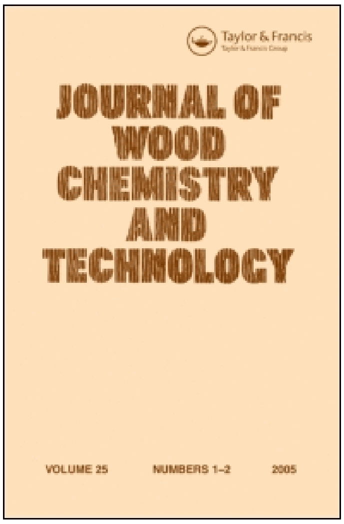

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Kringstad, K. P. , Stockman, L. G. and Strömberg, L. M.(1984) 'The Nature and Environmental Significance of Spent Bleach Liquor Toxicants: Present State of Knowledge', Journal of Wood Chemistry and Technology, 4: 3, 389 — 404

To link to this Article: DOI: 10.1080/02773818408070656

URL: http://dx.doi.org/10.1080/02773818408070656

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 4(3), 389-404 (1984)

THE NATURE AND ENVIRONMENTAL SIGNIFICANCE OF SPENT BLEACH LIQUOR TOXICANTS: PRESENT STATE OF KNOWLEDGE

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Paper dedicated to Dr. Joseph L. McCarthy
on the occasion of his 70th birthday.

ABSTRACT

This paper is a description of the present state of knowledge on the nature and properties of the compounds present in spent bleach liquors known to have acute toxic, mutagenic and/or carcinogenic effects. Included is also a discussion concerning bioaccumulation of spent bleach liquor material. Furthermore, the eventual risks involved in releasing such liquors into the rivers and lakes are briefly discussed.

INTRODUCTION

In the conventional bleaching of chemical pulp, 45-90 kg of organic material dissolve into the bleaching liquors per ton of pulp produced. The dissolved material is chlorinated and in the case of softwood kraft pulp contains 4-5 kg organically bound chlorine/ton of pulp.[1] The world production of bleached chemical pulp is presently of the order of 50 million tons per year. This leads to the conclusion that the annual discharge of organically bound chlorine from pulp bleach plants is about 200,000 tons. The discharge of spent bleach liquors has for some time been

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considered to be the most important environmental question within the pulp and paper industry.

In 1982 a comprehensive four-year Swedish research project was concluded entitled "Environmentally harmonized production of bleached pulp".[2] One conclusion was that according to the present state of knowledge, the environmental effects of spent bleach liquors are small or insignificant in "good" (high dilution) receiving water systems. However, much additional work is required to make possible a more complete evaluation of any risk involved. More knowledge concerning the nature, the quantities and the properties of toxic compounds formed during bleaching is particularly important. This paper presents a summary of presently available knowledge in this respect and points to some questions which need further investigation in order to improve risk evaluation.

DISCUSSION

Acute Toxicity and Sublethal Effects

It is well established that the spent liquors from the chlorination and the first alkali extraction stages in the conventional bleaching of a softwood kraft pulp exhibit a mild acute toxic effect with regard to fish.[2-4] Thus, neutralized bleached kraft effluents will have a 96-hr LC 50 concentration (to rainbow trout) of from 15-50 % by volume.

About 90 % of the acute toxic effect of spent alkali extraction liquor is due to the presence of 3,4,5-trichloroguaiacol, tetrachloroguaiacol, mono- and dichlorodehydroabietic acid and epoxystearic acid[5], see Fig. 1. Of these, the tetrachloroguaiacol is the most toxic. The acute toxic effect of the spent chlorination liquor is normally lower than that of the spent alkali extraction liquor. However, since the volume of the chlorination liquor produced is much larger, the total toxicity released with this liquor is greater.

