

Chlorinated Organics in Tropical Hardwood Kraft Pulp and Paper Mill Effluents and their Elimination in an Activated Sludge Treatment System

MURTEDZA MOHAMED, M. MATAYUN and T.S. LIM

Department of Chemistry,
Faculty of Science and Natural Resources,
UKM Sabah Campus, Locked Bag No. 62,
88996 Kota Kinabalu, Sabah, Malaysia.

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ABSTRAK

Identiti dan kepekatan sebatian-sebatian organik berklorin yang utama yang terkandung di dalam campuran efluen Kilang Pulpa dan kertas SFI di Sabah, Malaysia, telah ditentukan. Sebatian-sebatian organik berklorin yang didapati wujud dalam kuantiti yang relatif tinggi selepas efluen tersebut diolah secara biologi ialah asid trikloroasetik (838-994 µg/L), 1,1-diklorodimetil sulfon (DDS)(86-232µg/L), asid dikloroasetik (14-18 µg/L), dan triklorosiringol (5-18 µg/L). Perbandingan antara muatan sebatian-sebatian fenol serta asid organik berklorin dalam air buangan kilang pulpa kraf kayu keras SFI dengan muatan yang dilaporkan dalam air buangan beberapa kilang pulpa kraf kayu keras SFI dengan muatan yang dilaporkan dalam air buangan beberapa kilang pulpa kraf kayu lembut menunjukkan bahawa muatan sebatian-sebatian tersebut di dalam air buangan kilang SFI adalah kira-kira 3-8 kali lebih rendah. Keberkesanan sistem pengolahan enap cemar teraktif beroksigen dalam pelupusan sebatian-sebatian tersebut daripada air buangan kilang SFI adalah seperti berikut: fenol berklorin 20-70%, DDS 60%, dan asid asetik berklorin 30-99%.

ABSTRACT

The identity and concentration of major chlorinated organics in the combined effluents of the SFI Pulp and Paper Mill in Sabah, Malaysia, were determined. In the biologically treated effluent, chlorinated organics found to occur in a relatively higher concentration were trichloroacetic acid (838-994 µg/L), 1,1-dichlorodimethyl sulfone (DDS)(86-232 µg/L), dichloroacetic acid (14-18 µg/L), and trichlorosyringol (5-18 µg/L). Compared to those of a number of softwood kraft mills, the load of chlorinated phenols and acids in the wastewater of SFI hardwood kraft mill was 3-8 times lower. The effectiveness of oxygen activated sludge treatment system in eliminating these chlorinated organics was found to be as follows: chlorinated phenols 20-70%, DDS 60%, and chlorinated acetic acids 30-99%.

INTRODUCTION

Information gathered thus far clearly indicates that some of the chlorinated organics present in the wastewater of bleached pulp mills are toxic, mutagenic, and rather resistant to biodegradation (Kringstad and Lindstrom 1984; Leach *et al.* 1978; Mueller *et al.* 1977). Some of the compounds known to impart toxicity are 2,4,5-trichlorophenol, tetra- and pentachlorophenols, tetrachlorocatechol, 3,4,5-trichloroguaiacol, and tetrachloroguaiacol. With the

exception of the catechol, these compounds also exhibit a potential for bio-accumulation.

To date, the majority of studies on pulp-mill-originated chlorinated organics are on effluents of softwood mills operating in temperate countries (Kringstad and Lindstrom, 1984; Murtedza, 1987 and references therein). Similar studies on the effluent of hardwood mills operating in the tropics are scarce. This report presents results of an investigation performed in cooperation with the only Malaysian

pulp mill, the Sabah Forest Industries (SFI) Pulp & Paper Mill, to determine (i) the identity of major chlorinated organics present in the mill's wastewater, (ii) the rate they are produced during the bleaching process (per ton of pulp bleached), (iii) the effectiveness of the oxygen activated sludge effluent treatment system incorporated in the mill in removing the chlorinated organics, and (iv) their concentrations in the effluent before they are discharged into the receiving water (the Brunei Bay). The mill, which started its operation in April 1987, produces kraft pulp from mixed tropical hardwoods. The maximum annual production capacity of the mill is 94 000 tonnes of bleached kraft pulp, and the maximum volume of effluent discharged daily is 43 000 m³.

