WRC RESEARCH REPORT NO. 205

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DURING SIMULATED PAPER PULP BLEACHING

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REPORT
PROJECT NO. S-100-ILL

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ABSTRACT

Toxaphene is a persistent pesticide which is highly toxic to a broad range of organisms including freshwater fish. The sources of Toxaphene are still not clearly understood. Atmospheric transport from the cotton-growing districts of the southeastern United States is presently considered the most plausible hypothesis. This mechanism, however, does not adequately explain all of the data on Toxaphene concentrations in different geographical regions of the U.S. In particular, concentrations in the immediate vicinity of the Great Lakes have been increasing, whereas decreases have been observed at Midwestern sites not near these lakes. It is conceivable that environmental chlorination reactions, not involving the manufacture or application of Toxaphene at all, may be generating materials closely related to or indistinguishable from Toxaphene.

The objective of our research was to simulate pulp bleaching conditions in the laboratory and determine if Toxaphene-like materials could be produced.

The aqueous chlorination of the monoterpenes, camphene, limonene, α-pinene and β-pinene produced complex polychlorinated product mixtures. The extent of chlorination was primarily dependent on pH and light conditions. At pH 2 and exposed to sunlight product mixtures were obtained that had striking similarities to Toxaphene. At higher pH or in the dark, less extensive but still substantial chlorination took place; these lower chlorinated compounds could be mistaken for biologically degraded Toxaphene in environmental samples.

We conclude that Toxaphene-like mixtures may conceivably be formed under environmental conditions, but the actual extent of formation of such mixtures and the degree to which they may contribute to apparent Toxaphene in natural samples remain to be assessed.

INTRODUCTION

Toxaphene is an extremely toxic and apparently persistent chlorinated insecticide. Its production was curtailed and its use severely restricted in the United States in 1982. As of 1986 it is completely banned from use in the U.S. It has been described as "the most heavily used and least understood organochlorine insecticide." On a per-milligram basis, it has approximately the same gross acute toxicity as DDT (Registry Toxic Effects, 1976). Toxaphene is an extremely complex mixture of more than 200 polychlorinated compounds; no single compound predominates. The number of chlorine atoms range from 2-11 per molecule, with predominantly Cl_6-Cl_{10} isomers. It is typically represented by (<u>1</u>). It is known that some of these isomers are far more toxic than others (Turner et al., 1977), but it is not known whether the more toxic substances are the more environmentally persistent.
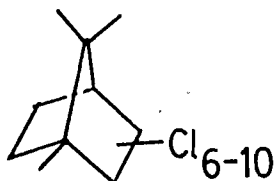
<u>1</u>

Not much Toxaphene has been used in the upper Midwest; it has been used mostly for the control of cotton pests. This is reflected in the high usage in the southern U.S. In the past thirty years this region has accounted for almost 90% of the total Toxaphene applied to farm acreage. By the early 1970's use of Toxaphene was rapidly increasing, from a yearly average of 30 million pounds to nearly 60 million pounds. The heaviest increase occurred in the Delta states (Louisiana and Mississippi) with the proportionate usage mounting to nearly 42% of total

Toxaphene usage (U.S. EPA, 1971). Neverthess, as early as 1973,

Toxaphene was detected as a residue in trout from Lake Michigan (Ribick,

et al., 1982). This year (1986) data have been obtained (Swackhamer and

Hites, unpublished) on carp from two Great Lakes sampling areas. Fish

from both Siskiwit Lake (a small, essentially undisturbed lake on Isle

Royale in Lake Superior) and Saginaw Bay (a heavily polluted site near

the Michigan shore of Lake Huron) contained roughly equal concentrations

of Toxaphene, on the order of 1 ppm on a whole-fish basis. These data

indicate no significant decrease in fish tissue Toxaphene concentrations

over the past 13 years.

Toxaphene has been used on crops in the Great Lakes Region since the

1960's. Its use has been mainly as a post-emergent corn insecticide, but

has also been used as an insecticide on hay, soybeans and small grains.

These uses have been quite small however, accounting for less than 1% of

Toxaphene used yearly (von Rumker et al., 1975).

Toxaphene concentrations in the Great Lakes have shown no sign of

declining, even though the levels of use in the southern states rapidly

decreased since the mid-70"s and it is now no longer used (Schmitt, et

al., 1983).

Toxaphene is produced commercially by the chlorination of camphene

(2), a monoterpene derived from the turpentine oleoresin of wood.

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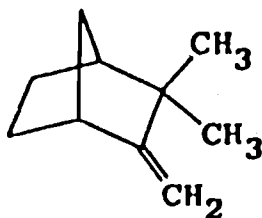
Terpenes have long been known to exhibit some insecticidal activity. It was then found their toxic activity could be enhanced by chlorination (Khanenia and Zhuraviev, 1964). The chlorination products of many terpenes have been studied including pinene, camphene, dipentene, fenchene, phellandrene, carene, thujone and others. Among these the chlorinated camphenes, Toxaphene, and the chlorinated α-pinenes, Strobane, are the best known and commercially significant. Strobane has been used primarily in the Soviet Union and European countries.

It is possible that environmental chlorination reactions, not involving the manufacture or application of Toxaphene at all, could be generating materials closely related to or indistinguishable from Toxpahene. The large scale bleaching of paper pulp is such a process. Terpenes related to camphene, such as α- and β-pinenes, are abundant in the softwoods used for papermaking. Although attempts are made to remove these terpenes (recovering them as turpentine) before the bleaching process, some always remain and may be chlorinated during bleaching.

