Reducing chlorinated organic compounds from bleached kraft mills through first stage substitution of chlorine dioxide for chlorine

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ABSTRACT: Concern about the chlorinated organic compounds in kraft bleach plant effluent has led the U.S. Environmental Protection Agency (EPA) to propose new regulations to limit discharge of AOX, chlorinated dioxins and furans, and certain chlorinated phenolic compounds. Several mills have either eliminated the routine use of elemental chlorine by substitution of chlorine dioxide in their bleach plants or conducted trials to evaluate this technology. This paper describes impacts on chlorinated organic compounds discharged during long-term operation of low-chlorine bleaching at one James River Corp. mill. Results show that complete substitution of chlorine dioxide for chlorine in the first bleaching stage reduced chlorinated dioxins and highly chlorine-substituted chlorinated phenolic compounds to nondetectable levels in the bleach plant effluent. The AOX level in final mill effluent, while above that proposed by EPA, is greatly reduced from that observed before the bleach plant modifications.

KEYWORDS: Adsorbable organic halogen, bleach plants, bleaching, bleaching effluents, chlorine compounds, chlorine dioxide, dioxins, EPA, phenols, regulations, substitutes, test methods.

The U.S. Environmental Protection Agency (EPA) has proposed numeric limitations for several chlorinated organic compounds as part of its periodic revision of the effluent guidelines for pulp and paper mills. Specifically highlighted for regulation in bleach plant effluent are dioxin (2,3,7,8-TCDD and 2,3,7,8-TCDF) and 12 chlorinated phenolic compounds. The agency has proposed stringent limitations for AOX in final effluent.

Several James River Corp. mills, along with much of the bleached pulp and paper industry, have implemented significant process changes over the last several years to reduce trace amounts of dioxin found in pulp and effluent. In addition to being very successful in reducing dioxin levels, the process changes have reduced levels of other chlorinated organic compounds in mill effluents. This paper will focus primarily on reductions at James River's Wauna, OR, mill because this mill has significantly changed its bleaching process and carefully documented the effects of the changes on the formation of chlorinated organic compounds. Also reported will be supporting data from two other mills: the Naheola mill in Pennington, AL, and the Marathon, ON, mill.

Wauna mill data

The Wauna mill is located on the Columbia River, about 40 miles upstream from the Pacific Ocean. Constructed in the late 1960s, the mill produces three main lines of products: consumer and commercial grades of bathroom tissue, paper

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towels, and napkins; groundwood specialty printing papers produced from a blend of 25% kraft and 75% refiner mechanical pulp; and printing and business papers from kraft pulp.

I. Dioxin levels in bleach plant effluent

Bleaching *sequence*	Percent *substitution*	Chlorine *factor**	Dioxin levels, ppq Bleach plant *TCDD*	*TCDF*	Final effluent *TCDD*	*TCDF*
(C+D)(EO)HHD	10	0.16	48	124	9	24
(CD)(E, O+P)DD	50	0.11	20	92	ND	17
(CD)(E, O+P)DD	70	0.07	ND	17	ND	15
(CD)(E, O+P)DD	90	0.02	ND	31	ND	13
D(E, O+P)DD	100	0.00	ND	ND	ND	ND

*Chlorine factor = percent Cl_2/kappa number

Technical description of the pulping and bleaching lines

Wood source and species. The mill produces about 850 tons/day of bleached kraft pulp from softwood chips and sawdust. The species are predominantly Douglas-fir and Western hemlock. The mill also produces a small amount of bleached hardwood kraft from Red Alder. More than 80% of the incoming wood is residual chips or sawdust from the timber industry, while the remainder is purchased as chips made from logs of too poor a quality to be made into solid wood products. Wauna also produces 300 tons/day of refiner mechanical pulp from 80% Western hemlock and 10% plantation cottonwood.

Kraft pulping. Softwood and hardwood chips are campaigned through a single-vessel Kamyr hydraulic digester operated at about 700 unbleached tons/day. Sawdust pulp is produced in an M&D digester at a rate of 250 unbleached tons/day. The kappa number for softwood from the two digesters averages about 31, while the hardwood kappa is about 18. Each digester has its own three-stage washing line. Each of the three pulps (chip softwood, chip hardwood, and softwood sawdust) is stored separately in high-density chests. Wauna has only one bleach line, so the three pulp grades are scheduled through the bleach plant in separate production runs. A typical run lasts about 5 hours.