MATERIALS AND METHODS

Sample Source and Sampling

Wastewater samples collected at the oxygen activated sludge effluent treatment plant at SFI Mill were a mixture of effluents, originating mainly from pulp mill, bleach plant and paper mill (Fig. 1), with small inputs from inorganic

chemical plants and sewage system. The pulp bleaching at SFI utilises a (C+D).Eo.D. sequence, comprising of pre-bleaching stage using a mixture of chlorine (C) and chlorine dioxide (D) followed by oxidative extraction (Eo), and subsequent brightening stages using chlorine dioxide. Samplings of effluents were carried out during July 1987 – August 1988. Five composite samples of the combined process wastewater were collected from the inlet and outlet points of the treatment plant (Fig. 1; points 1 and 2 for influent and effluent samples, respectively). During each sampling, 250 mL of wastewater samples were collected every 30 minutes over a period of 4 hours. Samples were immediately transported back to UKMS Laboratory and/or stored at 4°C if not immediately analysed.

Sample Preparation

Neutral Chlorinated Organics. 40 µL of a 62.8 µg/ml solution of 1,6-dibromobenzene in diethyl ether (internal standard) was introduced into a 50 mL sample and the pH of the solution adjusted to 12. The solution was then extracted with 25 mL diethyl ether; the ether layer was

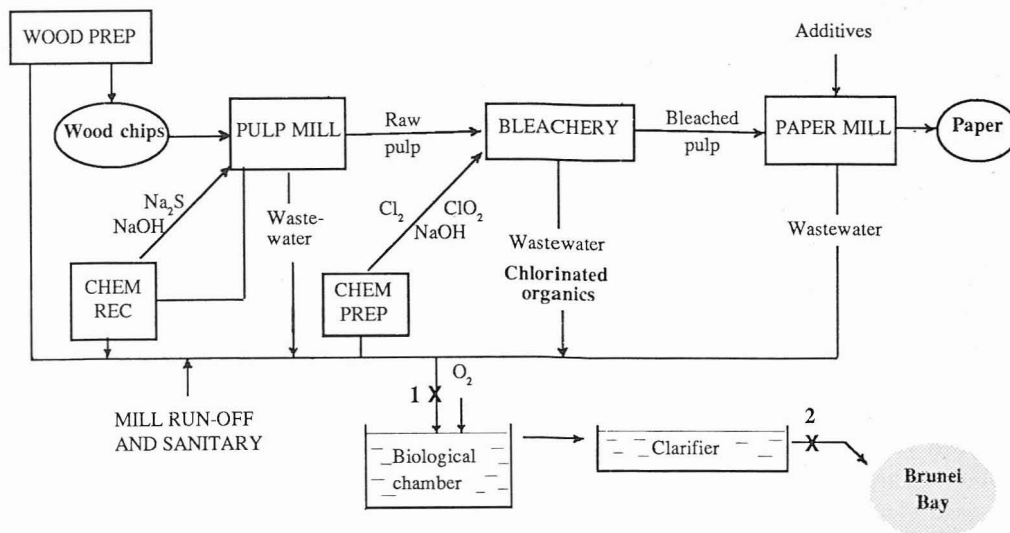


Fig. 1: A simplified scheme of the SFI integrated kraft pulp and paper mill operations showing among others, the process units, the source of chlorinated organics and the wastewater treatment system. Abbrev: CHEM REC-Chemical Recovery Plant; CHEM PREP-Chemical Preparation Plant. Points 1 and 2 were sites of influent and effluent samplings, respectively.

separated, dried (Na_2SO_4), evaporated to about 1 mL and analysed on GC.

Chlorinated Phenols. To a 25 mL sample, was added 1.25 mL of 2,6-dibromophenol solution in ethanol (0.268 $\mu\text{g}/\text{mL}$, internal standard), followed by 25 mL of 0.01 mol/L K_2CO_3 solution and 1 mL of acetic anhydride. The mixture was vigorously shaken for 1 min., after which chlorophenols were extracted twice with 5 mL portions of n-hexane. The hexane layer was separated (after centrifugation), and then washed with 50 mL of 0.1 mol/L K_2CO_3 solution. After drying, the extract was analysed on GC.

Chlorinated Acids. To a 10 mL effluent sample, was added 100 μL of bromoacetic acid solution in diethyl ether (236.6 $\mu\text{g}/\text{mL}$, internal standard). The pH of the solution was then adjusted to about 0.8 and the solution extracted with 5 mL diethyl ether. After separation, the ether layer was dried and methylated using *N*-nitroso-*N*-methyl-*p*-toluene-sulfonamide as described in detail elsewhere (Lindstrom and Osterberg 1986). The resulting solution was then analysed on GC.

