

**TWENTY-SIXTH CANADIAN SYMPOSIUM  
ON  
WATER POLLUTION RESEARCH**

**FEBRUARY 13 - 14, 1991**

***ABSTRACTS***

***ASSESSMENT AND REMEDIATION OF  
PULP AND PAPER MILL EFFLUENT EFFECTS***

***WATER POLLUTION  
CONTROL TECHNOLOGY***

***IMPACT OF POLLUTANTS  
ON AQUATIC ECOSYSTEMS***

**CANADA CENTRE FOR INLAND WATERS  
BURLINGTON, ONTARIO**

**SPONSORED BY:**

**CANADIAN ASSOCIATION ON WATER POLLUTION  
RESEARCH AND CONTROL**

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26th

**PROGRAM**  
*Wednesday, February 13, 1991*  
**ASSESSMENT AND REMEDIATION OF PULP AND PAPER MILL EFFLUENT EFFECTS**

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| <p>7:30 - 8:45 REGISTRATION (CCIW FOYER)</p> <p>8:45 - 9:00 OPENING REMARKS (AUDITORIUM)<br/>K.L. Murphy, President CAWPRC<br/>McMaster University</p> <p style="text-align: center;">SESSION I - AUDITORIUM</p> <p>PRESIDER: J.H. Carey<br/>National Water Research Institute</p> <p style="text-align: center;">EFFLUENT CHARACTERIZATION AND TREATMENT</p> <p>9:00 - 9:30 COMPREHENSIVE STUDY OF A BLEACHED KRAFT MILL SECONDARY TREATMENT SYSTEM<br/>J. Fein, M. Beavan, A. Effio, N. Gray, N. Moubayed and P. Cline</p> <p>9:30 - 10:00 A BATCH STUDY OF THE AEROBIC AND ANAEROBIC REMOVAL OF CHLORINATED ORGANIC COMPOUNDS IN AN AERATED LAGOON<br/>A. Chernysh, D.G. Allen and S. Liss</p> <p>10:00 - 10:30 ANAEROBIC AND AEROBIC TREATABILITY OF HIGH YIELD SULPHITE SPENT LIQUOR<br/>A. Schnell, E.R. Hall and S. Skog</p> <p>10:30 - 11:00 COFFEE BREAK - MAIN MALL AREA</p> <p>11:00 - 11:30 APPLICATION OF BIOLOGICAL AERATED FILTER FOR INDUSTRIAL WASTEWATER TREATMENT<br/>A. Kantardjiev and J.P. Jones</p> <p>11:30 - 12:00 FATE AND EFFECTS OF RESIN ACIDS UNDER AEROBIC AND ANAEROBIC TREATMENT CONDITIONS<br/>S.F. Liver and E.R. Hall</p> <p>12:00 - 12:30 A BIOLOGICAL AND CHEMICAL CHARACTERIZATION OF NEWSPRINT/SPECIALTY MILL EFFLUENTS<br/>T.G. Kovacs and R.H. Voss</p> <p>12:30 - 1:30 BUFFET LUNCHEON - MAIN MALL AREA</p> | <p>SESSION I - AUDITORIUM</p> <p>PRESIDER: E. Hall<br/>Wastewater Technology Centre</p> <p style="text-align: center;">ENVIRONMENTAL IMPACT OF PULP AND PAPER MILL EFFLUENTS</p> <p>1:30 - 2:00 EUTROPHICATION OF RIVERS BY NUTRIENTS IN TREATED KRAFT MILL EFFLUENTS<br/>M.L. Bothwell</p> <p>2:00 - 2:30 REPRODUCTIVE DYSFUNCTION AND MFO ACTIVITY IN THREE SPECIES OF FISH EXPOSED TO BLEACHED KRAFT MILL EFFLUENT: IMPACT OF SECONDARY TREATMENT<br/>K.R. Munkittrick, G.J. Van Der Kraak, M.E. McMaster and C. Port</p> <p>2:30 - 3:00 ENVIRONMENTAL IMPACT OF PRIMARY-TREATED BLEACHED KRAFT MILL EFFLUENT: A CASE STUDY<br/>J.H. Carey, B.K. Burnison and P.V. Hodson</p> <p>3:00 - 3:30 COFFEE BREAK - MAIN MALL AREA</p> <p>3:30 - 4:00 IMPACT OF A MODERN BLEACHED KRAFT MILL WITH SECONDARY TREATMENT ON WHITE SUCKERS<br/>M. Servos, J.H. Carey, M. Ferguson, G. Van Der Kraak, H. Ferguson, J. Parrott, K. Gorman and R. Cowling</p> <p>4:00 - 4:30 <u>IN-VIVO</u> TESTING OF BKME EXTRACTS FOR TOXIC AND CARCINOGENIC EFFECTS TO RAINBOW TROUT (<u>ONCORHYNCHUS MYKISS</u>)<br/>M.E. Nanni, N.M. Sculls and C.D. Metcalfe</p> <p>4:30 - 5:00 MIXED FUNCTION OXIDASE INDUCTION POTENTIAL OF RESIN ACIDS<br/>M. Ferguson, M. Servos and K. Munkittrick</p> <p>5:00 - 5:30 ESTIMATING EFFLUENT TOXICITY FROM MOLECULAR-CHLORINE-GAS-FREE BLEACHING IN TERMS OF TOXICITY EQUIVALENCE<br/>M.F. Holoran, R.F. Wiles, M.J. Palmiere and D.G. Wilson</p> |
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**PROGRAM**

*Thursday, February 14, 1991 (a.m)*

**IMPACT OF POLLUTANTS ON  
AQUATIC ECOSYSTEMS**

**WATER POLLUTION CONTROL  
TECHNOLOGY**

**SESSION II - SOUTH SEMINAR ROOM**

**SESSION III - AUDITORIUM**

**PRESIDER:** C. Gray  
National Water Research Institute

**PRESIDER:** P. Laughton  
R.V. Anderson and Associates

**MODELLING THE IMPACT OF PULP AND PAPER MILL EFFLUENTS**

**WATER POLLUTION CONTROL TECHNOLOGY**

9:00 - 9:30 **PREDICTING FOOD CHAIN  
ACCUMULATION OF CHLORINATED  
DIOXINS AND FURANS**  
D.C.G. Muir and W.L. Fairchild

9:00 - 9:30 **FEASIBILITY OF RETROFITTING FOR  
BIOLOGICAL PHOSPHATE REMOVAL IN  
QUÉBEC**  
Y. Commeau, L. Raymond and Jean F. Riel

9:30 - 10:00 **AQUATIC FOOD CHAIN UPTAKE OF  
2,3,7,8-T<sub>4</sub>CDD**  
M.E. Starodub, E. Lopes and R.F. Wiles