The hypothesis that toxaphene-like compounds could be produced by chlorination of of wood pulp has been proposed independently by two other researchers. In one case pulp waste liquor was chlorinated under controlled laboratory tests, but only compounds with up to three chlorine atoms were detected. After increased concern in Finland over the detection of Toxaphene residues, another area with no history of Toxaphene usage, it was shown that the spent bleach liquor of a pine kraft pulp mill contained compounds similar to Toxaphene (Pyysalo and Antervo, 1985).

The two bleaching technologies most commonly used in paper

manufacture are the <u>sulfite</u> and <u>kraft</u> processes, with the kraft process being by far the most widely used. FIGURE 1 is a schematic of a kraft pulp mill. In a typical kraft pulp bleaching process, the unbleached wood meal is treated by a series of operations which typically include (in this order) strong acid chlorination, alkaline extraction, basic (hypochlorite) chlorination, and ClO_2 treatment. Acidic and alkaline extracts are not combined, but are sewered separately. Both the alkaline and the acidic extracts contain many toxic constituents. Diterpene resin acids, chlorinated guaiacols, chloroacetones, fatty acids, "chlorolignin," and other unknown factors have been identified by several groups (Thakore and Oehlschlager, 1977; Landner et al., 1977; McKague et al., 1981). Mills processing pine species, which are high in resinous constituents, tend to afford the most toxic kraft effluents. Among the compounds found in resins are mono- sesqui-, and diterpenes. Some of these substances have been found near a kraft mill waste outfall (Yamoka, 1979; Voss, 1984).

In pulp bleaching the acidic chlorination step is done at a pH of 1 and a reaction temperature of 15-30°C (Dence and Sarkanen, 1960). These conditions insure that a majority of the chlorine applied will be in the form of free molecular chlorine, Cl_2, rather than HOCl or ClO^-, as in other water treatment procedures. When chlorine is dissolved in water, the following equilibria rapidly develop:

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl \qquad pK_a = 3.4$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad pK_a = 7.5$$
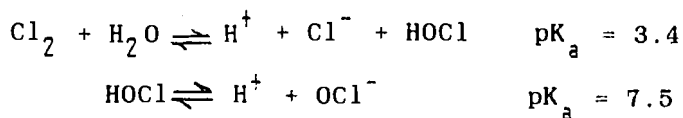
Molecular chlorine is also the form encountered in organic solvent-containing systems and has a different and greater reactivity toward many
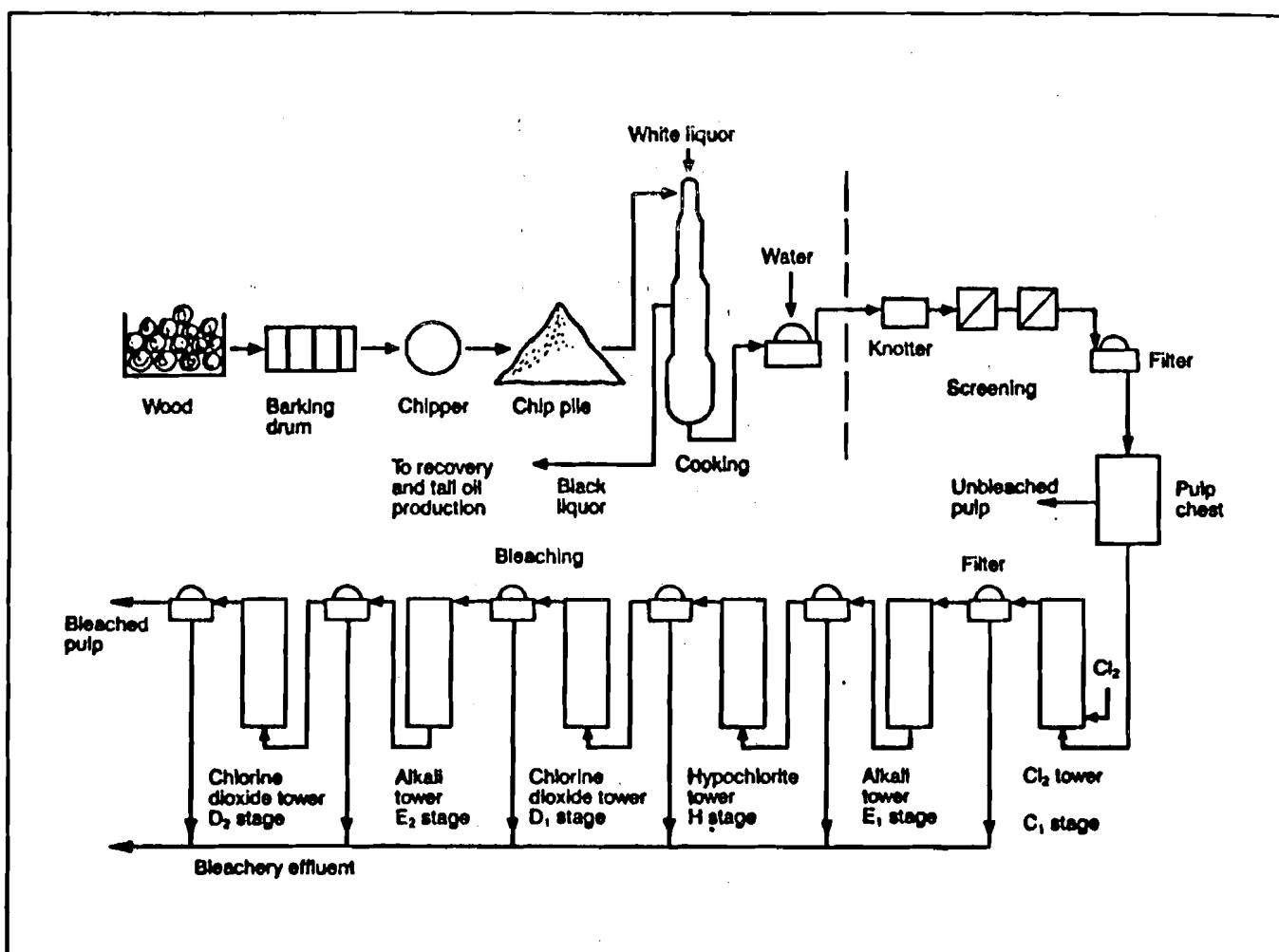
FIGURE 1 Kraft pulp mill, including a conventional bleach plant
(Rydholm, 1965)

classes of organic compounds than hypochlorites do.

