CASE STUDIES FOR TOXICITY TESTING AND RISK ASSESSMENT RELATED TO THE PLACEMENT OF TEXTILE FACILITIES.

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ABSTRACT

The Province of New Brunswick has been actively participating in the establishment of new textile facilities in northeastern and northwestern New Brunswick. A key component of these programs has been the need for detailed environmental studies dealing with the effluent chemical quality and effluent toxicity. In the first case study in northeastern New Brunswick toxicity testing and wastewater treatment process studies were conducted to identify the toxicity of individual process streams, as well as the final effluent. The approach allowed for adjustment of the wastewater treatment process and wastewater stream segregation to eliminate and treat sources of toxicity in the final effluent. As part of the project, a bioassay facility was constructed at the mill and plant operators trained to conduct their own toxicity testing. In the second case study, an environmental assessment was completed for two proposed mills in northwestern New Brunswick with treated wastewater being discharged to the Madawaska River. Toxicity testing is being conducted to determine the overall environmental impact of individual and collective process streams before and after treatment. Testing is being conducted on treated and untreated wastewater collected from existing textile facilities, located in the USA and Hong Kong, having similar processes. The purpose of this presentation is to show the role of toxicity testing as a valuable assessment tool to support standard chemical analysis in determining the potential environmental impact of effluent discharges.

INTRODUCTION

Pollutech Environmental Limited has been actively working within the Province of New Brunswick, concentrating on environmental studies to assist government agencies with the placement of textile facilities. The work conducted to date has included process evaluations for the design of waste treatment facilities, environmental impact studies under the provincial Environmental Assessment Act, and aquatic habitat studies to investigate the impact of the operations on the natural environment.

A key component of the studies to date has been the application of aquatic toxicity tests to assist the process engineering group in identifying potential problems with the effluent from the textile plants. In the first application at an integrated northeastern textile facility using, the toxicity tests were used to identify toxicity from individual process streams, the total plant effluent and the effluent after various stages of treatment. In the second application in northwestern New Brunswick, toxicity testing was completed on two proposed mills to identify the impact of the process streams, before and after treatment, in combination with other industrial and municipal wastes.

In the cases where the textile had not yet been constructed, it was necessary to collect effluent from similar process operations for the investigations. To achieve this, on-site investigations of the plants in Hong Kong and the United States were conducted, followed by treatability testing and toxicity evaluations.

The studies completed to date have shown that the application of toxicity tests is an important investigative tool for process engineering studies. A toxicity testing program can be used in conjunction with routine chemical analysis and treatability testing to better define the expected environmental impact of proposed industrial facilities.

DISCHARGE REQUIREMENTS

The Province of New Brunswick established effluent criteria on a "case-by-case" basis depending on the point of discharge. In the applications studied to date we have evaluated discharges directly to the Atlantic Ocean, discharge into a tidal basin and discharge to a major inland river. In addition to standard discharge criteria (ie. BOD_5, solids, phosphorus, nitrogen), the province has generally stated that the effluents must meet three prime criteria:

- the effluent must not impart a colour to the waterway into which the discharge takes place;
- the effluent discharge must not result in the creation of floating foam on the surface of the receiving waters; and
- the effluent must not show greater than 50 % mortality at 100 % concentration for any discharges entering into the receiving water.

Although not stated in the regulations, our dealings with the province have indicated a preference for an operation that does not allow for the use of chemicals or chemical processes that could result in a toxic discharge episode from a process failure. For that reason, a number of the toxicity trials looked at individual process streams and specific chemical formulations, to determine the impact that could arise from a process upset.

TREATMENT PROCESSES STUDIED

The placement of the textile facility dictates the discharge area for the effluent. The effluent criteria were therefore dictated by the carrying capacity of the receiving waters. To achieve the level of treatment required for the individual installations, the studies evaluated treatment of the textile wastes by various methods:

- direct discharge of the waste streams, or component waste streams, without any form of treatment;
- pretreatment of the waste streams for the removal of gross solids, adjustment of pH, and flocculation and sedimentation of coloured matter;
- discharge without pretreatment to existing municipal sewage treatment plants using either aerated lagoons or activated sludge processes;
- combinations of pretreatment with subsequent effluent polishing at the municipal treatment works; and
- treatment at on-site industrial waste facilities, with final treatment at municipal works.