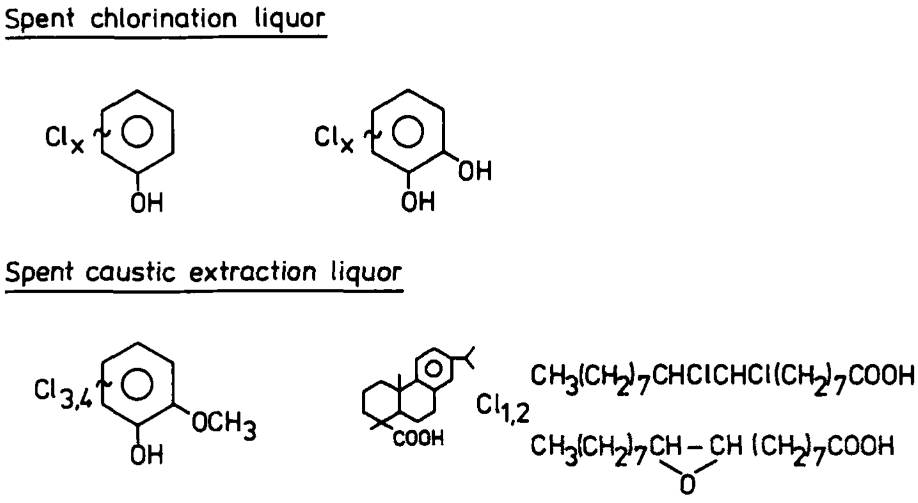

FIGURE 1. Some acute toxic compounds in spent bleaching liquors.

The identification of the compounds responsible for the toxicity of spent chlorination liquor has not progressed as far as it has for the alkali extraction liquor, although it is clear that chlorinated phenols, catechols and quinones contribute to significant degrees,[1,6-8] see Fig. 1. In the case of chlorinated phenols and catechols, toxicity increases with increasing number of chlorosubstitutents.[6] Non-chlorinated compounds (other than epoxystearic acid), such as various resin acids and unsaturated fatty acids, are also known to contribute to the acute toxic effects of spent bleach liquors.[9-10]

Information concerning the stability and tendency to bioaccumulation of the acute toxic compounds is important from an environmental point of view. Results from a number of investigations suggest, as indicated in Fig. 2, that chlorinated phenols are quite resistant to biodegradation.[2,9-11]

This is particularly true of compounds with a high degree of chlorine substitution. Similar investigations on chlorinated and non-chlorinated resin and fatty acids, suggest that these are less

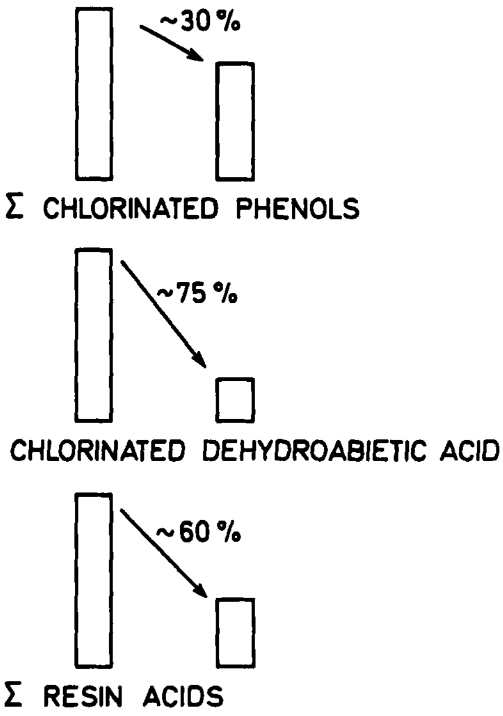

FIGURE 2. Approximate reductions in aerated lagoons of spent bleach liquor toxicants.[2,9-13]

resistant to biodegradation.[12,13] Apparently, this is also true for mono- and dichlorodehydroabietic acids.[2,9]

With regard to the tendency to bioaccumulation it has been found in both laboratory and field studies that 2,4,6-trichlorophenol, 3,4,5-trichloroguaiacol and tetrachloroguaiacol in particular accumulate in fish (14,15). Fig. 3 shows that an increasing degree of chlorine substitution leads to increasing lipophilicity of phenols.[16]

With regard to the bioaccumulation of chlorinated phenols, it is important to note that the degree of bioaccumulation is highly dependent upon the pH of the water[17] and when exposed fish are moved to non-polluted waters, the phenols are eliminated from the fish in a short period of time.

