J., and Somppi, L. (1973). Procedure for short-term bioassay tests on industrial effluents of low oxygen content. Can. Gov. Zool. 51(7):794.

Ozburn, G., Kraft, J., and Somppi, L. (1974). Short-term bioassays of low O_2 content effluents. Pulp and Paper Mag. Can. 75(9):(T318).

Parker, R. R. and Sibert, J. (1973). Effect of pulp mill effluents on dissolved oxygen in a stratified estuary. (1) Empirical model. (2) Numerical model. Water Res. 7:503.

Rainville, R. P., Copeland, B. J. and McKean, W. T. (1975). Toxicity of kraft mill wastes to an estuarine phytoplankton. J. Water Poll. Cont. Fed. 47:487.

Rogers, I. H. (1973). Isolation and chemical identification of toxic components of kraft mill wastes. Pulp Paper Mag. Canada. 74:T303.

Rogers, I. H. and Mahood, H. W. (1974). Removal of fish-toxic organic solute from whole kraft effluent by biological oxidation and the role of wood extractives. Tech. Rep. No. 434, Fish Res. Bd. Canada, West Vancouver, B.C.

Rosehart, R. G., Ozburn, G. W., and Mettinen, R. (1974). Origins of toxicity in sulphite pulping. Pulp and Paper Mag. Canada. 75:63.

Row, R. and Cook, R. H. (1971). Resin acid soaps—toxicity and treatability. Presented at the 6th Air and Stream Improvement Conf., Tech. Sect., Can. Pulp Paper Assoc., Quebec City, Quebec.

Schaumburg, F. D., Howard, T. E., and Walden, C. C. (1967). A method to evaluate the effects of water pollutants on fish respiration. Water Res. 1:731.

Seim, W. K. Lictatowich, S., Ellis, R., and Davis, J. E. (1977). Effects of kraft mill on production of juvenile salmon production in laboratory stream communities. Water Research 11:189.

Seppovaara, O. and Hynninen, P. (1970). On the toxicity of sulphate mill condensates. Paperi ja Puu. 52:11. (Ab. Bull. Inst. Paper Chem. 41: 487).

Seppovaara, O. (1973). The toxicity of the sulfate pulp bleaching effluents. Paperi ja Puu. 55:713. (Ab. Bull. Inst. Paper Chem. 44:10910).

Servizi, J. A., Gordon, R. W., and Martens, D. W. (1968). Toxicity of two chlorinated catechols possible components of kraft pulp mill bleach wastes. Progress Report No. 17, Int. Pacific Salmon Fish Comm. New Westminster, B.C.

Servizi, J. A., Stone, E. T., and Gordon, R. W. (1966). Toxicity and treatment of kraft pulp bleach plant waste. Prog. Rep. 13, Int. Pacific Salmon Fish. Comm., New Westminster, B.C.

Shireman, J. V. (1975). Utilization of a kraft effluent channel by fish and aquatic organisms. TAPPI Environmental Conf., Denver, CO., p. 185.

Shumway, D. L. (1968). Flavor of jack coho salmon. NCSAI Tech. Bull. No. 217.

Smith, L. L. and Kramer, R. H. (1964). Some effects of paper fibers on fish eggs and small fish. Proc. 19th Ind. Waste Conf., Purdue Univ., Lafayette, In.

Smith, L. L., Kramer, R. H., and MacLeod, J. C. (1965). Effect of pulp wood fibers on fathead minnows and walleye fingerling. J. Water Pollut. Control. Fed. 37:130.

Smith, L. L. and Oseid, D. M. (1972). Effect of hydrogen sulfide on fish eggs and fry. Water Res. 6:711.

Sprague, K. B. (1969). Measurement of pollutant toxicity to fish. I. Bioassay methods for acute toxicity. Water Res. 3:793.

Sprague, J. B. (1971). Measurement of pollutant toxicity to fish. III. Sublethal effects and "safe" concentrations. Water Res. 5:245.

Sprague, J. B. and Drury, D. W. (1969). Avoidance reactions of a salmonid fish to representative pollutants. Advances in Water Pollution Research, Vol. 4, pp. 169. Pergamon Press, Oxford.

Sprague, J. B. and McLeese, D. W. (1968). Toxicity of kraft pulp mill effluent for adult and larval lobsters, and juvenile salmon. Water Res. 2:753.

Springer, A. M. and Atalla, R. H. (1974). Cellulosic deposits in benthal environments: Occurrence, evaluation and decomposition. TAPPI. 1:120.

