Combining pilot-scale ozone and activated sludge treatments on newsprint mill effluents

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ABSTRACT

Low charges of ozone applied to the combined untreated effluents of a CTMP mill selectively remove resin and fatty acids and acute toxicity. Combining this with subsequent biotreatment may prevent highly toxic effluent streams from damaging a biotreatment system or causing toxic breakthroughs. Installation of pilot scale ozonation and activated sludge biotreatment systems allowed testing this idea. Continuous preozonation of woodroom effluent produced no adverse performance effects on the activated sludge system. To simulate a real treatment problem, the pilot activated sludge system underwent sufficient stressing to permit a substantial toxic breakthrough. Low-level preozonation of the most toxic in-mill effluent stream feeding the biotreatment system quickly eliminated the toxic breakthrough and restored the effluent to a nontoxic condition.

Application:

This study is an interim step demonstrating the potential of enzyme-mediator technology for pulp leaching. Further study may lead to the development of a more potent, less costly pulp delignifier.

ENVIRONMENTAL CONCERNS AND new effluent emission regulations have prompted most Canadian pulp and paper mills to investigate ways of improving their effluent treatment systems. A very common problem in both municipal and industrial activated sludge and aerated lagoon biotreatment systems is an upset or sudden change in the feed effluent. This can affect the microbial population and their degradative activities. Such disturbances frequently cause decreased treatment efficiency and elevated—noncompliant—levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and toxicity to reach the receiving waters. Recent results suggest that ozonation unlike biotreatment can instantly alter the effluent and may be a good way to prevent or combat such "toxic breakthrough."

Extensive work in the 1970s investigated ozonation as a potential tool to improve the quality of kraft mill effluents *(1–8)*. However, except for the work of Dorica and Wong *(9)*, our recent work *(10)* was the only publication on the application of ozone to the liquid wastes of thermomechanical pulp (TMP) and chemithermomechanical pulp (CTMP) mills. Recent ozone treatment trials at Paprican using softwood TMP and CTMP mill effluents have demonstrated that this oxidant selectively destroys acute toxicity measured by the Microtox, *Daphnia*, and trout assays *(10)*. This is due to the selective oxidation of resin and fatty acids (RFA) by ozone compared to total COD. This is most prominent when using small charges of ozone *(9, 10)*.

The RFA are a major group of tree-derived compounds responsible for TMP and CTMP effluent toxicity. RFA can reach 500–550 mg/L in CTMP effluents *(11)*. At lower levels than this, they are acutely toxic to fish and other aquatic life. As an example, Leach and Thakore *(12)* obtained a 96-h LC_{50} of 4–10% v/v for mechanical pulp mill effluent using juvenile trout. The resin acids (RA) were the major toxic components with LC_{50} values of 0.4–1.1 mg/L.

Because nearly stoichiometric and thus uneconomically large amounts of ozone would be necessary to remove most effluent COD *(10)*, ozone application would probably be best in conjunction with with biological treatment. This would be especially true for effluents having high or recalcitrant toxicity.

In this study, we have investigated the application of ozone as a secondary system pretreatment to control effluent toxicity and protect the sludge biomass. We have also tried using ozone after biotreatment to destroy residual toxicity. To this end, we constructed and used a pilot-scale ozonation unit with a 2 x 1.5 m^3 (two lines) activated sludge biotreatment unit at an eastern Canadian bisulfite chemimechanical pulp (BCMP) softwood newsprint mill.

The objective of this work was to demonstrate the prevention by ozone of "toxic breakthrough" in the activated sludge pilot. We achieved this both by preozonation of a particularly toxic mill effluent stream and by postozonation of the secondary clarifier outfall.

In the laboratory, both preozonation and postozonation were compatible with activated sludge. There was no detection of dissolved ozone. In the presence of the high COD typical of mechanical mill effluents, dissolved ozone quickly undergoes complete consumption. The effects of the two treatments were additive

CHARACTERISTICS	MILL A	MILL B	MILL B
	Primary clarifier effluent	Combined effluent[1]	Woodroom clarifier effluent
pH	6.1 ± 1.1 (5)[2]	7.31 ± 0.12 (15)	6.2 ± 0.3 (4)
Total suspended solids, mg/L	60 ± 28 (5)	3597 ± 789 (15)	NA[3]
COD_S, mg/L	1450 ± 212 (5)	3111 ± 817 (9)	1193 ± 33 (3)
BOD_5, mg/L	475 ± 170 (5)	1010 ± 57 (9)	NA
SO_3^{-2}, mg/L	32 ± 2 (2)	302 ± 81 (9)	Nil
SO_4^{-2}, mg/L	290 ± 11 (2)	272 ± 53 (9)	Nil
RFA, mg/L[4]	17.3 ± 5.9 (12)	15.4 ± 7.3 (3)	57.4 ± 2.34 (4)
Microtox, $100/EC_{50}$, % v/v	27.0 ± 16.8 (12)	61 ± 14.5 (6); 13.9[5]	133 ± 46 (7)
Daphnia magna, $100/LC_{50}$, 48 h, % v/v	6.6 ± 0.44 (2)	10.8[5]	NA
Trout, $100/LC_{50}$, 96 h, % v/v	5.6–10%[5]	8.3[5]	NA

[1]A mixture of the principal effluents produced by Mill B in the proportions of their production—BCMP/WR/WW:1.33:1:1
[2]Number of samplings
[3]NA = not available
[4]Thirteen identified resin/fatty acids and juvabione/dehydrojuvabiones
[5]Results obtained from mill

I. Typical effluent characteristics

but not complementary in detoxifying the combined effluents from the softwood newsprint mill.

Results obtained with the pilot activated sludge and ozonation units at the mill confirmed that combining ozone with activated sludge was feasible and effective. Low continuous ozone applications greatly reduced input effluent stream toxicity. This eliminated toxicity in the secondary clarifier. In this case, however, the activated sludge unit alone when properly functioning was very effective in producing a nontoxic, low BOD effluent. Adding ozone as a pretreatment or posttreatment would probably not be economically justifiable.

