Toxicity Reduction Evaluation Case Summary for the Pulp and Paper Industry

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This report reviews the causes of toxicity in discharges from the Pulp and Paper Industry and the actions taken to reduce this toxicity. Case studies from the USA and Canada where toxicity controls have been in place for 10 to 15 years were utilised as sources for this review. It was intended that this information would assist both the regulator and industry in toxicity identification and reduction programmes here in the UK resulting from the current toxicity-based licencing initiative.

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1. SUMMARY

Information on several toxicity reduction evaluation (TRE) studies conducted in the U.S. and Canada is provided to assist the pulp and paper industry in addressing new toxicity criteria for use in consenting to be considered soon by the Environment Agency. These studies focused on causes of toxicity that may be common to paper mill discharges: use of toxic additives in paper manufacturing (e.g. biocides), residual wood derivatives released from repulping (e.g. resin acids), toxic wastewater treatment chemicals (e.g. polymers), and incomplete treatment of mill wastewaters. The role of the chemical additives in pulp and paper effluents can be readily determined through bench-scale testing using the U.S. Environmental Protection Agency's (USEPA) toxicity identification evaluation (TIE) procedures. Other causes of toxicity such as organic compounds (either formed in the bleaching process or released in repulping) may be reduced through improvements in water management and biological treatment. Additional TRE examples are noted based on experience at similar U.S. industries.

2. INTRODUCTION

2.1 Background

The environmental regulators is developing a toxicity-based consent (TBC) programme to identify and control the discharge of toxicity to waters of the U.K. The purpose is to address toxic effects caused by complex effluents that are not readily explained by data on specific chemicals or by the interaction of effluent constituents in receiving waters. Direct toxicity assessment (DTA) using aquatic organisms in standardised tests will be applied to evaluate the net toxic effect of the various effluent constituents.

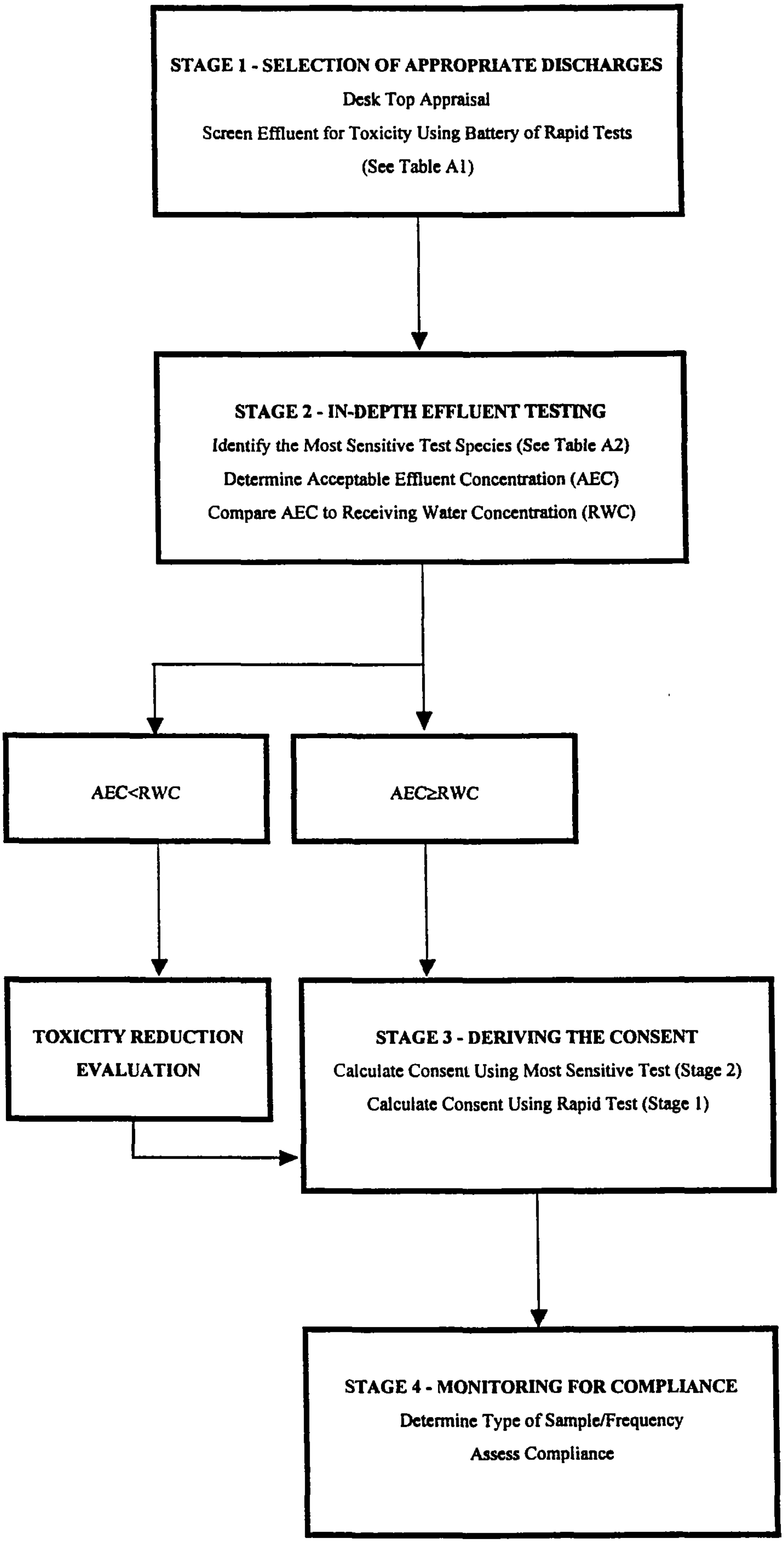
A protocol for deriving consents containing toxicity criteria is being evaluated. These studies will evaluate the available toxicity testing procedures (including low cost, rapid tests) and assess approaches for deriving TBCs that protect water quality. Comparisons of the test procedures will be made to determine the most appropriate tests to apply to particular types of effluents (e.g. metal fabricating, pulp and paper, municipal) and receiving waters (freshwater versus marine). The magnitude and frequency of effluent toxicity and the available dilution and mixing conditions, will be used to determine consents containing toxicity criteria.

The regulators draft protocol for TBCs is illustrated in Figure 1. Toxicity tests currently proposed for effluent monitoring by the regulators are shown in Appendix A.

2.2 Case Summary Information

Preliminary results of the NRA studies indicate a potential for toxicity in effluents from pulp and paper mills. This report provides information that can be used by the pulp and paper industry to identify and control the discharge of toxicity. Information on toxicity reduction studies performed in the U.S. and Canada over the last five years has been summarised with emphasis on the methods used, types of toxicants identified, and control measures successfully implemented. This report is intended to be a general guide on

Figure 1. The Environmental Regulators' Protocol For Deriving And Monitoring Compliance With Toxicity-Based Consents



approaches that may apply to pulp and paper mills. Each facility has unique manufacturing processes, effluent constituents, and receiving water conditions, which will influence the selection and use of TRE methods. Therefore, facility managers should develop a facility specific plan, preferably in consultation with an experienced team of toxicologists, engineers, and chemists.

2.3 TRE Process

Since the early 1980s, toxicity monitoring has been applied to effluents of nearly all industry types in the U.S., including the pulp and paper industry. Companies with permits issued under the National Pollutant Discharge Elimination System (NPDES) are required to perform a TRE if their effluents are suspected of causing unacceptable instream toxicity. Several guidance documents have been prepared by the U.S. EPA to assist dischargers in conducting TRE studies (USEPA, 1993a, 1993b, 1992, 1991, 1989a and 1989b). These documents describe why it is necessary to use a toxicity-based approach that relies on toxicity tests (instead of chemical measurements) to identify the cause(s) and source(s) of effluent toxicity. This approach will ensure that corrective measures will achieve compliance with the toxicity-based limit.

A generalised schematic of the TRE process is presented in Figure 2. Major steps in the TRE process are summarised below.

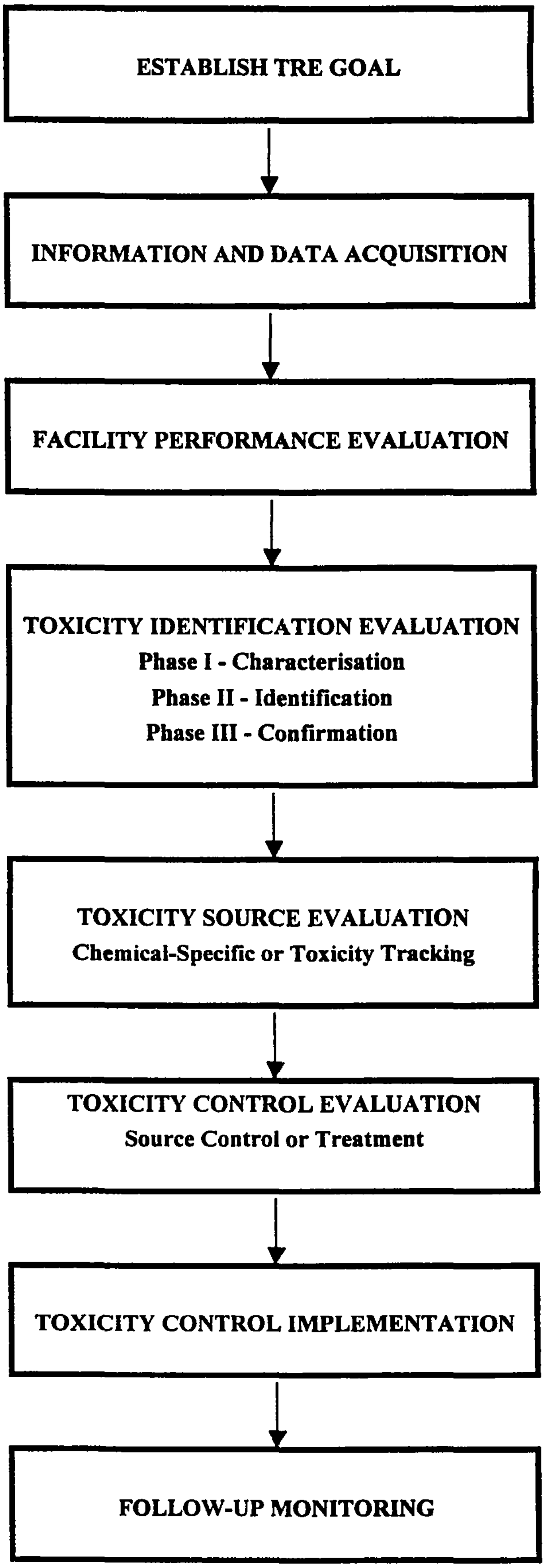
Establish the TRE Goal - so that the effluent compliance level and the duration of the TRE are understood. The goal and schedule of the TRE should be reviewd and agreed upon with the regulatory authority before testing is initiated.