The B&W recovery furnace, originally installed with the mill in the late 1960s as a direct-contact furnace, was rebuilt and converted to a noncontact furnace in 1986. The recovery furnace has insufficient capacity to process all of the spent liquor produced by the kraft digesters. About 6% of Wauna's black liquor is trucked to other mills for recovery of the kraft chemicals. This means that Wauna is dependent upon under-utilized recovery capacity at other mills to sustain its normal level of production.

Bleach plant. The original bleaching sequence at the Wauna mill was fairly typical of that used when this mill was designed. The first stage used elemental chlorine and 10% chlorine dioxide for pulp strength protection. The second stage was caustic extraction (oxygen reinforcement was added in 1986 to improve the extraction efficiency). The third and fourth stages were sodium hypochlorite. The final stage utilized chlorine dioxide to raise the pulp to its target brightness of 83–86.

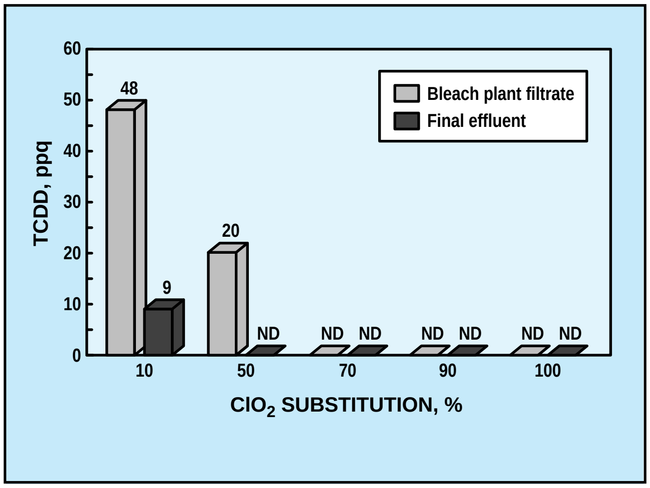
After the discovery that trace amounts of dioxin were formed in the chlorine bleaching process and, because some of the grades of paper produced at Wauna were used in food-contact applications, James River started a dioxin reduction program to implement the company's commitment to the industry's goal of achieving less than 2 ppt in pulp used for food-contact packaging. Research into possible process modifications indicated that substitution of chlorine dioxide for some of the elemental chlorine used in the first bleaching stage reduced dioxin in pulp and final mill effluent to nondetectable levels.

At approximately the same time as dioxin concerns were being addressed by the mill, the state of Oregon issued a National Pollutant Discharge Elimination System (NPDES) permit to the Wauna mill, which included a requirement to reduce AOX levels in final effluent to below 1.5 kg/ton. Laboratory-scale testing indicated that this level of AOX could possibly be achieved at a substitution level of about 90%. Since it appeared that substantial substitution of chlorine dioxide for chlorine would both reduce dioxin and lower AOX, the strategy was adopted for the Wauna mill and resulted in the startup of a modified bleach plant in the middle of 1992.

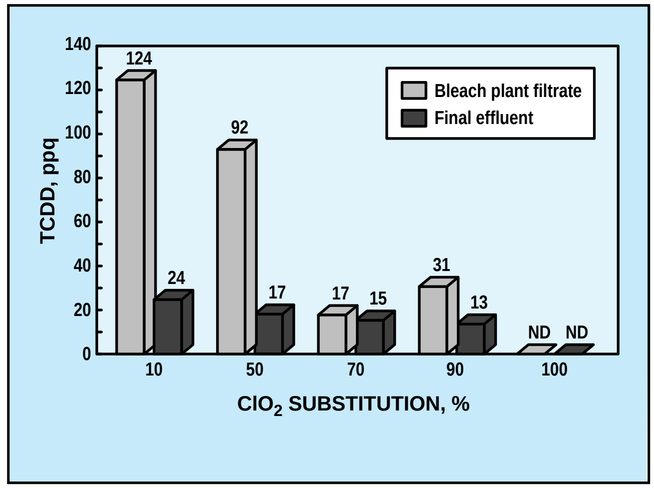
Following is a summary of the startup events of the new bleaching sequence and the eventual conversion to complete substitution of chlorine dioxide for chlorine in the first stage:

- May 1992. The chlorination stage was converted to medium-consistency operation. The bleaching sequence was (C + D)(EO)HD.
- July 1992. A new R-8 chlorine dioxide generator was started up. The substitution of chlorine dioxide for chlorine was raised to 70%, making the bleach sequence (CD)(EO)HD.

1. 2,3,7,8 TCDD in Wauna bleach plant filtrate and final mill effluent (ND = nondetectable)



2. 2,3,7,8 TCDF in Wauna bleach plant filtrate and final mill effluent (ND = nondetectable)



- August 1992. Hypochlorite was eliminated from the bleaching sequence, and a second chlorine dioxide stage was added. Sequence was (CD)(EO)DD.

- September 1992. Peroxide addition to the (EO) stage was started, making the sequence (CD)(E, O+P)DD.

- November 1992. Chlorine dioxide substitution level was raised to 90% for a one-month trial. The second, third, and fourth stages were not changed.

- December 1992. Chlorine dioxide substitution was lowered to 50% for an extended period to gain long-term operating experience. Substitution was raised to 70% for certain production runs during this time.

- June 1993. The chlorine mixer failed due to a corrosion problem. The mill determined that it was not cost-effective to spend the capital necessary to replace the chlorine mixer and make some required upgrades to the chlorine car unloading system. The mill is now operating with the D(E, O+P)DD sequence.

Wastewater treatment system. Wauna operates a standard activated-sludge wastewater treatment system. Fiber containing wastewaters go to a primary clarifier. Primary clarifier effluent is combined with acidic bleach plant effluent, and the combined waste stream enters an unaerated holding pond with an 8-hour retention time. All samples referenced as secondary treatment influent were collected at the holding pond outlet.

At the outlet of the holding pond, wastewater is mixed with recycled secondary sludge, and the mixture enters an aeration basin equipped with 36 floating aerators. The residence time in the aeration basin is about 6 hours, and the mixed-liquor suspended solids is maintained at about 2000 mg/L. The BOD feed to the aeration basin averages 46,000 lb/day, and overall BOD removal averages 88%. Downstream from the aeration basin, biological sludge is separated from treated effluent in two parallel secondary clarifiers and recycled to the aeration basin inlet. Treated effluent is discharged into the Columbia River.

Chlorinated organics reduction

Dioxin. Through each of the bleach plant modification steps, the mill collected data on dioxin levels both in bleach plant filtrate (combined acid and alkaline sewers) and in final mill effluent. The data in **Table I** and **Figs. 1 and 2** are results from each operating scenario. There is a progressive reduction in dioxin formation with increasing levels of substitution. More detailed data, including detection levels, are included in **Table II**.

TCDD was reduced to nondetectable (less than 10 ppq) levels in final effluent when the level of chlorine dioxide substitution was raised to 50% and remained consistently nondetectable as more chlorine dioxide was introduced into the first stage. TCDF remained slightly above the detectable level until elemental chlorine was completely eliminated.

TCDD in combined bleach plant filtrates was reduced to nondetectable levels when substitution of chlorine dioxide reached 70%. Both TCDD and TCDF were nondetectable when only chlorine dioxide was used in the first stage. Note that these levels were achieved on a conventional unbleached-softwood pulp with a kappa number about 31.

AOX. AOX reduction in final effluent was monitored throughout the bleach plant modification project. **Table III** and **Fig. 3** show AOX reduction in treatment plant influent and effluent with increasing chlorine dioxide substitution.