Spruil, E. L., Jr. (1974). Color removal and sludge disposal [Process] for kraft mill effluents. Paper Trade Journ. 158(33):24.

Stein, J. E., Petersen, R. E., Denison, J. G., Clark, G. M., and Ellis, I. E. (1959). The spawning of Olympic oysters (Ostrea lurida) kept in spent sulphite liquor (SSL). Olympia Research Div. Report Rayonier, Inc. Shelton, WA.

Stiles, D. (1977). Effects of chlorinated biologically stabilized kraft mill effluent on the mortality and growth of coho salmon. M.S. Thesis, Oregon State Univ., Corvallis.

Stone, D., Griffing, T. C., and Knight, M. C. (1974). Biological monitoring of the Fraser River near Prince George, B.C. Pulp and Paper Mag. Can. 75(c):100.

Tabata, K. (1965). Systematic studies on toxic components in industrial wastes with reference to the tolerance of aquatic lives. II. On acute toxic components in digested waste from ammonium-base semichemical pulp mills. Bull. Tokai Reg. Fish. Res. Lab. #42. 11-16. (Japanese with English summary).

Tokar, E. M. and Owens, E. L. (1968). The effects of unbleached kraft pulp mill effluents on salmon. I. Growth, food consumption and swimming ability of juvenile chinook salmon. Tech. Bull. No. 217, NCASI, New York, N.Y.

Tsai, Chu-Fa. (1973). Water quality and fish life below sewage outfalls. Trans. Am. Fish. Soc. 102:281.

Van Horn, W. M. (1961). Aquatic biology and the pulp and paper industry. (Report No. 1), Tech. Bull. No. 148, NCSAI, New York, N.Y.

Van Horn, W. M. (1971). Aquatic biology and the pulp and paper industry (Report No. 2). Tech. Bull. 251, NCASI, New York, NY.

Van Horn, W. M., Anderson, J. B., and Katz, M. (1949). The effect of kraft pulp mill wastes on some aquatic organisms. Trans. Am. Fish. Soc. 79:55.

Van Horn, W. M., Anderson, J. B., and Katz, M. (1950). The effect of kraft pulp mill wastes on fish life. TAPPI. 33:209.

Walden, C. C. (1976). Review paper. The toxicity of pulp and paper mill effluents and corresponding measurement procedures. Water Res. 10:639.

Walden, C. C. and Howard, T. E. (1971). The nature and magnitude of the effect of kraft mill effluents on salmon. Proc. Int. Symp. Ident. Measurement of Environmental Pollutants. p. 363. Nat. Res. Council of Canada.

Walden, C. C., Howard, T. E., and Froud, G. D. (1970). A quantitative assay of the minimum concentration of kraft pulp mill effluents which affect fish respiration. Water Res. 4:61.

Walden, C. C., Howard, T. E., and Sheriff, W. J. (1971). The relationship of kraft pulp mill operating and process parameters to pollution characteristics of the mill effluents. Pulp Paper Mag. Canada. 72:T82.

Walden, C. C. and McLeay, D. J. (1974). Interrelationships of various bioassay procedures for pulp and paper mill effluents. CPAR Report No. 165-1. Canadian Forestry Service, Ottawa, Ontario.

Walden C.C ., McLeay D. J. and Monteith D. D. (1975) Comparing bioassay procedures for pulp and paper effluents. Pulp Paper Mag. Canada 76, T130-T134.

Warren, C. E. (1972). Laboratory and controlled experimental stream studies of the effects of kraft effluents on growth and reproduction of fish. Tech. Bull. No. 259, NCASI, New York, N.Y.

Warren, C. E. and Doudoroff, P. (1958). The development of methods for using bioassays in the control of pulp mill waste disposal. TAPPI. 41:211.

Warren, C. E., Seim, W. K., Blosser, R. O., Caron, A. L., and Owens, E. L. (1974). Effect of kraft effluent on the growth and production of salmonid fish. TAPPI. 57(2):127.

Washington, State of. (1967). Pollutional effects of pulp and paper mill wastes in Puget Sound, State of Washington Pollution Control Comm., Olympia. 474 pp.

Webb, P. W. and Brett, J. R. (1972). The effects of sublethal concentrations of whole mill bleached kraft pulp mill effluent on the growth and food conversion efficiency of underyearling sockeye salmon. J. Fish. Res. Bd. Canada. 29:1555.

Werner, A. E. (1963). Sulfur compounds in kraft pulp mill effluents. Can. Pulp and Paper Ind. 16(3):35.