MATERIALS AND METHODS

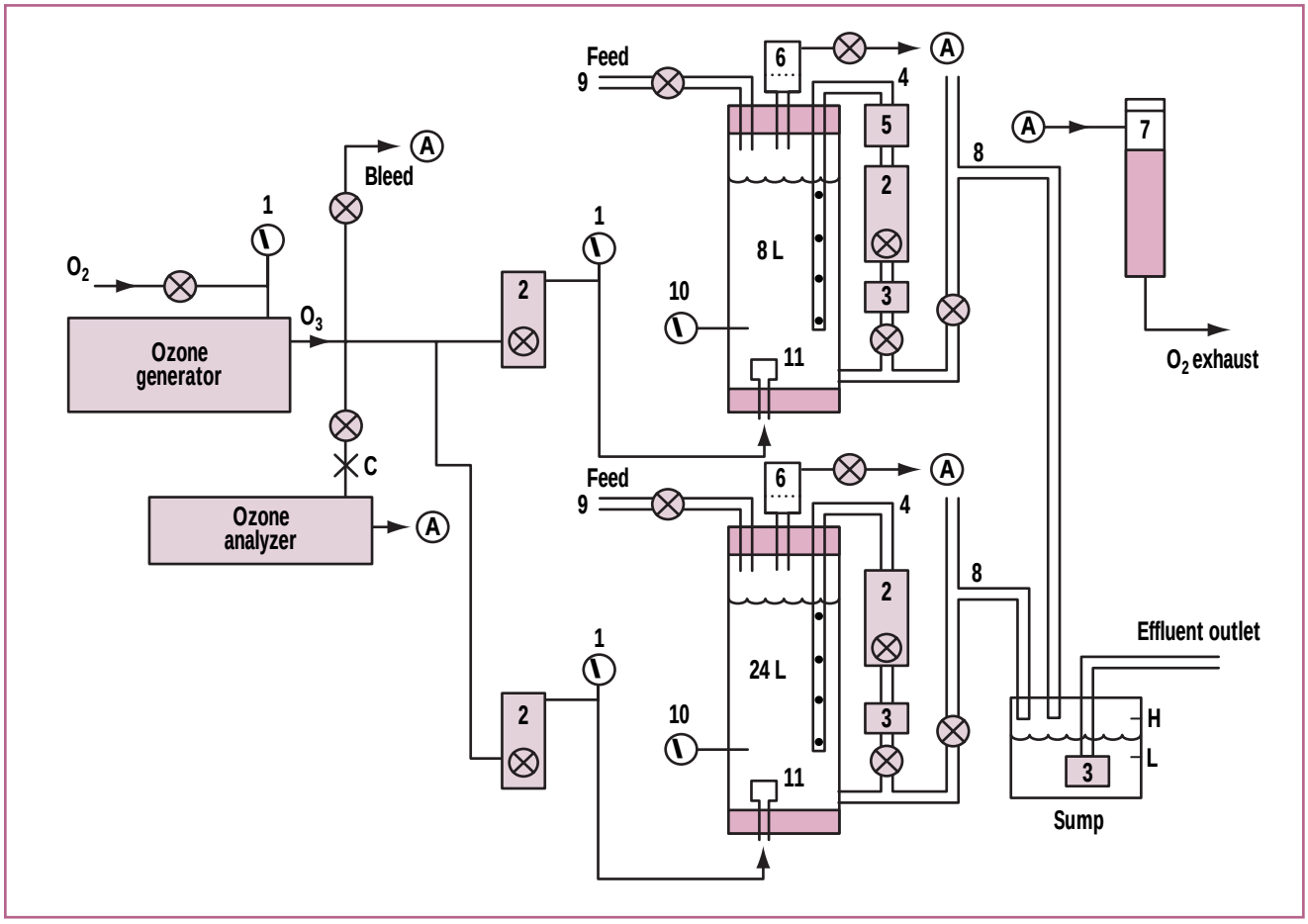
Effluents employed

The effluents used for the laboratory scale ozonation trials came from two eastern Canadian CTMP mills. Mill A produces 400 a.d. tons/day of peroxide bleached pulp typically using a 70% fir, 25% spruce, and 5% aspen furnish. The combined primary clarifier effluent includes all mill streams except cooling water. The flow rate is 20,700–30,500 m^3/day. Table I gives a typical characterization of the primary clarifier effluent. The mill effluent samples arrived within 48 h of collection. We stored them at 4°C for a maximum of 7 days. We usually used the effluents within 3 days of collection. The effluents had no treatment as received except pH and temperature adjustment as required.

Mill B produces 710 a.d. tons/day of mechanical (50–65%) and BCMP (50–35%) from black spruce and balsam fir. There are two effluents: woodroom clarifier effluent (WR) and a combined effluent containing BCMP, WR, and whitewater (WW) in a 1.33:1:1 ratio. Although this is the typical production ratio, we later changed it to 1:1.62:0.73 to increase the proportion of the most toxic stream during the pilot ozonation trial. The pilot work was at Mill B.

Chemical analyses

Gas chromatography (GC) *(13)* was used to measure effluent total RFA, juvabione, and dehydrojuvabione contents with minor method modifications as reported previously *(10)*. Using their peak areas calibrated against standards quantified seven different RA, four fatty acids, and two juvabiones. CPPA Method H.3P measured COD except absorbance determination used a spectrophotometer at 620 nm. Soluble COD (COD_S) was measured in supernatants of 2400-g samples centrifuged for 5 min. Total COD was measured in untreated samples. BOD measurement used CPPA Method H.2. Measurement of sulfite and sulfate used a Dionex QIC ion chromatograph with a Dionex AS4A Ion Pac column. Addition of 2% isopropanol to the samples pre-



1. Pilot effluent ozonation apparatus

vented the oxidation of sulfite to sulfate.