The studies conducted at the laboratory scale used standard bench scale processes to evaluate the effectiveness of the treatment on both the individual waste streams from and industry and the combined plant effluents. The potential for toxicity from the waste streams were evaluated using three levels of toxicity screening, all of which had a specific objective:

- standard OUR tests (Oxygen Uptake Rate) were conducted to determine if the waste had a specific concentration at which point toxicity would occur within a biological treatment plant from a sudden and irreversible discharge;
- biological degradation studies were completed on the various mixtures at different hydraulic and solids retention times to determine if the biological treatment plants could acclimatize to the wastes, or whether the wastes would result in eventual failure of the plant from selective toxicity (ie. destruction of colonial ciliates); and
- routine effluent toxicity test (*Daphnia magna* and Rainbow Trout) were undertaken on the virgin chemicals used in the process, the effluent streams from the individual processes, the pretreated effluent streams and the final effluent after any polishing stages.

Where a specific waste stream or chemical was identified as having an unacceptable level of toxicity, the alternative chemical formulations were then examined. If no alternative was available then means to control the toxicity were evaluated. Each of the process streams were evaluated at concentrations expected from the plant, plus concentrations that could arise during an unforseen process upset.

TEXTILE PLANTS STUDIED

The three major groups of textile plants studied included:

- an integrated printing and dyeing operation using cotton and polyester materials, a wide range of interim fabric process stages (singeing, starching, PVA, CMC, fire retardants) followed by application of a wide variety of organic dyes, several of which contained heavy metals;
- a dyeing operation with cotton fabric only, using a limited number of processes for fabric preparation and base colour dyeing only;
- an indigo slashing and dyeing operation for the production of denim materials from a cotton fabric, with limited amounts of starching.

In each of the studies completed there were a number of benefits achieved from the evaluation of the toxicity of the chemicals used in the manufacturing, the processes carried on at the mill, or the operations within the treatment facilities.

At the existing mill where the studies concentrated on the development of treatment processes to combat toxicity, the tests were clearly beneficial in the following areas:

- a number of the chemicals used in the processes were identified as being extremely toxic, providing the operators with the information necessary to approach the chemical suppliers regarding replacement chemicals or formulations;
- process operations (ie. polyester singeing) were identified as steps that resulted in the formation of toxic compounds that were collected in the effluent after fabric washing, therefore requiring specific attention at the treatment plant (ie. powdered activated

carbon);
- pretreatment needs could be developed to handle the individual waste streams, prior to being combined in a final effluent stream, which allowed for optimization of the pretreatment, avoiding contamination of the total plant effluent;
- the ability of the manufacturing operation and treatment plant to achieve the objectives established by the regulatory agencies could be clearly established and maintained on a routine basis; and
- the general public could be assured of the success of the facility in meeting the "non-toxic" discharge criteria, a critical component given the dependency of the area residents on the aquatic resources.

The same general benefits were also available to the promoters of the two proposed textile facilities, allowing changes to be made early in the process, thus avoiding the cost for expensive remedial treatment. In particular, testing conducted at the plants in the United States and Hong Kong enabled the developers and the regulator agencies to work together to achieve the following:

- individual process streams were evaluated enabling the owners to identify which processes produced a highly toxic effluent, resulting in adjustment to the processes proposed for the facility;
- chemical formulations were checked and tested, allowing the chemical suppliers the opportunity to suggest alternative formulations;
- treatment needs could be determined early in the process, allowing for the inclusion of these costs in the overall planning for the facility, particularly where process changes could be compared to treatment needs;
- the regulatory agencies and general public could be assured early in the review process of the general acceptance of the facility relative to the achievement of the effluent objectives; and
- baseline conditions could be established for future examinations of the manufacturing processes, in anticipation of future phases to the production facilities.

TOXICITY PROBLEMS IDENTIFIED

The results of the investigations were unique in that a number of areas were identified as being critical to the achievement of the "non-toxic" effluent. Conducting the tests on the individual process streams as well as the combined plant effluents allowed us to study the synergistic impact of toxic components, the toxicity reduction from total plant effluent dilution, the production of toxins within the process, and the effectiveness of various waste treatment alternatives.

A number of sources of toxicity were identified as a result of the combination of the process investigations and toxicity tests completed:

- pH imbalances were common for individual process streams, thus enabling operations to plan for pH adjustment, equalization prior to discharge, or establishment of alarm conditions;
- high strength organic wastes were shown to impact on the toxicity tests from oxygen depletion, demonstrating the need for adequate biological treatment prior to discharge and containment in the event of spills;

- high ionic strength chemicals resulting in imbalances to the osmotic pressure in the effluent were identified and corrected (ie. chlorides, sulphates);
- specific toxic chemicals (ie. chrome, chlorine) were identified and formulation changes were made or treatment processes added;
- by-products from the processing of the fabric (ie. singeing) could be traced back to areas in the production facility; and
- failures in the treatment plant could be characterized relative to the impact on toxicity results.