Toxaphene is synthesized by bubbling chlorine gas (molecular Cl_2) into a mixture of monoterpenes and other organic liquids. It is not known whether Toxaphene would be similarly produced by reaction with chlorine in acidic, aqueous solution, although mechanistic considerations suggest that some Toxaphene-like compounds should be formed. There is extensive literature on the organic synthesis of chlorinated terpene derivatives in organic solvents (Jennings and Herschbach, 1963; Richet et al., 1965). Very little, however, has been published on their chlorination reactions in water, particularly under pulp bleaching conditions. Mono- and dichlorocamphenes were produced by chlorinating camphene with hypochlorous acid in aqueous acetone (Buchbauer et al., 1984). α-terpineol was chlorinated to a variety of mono- and dichloro compounds in water (Bjorseth et al., 1977)

The presence of Toxaphene in the environment in, or close to, the areas of use has been studied for a long time. During the 1970's it was routinely detected in water and sediment samples in the southern agricultural regions of the U.S. In some analyses, it was also detected in air samples (Stanley et al., 1971). Toxaphene was detected in air samples after the 1973-74 application season in the southeastern U.S. over the western North Atlantic ocean, thus establishing the long range transport of Toxaphene (Bidleman and Olney, 1975). Since the level of Toxaphene usage in the Great Lakes region has been relatively little compared to the southern United States, it has been suggested that the only means of explaining its occurrence in the Great Lakes is by atmospheric transport (Rice and Evans, 1984). However, this hypothesis

does not fully explain the patterns of distribution of Toxaphene and alternative suggestions should be examined (cf FIGURE 2).

Confirmation and quantification of Toxaphene residues in the environment has been a difficult task for analytical chemists. Due to its multi-component nature the detection limit for Toxaphene is in the range of 250-500 ppb, for DDT it is 5 ppb (Rice and Evans, 1984; Schneider et al., 1984). There are also interferences from other halogenated hydrocarbons such as PCB's, DDT and chlordanes. It has been estimated that in the early years of Toxaphene analysis, that these interferences could have led to a false positive detection of PCB's (Swain et al., 1982). In recent years methods have been developed which have increased the sensitivity and reliability of these analyses. These include fractionation (Kaiser et al., 1981), dual capilllary column confirmation (Schneider et al., 1984), negative ion chemical ionization (Ribick et al., 1982), SIMCA, a statistical analysis approach (Stalling et al., 1982), and Selected Ion Monitoring (Budde and Eichelberger, 1977).

It has also been shown that Toxaphene is dechlorinated under environmental conditions, such as photolysis or metabolic degradation (Saleh and Casida, 1978). Generally, the weathered or metabolized product shows the loss of the higher chlorinated compounds and an increase in the lower chlorinated compounds.

The objective of our research was to simulate pulp bleaching conditions in the laboratory and determine if Toxaphene-like materials could be produced.
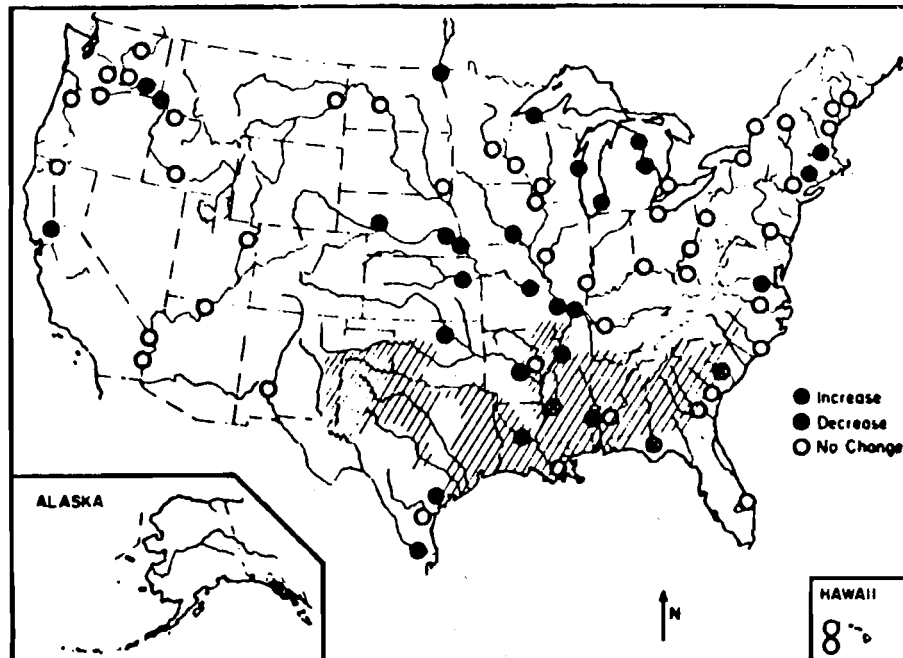
FIGURE 2 Location of monitoring stations for National
Pesticide Monitoring Program where changes in lipid-weight
residues of Toxaphene in fish are compared over time,
1974-1979 (Schmitt et al., 1983).