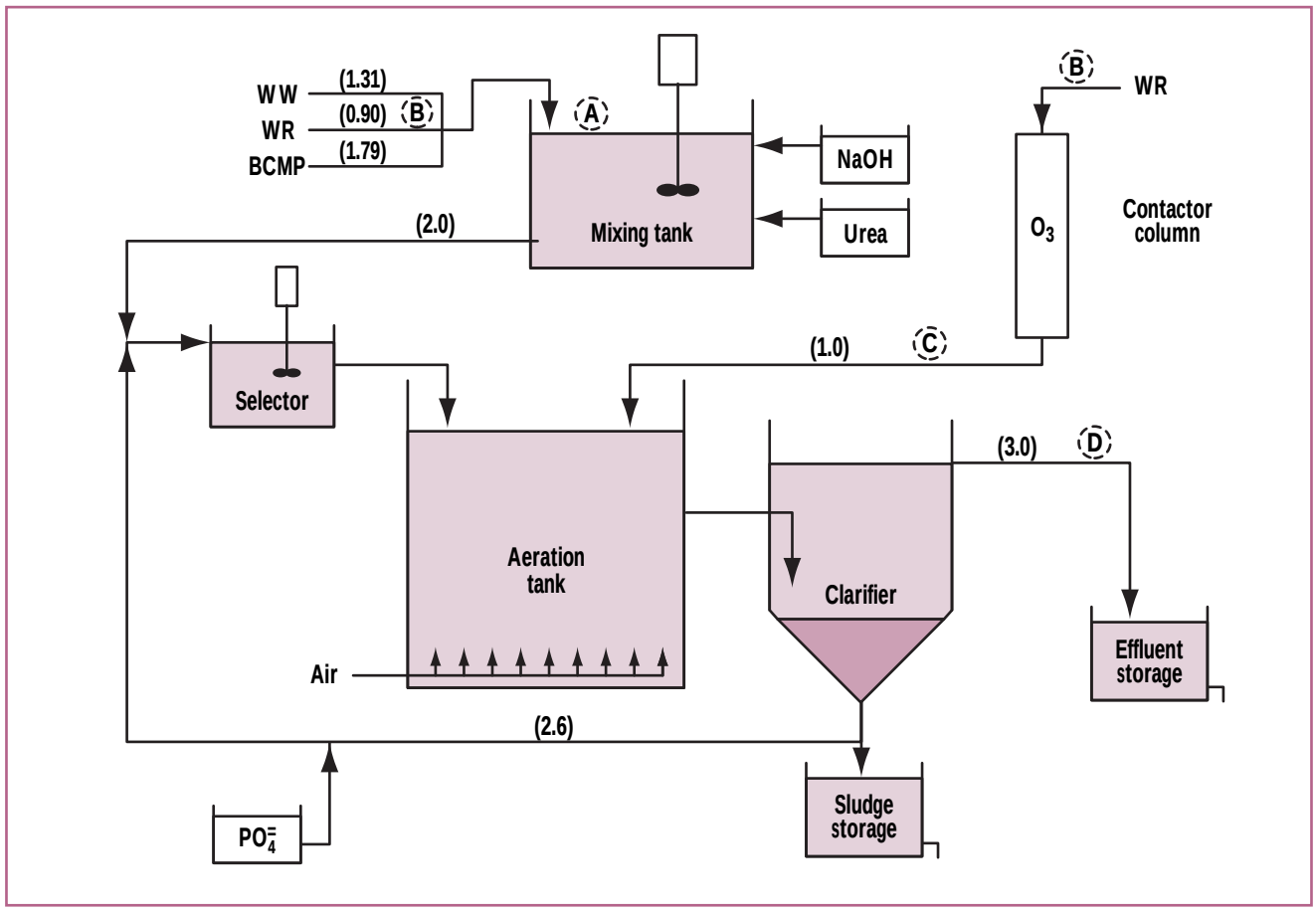
Toxicity tests

Microtox *Photobacterium* luminescence assay provided an estimation of toxicity. We followed the manufacturer's (Microbics Corp., Carlsbad, CA) recommended procedure except reconstitution and dilutions of Microtox reagent were with 10 m*M* Tris buffer with 2% NaCl. This assay measures toxicity by the ability of the effluent to suppress the luminescence of a marine bacterium by interfering with its membrane or central metabolic processes. Effluent toxicity is the reciprocal of the effluent dilution that reduces the bacterial light output by 50%. Confidence intervals were calculated with a significance threshold of 20% (a = 20%). The *Daphnia magna* toxicity assays were according to the standard procedure *(14)*. Samples were sent cool and analyzed immediately upon their arrival.

Ozonation

Figure 1 is a diagram of the pilot ozonation apparatus employed at the mill. It shows pressure gauges (1), gas or liquid flowmeters with needle valves (2), liquid pumps (3), effluent recirculation loops (4), a 1.5 kW immersion heater (5), foam traps (6), an ozone catalytic destruction unit (7), adjustable height column outlets with anti-siphon (8), and effluent feed points (9). Effluent pumps were at these points. In addition, the diagram shows a thermometer (10) and sintered alumina ozone spargers. The exhaust points (A) all connect to the catalytic ozone destruction unit (7). The designations H and L are the high and low points, respectively, for the range of sump pump level regulation. To measure the unconsumed ozone exiting an ozone contactor column, point C is connected to point A exiting from a foam trap (6).

All parts in contact with ozone were stainless steel, Plexiglas, Norprene, polytetrafluoroethylene (PTFE), polyvinyl chloride, or silicone rubber. A Griffin GTC-0.5B generator (Griffin Technics Corp., Lodi, NJ) produced gaseous ozone in oxygen for measurement with an AFX H1 ozone analyzer (IN/USA, Newtonville, MA). A 1.5 kW immersion heater in the effluent recirculation loop raised contactor column temperature in the 8-L column. Adjusting



