Organochlorine in bleached kraft pulp

Douglas W. Reeve

The amount of AOX and the water-insoluble chlorine in pulp add up to the total amount of organochlorine—the chlorine chemically bound to carbon.

In recent years, there has been growing concern about chlorinated organic matter in the effluent from bleached kraft pulp mills (*1*). Regulations to limit the discharge of adsorbable organic halogens (AOX) have been established in Sweden, Germany, Finland, and Canada. In the United States, all bleached kraft mill effluent is biologically treated, eliminating 25-60% of AOX before discharge. The conclusion from a recent comprehensive review is that no detrimental environmental impact arises from the effluent from well-operated bleached kraft mills with properly designed and operated effluent treatment systems (*2*).

Nevertheless, there is a drive in some quarters to completely eliminate organochlorine discharges. This initiative is perhaps based on the misconception that all organochlorine has the same properties as the notorious organochlorine compounds—polychlorinated dibenzofurans and dioxins—or organochlorines that are deliberately designed to be toxic and persistent—pesticides, herbicides, and some wood preservatives (PCP, or pentachlorophenol). These organochlorine compounds are indeed hazardous in the environment because of their persistence, toxicity, and tendency to bioaccumulate. Dioxin in pulp has been the subject of extensive studies in several countries (*3-5*). A number of congeners of polychlorinated dibenzo-*p*-dioxin and dibenzofuran have been found. The predominant congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, is also the most toxic.

Organically-bound chlorine, arising from the chlorination of lignin and extractives, is found in significant concentrations in bleached kraft pulp. As early as 1964, Howard and Histed (*6*) showed that fully bleached softwood kraft and sulfite pulps contain approximately 0.5 kg Cl/metric ton of pulp. The organochlorine content in these pulps represents a large portion of the total organochlorine in effluents, which is limited to approximately 1.5 kg/metric ton of pulp.

Our research presented here has been focused on the characterization and identification of chorinated organic matter in bleached kraft pulp (*7-9*).

Reeve is associate professor, Dept. of Chemical Engineering and Applied Chemistry, and director, Pulp and Paper Centre, University of Toronto, 200 College St., Toronto, Ont., Canada M5S 1A4.

Concern about organochlorine in pulp

There is growing concern about the fate and effects of organochlorine in the life cycle of products made from bleached kraft pulp. In many countries, consumers are concerned about toxic chemicals in personal-use products, in foods, and in food packaging. Paper products made from chlorine-bleached kraft pulp have been used safely for many years. However, little has been published about the nature of organochlorine in pulp, its behavior in various products, or its toxicological properties.

Organochlorine in pulp may be dissolved when the pulp is made into paper, and it may then become part of the effluent from the paper mill. German buyers of pulp have become increasingly sensitive to this issue. Environmental activists have raised questions about the fate of organochlorine in municipal refuse, particularly in municipal incinerators, where it is conceivable that chlorinated dioxins could be formed.

Concern about organochlorine in pulp has been voiced in many sectors of society—by environmental activists, government regulators, and consumer advocates:

"Paper contains a lot of chlorine"

"Dioxins are only the tip of the iceberg. Preliminary research shows organically-bound chlorine in paper is in the range of several hundred parts per million."

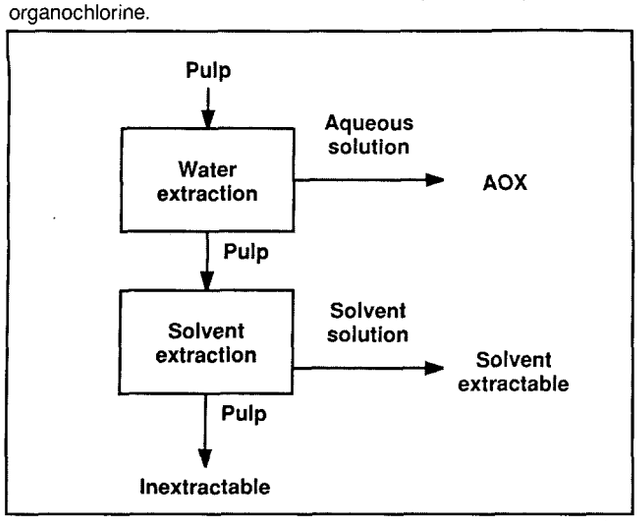
—G. Bryntse, B. Johansson, and G. Ladberg
Paperet och Miljön (Paper and The Environment), Svenska Naturskydds-föreningen och Miljöförbundet, Stockholm, 1988

"If we get chlorine-bleached paper out of consumer products, we will also lose huge amounts of chlorine from the industrial process."