9:30 - 10:00 **WASTEWATER CHARACTERIZATION FOR  
ACTIVATED SLUDGE MODELLING**  
J. Gibson and P.L. Dold

10:00 - 10:30 **MODELLING THE TRANSPORT AND FATE  
OF PERSISTENT ORGANIC COMPOUNDS  
IN THE AQUATIC ENVIRONMENT:  
APPROACHES TO MODELLING AND CASE  
STUDIES OF PCDD AND PCDF**  
M.F. Holoran and D.G. Wilson

10:00 - 10:30 **FACTORS AFFECTING DISPERSION OF  
ACTIVATED SLUDGE FLOCS**  
D. Li and J.J. Ganczarczyk

10:30 - 11:00 **COFFEE BREAK - MAIN MALL AREA**

10:30 - 11:00 **Coffee - Main Mall Area**

**PRESIDER:** E. McBean  
University of Waterloo

11:00 - 11:30 **FIELD VALIDATION OF THE 7-DAY  
FATHEAD AND CERIODAPHNIA SHORT-  
TERM CHRONIC TOXICITY PROTOCOLS  
FOR PREDICTING RECEIVING WATER  
IMPACTS OF PULP MILL EFFLUENTS**  
R.D. Robinson, J.H. Carey, K.R. Solomon,  
M.R. Servos, P.E. Kapteyn and P.V. Hodson.

**WASTE MANAGEMENT TECHNOLOGY**

11:00 - 11:30 **SELECTION CRITERIA OF APPROPRIATE  
SITES FOR ELIMINATION OF MUNICIPAL  
SOLID WASTE IN METROPOLITAN AREAS**  
M. Elekrowicz, J. Hadjicicolaou and R.N. Yong

**IMPACT OF POLLUTANTS ON AQUATIC ECOSYSTEMS**

11:30 - 12:00 **PREDICTIONS OF PCB CONTAMINATION IN  
LAKE ONTARIO SPORT FISH**  
D.R.S. Lean, W.A. Scheider, J.H. Carey and  
J.B. Rasmussen

11:30 - 12:00 **USE OF THE AERIS MODEL TO ASSESS  
RISKS ASSOCIATED WITH THE  
DECOMMISSIONING OF INDUSTRIAL SITES**  
K.R. Hosler, T.L. Bulman and T.W. Constable

12:00 - 12:30 **EFFECTS OF EROSION BY RAINFALL ON  
AGRICULTURAL RUNOFF WATER  
QUALITY**  
D. Couillard, J.F. Li

12:00 - 12:30 **WASTE REDUCTION PLANNING IN THE  
PETROLEUM AND PETROCHEMICAL  
INDUSTRY**  
H. Roberge and B.W. Baetz

12:30 - 1:30 **BUFFET LUNCHEON - MAIN MALL AREA**

12:30 - 1:30 **BUFFET LUNCHEON - MAIN MALL AREA**

**PROGRAM**

*Thursday, February 14, 1991 (p.m.)*

**IMPACT OF POLLUTANTS ON  
AQUATIC ECOSYSTEMS**

**WATER POLLUTION CONTROL  
TECHNOLOGY**

**SESSION II - SOUTH SEMINAR ROOM**

**PRESIDER:** M.N. Charlton  
National Water Research Institute

**POLLUTION ASSESSMENT AND REMEDIATION:**

**PROGRESS IN HAMILTON HARBOUR**

- 1:30 - 2:00 **COAL TAR IN HAMILTON HARBOUR**  
T. Murphy
- 2:00 - 2:30 **HAMILTON HARBOUR CLARITY  
RESPONSE TO NUTRIENT ABATEMENT**  
S. Painter
- 2:30 - 3:00 **SPATIAL VARIATION IN WATER QUALITY  
AND CONTAMINANTS IN HAMILTON  
HARBOUR**  
M. Charlton

3:00 - 3:30 **COFFEE BREAK - MAIN MALL AREA**

3:30 - 4:00 **ANNUAL LOADING OF PCBs AND PAHs  
FROM HAMILTON HARBOUR TO LAKE  
ONTARIO**  
M. Fox, R. Khan

4:00 - 4:30 **BIOLOGICAL SEDIMENT CRITERIA**  
T.Reynoldson

4:30 - 5:00 **FISH AND FISH HABITAT IN HAMILTON  
HARBOUR**  
C.K. Mirns and V. Cairns

5:00 - 7:00 **RECEPTION - CAFETERIA**

**SESSION III - AUDITORIUM**

**PRESIDER:** D. Averil  
Wastewater Technology Centre

**POTABLE WATER TECHNOLOGY**

1:30 - 2:00 **SIMULATION OF PARTICLE GROWTH  
KINETICS IN A SUPERSATURATED  
COAGULATION-FLOCCULATION SYSTEM**  
G.T. Eastwood, W.J. Snodgrass

2:00 - 2:30 **THE ANALYSIS OF  
N-NITROSODIMETHYAMINE IN WATER BY  
GAS CHROMATOGRAPHY-MASS  
SPECTROMETRY**  
R.L. Hong-You, P.S. Adah, P.J.A. Fowie

2:30 - 3:00 **SOURCE OF NDMA IN A WATER SUPPLY**  
P. Child

3:00 - 3:30 **COFFEE BREAK - MAIN MALL AREA**

**PRESIDER:** K. Murphy  
McMaster University

**WATER POLLUTION CONTROL TECHNOLOGY**

3:30 - 4:00 **GROUNDWATER CONTAMINATION BY  
TOXIC ORGANICS: THE CASE STUDY OF  
VILLE MERCIER, QUEBEC, CANADA**  
M. Halevy, R. Booth, J.W. Schmidt

4:00 - 4:30 **BACTERIAL LEACHING OF SLUDGE  
INACTIVATED BY COPPER SULPHATE**  
G. Henry, D. Prasad, A. Mavi

4:30 - 5:00 **SIMULTANEOUS MUNICIPAL SLUDGE  
DIGESTION AND MICROBIAL METAL  
LEACHING**  
R.D. Tyagi, J.F. Blais, and J.C. Auclair