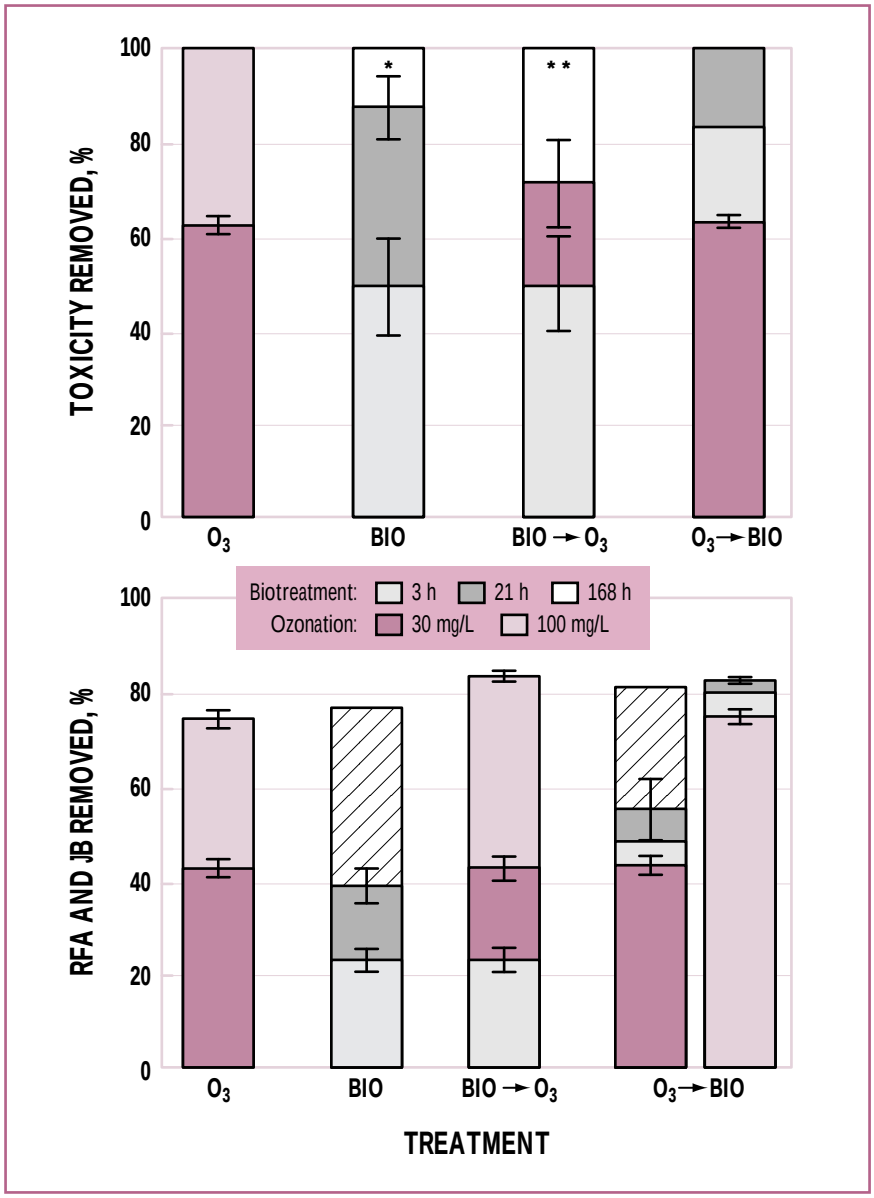
2. Mill B activated sludge pilot system with letters indicating the sampling points for data displayed in Figs. 5–7 and flow values in L/min

the feedline inlet valves or using a peristaltic metering pump on the feedline (not shown) regulated the effluent flow rates through the columns. Raising or lowering the anti-siphon overflow type column outlet tube—item 8 of Fig. 1—regulated the column liquid levels. The two ozone contactor columns had working volumes of 8–10.8 L and 24–28 L.

Contactor column headspace (unconsumed) ozone was measured by switching the AFX H1 gaseous ozone analyzer into a column exhaust line. The ozone values given are always the consumed or transferred doses. Ozonations used concentrations of 20–50 mg ozone/L in oxygen. Both columns employed centrifugal pump-driven effluent recirculation loops using exhaust tubes with lateral holes (one side only) to impart an effective circular mixing action to the effluent and gas bubbles. This optimized bubble retention time and path length.

The complete 2-contactor ozonation system was mounted in a 2.2 x 3 m (8 ft x 10 ft) mobile construction van adjoining the activated sludge pilot van and was fed directly from mill effluent lines. Effluents exiting the contactor columns accumulated by gravity in a 20-L sump with a liquid sensor providing automatic pumpout each time 5 L had accumulated. Excess gaseous ozone was converted into oxygen in a catalytic destruction unit employing alumina pellets coated with cupric and manganic oxides.

The laboratory-scale ozonation unit was a smaller version of the pilot unit. Batch ozonations used a concentration of 12–15 mg O_3/L O_2. This gas was sparged into 2.4 L of effluent at 0.4 L/min. The ozonation column was Pyrex tubing (90 cm x 7.5 cm) (2.0–2.8 L working volume) with polyvinyl chloride caps and stainless steel fittings. It included a sintered alumina sparger. A recirculation loop employing a centrifugal pump (8 L/min) ensured constant mixing and liquid downflow. Column temperature was controlled with a Barnant Model 621-8620 controller and heating tape.



*3. Removal of toxicity, RFA, and juvabiones by ozone (O_3), biotreatment (BIO), or by a combination of the two with each datum (bar height) the mean of two or three replicates. *72 h biotreatment removed all toxicity. ** All toxicity removed by 75mg O_3/L after 3h biotreatment*

Activated sludge effluent treatment

Laboratory trials. The activated sludge used as inoculum for Mill A effluent was produced in two 2-L fermenters operated as sequential batch reactors. Every 24 h, after l h of sedimentation, 1 L of the total 1.5-L working volume of each fermenter was replaced with fresh primary clarifier effluent from Mill A. Biotreatment temperature, dissolved oxygen, and mixed liquor suspended solids (MLSS) were 25°C, 2 mg/L, and 2 g/L, respectively. For Mill B effluent biotreatment, the inoculum was produced in a 5-L fermenter fed combined BCMP:WR:WW (1.33:1:1) effluents from Mill B. The reactor was operated with hydraulic retention time (HRT) of 24 h, 2,300 mg/L of MLSS, 0.4 food to microorganism ratio (F/M), and 10 days solid retention time (SRT). For the biotreatment assays, 200-mL aliquots of either raw or preozonized (30 or 100 mg 0_3/L) effluent were inoculated with 400 mg/L MLSS and then agitated in 500-mL baffle flasks for up to 96 h at 200 rpm.

To keep ozone costs within the economic range for mill-scale applications, the maximum ozone charge applied was 100 mg/L. For postozonation of biotreated effluent, 3-L effluent aliquots were also inoculated and agitated in a 4-L container at 25°C for 3 h at 200 rpm and aerated using an air stone. The suspended sludge settled for 30 min. Then the supernatant was decanted and ozonized. Ammonium-phosphate buffer was added to maintain a 100:5:1 ratio of BOD:N:P. The pH of the effluents was adjusted to 7.

Mill pilot trials. Figure 2 shows the biotreatment employing a continuously activated sludge pilot unit installed at Mill B a few months earlier. This consisted of two parallel treatment lines each with an anoxic chamber (62-L selector). Initially there were three 550 L sequential aeration tanks, and a secondary clarifier (165 L). Both lines came from a common mixing tank (550 L) where BCMP, WW, and WR were mixed in a 1.33:1:1 ratio to mimic the effluent flows and loadings projected for the mill in the future. Urea was added to the mixing tank and phosphoric acid to the sludge recycle line to maintain the BOD:N:P ratio at 100:5:1. A pH controller maintained the mixing tank pH from 6.5–7.5. Dissolved oxygen was manually measured every 3 h, and values of 3.0–4.0, 2.0–3.0, and 1.0–2.0 mg/L were maintained in tanks 1, 2, and 3, respectively. Treated effluents were stored in two 2-m^3 tanks where they were mixed and

sampled twice daily. Purged sludges were stored in two 350-L tanks where they were measured and sampled once daily.