AOX levels showed a steady decline with increased substitution of chlorine dioxide, reaching a minimum of about 0.5 kg/unbleached metric

II. Dioxin reduction at Wauna

A. Premodification: January to July, 1992
Bleaching sequence: (C+D)(EO)HHD

	Bleach plant sewer		Final effluent	
	TCDD, ppq	*TCDF, ppq*	*TCDD, ppq*[1,2]	*TCDF, ppq*
	38	70	10	20
	32	44	8	12
	39	81	ND(7.6)	26
	27	65	8	20
	53	190	ND(4.9)	19
	50	130	11	22
	98	290	15	51
Average	48	124	9	24

B. Post modification: August to December, 1992

	Bleach plant sewer		Final effluent	
Bleach sequence	*TCDD, ppq*	*TCDF, ppq*	*TCDD, ppq*	*TCDF, ppq*
(CD)(EO)DD (70% substitution)	ND (6.4)	20	ND(6.4)	27
(CD)(E, O+P)DD (70% substitution)	ND (8.9)	13	ND (3.3)	9
(CD)(E, O+P)DD (70% substitution)	8	17	2.6	13
Average	ND	17	ND	15
(CD)(E, O+P)DD (90% substitution)	ND (3.2)	9	ND (1.4)	11
(CD)(E, O+P)DD (90% substitution)	7	54	ND (3.3)	15
Average	ND	31	ND	13

C. Post-modification: December to May, 1993
Bleaching sequence: (CD)(E, O+P)DD (50% substitution)

	Bleach plant sewer		Final effluent	
	TCDD, ppq	*TCDF, ppq*	*TCDD, ppq*	*TCDF, ppq*
	25	100	ND (4.4)	12
	12	30	48	7
	37	220	ND (4.5)	35
	6	19	ND (3.4)	13
Average	20	92	ND	17

D. Post-modification: June 1993 to February 1994
Bleaching sequence: D(E, O+P)DD

	Bleach plant sewer		Final effluent	
	TCDD, ppq	*TCDF, ppq*	*TCDD, ppq*	*TCDF, ppq*
	ND (2.3)	7.6	ND (2.7)	17
	ND (2.8)	10	ND (3.2)	9
	ND (1.6)	ND (1.8)	ND (1.3)	ND (3.3)
	ND (1.4)	ND (1.9)	ND (1.3)	ND (1.7)
	ND (3.4)	ND (2.4)	ND (2.8)	ND (3.5)
	ND (5.5)	ND (6.5)	ND (1.9)	3.2
	ND (8.0)	ND (10.0)	ND (3.8)	ND (2.3)
	ND (2.5)	ND (1.9)	ND (1.4)	ND (1.9)
			ND (2.7)	ND (3.0)
Average	ND	ND	ND	ND

[1]Average determined using Cohen's Technique (NCASI Technical Bulletin No. 621, December, 1991).
[2]Numbers in parentheses indicate detection levels.

III. AOX levels (kg/a.d. unbleached metric ton)

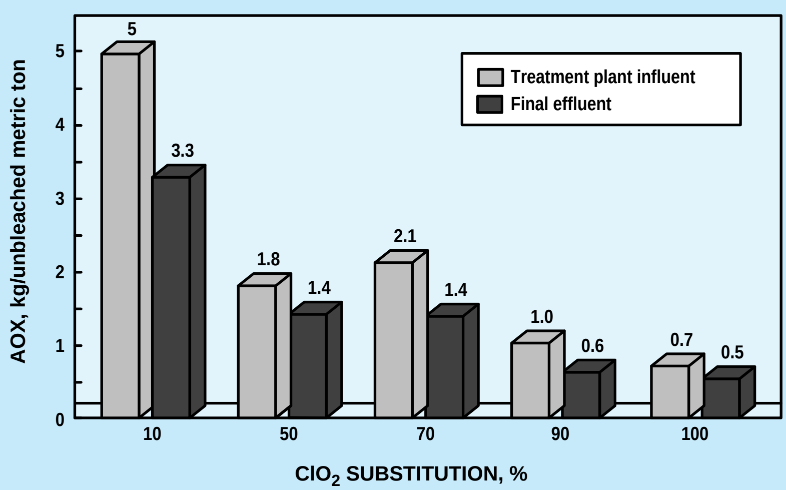
Bleaching sequence	*Substitution, %*	*Kappa factor*	*AOX level Influent*[1]	*Effluent*	*Treatment plant removal, %*[2]	*No. of samples*[3]
(C+D)(EO)HHD	10	0.18	5.0	3.3	28	26
(CD)(E, O+P)DD	50	0.22	1.8	1.4	26	23
(CD)(E, O+P)DD	70	0.24	2.1	1.4	28	10
(CD)(E, O+P)DD	90	0.19	1.0	0.6	33	11
(D)(E, O+P)DD	100	0.19	0.7	0.5	27	21

[1]Holding pond outlet.

