A comparison of chlorinated phenolic compound concentrations and loadings in bleach-plant and treatment-system samples at eight mills

Douglas B. Spengel, Betsy Bicknell, Donald F. Anderson, Marla Smith, and Danforth G. Bodien

ABSTRACT: Twenty-eight chlorinated phenolic compounds were analyzed in samples of raw water, bleach-plant effluent, bleached pulp, and in the influent, effluent, and sludge of wastewater-treatment systems at eight U.S. pulp mills. Chlorinated phenolic compounds are examined in relation to several process variables. The lowest loadings of chlorinated phenolic compounds were observed at mills with oxygen delignification and 100% chlorine dioxide substitution. Trends in the distribution of chemical families and attached chlorine atoms also are identified. Finally, removal of chlorinated phenolic compounds in wastewater-treatment systems is compared with the removal of AOX and BOD_5 to assess whether wastewater-treatment performance is related to removal of chlorinated phenolic compounds.

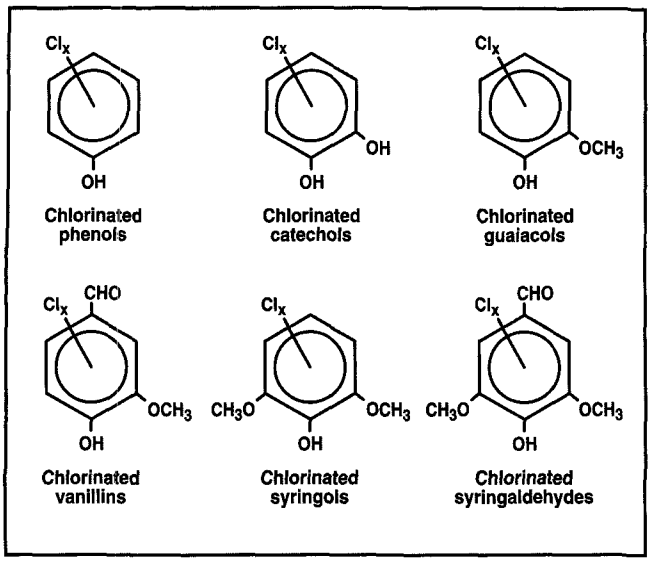
KEYWORDS: Adsorbable organic halogen, aerobic process, biodegradability, bleaching, bleach plants, chlorine compounds, effluent treatment, loading, phenols.

The use of chlorine and chlorine-containing bleaching agents in the production of bleached chemical pulp from wood leads to the formation of a variety of chlorinated organic compounds that are discharged in bleach-plant wastewaters *(1)*. These compounds are formed primarily as a result of chemical reactions between chlorine or chlorine-containing bleaching agents and lignin remaining in the pulp after the preceding chemical (kraft or sulfite) pulping process *(1)*. These compounds include unidentifiable high-molecular-weight compounds and identifiable low-molecular-weight compounds, including chlorinated phenolic compounds. The molecular weight of the compounds is determined by the degree to which lignin fragments are broken down during pulping and bleaching. The chlorinated phenolic compounds are known to be toxic, bioaccumulative, and persistent in the environment *(1–3)*.

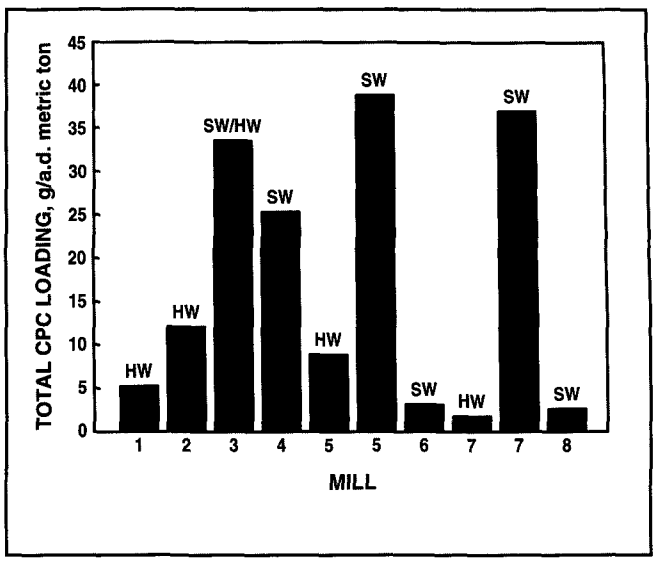
The chlorinated phenolic compounds investigated in this study include several groups of compounds characterized by a benzene ring with one hydroxyl group (phenols) and at least one chlorine atom (chlorinated phenolics). Figure 1 shows the molecular structure of each compound class. Ring substituents may be a second hydroxyl group at the ortho position (catechols), a methoxy group at the ortho position (guaiacols), a methoxy group at the ortho position and an aldehyde group at the para position (vanillins), and methoxy groups at both ortho positions and a

Spengel, staff chemical engineer, and Bicknell, senior environmental engineer, are affiliated with Radian Corp., 2455 Horsepen Road, Suite 250, Herndon, VA 22071. Anderson, chief of the commodities branch, and Smith, statistician, are affiliated with the U.S. Environmental Protection Agency, Engineering and Analysis Division, 401 M St. SW, Washington, DC 20460. Bodien, senior environmental engineer, is affiliated with the U.S. Environmental Protection Agency, Region X, 1200 Sixth Ave., Seattle, WA 98101.

1. Structures of chlorinated phenolic compounds



2. Total loadings of chlorinated phenolic compounds in bleach-plant effluent from eight mills



hydroxyl or aldehyde group at the para position (syringols and syringaldehydes).

Sampling program

The results presented here were obtained as part of a more comprehensive study (that included more analyses) at eight U.S. mills producing bleached chemical pulp. The study was conducted from June 1991 through February 1992 and was a joint effort of the U.S. Environmental Protection Agency (EPA), the American Paper Institute (now the American Forest and Paper Association, AF&PA), and the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). Mills were selected to participate in this sampling program based upon particular fiber furnishes, pulping or bleaching technologies, products, or wastewater-treatment systems. Table I summarizes the furnish, pulping process, bleaching process, and type of treatment system for each mill. Table I also identifies each mill by number for use in the figures presented in this paper.

The sampling points at each mill included raw water, bleach-plant effluent, bleached pulp, and influent to and effluent from the wastewater-treatment system. At some mills, wastewater-treatment sludge was also sampled. Bleach-plant effluents were characterized by collecting samples that represent all discharges from a bleach line, typically the first acid-stage filtrate (or acid sewer) and the first alkaline-stage filtrate (or alkaline sewer), and other filtrates if discharged separately.

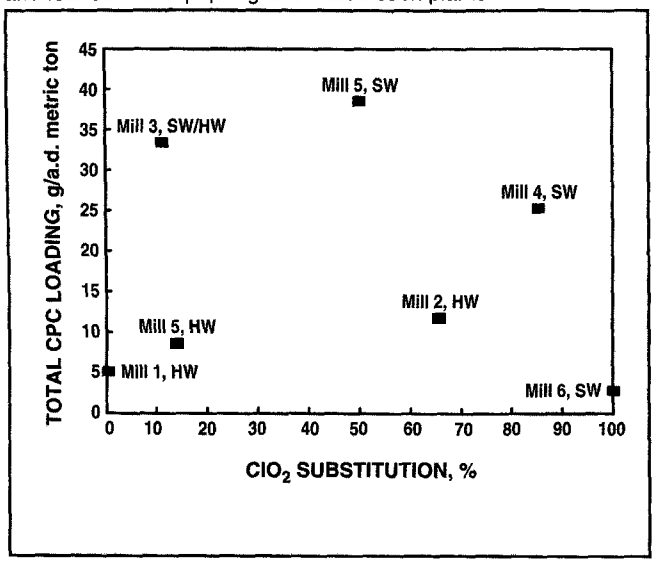
Samples were collected during one 24-hour period each week for nine weeks from June through September 1991 (summer). This regime was repeated each week for nine weeks from December 1991 through February 1992 (winter). Approximately 540 wastewater samples were collected. Detailed sampling plans were prepared by EPA and reviewed with mill personnel prior to the first week of sampling *(4)*. NCASI and EPA contractor staff were on-site during the first week of sampling at each mill during the summer program.