Gas Chromatographic Analysis

Gas chromatographic analyses were carried out using a Hitachi Model 163 Gas Chromatograph with a ^{63}Ni electron capture detector (ECD) and a fused silica capillary column (25 m \times 0.25 mm i.d., BPI methyl silicon). The oven temperatures were isothermic in all analyses, i.e. 55°C for chlorinated acids determination, 90°C for chlorinated neutrals, and 175°C for chlorinated phenols determination. Injector and detector temperatures were maintained at 300°C. Nitrogen was used both as the carrier gas (0.6 mL/min) and the make-up gas (30 mL/min). The injector split ratio was 1 : 20.

Quantification was based upon the internal standard method, making use of peak areas and the relative response factors of individual compounds. Calibration (i.e. determination of response factors and retention times relative to the internal standard) was performed by injecting standard mixtures in appropriate solvents containing known amounts of the reference compounds and the internal standard.

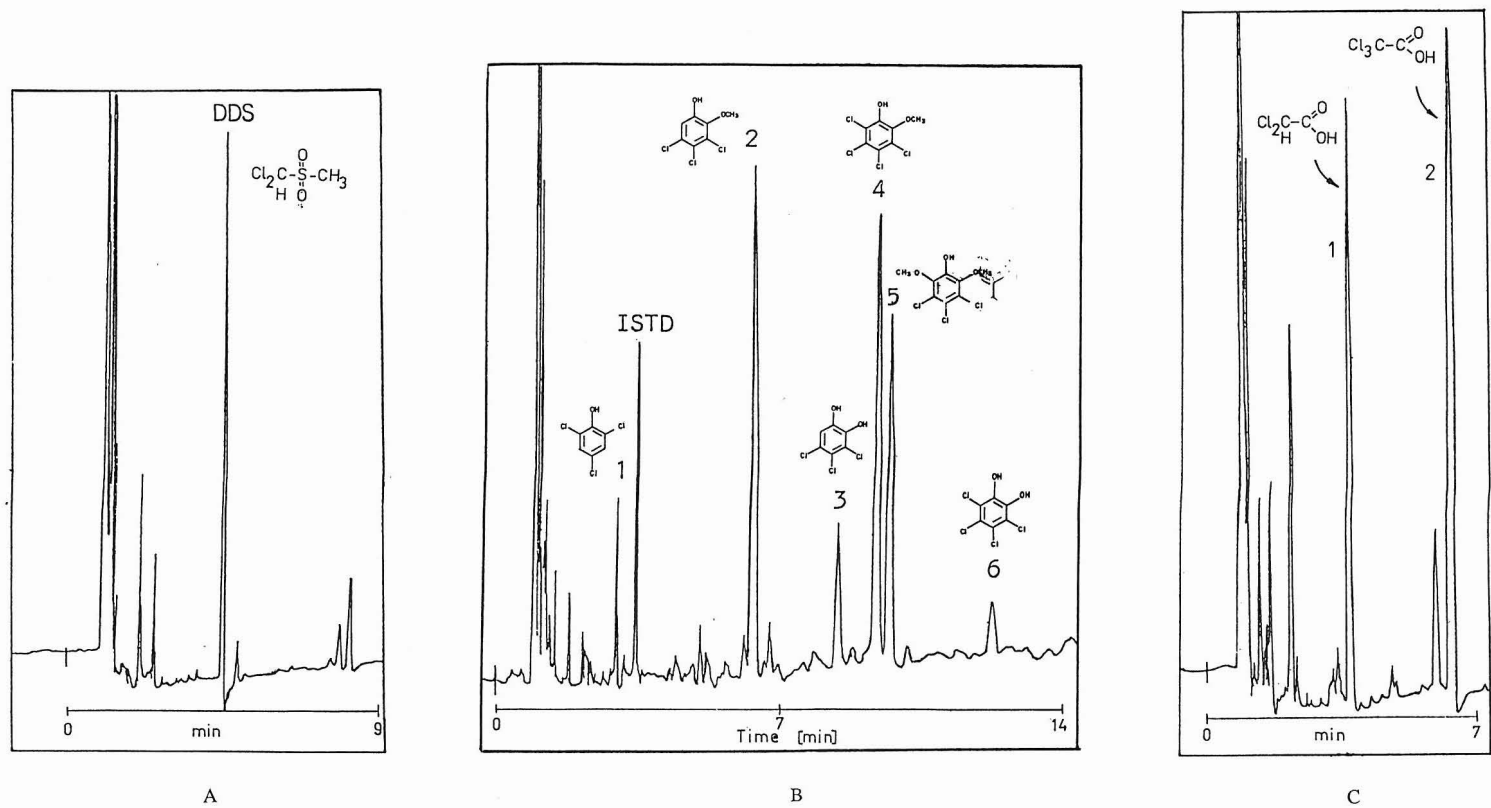
RESULTS AND DISCUSSION

Extraction of the SFI Pulp and Paper Mill combined wastewater samples at different pH, followed by derivatisation where necessary, gave satisfactory separations of chlorinated neutral organics, chlorinated phenols, and chlorinated organic acids, as reflected in their respective chromatograms (Figs. 2A-C). Major chlorinated organics extracted and their respective concentrations and loadings in the influent and effluent are given in Table 1. Also presented in the table are their removal efficiencies upon treatment in the oxygen activated sludge treatment system. Although the primary role of the effluent treatment plant was to remove most of the oxygen demanding organics present in the wastewater, the treatment process did show a certain degree of efficiency in removing chlorinated organics.