[2]Average of individual percentage reduction calculations for all AOX tests at the indicated substitution levels.

[3]All AOX samples are daily composites.

3. AOX in Wauna wastewater treatment plant influent and effluent (solid line = proposed EPA regulation, 0.16 kg/ton)



ton when only chlorine dioxide was used in the first stage. The final level, however, remains significantly above the regulatory level of 0.156 kg/ton (monthly average) stipulated by EPA in the proposed effluent guidelines revision *(1)*. The reduction efficiency of AOX through the primary and secondary treatment system remained relatively constant as the bleaching sequence was modified.

Chlorinated phenolic compounds. EPA has proposed to establish limits for 12 chlorinated phenolic compounds in bleach plant filtrate. Since the agency's intention to regulate these compounds in bleach plant filtrates was not announced until after Wauna had already converted to complete substitution of chlorine dioxide for chlorine, the mill analyzed chlorinated phenolics only in waste treatment influent and final mill effluent during the progressive changes from the original bleaching sequence through high substitution. Also, because the list of the 12 proposed compounds had not been made public, no data were collected on 3,4,5-trichloroguaiacol or 3,4,6-trichlorocatechol, except at complete substitution.

IV. Wauna mill chlorinated phenolics in treatment plant influent and final mill effluent[1,2]

		May 1991		*February 1992*		*October 1992*		*December 1992*	
		10% substitution		*50% substitution*		*70% substitution*		*90% substitution*	
		Influent	*Effluent*	*Influent*	*Effluent*	*Influent*	*Effluent*	*Influent*	*Effluent*
Compound	*MLR*[3]	*Concentration, ppb*							
2,4,6 Trichlorophenol	5	13	ND	5	ND	ND	ND	ND	ND
2,4,5 Trichlorophenol	5	ND	ND	ND	ND	ND	ND	ND	ND
2,3,4,6 Tetrachlorophenol	5	ND	ND	ND	ND	ND	ND	ND	ND
Pentachlorophenol	5	ND	ND	ND	ND	ND	ND	ND	ND
3,4,6 Trichloroguaiacol	...	...	...	...	...	...	...	...	...
3,4,5 Trichloroguaiacol	5	35	ND	10	ND	9	ND	ND	ND
4,5,6 Trichloroguaiacol	5	14	52	ND	ND	ND	ND	ND	ND
Tetrachloroguaiacol	5	16	ND	ND	ND	6	ND	ND	ND
3,4,6 Trichlorocatechol	...	...	...	...	...	...	...	...	...
3,4,5 Trichlorocatechol	20	1140	ND	14	ND	ND	ND	ND	ND
Tetrachlorocatechol	20	252	ND	ND	ND	ND	ND	ND	ND
Trichlorosyringol	5	ND	ND	ND	ND	ND	ND	ND	ND

[1]Testing procedure: NCASI Method CP 86.01
[2]Samples are daily composites.
[3]Method reporting limit

V. AOX and dioxin levels in Marathon mill effluent

		Dioxin[2]*, ppq*		*AOX*	*No. of AOX*
Bleaching sequence	*Substitution, %*	*TCDD*	*TCDF*	*level*[1,2]	*samples*
(C+D)(EO)HED	10	160	500	7.2	26
(CD)(EO)HED	50	ND	6.6	4.6	43
D(E, O+P)DED	100	ND	ND	1.2	280

[1]AOX, kg/bleached a.d. metric ton
[2]Daily composites

Table IV presents test results in the waste treatment plant influent and final mill effluent of 10 of the chlorinated phenolic compounds proposed by EPA for regulation as analyzed by National Council for Air and Stream Improvement (NCASI) Method CP 86.01 *(2)*. All of the compounds were at the nondetectable level in final mill effluent at 50% and higher chlorine dioxide substitution. At 90% substitution, all are nondetectable in treatment plant influent.