I. Summary of mills included in this study

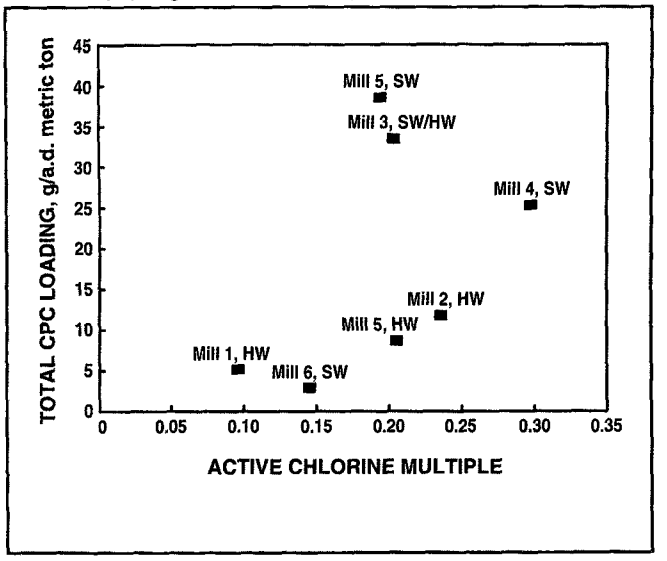
Mill	*Pulping process*	*Fiber furnish* [a]	*Oxygen delignification*	*Bleaching process, % ClO_2*	*Wastewater treatment* [b]
1	Bleached kraft	HW	No	0	ASB
2	Bleached kraft	HW	No	70	ASB & AST
3	Bleached kraft	SW & HW	No	5–10	AST
4	Bleached & unbleached kraft	SW	No	85	AST
5	Bleached kraft	SW	Yes	50	ASB
		HW	Yes	15	ASB
6	Bleached kraft	SW	Yes	100	ASB
7	Dissolving kraft	SW & HW	No	0–30	ASB
8	Dissolving sulfite	SW	Yes	100	ASB

[a] HW = hardwood; SW = softwood
[b] ASB = aerated stabilization basin; AST = activated sludge treatment

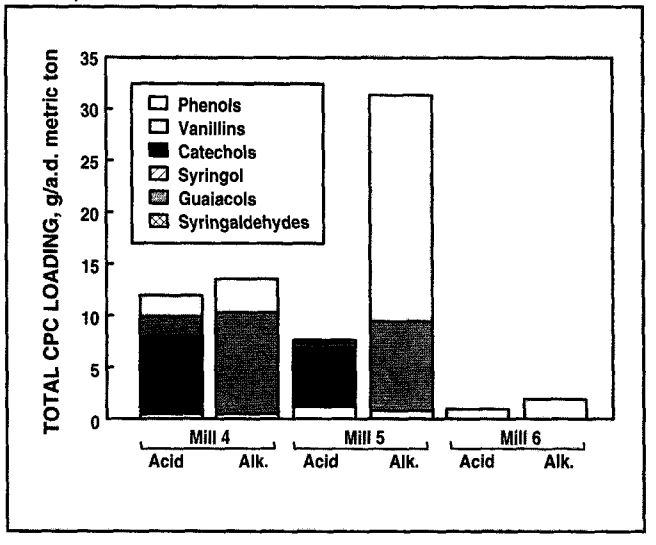
3. Total loadings of chlorinated phenolic compounds in bleach-plant effluent vs. percent chlorine dioxide substitution for three hardwood and four softwood paper-grade kraft bleach plants



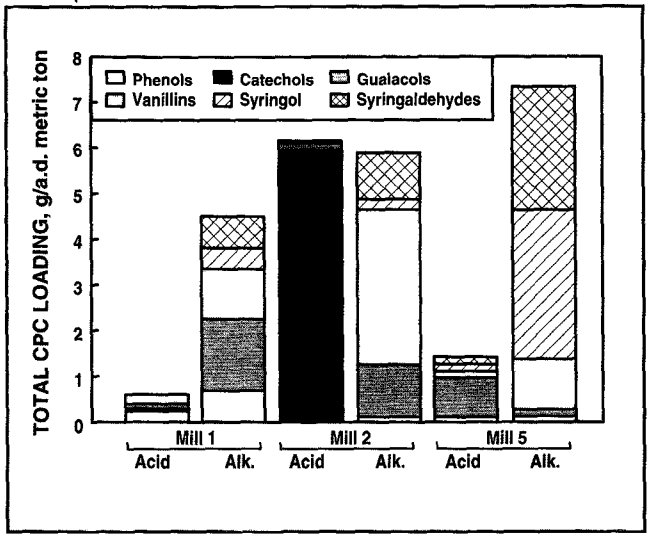
4. Total loadings of chlorinated phenolic compounds in bleach-plant effluent vs. active-chlorine multiple for three hardwood and four softwood paper-grade kraft bleach plants



5. Loadings of chlorinated phenolic compounds by chemical family in acid and alkaline filtrates for three softwood paper-grade kraft bleach plants



6. Loadings of chlorinated phenolic compounds by chemical family in acid and alkaline filtrates for three hardwood paper-grade kraft bleach plants

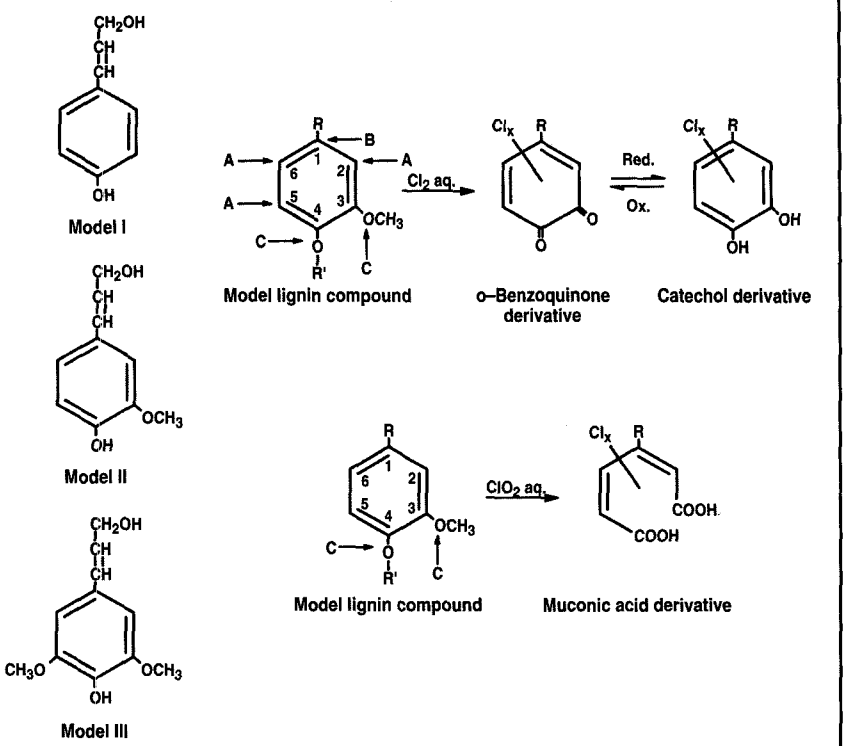


Mill personnel were responsible for collecting the samples and accurately reporting wastewater flow, bleached pulp production, and mill operating conditions. EPA audited sampling performance in the eighth or ninth week of the summer program, and again during the winter program, to assess whether mill personnel were following the site-specific sampling plans. The audits revealed a very high rate of mill compliance with established sampling and sample-handling protocols *(5)*. Data for only two samples were not considered valid for purposes of this study on the basis of field sample handling. These samples had been collected during a bleach-plant shutdown, and the data were not representative of normal operations.