Information and Data Acquisition - regarding facility activities and effluent monitoring is need to prepare a plan of study. This information should include data on chemical use management, waste generating activities, and wastewater treatment operations and performance. TREs are an iterative process; therefore, the plan will change depending on the outcome of each step of the study.

Facility Performance Evaluation - involves a review of the manufacturing processes and wastewater treatment system to identify problem areas that may be contributing to effluent toxicity. This evaluation usually does not establish a "cause and effect" relationship between a suspect toxicant and effluent toxicity; therefore, simple, low cost corrective measures (e.g., waste minimisation, chemical use optimisation, and improved operational strategies) that have the potential to reduce toxicity are generally recommended. This step is most effective in cases where facility deficiencies or concentrations of known toxicants appear to be related to effluent toxicity.

Toxicity Identification Evaluation - is generally performed in three phases: toxicity characterisation (Phase I), toxicant identification (Phase II), and toxicant confirmation (Phase III). Phase I characterises the types of effluent toxicants by testing the toxicity of aliquots of effluent sample that have undergone bench-top treatments (USEPA, 1992 and 1991). Treatment steps include pH adjustment, filtration, aeration, oxidant reduction, chelation of metals, and removal of non-polar organic compounds by a C_{18} solid phase extraction (SPE) column. Removal of toxicity by one or more of these steps provides

Figure 2. Generalised Flow Chart For Toxicity Reduction Evaluation



information on the class of the toxicants (e.g., ammonia, chlorine, metals, non-polar organic compounds, etc.). Phases II and III involve further treatments in conjunction with chemical analyses to identify and confirm the compound(s) causing effluent toxicity (USEPA, 1993a and 1993b). It is not always necessary to identify the actual toxicant(s) if toxicity can be effectively removed through source control or other means.

Source Identification - involves sampling and analysis of samples of individual waste lines to locate the source(s) of toxicity. Chemical tracking is recommended when the toxicants have been identified and confirmed in the TIE. However, toxicity tracking may be needed if the TIE results are inconclusive. In this latter approach, samples are first collected from the main sewer lines and results of toxicity tests are used to identify toxic tributary waste streams and, ultimately, the specific sources of toxicity. Samples must be subjected to the same treatment as is practiced in the facility's treatment process to provide an accurate measure of the toxicity that passes through in the final effluent.

Toxicity Control Evaluation - selects the most appropriate control method based on a thorough review of the technical and cost considerations of the available alternatives. The selected control method(s) is implemented and follow-up monitoring is conducted to ensure that it reduces effluent toxicity to compliance levels. Many TREs in the U.S. have identified relatively low cost operational or chemical use changes, rather than large-scale treatment plant modifications or additions, as the preferred toxicity control methods.

3. INDUSTRY DESCRIPTION

Little virgin pulp is produced in the U.K.; the main fibrous raw materials used by mills are imported pulp and wastepaper. Pulp comes mainly from North America, Scandinavia, Spain/Portugal and Brazil. The majority is bleached chemical pulp (mainly kraft), but includes some mechanical pulp (e.g. from Canada for newsprint mill). These pulps may contain chemicals not otherwise used at the mill (e.g. chlorinated organic compounds from chlorine bleached pulps).

Mechanical pulps are produced in the U.K. at three mills, which are integrated with paper/board manufacture and one also has a deinking plant. There are no stone ground wood or chemithermomechanical pulping (CTMP) processes currently in the U.K.

One chemical wood pulp mill uses the neutral sulphite semi-chemical (NSSC) process to produce a pulp (25 000 t.p.a.) for corrugating medium. There are also five small mills (<25 000 t.p.a.) carrying out chemical pulping of non-wood fibres such as hemp and cotton. Three of these mills use a sulphite process and one uses hydrogen peroxide. There are no mills using the kraft process in the U.K.

Wastepaper is used after deinking to make newsprint, and printing/writing papers. The majority of wastepaper is used without deinking to make packaging grades such as fluting. All but two of the deinking plants are integrated with paper production.

Most U.K. mills are not integrated (involving the whole cycle from pulping, or deinking, through to paper-making) as there are neither deinking nor pulping plants. Instead virgin pulp or wastepaper is used to make paper and/or board. Coating processes are also performed, commonly using an aqueous coating with a mixture of pigment and binder.

Coating machines are either integrated on-line or operated off-line.

3.1 Chemicals Used

Chemicals used in U.K. mills include retention/drainage aids, deposit control chemicals, preservatives, foam control agents, sizing agents, dry strength material, wet strength chemicals, colours and brighteners. A list of commonly used chemicals is shown in Appendix A (Table A-3).

The degree to which a material may contribute to mill effluent toxicity depends on its toxicity, the amount used, recovery and reuse practices in the manufacturing area, interaction with other waste constituents, and its removal in the wastewater treatment system. These factors make it difficult to identify particular chemicals of concern from the list in Table A-3. Nonetheless, three types of chemicals used at mills have been identified as effluent toxicants in other TRE studies: biocides (USEPA, 1988), surfactants (Diehl and Moore, 1987 and Botts *et al.*, 1994), and polymers (Hall and Mirenda, 1991). A thorough review of the TRE case study literature indicates biocides and polymers to be causes of toxicity in pulp and paper mill effluents; surfactants were not found to be a problem. The TRE examples presented below discuss the contribution of biocides and polymers to toxicity in pulp and paper mill effluents.

3.2 Wastewater Treatment

Approximately 40 percent of U.K. mills discharge to central treatment facilities. The remainder discharge directly to freshwaters (34%) and tidal waters (26%) where TBCs may be applied. The reader is advised to consult Tables A-1 and A-2 in Appendix A regarding the test species proposed for monitoring discharges to these waters.

Of the mills discharging to surface waters, about half have primary treatment only and the remainder have both primary and secondary (biological) treatment. As noted below in the TRE case studies, biological treatment can achieve significant toxicity reduction, especially for pulp mill effluents.

4. TRE CASE STUDIES

Information on eight TRE studies is included in this summary. Key elements of each study are discussed, including the methods for toxicant identification, sources of toxicity, and approaches for controlling effluent toxicity. The following literature review also provides background information on the toxicity of pulp and paper mill effluents.

4.1 Literature Review

Most toxicological studies of the pulp and paper industry have focused on the effluents from pulping and bleaching processes (McLeay *et al.*, 1987; Owens, 1991 and Colodey and Wells 1992). Delignification of the wood fibres in the pulping process releases significant quantities of organic materials, including resin and fatty acids, which are highly toxic to aquatic life (McLeay *et al.*, 1987). Brighting of the pulp in the bleaching process can lead to the formation of even more toxic chlorinated organic compounds such as chlorinated resin acids and chlorinated phenolics (Owens, 1991). However, as noted above, only nine mills in the U.K. are involved in pulp production. Most U.K. mills process imported, bleached pulps or wastepaper to make newsprint and specialty papers. This summary will focus, therefore, on the paper production side of the industry. Some background on the toxicity of unbleached/ bleached pulp mill effluents is also provided to address potential concerns at the few U.K. pulp mills and to describe the nature of residual toxicants that may be present in pulps used for paper/board production.

4.1.1 Toxicity of Unbleached and Bleached Pulp Mill Effluents

Spent cooking liquor (black liquor) is generated during washing of the pulp and contains wood extractives, lignin, and carbohydrates. In recent years, waste loads from pulping operations have been minimised through a variety of in-plant controls including conversion from wet debarking to dry debarking, extended cooking, oxygen delignification, black liquor spill control in the cooking and recovery areas, improved recovery of turpentine and tall oil, and condensate recovery (Confidential Report, Shimp and Owens, 1993). Also, the black liquors are usually concentrated in evaporators and incinerated in furnaces to recover pulping chemicals and produce energy. As a result, the discharge of process wastewater is minimised.

The acute toxicity of untreated chemical or mechanical pulp mill effluents is mostly due to volatile materials such as methylated sulphur compounds and non-volatile, organic constituents such as resin acids and neutral diterpenes (Leach *et al.*, 1978). A summary of toxic organic compounds by pulp mill type is shown in Table 1.

Resin acids have been found to be a primary cause of untreated effluent toxicity in virtually all types of pulp mills. Like many researchers, Lo *et al.*, (1994) observed a significant correlation between resin acids and effluent toxicity at two integrated newsprint mills ($r^2 = 0.99$ and 0.98). Diterpene alcohols and juvabiones also contribute moderate toxicity in untreated mechanical and sulphite pulp mill effluents, respectively. Unsaturated fatty acids generally do not contribute significant toxicity. Each of these toxicants can be removed by effective conventional biological treatment (Leach *et al.*, 1978).

Table 1. Organic compounds toxic to fish in pulp mill effluents.

Type of Chemical Compound	Relative Toxicity Contribution		
	Major	Intermediate	Minor
Resin Acids: Abietic, dehydroabietic, isopimaric, palustric, pimaric, sandaraco-pimaric, neoabietic	KP D M S		
Unsaturated fatty acids: Oleic, linoleic, linolenic, palmitoleic		KP	S D M
Diterpene alcohols: Pimarol, isopimarol, abienol, 12E-abienol, 13-epimanoöl		M	D D
Juvabiones: Juvabione, juvabiol, todomatuic acid, 3 -deoxy-3 -hydroxytodomatuic acid, 1' -dehydrojuvabione 1' -dehydrojuvabiol		S	M
Lignin degradation products: Eugenol, isoeugenol, 3,3 -dimethoxy-4,4 -dihydroxystilbene			S
Chlorinated resin acids: Monochloro- and dichloro-dehydroabietic		KC	
Unsaturated fatty acid derivatives: Epoxystearic, dichlorostearic		KC	
Chlorinated phenolics: Trichloro- and tetrachloro-guaiacol		KC	
Miscellaneous: Non-ionic pitch dispersants			KC

K = kraft   P = pulping   C = caustic extraction
S = sulphite pulping   D = debarking   M = mechanical pulping
Source: Leach *et al.*, 1978

The fibres from pulping are further treated to remove or decolourise residual lignin in the bleaching process. Residual lignin in bleached pulp is measured as "kappa number". The lower the kappa number, the more refined and brighter the pulp, and, correspondingly, the greater the wasteload of extracted organic substances (Owens, 1991). In the bleaching process, chemicals such as elemental chlorine, chlorine dioxide, and hypochlorite are used to solubilise the lignin, and sodium hydroxide is used to extract the lignin. The resulting bleaching liquor can not be recycled through the recovery boiler, like the black liquors, because it is corrosive. Consequently, bleaching wastes can represent a major loading in mill effluents.