Ultimately, the chemical formulations approved for use and the treatment processes selected, were based on the results of the toxicity evaluations. In particular instances, spills response programs were developed to handle potentially toxic episodes, such as the addition of PAC (powdered activated carbon) to the effluent lagoons.

TOXICITY TESTS COMPLETED

Process testing for the mill evaluations were conducted either at the mill sites in Hong Kong or the United States, or at Pollutech's Oakville process engineering laboratory. All samples for toxicity evaluations were transported to Pollutech's Sarnia biological research facility. Standard toxicity testing protocols were used that responded to the requests of the regulatory agencies as well as those that provided insight into the potential for effluent toxicity from the manufacturing processes. For example,lethality toxicity tests that incorporated other sublethal endpoints, such as an EC_{50} or TLOE (Total Loss of Equilibrium), were of particular importance to the process group to identify areas that required further attention. By paying attention to these sublethal responses, process upsets and toxicity problems could be expediently isolated. The standard LC_{50} tests were of greater importance to the regulatory agencies as a result of the lethality compliance requirement.

The *Daphnia magna* 48 hour acute lethality test highlighted both mortality data and mobility. The standard Rainbow Trout 96 hour lethality test provided data regarding partial and total equilibrium loss.

The tests conducted are summarized as follows:

- *Daphnia magna* 48 hour acute lethality testing provided data on acute as well as sublethal response (ie. loss of mobility);
- Rainbow Trout 96 hour acute lethality testing provided data on acute as well as sublethal responses (ie. Total Loss of Equilibrium -TLOE).

PROGRAM TEST RESULTS

To demonstrate the results that were achieved from the individual test programs, we have highlighted important findings to the process investigations for the three case studies.

In the first case at the existing textile facility, Pollutech conducted treatability testing and toxicity evaluations to optimize the treatment process. In the latter stages of the project, Pollutech assisted with the design, construction and commissioning of an on-site toxicity laboratory at the textile plant.

During the commissioning of the treatment plant, a series of tests provided the following results:

Date	*Daphnia magna* 48 hour EC_{51} [1]	*Daphnia magna* 48hour LC_{50} [2]	Rainbow Trout % TLOE [3]	Rainbow Trout Pass/Fail
Nov. 9	no immobility	non-lethal	0	non-lethal
Nov. 12	not run	not run	0	non-lethal
Nov. 15	no immobility	non-lethal	0	5 %
Nov. 16	no immobility	non-lethal	0	non-lethal
Nov. 23	no immobility	non-lethal	100	50 %
Nov. 23	no immobility	non-lethal	100	60 %

- 1. The effective concentration of the chemical or effluent which causes immobility in 50 % of the test organisms.
  2. The lethal concentration at which mortality occurs to 50 % of the organisms.
  3. Total Loss of Equilibrium
  4. % Mortality

The test results were critical in that the operating permit during the commissioning period allowed the plant exceed the BOD_5 and Suspended Solids effluent criteria but explicitly disallowed any releases of toxic effluents. The availability of the results at the site allowed staff time to divert the treated effluent to the holding lagoon where it could be further treated with activated carbon to reduce the toxicity. Activated carbon had been identified in the lab scale trials as a viable means to control toxicity form the singeing operation. As a result of this episode, the production team made changes to the process that corrected this problem.

It is important to note that the *Daphnia magna* tests, although they provided a good screening tool in the design stage of the project, did not highlight the effluent toxicity associated with the singeing operation. The protocol for conducting toxicity tests on the treated effluent and the individual process streams became an important aspect in the operation and compliance monitoring for the facility.

In the second case study, the similarities of the existing process in northeast New Brunswick discharging to the Atlantic Ocean was evaluated against a proposed facility in northwest New Brunswick discharging to an inland river. Three sets of samples from supposedly "similar" operations were evaluated with the *Daphnia magna* 48 hour LC_{50} protocol. The results obtained are detailed as follows (% by volume):

Sample	Northwest Plant 48 hour LC_{50}	Northeast Plant 48 hour LC_{50}
A	<0.25	11.3
B	<0.25	>100
C	<0.25	34.1

For the northwest plant, no specific 48 hour LC_{50} value could be obtained as 100 % toxicity occurred at the lowest concentration tested (0.25 % by volume). Toxicity was observed to occur very rapidly. Even at the lowest concentrations studied, 60 to 100 percent of the

Daphnia were immobile within 24 hours of initiating the test. These preliminary screening trials showed that the effluent from the Northwest (proposed) facility was at least 136 time more toxic than the existing facility. As the proponents of the mill had claimed that the operation was "non-toxic" there was a definite change in the operations plan for the proposed facility.