Analytical program

The analytical method used to determine concentrations of chlorinated phenolic compounds in liquid samples was EPA Method 1653. This method is based on NCASI Method CP-86.01 and draft APHA (American Public Health Association) Method 6240. Method 1653 measures compounds in water and wastewater amenable to *in-situ* acetylation, extraction, and determination by high-resolution gas chromatography (HRGC) combined with low-resolution mass spectrometry (LRMS). In this method, chlorinated phenolics are derivatized *in*

7. Left: Three model lignin compounds. Right: Reactions of chlorine and chlorine dioxide with a model lignin compound; aromatic substitution, electrophilic displacement, and oxidation.



II. Maximum concentrations in bleach-plant effluent

Chlorinated phenolic compounds	*Maximum concentration, µg/L*
Acid filtrate	
4,5-dichlorocatechol	820
4-chlorocatechol 6-chlorovanillin 3,4-dichlorocatechol 3,6-dichlorocatechol 4,5-dichloroguaiacol 2,4,6-trichlorophenol 3,4,5-trichlorocatechol	60–750
all others	<60
2,4,5-trichlorophenol pentachlorophenol	Not detected
Alkaline filtrate	
6-chlorovanillin	7500
5-chlorovanillin 2-chlorosyringaldhyde 2,4-dichlorophenol 4,5-dichlorocatechol 3,4-dichloroguaiacol 4,5-dichloroguaiacol 5,6-dichlorovanillin 2,6-dichlorosyringaldehyde 2,4,6-trichlorophenol 3,4,5-trichlorocatechol 3,4,5-trichloroguaiacol 4,5,6-trichloroguaiacol trichlorosyringol tetrachlorocatechol tetrachloroguaiacol	60–500
all others	<60
2,6-dichlorophenol 2,4,5-trichlorophenol	Not detected
Combined sewer	
6-chlorovanillin	600
5-chlorovanillin 4,5-dichloroguaiacol 5,6-dichlorovanillin 2,4,6-trichlorophenol 3,4,5-trichlorocatechol 4,5,6-trichloroguaiacol	60–275
all others	<60
2,6-dichlorophenol 3,4,5-trichlorophenol pentachlorophenol	Not detected

situ to form acetic-acid phenolates, which are extracted in the laboratory with hexane, concentrated, and injected into the HRGC/LRMS, where separation and detection occur. Detected compounds are quantified by isotope dilution if a labeled analog is available. Where labeled analogs are not available, detected compounds are quantified by an internal-standard technique.

Method detection limits (MDLs) for Method 1653 for specific compounds depend upon matrix interferences rather than upon instrument limitations. With no interferences present, MDLs of 0.09–1.39 µg/L (ppb) have been achieved for these compounds in water. Based upon these MDLs and on calibration of the HRGC/LRMS instrument, minimum reporting levels have been determined by EPA to be 1.25 µg/L, 2.5 µg/L, or 5.0 µg/L, depending upon the specific compound. For solid samples, detection limits are approximately 600 µg/kg, 1200 µg/kg, or 2400 µg/kg, depending upon the specific compound.

EPA's analytical-methods staff and NCASI jointly reviewed the quality of the analytical data to ensure that appropriate quality assurance/quality control (QA/QC) criteria were met. Data that did not meet appropriate QA/QC criteria were excluded from the resultant database. Details of these reviews are provided elsewhere *(6–9)*. As a result of these reviews, approximately 93% of the chlorinated phenolic determinations in liquid samples were accepted as valid. Most of the determinations in water samples that did not meet the QA/QC criteria were for the seven catechols, 2-chlorosyringaldehyde,

III. Key to chlorinated phenolic compounds in Figs. 10–13

	Phenols
1	4-chlorophenol
2	2,4-dichlorophenol
3	2,6-dichlorophenol
4	2,4,5-trichlorophenol
5	2,4,6-trichlorophenol
6	2,3,4,6-tetrachlorophenol
7	pentachlorophenol
	Catechols
8	4-chlorocatechol
9	3,4-dichlorocatechol
10	3,6-dichlorocatechol
11	4,5-dichlorocatechol
12	3,4,5-trichlorocatechol
13	3,4,6-trichlorocatechol
14	tetrachlorocatechol
	Guaiacols
15	4-chloroguaiacol
16	3,4-dichloroguaiacol
17	4,5-dichloroguaiacol
18	4,6-dichloroguaiacol
19	3,4,5-trichloroguaiacol
20	3,4,6-trichloroguaiacol
21	4,5,6-trichloroguaiacol
22	tetrachloroguaiacol
	Vanillins
23	5-chlorovanillin
24	6-chlorovanillin
25	5,6-chlorovanillin
	Syringol
26	trichlorosyringol
	Syringaldehydes
27	2-chlorosyringaldehyde
28	2,6-dichlorosyringaldehyde

IV. Chlorinated phenolic compounds detected in sludge *

	Influent load in sludge, %				
Compound	*Mill 1 (primary sludge)*	*Mill 3 (combined sludge)*	*Mill 4 (combined sludge)*	*Mill 5 (primary sludge)*	*Mill 6 (primary sludge)*
4-chlorophenol	0.8	9	0.4	...	2.8
2,4-dichlorophenol	...	29	...	...	...
2,4,6-trichlorophenol	0.1	18	...	...	...
3,4-dichlorocatechol	...	10	82	...	...
4,5-dichlorocatechol	...	86	5.5	...	...
3,4,5-trichlorocatechol	...	9	1.9	...	...
4-chloroguaiacol	...	...	...	...	3.6
3,4-dichloroguaiacol	...	25	5.2	...	...
4,5-dichloroguaiacol	0.6	24	0.5	2.1	...
4,6-dichloroguaiacol	...	8	...	...	...
3,4,5-trichloroguaiacol	0.6	44	5.7	...	...
3,4,6-trichloroguaiacol	...	21	...	...	...
4,5,6-trichloroguaiacol	...	46	16	...	...
tetrachloroguaiacol	...	29	...	...	...
5-chlorovanillin	...	...	...	...	0.5
6-chlorovanillin	0.4	4	0.1	0.25	1.4
trichlorosyringol	0.1	27	...	...	...
2-chlorosyringaldehyde	0.4	2	...	...	...
2,6-dichlorosyringaldehyde	0.1	0.8	...	...	...

* No compounds detected in sludge at Mill 2

and 4,6-dichloroguaiacol. All of the determinations in solid samples were accepted as valid.