Chlorine bleaching causes the formation of numerous toxic chlorinated organic compounds, such as chlorinated resin acids (mono and dichlorodehydroabietic acid) and chlorinated phenolics (chloroguaiacols, chlorocatechols, and chlorophenols). The toxicity of chlorophenolics increases with the number of chlorine atoms bound to the phenolic molecules (Salkinoja-Salonen *et al.*, 1981, Voss *et al.*, 1980, Shigeoka *et al.*, 1988). Adsorbable organic halogens (AOX), a measure of the sum of chlorinated organic compounds, averages about 4 to 5 kg per tonne of pulp in untreated effluents of mills using primarily elemental chlorine for bleaching (O'Connor *et al.*, 1993). This concentration can be reduced to 1 to 2 kg/tonne by biological treatment and <1 kg/tonne through the use of other bleaching chemicals (with treatment).

Although chlorinated organic compounds often cause toxicity in mill effluents, AOX is not a good indicator of toxicity (O'Connor *et al.*, 1993). Some investigators have found a significant correlation between the low molecular weight fraction of AOX and toxicity in mill effluents (Firth and Backman 1990); however, AOX consists largely (80%) of high molecular weight material (Colodey and Wells 1992), which is thought to be too large to pass through organism membranes.

In response to the need to reduce the discharge of chlorinated organic compounds, including dioxin and furans, the industry has substituted new bleaching chemicals (including chlorine dioxide, hydrogen peroxide, and ozone) for elemental chlorine. Chlorine dioxide substitution reduces total AOX levels, and shifts the character of AOX from highly chlorine substituted species to those with only one to two chlorines (Shimp and Owens, 1993). O'Connor *et al.*, (1994) observed a greater than 90 percent decrease in effluent AOX and chlorinated phenolics in going from conventional bleaching to chlorine dioxide addition with oxygen delignification. Effluent toxicity also decreases with increasing chlorine dioxide substitution and addition of oxygen delignification (Graves *et al.*, 1993 and O'Connor *et al.*, 1994).

Some mills have adopted totally chlorine free (TCF) bleaching processes, which have further reduced effluent AOX levels. However, effluent toxicity from TCF processes is not necessarily decreased compared to elemental chlorine free (ECF) effluents. In laboratory bleaching experiments, O'Connor *et al.*, (1994) found TCF effluents to be more chronically toxic to *Ceriodaphnia* than ECF effluents. Chlorine dioxide addition in combination with oxygen delignification was the least toxic bleaching sequence to both *Ceriodaphnia* and fathead minnows. In contrast, Kovacs *et al.*, (1995) observed lower chronic toxicity to fathead minnow, *Ceriodaphnia*, and *Selenastrum* when a mill changed from ECF bleaching to a TCF process. Only the sea urchin was more sensitive to the TCF mill effluent. This inconsistency has been observed in other studies, leading some to speculate that natural wood components, rather than compounds created by bleaching, may be responsible for effluent toxicity (Kovacs *et al.*, 1995).

Another benefit of TCF processes is an overall reduction in wastes discharged. Some TCF bleaching effluents can be combined with weak black liquors and sent to a recovery boiler. Waste loadings have also been decreased through improved washing, mixing, and process control. As a result, bleach liquor volumes have been reduced from 30 000 gallons per ton of bleached pulp to 3 000 to 10 000 gallons per ton (Confidential Report).

Biological treatment can substantially reduce the toxicity of pulp and paper mill effluents (see reviews by McLeay *et al.*, 1987 and Colodey *et al.*, 1992). O'Connor *et al.*, (1994) found 10 times less chronic toxicity to *Ceriodaphnia* and fathead minnows after secondary treatment. Effluent toxicity at Canadian mills was also consistent with the level of treatment; lower toxicity was observed at mills with biological treatment (Robinson *et al.*, 1994). Effluent toxicity at bleached and unbleached pulp mills is primarily due to resin and fatty acids, which are largely removed by biological treatment (McLeay *et al.*, 1987). Lo *et al.*, (1994) achieved substantial toxicity removal by treating integrated mill effluents (bleaching and paper production) at hydraulic residence times (HRTs) as low as 8 hours. In general, treatment of resin acids and unsaturated fatty acids to less than 1 mg/l should not cause acute toxicity to trout (Leach *et al.*, 1978). Nonetheless, investigators are finding that bleach plant effluents at integrated mills may not necessarily be the cause of total mill effluent toxicity (O'Connor *et al.*, 1994).

Inconsistent treatment of mill waste streams, especially concentrated pulping effluents, can cause effluent toxicity. Treatment deficiencies may be related to sludge bulking, unstable mixed liquor suspended solids (MLSS), short sludge age, and low HRT (Lo *et al.*, 1994). Suboptimal operation of biological treatment systems, including concentrated black liquor spills, nutrient deficiencies, and short-circuiting in treatment, may also allow the pass-through of toxic materials (Leach *et al.*, 1978).

4.2 TRE Case Examples

Key elements of the TRE studies summarised herein are presented in Table 2. A description of each study is given below.

Table 2. Key elements of the summarised TRE case studies.

Mill	Goal (Permit Limit)	Toxicants Identified	Sources Identified	Control Method
E B Eddy - Ottawa Hull Div.	96h $LC_{50} \geq 100\%$ Rainbow trout	Biocide	Paper machine	Product substitution
E B Eddy - Port Huron	48h $LC_{50} \geq 100\%$ *Daphnia magna*	Biocide	Paper machine	Reduced product use; Optimised treatment
Procter & Gamble Green Bay	$IC_{25} \geq 2.9\%$ *Ceriodaphnia*	Resin acids from repulping	Paper machine	Diverted whitewater to municipal plant
Northeast US	NOEC≥6.2% *Ceriodaphnia*	Polyacrylamide polymer	Treatment plant	Substituted product; Reduced product use

Mill	Goal (Permit Limit)	Toxicants Identified	Sources Identified	Control Method
Simpson Paper	$TU_c \leq 46$ echinoderms	Not identified	Not identified	Activated sludge treatment
Appleton Papers, Inc., Locks Mill	NOEC=100% *Ceriodaphnia*	Filterable material	Not identified	Optimised treatment with constant MCRT
Canadian Kraft	96h $LC_{50} \geq 100\%$ Rainbow trout; 48h $LC_{50} \geq 100\%$ *Daphnia magna*	Ammonia and unidentified toxicant(s)	Nutrient feed to biological treatment	Eliminated ammonia addition to treatment system
Eastern Canada	$LC_{50} \geq 100\%$ Rainbow trout *Daphnia magna*	Resin acids from repulping	Whitewater in manufac-turing process	Improved water management through whitewater recycling

4.2.1 E B Eddy Hull Paper Mill

This case study provides an example of a TRE that focused on the identification and control of toxicity within the paper production process (Fein *et al.*, 1994). E B Eddy's mill located in Hull, Quebec (Ottawa Hull Division) is an alkaline mill that operates a single paper machine. Prior to the TRE, E B Eddy evaluated the use of a high-rate biofilter (ActiContact Process) to meet new discharge limits for BOD, TSS, and acute toxicity that were to go into effect in 1995. Site-specific constraints prevented the consideration of other treatment approaches such as conventional activated sludge or tertiary treatment options. The biofilter did not consistently remove acute toxicity; therefore, E B Eddy decided to initiate a TRE to better identify and control the sources of the toxicity rather than evaluate other "end-of-pipe" control options. Prior to implementing the study, E B Eddy performed a series of tests to select an inexpensive, surrogate procedure that compared well with the acute toxicity tests required for discharge monitoring (i.e. 48-hour *Daphnia magna* test for the Port Huron mill and 96-hour rainbow trout test for the Hull mill). The Microtox™ 15 minute procedure was chosen based on a good correlation between test results and results of permit specified tests.

4.2.1.1 Preliminary Toxicity Evaluation

As shown in Table 3, E B Eddy initiated the TRE by evaluating effluent toxicity variability and by performing toxicity tests on individual waste streams from the paper machine. Results showed the mill effluent toxicity to be somewhat consistent (i.e. Microtox™ EC_{50} values ranged from 5 to 30 percent effluent). All process-related streams were toxic, especially the whitewater chest and silo, quaternary cleaner rejects, clarified whitewater, and paper machine final effluent. The data showed intermittent slugs of toxicity from several paper machine processes.

Table 3. Toxicity results for waste streams from #14 paper machine - E B Eddy Hull Mill

Process Stream	**Microtox™ EC_{50} (Percent Sample)**			
	July 9/91	**July 10/91**	**July 16/91**	**July 24/91**
Electric Room & Compressor Cooling Water	>100	>100	--	--
Rewinder Cooling Water	>100	>100	--	--
Vacuum Pump Sealing Water	>100	>100	--	--
Hot Water Tank Overflow	>100	>100	--	--
Starch Run Tanks & Starch Converters (Drains)	74.6	6.1	61.8	3.7
Size Press Floor Drain	64.0	13.1	66.9	51.1
Additive & Acticontact Pilot Plant Area	43.8	0.9	31.8	23.3
Jonsson Screen Overflow Rejects	35.7	27.2	14.5	7.0
Quaternary Cleaner Rejects	17.9	22.3	3.2	6.4
Whitewater Chest	19.8	14.0	8.2	6.6
Clarified Whitewater	13.2	11.6	2.2	3.6
Silo	1.7	14.7	3.2	3.0
Whole Effluent Before Pumping Station	17.0	5.9	7.3	5.5

-- not determined. Source: Fein *et al.*, (1994)

4.2.1.2 Toxicity Identification Evaluation

TIE Phase I tests were performed on two final effluent composite samples (24-hour). Results of these tests, summarised in Table 4, were calculated as toxic units, which is the inverse of the EC_{50} value (i.e. TU = 100/EC_{50}). The TIE treatments that removed toxicity in both samples included pH adjustment to pH 11, oxidant reduction with sodium thiosulphate, and C_{18} solid phase extraction (SPE) column treatment at various pHs. Toxicity was also reduced by graduated pH adjustment (pH 8) in the February 17 sample. These results indicated the toxicants to be unstable at alkaline pH, detoxified by a reducing agent (thiosulphate), and, perhaps, non-polar organic (i.e. removed by C_{18} SPE column). These characteristics are consistent with biocides used to prevent biofouling in the paper machine process.

Paperforming is achieved by suspending the pulped fibres in a water slurry which transfers the fibres to a screen for forming. Microorganisms grow in the slurries (called "whitewater"); therefore, slimicides/biocides are added to prevent growth. Main process chemicals, including biocides, defoamers, sizing agents, fillers, and polymers, were screened for toxicity using Microtox™. As shown in Table 5, six of the chemicals were found to be acutely toxic. The least toxic additive, Defoamer B, had an EC_{50} of 1.78E-02 percent (i.e., toxic at 5 600:1 dilution). Although very toxic, Defoamer B was not expected to contribute to effluent toxicity because of its low usage rate and the high dilution provided by the whitewater flow.