METHODS

Chemicals. Camphene, 95% grade, limonene, α-pinene and β-pinene
were obtained from Aldrich Chemical Company (Milwaukee, WI) and used
without further purification. Toxaphene was supplied from Supelco
(Bellefonte, PA).

Chlorination procedure. Terpenes were suspended in 1.0 N HCl
solution and equilibrated for 24 hours by shaking gently on a wrist-
action shaker. A 5.25% sodium hypochlorite solution ("Clorox") was then
added. The final pH of the solution was 1.8-2. In order to facilitate
analysis of the products, higher concentrations of terpenes than those
normally found in the pulp bleaching process were used, ranging from
0.007 $\underline{M}$ to 0.02 $\underline{M}$, with chlorine in a 10 molar excess. For chlorinations
at pH 8, a 0.1 $\underline{M}$ borate buffer was used with subsequent addition of the
NaOCl solution. After each reaction, sodium sulfite was added to consume
any remaining chlorine and stop the reaction. In each case blanks were
prepared, with no addition of chlorine.

The reaction mixtures were extracted with portions of methylene
chloride, dried over $MgSO_4$, and stored in a 0°C freezer. If necessary,
for improved detection on the GC-MS, a portion of the extract was reduced
in volume by gentle evaporation with N_2.

GC-MS Conditons. A Hewlett-Packard Model 5985A GC-MS instrument was
used. The GC was equipped with DB-1 (J&W Scientific) fused silica
capillary column (30 m x 0.32 mm id, 0.25 micron film thickness) which
was vented directly into the ion source of the mass spectrometer. Helium
was used as the carrier gas. Splitless, on-column injections were made;

sample size was typically 2.0 μl. The GC oven temperatures were programed from 40-240 °C or 150-240 °C at 3 °C/min (after a 5 min hold). Injection port, transfer lines and ion source were kept at 200 °C. Mass spectra were collected in the electron ionization mode operating at 70 eV. Data was collected either in the Total Ion (TI) or Selected Ion Monitoring (SIM) modes. For SIM the fragment ions at 159, 161, 195 and 197 are the most significant in the chlorinated hydrocarbons in the Toxaphene mixture and are not present in potentially interfering substances such as PCB's and other chlorinated hydrocarbons (Budde and Eichelberger, 1977).

Stock solutions of Toxaphene were prepared and analyzed by GC-MS by both TI and SIM. The resulting fingerprint chromatograms were then used as references for retention times and peak patterns. All 200 components of Toxaphene are not separable by capillary GC; approximately 70-80 sharp peaks can be resolved. This is an established method used in pesticide residue analysis for identifying Toxaphene (Saleh, 1983). Mass spectra were examined to attempt to determine molecular weight and number of chlorines, however exact assignment was limited to the lower chlorinated compounds, Cl_1's-Cl_4's; for the higher chlorinated molecules, assignments were based on the partial spectra available and comparison to the retention times of known Cl_6-Cl_{10} isomers of Toxaphene. In the EI mode the M^+ ion is seldom visible and the isotope ratios are not always reliable, especially for highly chlorinated compounds.

Ultraviolet light was generated by a 200 watt Canrad-Hanovia medium pressure quartz mercury vapor lamp (Ace Glass, Inc. Vinland, NJ). A water-cooled borosilicate immersion well was used to absorb IR and shortwave UV from the lamp. Dark samples were always wrapped in aluminum

foil. Sunlight was that of a typical summer day in Urbana IL (40° North latitude); intensity was measured with a UVX Radiometer (UVP, Inc. San Gabriel CA).

RESULTS

Initially, comparisons were made between chlorinations of camphene under light and dark conditions. In every case a large number of chlorinated products were observed. (cf. Table 1) The extent of chlorination seemed to be dependent on the length of the reaction and the light conditions to which the mixture was exposed. Under dark conditons, at short reaction times (30-60 min) mono- and dichlorocamphenes were observed. At longer reaction times (up to four hours) Cl_2-Cl_3 isomers predominated, and up to Cl_5 compounds were also present. When a mixture was left to react overnight (T=15 hr), the predominant products shifted to the Cl_4-Cl_5 isomers. In each case the camphene was rapidly consumed, only a small amount remained after the 30 minute reaction time and by 60 minutes it was no longer detectable. Thus as the reaction proceeded, the camphene was initially chlorinated, and then additional chlorinated compounds were formed, proceeding from the lower to the higher chlorinated isomers.

When exposed to a mercury arc lamp (to simulate sunlight exposure) up to Cl_6 compounds were formed with mostly Cl_3-Cl_4's present. After exposure to actual sunlight a highly complex mixture of chlorinated camphenes was observed: up to 78 different compounds were resolved on the GC column. Many of the chlorinated products had mass spectra typical of Toxaphene isomers. FIGURE 3 shows the GC-MS trace of the product mixture and a comparison to authentic Toxaphene. They are virtually identical.