5:00 - 7:00 **RECEPTION - CAFETERIA**

POSTER SESSION

1. **MODELLING THE ENVIRONMENTAL FATE OF 2,3,7,8-T4CDD INTRODUCED TO RECEIVING WATERS VIA PULP MILL EFFLUENTS**  
A. Sardella, M.E. Starodub, and R.F. Wiles
2. **BIOACCUMULATION OF HEAVY METALS IN *GAMMARUS FASCIATUS* (CRUSTACEA: AMPHIPODA) IN RELATION TO CONTAMINATION OF SEDIMENTS AND WATER CHEMISTRY.**  
Marc Amyot, Bernadette Pinel-Aloul and Peter G.C. Campbell
3. **A NEW METHOD FOR TESTING SOIL AND SEDIMENT SAMPLES**  
Anthony Bulch and Grace Scheibner
4. **DEGRADATION OF PHENOLS BY ALGAE**  
V. Klekner and N. Kosaric
5. **USE OF FLY ASH IN THE REMOVAL OF COPPER, NICKEL AND ZINC FROM WASTEWATER**  
M.M. Dronamraju and T. Viraraghavan
6. **APPLICATION OF ROBOTICS AND DATA QUALITY MONITORING/CONTROL TO REDUCE OPERATOR INTERVENTION IN AUTOMATED ION TESTING OF DRINKING WATER**  
Craig B. Ranger and Jean Wong-Chong
7. **COMPARAISON ENTRE LA CAPACITE DE BIOACCUMULATION DU MERCURE DES GASTEROPODES DE FAIBLE LONGEVITE ET DES PELECYPODES DE L'ESTUAIRE D'EAU DOUCE DU SAINTE-LAURENT**  
Louis Tessier, Guy Vaillancourt, and LeRoy Pazdernik
8. **EFFECT OF TILLAGE PRACTICES AND AGRICULTURAL IMPACTS ON WATER QUALITY IN EASTERN WASHINGTON**  
B. Danesh, B.C. Moore and W.H. Funk
9. **THE EFFECTS OF CONCENTRATED PULP MILL EFFLUENTS ON MIXED FUNCTION OXIDASE ACTIVITY (MFO) IN RAINBOW TROUT AS MEASURED BY 7-ETHOXYRESORUFIN-O-DEETHYLASE (EROD).**  
T.G. Williams, L.M. Hewitt, J.H. Carey, B.K. Burnison, J. Parrott, M.R. Servos, D.G. Dixon, K.R. Milar, V. Martin, and A. Rosner
10. **ISOLATION OF HIGH MOLECULAR WEIGHT ORGANICS FROM KRAFT MILL EFFLUENT BY NANOFILTRATION**  
Burnison, K., V. Martin, A. Rosner, M. Hewitt, K. Milar, and T. Williams

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## COMPREHENSIVE STUDY OF A BLEACHED KRAFT MILL SECONDARY TREATMENT SYSTEM

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Conventional secondary treatment systems used by bleach kraft mills in Canada have been designed to effectively lower suspended solids, biological oxygen demand and acute toxicity to meet regulated environment guidelines. These systems were not designed for removing organochlorines (measured as adsorbable organic halide; AOX) or chronic toxicity. Depending on the mill, using secondary treatment systems, the AOX removed is usually 5-30%, although some mills have reported up to 50%. These systems have not been examined for their potential to increase AOX removal.

A study was undertaken at the E.B. Eddy Forest Products Ltd. mill in Espanola, Ontario to profile the secondary treatment system from a physical, chemical, toxicological and microbiological perspective. This is a state-of-the-art mill, using BATEA technology, including oxygen delignification, and high chlorine dioxide substitution. The effluent treatment system consists of a primary clarifier, followed by a settling basin, two aeration cells in tandem (aerated stabilization basins) and a quiescent zone.

The fate and distribution of different AOX fractions, based on apparent molecular weight and hydrophobicity, was determined in various parts of the system. The results of the study demonstrated that the first cell of the aeration lagoon was responsible for most of the removal of AOX, biotoxicity, and BOD. Most microbial activity (based on cell counts and nutrient availability) was observed in Cell 1. Cell 2 was primarily responsible for the removal of suspended solids. There was no appreciable accumulation of organic sediment in the aeration lagoon, which has been in continuous operation since 1983. The effluent discharged from this state-of-the-art bleached kraft mill is one of the cleanest in the world, consistently surpassing all regulatory environmental parameters.

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# A BATCH STUDY OF THE AEROBIC AND ANAEROBIC REMOVAL OF CHLORINATED ORGANIC COMPOUNDS IN AN AERATED LAGOON

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Public concern about the environmental effects of the chlorinated organic compounds contained in bleached kraft pulp mill effluent has resulted in governmental regulations on their discharge and a search for improved treatment technologies.

At the present time, many kraft mills use aerated lagoons for the removal of biochemical oxygen demand (BOD) and suspended solids (TSS). In addition to the removal of BOD and TSS, aerated lagoons also remove a substantial fraction of chlorinated organic compounds, measured as adsorbable organic halogen (AOX). For example, in a recent study of an operating lagoon in Northern Ontario (Tomar and Allen, 1990) 30 to 40% of the AOX was removed across the lagoon. Despite the established capability of lagoons and other biological treatment systems to remove AOX, the mechanisms of the removal are poorly understood. Some researchers suggest that the major pathways for the removal of AOX in an aerated lagoon include biosorption in the aerobic zone with subsequent deposition into the benthic layer, followed by anaerobic degradation and dehalogenation within the anaerobic zone. Of particular relevance is the relatively long residence time that compounds would spend in the benthic region.

The objectives of this study were to determine: 1) the relative significance of aerobic and anaerobic processes on AOX removal in an operating lagoon; 2) whether or not dehalogenation of AOX occurs; and 3) if decomposition of high molecular weight chlorinated organic compounds takes place in the lagoon.

Two phases of batch experiments, aerobic and anaerobic, have been conducted at temperatures of 20 and 30 C. The materials used were bleached kraft mill effluent collected after the clarifier and sludge from an existing lagoon located in Dryden, ON. Enough wastewater was collected for all experiments and was stored frozen until it was used. Fresh sludge was collected before each experiment and kept cool during transportation (1 or 2 days). Viability studies of the sludge were done before and after each experiment using the dehydrogenase enzyme method. Wastewater and sludge were mixed in proportions to achieve mixed liquor volatile suspended solids concentrations (VSS) of approximately 3000 mg/L. Aerobic experiments were run at approximately the same residence time as that in the lagoon (10 days) and anaerobic experiments were run for 40 days. In order to assess the significance of non-biological removal processes (stripping, sedimentation and chemical reactions) the experiments were also conducted in control reactors, which contained no biomass.

After each experiment, the liquid was separated from the solids and samples of wastewater were analyzed for total (<1.2 $\mu$ m) AOX and low molecular weight (<1000 daltons) AOX using a Mitsubishi Total Halogen Analyzer. The low molecular weight

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fraction was separated using ultrafiltration. Sludge samples were analyzed for organically-bound chlorine using neutron activation analyses (NAA). Total chlorine concentration was determined by NAA in both the liquid and solid phases.