The five remaining toxic chemicals were subjected to TIE testing to determine which additives matched the characteristics of effluent toxicity indicated in earlier TIE tests. TIE treatments focused on thiosulphate addition (oxidant reduction), pH adjustment to pH 3 and 11, and graduated pH adjustment (pH 6,7 and 8). As shown in Table 6, the toxicity of all of the chemicals except Defoamer A was reduced by thiosulfate addition. Biocide A exhibited the greatest instability at alkaline pH (pH 11), while Biocide B showed only slight sensitivity and Defoamer A was not affected. Finally, in the graduated pH test, only Biocide A exhibited the same pattern of reduced toxicity at higher pH (especially pH 8) as the mill effluent samples (results not shown).

Table 4. TIE phase I characterisation tests results - E B Eddy Hull Mill

Phase I Treatment	Microtox™ Toxic Units*	
	Jan 16	Feb 17
Effluent Stability		
Initial test	13.2	17.6
24h Baseline	--	14.0
48h Baseline	13.1	13.1
144h Baseline	8.0	--
pH Adjustment		
pH 3	9.3	12.7
pH 7	13.1	13.1
pH 11	6.8	5.2
pH Adjustment/Filtration		
pH 3	7.9	12.2
pH 7	8.0	10.9
pH 11	4.9	5.5
pH Adjustment/Aeration		
pH 3	8.4	10.2
pH 7	1.8	8.1
pH 11	6.1	2.5
pH Adjustment/C_{18} SPE		
pH 3 (early)	3.4	6.0
pH 3 (late)	6.0	7.7
pH 7 (early)	3.6	6.0
pH 7 (late)	7.0	7.0
pH 9 (early)	1.9	1.6
pH 9 (late)	1.3	1.3
Sucrose Test (20.4%)		
24h Baseline	--	9.1
48h Baseline	8.0	--
Sodium Thiosulphate (0.25M)	2.1	3.5
EDTA (0.5 g/L)	8.6	10.2
Graduated pH		
pH 6.0	--	8.5
pH 7.0	--	6.2
pH 8.0	--	3.2

* Toxic Units (TUs) = $100/EC_{50}$.
Source: Fein *et al.*, (1994).

Table 5. Toxicity results of mill process chemicals - E B Eddy Hull Mill

Process Chemical	Microtox™ EC_{50} (Percent)
Biocide "A"	1.09E-05
Biocide "B"	5.73E-04
Biocide "C"	8.55E-04
Defoamer "A"	1.43E-03
Sizing Agent "A"	3.60E-03
Defoamer "B"	1.78E-02
Alum	Non-toxic
Filler "A"	Non-toxic
Filler "B"	Non-toxic
Polymer "A"	Non-toxic
Filler "C"	Non-toxic
Polymer "B"	Non-toxic
Polymer "C"	Non-toxic
Felt Cleaner "A"	Non-toxic
Talc	Non-toxic
Filler "D"	Non-toxic

Source: Fein *et al* (1994).

Table 6. Effect of selected TIE phase I treatments on process chemicals - E B Eddy Hull Mill

Process Chemical	Toxicity Reduction (%)	
	Sodium Thiosulphate Addition	pH Adjust. (pH 11)
Mill Effluent	66.2	53.9*
Biocide A	87.0	85
Biocide B	89.3	33
Biocide C	81.6	--
Defoamer A	0	0
Sizing Agent A	100	--

* Mean of results for TIE Phase I tests performed on Jan. 16 and Feb.17 samples (See Table 4).
-- Not determined
Source: Fein *et al.*, (1994).

4.2.1.3 Toxicity Control

Based on the TIE results, Biocide A was identified as the principal effluent toxicant. E B Eddy contacted the product vendor and selected a less toxic, alternative biocide. Following chemical substitution, the mill effluent immediately became less toxic. As a result, the mill has met the acute toxicity permit requirement.

4.2.2 E B Eddy Port Huron Paper Mill

E B Eddy operates another mill in Port Huron, Michigan. The Port Huron mill utilises four lightweight specialty paper machines with a total daily production of approximately 320 tonnes/day.

In 1989, E B Eddy submitted a biomonitoring plan for the Port Huron mill, as required under the Michigan discharge permit. The plan specified routine acute toxicity tests using *Daphnia magna* and a TRE study, if unacceptable toxicity was observed in the mill effluent. Acute effluent toxicity was occasionally observed when monitoring began, and in early 1993 the mill initiated a TRE with the goal of achieving compliance with the toxicity limit by December 31, 1993.

It was anticipated that the TRE would be more complex than the Ottawa mill TRE, because four paper machines (instead of one) are operated at the Port Huron mill. Wastewater from the four paper machines is collected and pumped via two lift stations to a neutralisation/equalisation tank. After pH adjustment, the wastewater flows to a mix tank where polymer is added to promote solids clarification and hypochlorite is used to prevent bacterial growth. Coagulated solids are removed in two dissolved air flotation (DAF) units and the effluent is dechlorinated with sodium metabisulphite (MBS) before discharge to the St. Clair River.

4.2.2.1 Toxicity Identification Evaluation

Four effluent samples were evaluated in TIE Phase I tests. Toxicity was reduced by pH adjustment to pH 11, C_{18} SPE column treatment at pH 3, 7, and 9, aeration, and oxidant reduction (thiosulphate addition). These results are generally similar to the Ottawa mill study, which suggested the toxicity was related to biocides or organic process chemicals.

The most interesting TIE result was the reduction in toxicity achieved by thiosulphate addition. As noted, the mill treatment plant uses a similar reducing agent, MBS, for effluent dechlorination. Samples collected before and after the MBS addition point demonstrated a significant decrease in toxicity that appeared to be related to the MBS. Laboratory tests showed that the majority and, in some cases, all of the effluent toxicity was removed by adding MBS.

4.2.2.2 Toxicity Source Evaluation

Another important observation from TIE testing was the highly variable nature of the effluent toxicity. E B Eddy decided to collect and test samples from the two lift stations and relate the results to activities in the paper mill. Based on the cyclic nature of the toxicity at the lift stations (Figure 3), the process engineers identified a major source of toxicity to be the whitewater holding chest on paper machine #8. The level of whitewater in the chest was correlated with the occurrence of toxicity at one of the lift stations. The metering pump used to add the biocide had been incorrectly set to deliver exceptionally high doses. The pump was recalibrated and MBS-resistant toxicity was no longer observed in the plant effluent.

Toxicity at the other lift station appeared to be related to the whitewater discharge from paper machine #5. The toxicant was identified to be a biocide that was being added to a tank in the thick stock system. Several times a day, a timer would activate a pump that would add biocide to the tank. Some days, whitewater in the tank was not used in production; therefore, the biocide would build up to toxic levels. Excess whitewater from the tank would overflow to the lift station when it was not being used for pulper fill, which caused occasional toxicity in the mill effluent.

4.2.2.3 Toxicity Control

The solution involved changing the biocide pump from the timer to a flow weighted device that matched biocide addition to the flow of whitewater into the tank. This modification prevented the build-up of toxic biocide concentrations in the tank. The use of other process chemicals was also optimised to prevent the potential discharge of toxicity. In addition, MBS addition in the treatment plant was adjusted to optimise both toxicity reduction and dechlorination of the final mill effluent.

4.2.3 Procter and Gamble Paper Products Company

Procter and Gamble Paper Products Company (P&G) operates a towel and tissue products plant in Green Bay, Wisconsin. High BOD wastewaters are treated at a local municipal wastewater treatment plant. Whitewater and other low strength wastewaters are treated onsite (using dissolved air flotation) before discharge to the Fox River (Buttke *et al.*, 1994).

In 1989, Wisconsin issued a permit that required P&G to monitor its direct discharge for toxicity using a battery of tests. Initial tests performed by P&G found no toxicity to fathead minnow (acute and chronic), *Ceriodaphnia* (acute and chronic), and *Daphnia magna* (acute). However, in May 1990, three consecutive *Ceriodaphnia* tests showed chronic toxicity that exceeded the no observed effect concentration (NOEC) limit of 2.9 percent effluent (which is equivalent to the instream waste concentration). These results prompted P&G to voluntarily initiate a TRE (Buttke *et al.*, 1994).

The first step of the TRE was a housekeeping evaluation of the production processes and the wastewater treatment system. No deficiencies were found; therefore, P&G proceeded with further testing.

4.2.3.1 TRE Approach

Based on plant personnel's knowledge of the facility, TIE testing, the next step recommended in EPA guidance (1989b), was dropped in favour of an evaluation of the toxicity contribution from the various plant waste streams. Due to the large number of

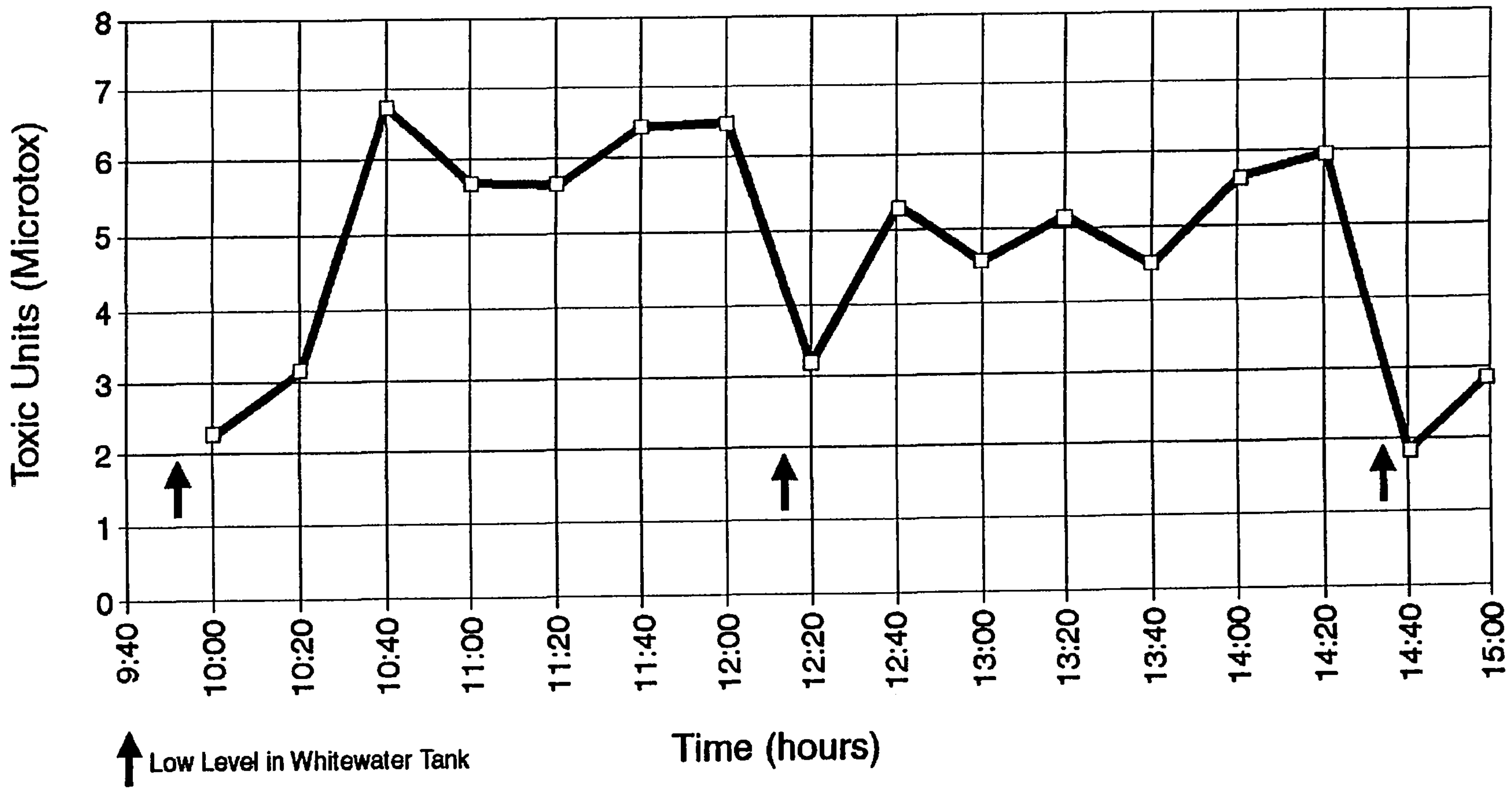


Figure 3. Toxicity variability at lift station #2 on 23 March 1993, (adapted from Fein et al. 1994).