The Cl_1-Cl_2 compounds in the "dark" reaction mixtures are relatively

Table 1. Chlorinated Products Produced at pH 2

Terpene	Light Conditions		Range*	Predominant
Camphene	dark	T = 30 min	$Cl_1 - Cl_2$	Cl_2
		= 60 min	$Cl_1 - Cl_2$	Cl_2
		= 4 hr	$Cl_1 - Cl_5$	$Cl_2 - Cl_3$
		= 15 hr	$Cl_3 - Cl_7$	$Cl_4 - Cl_5$
	Mercury arc	T = 4 hr	$Cl_2 - Cl_6$	$Cl_3 - Cl_4$
	Sunlight	T = 4 hr	$Cl_2 - Cl_{11}$	$Cl_6 - Cl_9$
	Sunlight T = 4 hr (UVA ≈ 1200 µW/cm^2) (UVB ≈ 570 µW/cm^2)		$Cl_2 - Cl_9$	$Cl_2 - Cl_5$
	Sunlight T = 4 hr (UVA ≈ 1900 µW/cm^2) (UVB ≈ 940 µW/cm^2)		$Cl_3 - Cl_9$	$Cl_4 - Cl_6$
β-pinene	dark	T = 15 hr	$Cl_2 - Cl_5$	Cl_3
	Sunlight T = 4 hr (UVA ≈ 200 µW/cm^2) (UVB ≈ 110 µW/cm^2)		$Cl_1 - Cl_9$	$Cl_3 - Cl_4$
	Sunlight T = 4 hr (UVA ≈ 1200 µW/cm^2) (UVB ≈ 570 µW/cm^2)		$Cl_4 - Cl_{11}$	$Cl_6 - Cl_9$
	Sunlight T = 4 hr (UVA ≈ 1900 µW/cm^2) (UVB ≈ 940 µW/cm^2)		$Cl_2 - Cl_9$	$Cl_4 - Cl_6$
α-pinene	dark	T = 15 hr	$Cl_2 - Cl_5$	Cl_2
	Sunlight T = 4 hr (UVA ≈ 1600 µW/cm^2) (UVB ≈ 610 µW/cm^2)		$Cl_2 - Cl_9$	$Cl_6 - Cl_9$
	Sunlight T = 4 hr (UVA ≈ 1900 µW/cm^2) (UVB ≈ 940 µW/cm^2)		$Cl_2 - Cl_9$	$Cl_4 - Cl_6$
Limonene	dark	T = 15 hr	$Cl_4 - Cl_9$	$Cl_5 - Cl_7$
	Sunlight T = 15 min (UVA ≈ 200 µW/cm^2) (UVB ≈ 110 µW/cm^2)		$Cl_2 - Cl_9$	$Cl_6 - Cl_9$
	Sunlight T = 4 hr (UVA ≈ 1200 µW/cm^2) (UVB ≈ 570 µW/cm^2)		$Cl_4 - Cl_9$	$Cl_6 - Cl_9$
	Sunlight T = 4 hr (UVA ≈ 1900 µW/cm^2) (UVB ≈ 940 µW/cm^2)		$Cl_4 - Cl_9$	$Cl_6 - Cl_9$

* For comparison, Toxaphene has a range of $Cl_2 - Cl_{11}$ isomers, predominantly in the $Cl_6 - Cl_9$ range (cf Figure 2).
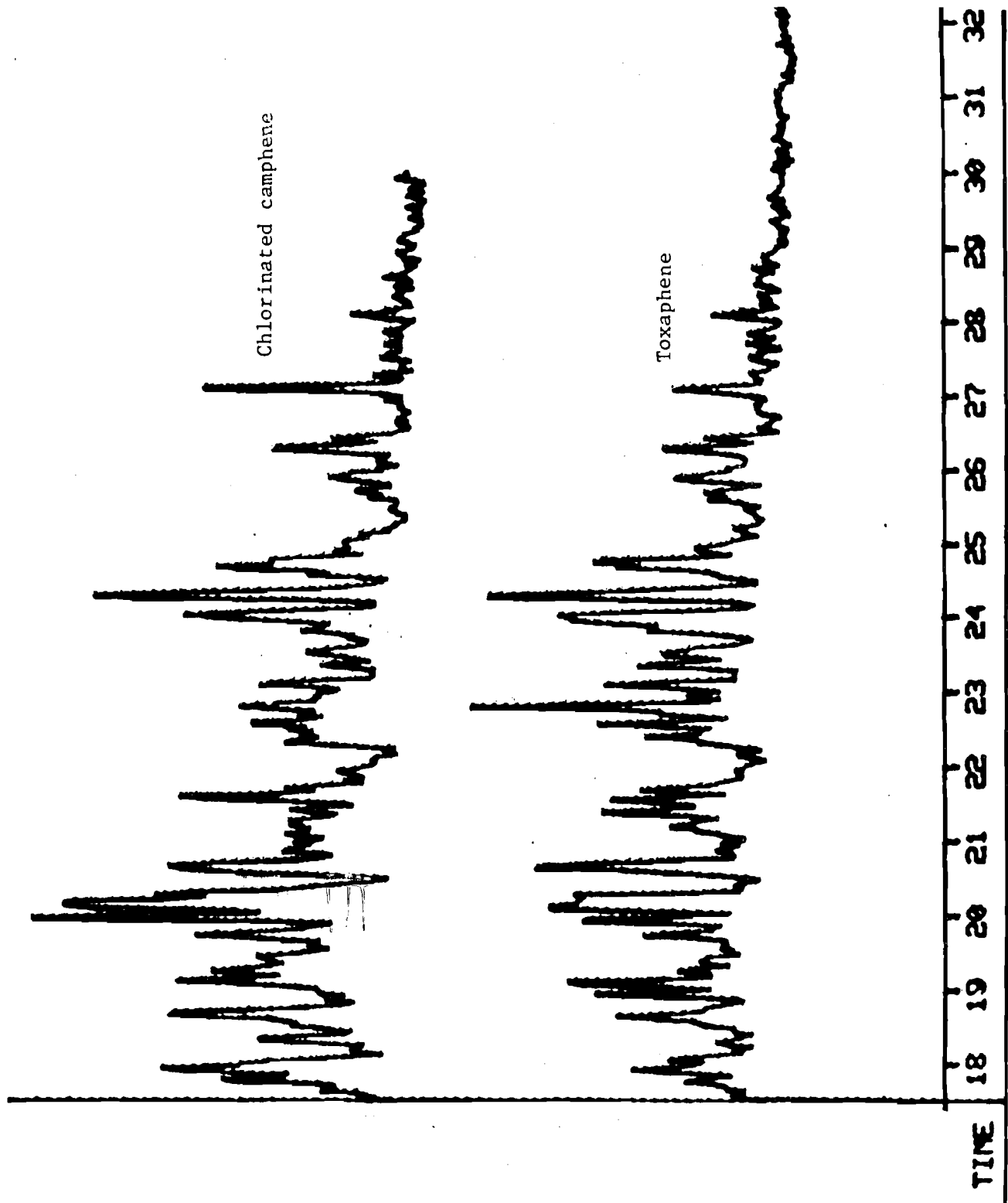
14