The wastewater treatment plant appears to be very effective in removing these compounds. Phenolics detected in treatment plant influent were reduced to nondetectable levels in final effluent at substitution levels higher than 10%. At 10% substitution (the premodification case), only 3,4,5-trichloroguaiacol was detected in final effluent.

In July 1993, Wauna collected samples of alkaline and acid bleach plant filtrates, waste treatment influent, and final mill effluent to document chlorinated phenolic levels after conversion to complete chlorine dioxide substitution. These samples were analyzed using EPA Method 1653. The results for all 10 samples were nondetectable for all of the 12 compounds of interest at the detection levels specified in Method 1653. Especially significant is that the 12 chlorinated phenolics were not detected in any bleach plant filtrates before dilution with other mill waste streams.

To confirm this observation, seven samples were collected over a three-week period in October and November from combined bleach plant sewer streams (containing both acid and alkaline filtrates before dilution with any other streams). The results confirmed that all of the chlorinated phenolics of concern are nondetectable in bleach plant filtrates, again using EPA Method 1653. These data show that the normal process variability in the Wauna mill's bleach plant did not result in detectable amounts of chlorinated phenolics in the bleach plant effluent.

VI. Dioxin reduction in final effluent of Marathon mill

April 1989 to January 1990		*January 1990 to February 1991*		*May 1991 to July 1993*	
(C+D)(EO)HED		*(CD)(EO)HED*		*D(E, O+P)DED*	
TCDD, ppq	*TCDF, ppq*	*TCDD, ppq*[1]	*TCDF, ppq*[2]	*TCDD, ppq*	*TCDF, ppq*
200	520	ND (5.4)	6.3	ND (3.9)	ND (2.3)
190	660	ND (5.9)	5.6	ND (4.4)	ND (2.3)
180	500	ND (4.6)	6.7	ND (3.6)	ND (2.5)
70	320	ND (8.2)	ND (0.8)	ND (3.1)	ND (5.4)
Avg.160	500	ND (5.5)	ND (2.9)	ND (2.9)	ND (2.4)
		ND (4.1)	ND (3.9)	ND (4.2)	ND (3.0)
		ND (4.3)	25	ND (2.4)	ND (4.0)
		ND (7.4)	15	ND (2.4)	ND (2.1)
	Avg.	ND	6.6	ND (2.3)	ND (2.6)
				ND (9.2)	ND (11.0)
				ND (3.0)	ND (2.6)
				ND (3.2)	ND (2.2)
				ND (3.3)	ND (2.6)
				ND (4.1)	ND (3.3)
			Avg.	ND	ND

[1]Numbers in parentheses indicate detection levels.
[2]Average determined using Cohen's Technique (NCASI Technical Bulletin No. 621, December, 1991).

The Wauna data show that using only chlorine dioxide in the first stage of bleaching, even on unbleached pulp at a conventional kappa number (approximately 31), results in nondetectable levels of chlorinated phenolics in both bleach plant filtrate and final effluent.

Chloroform. In conventional bleach plants similar to the Wauna mill before modifications, the majority of chloroform formation occurs in the hypochlorite stage *(3)*. Even in hypochlorite-free mills, some chloroform is formed in the first stage of bleaching as a result of the reaction of chlorine with residual lignin. Substitution of chlorine dioxide for chlorine has been shown to significantly reduce chloroform in hypochlorite-free mills *(4)*.

Prior to the modification of the (C+D)(EO)HHD bleaching sequence at Wauna, a survey of total chloroform formation showed about 1.09 lb of chloroform per ton of pulp produced. After elimination of hypochlorite and raising chlorine dioxide substitution to 70%—the (CD)(EO)DD sequence—chloroform formation was reduced to 0.06 pounds per ton of pulp. This represents a 94% reduction in total chloroform formation.