RESULTS

Laboratory

Ozonation and biotreatment trials. For consideration as a pretreatment or posttreatment of a particular effluent, ozone must do the following:

- Selectively attack that effluent's toxicity
- Not adversely affect the subsequent biotreatment when used for preozonation
- Not create excessive new BOD from recalcitrant COD when used for postozonation.

To evaluate preozonation, we developed a laboratory assay in which the test effluent was first ozonized and then biologically treated for up to 96 h in shaking 500-mL baffle flasks. For postozonation, the effluent was first treated with activated sludge. Then the biomass sedimented naturally and the decanted supernatants were ozonized.

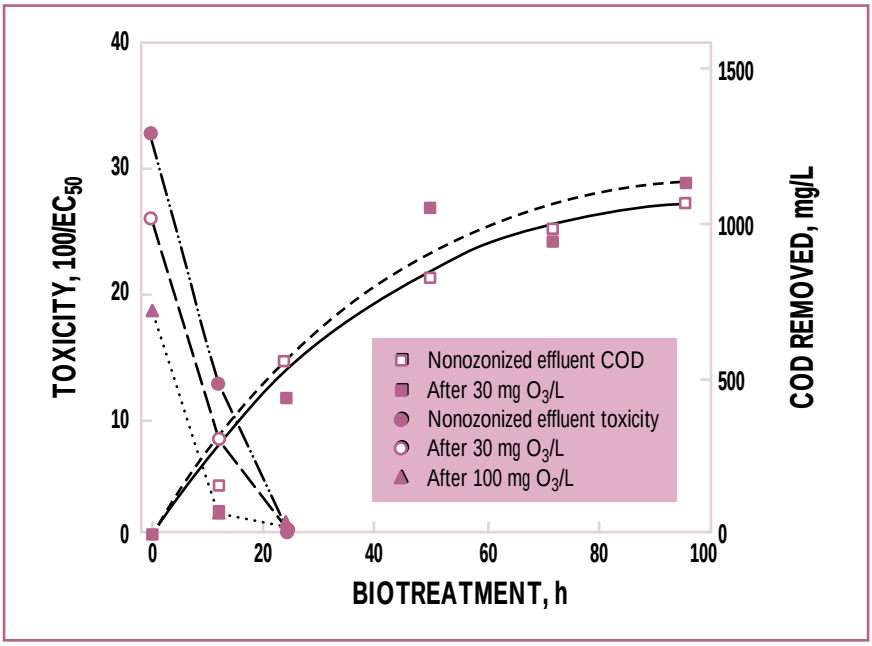
Figure 3 shows that the effects of ozone and biotreatment on both toxicity and RFA concentration of Mill A primary clarifier effluent were additive when ozone was applied as a pretreatment or posttreatment. Initial toxicity and RFA and juvabione contents were 38 toxicity units ($100/EC_{50}$) and approximately 15 mg/L, respectively. The two treatments could be applied in various proportions to reach zero toxicity or low RFA and juvabione content. The per unit removal efficiencies of both treatments decreased as the extent of effluent toxicity and RFA and juvabione removal increased. Rates of these removal efficiency changes appeared similar for ozone and biotreatment (not shown). For toxicity removal, Fig. 3 shows that ozone and biotreatment had additive but not complementary or synergistic effects on RFA and juvabione removal.

Both treatment sequences (ozone first or biotreatment first) showed simple additive effects. Both treatments applied separately or in combination left a small nondegraded RFA fraction of approximately 2.5 mg/L that did not produce acute Microtox toxicity. Thirteen specific RFA and juvabiones were quantified in these assays *(10)*. Using chromatographic peak areas, ozone and biotreatment degraded the RA approximately equally—dehydroabietic acid was more sensitive to biodegradation. The fatty acids showed large discrepancies between their sensitivities to the two treatments, but juvabione was far

	BOD, mg/L[1]	COD_5, mg/L[2]
Untreated effluent[3]:	613	1434 ± 34
30 mg O_3/L	563	1392 ± 42
100 mg O_3/L	506	1316 ± 20
Untreated effluent[3]:	660	1541 ± 69
3-h biotreatment	610	1379 ± 74
3-h biotreatment with 10 mg O_3/L	570	1263 ± 138
3-h biotreatment with 30 mg O_3/L	560	1313 ± 113
3-h biotreatment with 100 mg O_3/L	460	1185 ± 92

[1]Mean of duplicates
[2]Mean of triplicates ± standard deviation
[3]Different batches

II. Effect of preozonation and postozonation on BOD and COD



4. Effects of biotreatment and ozone on combined Mill B effluents

		Normal operation		With additional WR line		
HRT, h	24	18	12	6	4	
SRT, days	10	10	4.2	2.3	1.8	
MLSS, mg/L	4400	4530	3540	3562	2336	
F/M, kg BOD/kg MLSS/day	0.23	0.28	0.51	1.1	2.2	
Suspended solids, mg/L[1]	56	117	123	162	421	
BOD, inlet, mg/L	909	860	903	1010	715	
BOD removed, outlet, %	96	98	93	82	51	
COD, inlet, mg/L	2930	2940	2807	3513	2738	
COD removed, outlet, %	56	60	57	47	25	
Daphnia, inlet[2,3]	14.1	10.8	NA[4]	NA	NA	
Daphnia, outlet[5]	1	1	NA	NA	NA	
					No O_3	With O_3
Microtox, inlet[6]	53	13.9	11.6	50	97	60
Microtox, outlet	<1	<1	<1	<1–2.5	36	5.1
RFA, outlet, mg/L	NA	NA	NA	NA	7.85	3.86

[1]From the secondary clarifier
[2]*Daphnia magna*, 100/LC_{50}, 48 h, %v/v
[3]Inlet: mixing tank fed to the aeration tanks
[4]Not available
[5]Outlet: secondary clarifier outfall
[6]Microtox toxicity test: 100/EC_{50}, 15°C, 5 min, % v/v

III. Summary of the performance of the activated sludge pilot unit line #1

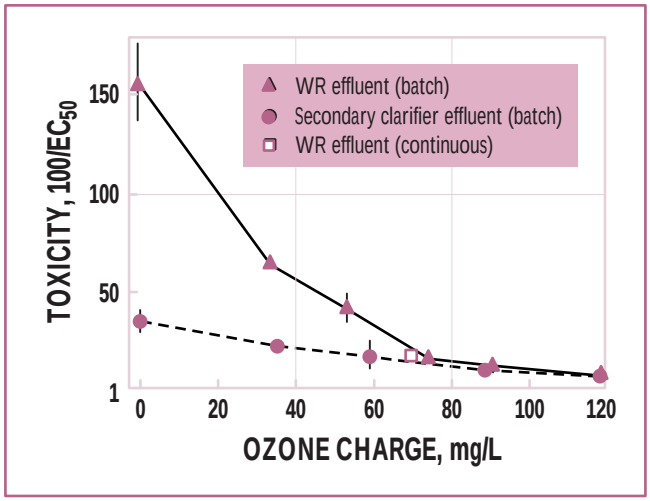
more sensitive to ozone. Even 168 h of biotreatment corresponding to the removal of all the BOD (results not shown) did not alter this residual fraction of toxicants.