In the third case study, currently in progress, the individual chemical components of the process are being evaluated along with the process streams, the final effluent, and mixtures of the wastes with other industrial and municipal streams. Each chemical is being tested at the expected concentration in the process, as determined by a mass balance, and at three times the expected concentration. The preliminary results of the *Daphnia magna* tests are as follows:

Chemical	Daily Usage (lbs)	Yarn Uptake (%)	Chemical (mg/L)	3 X (mg/L)	EC_{50} (mg/L)	LC_{50} (mg/L)
Indigo Dye	120	85	57	172	>200	>200
Sodium Hydrosulphite	240	85	115	344	222	222
Soda Ash	32	85	15	46	>50	>50
Subitol San	40	85	19	57	1.1	1.1
Tapioca Flour	882	85	421	1264	>1300	>1300
Bev 4118	100	85	48	143	>150	>150

The test results clearly show that one particular compound (Subitol San) will create a toxicity problem if the formulation can not be modified or the waste can not be appropriately treated.

Ten treatment processes and combinations were evaluated with both the *Daphnia magna* and the Rainbow trout test protocols. The tests were undertaken to determine the efficiency of the waste treatment process with the various alternatives under the following conditions:

- the treatment plant receiving domestic sanitary sewage only, representing the base case if no industries discharged to the facility;
- the treatment plant receiving sanitary waste plus an existing effluent stream from a local pulping operation;
- the treatment plant receiving sanitary sewage plus the proposed textile effluent, without the pulping waste; and
- the combination of sewage, pulping waste and textile effluent.

Each test was completed at 50 %, 100 % and 200% of the expected feed concentration, with a 12 and 24 hour HRT (hydraulic retention time) and a 10 day, 20 day and 30 day SRT (Solids Retention Time). These conditions had been previously identified as the critical design parameters for the biological treatment facility.

Preliminary test results are available on the effluents collected during the acclimatization period of the biological treatability tests, as depicted below:

Bioassay Test	Rainbow Trout 96 hour Pass/Fail	*Daphnia magna* 48 hour LC_{50} (% by volume)
Sewage Only	pass	84
50 % Textile	pass	75
100% Textile	pass	80
200 % Textile	fail[1]	>100
50 % Pulp Waste	pass	85
100% Pulp Waste	pass	NT
200 % Pulp Waste	pass	NT
50 % Mixture	pass	>100
100% Mixture	pass	NT
200% Mixture	pass	NT

[1] 60 % mortality at 100 % effluent concentration

The effluent toxicity results showed that there was a toxicity problem associated with the sanitary sewage alone when it had not been fully treated. The textile and pulp mill wastes showed signs of toxicity that can be addressed with adequate biological treatment, provided the concentrations are not excessive. The individual chemical toxicity results assisted in the identification of the Subitol San as a major toxicity concern.

The test results that we have obtained from the case studies have demonstrated that the textile manufacturing process would have to be operated to ensure that there was:

- no dumping of acids or bases
- no production with sulphide based dyes
- treatment after singeing of polyester fibres
- control of dyes with trace metals
- no spillage of high strength organics, and
- no treatment plant failures

CONCLUSIONS

The studies conducted to date have been critical to the evaluation of the environmental impact of these textile facilities. In general the tests have shown that:

- the *Daphnia magna* is a useful screening tool for identifying potential problems with individual chemicals or treatment alternatives;
- Rainbow trout testing is required for compliance testing as not all effluents responded equally to *Daphnia magna* and Rainbow Trout toxicity tests;
- the investigator must screen component streams to ensure that the treatment facilities are not designed to treat large volumes of waste that are created toxic by a small side stream;
- it is essential to account for process upsets in the studies resulting in the formation of toxic streams from otherwise normal operations;

- the study must evaluate both raw and treated wastes to provide information on the toxicity reduction with treatment and the potential impact from treatment plant failures; and
- the evaluation must screen a series of concentrations for process chemicals, given the wide range of process changes experienced at the operating facilities.

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