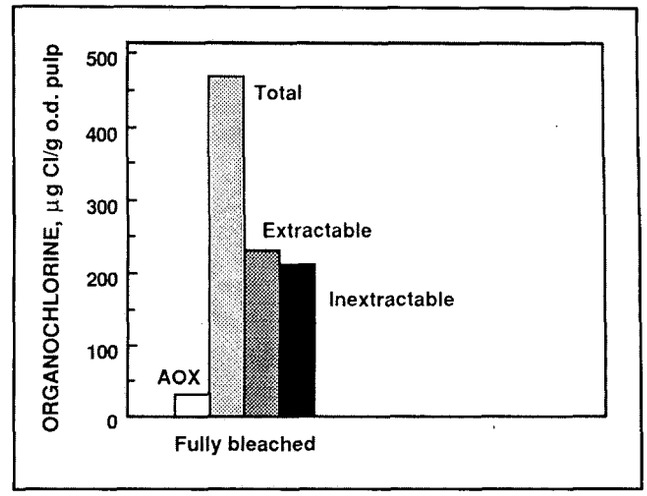
"Consumers will not be required to live with an environmental threat on their breakfast tables, in their bathrooms, and in large parts of their everyday life."

—Brigitta Dahl
Environment Minister, Sweden (Quoted by Reuter News Agency, Stockholm, June 20, 1988)

1. Separation of various forms of chlorine in pulp. The AOX quantity is minor and is added to that not extracted by water to give the total organochlorine.



2. Organochlorine in softwood



"We want the pulp industry to know that there is a potentially huge market for organochlorine-free paper products."

—Ada Brown
President, B.C. Branch, Consumers' Association of Canada, Vancouver (Oct. 25, 1988)

"These products (regarding some paper products from Sweden) are free of organochlorines, and they are in stores and selling like hotcakes in Europe. There is no reason our Canadian companies couldn't produce organochlorine-free products for the Canadian and world market for healthy paper products."

—Renate Kroesa
International Pulp & Paper Campaign Coordinator, Greenpeace, Vancouver, Oct. 25, 1988

Finally, the West Coast Environmental Law Association has as one of its goals to promote "paper products free of organochlorine" for the Canadian "Environmental Choice" label.

In response to these concerns, some in the corporate sector are promoting paper products as "bleached without chlorine." In Sweden, a grocer's association publishes a newsletter entitled "News About Environmental Friendliness." In the first issue, they categorized all paper products sold in their shops as being "chlorine-free" paper, "mini-chlorine" paper, or "chlorine" paper. Potential environmental problems associated with chlorine and paper products were listed (*10*).

Measuring chlorine in pulp

The measurement of chlorine in any combustible material is straightforward. The combustible material is burned, and organically-bound chlorine is converted into hydrochloric acid gas that is captured in aqueous solution. The chloride ion in the solution is then measured.

This technique has been applied to paper products and pulp using various techniques, such as volumetric titration (*11*), ion chromatography (*12*), and microcoulometric titration (*13*), for the determination of chloride. The AOX analyzers developed for burning activated carbon onto which organochlorine has been absorbed provide accurate and expedient analysis (*7, 13*). These analyzers combine a simple, reliable combustion technique with microcoulometric titration. Neutron activation analysis can be used to directly determine the organochlorine in pulp (*7*).

Functional types of chlorine in pulp

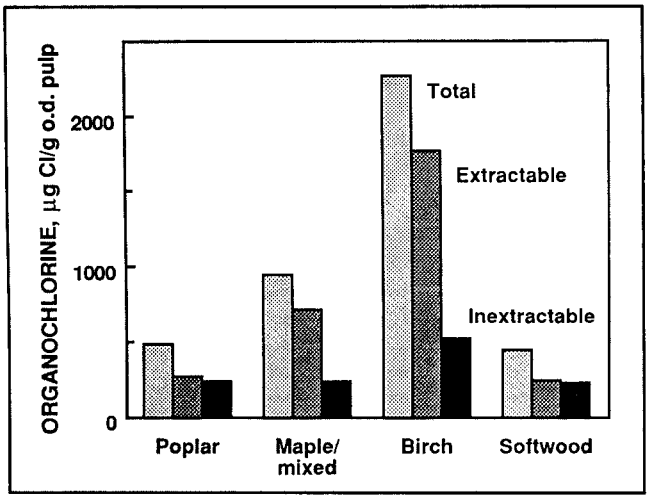
Some of the chlorine in pulp and paper products is present in the form of chloride ion. This ion can be removed by extraction with water or a dilute solution of sodium bicarbonate. Chloride ions may be present as spent bleaching chemical or may be added during papermaking, to control static electricity in dryers, for instance.