samples to be tested, P&G evaluated the use of several short-term screening tests, including Microtox™. Comparisons were made by testing reference toxicants (sodium chloride and pentachlorophenol). A modified two-day, single brood *Ceriodaphnia* chronic test was chosen based on the similarity in results with the seven-day, three brood *Ceriodaphnia* chronic test specified in the discharge permit (Buttke *et al.*, 1994).

All paper machine whitewater waste streams and the influent and discharge from the DAF treatment process were screened using the two-day *Ceriodaphnia* procedure. Water extracts of pulp were also prepared and tested (a five percent slurry of pulp was cooked for three hours at 43°C to simulate the repulping process and the filtered water was tested for toxicity). Finally, literature data on process additives were reviewed and potentially toxic chemicals were selected for testing.

4.2.3.2 Results

Toxic levels of residual chlorine were found in some whitewater waste streams; however, chlorine is typically diluted when combined with other waste streams and becomes essentially non-toxic in the final effluent (Buttke *et al.*, 1994). Therefore, it was necessary to dechlorinate the whitewater samples in order to observe the contribution of non-chlorine related toxicity. Results of these tests, shown in Figure 4, identified paper machine #9 as a major source of toxicity.

Tests of the water extract from pulps used on paper machine #9 indicated toxicity in only one pulp (Y). The toxicity of this pulp extract was sufficient to cause effluent toxicity based on dilution of the whitewater in the combined plant waste stream. Subsequent tests of sequential water extracts from Pulp Y showed equal toxicity among the extracts. These results indicated the toxicant to be water soluble, which is a characteristic of resin acid compounds.

One process additive, a cationic polyamide epichlorohydrin adduct, was found to be acutely and chronically toxic at levels expected to occur in the final effluent (based on usage and dilution). Further review of the literature revealed that the additive was formulated to bind to cellulose fibres, which are removed to some degree in towel/tissue making process and more completely in the DAF treatment unit (Buttke *et al.*, 1994). Therefore, it was unlikely that this additive would be present in the effluent at concentrations that are acutely and chronically toxic.

4.2.3.3 Control Strategy

The immediate control strategy was to isolate and divert the paper machine #9 whitewater to the local municipal wastewater treatment plant. As a result of this change, the P&G mill has passed the effluent toxicity limit, as recorded by three consecutive toxicity tests (IC_{25} values = 7.3 to 33 percent) performed after the TRE.

Long-term toxicity control efforts involve a management system to track the effects of production changes, such as the use of new chemical additives, on final effluent toxicity (Buttke *et al.*, 1994). Where possible, the two-day *Ceriodaphnia* test is used to measure the toxicity resulting from the proposed changes. In this manner, potential toxicity problems are corrected before the changes are implemented.

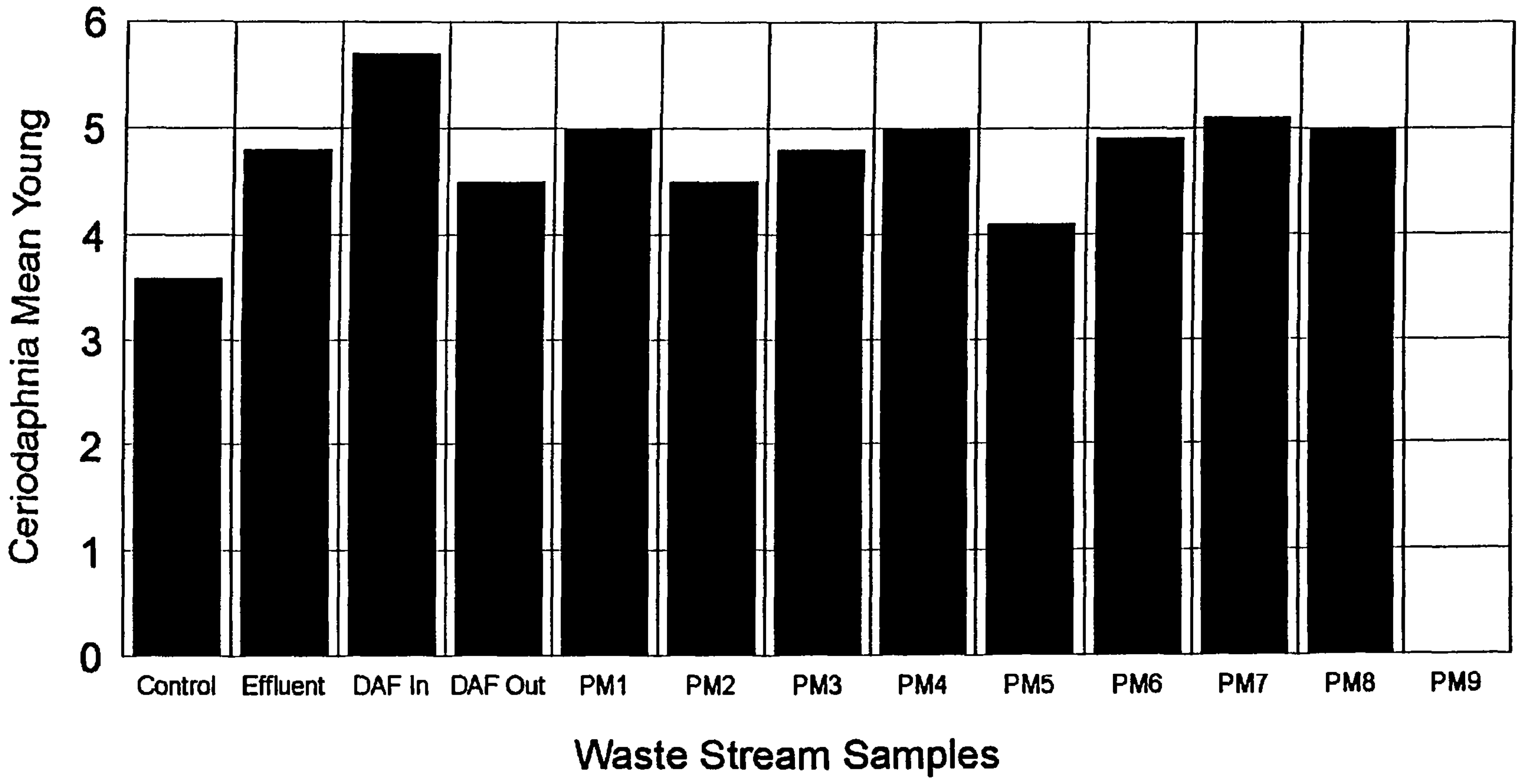


Figure 4. Waste stream toxicity results (after dechlorination)— Procter & Gamble Green Bay Plant (adapted from Buttke et al. 1994).

4.2.4 Confidential Pulp and Paper Mill - Northeast US

An integrated pulp and paper mill in the northeastern U.S. could not consistently meet its effluent toxicity guideline of no chronic toxicity in 6.2% effluent (measured as the NOEC). The regulatory authority required the company to conduct a TRE to identify the cause(s) of effluent toxicity and implement corrective actions to reduce the toxicity to compliance levels.

The mill produces bleached hardwood and softwood kraft pulp that is used to manufacture uncoated printing and reprographic papers. The mill's wastewater treatment plant consists of primary clarification and biological treatment in an aeration stabilisation basin (ASB), followed by secondary and tertiary clarification. Polymers are added after the ASB to enhance colour and suspended solids removal in the clarifiers. A polyamine coagulant is added to the ASB effluent and polyacrylamide flocculating agents are injected into the influents of the secondary and tertiary clarifiers.

Initial work involved collecting toxicity data on chemicals used in the production process. None of the production chemicals were expected to contribute significantly to effluent toxicity; however, there was concern about the polyacrylamide polymers used in the treatment process. Hall and Mirenda (1991) found some polymers, especially acrylamide-based polymers, to be toxic to *Daphnia pulex*, a species with sensitivity that is often similar to the mill's permit species (*Ceriodaphnia*).

The mill staff decided to collect and test samples of the ASB effluent before and after addition of the polymers in the secondary/tertiary clarifiers. Results showed the effluent to be about 40 percent less toxic before polymer addition than after.

Based on these results, the mill staff identified and substituted a less chronically toxic polymer for use in the clarifiers. Polymer doses were also reduced to the minimum levels that would achieve optimal coagulation and removal of suspended solids. As a result, the mill has consistently met the chronic effluent toxicity limit.

4.2.5 Simpson Paper Mill

Simpson Paper was required by the California Regional Water Quality Control Board to conduct a TRE at their bleached kraft mill. The mill discharged untreated wastewater to marine waters. It was anticipated that conventional treatment of the effluent would reduce chronic toxicity to acceptable levels; therefore, a toxicity treatability study was planned and implemented (Hickman *et al.*, 1992).

4.2.5.1 TRE Approach

An activated sludge pilot plant was designed and constructed for the study (Hickman *et al*, 1992). The pilot plant consisted of a grit chamber, pH control tank, primary clarifier, aeration basin, nutrient feed system, antifoam tank, and secondary clarifier. Untreated effluent from the mill was fed to the grit chamber. A pH control system used caustic soda and sulfuric acid to maintain pH in the optimum treatment range of 6.5 to 8.5. The primary clarifier overflow entered the aeration basin, which had a 1 063 gal working volume. Mixing was provided by two mixers. Air was supplied through four coarse bubble diffusers. Nutrients and antifoam were added as needed. Following activated sludge treatment, the suspended solids were removed in the secondary clarifier. Settled, thickened sludge was returned to the aeration basin by a peristaltic pump. Composite samplers were used to collect twenty-four samples of the primary clarifier influent and effluent, and secondary clarifier effluent for testing.