The most abundant chlorinated organics found to be present in the wastewater were di- and tri-chloroacetic acids. On the average, loadings of the two acids in treated effluent amounted to about 13.6 tonnes/year. Of the two, dichloroacetic acid is the most biodegradable, although the trichloro analogue can be equally efficiently removed by prolongation of retention time in the treatment plant (Lindstrom and Murtedza 1988). The acids are not Ames mutagenic (McKague 1979) but toxic to a variety of organisms, including mammals.

Although it is apparent in Table 2 that SFI Mill produces DDS several times more than those of the softwood pulp mills A and B, there are softwood mills producing just as much DDS; a survey on nine softwood kraft pulp mills in Canada showed that DDS was present in concentrations 64-429 $\mu\text{g}/\text{L}$ in their biologically treated effluents (Table 3) (Voss 1983). As far as environmental implication of DDS is concerned, the compound has been shown to be neither toxic to rainbow trout nor Ames mutagenic (McKague 1986).

Major chlorinated phenols occurring in SFI Mill wastewater, in their declining order of loadings, were trichlorosyringol, 3,4,5-trichloroguaiacol, tetrachlorocatechol, 3,4,5-trichlorocatechol, and tetrachloroguaiacol. Comparison between constituents of chlorinated organics in the hardwood kraft pulp mill effluents with



Figs. 2 (A-C) Representative chromatograms of the three classes of chlorinated organics. Chromatogram A: diethyl ether extract of effluent adjusted to pH 12, showing DDS peak; Chromatogram B: n-hexane extract of effluent at pH 7, showing peaks of acetylated 2,4,6-trichlorophenol (1), 2,6-dibromophenol (internal standard, ISTD), 3,4,5-trichloroguaiacol (2), 3,4,5-trichlorocatechol (3), tetrachloroguaiacol (4), trichlorosyringol (5) and tetrachlorocatechol (6); Chromatogram C: diethyl ether extract of influent adjusted to pH 0.8, showing peaks of dichloroacetic acid (1), and trichloroacetic acid (2).