As opposed to chloride ion, organochlorine is found in various forms. Some water-soluble organochlorine may be removed during aqueous extraction. The organochlorine content of the aqueous extract can be tested by carbon adsorption, as in the AOX technique. The chlorine remaining in the pulp is assumed to be covalently bound to carbon atoms—making it "organochlorine." There is no absolute measure of organochlorine in pulp; rather, we must define its measurement according to a prescribed methodology. Total organochlorine in pulp is therefore the sum of the AOX and the water-insoluble chlorine in pulp.

Figure 1 presents a scheme for determining the functional types of chlorine in pulp (*7*). The pulp, which has been water extracted, is extracted using a neutral solvent to determine the "extractable" and the "inextractable" organochlorine. Extractable organochlorine may be important in personal-use products and food packaging. It is this fraction of the organochlorine which will be mobile.

The results of a survey of 34 softwood bleached kraft pulps are illustrated in **Fig. 2**. AOX is only a small fraction (6%) of the total organochlorine (440 µg/g of o.d. pulp). About 50% of the organochlorine is solvent extractable, and 50% is inextractable.

3. Organochlorine in hardwood



I. Forms of organically bound chlorine in kraft pulp (7)

	Average found, µg/g o.d. pulp		
	Semi-bleached softwood	Fully-bleached	
		Softwood	Hardwood
Total	800	400	1000
AOX	50	30	40
Solvent extractable	400	200	700
Inextractable	400	200	300

II. Extractable organochlorine (8)

	Total organochlorine, µg/g o.d. pulp	Organochlorine extracted by acetone, %	Cl content of extractives, %
Birch	2200	80	25
Eucalyptus	600	40	12
Hemlock/balsam	500	40	13
Western red cedar	600	20	8
Aspen	400	40	7.5
Jack pine/spruce	300	10	7.5

The results of a survey of 12 hardwood pulps are illustrated in **Fig. 3**. Organochlorine content differs between species. The birch sample contained almost 2300 µg/g, of which 70% was extractable. The poplar samples were almost identical in organochlorine content and percentage extractable to the softwood samples. Note that the overall average AOX for all the hardwoods was 4% of the total or 40 µg/g.

An important finding of this work was that in semi-bleached pulp (with brightness ranging from 56 to 78), the organochlorine content was almost twice as high as the fully bleached softwood kraft; about 50% was solvent extractable.

The results from this survey work (*7*) are summarized in **Table I.**

Characterizing the extractable organochlorine

Different analytical techniques have been applied to the extracts from six pulp types: birch, eucalyptus, hemlock-balsam fir, western red cedar, aspen, and jack pine-spruce (*8*). The extracts have been found to be highly diverse in character, with considerable variation among wood species.

Table II highlights the results. The percentage extractable was the highest for birch. The fraction extractable for the jack pine-spruce and western red cedar was very low, perhaps due to the poor efficiency of the acetone extraction. (Previous extractions were by ethanol-toluene soxhlet extraction.) Interestingly, the chlorine content of the extractives varied quite widely, from 25% to 7.5%. This finding is important because the chlorine content affects a number of environmental parameters. As chlorine content in a family of chemicals such as phenols increases, the toxicity and the lipophilicity most often increases.

The pulp extracts were highly lipophilic. Lipophilicity is usually measured in terms of the partition coefficient between octanol and water. Octanol is a good mimic for fatty tissue in fish and other organisms. If the octanol-water partition coefficient is greater than 1000 (that is, if the concentration in octanol in contact with an aqueous solution is more than 1000 times greater than the concentration in the aqueous solution), then the potential for bioaccumulation is significant. Partition coefficient is usually expressed as a log value, so that values for log P_{ow} greater than 3 indicate a statistically significant potential for bioaccumulation. More than 80% of the organochlorine in the pulp extract was found to have a log P_{ow} greater than 4. A significant fraction had a log P_{ow} greater than DDT (log P_{ow} = 6.2). This finding is important because it suggests that the extractable organochlorine is not only mobile but is highly attracted to fatty tissue such as fatty foods and oil in the skin.