In addition to the QA/QC reviews, an engineering review of the data was performed to determine whether any deviations from established sampling and sample handling protocols (documented in the audit reports) affected the analytical results. Based on this review, data for the two filtrate samples that were collected during a bleach-plant shutdown (56 data points) were excluded *(10)*. As a result of using established and documented sampling and analytical protocols, and these extensive data reviews, the remaining database contains high-quality data that are representative of samples obtained.

Results and discussion

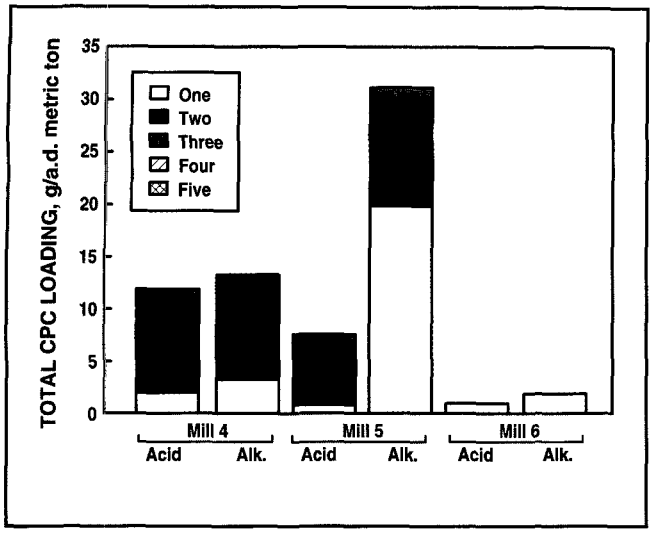
Raw water and bleached pulp

None of the chlorinated phenolic compounds were detected in any of the 16 raw-water samples (one sample from each mill in summer and in winter). During this sampling program, 99 samples of bleached pulp were collected (from 9 to 16 samples per bleach line, with an average of 11). None of the chlorinated phenolic compounds were detected in any sample of bleached pulp.

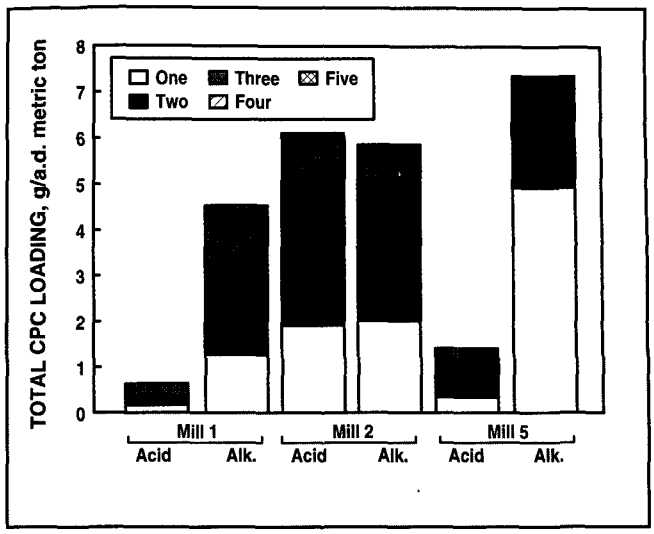
Bleach-plant effluents

Concentrations. At seven mills, separate acid and alkaline filtrate (or sewer) samples were collected to represent the bleach-plant effluent. At one mill, samples of a single combined sewer were collected. The concentrations of each chlorinated

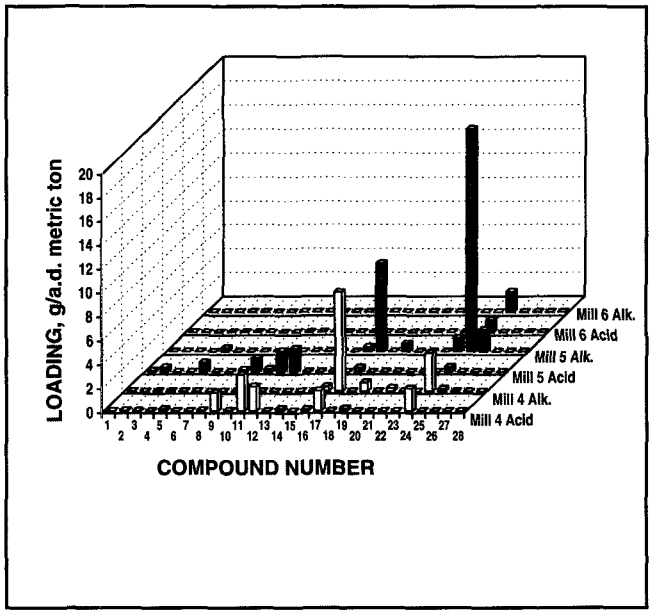
8. Loadings of chlorinated phenolic compounds by number of attached chlorine atoms in acid and alkaline filtrates for three softwood paper-grade kraft bleach plants



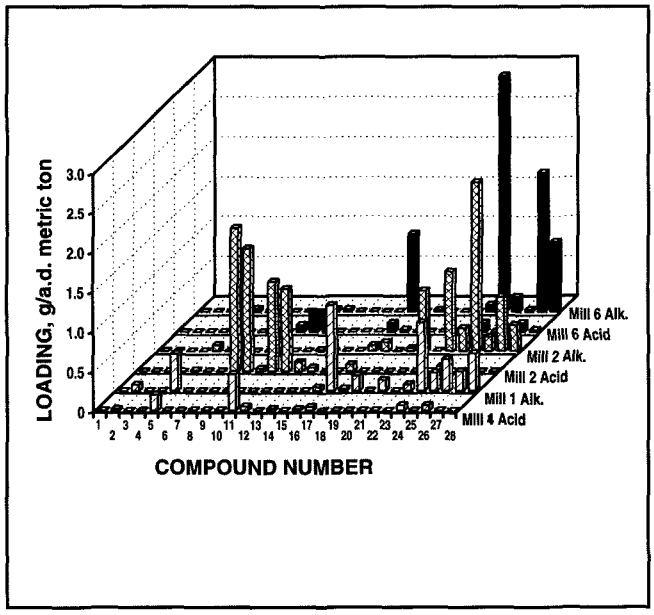
9. Loadings of chlorinated phenolic compounds by number of attached chlorine atoms in acid and alkaline filtrates for three hardwood paper-grade kraft bleach plants



10. Loadings of individual chlorinated phenolic compounds in acid and alkaline filtrates for three softwood paper-grade kraft bleach plants. See Table III for definitions of "compound number."



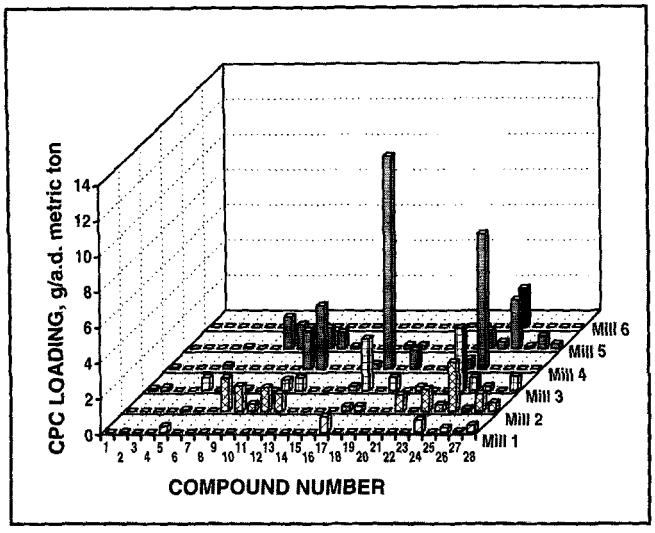
11. Loadings of individual chlorinated phenolic compounds in acid and alkaline filtrates for three hardwood paper-grade kraft bleach plants. See Table III for definitions of "compound number."