Figure 3   Comparison of chlorinated camphene mixture with authentic Toxaphene

easy to rationalize. Addition of chlorine would occur only at the double bond of camphene, resulting in a few mono- and dichloro compounds, and with possible rearrangement of the bornane structure (Buchbauer et al., 1984), perhaps a few more isomers could be formed. The highly chlorinated products can form only by a substitution reaction, chlorine atoms incorporated into the molecule in place of the hydrogen atoms. This reaction would proceed almost certainly via a free radical chain mechanism. Chlorine free radicals can be generated by thermal activation ($\geq$ 250 °C), exposure to UV light (300-500 nm) or by one-electron redox reactions (organic peroxides, metal ions, etc.). For the reactions exposed to the mercury arc lamp or to sunlight, the free radical present would be Cl· Chlorine absorbs in the UV region with a maximum absorption at 330 nm resulting in homolytic Cl-Cl bond cleavage and formation of Cl· radicals from the excited state. It is not clear how the Cl_3-Cl_6 isomers were produced in the dark. A radical chain initiaton mechanism involving conversion of organochlorine isomers to free radicals, or a surface reaction involving metal ion catalysis in which free radicals are generated, are two alternatives. These possibilities require further investigation.

In other experiments, monoterpenes which could also be present in wood pulp bleaching processes also became chlorinated. Table 1 presents a summary of these studies. Each of the terpenes did react to give polychlorinated mixtures in much the same way as camphene. FIGURE 4 shows a comparison of the product mixtures resulting when these terpenes were exposed to bright sunlight.
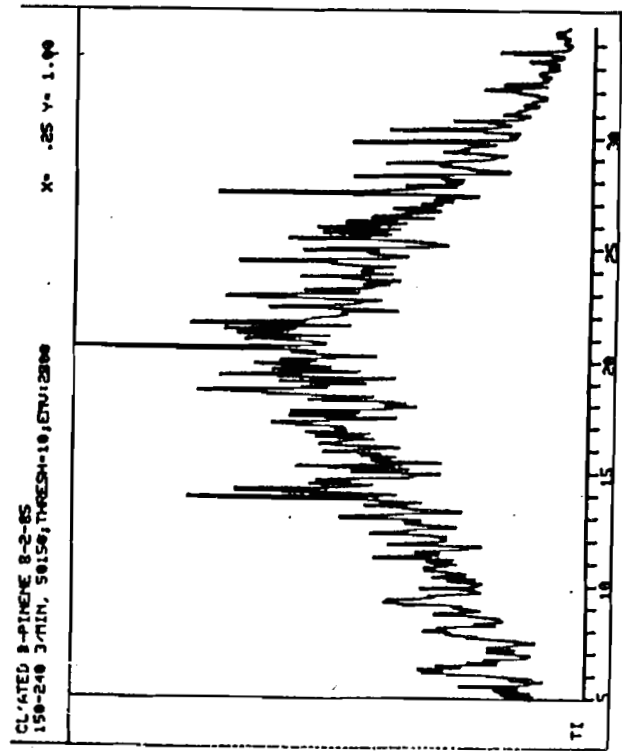