Preliminary results indicate that AOX removal at anaerobic conditions is higher than at aerobic conditions (70 and 56% respectively). Removal in the control reactors was approximately one third of the removal observed during treatment with biomass. There was no significant difference in the AOX concentration in the liquid phase over time during the anaerobic experiment after 10 days of incubation. Over the course of the aerobic experiment the amount of organically-bound chlorine in the sludge increased slightly. In the anaerobic experiment a slight decrease in sludge-bound chlorine was observed. In either case, the change in sludge-bound chlorine was not statistically significant and could not account for the removal of AOX from the liquid phase. Total chlorine concentration was also constant during the experiments. Further analysis will be available during the presentation and the directions of future research will be discussed.

## ANAEROBIC AND AEROBIC TREATABILITY OF HIGH-YIELD SULPHITE SPENT LIQUOR

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Many integrated newsprint mills in Canada employ sodium base high-yield and ultra-high-yield sulphite pulping. Very few of these mills recover the spent sulphite cooking liquor (SSL) and none practice external effluent treatment. Consequently, mill discharges contain a substantial load of dissolved organics and toxicity, comprised mainly of lignosulphonates, wood sugars and extractives. Secondary treatment appears to be the least-cost approach for meeting increasingly stringent effluent discharge regulations. However, availability of essential information on the composition and treatability of higher-yield sulphite spent liquors is limited.

The Wastewater Technology Centre (WTC) has conducted a preliminary investigation on the chemical characteristics and batch treatability of SSL, to determine the technical suitability of anaerobic and aerobic biotreatment technologies. Samples of digester spent liquor from both a high-yield sulphite (HYS; 70% pulp yield) and an ultra-high-yield sulphite mill (UHYS; 90% yield) were tested.

HYS waste liquor contained 79 g/L of total solids (TS), with corresponding COD (soluble) and BOD<sub>5</sub> (total) concentrations of 73 g/L and 26 g/L, respectively. The total sulphur content was 14 g/L, including 5.1 g/L of SO<sub>4</sub>-S and 4.8 g/L of SO<sub>3</sub>-S. Spent liquor from the UHYS process was less concentrated (i.e., 32 g TS/L, 36 g COD/L, 9.8 g BOD<sub>5</sub>/L, 3.6 g/L total sulphur, 1.8 g SO<sub>4</sub>-S/L and 1.3 g SO<sub>3</sub>-S/L), owing to an inherently lower degree of chemical treatment and wood solubilization. Dilution of both high-strength SSL samples was required prior to biological treatment. Comparative assessments of anaerobic and aerobic treatability were made using batch bioassays at SSL concentrations of 5, 10, 15 and 20% (v/v).

Anaerobic serum bottle tests indicated considerable toxic effects of HYS and UHYS spent liquors on the unacclimated biomass. Treatment efficiencies decreased and inhibition of methane production worsened as bioassay concentrations of SSL increased within the 5-20% v/v range. Severe inhibitory effects on the rate of methane production were exhibited by both waste liquors at volumetric concentrations as low as 5%. Furthermore, despite this 20-fold dilution, only moderate treatment efficiencies were obtained for HYS spent liquor over a 70-day incubation period. Removals of soluble BOD<sub>5</sub>, COD and DOC were 75%, 30% and 30%, respectively. A low methane yield of 0.06 L/g COD removed, was presumably due to a high degree of biological sulphur reduction. Observed SO<sub>4</sub> and SO<sub>3</sub> reductions were >99% and 70%, respectively. A somewhat better performance was achieved with UHYS waste liquor, as indicated by the 70% BOD<sub>5</sub> (soluble), 50% COD (soluble) and 45% DOC removals from 10% v/v samples incubated for 75 days. The methane yield was 0.13 L/g COD removed.

Toxic effects of SSL on the anaerobic process were most likely attributable to the elevated levels of inorganic sulphur, particularly sulphite. An extreme example was the negligible degree of anaerobic activity observed at HYS spent liquor concentrations of 15% and 20% v/v (i.e., BOD<sub>5</sub> removal, sulphur reduction, organic acid formation as well as biogas

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production were all virtually completely inhibited). It is noteworthy however, that although the batch experimental results have indicated potential difficulties in anaerobically treating higher-yield sulphite spent liquors, it is possible that acclimated continuous-flow systems could attain improved treatment efficiencies as well as lower SSL dilution requirements.

Aerobic bioassays, which involved a 20-day batch treatment of diluted HYS and UHYS spent liquors, revealed a high degree of treatability. Reductions of BOD<sub>5</sub> (soluble), COD (soluble) and DOC in the HYS waste liquor were >98%, 60-65% and 55-60%, respectively. Even higher treatment efficiencies were obtained for UHYS spent liquor, including removals of >98% BOD<sub>5</sub>, 70-75% COD and 70-75% DOC. Aerobic treatment effectively reduced resin and fatty acid concentrations to non-detectable levels in both HYS and UHYS spent liquors. Furthermore, these high aerobic treatment efficiencies were obtained at all HYS and UHYS waste liquor concentrations tested (i.e., 5-20% v/v), in contrast to the poorer dilution-dependent performances with the anaerobic bioassays.

# APPLICATION OF BIOLOGICAL AERATED FILTERS FOR INDUSTRIAL WASTEWATER TREATMENT

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The Biological Aerated Filter is a high rate, fixed film, wastewater treatment system. The process is capable of removing both soluble and suspended organic material from wastewater. The media provides a surface for the growth of microorganisms which assimilate the organic matter in the wastewater, municipal or industrial. Air is introduced directly in the packed bed, providing oxygen for biological growth. Excess biological growth and trapped suspended solids are removed from the bed by periodic backwashing of the entire media with treated effluent.

While most of the European and Canadian operating experiences with the biological aerated filter process are with domestic wastewaters, several operational facilities, treating industrial effluents exists in Japan. The Japanese technology has been put to use for a variety of industrial effluents, including the following:

| Type of industry                | Operational facilities | Inlet BOD (mg/L) |
|---------------------------------|------------------------|------------------|
| Food processing                 | 53                     | 300 - 6000       |
| Chemicals and<br>Pharmaceutical | 29                     | 20 - 4200        |
| Textile & Dyeing                | 13                     | 10 - 6200        |
| Pulp and Paper                  | 14                     | 100 - 3000       |

The first installation in the pulp and paper industry was made in November 1983, followed by some fourteen operational facilities up to 1990 plus two in design stage. The biggest biological aerated filter installation treats some 150 000 m<sup>3</sup> of flow per day, and 23 000 kg of BOD per day. The range of BOD levels treated by these operational facilities is very wide, starting from 100 mg/L and going as high as 1400 mg/L. The removal efficiencies obtained are in accordance with the individual discharge requirements for each mill and cover the range of 60 % to 92 %. A fixed film wastewater treatment system, such as the biological aerated filter, usually allows specific design for the precise removal efficiency needed. The Japanese operational facilities are treating wastewaters produced by different type of mills including: used paper, bleached kraft, deinked pulp and unbleached kraft. The strongest wastewater is the fouled condensate which originates from the pulp manufacturing stripping

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process. The levels of suspended solids acceptable by the biological aerated filter vary from 10 mg/L to 500 mg/L, indicating a good tolerance to eventual accidental spills.

