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Effect of 20- to 30-Day Continuous Exposure of Treated Bleached Kraft Mill Effluent on Selected Freshwater Species

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Large volumes of wastewater are produced during the mechanical and chemical operations used in the pulp and paper industry. WALDEN (1976) reported that a small groundwood mill, processing 4.54×10^4 kg/day (50 tons/day), can discharge $1.14\text{-}1.89 \times 10^6$ L waste/day (300,000-500,000 gallons waste/day). This author also stated that a bleached kraft pulp mill with a production of 6.80×10^5 kg/day (750 tons/ day) may discharge up to 1.14×10^8 L effluent/day (30 million gallons effluent/day).

Several studies have been conducted to assess the ecological impact these woodwastes and treatment by-products have on the aquatic environment (SMITH & KRAMER, 1965; DAVIS & MASON, 1973; ZIMMERMAN & LIVINGSTON, 1976; STOCKNER & CLIFF, 1976 and KELSO et al., 1977). Mechanical, chemical and biological waste treatment systems have been developed to reduce potential environment impact (BETTS & WILSON, 1966; LEACH et al., 1978; ULLRICH, 1978; NG et al., 1978; and WANG et al., 1979). Biological treatment such as storage oxidation basins, activated sludge systems and aerated stabilization basins (ASB) have proven useful in lowering the toxicity of pulp and paper mill wastewaters. CHANDRASEKARAN et al. (1978) have reported a 90% reduction in toxicity, biochemical oxygen demand (BOD) and resin acids at a mill which employs an ASB. Similar results have been found by SERVIZI & GORDON (1973) and GORDON & SERVIZI (1974).

The objective of this study was to evaluate the efficiency of an ASB waste treatment system employed at a large southern United States pulp and paper mill. Continuous-flow long term (20-30 day) exposures to a treated composite effluent were conducted on green sunfish (*Lepomis cyanella*), golden shiners (*Notemigonus crysoleucas*), hybrid bream (*Lepomis macrochirus x Lepomis microlophus*), channel catfish (*Ictalurus punctatus*) and red swamp crayfish (*Procambarus clarki*).

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MATERIALS AND METHODS

Test Animals

Green sunfish, golden shiners, hybrid bream and channel catfish were obtained from Easterling's Fish Hatchery in Clio, Alabama. Crayfish were obtained from the Louisiana Department of Agriculture's crayfish culturing pond in Breaux Bridge, Louisiana. All species, which included males and females, were held in separate 1200 L continuous flow holding tanks two weeks prior to testing. Basic water quality during acclimation was as follows: mean temperature (± S.D.) 9.5°C (±0.37); salinity 0 ^{o}/oo (±0.0); dissolved oxygen 10.1 mg/L (±0.31) and pH 7.2 (±0.19). All fish were fed Purina Trout Chow daily throughout the acclimation period. Crayfish were fed fresh fish.

The average wet weight of the test animals (±S.D.) was as follows: Green sunfish 10.9 g (±5.16); golden shiners 11.6 g (±4.44); hybrid bream 0.3 g (±0.32); channel catfish 4.6 g (±1.42) and crayfish 12.6 g (±3.23). Their mean corresponding total lengths (±S.D.) were 8.6 cm (±1.48); 10.0 cm (±1.36); 3.0 cm (±0.60), 8.4 cm (±0.89) and 8.1 cm (±0.61), respectively.

Effluent and Water Supply

Test effluent was obtained from Scott Paper Company in Mobile, Alabama. This mill produces a total of 1.27 x 10^6 kg/day (1400 tons/day) of bleached and unbleached pulp and paper. Approximately 90% of the pulp was bleached. Waste treatment consisted of neutralization, nutrient addition, primary settling, secondary treatment (activated sludge) and additional secondary treatment in the form of an aerated stabilization basin (1 day retention time). The effluent discharge volume was approximately 2.27 x 10^8 L/day (60 million gallons/day).

Treated effluent used during the bioassay studies was pumped continuously from an intake located near the terminus of the mill's aerated stabilization basin. Control and dilution water was pumped from the Mobile River to the laboratory from an intake (~ 1 m in depth) located ~ 0.6 km north of the mill's outfall. Since the Mobile River's basic flow is from north to south this placement was free from the influence of discharged effluent.

The delivery system used to provide a continuous flow of test concentrations was a modified version of the one described by VANDERHORST et al. (1977). A flow of 2 L/min at test concentrations (v/v±S.D.) of 0%

(±0.00), 17% (±6.4), 38% (±7.4), 60% (±1.1), 80% (±2.6) and 100% (±0.0) were used for exposures. When necessary, airstones were supplied to the treatment aquaria to maintain appropriate dissolved oxygen levels.

Exposure

Green sunfish, golden shiners and channel catfish

Thirty fish of each species were placed in 114 L treatment aquaria to evaluate the effects of exposure to the various effluent concentrations mentioned above.

Hybrid Bream

Experimental chambers were plastic baskets (volume 4 L) with 0.8 cm diameter holes (0.3 inch). Thirty fish were placed in each test basket then immersed into their appropriate treatment aquaria.

Crayfish

Plastic test chambers (volume 216 mL) fitted with mesh on both ends were used for exposures. Thirty crayfish (one per chamber) were immersed in each of the treatment aquaria.

All tests were performed in duplicate. Water quality (D.O., temperature, salinity and pH) during the experiment was determined as outlined in *Standard Methods* (AMERICAN PUBLIC HEALTH ASSOCIATION et al., 1976) and is presented in Tables 1 and 2.

RESULTS AND DISCUSSION

No mortality was observed for the channel catfish at effluent concentrations up to 100% (v/v) during the 30-day exposure period. Approximately 20% mortality at day 10, in both control and treatment aquaria occurred for golden shiners. Close examination of the dead fish revealed that these fish died of a fungal infection. Because of this, these fish were discontinued as a test species and the hybrid bream were substituted. No mortality was observed for the hybrid bream for the remaining 20 days of the study period.