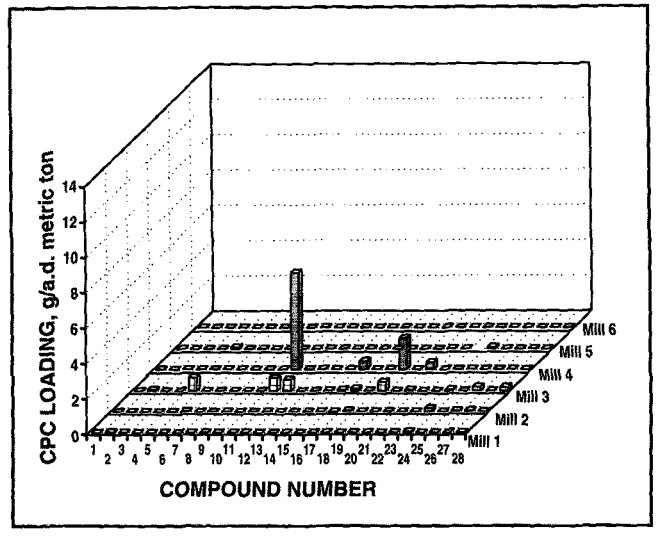
phenolic compound ranged from less than the detection limit to the maximum value listed in Table II.

Total mass loadings related to process variables. The total mass loading of chlorinated phenolic compounds in the bleach-plant effluent from each mill is illustrated in Fig. 2. These loadings are production-normalized based on the brownstock pulp entering the bleach plant (after oxygen delignification). The totals were calculated by determining the average loading for each compound in each stream (separate acid and alkaline streams) during the sampling program, summing the acid and alkaline results for each compound, and then summing the results for all 28 compounds for each bleach plant. For compounds that were not detected, a mass loading of zero was included in the average. In the analyses presented in this paper, compounds reported below the detection limit were assumed to be not present. The reported detection limits for these data were sample-specific and consisted of a broad range of values. The true value of a compound reported to be not detected may range from zero to the reported detection limit. Thus, zero is a lower bound on

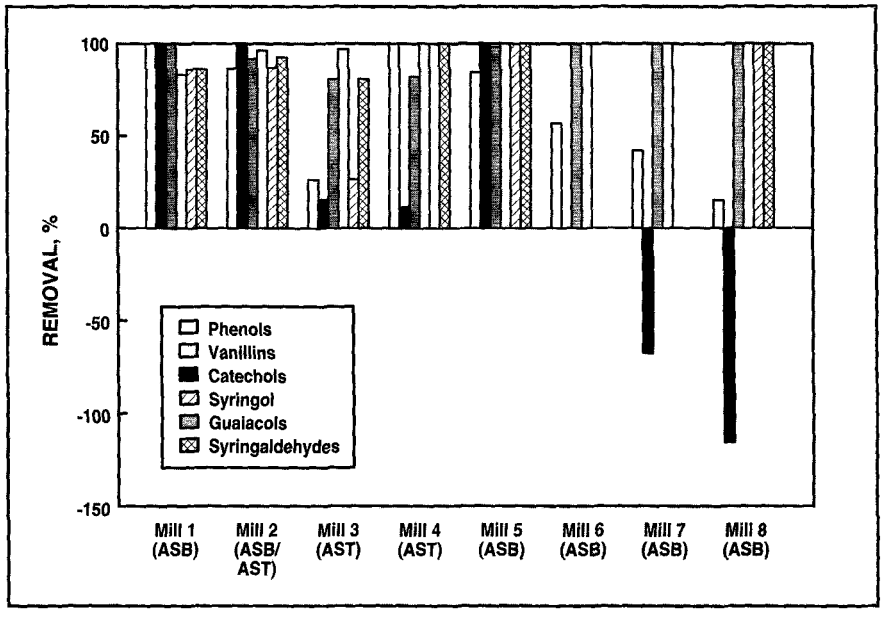
12. Loadings of individual chlorinated phenolic compounds in wastewater-treatment-plant influent for six paper-grade kraft mills. See Table III for definitions of "compound number."



13. Loadings of individual chlorinated phenolic compounds in wastewater-treatment-plant effluent for six paper-grade kraft mills. See Table III for definitions of "compound number."



14. Removal of chlorinated phenolic compounds by chemical family across wastewater-treatment plants at eight mills



the true value, and the use of zero for nondetect values biases calculated mass loadings on the low side.

Figure 2 (and Table I, which lists the pulping and bleaching processes used at each mill) shows that loadings of chlorinated phenolic compounds are related to furnish and to pulping and bleaching processes. The loadings for paper-grade kraft hardwood lines at Mills 1, 2, and 5 are lower than for the paper-grade kraft softwood lines at Mills 3, 4, and 5. The loading for Mill 3, which makes paper-grade kraft from approximately half softwood and half hardwood, is similar to the loadings for the softwood mills. The loadings for Mill 7, which makes dissolving kraft pulp from mostly hardwood with occasional production of softwood, also has a greater loading during softwood production. Mills 6 and 8 have the lowest loadings. These mills both pulp softwood but use oxygen delignification and 100% chlorine dioxide substitution for bleaching. The finding that oxygen delignification reduces the formation of chlorinated phenolic compounds at these mills is consistent with previous research *(1)*.

Figure 3 shows the same total loadings plotted against percent chlorine dioxide substitution for six bleached paper-grade kraft mills. Note that two of the mills (Mill 5 and Mill 6) use oxygen delignification. According to laboratory experiments by Axegard *(3)* and results of a mill trial reported by Munro *(11)*, softwood bleach-plant effluent loadings of chlorinated phenolic compounds decrease linearly with increasing chlorine dioxide substitution. In contrast, Kringstad and Lindstrom *(1)*, discussing work reported by Voss, *et al.*, stated that softwood bleach-plant effluent loadings of chlorinated phenolic compounds increase with chlorine dioxide substitution up to 50% and decrease linearly as substitution is increased further. Voss *(12)* recently summarized work performed over the past 14 years by Paprican that has shown a relation-

ship between the level of chlorinated phenolics in bleach-plant effluent and the amount of chlorine dioxide substitution in the first stage of bleaching. Paprican studies have found either no change or a slight increase in the loading of chlorinated phenolic compounds in bleach-plant effluent as chlorine dioxide substitution was increased from zero to 50%. Between 50% and 100% substitution, bleach-plant-effluent chlorinated phenolic loadings decreased, with a shift to less highly chlorinated phenolic compounds.

The data reported here, for mills pulping mostly softwood, clearly show that higher substitution is associated with lower chlorinated phenolic compound loadings at mills that do not use oxygen delignification (Mill 4 compared with Mill 3). The total chlorinated phenolic loading from Mill 4 is lower than at Mill 3, even though about half of the furnish at Mill 3 is hardwood, which reduces the loading. High substitution is also associated with lower loadings at mills that use oxygen delignification (Mill 6 compared with Mill 5-SW). The data reported here for hardwood mills do not support any relationship between chlorine dioxide substitution and chlorinated phenolic compound loadings.