The retention time (EBCT = empty bed contact time) in the operational facilities varies from 1 hour to 2.5 hours with the exception of the biofilter treating the fouled condensate wastewaters (20 hours). Depending on the effluent requirements, the design organic loadings cover the range of 2 to 7 kg BOD per m<sup>3</sup> of media.

The presence of chlorinated organics in bleached kraft mill wastewaters has become a major challenge for the Canadian pulp and paper industry and the heart of the new federal and provincial regulations. The reported removal efficiencies by the conventional processes varies from 34 % (ASB) to 43 % (activated sludge). Several researchers believe that a better secondary effluent treatment can be part of the solution to higher AOX removal. At one of the Japanese operational facilities (ECBT = 1 hour) AOX removal efficiency was measured to be 30 %. Laboratory work indicates however that biofiltration will be able to achieve at least 57 % AOX removal efficiency, provided a design with lower BOD loadings. It is believed also that a final treated effluent of 50/50 (BOD/SS) will be non toxic in accordance with the new federal regulations.

## FATE AND EFFECT OF RESIN ACIDS IN BIOLOGICAL ASSAYS

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The behaviour of resin acids, a key group of toxic constituents found in Chemithermomechanical pulping (CTMP) wastewaters, was studied in batch anaerobic and aerobic biodegradation assays. Methanol (6000 mg COD/L) was added to the assays to act as both a solvent for the resin acids and as a substrate for the assay inoculum. Three anaerobic biomass concentrations (1100 to 10600 mg VSS/L) and two aerobic biomass concentrations (1300 and 5000 mg VSS/L) were studied at high and low resin acid levels (from 22 to 265 mg/L).

The anaerobic biomass was found to be incapable of degrading the resin acids over the course of a two-week assay. The aerobic biomass reduced the resin acids to non-detect levels in two to three days. The time required to aerobically reduce the resin acids to non-detect levels was slightly longer when the concentration of resin acids was increased five-fold. However, the time required for resin acid removal was independent of aerobic biomass concentration. The presence of resin acids did not measurably alter the biomass concentration in the aerobic batch tests completed.

Resin acids were inhibitory to unacclimated anaerobic methanogenic bacteria under batch test conditions. The extent of inhibition increased at higher resin acid concentrations and at lower anaerobic biomass concentrations. There appeared to be a threshold resin acid concentration below which no inhibition was apparent at high biomass concentrations.

These results may have several implications for full scale biological treatment system selection. Since biogas production was not inhibited at high anaerobic biomass levels, high rate anaerobic systems for BOD removal may be suitable in pre-treatment applications. Under aerobic conditions, time appeared to be a more critical factor for resin acid biodegradation, than biomass concentration. This might suggest that there would be no advantage to the selection of a short retention time, high biomass aerobic treatment system such as an activated sludge process. The longer retention times provided by aerobic stabilization basin systems may be adequate for resin acid removal. The batch tests indicated that a five-fold increase in initial resin acid concentrations required only 30% more treatment time. This suggests that small changes in the influent resin acid concentrations should not adversely affect treated effluent quality.

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## A BIOLOGICAL AND CHEMICAL CHARACTERIZATION OF NEWSPRINT/SPECIALTY MILL EFFLUENTS

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A biological and chemical characterization of primary-treated and secondary-treated effluents from Canadian newsprint/specialty mills was completed. Biological characterization included acute lethal toxicity tests with rainbow trout, fathead minnow, *Ceriodaphnia*; sublethal tests examining effects on minnow growth and *Ceriodaphnia* reproduction; and microbiological tests with *Photobacterium phosphoreum* (Microtox) and *Selenastrum capricornutum*. Chemical characterization involved chemical analysis of the effluents for conventional environmental parameters (e.g., COD, BOD) and wood extractives (e.g., resin and fatty acids). The acute lethal toxicity of the primary-treated effluents, expressed as LC<sub>50</sub>s, ranged from approximately 5% to 50%. For the same effluents, the reproduction of *Ceriodaphnia* was found to be the most sensitive sublethal endpoint. The concentrations of wood extractives in the effluents correlated well with acute lethal toxicity, but could not fully explain all toxic effects. Conventional secondary-treatment was found to eliminate acute lethal toxicity and substantially reduce sublethal effects, conventional environmental parameters and wood extractives.

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## EUTOPHICATION OF RIVERS BY NUTRIENTS IN TREATED KRAFT MILL EFFLUENTS

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The nitrogen and phosphorus content of kraft pulp mill effluents (KME) which have been secondarily treated in extended aeration lagoons can cause algal blooms in receiving rivers. In some cases the increases in primary production have been large enough to alter the trophic structure of the river ecosystem. However, the role of pulp mill effluents in the eutrophication of rivers is not widely appreciated. In part, this is because of the common misconception that concentrations of nutrients must be greatly elevated to have a measurable impact on algal production.

In 1972 the start up of a 1200 ADT/day bleached kraft pulp mill in Kamloops, British Columbia resulted in a massive increase in algal standing crop in the Thompson River below Kamloops Lake. While phosphorus loading from the pulp mill was believed to be responsible for this change, the actual measured elevation in phosphorus concentration downstream of the discharge was below the detection limit (3 ppb P) of the analytical procedure used in the joint Federal-Provincial Task Force Study of the Thompson River in 1973-75. Research at Environment Canada's Experimental Troughs Apparatus (EXTRA) located at Chase, B.C., has now proven that the ambient concentrations of phosphorus required to saturate the specific growth rates of attached diatom communities with a concomitant increase in algal standing crop are very low (ca. 1 ppb). Hence, although the concentration of dissolved phosphorus in fully treated KME mill effluents is typically only around 0.55 ppm (ca. 1 ppm total phosphorus), even at in-river dilutions of 100:1 the steady-state elevation of soluble phosphorus is high enough to greatly stimulate algal production in rivers which are phosphorus-limited.

Likewise, in rivers that are nitrogen-limited, nitrogen in fully treated KME stimulates in algal production. The atomic N:P ratio in the McKenzie River, Oregon, is ca.1:1 indicating a clearly nitrogen-limited system. The discharge of treated KME to this river near Springfield, Oregon resulted in a great increase in algal production. Stream-side flume experiments measuring the effect of treated KME additions on algal growth have shown that the concentrations of ammonia-N (0.1-0.1 ppm) and nitrate-N (0.05-0.1 ppm) in KME are enough to increase specific growth rates from 0.3 to 0.63 divisions/day during the summer, even when the effluent is completely mixed in the river (dilution 100:1). At other seasons of the year, lower temperatures and light levels combined with greater dilution prevent nitrogen stimulation from having a significant impact on algal growth rates in the river as a whole.