TABLE 1
Major chlorinated organics in the influent and effluent of the SFI Mill

Compound	Concentrations ($\mu\text{g/L}$)				Average removal %	Loading ¹	
	Influent		Effluent			tonne yr(g/tonne pulp)	
	Average ²	Range	Average ²	Range		Influent	Effluent
<i>Chlorinated neutral</i>							
1,1-Dichlorodimethyl sulfone	424	286 - 580	170	86 - 232	60	6.190 (68.78)	2.482 (27.57)
<i>Chlorinated phenols</i>							
2,4,6-Trichlorophenol	2.07	0.95 - 4.46	1.38	0.45 - 3.71	33	0.030 (0.34)	0.020 (0.22)
4,5-Dichloroguaiacol	1.67	1.10 - 2.45	1.27	0.21 - 2.21	24	0.024 (0.27)	0.018 (0.21)
2,3,4,6-Tetrachlorophenol	1.21	0.80 - 2.22	0.36	0.10 - 0.95	70	0.018 (0.20)	0.005 (0.06)
3,4,5-Trichloroguaiacol	10.05	7.13 - 18.70	6.49	2.86 - 11.20	35	0.146 (1.63)	0.095 (1.05)
4,5,6-Trichloroguaiacol	0.46	0.34 - 0.67	0.25	0.14 - 0.44	46	0.007 (0.07)	0.004 (0.04)
3,4,5-Trichlorocatechol	8.87	2.65 - 17.50	4.80	2.12 - 10.50	46	0.130 (1.43)	0.070 (0.78)
Tetrachloroguaiacol	7.06	2.55 - 14.19	5.62	1.79 - 12.30	20	0.103 (1.14)	0.082 (0.91)
Trichlorosyringol	17.43	12.04 - 21.90	13.81	5.49 - 18.35	21	0.254 (2.82)	0.202 (2.24)
Tetrachlorocatechol	9.92	4.65 - 16.70	3.81	0.27 - 10.70	62	0.145 (1.61)	0.056 (0.61)
<i>Chlorinated acids</i>							
Dichloroacetic acid	1424	1102 - 1747	16	14 - 18	99	20.790 (231)	0.234 (2.60)
Trichloroacetic acid	1314	853 - 1775	916	838 - 994	30	19.184 (213)	13.374 (148.60)

¹ Based on effluent volume of 40 000 m³/day and a production level of 90 000 tonnes pulp a year.

² Averaged from 5 composite samples, except for chlorinated acids (2 samples)

TABLE 2
Comparison of loadings of major chlorinated organics in the influent of three kraft mills (g/tonne pulp)

Compound	Mill A ¹	Mill B ²	SFI Mill ³
1,1-Dichlorodimethyl sulfone	12.20	9.98	68.78
2,4,6-Trichlorophenol	3.03	0.77	0.34
3,4,5-Trichloroguaiacol	6.22	4.25	1.63
4,5,6-Trichloroguaiacol	2.07	0.45	0.07
3,4,5-Trichlorocatechol	17.79	9.00	1.43
Tetrachloroguaiacol	3.23	1.86	1.14
Tetrachlorocatechol	3.98	0.85	1.61
Dichloroacetic acid	480	294	231
Trichloroacetic acid	631	892	213

¹ Mill A (in Sweden) processed mainly softwood; the bleaching sequence employed was CEHDED; values given were averaged from three composite samples (Source: Lindstrom and Murtedza 1988)

² Mill B (also in Sweden) processed only softwood; the bleaching sequence was O(C+D)EoDD; values given were averaged from three composite samples (Source: Lindstrom and Murtedza 1988).

³ SFI Mill processed only hardwood; the bleaching sequence was (C+D).Eo.D; values given were averaged from five composite samples, except for chlorinated acids (2 samples).

those of softwood mill effluents revealed that the most abundant chlorinated phenol in the hardwood pulp mill effluents was trichlorosyringol, whereas the dominant chlorinated phenol in softwood pulp mill effluents was 3,4,5-trichlorocatechol (Table 3). The higher quantity of trichlorosyringol in the hardwood mill effluents is attributable to the difference in the type of lignin present in hardwood and softwood. Hardwood lignin is of guaiacyl-syringyl type, whereas softwood lignin is of guaiacyl type (Sjostrom 1981).

Compared to the conventional method of bleaching (CEHDED, Mill A in Table 2) and a bleaching sequence incorporating oxygen prebleaching, O(C+D)Eo.D (Mill B in Table 2), the (C+D).Eo.D. sequence employed at SFI Mill generally resulted in lesser (3-8 time less) load of chlorinated phenols and acids in the wastewater. For chlorinated phenols, this finding is in agreement with that noted by Voss *et al.* (1981). Also, concentrations of chlorinated organics in the treated effluent of SFI Mill were generally less than the average levels reported for biologically treated effluents of a number of softwood kraft pulp mills in Sweden and Canada (Table 3). Graphical comparison of the aver-

TABLE 3
Comparison of levels of major chlorinated organics in
biologically treated effluents of kraft mills (mg/L)

Compound	Swedish Mills		Canada and	Malaysia
	Mill A ¹	Mill B ²	US Mill ³	SFI Mill ⁴
1,1-Dichlorodimethyl sulfone	40	41	223 ⁵	170
2,4,6-Trichlorophenol	8	2	6	1
Trichloroguaiacols	22	15	20	7
3,4,5-Trichlorocatechol	37	30	na	5
Tetrachloroguaiacol	9	7	12	6
Tetrachlorocatechol	9	3	na	4
Dichloroacetic acid	79	123	na	16
Trichloroacetic acid	1758	40	na	916

¹ See notes for Mill A in Table 2; wastewater was treated in an aerated lagoon of 2.5-day retention time.