Ozone and biotreatment also showed additive effects in the removal of COD. Whether ozone was applied on fresh or on biotreated effluent did not significantly (a = 95%) change the size of the ozone-oxidized COD fraction. The sequences 30 mg O_3/L followed by 3-h biotreatment and 3-h biotreatment followed by 30 mg O_3/L gave 15.6 ± 5.2% and 14.9 ± 5.9% total COD removal, respectively. The same result occurred with higher COD removal (17–23%) when applying an ozone charge of 100 mg/L in combination with a 3-h biotreatment. Ozone degraded BOD and COD equally. Table II shows that even an application of 100 mg O_3/L did not result in a significant net conversion of COD to BOD. This is in contrast to ozonation of primary and secondary kraft effluents where ozonation frequently appears to result in production of BOD from the COD *(2–4, 7)*.

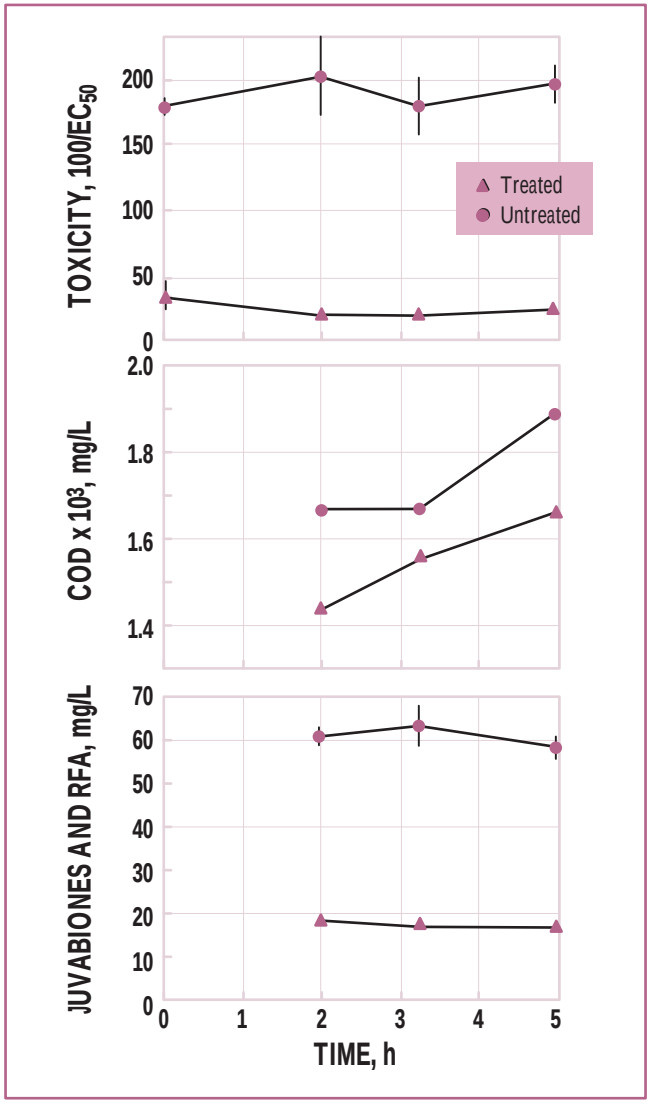
Figure 4 shows that application of 30 and 100 mg O_3/L charges to Mill B combined effluent removed much of the total acute toxicity within minutes. As with Mill A effluents, ozone only slightly decreased its COD. Also consistent with Mill A results, the preozonation of the combined Mill B effluents did not reduce the efficiency of a subsequent biotreatment. With or without this preozonation, however, the toxicants in the Mill B combined effluent were biodegradable. Figure 4 shows that they disappeared in less time than that required to destroy the biodegradable fraction of COD. All COD degraded in 120 h is considered BOD in the standard 5-day test for BOD. Preozonation of these combined effluents for destruction of toxicity did not decrease the HRT required to reach compliance because of the time required for BOD removal.

Mill pilot trials

Upon starting the pilot-scale ozonation trials, both lines of the activated sludge pilot plant were producing nontoxic secondary clarifier effluents from combined mill effluent. To challenge this system, we substantially increased the feed rates of the three in-mill streams to the mixing tank. The HRT values were reduced in steps from 24 h to 6 h. To stress the system further, two of three aeration tanks were removed—reducing the system's "plug-flow" character—before the present work began. Table III shows these conditions. Since the biotreatment system was working very well at an HRT of 24 h, toxic breakthrough appeared only after the HRT decreased to 6h. To achieve continuous toxicity, the HRT had to be decreased to less than 4 h by the addition of more WR effluent. The additional WR feed line was run through the 24-L ozone contactor column to the aeration tank. The most toxic in-mill stream—the WR



5. Batch and continuous ozonation of Mill B effluents with bars representing data within standard deviation



6. Effects of continuous ozonation of Mill B WR effluent on its toxicity, COD, RFA, and juvabione content with bars representing data within standard deviation

effluent—then accounted for approximately 50% of the total effluent treated. This approach to disturbing the system simulated a large volume spill or bolus of highly concentrated effluent arriving at the treatment system. Both are relatively common occurrences in mills. The effects of this on biotreatment system characteristics and performance included an elevated F/M ratio, poorer sludge floc formation, a larger sludge volume index (SVI) resulting in a sludge accumulation in the secondary clarifier, and substantially increased release of COD, BOD, and acute toxicity in the treated effluent. Table III shows specific results.