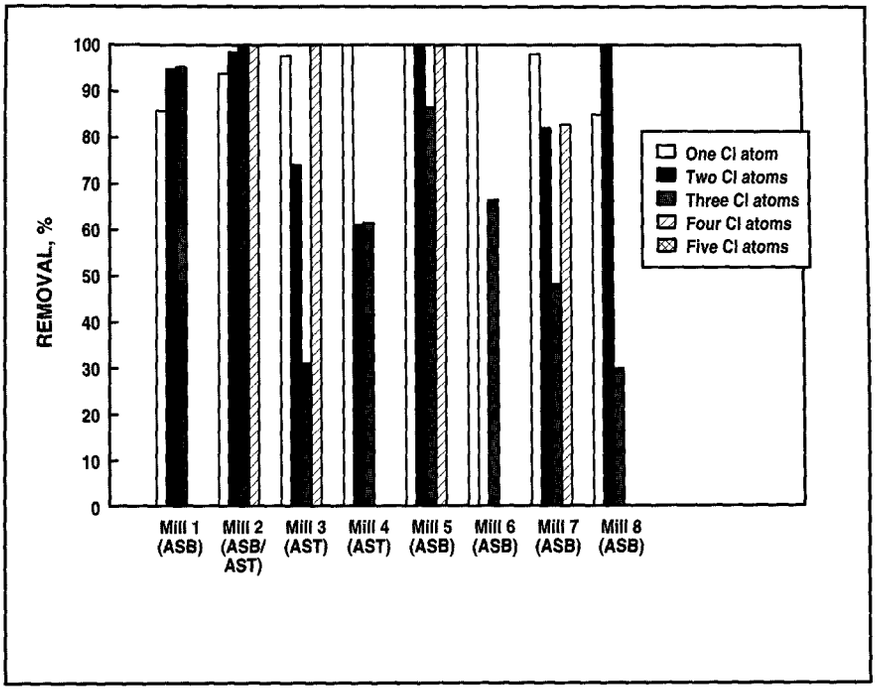
Figure 4 shows the same total loadings plotted against the active-chlorine multiple (ACM). The ACM is the equivalent chlorine (Cl_2 and ClO_2) charged in the first stage [expressed as a percent on air-dried (a.d.) pulp] divided by the kappa number of brownstock (BS) pulp entering the first stage:

{[(kg Cl_2/a.d. metric ton BS) + 2.63(kg ClO_2/a.d. metric ton BS)]/(1000 kg/metric ton)} x 100 = equivalent Cl, %

equivalent Cl/BS kappa number = ACM

Figure 4 indicates that the total loading decreases as the active-chlorine multiple decreases for the hardwood mills. The data reported here for the softwood mills do not support any relationship between the total loading and the active-chlorine multiple.

15. Removal of chlorinated phenolic compounds by number of attached chlorine atoms across wastewater-treatment plants at eight mills

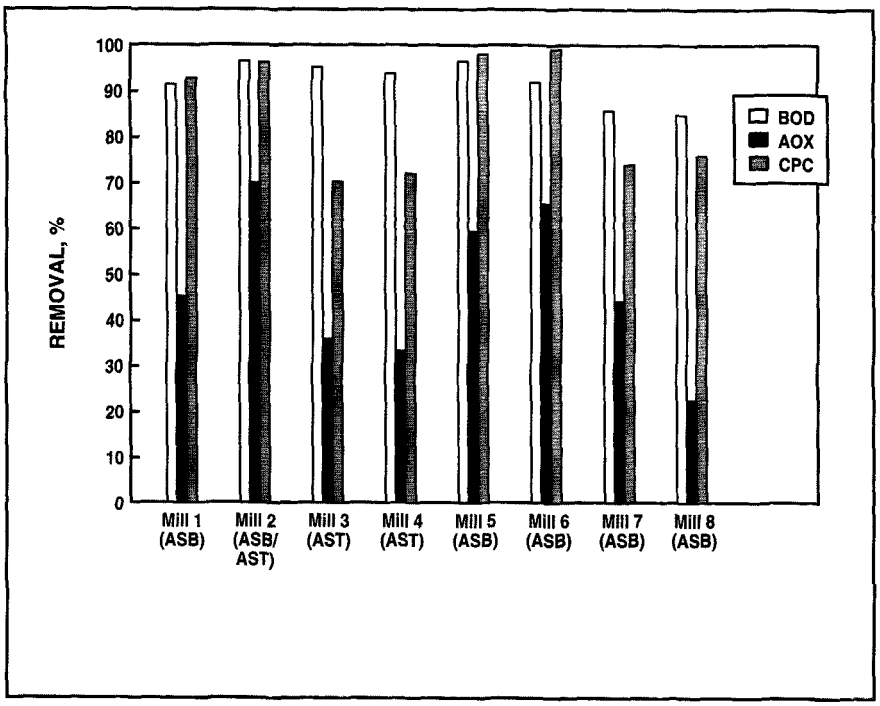


Trends in chemical family. The distribution of loadings by chemical family of chlorinated phenolic compounds is illustrated in **Figs. 5 and 6** for three softwood and three hardwood kraft pulp mills, respectively. Results are presented for both acid and alkaline filtrates. Figures 5 and 6 show that the total loadings of all compounds in alkaline filtrates are generally greater than the loadings in acid filtrates. Guaiacols and vanillins follow this trend, with greater loadings in alkaline filtrates. The catechol family did not follow the trend; catechol loadings were greater in acid filtrates than in alkaline filtrates.

Figure 5 shows similarities in the families of chlorinated phenolic compounds detected in bleach-plant filtrates from Mills 4 and 5, which bleach with both chlorine and chlorine dioxide. In contrast, vanillins were the primary compounds detected at Mill 6, which uses 100% chlorine dioxide substitution. For Mills 4 and 5, phenols, catechols, guaiacols, and vanillins were detected, but loadings of phenols and catechols were greater in acid filtrates, while loadings of guaiacols and vanillins were greater in alkaline filtrates. This has been reported previously *(1, 13)*.

Syringol and syringaldehydes were rarely detected in softwood acid or alkaline filtrates. However, these compounds contribute to the total loadings at hardwood mills, particularly in the alkaline filtrates, as seen in Fig. 6. As with the softwood mills, some compounds in each family were detected, but loadings of catechols were greater in acid filtrates, while loadings of guaiacols and vanillins were greater in alkaline filtrates. It can also be seen that catechols represent most of the loadings in acid filtrates at Mills 2 and 5, where some chlorine dioxide substitution is used in bleaching. In contrast, phenols represent most of the loadings in acid filtrate at Mill 1, where only chlorine is used. In a similar study, increased chlorine dioxide substitution was associated with an increase in the detection of guaiacols and

16. Removal of BOD_5, AOX, and chlorinated phenolic compounds across wastewater-treatment plants at eight mills



vanillins and a decrease in the detection of catechols *(11)*.

Many of these observations can be explained through a review of the chemistry involved in the first bleaching stage(s). **Figure 7** shows the prominent structures in softwood lignin and several possible reactions that can occur with molecular chlorine. The following notes on the chemistry of lignin chlorination were presented by Dence and Annergren *(14)*. For hardwood lignin, approximately 50% of the prominent lignin structures have a methoxy group at Position 5 (see model compound III in Fig. 7). The structures formed during chlorination of lignin depend upon the number of substituents attached to the phenolic ring and the amount of chlorine applied. In the model compound, one site is available for electrophilic displacement (Position 1), three for aromatic substitution (Positions 2, 5, and 6), and two for oxidation (Positions 3 and 4). Of the three, electrophilic (displacement) substitution is believed to be the least important. For aromatic monosubstitution, chlorine exhibits a preference for the available sites in the order 6 > 5 > 2. During oxidation at Position 3, methanol is formed. When chlorine dioxide is applied, oxidation of the phenolic compounds occurs, resulting in the formation of nonaromatic compounds (e.g., dicarboxylic acid fragments) rather than phenolic compounds.