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# REPRODUCTIVE DYSFUNCTION AND MFO ACTIVITY IN THREE SPECIES OF FISH EXPOSED TO BLEACHED KRAFT MILL EFFLUENT: IMPACT OF SECONDARY TREATMENT.

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Pulp mills are the single largest producer of effluent in Ontario, and the Canadian side of the Great Lakes is the receiver for effluent from 19 pulp mills. Within the Great Lakes, increased levels of hepatic enzyme (MFO) activity have been found in fish collected at Thunder Bay (GLFP), Cornwall, Terrace Bay, Marathon, and Espanola, as well as at pulp mills in Quebec and B.C.. Jackfish Bay, Lake Superior has been identified as an area of concern by the IJC, due to the presence of a 1200 ADMT bleached kraft mill at Terrace Bay. This mill releases approximately 120,000 m<sup>3</sup> d<sup>-1</sup> of bleached kraft mill effluent (BKME) into Blackbird Creek, which takes the effluent 15 km to Jackfish Bay. Up until the initiation of secondary treatment in October of 1989, Jackfish Bay had received the primary-treated effluent for 40 years. Studies conducted during 1988 and 1989 were completed prior to the initiation of secondary treatment, and present studies are characterizing changes in the fish populations during ecosystem recovery and attempting to document the impacts of BKME on fish performance.

Over the past 3 years, we have found increased levels of hepatic MFO activity in white sucker (20-fold), longnose sucker (16-fold), lake whitefish (8-fold) and lake trout (12-fold) collected from Jackfish Bay. MFO activity levels, measured as EROD or PPO, have not declined detectably since the initiation of secondary treatment. Steroid levels have been examined in three species of fish (white and longnose sucker and lake whitefish), and fish exposed to the pulp mill effluent have significantly lower levels of steroid hormones, reduced secondary sexual characteristics and dramatic increases in age to maturity. Fewer than 10% of lake whitefish captured in 1990 were sexually mature, while white sucker show a 2 to 4 year delay in maturity. Longnose sucker show no changes in gonadal size, but females steroid levels are 30% of reference fish. Our 1990 studies have demonstrated impacts of BKME at multiple sites in the hypothalamic-pituitary-gonadal axis. Although previous hypotheses relating to impacts of lipophilic contaminants on reproduction related to the possible impacts of elevated MFO activity on circulating steroid levels, our evidence strongly suggests that the phenomena of induced MFO activity and dysfunction of the h-p-g axis are acting independently.

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## ENVIRONMENTAL IMPACT OF PRIMARY-TREATED BLEACHED KRAFT MILL EFFLUENT: A CASE STUDY

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Recently, the presence of organochlorine compounds in effluents from pulp mills has come under scrutiny and a number of regulatory authorities have come under pressure to limit the discharge of organically-bound chlorine, commonly expressed as AOX (absorbable organic halogen).

Much of the current concern about the discharge of chlorinated organic material from pulp mills stems from the results of the Environment/Cellulose Project established in 1982 by the Swedish National Environment Protection Board. The studies under that project examined the biological/ecological, pathological, and physiological impacts of bleached kraft mill effluent on the Gulf of Bothnia and observed a number of effects. The applicability of the Swedish results to the North American situation has been questioned. Factors which are cited are: (i) that unique aspects of the Gulf of Bothnia, such as salinity variations, historical pollution, other contaminant sources and low flushing rate, make it a poor model for other water bodies; (ii) that the mill had no effluent treatment and mill operations were not representative a normally operating North American pulp mill; and (iii) that no cause-effect links were demonstrated to implicate chlorinated organics as causative agents.

In order to provide a Canadian perspective to this dispute, a collaborative, multi-agency project into the aquatic fate and effects of chlorinated organic material in effluents from Canadian pulp mills was begun in 1988. The first phase of the project involved a field study of the environmental impacts of a bleached kraft mills employing older bleaching practices and minimal effluent treatment. An examination of white sucker (Catostomus commersoni) and northern pike (Esox lucius) from the river indicated that a variety of effects similar to those observed in Sweden were present. However, the geographical distribution of these effects did not correlate well with the persistence of AOX in the river, suggesting that AOX is of limited utility as a predictor of the "Swedish-style" responses.

A number of the components of Environment Canada's proposed Environmental Effects Monitoring (EEM) Program for pulp mills were incorporated in the study design to evaluate their utility. The results of this partial 'case study' will be discussed.

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## IMPACT OF A MODERN BLEACHED KRAFT MILL WITH SECONDARY TREATMENT ON WHITE SUCKERS

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The environmental impact of bleached kraft mill effluent (BKME) has been widely reported. Untreated BKME is often acutely toxic to fish and numerous impacts on fish communities in the receiving waters have been observed. A variety of process changes (e.g., chlorine dioxide substitution) and secondary treatment of the effluent can dramatically alter the chemical composition of the final effluent. Secondary treatment can reduce the adsorbable organic halide (AOX) by more than 50% and eliminate acute and even sublethal toxicity (i.e., fathead minnow growth and survival). However, modernization of bleaching processes and installation of secondary treatment does not guarantee the elimination of impacts on the aquatic community in the receiving waters. The characteristics of the receiving waters, particularly the dilution ratio, must be considered as an additional factor modifying toxicity.

In this study, the impact of a modern bleached kraft mill, utilizing oxygen prebleaching, chlorine dioxide substitution, and secondary treatment (aerated lagoon), on the Spanish River was examined. Even though the mill produces <1 kg AOX/air dried metric tonne (ADMT) of pulp the dilution ratio at low flow is only 10:1 resulting in an AOX concentration in the receiving waters of approximately 0.2 mg/L. This value is similar to AOX concentration measured in the St. Maurice River which receives primary treated effluent from a mill producing >8 kg AOX/ADMT of pulp. A significant response of white suckers downstream of the mill has been observed in the St. Maurice River other researchers.

In early August, 1990, 14 to 30 live white sucker were collected at each of two sites upstream and three sites (2, 28, 51 km) downstream of the outfall. Each fish was examined for gross pathology, several condition indices, haematocrit, blood chemistry including sex steroids, and liver enzyme activity (ethoxyresorufin-o-deethylase). Selected samples also underwent histopathological examination of liver, gill, kidney, spleen, heart, muscle and gonad. There were no obvious differences between the upstream and downstream fish in condition factor or haematocrit and there were no unusual histopathological abnormalities. The liver somatic indices of male and female fish were 24 and 14% higher, respectively, in fish collected downstream. This effect was most pronounced at the site immediately below the outfall. EROD activity was 3 to 6 fold higher in downstream fish and this response persisted even 51 km downstream. This result is consistent with the minimal reduction of AOX observed in the river water. The removal of chlorophenolics from the receiving waters downstream of the outfall will also be described and related to the effects observed in the fish.