Data from the Marathon mill

The Marathon, ON, mill produces about 550 tons/day of market softwood pulp from approximately 50% spruce and 50% jack pine, with the entire chip supply being sawmill residuals. The mill uses conventional batch digesters to produce brownstock of about 30–32 kappa number. The bleaching sequence operated in 1989 was (C+D)(EO)HED. Final pulp brightness is 90 ISO. The mill is currently installing a secondary treatment plant.

AOX/Dioxin

The Province of Ontario established an AOX discharge limitation of 2.5 kg/ton, effective January 1992. During 1990 and 1991, the bleaching sequence was changed first to (CD)(EO)HED (50% ClO_2 substitution) and then to a five-stage elemental-chlorine-free sequence, D(E, O+P)DED.

AOX and dioxin in the untreated effluent were measured during the bleach plant modification. **Table V** shows the progressive reduction of both with increased use of chlorine dioxide in the first stage and elimination of hypochlorite. (The complete set of dioxin data is shown in **Table VI**.)

As was the case at the Wauna mill, TCDD was reduced to nondetectable levels in mill effluent as substitution of chlorine dioxide for elemental chlorine was increased to 50%. TCDF was slightly detectable at the 50% level and completely nondetectable when chlorine dioxide was completely substituted for chlorine. AOX at Marathon declined to levels within compliance with Ontario limitations.

Chlorinated phenolics

All 12 chlorinated phenolic compounds being proposed for regulation by the U.S. EPA were nondetectable in final mill effluent as measured by NCASI Method 86.01.

Data from the Naheola mill

James River's Naheola mill, located in Pennington, AL, produces about 1500 tons/day of bleached pulp for food packaging and for consumer and industrial tissue, toweling, and napkins. The mill uses conventional batch digesters to produce hardwood kraft and a single-vessel Kamyr hydraulic digester to produce softwood kraft pulp. Both digesters cook to conventional kappa numbers of 30 for softwood and 17 for hardwood. Overall, the mill produces about 70% hardwood and 30% softwood. Hardwood pulp is bleached in a three-stage sequence—(D, C + D)(EO)D—to a final brightness of 86. A four-stage softwood bleach plant—(D, C + D)(EO)DD—produces pulp at 86 brightness. Fifty percent chlorine dioxide substitution is used on both lines. Final effluent from the mill is now nondetectable for both TCDD and TCDF at typical detection levels of 10 ppq or less.

The Naheola mill operates an aeration stabilization basin (ASB) treatment system. All wastewater from the mill flows to a primary clarifier. Primary clarifier effluent enters the ASB equipped with 53 floating aerators. Residence time in the basin is about nine days. Prior to discharge to the Tombigbee River, treated effluent is held in a polishing pond with about four days' retention time. BOD feed to the basin is approximately 100,000 lb/day, and overall BOD removal averages about 98%.

Chlorinated phenolics and dioxin in bleach plant effluent

The mill conducted a trial in January and February 1993 to determine the effect of raising the chlorine dioxide substitution level from 50% to 100% on dioxins and chlorinated phenolics in softwood bleach plant filtrates. Four daily grab samples of both acid and alkaline filtrates were collected and analyzed for chlorinated phenolics using EPA Method 1653 and dioxin and furan using NCASI Method 551.

All of the 12 chlorinated phenolic compounds proposed for regulation were nondetectable at complete substitution in both acid and alkaline filtrates at the detection levels specified in Method 1653. This finding was consistent in separate samples taken on four different days. Both 2,3,7,8-TCDD and 2,3,7,8-TCDF were likewise nondetectable (less than 10 ppq) in both the acid and alkaline filtrates.

A second (confirming) trial was conducted at Naheola during February 1994. During this trial, elemental chlorine was eliminated from both the hardwood and softwood bleach plants. As in the earlier trial, 2,3,7,8-TCDD, 2,3,7,8-TCDF, and the 12 chlorinated phenolic compounds using the same test method as the previous trial were nondetectable in bleach plant filtrates from both the hardwood and softwood bleach plants.