² See notes for Mill B in Table 2; wastewater was treated in an aerated lagoon of 5-day retention time.

³ Average concentrations found in biologically treated effluents of six kraft mills in the United States (Source: Claeys *et al.* 1980), except for DDS.

⁴ SFI mill incorporated oxygen activated sludge system for wastewater treatment; retention time of the treatment plant was 10-12 h.

⁵ Average concentration found in biologically treated effluent of nine kraft mills in Canada (Voss 1983).

age concentrations of three chlorinated phenols in biologically treated effluents of different kraft mills is given in Fig. 3.

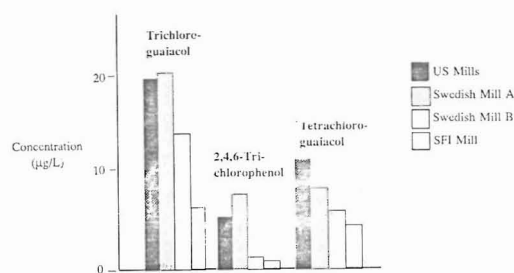


Fig. 3: Comparison of the average concentrations of three chlorinated phenols in biologically treated effluents of six mills in the United States (Claeys 1980), two mills in Sweden (Lindstrom and Murtedza 1988), and the SFI mill.

The efficiency of oxygen activated sludge effluent treatment system at SFI in removing chlorinated organics was found to be comparable or slightly better than those exhibited by aerated lagoons and air activated sludge systems (Table 4). Removal of chlorinated phenols in the oxygen activated sludge system was between 20-70%, against 13-54% reported for

air activated sludge system (Leuenberger *et al.* 1985). For the former, high efficiencies were observed in the removal of DDS, 2,3,4,6-tetrachlorophenol, tetrachlorocatechol, and dichloroacetic acids. DDS was reported to be poorly degraded in aerated lagoons (Lindstrom and Murtedza 1988)

CONCLUSION

The period during which this study was carried out may be considered as a 'start-up' period for the SFI Mill. During such a period, significant fluctuation in the process parameters can occur and loading of pollutants in the effluent fluctuated accordingly. Nevertheless, under the operational conditions prevailing during the time of samplings and based on the described analytical procedures, the following consistencies were observed:

1. Major chlorinated organics occurring in the wastewater of the SFI hardwood kraft pulp and paper mill were di- and trichloroacetic acids, 1,1-dichlorodimethyl sulfone (DDS), and trichlorosyringol.
2. Loadings of chlorinated phenols and organic acids in the wastewater of the SFI Mill were 3 to 8 times lower than levels normally found in wastewaters of softwood bleached pulp mills.

TABLE 4
Efficiency in the removal of chlorinated organics by activated sludge treatment system compared to aerated lagoon treatment system (% removed)

Compound	Aerated Lagoon		Activated Sludge	
	Mill A ¹ (2.5 d)	Mill B ² (5 d)	Mill C ³ (12 h)	SFI Mill ⁴ (12 h)
1,1-Dichlorodimethyl sulfone	8	17	na	60
2,4,6-Trichlorophenol	24	57	28	33
2,3,4,6-Tetrachlorophenol	na	na	33	70
3,4,5-Trichloroguaiacol	29	33	36	35
4,5,6-Trichloroguaiacol	23	53	35	46
3,4,5-Trichlorocatechol	41	32	na	46
Tetrachloroguaiacol	20	21	13	20
Tetrachlorocatechol	38	34	na	62
Dichloroacetic acid	95	91	na	99
Trichloroacetic acid	22	99	na	30

¹ See notes for Mill A in Table 2 and Table 3.

² See notes for Mill B in Table 2 and Table 3.

³ Mill C (in Switzerland) was a sulphite mill processing softwood; wastewater was treated in an air activated sludge system with a retention time of 12 h. (Source: Leuenberger *et al.* 1985)

⁴ See notes for SFI mill in Table 1, Table 2 and Table 3.

3. Upon treatment in an oxygen activated sludge effluent treatment plant, DDS and dichloroacetic acids were efficiently removed from the wastewater. Removal of chlorinated phenols by this method of effluent treatment was 20-70%, an efficiency slightly better than those reported for air activated sludge and aerated lagoon treatment methods.

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