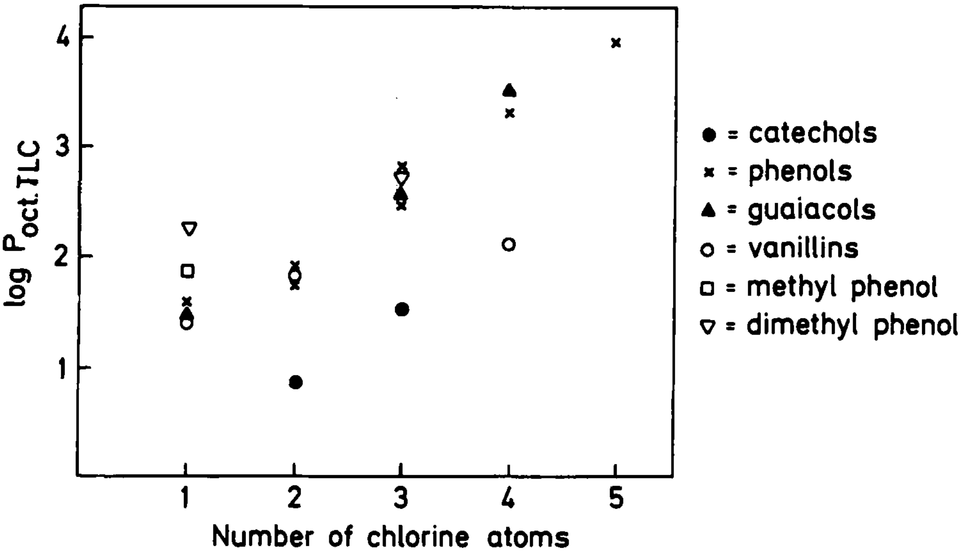

FIGURE 3. Partition coefficients derived from reversed phase thin layer chromatography as a function of the degree of chlorine substitution of various phenols.[16]

Chlorinated phenols are not the only type of compounds which may bioaccumulate. Recently, 1,1-dichlorodimethylsulfone was found in fish (flounder) caught in the vicinity of a pulp mill.[18] 1,1-Dichlorodimethylsulfone is a spent bleach liquor compound with a high degree of resistance to biodegradation (see further below, Ref. 42).

Several studies have been made of the effects on fish of spent bleach liquors at sublethal concentrations.[2,4,19] These include effects on reproduction, late effects, effects on behaviour and different physiological and histological sublethal effects. The sensitivity varies considerably. Probably the most sensitive test known so far is one for parasitic cysts in gills of flounder.[2] Effects are here clearly detectable at concentrations which are 25-30 times lower than the 96-hr LC 50 concentration.

The other effects are observed at concentrations above about 5 % of the 96-hr LC 50 .

Hardly any information is presently available as to which compounds are responsible for the effects at sublethal concentrations. Some preliminary results indicate that these are not necessarily the same as those responsible for the acute toxic effects.[2] Research to improve knowledge in this field should be given priority.

Genotoxic Effects

It is now well established that spent chlorination liquor from the bleaching of softwood kraft pulp (and most other pulp types) exhibits a mutagenic effect.[20,21] This was determined by testing the spent liquor according to the Ames-test[22] as well as by other laboratory techniques for testing for genetic effects.[23-25]

Of the mutagenic compounds which have so far been identified (see Table 1) 1,3-dichloroacetone,[26,27] 2-chloropropenal,[26,27] 2,3-dichloropropanal[28] and 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone[29] are strong mutagens in the pure state. Chloroacetones,[25] the chlorinated furanone derivative and the 2-chloropropenal are regarded as major contributors to the mutagenicity of the spent chlorination liquor. However, additional mutagens remain to be identified. Bromo-p-cymene and dichloro-p-cymene contribute to the mutagenicity of spent chlorination liquor from the bleaching of softwood sulfite pulp.[21,33]

Spent chlorination and alkali extraction liquors and spent liquors from bleaching with hypochlorite contain chloroform and carbon tetrachloride which have been classified as carcinogens using standard methods of animal testing.[1] Other compounds present including various chlorinated benzenes and phenols, epoxystearic acid and dichloromethane, have been classified as suspected carcinogens.[23]

TABLE 1.

Ames-Test Positive Compounds Identified in the Spent Chlorination Liquor from the Bleaching of Softwood Kraft Pulp.[23-32]

Compound	Strain, Salmonella typhimurium	g/ton pulp
Dichloromethane	TA 100	-
Bromodichloromethane	TA 100	-
Dibromochloromethane	TA 100	-
Trichloroethene	TA 100	0.5
Tetrachloroethene	TA 100	-
Tetrachloropropene	TA 98, TA 100, TA 1535	
Pentachloropropene	TA 100, TA 1535	
1,3-Dichloroacetone	TA 100, TA 1535	0.7
1,1,3-Trichloroacetone	TA 100	
1,1,3,3-Tetrachloroacetone	TA 100	12
Pentachloroacetone	TA 100	
Hexachloroacetone	TA 100	0.4
Monochloroacetaldehyde	TA 100, TA 1535	0.2
2,3-Dichloropropanal	TA 100, TA 1535	0.5
2-Chloropropenal	TA 100, TA 1535	1.5
3-Chloro-4-dichloromethyl-5- -hydroxy 2(5H)-furanone	TA 100	-