Operational parameters are shown in Table 7. Treatment performance was monitored by routine measurements of mixed liquor [mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS)] and sludge settling characteristics [zone settling velocity (ZSV) and sludge volume index (SVI)]. The food to microorganism (F/Mv) ratio was kept low (0.23 day^{-1}) relative to conventional activated sludge processes for pulp and paper plants to enhance BOD and toxicity removal (Hickman *et al.*, 1994).

Table 7. Pilot plant operating parameters and wastewater characteristics.

Parameter	Average Value
MLSS	3 135 mg/l
MLVSS	2 482 mg/l
F/Mv	0.23 day^{-1}
Sludge age	9.2 days
Return sludge flow	90%
Hydraulic retention time	6.2 hours
Influent total BOD	147 mg/l
Effluent total BOD	18 mg/l
Effluent soluble BOD	5 mg/l
ZSV	4.0 ft/hour
SVI	146 ml/gm

Source: Hickman *et al.*, 1994.

4.2.5.2 Results

The pilot plant achieved greater than 80 percent removal of chronic toxicity as measured using echinoderm tests (Figure 5). Toxicity removal was highest in the biological treatment process. The toxicity of the biological treatment process influent (primary effluent) was variable, ranging from 6.6 to 135.1 chronic toxic units (TU_cs) based on the Dinnel inhibition concentration (IC_{15}) measurement criteria. However, treated effluent toxicity was more consistent, averaging 8 TU_cs. Overall, toxicity was reduced to well below the permit limitation of 46 TU_cs (Hickman *et al.*, 1992).

Toxicity removal was not as good when measured using chronic abalone tests. Primary influent toxicity was 34 TU_cs as compared to 25 TU_cs for the final effluent. Giant kelp tests performed on two sets of influent and effluent samples showed 69 and 90 percent reduction in toxicity (Hickman *et al.*, 1992).

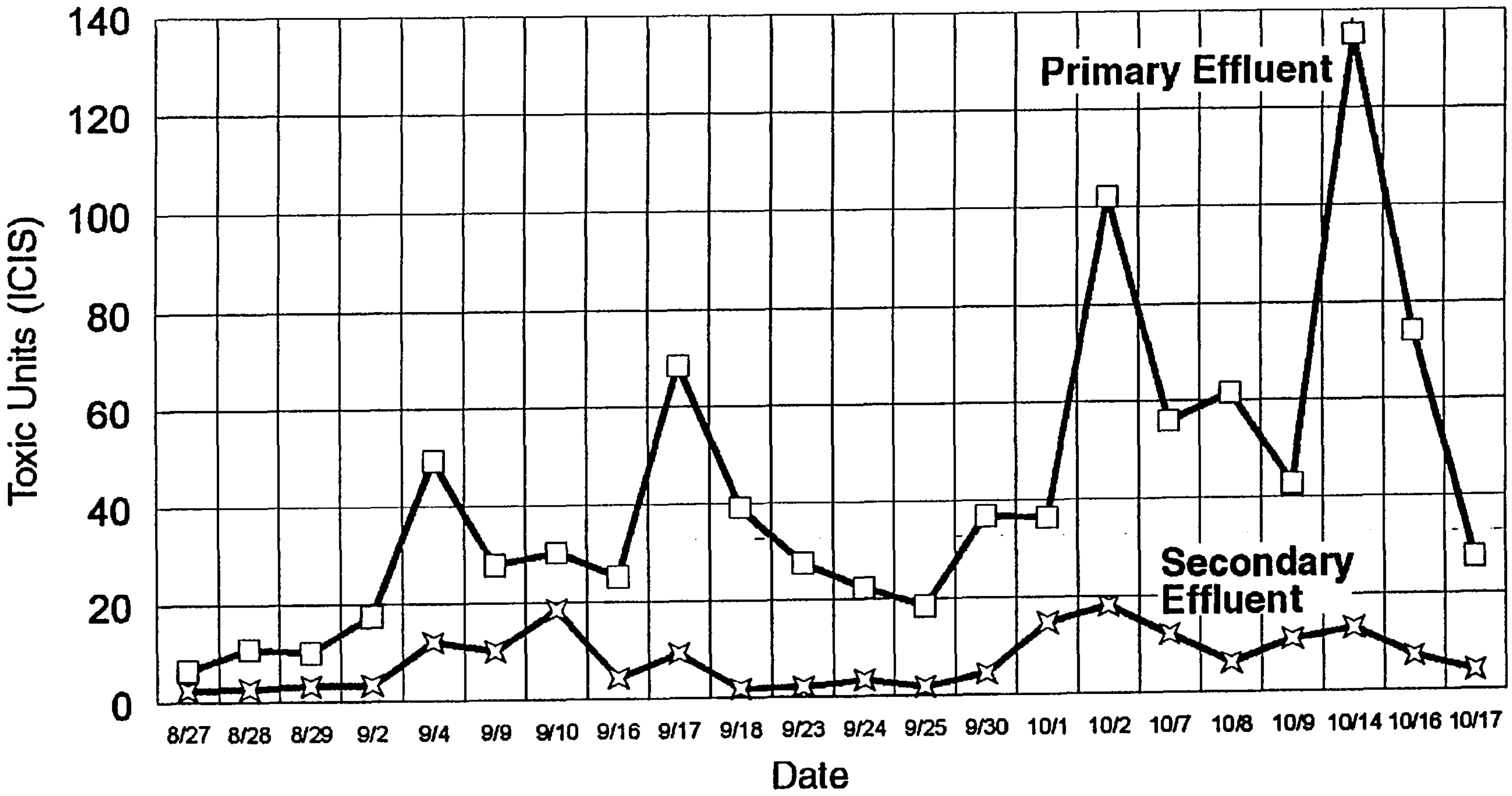


Figure 5. Pilot plant influent and effluent toxicity to echinoderms—Simpson Papermill TRE.

4.2.5.3 Toxicity Control

Although the pilot plant was operated only a short period (9 weeks), it achieve steady-state operation with no major upsets. It was anticipated that the toxicity reduction observed for the pilot plant would be similar to that of a full-scale activated sludge treatment process. Biological treatment was considered to be a viable option for achieving compliance with the toxicity limitation (Hickman *et al.*, 1992).

4.2.6 Appleton Papers, Inc., Locks Mill

Appleton Papers, Inc., Locks Mill operates an integrated pulp and paper mill in Combined Locks, Wisconsin. A TRE was required based on results showing chronic effluent toxicity to *Ceriodaphnia*. Initial testing focused on the identification of effluent toxicants using TIE procedures.

TIE Phase I tests were conducted on several effluent samples. Phase I treatments included filtration, aeration, C_{18} SPE treatment, EDTA addition, and sodium thiosulphate addition. Seven-day chronic *Ceriodaphnia* tests were used to evaluate the effect of the treatments on effluent toxicity. Results showed that filtration was the only Phase I treatment that reduced chronic toxicity. Additional tests confirmed toxicity removal by filtration through a 1.0 m glass fibre filter (Table 8).

Table 8. Effect of filtration on effluent toxicity - Appleton Papers, Inc., Locks Mill.

Sample	*Ceriodaphnia* Mean Young in Effluent Samples	
	Untreated	Filtered
8/8/91	4.4 ±2.3	18.3 ±8.0
8/23/91	0	21.4 ±3.0
9/20/91	12.1 ±6.9	23.6 ±7.4
10/11/91	8.8 ±7.1	23.8 ±3.3
12/6/91	0	13.2 ±0.8
1/17/92	26.1 ±2.3	28.2 ±1.5

Source: AScI Corporation, Inc. (Duluth, Minnesota).

Additional TIE tests were performed to isolate and identify the toxicant removed by filtration. A filter used in the filtration tests was soaked in methanol and the methanol extract was analysed for toxicity. Results demonstrated that toxicity could be recovered from the filter. The extract was analysed by GC/MS in an attempt to identify the toxic compound(s); however, it was not possible to isolate the toxicant(s) from the large number of peaks on the chromatograph.

Further testing focused on the sources of filterable toxicity. Initial testing was performed on samples from various waste streams in the treatment plant. Samples were collected from the effluent of the primary sedimentation process, at an intermediate treatment stage, and the final effluent. As shown in Table 9, the toxicity of the primary effluent was only slightly improved by filtration. Samples taken following biological treatment, however, were greatly affected by filtration. Toxicity appeared to be associated with the residual biological solids from the treatment process.

A thorough review of the treatment plant was undertaken to determine if improved operation would reduce toxicity. Appleton Papers implemented a plan to optimise the activated sludge treatment system by maintaining a constant sludge age (sometimes referred to as mean cell residence time or MCRT). The sludge wasting rate was adjusted to maintain a constant MCRT, which resulted in a consistent level of treatment. Toxicity tests were performed during the operational change to monitor the effect on effluent toxicity. After steady-state operation had been achieved, monitoring results indicated that chronic toxicity had been eliminated. Further testing over time confirmed that chronic effluent toxicity had been reduced to below the compliance limit. Although the filterable toxicant had not been identified, sufficient evidence was provided to direct the mill to reduce toxicity through relatively simple treatment modifications.

Table 9. Effect of filtration on samples from various stages in the treatment plant - Appleton Papers, Inc., Locks Mill.

Sample	Treatment	Ceriodaphnia Mean Young
Control	None	22.6 ±9.5
	Filtered	21.0 ±7.5
Primary Effluent	None	0
	Filtered	3.2 ±2.8
3rd Stage Effluent	None	0
	Filtered	14.4 ±1.7
Final Effluent	None	0
	Filtered	13.2 ±0.8

Source: AScI Corporation, Inc. (Duluth, Minnesota).

4.2.7 Canadian Kraft Mill

The mill is a modernised kraft mill producing about 900 tons per day of bleached softwood pulp. Mill wastewaters receive primary treatment as well as biological treatment in an aerated stabilisation basin (ASB). Prior to the TRE, mill effluent was routinely meeting regulatory requirements stipulating that effluent not be acutely lethal to either rainbow trout or *Daphnia magna* (i.e., LC_{50} 100%). Following a maintenance shutdown that was accompanied by particularly cold weather, the mill effluent became acutely toxic to rainbow trout. A TRE was initiated.

4.2.7.1 TRE Approach and Results

Numerous TIE Phase I tests were conducted using modified EPA procedures (USEPA 1992 and 1991).

Phase I results showed:

Effluent was lethal to trout (LC_{50}s of 70 to 100 percent), but not to *Daphnia magna* (LC_{50}s 100%).

Effluent toxicity to trout increased dramatically as pH was increased, especially from pH 8.5 to 9.0.

Toxicity was consistently removed by passing effluent samples through columns packed with zeolite resin.

No other Phase I treatments consistently removed toxicity.