For individual chlorinated phenolic compounds to form, the linkages with lignin at Positions 1 and 4 must be broken. This can apparently occur in a chlorination stage or in an extraction stage. If it occurs in a chlorination stage (where both aromatic substitution and oxidation can occur), the most likely compounds to be formed are catechols (by oxidation at two positions) and phenols, although compounds in other families can also be formed. For chlorinated guaiacols, vanillins, syringols, and syringaldehydes to form, aromatic substitution of chlorine most likely occurs rather than oxidation of the methoxy group at Positions 3 and/or 5. For these compounds to be detected in filtrates from extraction stages (where little chlorine is available), chlorine most likely reacts aromatically during chlorination, and the linkages with lignin then break during the extraction.

Trends in number of attached chlorine atoms. The distribution of chlorinated phenolic compounds by the number of attached chlorine atoms is illustrated in **Figs. 8 and 9** for three softwood and three hardwood kraft mills, respectively. Results are presented for both acid and alkaline filtrates. For Mills 4 and 5, which bleach with both chlorine and chlorine dioxide, Fig. 8 shows that mono-, di-, and tri-substituted compounds were detected in both acid and alkaline filtrates, with mono- and di-substituted compounds accounting for most of the loading in each filtrate. At Mill 6, which bleaches with 100% chlorine dioxide substitution, mono-substituted compounds accounted for most of the loading. Figure 9 shows that mono-, di-, and tri-substituted compounds also predominated in hardwood bleach-plant effluents. It has been previously reported that the amount of highly substituted chlorinated phenolic compounds decreases as the percent of chlorine dioxide substitution increases *(3, 11, 12)*. This trend cannot be distinguished in these data because of the variety of furnishes and processes used by mills in this study.

Specific chlorinated phenolic compounds. Loadings of specific compounds are illustrated in **Figs. 10 and 11** for three softwood and three hardwood kraft mills, respectively. Results are presented for both acid and alkaline filtrates. The "compound numbers" on the x-axes are defined in **Table III**. Of 28 compounds studied, only 2,4,5-trichlorophenol (Compound 4) was never detected in any bleach-plant filtrate sample from these six mills.

In Fig. 10, 6-chlorovanillin (Compound 24) and 4,5-dichloroguaiacol (Compound 17) account for most of the alkaline loading from the three softwood bleach lines. In acid fil-

trates, 4,5-dichloroguaiacol, 3,4-dichlorocatechol (Compound 9), 4,5-dichlorocatechol (Compound 11), 3,4,5-tricholorocatechol (Compound 12), and 6-chlorovanillin account for most of the loading. At Mill 6, which uses oxygen delignification and 100% chlorine dioxide substitution, 6-chlorovanillin is almost the only compound detected. This has also been observed at other mills that bleach with these processes *(1, 15)*.

As shown in Fig. 11, the same compounds contribute most of the loading in filtrates from hardwood bleach lines. However, trichlorosyringol (Compound 26), 2-chlorosyringaldehyde (Compound 27), and 2,6-dichlorosyringaldehyde (Compound 28) are also important, particularly in alkaline filtrates.

Wastewater-treatment influent and effluent

Samples of influent to wastewater-treatment systems showed concentrations of less than 100 µg/L for all but two of the chlorinated phenolic compounds. The maximum concentration of 6-chlorovanillin was 2150 µg/L, and for 4,5-dichloroguaiacol it was 764 µg/L. Two compounds—2,4,5-trichlorophenol and pentachlorophenol—were never detected.

In effluent samples, the maximum concentration of any chlorinated phenolic compound was 39 µg/L, for 4,5-dichlorocatechol. All other compounds that were detected were below 18 µg/L. Nine of the chlorinated phenolic compounds were never detected.

Figures 12 and 13 show the compounds detected in the influent and effluent, respectively, of wastewater-treatment systems at six bleached paper-grade kraft mills. Individual compound loadings are the average over the 18-week sampling program. Again, a mass loading of zero was included in the average for a nondetected compound, so the average may be biased low. Comparison of the results in Fig. 12 with Figs. 10 and 11 indicates that the same chlorinated phenolic compounds detected in the bleach-plant effluent are also detected in the influent to the wastewater-treatment system. For each mill and for most compounds, the average bleach-plant loading and treatment-system influent loadings were the same, showing that bleach-plant effluent is the major source of these compounds discharged to the treatment system. For some compounds present in low concentrations in bleach-plant effluents, the treatment-system influent loading was lower than the bleach-plant loading. This is most probably the result of dilution of these compounds to below detectable concentrations in the influent to the wastewater-treatment system.

Using the 18-week average loadings for treatment-system influent and effluent, the overall percent removal for each compound at each mill was estimated. Note that the removals were not calculated weekly and then averaged. Instead, the 18-week average influent loading and 18-week average effluent loading were used in an attempt to minimize the calculation of removals using compounds not detected and to minimize the impact of treatment-system retention time. Nevertheless, because few compounds were routinely detected in the effluent, and because of the low bias introduced by assigning a value of zero to all concentrations below the detection limit, the estimated percent removal of these compounds is near 100%. An additional complicating factor is that for some compounds at some mills, the calculated percent removal is negative. Negative removals could result from transformation of one compound into another during treatment (e.g., microbial dechlorination of a trichlorophenol to a mono- or dichlorophenol). Negative removals could also result from a "slug" of compound that was not present in the influent during weekly sampling but, because of treatment-system retention time, was present in effluent at a higher-than-average loading.

Figures 14 and 15 show the overall percent removal by chemical family and by number of attached chlorine atoms, respectively, for each mill. These data do not explain the mechanism by which chlorinated phenolic compounds are removed from wastewaters. Possible mechanisms are volatilization, biodegradation, and adsorption to wastewater-treatment sludges. Because of the low volatility of these compounds and the very low concentrations detected in sludge, we conclude that biodegradation is the major removal mechanism. The low (and sometimes negative) removals for phenols and catechols shown in Fig. 14 indicate that compounds in these families are difficult to biodegrade in some treatment systems. Similar studies have also shown that guaiacols and vanillins degrade more easily than catechols *(13, 16)*. The low removals of tri-substituted compounds relative to the removals of mono- and di-substituted compounds shown in Fig. 15 may indicate that tri-substituted compounds are difficult to degrade in some treatment systems. Another study has also shown that more highly chlorine-substituted compounds are more difficult to biodegrade *(17)*.

Wastewater-treatment sludge samples were collected at six mills. The loading of each chlorinated phenolic compound in sludge was calculated and compared with the treatment-system influent loading. The compounds detected in sludge and the fraction of this load as compared with the influent load are summarized in **Table IV**. None of the compounds were detected at Mill 2. At mills where primary sludge was collected, the sludge loading was less than 4% of the influent load. At Mills 3 and 4, where a combined primary and secondary sludge was collected (mills with activated-sludge treatment), the sludge loading ranged from zero to 86% of the influent load.