With current knowledge it is not possible to assess correctly the risks involved in releasing such compounds into rivers, lakes and the ocean.[34] This is in part due to the lack of animal carcinogenicity data for the combined spent liquor compounds. Nevertheless, in a recent evaluation of the three major inland receiving waters in Sweden this risk was estimated to be extremely low to non-existent.[2] This conclusion was reached from figures showing that the spent bleach liquors released into these receiving waters were diluted to low levels with respect to chloroform, carbon tetrachloride and some of the identified mutagenic compounds. These levels were actually far below those of identical compounds formed in the disinfection of drinking water by chlorination. It is well known that chloroform is formed in reactions between humic and fulvic acid and chlorine, and so are many of the spent bleach liquor mutagenic compounds as shown in Table 2.

The conclusion that the risk is low is supported by observations showing that chloroform (see further below) and a major part of the mutagenic compounds are fairly unstable[28] under conditions prevailing in the receiving waters. However, additional information on the fate of the genotoxic compounds in the receiving waters and in organisms living in these waters is necessary for a better risk evaluation. Recent investigations on the tendency to bioaccumulation of the mutagenic compounds in spent chlorination liquor from the bleaching of softwood kraft pulp have shown that about 2 % of the mutagenicity originates from compounds with partition coefficients of between 1,000 and 10,000.[36] The identification and characterization of such compounds deserve future interest.

Toxicants in Spent Liquors from Alternative Bleaching Sequences

In the Swedish research project "Environmentally harmonized production of bleached pulp" an attempt was made to rank various

TABLE 2

Formation of Various Mutagenic Compounds by Chlorination of Humic Acid.[35] The Values are Given as Nanograms per Milligram Organic Carbon Chlorinated.

	Cl_2:C ratio				
	0.1:1	0.5:1	1:1	2:1	4:1
2-Chloropropenal	-	-	13.5	44.6	110.8
1,3-Dichloroactone	1.9	2.7	5.7	27.2	59.2
1,1,3,3-Tetrachloroacetone	2.1	30.4	416.0	444.0	541.6
Pentachloroacetone	6.4	26.7	352.0	856.0	1730.0
Hexachloroacetone	-	-	9.9	28.2	66.4

alternative bleaching processes according to their environmental impact.

Results from a number of chemical and biological tests formed the base for ranking the processes, a certain priority being given to the biological test results.[2] As can be seen in Table 3, prebleaching with oxygen and/or partial replacement of chlorine by chlorine dioxide in the first bleaching stage and/or biological treatment of the effluents are all important ingredients in these processes and are well-known techniques for reducing the toxicity, mutagenicity, color, COD and/or BOD of bleach plant effluents.

There is as yet very little knowledge available concerning the way these techniques influence the organic chemical composition of the bleach plant effluent.

In recent investigations it was shown that oxygen prebleaching does not seem to alter significantly the spectrum of compounds present in the spent chlorination and alkali extraction liquors.[37] However, when properly conducted, prebleaching with oxygen generally results in the formation of smaller quantities of the compounds. Bleaching sequences including oxygen do not

TABLE 3.

Ranking of Alternative Bleaching Processes for Softwood Kraft Pulp in order of Decreasing Environmental Impact (Top to Bottom).[2]

Process (+ treatment)	Comment
C_{90}/D_{10}EHDED	- Present technique
C_{90}/D_{10}EHDED	- Better washing compared with present technique
C_{90}/D_{10}EHDED+UF(E_1)	- Ultrafiltration of E_1-effluent
O(C_{85}+D_{15})EDED	- Oxygen bleaching to Kappa number 20 + washing to 10-12 kg/t_{90} as COD
C_{90}/D_{10}EHDED+UF+OZ	- Ozone treatment of permeate and C-stage effluent
O(C_{85}+D_{15})EDED	- Oxygen bleaching to Kappa number 20 + washing to 4-6 kg/t_{90} as COD
C_{90}/D_{10}EHDED + aerated lagoon	- Total effluent through aerated lagoon
C_{90}/D_{10}EHDED + ion exchange	- Ion exchange of total bleach plant effluent
D_{85}/D_{10}EDED	
O(C_{85}+D_{15})EDED + aerated lagoon	- Oxygen bleaching to Kappa number 20
O(D_{85}+C_{15})EDED	- Oxygen bleaching to Kappa number 17

normally contain a hypochlorite stage. Therefore, only very small quantities of chloroform are formed in such sequences.[37]