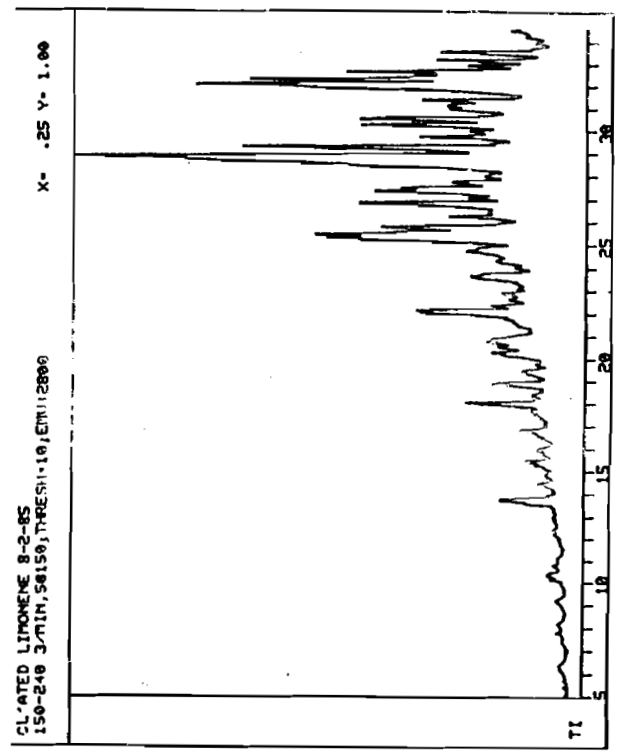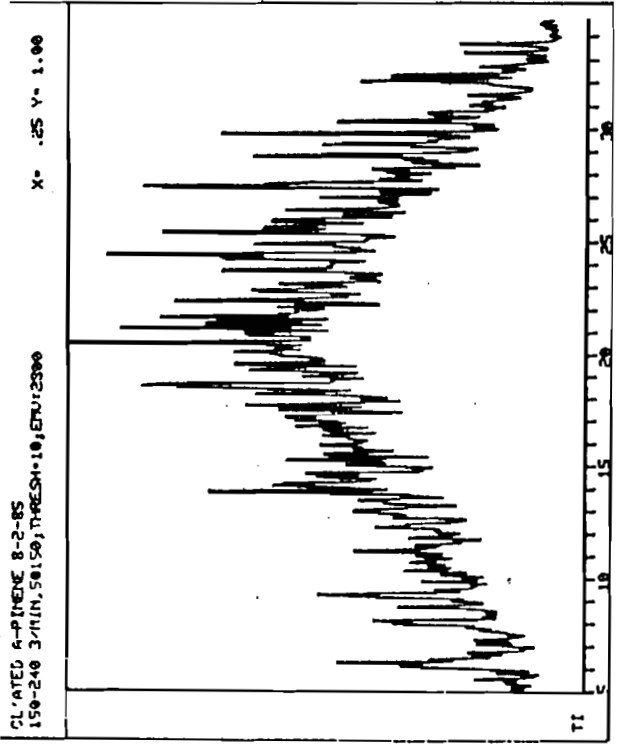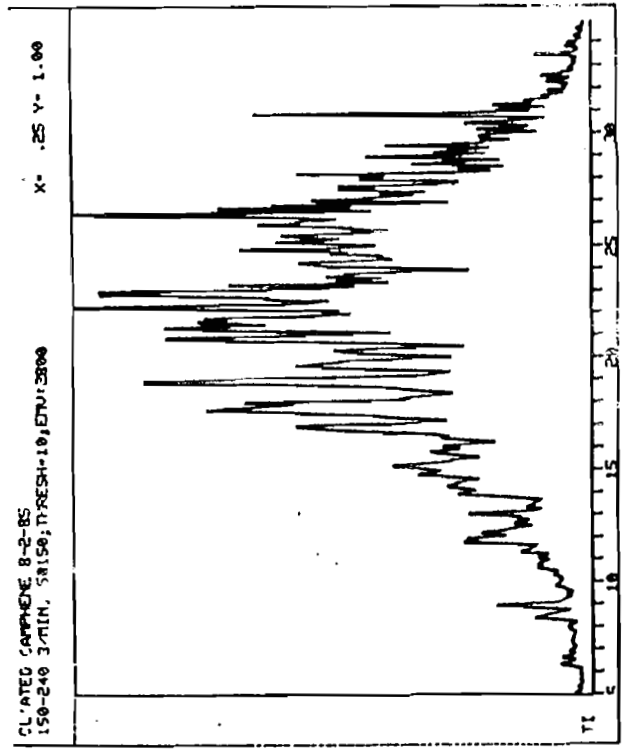In the initial experiment that produced an exact match for

FIGURE 4. TI chromatograms of product mixtures from the chlorination of terpenes while exposed to bright sunlight (UVA $\cong$ 1900 $\mu W/cm^2$; UVB $\cong$ 940 $\mu W/cm^2$

Toxaphene-like compounds, the sunlight intensity was not measured. Later experiments were done to assess the degree of chlorination and sunlight intensity. On a cloudy day, when sunlight intensity was low, the lower range of chlorinated compounds were formed. When sunlight intensity was higher, as on a cloudless day, the reactions produced mixtures with a higher degree of chlorination. However, the data are scattered and there seems to be no direct relationship between the sunlight dose and chlorinated products. A day with much greater intensity, no clouds, produced compounds that were in the middle range of chlorination (Cl_4-Cl_6); a day that was partly cloudy produced compounds in the Cl_6-Cl_9 range, the "Toxaphene" range. The measurement of sunlight intensity with the UVX radiometer was only a point measurement and not integrated over the period of exposure; therefore, it is only a rough approximation of the sunlight dose. A chemical actinometer (Dulin and Mill, 1982) is the preferred method but was not available at the time of these experiments. It is interesting to note that even in a chlorinated camphene mixture that was not an exact match for Toxaphene, Toxicant A was formed (cf. FIGURE 5). Toxicant A has been isolated and identified as a mixture of two octachlorbornanes, each contributing a significant portion to the toxic and mutagenic activity of Toxaphene (Turner at al., 1975).

Limonene showed the greatest reactivity, consistently producing highly chlorinated material. This is probably due to the second double bond in its chemical structure.