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## IN VIVO TESTING OF BKME EXTRACTS FOR TOXIC AND CARCINOGENIC EFFECTS TO RAINBOW TROUT (ONCORHYNCHUS MYKISS)

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In this study, "grab" samples of bleached kraft mill effluent (BKME) were filtered through a 0.3 m glass fibre filter to remove suspended solids which otherwise inhibited flow rates through the chromatography columns. The filters were then Soxhlet extracted into methanol. The filtered effluent was extracted using the macroreticular resins XAD-4 (non-polar to medium polarity) and XAD-7 (polar). Non-polar to medium polarity compounds were eluted from XAD-4 with diethyl ether while the polar compounds were eluted from XAD-7 with methanol. These extracts; 1) XAD-4, 2) XAD-7, and 3) Filter, are being used for intraperitoneal injections of rainbow trout to determine toxicological responses to these classes of BKME compounds.

Chronic as well as acute exposures of fish to BKME induce P450 dependent-monoxygenases. The effluent extracts are currently being tested for ability to induce the monoxygenases, aryl hydrocarbon hydroxylase (AHH) and 7-ethoxyresorufin-o-deethylase (EROD) in trout liver. Preliminary data indicate that both of the XAD extracts induce monoxygenase activity, but the XAD-4 extract has greater inductive potency.

Proliferation of hepatocytic microbodies which resemble peroxisomes have been observed by TEM in trout exposed to the XAD-4 extract, and a positive control compound, diethylhexyl phthalate (DEHP). Chronic exposure of rodents to compounds that induce peroxisome proliferation has been correlated with the development of hepatic tumours. Similar carcinogenic mechanisms may occur in fish species. Hepatic catalase activity resulting from the proliferation of peroxisomes may be a useful indicator of chronic exposure to BKME. In vivo bioassays with rainbow trout are currently being used to determine catalase activity.

These studies are being conducted in association with in vivo carcinogenicity assays of BKME extracts using the rainbow trout model. There are field data which indicate that BKME are carcinogenic to bottom-dwelling fish species in Lake Superior and off the coast of Japan. These assays are designed to test for carcinogenic activity of extracts, as well as the promotional activity of the extracts after exposure to a known carcinogen, aflatoxin B<sub>1</sub>. These studies will indicate whether BKME are carcinogenic, and will also provide insight into the mechanisms of carcinogenicity and/or toxicity in fish chronically exposed to these effluents.

Keywords: BKME, AHH, EROD, peroxisomes, carcinogenicity

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## MIXED FUNCTION OXIDASE INDUCTION POTENTIAL OF RESIN ACIDS

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Recent studies have demonstrated the induction of mixed function oxidases (MFOs) in native fish populations downstream of kraft pulp mills. Although the chemicals responsible for this induction have not yet been identified, dioxin/furans have been cited as the most likely contaminants causing this response. However, the concentrations of dioxins and furans are usually several orders of magnitude lower than other components in the effluent. Relatively high concentration of resin acids have been reported in both untreated effluent and receiving waters. Resin acids are responsible for a large proportion of the acute toxicity reported in untreated BKME. A recent study has also reported resin acids as potential inducers of MFO activity, i.e. ethoxyresorufin-o-deethylase (EROD). If this can be verified it will have important management and regulatory implications.

This study was designed to test the EROD induction potential of resin acids in rainbow trout. A mixture of ten resin acids (pimaric, sandaracopimaric, isopimaric, palustric, dehydroabietic, abietic, neoabietic, 12-chlorodehydroabietic, 14-chlorodehydroabietic, 12,14-dichlorodehydroabietic) were injected i.p. at 3.7 or 37 mg/kg each. Six fish were sacrificed after 4, 8 and 16 days, the livers were excised, weighed and then assayed for EROD activity. The same mixture of resin acids was also used for a water borne exposure of fish to a nominal concentration of 10 ug/L of each individual component. Fish were again sacrificed at 4, 8 and 16 days. The concentration of each resin acid component in the water was monitored every second day during the experiments. A separate group of fish were injected i.p. with B-naphthaflavone (BNF) at 0.1 mg/kg to act as a positive control. Additional experiments were conducted using i.p. injections of abietic and dehydroabietic acid at 1, 10 and 50 ug/kg and fish were sacrificed at 2, 4 and 10 days.

Injection of BNF at only 0.1 mg/kg resulted in induction of EROD activity. However, exposure of fish to 50 mg/kg abietic or dehydroabietic acid did not induce EROD activity. Neither exposure to 370 mg/kg (total) resin acid mixture administered i.p. or exposure to 10 ug/L via water over 16 days resulted in EROD induction. Fish injected i.p. at the high dose were discoloured and lethargic but appeared to recover by day 16. Under the experimental conditions of this study, the mixture of ten resin acids did not cause a significant induction of the EROD activity.

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## ESTIMATING EFFLUENT TOXICITY FROM MOLECULAR-CHLORINE-GAS-FREE BLEACHING IN TERMS OF TOXICITY EQUIVALENCE

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A procedure for characterizing mill effluent toxicity in terms of toxic equivalence based on pentachlorophenol (pcp), resin acids, and fatty acids was developed. The procedure is similar to the classification of dioxin and furan congeners in terms of their 2,3,7,8, TCDD equivalence. The procedure was used to estimate the toxic equivalence of bleaching effluent from molecular-chlorine-gas-free bleaching of hardwood and softwood. Lab scale pulping and bleaching trials were conducted to simulate MCC cooking, oxygen delignification, and  $D_{100}E_{PO}D_N$  bleaching of hardwood and softwood to market brightness. The results obtained demonstrated a reduction in AOX, and a far greater reduction in toxic equivalence in combined acid and alkaline filtrates from the molecular-chlorine-gas-free bleaching sequence compared to data from conventional cooking and bleaching processes. Untreated mill effluent is predicted to be non acutely toxic, secondary treated mill effluent is predicted to be non-chronically toxic based on chlorophenolic, resin acid, and fatty acid toxicity equivalence. The value of AOX as a meaningful regulatory parameter for the protection of receiving waters is questioned.

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# PREDICTING FOOD CHAIN ACCUMULATION OF CHLORINATED DIOXINS AND FURANS

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The contamination of fish and invertebrates with 2,3,7,8-tetrachlorobibenzo-p-dioxin (TCDD) and dibenzofuran (TCDF) near bleached kraft mills has been documented in recent surveys by Fisheries and Oceans and Environment Canada (Whittle 1990; Harding 1990). These findings have prompted the questions such as, what is the pathway of the contaminants from effluent to the fish, and can observed TCDD/TCDF concentrations in biota be predicated from concentrations in the mill effluent?