These results were consistent with ammonia as the cause of effluent toxicity. Chemical analyses confirmed that ammonia was removed by the zeolite treatment; however, ammonia levels in the effluent (2 to 5 mg/L total ammonia) were lower than the concentrations reported to be lethal to fish at similar exposure pHs (USEPA, 1993a and 1993b). As shown in Figure 6, effluent LC_{50}s expressed on the basis of un-ionized ammonia concentration were consistently lower than LC_{50}s for ammonia in laboratory water. This comparison suggested that either ammonia was not, in fact, responsible for toxicity or that one or more substances contributed to effluent toxicity in addition to ammonia.

A series of tests were performed to identify whether the toxicity reduction in the zeolite tests was caused by ammonia removal or the removal of some other effluent constituent. These tests involved spiking ammonia back into effluent samples treated with zeolite and measuring the resulting toxicity. As shown in Figure 7, the toxicity of the spiked samples was similar to that of the whole effluent samples, confirming that ammonia was a primary toxicant and zeolite treatment did not remove other toxicants. It was concluded that ammonia acted together with another effluent toxicant to cause the observed toxicity.

Ammonia had traditionally been added to the ASB as a nutrient, but the results of the TIE prompted the mill to halt all ammonia addition to the system. Effluent toxicity immediately decreased.

Although effluent toxicity was eliminated, a sufficient number and volume of samples was archived to permit further testing. Toxicity tests conducted up to two months after sample collection showed that effluent toxicity was unchanged. Therefore, the study continued with the objective of identifying the other, unknown toxicant(s) that was causing the additive toxicity with ammonia.

Solid phase extraction (SPE) using a C_{18} column was the only other treatment occasionally effective in reducing toxicity. However, attempts to recover the toxicity from the C_{18} SPE column using methanol and acetone were not successful. To evaluate the apparent

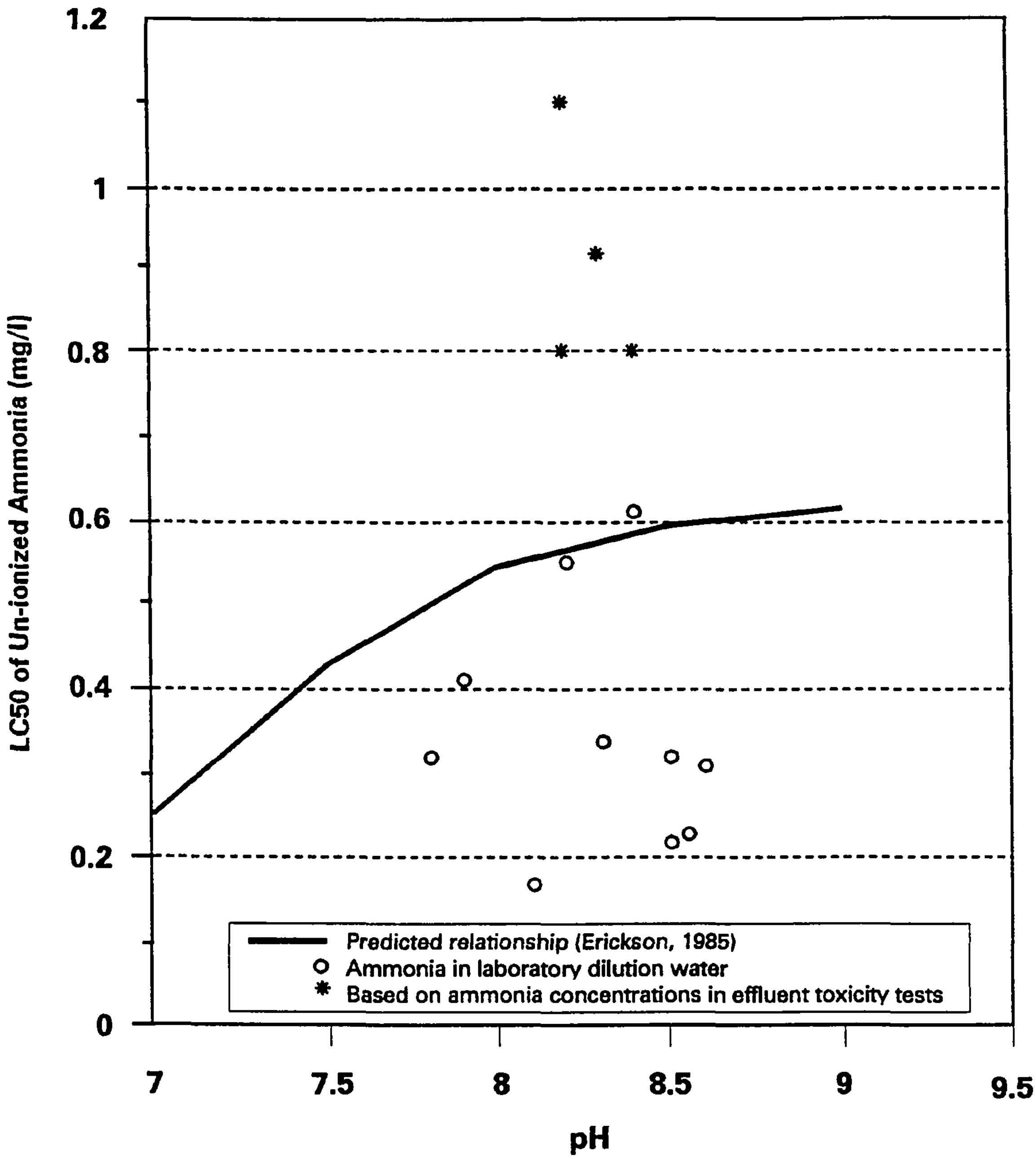


Figure 6. Acute lethality of un-ionized ammonia to rainbow trout—Canadian Kraft Mill.

Source: Beak Consultants, Ltd.

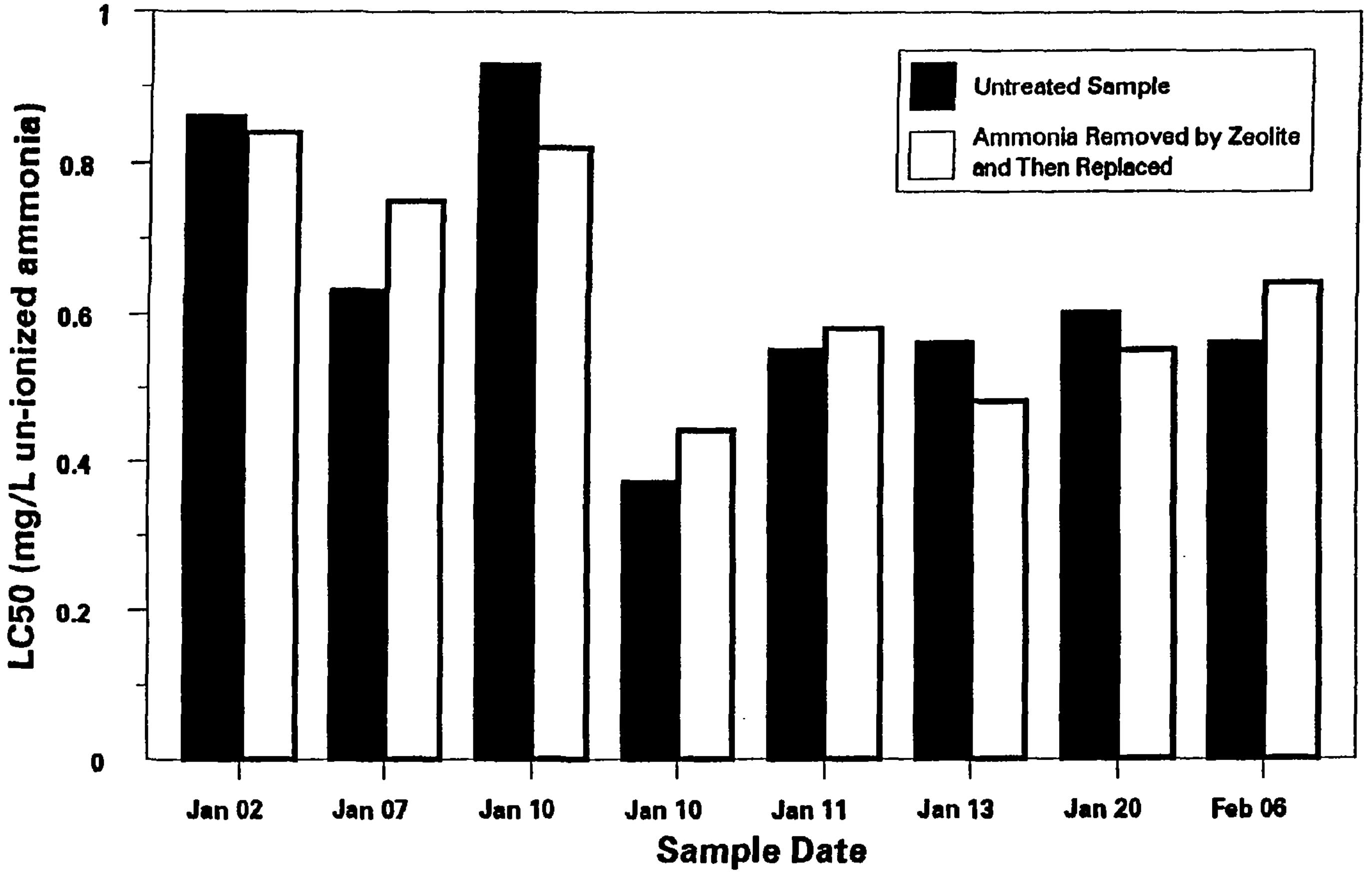


Figure 7. LC50 of effluent samples to fathead minnow* (expressed as un-ionized ammonia concentration)

*Used as surrogate for trout in TIE. Periodic testing confirmed that both species gave similar results.
Source: Beak Consultants, Ltd.

additive toxicity effect, ammonia was spiked into the methanol extracts to original effluent concentrations. The resulting toxicity was equivalent to the toxicity observed in the whole effluent samples, which confirmed the additive nature of the toxicity. Apparently, an effluent constituent(s) was causing ammonia to be more acutely toxic than would be expected based on the measured ammonia levels.

Gas chromatography (GC) and liquid chromatography (LC) analyses showed that C_{18} column extracts contained too many chemicals to positively identify the toxicant. Attempts to further separate the toxicants by sequentially extracting C_{18} columns with a series of solvent-water concentrations did not produce consistent recovery of toxicity. By this time, the mill effluent had become consistently non-lethal; therefore, the investigation was terminated.

Although additive toxicity with ammonia is highly unusual, discussion with an environmental representative from another mill in the region indicated that other facilities must maintain extremely low ammonia residuals in their effluents (e.g. less than 2 mg/L) in order to avoid ammonia-related toxicity. This is anecdotal evidence that low levels of ammonia may interact with other effluent constituents to cause effluent toxicity at pulp mills.