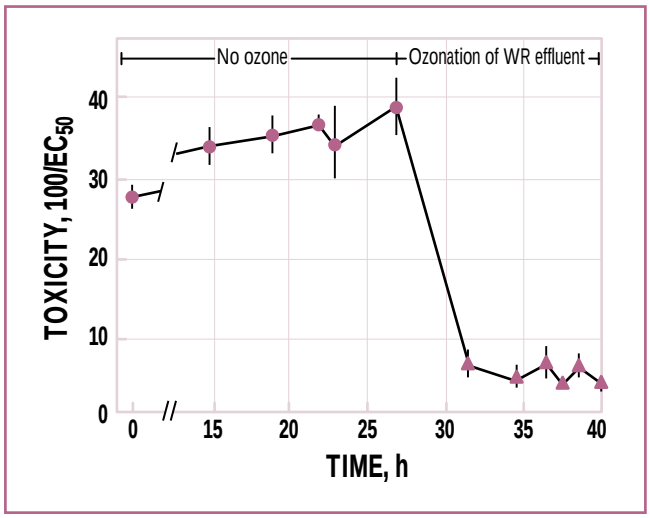
Batch postozonation of WR clarifier and secondary clarifier effluents. Because it is possible to tailor the rate and extent of ozone application to follow rapid effluent composition fluctuations, a rapid and economical postozonation treatment of the effluent could efficiently destroy intermittent or continuous residual toxicity.

While line no. 1 of the stressed pilot treatment system was releasing toxic effluent, the batch ozonations of the primary WR and the secondary clarifier outfalls were performed (Fig. 5). Continuous ozonation was applied at a rate of 2.46 mg O_3/L/min, 11.0–0 kPa above atmospheric in the 24-L column at temperatures of 21°C (clarifier) and 15°C (WR). Effluent and gas flows were 0.5 and 1.0 L/min, respectively.

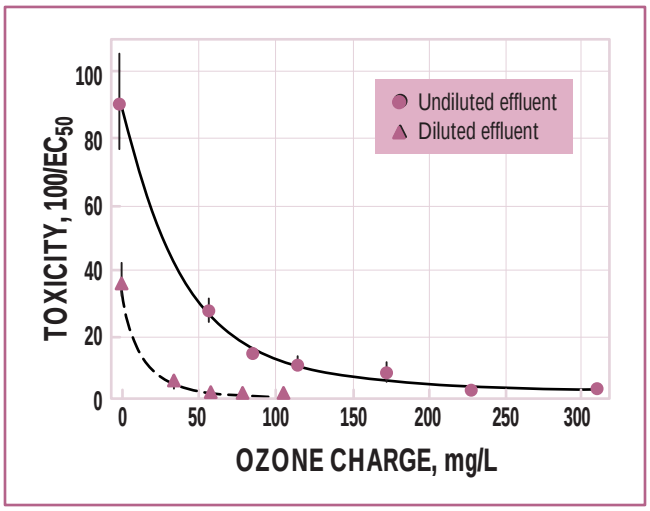
Probably because of the lower rate and extent of ozone detoxification and the resulting high ozone charge required to reach the Microtox zero toxicity level, postozonation of secondary clarifier effluent is a less interesting option than preozonation (Fig 5).

Continuous preozonation of WR clarifier effluent. Figure 6 shows that the raw WR effluent stream response to continuous ozonation was more promising. In this figure, untreated corresponds to WR effluent before ozonation and ozonized corresponds to WR effluent at the outlet of the ozone contactor column before its entry in the aeration tank. Ozonation was applied to effluent in the 24-L column at 2.45 mg O_3/L/min to a total charge of 71 mg O_3/L. Effluent temperature and flow and gas flow were 12.5°C, 0.5 L/min, and 1.0 L/min, respectively.

With a 70 mg O_3/L charge, toxicity decreased by approximately 88%. Comparing batch to continuous ozonation of a WR effluent stream at the same ozone charge in Figs. 5 and 6 shows similar detoxification efficiencies. The performance of ozone in treating small batches of



7. Effect of continuous preozonation of Mill B WR effluent on the secondary clarifier residual toxicity with and without ozonation with bars representing mean data values within standard deviation



8. Effect of Mill B WR effluent dilution on the ability of batch ozonation to destroy its toxicity with bars representing mean data values within standard deviation

Effluent	Upper limit	100/EC_{50} [1] Median	Lower limit
Whitewater (WW)	33.2	31.0	28.9
Woodroom (WR)	67.0	54.0	43.4
BCMP	46.9	42.9	39.3
Calculated combined[2]	48.8	42.6	37.4
True combined[3]	45.6	40.9	36.7

[1]Obtained at 15°C and 15 min with 80% confidence limits of the data
[2]Calculation based on a WW:WR:BCMP = 1:1:1.33 mixture using the measured toxicities of the individual streams
[3]Measured toxicity of a mixture of WW:WR:BCMP = 1:1:1.33. which was typical of the combined effluents

IV. Additive effects of in-mill stream toxicities

effluent therefore was comparable to that seen in continuous treatment of an effluent stream. As expected from the mill effluent's high acute toxicity, the RFA concentration in the WR effluent was high at 61.1 ± 7 mg/L compared to the combined effluent which contained 19.3 ± 5.9 mg/L. The data in Fig. 6 confirm earlier findings that a strong correlation exists between the acute Microtox toxicity of an effluent and its total RFA content *(10)*. There is no information on whether ozone is completely degrading the RFA or simply partially oxidizing them to forms no longer acutely toxic that do not register as RFA in the standard GC assay, however.

Data on toxicity, COD, and RFA and juvabiones before and after continuous ozonation of WR effluent appear in Figure 6. Combined with results in Fig. 4, they corroborate batch results showing that ozonation of CTMP effluent results in large decreases in toxicity and RFA content and only small decreases in COD.

Continuous preozonation of WR effluent before activated sludge treatment. The "control" phase of pilot operation—WR feed with no preozonation—was monitored for 27 h. Then ozone was continuously applied to the WR effluent (16°C) stream via the 24-L ozonizer column at 3.7 mg O_3/min/L for an absorbed charge of 70 mg O_3/L for 13 h. Effluent and gas flows were 1 L/min and 1.5 L/min, respectively. Figure 7 shows that ozonation of WR effluent before biological treatment substantially lowered the toxicity of the secondary clarifier outfall. To determine the contribution of the activated sludge to the removal of the total toxicity, we calculated toxicity balances for the control and ozonation phases of the pretreatment. These balances required knowing the total toxicity entering the line no. 1 aeration tank and leaving the secondary clarifier. Since two lines were going to the aeration tank (the mixing tank and the extra WR lines), we calculated a mean toxicity assuming that toxicities were additive. A separate experiment verified this assumption by measuring the toxicity of the individual feeds and of the mixture, as Table IV shows.