At Mill 4, the loadings for two compounds in sludge were greater than 10% of the influent load, but these compounds were only detected in approximately 30% of the samples. At Mill 3, the loadings of ten compounds in sludge were greater than 10% of the influent load, and these compounds were detected in nearly 100% of the samples. With the possible exception of Mill 3, the partitioning to sludge is a minor part of the overall removal efficiency. This is also the conclusion reached by other authors who analyzed the same data *(18)*. These authors handled the data differently, but they concluded that, compared with the biological degradation that occurred, partitioning to sludge and volatilization were minor removal mechanisms.

A parameter of interest is the fraction of the AOX (adsorbable organic halides) loading represented by chlorinated phenolic compounds. For influent samples at a particular mill, the percent of the AOX loading represented by chlorinated phenolic compounds ranged from 0.03% to 3.9%. Another study indicated that this relationship was on the order of 1% *(16)*. For effluent samples, where many chlorinated phenolic compounds were not routinely detected, the fraction ranged from 0.025% to 0.5%. These differences may relate to furnish or to pulping and bleaching processes, but particular trends have not been identified.

Figure 16 relates the percent removal of BOD_5 (five-day biochemical oxygen demand), AOX, and the total chlorinated phenolic compound loading for each mill. All eight mills achieved greater than 85% BOD_5 removal (and all but two were greater than 90%). At four mills, all operating aerated stabilization basins (ASBs), the removal of chlorinated phenolic compounds was the same or better than the BOD_5 removal. At the other four mills, the removal of the total chlorinated phenolic compound loading was 70–75%. Two of these mills produce dissolving-grade pulp and operate ASBs; the other two mills produce paper-grade kraft pulp and operate activated-sludge treatment (AST) systems. In comparison, AOX removals were 45–70% for the four kraft ASB mills, 43% at the dissolving kraft mill, 22% at the dissolving sulfite mill, and near 35% for the two kraft AST mills.

The data from this study also allow comparison of winter and summer removal of various pollutant parameters. Removals of BOD_5 were essentially the same during summer and winter, with a small (5%) decrease in BOD_5 removal in winter at two mills operating ASBs. The removal of total loadings of chlorinated phenolic compounds was also essentially the same during summer and winter. (It actually improved at six of eight mills in winter.) AOX removals in summer ranged from 26% to 75%. In winter, removals were somewhat lower, ranging from 20% to 70%. It should be noted, however, that the summer AOX removals are based on data that may be biased low because of column breakthrough during analysis. Thus, it cannot be concluded from comparison of these data that the lower AOX removals in winter are due to temperature effects. In contrast to the results of this study, a recent study of secondary-treatment-system performance at Ontario paper mills found less seasonal variation in AOX removal than for removal of BOD_5 and total suspended solids *(19)*.

In this study, the mill-to-mill differences in AOX removal are much greater than the differences in BOD_5 removal, possibly because the wastewater-treatment systems were designed for optimal BOD_5 removal. Factors influencing AOX removal may include aerobic vs. anaerobic stages, pH, retention time, and temperature.

Conclusions

A long-term study of chlorinated phenolic compounds in bleach-plant effluent and in flows to and from wastewater-treatment plants confirmed several important phenomena reported in the literature from laboratory or controlled studies:

- The lowest loadings of chlorinated phenolic compounds (and AOX) were observed at mills using oxygen delignification and 100% chlorine dioxide substitution.
- At softwood mills, the total loading of chlorinated phenolic compounds decreased as chlorine dioxide substitution increased for two mills that use oxygen delignification. Loadings also decreased with increased substitution at two mills that do not use oxygen delignification.
- At softwood and hardwood mills, loadings of catechols are greater in acid filtrates than in alkaline filtrates. Loadings of guaiacols and vanillins are greater in alkaline filtrates than in acid filtrates.
- Syringol and syringaldehydes are detected more often in bleach-plant filtrates at hardwood mills than at softwood mills.
- The removal of BOD_5 and total loadings of chlorinated phenolic compounds in treatment systems do not appear to vary seasonally. AOX removal appears to vary more from mill to mill than BOD_5 removal.

Literature cited

1. Kringstad, R. P. and Lindstrom, K., *Environ. Sci. Technol.* 18(8): 236(1984).
2. Suntio, L. R., Shiv, W. Y., and Mackay, D., *Chemosphere* 17(7): 1249(1988).
3. Axegard, P., *Tappi J.* 69(11): 54(1986).
4. "Generic sampling and analysis plan for U.S. Environmental Protection Agency and Paper Industry cooperative long term variability study," Radian Corp., Herndon, VA, July 31, 1991.
5. "Non-CBI audit report for the U.S. EPA/ Paper Industry long term variability study," Radian Corp., Herndon, VA, January 1993.
6. "Quality assurance project plan for the pulp and paper industry study final draft," Radian Corp., Herndon, Va, June 1991.
7. "Sample Control Center data review guidelines for the pulp and paper industry study final draft," U.S. EPA, Sample

Control Center, Viar and Co., Alexandria, VA, June 1991.
8. "Summer data review," U.S. EPA, Sample Control Center, Viar and Co., Alexandria, VA, 1992.
9. "Winter data review," U.S. EPA, Sample Control Center, Viar and Co., Alexandria, VA, 1992.
10. "Summary of preliminary engineering review of long term study data," memorandum from Radian Corp. (D. Spengel) to U.S. EPA (G. Heath), April 26, 1993.
11. Munro, F. C., *Appita* 43(6): 421(1990).
12. Voss, R. H., "Changes in the chlorinated phenolics content of the pulp bleaching effluents as a result of chlorine dioxide substitution," in NCASI Special Report 94-01, NCASI, New York, 1994.
13. O'Conner, B. I. and Voss, R. H., *Environ. Sci. Technol.* 26(3): 556(1992).
14. Dence, C. W. and Annergren, G. E., in *Chlorination in the Bleaching of Pulp* (R. P. Singh, Ed.), third edn., TAPPI PRESS, Atlanta, 1979.
15. Mackay, F. M. and Galloway, L. R., "Start up and initial operation of Celgar Pulp's low-rate air activated sludge treatment system," *CPPA 1993 Environment Conference*, CPPA, Montreal.
16. Parker, W. J., Farquhar, G. J., and Hall, E. R., *Environ. Sci. Technol.* 27(9): 1783(1993).
17. Jokela, J. K., Laine, M., Ek, M., *et al.*, *Environ. Sci. Technol.* 27(3): 547(1993).
18. Wiegand, P., Barton, D., and LaFleur, L., "Factors influencing the generation and treatability of chlorinated phenolic compounds and AOX in bleached chemical pulp mill wastewaters," in NCASI Special Report 94-01, NCASI, New York, 1994.
19. McCubbin, N., Folke, J., Stewart, A., *et al.*, *Tappi J.* 77(1): 172(1994).

The chemical analytical data upon which this paper is based were reviewed by the EPA Engineering and Analysis Division Sample Control Center operated under contract to EPA by DynCorp/Viar. The authors would like to acknowledge the contributions to data quality made by William Telliard (EPA) and Jim King, Harry McCarty, Lynn Riddick, and Carrie Buswell (Viar). The authors also wish to thank Amy Brockman, Kirsten Vice, and Gary Amendola for their contributions to the design and interpretation of this study.

The conclusions and opinions presented in this paper are those of the authors and not of Radian Corp. or U.S. EPA.

Received for review June 16, 1994.

Accepted July 19, 1994.

Presented at the TAPPI 1994 International Pulp Bleaching Conference.