4.2.8 Confidential Paper Mill - Eastern Canada

A company in eastern Canada operates a small mill which manufactures paper plates from virgin bleached kraft fibre, as well as other molded fibre products such as egg cartons, berry boxes and drink trays. The latter products are manufactured using recycled groundwood, unprinted newsprint, and post-consumer newsprint as furnish. During the TRE, the mill discharged a total of about 6,000 m^3/day from three outfalls. None of the discharges received treatment. One outfall was consistently non-lethal to rainbow trout and *Daphnia magna* in acute testing, but the other two discharges were often toxic (i.e. LC_{50} <100%). Regulations recently promulgated by the federal government require the effluents of all pulp and paper mills to be non-lethal to both species. The company initiated a TRE to achieve compliance with the regulation.

4.2.8.1 TRE Approach and Results

The mill's potable water supply was initially suspected as a source of toxicity when tests of the water showed acute lethality. However, a site visit determined that samples of the main water supply were being collected from a copper pipe. When samples were subsequently taken directly from the main water supply, no toxicity was observed, suggesting that metals leached from the copper pipe may have been responsible for the apparent toxicity of the incoming water.

A review of the mill operations found that up to seven process lines may be operating concurrently; although, the production schedules and the types of products manufactured on each line are typically different. The mill processes discharging to the two toxic outfalls utilise similar manufacturing steps. In each case, furnish is re-pulped and several chemical reagents are added as the fibre is dewatered and molded into the final product. Chemical additions typically follow the sequence of alum, rosin size, wax, defoamer, and sometimes wet strength or polymer (depending on the product). One or more dyes are also usually added.

As mill effluent did not receive treatment and the manufacturing processes on each line were similar, the toxicity contribution of any one process was assumed to be representative of the whole production system. Therefore, trial tests were conducted on a dedicated unit process to evaluate the toxicity of various waste streams generated by the production system. As depicted in Figure 8, the toxicity of whitewater in the system was sequentially measured in samples taken after each process reagent was introduced.

Each of the three major furnish types and each of the chemicals typically used in product manufacturing were evaluated, except dyes (which would be the subject of subsequent investigation, if necessary).

The trials showed that most of the toxicity discharged from the system was contributed by the furnish repulping step. Resin acid concentrations in the whitewater were sufficient to account for the amount of toxicity observed, except for one case in which toxicity to *Daphnia magna* was greater than could be explained by the measured resin acid levels. It was concluded that another agent contributed, at least on occasion, to effluent toxicity.

4.2.8.2 Toxicity Control

Although secondary (biological) treatment is generally successful in removing resin acid toxicity, it was not an economically viable solution for a relatively small operation, like this mill. A series of bench-scale (laboratory) and full-scale (mill) trials were initiated to identify whether alteration of the quantities or brands of the various chemical additives may enhance adsorption of resin acids to the product, thereby minimising loss to the sewer. While some of these measures reduced toxicity, none consistently eliminated it.

During this period, the company began combining the three outfalls to dilute the two toxic effluents with the third, non-toxic effluent. Water use practices were also reviewed to identify areas where clean water (e.g., cooling, seal waters) could be prevented from mixing with and displacing the toxic whitewater, thereby reducing whitewater loss to the sewer. These measures removed mill effluent lethality to rainbow trout, but lethality to *Daphnia magna* continued to be observed.

TIE Phase I testing was initiated using final mill effluent. Toxicity to *Daphnia* was removed by adjustment of the sample to pH 11, treatment by C_{18} SPE column at neutral pH (pHi), and adsorption with activated carbon at neutral pH. As the identity of the toxicant was not immediately obvious and substantial additional effort was anticipated, the company elected to proceed with further improvements in water management. A whitewater recycle system was implemented that achieved closure of eight of nine whitewater process lines. As a result, acute effluent lethality to rainbow trout and *Daphnia magna* was eliminated.

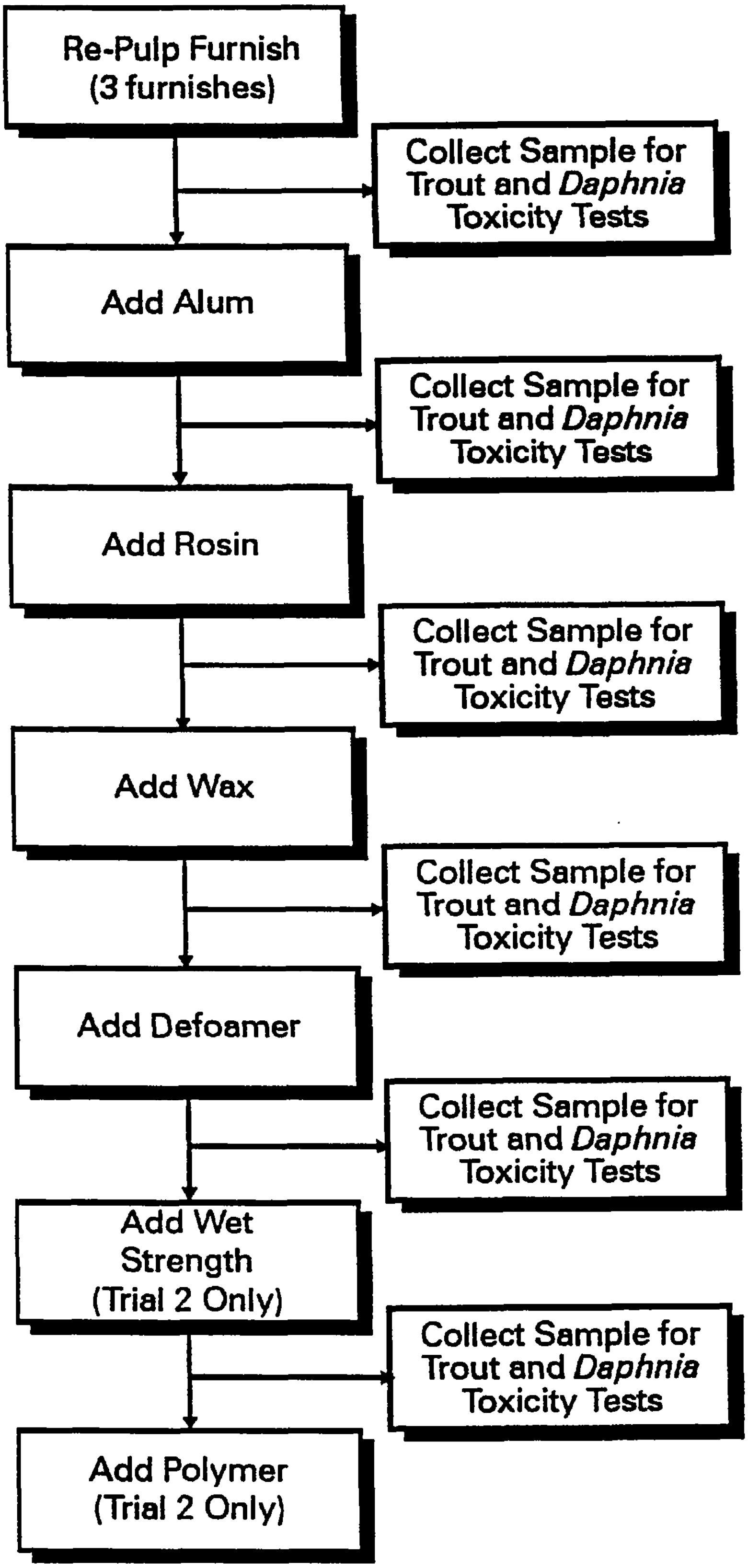


Figure 8. Study design for comparison of toxicity at various stages of manufacturing process.

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Procter and Gamble TRE - George Buttke, Environmental Specialist, Procter and Gamble

Simpson Paper TRE - Gary Hickman, Environmental Engineer, CH2M Hill

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APPENDIX A

Table A-1. Screening tests recommended for use in selecting appropriate effluents for toxicity-based control.

Toxicity Test	Receiving Water	
	Freshwater	Marine Waters
5-30 minute Microtox™ (*Photobacterium phosphoreum*) bioluminescence test (Butler *et al* 1991)	+	+
24 hr water flea (*Daphnia magna*) immobilisation test (OECD 1984)	+	
24 hr oyster (*Crassostrea gigas*) embyro-larval development test (ICES 1991)		+

Table A-2. Algae, invertebrates, and fish recommended for use in the testing of the toxicity of effluents discharged to fresh and marine waters.

Type of Organism	Freshwaters	Marine Waters
ALGAE	*Selenastrum capricornutum* 72 hr inhibition of growth (OECD 1984)	*Phaeodactylum tricornutum* *Skeletonema costatum* 96 hr inhibition of growth (ISO 1988)
INVERTEBRATES	*Daphnia magna* (water flea) 48 hr immobilisation (OECD 1984)	*Crassostrea gigas* (Pacific oyster) embryos 24 hr inhibition of development (ICES 1991)
FISH	*Salmo trutta* (Brown trout) *Oncorhynchus mykiss* (Rainbow trout) 96 hr mortality (OECD 1984)	*Pleuronectes platessa* (Plaice) *Scopthalmus maximus* (Turbot) 96 hr mortality

Table A-3. Chemicals typically used at U.K. pulp and paper mills.

Category	Materials	Category	Materials
Retention/ Drainage Aids	Aluminum sulphate (Alum) Polyacrylamides (PAM) Polyethyleneimines (PEIs) Polyamines Polydadmacs Polyethylene oxide Cationic starch (used with anionic polyacrylamide, colloidal silica, or alum) Bentonite (used with organic polymer such as polyacrylamide) Colloidal silica (with cationic starch)	Preservatives	Pentachlorophenol (previously used, but not currently) Brominated organics Carbamates Thiazoles Copper-8-hydroxyquinolate
Deposit Control Chemicals	Alum, talc, dispersants - for pitch control Polymer, surfactants, zirconium salts - for control of "Stickies" - adhesive contaminants Chlorine/hypochlorite, chlorine dioxide, Dichlorphen, bromonitrostyrene, methylene biocyanate and benzisothiazalones, guanidine and quaternary ammonium compounds, aldehydes - to control slime	Foam Control	Aqueous mixtures of fatty acids/esters/ alcohols/amides Pre-treated silica Silicones Ethoxylated nonionic polymers
Sizing	Rosin Alkyl ketene dimer (AKD) Alkenyl Succine Anhydride (ASA)	Wet Strength	Acid-curing formaldehyde based resins with urea (UF) or melamine (MF) Neutral-curing polyamidoamine-epichlrohydrin (PAE) resins, often used with carboxymethylcellulose Poly ethyleneimine and dialdehyde starches
Dry Strength	Starch (mainly raw or modified wheat, maize or potato starches Polyacrylamides Gums such as guar Carboxymethylcellulose	Colours and Brighteners	Water soluble dyes (e.g., iron oxides, carbon black or phthalocyanines). Fluorescent brightening agents (e.g.,derivatives of 4,4'-diaminostilbene-2,2' - sulphonic acid)