	Toxicity[2], inlet			Toxicity, outlet	Toxicity removed by biotreatment
	Mixing tank	WR clarifier	Total	Clarifier	
Without ozone	130	160	290	108	182
With ozone	152	30	182	15	167

[1]Toxicity balances calculated from the following stream flow rates and mean toxicities: Mixing tank [2.0 L/min and EC_{50} (% v/v) of 1.53], WR clarifier effluent (1.0 L/min and EC_{50} of 0.625), clarifier (3.0 L/min and EC_{50} of 2.78). During the ozonation trial, the mixing tank, the nonozonized and ozonized WR clarifier effluents, and the secondary clarifier toxicities were 1.32, 0.51, 3.28, and 19.5, respectively.
[2]Toxicity units are the product of ($Q \times 100/EC_{50}$) where Q is in L/min.

V. Total toxicity degraded by the biotreatment with and without the ozonation of the WR effluent stream[1]

KEYWORDS
Activated sludge process, biological treatment, chemithermomechanical pulps, effluent treatment, newsprint mills, ozone, ozonization, resin acids, softwoods, toxicity.

Those data show that the toxicities contributed by these streams were simply additive and did not interact to enhance or diminish each other.

Although the system was very perturbed, the toxicity balances of Table V indicate that the activated sludge maintained its level of detoxifying activity despite the lowering of the mean toxicity feeding the aeration tank by the preozonation. Preozonation therefore both prevented toxic breakthrough and had no detrimental effect on the activated sludge.

Effects of temperature, application rate, and dilution on detoxification by ozone. As previously noted in laboratory trials, ozonation at an elevated temperature (50°C) induced better detoxification *(10)*. When continuously ozonizing an effluent during commercial practice, Table VI shows that ambient temperature gave good results. There was extensive detoxification of WR effluent under continuous ozonations at 15°C. Toxicities decreased from 140–155 ($100/EC_{50}$) to 17–21 with an ozone charge of 71 mg/L.

Table VI shows that decreasing the rate of ozone application from 5.3 to 2.7 mg O_3/L/min resulted in a small but significant improvement of clarifier outfall detoxification. The effluents consumed the same total amount of ozone (114 mg/L) and completely consumed the ozone applied to the contactor column.

Figure 8 shows that complete detoxification of WR effluent did not occur even after an application of 300 mg O_3/L. Ozonations were in the 10.8-L column at 50°C with 4.26 mg O_3 applied per L per min. Was this "detoxification plateau" caused by recalcitrant residual toxicity, new ozonation by-products, or pH? Previous work has shown that 100 mg/L ozonations of combined CTMP primary clarifier effluents usually resulted in pH decreases from 7 to 5 *(10)*. It is known that the ozonation pH determines the active oxidizing species. Molecular O_3 is dominant in acidic conditions, and hydroxyl and related radical species are more important in alkaline conditions *(15)*.

Diluting the effluent by 50% (effluent to water dilution was 1:1) with tap water allowed complete detoxification with an ozone charge of 100 mg/L. This suggested that there was no recalcitrant toxicity in the untreated effluent. The pH fell from 7.2 to 7.0 in the diluted WR and from 7.2 to 6.2 in the undiluted WR effluent after applying 100 mg O_3/L. Complete detoxification occurred in diluted WR, and the detoxification rate was significantly higher.

CONCLUSIONS

Using the data compiled from the work reported here, we offer the following conclusions:

1. Ozone or biotreatment alone or in combination can accomplish complete detoxification of CTMP primary clarifier effluent—measured by the Microtox assay—and RA, fatty acid, and juvabione removal. Neither treatment greatly improves nor detracts from the rate of the other treatment applied subsequently. The two treatments are additive but not complementary for toxicity.
2. Ozone alone removed stoichiometric amounts of COD from CTMP primary clarifier effluent and combined (WR, WW, and BCMP) effluents.
3. While ozone removed toxicity from effluents very rapidly and efficiently, biotreatment alone removed toxicity faster than BOD. This makes BOD removal

Effluent	Application rate, mg O_3/L/min	Total O_3 charge, mg/L	Temperature, °C	Toxicity, 100/EC_{50}
Clarifier	0	0	17	28.4 (27.0–29.8)[1]
	5.3	114	17	17.6 (16.5–19.1)
	2.7	114	17	16.1 (15.6–16.3)
	2.7	114	30	14.4 (13.0–-15.9)
WR	0	0	18	67.2 (64.5–70.0)
	4.3	92	18	19.2 (17.9–20.6)
	4.3	92	50	12.2 (9.0–16.5)

[1]Lower and upper limits of the 80% confidence intervals

VI. Effects of temperature and ozone application rate on toxicity removal

the rate-limiting step in obtaining regulatory compliance. In this system, ozone therefore did not greatly decrease the biotreatment times required.

4. Continuous preozonation of WR effluent greatly lowered the toxicity and was compatible with the activated sludge pilot system.
5. Increasing effluent temperature, diluting the effluent, and decreasing the rate of ozone application all improved the efficiency of ozone-mediated effluent detoxification.
6. Preozonation of the most toxic in-mill stream (WR) quickly eliminated the toxic breakthrough appearing in the secondary clarifier outfall caused by a poorly functioning biotreatment system.

One can extrapolate these results with woodroom effluent to the whole mill and assume an over-the-fence ozone cost of US$ 2/kg. Further assuming production of 30 m^3 effluent (9 m^3 WR) per ton of pulp, the cost for the temporary ozonation in the system and mill employed in this study will be US$ 1.42 per ton of pulp delivered. If 50 mg O_3/L were sufficient, then the cost would fall to US$ 0.90 per ton of pulp produced.

The cost of ozone treatment at a particular mill will depend on the following factors:

- Local power cost
- Whether the mill presently uses oxygen such as for E_o or oxygen delignification stages
- Whether ozone application is continuous or intermittent
- The amount and susceptibility to ozone of the problem toxicity in the effluent
- Whether there is ozone pulp bleaching
- Whether treatment will be for a single stream or the combined effluent
- The degree of closure or water economy in the mill
- The degree of toxicity reduction desired, since ozone becomes a less efficient detoxicant as effluent toxicity approaches zero. TJ

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