Another important question is whether or not these extractable components are aromatic. Aromatic chlorine is often more persistent and more toxic than other types of organochlorine. NMR studies show very little aromatic content in the extracts.

Gas chromatography and gas chromatography/mass spectrometry are not very effective in identifying the complex mixture of chlorinated organic compounds found in pulp extracts. With the number average molecular weight in the range of 300-900, some extracts will contain moderately high-molecular-weight components.

A mass spectrometry technique called "negative desorption chemical ionization" was found to be useful in separating the complex mixture of chlorinated compounds. The technique is particularly sensitive to halogenated compounds (*14*). Various chlorination products of linoleic acid containing 1, 2, 3, and 4 chlorine atoms have been found. A number of chlorinated terpenoids and chlorinated and hydroxylated prenols are suspected (*9*).

The influence of pulp processing

Organochlorine in pulp may be decreased by a number of modifications to processes ahead of bleaching that result in improved removal of lignin or extractives. These process modifications would include improved debarking, extended delignification in the digester, oxygen delignification, and improved brownstock washing. Steps to be taken in bleaching include high chlorine dioxide substitution, use of pitch dispersant rather than talc, aggressive extraction stages, and bleaching to high brightness. (The samples analyzed in this study were collected in 1988. Many of the changes listed have become accepted technology.)

Concluding remarks

The influence of chlorinated organic compounds on users of paper products from bleached kraft pulp is probably negligible. However, it is vital that the chemistry and behavior of this material be more thoroughly understood to verify this contention. If necessary, action must be taken to minimize the possibility of negative effects to the user. Corporate, environmental, and governmental activities concerning organochlorine in pulp may have an impact on the marketing of bleached kraft pulp and its paper products.□

Literature cited

1. Reeve, D. W. and Earl, P. F., Pulp Paper Can. 90(4): T128(1989).
2. Pulping effluents in the aquatic environment, The Procter and Gamble Co., Cincinnati, Ohio, Aug. 11, 1989.
3. U.S. Environmental Protection Agency/Paper Industry cooperative dioxin screening study, National Council Paper Industry Air Stream Improvement (NCASI), Tech. Bull. No. 545, May 1989.
4. Kringstad, K. P., Johannsson, L., Kolar, M-C., and de Sousa, F., Tappi J 72(4): 147(1989) and 72(6): 163(1989).
5. Voss, R. H., Luthe, C. E., Fleming, B. I., Berry, R. M., *et al.*, Pulp Paper Can. 89(12): 151(1988).
6. Howard, E. J. and Histed, J. A., Tappi 47(11): 653(1964).
7. Reeve, D. W. and Weishar, K. M., J. Pulp Paper Sci. 16(4): J118(1990).
8. Reeve, D. W. and McKague, A. B., Chlorinated organic matter in bleached chemical pulp production, Part VII: Characterization of extractives, Proceedings of the CPPA Technical Section 76th Annual Meeting, CPPA, Montreal, 1990, p. 253.
9. Reeve, D. W. and McKague, A. B., Identification of chlorinated compounds in bleached pulp extracts, Proceedings of the 24th EuCePa Conference, EuCePa, Helsinki, 1990, p. 468.
10. Miljovanligt, Nr. 1, Mars, published by ICA-forbundet, Stockholm, Sweden, 1988.
11. Rioux, J. P. and Hurtubise, F. G., Tappi 48(1): 11(1965).
12. Douek, M. and Ing, I., J. Pulp Paper Sci. 15(2): J72(1989).
13. Stevens, B. J., Sell, L. O., and Easty, D. B., Tappi J. 72(7): 181(1989).
14. Budzikiewiz, H., Mass Spectrom. Revs. 5: 345(1986).

This work has been supported by Albright and Wilson Americas and by an industry consortium including Albright and Wilson Americas, Aracruz Celulose S.A., Champion International Corporation, CRS Sirrine, Fletcher Challenge Canada Ltd., International Paper, ITT Rayonier Incorporated, James River Corporation, Noranda Inc., The Procter and Gamble Cellulose Co., and Weyerhaeuser Company. Matching funding has been provided by The Ontario Ministry of Colleges and Universities' University Research Incentives Fund.

Received for review July 31, 1990.

Accepted Sept. 17, 1990.

Presented at the TAPPI 1990 Pulping Conference.