When softwood kraft pulp is bleached with a partial replacement of chlorine by chlorine dioxide, the quantity of chlorinated phenols decreases with increasing degree of replacement.[37,38] In a recent investigation where 100 % chlorine dioxide was used, the only phenolic compound that could be found in the spent liquor was 6-chlorovanillin.[10] Total replacement of chlorine by chlorine dioxide also significantly influences the elemental composition of the high relative molecular mass material, with a strong reduction in the content of organically bound chlorine. Only very small quantities of chloroform (about 1 g/ton of pulp) are found in such liquors.[37]

In a recent investigation it was found that the bladder wrack population was reduced in an area of receiving waters in the Baltic Sea surrounding the effluent outlet tube from a Swedish bleached kraft mill equipped with an aerated lagoon.[39] The disappearance of the bladder wrack began at a time when the mill introduced changes in the bleach plant involving amongst other changes the use of oxygen and chlorine dioxide. Several possible explanations for the damage were presented in the report which concluded by recommending that until further notice no further oxygen bleach plant should be installed.[39] As has now been shown, the damage was not a result of oxygen bleaching, but was due to the combined effects of the chlorate formed, a particular high degree of closure of the mill and shallow receiving waters.[40]

Biodegradability

Biological treatment reduces the content of organically bound chlorine to some degree.[37] This must, at least in part, be due to a reduction in the content of chlorinated neutral organic compounds. It is well established that aerated lagoons are efficient in removing chloroform,[41-44] possibly this may not only be due to biodegradation but also to evaporation into the atmosphere. In a recent investigation, various chlorinated dimethyl sulfones were the only detectable chlorinated neutral organic compounds (other than chloroform) in biologically treated, bleached kraft total mill effluents.[44]

Chlorinated phenols are also biodegradable.[7,45] However, the rate of removal is highly dependent on treating conditions and

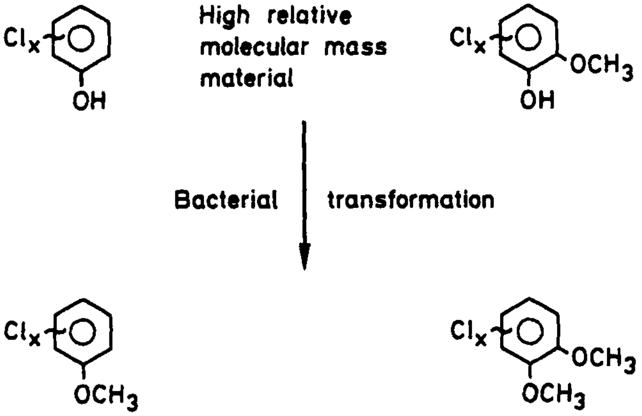

FIGURE 4. Chlorinated phenols, guaiacols and chlorinated high relative molecular mass material from spent bleach liquors are tranformed by bacteria to chlorinated anisoles and veratroles.[50]

can be quite low.[10,46-48] Thus chlorinated phenols and guaiacols are easily detectable in biologically treated, bleached kraft total mill effluents,[42] and also often in receiving waters.[49] Similar observations have been made with regard to various chlorinated resin acids.[49]

A new aspect of the biological treatment of spent bleach liquor arises from recent investigations. In these it was found that chlorinated phenols, guaiacols and high relative molecular mass material are transformed by bacteria isolated from sediments in receiving waters into chlorinated anisoles and veratroles,[50] see Fig. 4. Methylated chlorinated phenolic compounds are highly lipophilic and could if formed in aerated lagoons (or in the receiving waters) bioaccumulate in higher organisms. Research to identify such products in receiving waters and organisms and to characterize their properties also deserves high priority.

Conclusions

Much research has been carried out in recent years to characterize the chemical composition and the biological effect of spent bleach liqours. This has resulted in a significantly greater understanding of the nature and properties of the toxic compounds present in such liquor. Less research has so far been carried out with the aim of identifying and evaluating any risks involved in releasing spent bleach liquors into the aquatic environment. A major part of future research efforts concerning environmental aspects of bleach plant effluent should be directed towards such studies.

This manuscript is based on a paper presented at the XXI EUCEPA International Conference 1984 in Torremolinos, Spain.

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