Chlorinations were also done at pH 8. At this pH, chlorine is in the form of OCl^-, which would more likely be encountered in water treatment systems. For each terpene chlorinated small amounts of mono- and

dichloro compounds were produced. The major products were possibly ring-opened oxygenated products. The product mixtures were basically the same under both light and dark conditions.
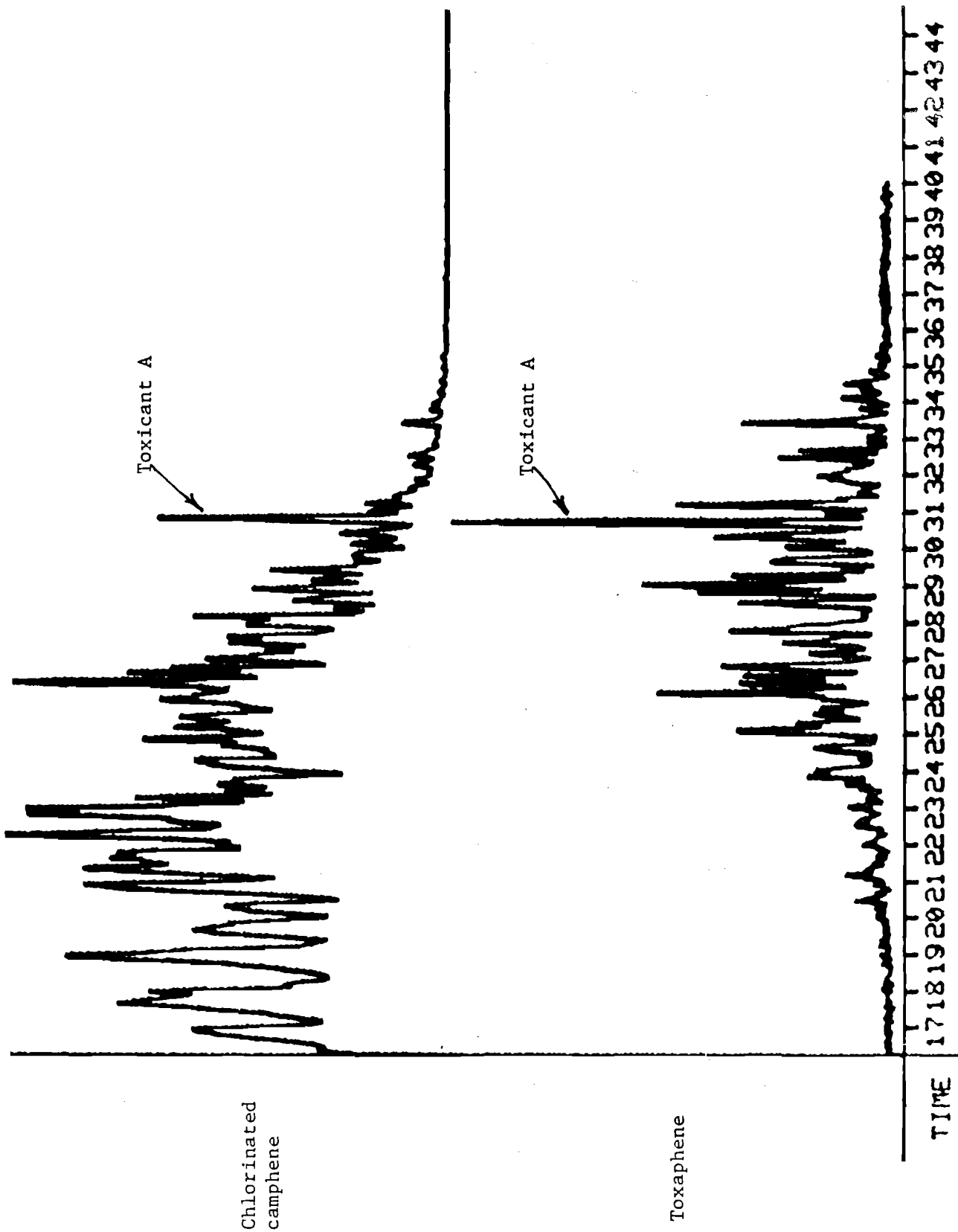
FIGURE 5 Toxicant A in 1) Toxaphene; 2) chlorinated camphene mixture

CONCLUSIONS

Complex chlorinated terpenes (similar to Toxaphene) can be produced in an aqueous system when chlorine is in the form of Cl_2, conditions similar to the acid chlorination stage of pulp bleaching. In addition, less heavily chlorinated compounds, which may possibly be mistaken for biologically degraded Toxaphene constituents or other chlorinated compounds, are produced.

The production of the highly chlorinated material proceeds by a free radical mechanism. To generate the free radicals an initiator must be present. In the case of the sunlight reactions, the initiator was ultraviolet light. Pulp bleaching is carried out in a closed system, with no sunlight present. There are indications that the hemicelluloses that are present in the pulp bleaching process react with chlorine in its free radical form (Kringstad and Lindstrom, 1984). It is not known for certain what initiators may be present, again surface reactions may be possible. Even if the chlorination of terpenes were not high yield processes, the large volume of material involved may mean that large absolute quantities of Toxaphene-like material could be produced. Production of bleached chemical pulp is about 50 million tonnes/year. The discharge of organically bound chlorine has been estimated at 5 kg/tonne of pulp for an approximate total of 250,000 tonnes per year (Kringstad and Lindstrom, 1984). Of this amount, only a very small fraction (~1%) has been characterized with respect to specific chlorinated compounds (Voss et al., 1981).

The relative importance of atmospheric transport of Toxaphene over

great distances (the prevailing theory) versus more localized production and transport of Toxaphene-like material (the hypthesis outlined in this report) remains to be assessed and will require further research.

RECOMMENDATIONS

1) Studies on the kinetics of terpene photochlorination in homogeneous solution and in the presence of surfaces such as clay minerals and metal oxides.

2) Field sampling of paper mill wastes, effluents and downstream sediments; comparison with existing data.

3) Studies of the effects of light on chlorination of other wood pulp constituents such as phenolic compounds.

PRESENTATIONS

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