Results for the green sunfish showed that at day 14 only one fish had died in the 20% (v/v) effluent treatment aquaria with no other death at the other test concentrations. At day 16 one more sunfish died in the 20% effluent tank. One fish also died in the 60% and 80% treatment aquaria. Mortality observations made at day 18 showed a total of three dead at 20%; one at 40%,

TABLE 1

Water Quality Summary (30-day Exposure) for Channel Catfish, Golden Shiners, Green Sunfish and Red Swamp Crayfish[+]

Tank #	Temperature (°C)		Salinity (°/oo)		pH		Dissolved Oxygen (mg/L)		Percent Effluent	Concentration (v/v)
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
1	11.1	1.62	0.4	0.26	7.24	0.132	9.42	0.505	0	0.0
2	11.3	1.68	0.4	0.26	7.24	0.106	9.37	0.482	0	0.0
3	12.5	1.67	0.4	0.21	7.27	0.092	8.94	0.438	17	6.4
4	12.6	1.75	0.4	0.20	7.31	0.088	8.91	0.376	17	6.4
5	14.3	1.77	0.5	0.12	7.41	0.103	8.43	0.455	38	7.4
6	14.3	1.75	0.5	0.12	7.46	0.114	8.48	0.488	38	7.4
7	16.2	2.08	0.6	0.09	7.50	0.111	7.85	0.541	60	1.1
8	16.2	1.95	0.6	0.09	7.56	0.110	8.10	0.505	60	1.1
9	17.9	2.21	0.6	0.06	7.56	0.104	7.29	0.552	80	2.6
10	18.0	2.32	0.6	0.05	7.61	0.092	7.60	0.561	80	2.6
11	19.7	2.46	0.7	0.06	7.66	0.087	7.31	0.573	100	0.0
12	19.6	2.48	0.7	0.06	7.63	0.085	7.02	0.752	100	0.0
13*	18.8	1.95	0.7	0.14	7.53	0.505	7.89	0.569	0	0.0

[+]N = 30 for each tank
* = Salinity control tank

TABLE 2

Water Quality Summary (20-day Exposure) for the Hybrid Bream+

Tank #	Temperature (°C)		Salinity (°/oo)		pH		Dissolved Oxygen (mg/L)		Percent Effluent	Concentration (v/v)
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
1	11.5	1.81	0.5	0.28	7.16	0.069	9.23	0.490	0	0.0
2	11.7	1.84	0.5	0.27	7.17	0.046	9.17	0.414	0	0.0
3	13.0	1.78	0.5	0.24	7.21	0.039	8.76	0.413	17	6.4
4	13.0	1.88	0.5	0.23	7.26	0.038	8.81	0.436	17	6.4
5	14.7	2.10	0.6	0.14	7.36	0.083	8.31	0.482	38	7.4
6	14.7	2.05	0.6	0.13	7.36	0.057	8.36	0.518	38	7.4
7	16.8	2.37	0.6	0.10	7.44	0.064	7.68	0.516	60	1.1
8	16.7	2.17	0.6	0.10	7.50	0.069	7.92	0.528	60	1.1
9	18.5	2.49	0.6	0.05	7.51	0.062	7.20	0.526	80	2.6
10	18.6	2.60	0.6	0.05	7.56	0.057	7.51	0.562	80	2.6
11	20.3	2.74	0.6	0.05	7.64	0.078	7.35	0.582	100	0.0
12	20.2	2.81	0.6	0.05	7.62	0.073	7.12	0.659	100	0.0
13*	19.2	2.10	0.7	0.15	7.35	0.505	7.74	0.588	0	0.0

+N = 20 for each tank
* = Salinity control tank

one at 60% and one at 80%. No further mortality was observed for the remaining 12 days of the 30-day exposure period.

Only two crayfish died during the exposure period. One animal died in the 80% treatment aquaria on day 4, while another died in the control tank on day 12.

Although some random mortality was observed during this long-term exposure study, no substantial toxic effects to the test species can be attributed directly to the effluent. Therefore, the performance of the treatment system employed at this pulp and paper mill seems to be adequate to prevent "harmful" toxic effects to the aquatic biota in the receiving waters surrounding the mill. Earlier studies by GORDON & SERVIZI (1974), using a bench scale treatment unit system, showed that a 99-h retention time was required for 65% survival of sockeye salmon (*Oncorhynchus nerka*) and pink salmon (*O. gorbuscha*) at an effluent concentration of 100% (v/v). Likewise, LEACH et al. (1978) have found that a well-operated treatment system, at a bleached kraft mill, should be capable of removing dehydroabietic acid, primaric acid and primorol under normal loading conditions. They also conclude that aerobic stabilization should provide adequate toxicity removal of chlorination stage effluents at most kraft mills.

This study dealt with a particular biological treatment system (ASB) used to treat pulp and paper mill wastes. Detoxification of such wastewaters through addition of sulphur dioxide to chlorination stage effluent was reported by BETTS & WILSON (1966). In addition, the treatment of pulp-bleaching wastewater with aluminium oxide followed by activated sludge treatment has proven useful in the removal of sulphonic acids, humic acids and 95% of the color (ULLRICH, 1978). Toxicity removal has also been accomplished through the use of a foam separation process. (NG et al., 1973; MUELLER et al., 1976 and NG et al., 1978).

In conclusion, this study shows that although there are various detoxification systems which have proven successful, the system at the mill under study (which employs an aerated stabilization basin as a final biological treatment) seems adequate to prevent deleterous toxic effects to the aquatic environment surrounding the mill's discharge.

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