AOX from the Naheola mill has averaged about 0.45 kg/a.d. unbleached metric ton at the normal 50% substitution level. When elemental chlorine was eliminated for this trial, AOX was lowered to about 0.20 kg/a.d. unbleached metric ton. Because Naheola is a predominantly hardwood mill, the AOX level is lower than Wauna's but still significantly higher than would be necessary to meet the proposed regulatory level of 0.156 kg/a.d. unbleached metric ton.

Conclusions

- Using unbleached softwood pulps of conventional kappa number, complete substitution of chlorine dioxide for chlorine in the first stage of bleaching reduced chlorinated dioxins (2,3,7,8-TCDD and 2,3,7,8-TCDF) and 12 chlorinated phenolic compounds to nondetectable levels in bleach plant effluent and final mill effluent. Detection levels for chlorinated dioxins were less than 10 ppq and for chlorinated phenolics matched those specified in the test method (either EPA Method 1653 or NCASI Method 86.01). At all mills studied, these levels would comply with dioxin and chlorinated phenolic limits proposed by EPA in its revision of the effluent guidelines. AOX in final effluents, however, was above proposed regulatory levels at all three mills. Further modifications, therefore, would be required were the AOX limits to be promulgated.
- TCDD was reduced to nondetectable levels (less than 10 ppq) in final mill effluent at substitution levels of 50% and above at all three mills. TCDF was reduced to nondetectable (less than 10 ppq) at substitution levels greater than 50%.
- TCDD in bleach plant effluent was reduced to nondetectable levels (less than 10 ppq) at 70% substitution in all mills studied.
- Chlorinated phenolic compounds were nondetectable in final mill effluent at substitution levels of 50% and above as measured by either EPA Method 1653 or NCASI Method 86.01.
- The 12 chlorinated phenolic compounds of interest were completely removed in the activated sludge secondary treatment plant.
- Between 27% and 33% of incoming AOX was removed in an activated sludge secondary treatment plant.
- At 100% substitution of chlorine dioxide for chlorine in the first stage, all tests of chlorinated phenolic compounds in bleach plant filtrates are consistently at nondetectable levels as measured by EPA Method 1653.
- AOX was consistently reduced as elemental chlorine was removed from the bleach plant but was not reduced below 0.5 kg/ton, even at

- complete substitution of chlorine dioxide for chlorine.
- AOX is not an indicator of the presence of detectable levels of either chlorinated dioxins or phenolic compounds in final mill effluent.

Experimental

Wauna mill

AOX. All AOX tests were obtained from three-day composite samples. The analytical method used was SM 506 for tests prior to 1993. EPA Method 1650A was used for all subsequent tests.

Dioxin. All dioxin tests on final effluent were made on three-day composites; those in bleach plant effluent were one-day composites. Analytical methods used were NCASI 551 for data prior to December 1993. After that date, EPA Method 1613 was used.

Phenolics. All chlorinated phenolic tests from final effluent were made on three-day composites; those in bleach plant effluent were one-day composites. Analytical methods used were NCASI Method 86.01 for data prior to July 1993. After that date, EPA Method 1653 was used.

Chloroform. Total chloroform formation was determined by analyzing samples from bleach plant vents and effluent. Vent samples were collected in SUMMA canisters. Liquid samples were collected according to procedures developed by NCASI *(5)*. Analysis for chloroform was performed using EPA Methods 5030 and 8010.

Naheola mill

Dioxin. All dioxin tests in final effluent are one-day composites; those from bleach plant effluent were grab samples. Analytical method used for the January–February 1993 trial was NCASI 551. EPA Method 1613A was used for the February 1994 trial.

Phenolics. All chlorinated phenolic tests from bleach plant effluent were grab samples. Analytical method used was EPA Method 1653.

Marathon mill

AOX. All AOX tests were obtained from one-day composite samples. Analytical method used was the standard Canadian Municipal/Industrial Strategy for Abatement protocol for all tests.

Dioxin. All dioxin tests were made on one-day composites. Analytical method used was Environment Canada Reference Method for PCDDs and PCDFs in Pulp and Paper Mill Effluents, Report EPS 1/RM/19.

Phenolics. All chlorinated phenolic tests from final effluent were made on one-day composites. Analytical work was performed using NCASI Method 86.01.

Literature cited

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