Williams, R. W., Mains, E. W., Eldridge, W. E., and Lasater, J. E. (1953). Toxic effects of sulfite waste liquor on young salmon. Res. Bull. No. 1. State of Washington Dept. of Fisheries, Olympia, WA.

Wilson, B. and Rennerfelt, J. (1971). Technical and economic evaluation of internal versus external paper mill wastes treatment. Pulp and Paper Mag. Canada. 72:84.

Wilson, M. A. (1975). Assessment of the sensitivity of major aquatic food chain organisms to newsprint mill effluents which are not acutely toxic to fish. CPAR Report No. 328-1, Canadian Forestry Service, Ottawa, Ontario.

Wilson, M. A. and Chappel, C. I. (1973). Reduction of toxicity of sulphite effluents. CPAR Report No. 49-2, Canadian Forestry Service, Ottawa, Ontario.

Wilson, R. C. H. (1972). Acute toxicity of spent sulphite liquor to Atlantic salmon (Salmo salar). J. Fish. Res. Bd. Canada. 29:1225.

Woelke, C. E. (1960). Effects of sulfite waste liquor on the normal development of Pacific oyster (Crassostrea gigas) larvae. Res. Bull. No. 6, State of Washington Dept. of Fisheries, Olympia, WA.

Woelke, C.E. (1965). Bioassays of pulp mill wastes with oysters. Biological Problems in Water Pollution, Third Seminar. Tech. Rep. No. 999-WP-25. Robert A. Taft Sanitary Engineering Center, U.S. Public Health Service, Cincinnati, OH.

Woelke, C. E. (1976). Measurement of water quality with the Pacific oyster embryo bioassay. Water Quality Criteria, ASTM STP 416. Am. Soc. Testing Materials, Philadelphia, PA.

Woelke, C. E., Schink, T. D., and Sanborn, E. W. (1970). Development of an in situ marine bioassay with clams. Ann. Rep. to the U.S. Fed. Water Quality Admin., Dept. of the Interior Grant No. 18050 DOJ, Washington, D.C.

Woelke, C. E., Schink, T., and Sanborn, E. (1972). Effect of biological treatment on the toxicity of three types of pulping wastes to Pacific oyster embryos. Report prepared under EPA contract No. 68-01-377, Washington, D.C.

Wong, A. (1976). Physical-chemical treatment—Proceedings of Seminars on water pollution abatement technology in the pulp and paper industry. Environmental Protection Service: Can. EPS 3-WP-76-4.

Worster, H. E. and Pudek, M. F. (1973). Effects of oxygen pulping on toxicity and color of effluents. Pulp and Paper Mag. Can. 95:793.

Zitko, V. and Carson, M. V. (1971). Resin acid and other organic compounds in groundwood and sulfate mill effluents and foams. Ms. Rep. Ser. No. 1134, Fish. Res. Bd. Canada, Biological Station, St. Andrews, N.B.

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Project Officer: F.E. Hutchins, 8-420-4735, Corvallis, OR (comm. (503)757-4735)

16. ABSTRACT

This review of pulp and paper mill effluents considers the need for additional toxicity data to insure effective effluent regulation. Effluent characteristics and problems of toxicity testing particular to pulp and paper mill effluents are discussed; however, the emphasis is on toxic effects of these effluents to aquatic life. Untreated pulp and paper mill effluents are very toxic to most aquatic life. Concentrations as low as two percent can be acutely toxic to fish. Sufficient treatment can render the effluent essentially nontoxic much of the time; however, treatment processes used by most mills reduce toxicity but do not eliminate it. Even effluents receiving "good" treatment may exhibit sporadic and dynamic increases in toxicity (due in part to spills or dumping of spent pulping chemicals). Sublethal exposures of aquatic organisms to pulp effluent may affect a number of their physiological and behavioral functions. The more sensitive functions, growth rate, coughing reflex, and temperature tolerance, are affected at concentrations less than 1/10th of the 96-hr LC50. Many other systems such as respiration, and circulation may be affected at concentrations near 1/10th of the 96-hr LC50. The principal toxic components in pulp and paper mill effluents are resin acids and fatty acids naturally occurring in the wood pulped, and in effluents from bleaching processes toxic chlorinated compounds predominate. Untreated effluents have caused considerable environmental damage, but well-treated effluents have had minimal effects on fish production, although shifts in biological diversity have occurred.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pulp mill effluent, water-pollution, acute toxicity, subacute toxicity, bioassay, physiological effects, toxic components, review	Pulp mill effluent toxicity review	06/F

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