Food chain transfer is generally recognized as the most important pathway of accumulation of most hydrophobic organochlorine pollutants, such as PCBs and 2,3,7,8-substituted chlorinated dioxins (PCDDs) and furans (PCDFs), in fish. Models have been developed to predict accumulation of hydrophobic pollutants in Great Lakes pelagic food chains (Thomann, 1981) and in riverine ecosystems (Connolly and Tonelli 1985). These models require reliable data on assimilation efficiency from food and elimination rates, along with information on growth, feeding relationships, water and sediment concentrations, to predict levels in fish. This presentation will describe our research to develop pharmacokinetic data on PCDD/PCDF uptake and elimination by fish and invertebrates, particularly 2,3,7,8-TCDF, and the use of a simplified Thomann/Connolly model to predict contamination of fish near Canadian bleached kraft mills.

The assimilation from food and the elimination of 2,3,7,8-TCDF by rainbow trout was studied by feeding food treated at 0.36, 3.6, 7.2 and 43 ng g<sup>-1</sup> concentrations daily for 30 days followed by a 180 day clearance phase. Half-lives of elimination of TCDF ranged from 58 to 69 days, and assimilation efficiency from 54 to 69%. When combined with data from other PCDD/PCDF congeners, the results indicate that assimilation efficiency and elimination rates are negatively correlated with log K<sub>ow</sub> of PCDD/PCDF. This empirical relationship may prove useful in modelling the food chain dynamics of these compounds.

Bioaccumulation of TCDF in lower food chain organisms was studied under field conditions using lake enclosures (5 m diameter x 2 m depth) in the littoral zone of a small oligotrophic lake at the Experimental Lakes Area in northwestern Ontario. TCDF was added to the enclosures sorbed to small quantities of bottom sediment. Sediment concentrations of about 20 pg g<sup>-1</sup> (dry wt) TCDF were achieved and remained relatively constant for a 100 day period after treatment. Dissolved concentrations of TCDF in the water column and in sediment pore waters were <10% of total TCDF because most of the compound was associated with dissolved and particulate organic carbon. Bioavailability indices (BI; concentration in organism on a lipid basis/concentration in sediment organic carbon) ranged from 0.07 for *Hexagenia*, to 0.35 for chironimids and 1.63 for crayfish. BI's ≥ 1 suggest similar assimilation efficiencies and half-lives to those observed in fish. Ingestion of particulates and assimilation of sorbed TCDF appeared to be the major pathway of exposure of the benthic organisms.

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The bioaccumulation data for benthic organisms and pharmacokinetic data for fish for 2,3,7,8-TCDF were used to predict concentrations of TCDF in fish near bleached kraft pulp mills at sites in Alberta and British Columbia. A steady state version of the food chain model of Thomann (1981) was used. Effluent concentrations from the 1988 CPPA survey and average annual flows were used to generate concentrations in water and on particles. TCDF concentrations on particulates available to benthic organisms were assumed to be in equilibrium with dissolved concentrations in the receiving waters after dilution of the mill effluent. Despite these simplifying assumptions results indicated good agreement between predicted and observed levels in fish downstream from bleached kraft mills.

In conclusion, knowledge of the pathways, rates and efficiencies by which sediment-sorbed PCDD/PCDFs are transferred to lower food chain organisms is critical to predicting the food chain accumulation of these compounds. A simplified food chain model adequately predicted levels in fish near Canadian pulp mills from 1988 effluent data. Recent reductions in emissions of TCDD/TCDF may require the use of non-steady state models where river sediments are the only major source of the contaminants.

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## AQUATIC FOOD CHAIN UPTAKE OF 2,3,7,8-T4CDD

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Aquatic food chain uptake of 2,3,7,8-T4CDD resulting from bleached kraft pulp mill effluents discharged to two river systems, Rainy River and Athabasca River, was modelled using the Age-Dependent Food Chain Model developed by HydroQual (1988) as updated by Connolly (1990). Unlike earlier simplified food chain models the Age-Dependent Food Chain Model predicts changes in chemical body burdens with respect changes in age-class due to bioenergetics and predator-prey interactions for aquatic species modelled. Steady state environmental concentrations of 2,3,7,8-T4CDD in the water column and benthic sediments estimated by EXAMS for the Rainy River and Athabasca River systems, under average flow conditions, receiving a constant 2,3,7,8-T4CDD loading rate, representative of the estimated 2,3,7,8-T4CDD discharged by local pulp mills, were input to the food chain model. Age-dependent 2,3,7,8-T4CDD whole body concentrations were predicted for aquatic organisms inhabiting river waters downstream of pulp mill outfall(s); predicted 2,3,7,8-T4CDD body burdens were compared with site specific field data. The aquatic species modelled were: phytoplankton, benthic invertebrates, polychaete, clam, crayfish, *Mysis relicta* (a freshwater shrimp), perch, bottom feeding fish, pike and lake trout.

The results of the Age-Dependent Food Chain Model demonstrated the propensity of 2,3,7,8-T4CDD to accumulate in biological tissues to concentrations greater than the corresponding environmental concentrations and the importance of food as the predominant exposure route. Predicted concentrations of 2,3,7,8-T4CDD in the aquatic species modelled related to the environmental concentration, predator-prey interactions, predator growth rates and the percent lipid content of the organism. Body burdens of 2,3,7,8-T4CDD in fish tended to be the highest in the early age classes, followed by a decrease in 2,3,7,8-T4CDD concentrations. Then a gradual increase which leveled off in the older age classes. Good agreement was observed between the results of the Age-Dependent Food Chain Model and concentrations of 2,3,7,8-T4CDD detected in Northern Pike and Sucker collected from the Rainy River and Athabasca River near bleached kraft pulp mills.

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# MODELLING THE TRANSPORT AND FATE OF PERSISTENT ORGANIC COMPOUNDS IN THE AQUATIC ENVIRONMENT: APPROACHES TO MODELLING, AND CASE STUDIES OF PCDD, AND PCDF

M.F. Holloran<sup>1</sup> and D.G. Wilson<sup>1</sup>

Estimating the body burden of persistent organic compounds through food web uptake requires knowledge of the appropriate physical transport mechanisms, reaction pathways, and reaction kinetics, as well as the food chain interactions. Approaches have typically involved mixed time dependent, and steady state analyses of hydrodynamic, water quality and food web interactions. In this paper the rationale for model selection is examined. The extremes of approach are investigated in the context of aquatic food web body burden estimates of 2,3,7,8, TCDD and 2,3,7,8, TCDF in Howe Sound on the west coast of British Columbia, and in the Athabasca River Basin of Northern Alberta. For Howe Sound, results obtained from complex time dependent hydrodynamic, water quality and food web modelling are compared to results obtained from simplified steady state water quality and food web models. For the Athabasca River, results from time dependent water quality and food web modelling are compared to results from steady state modelling. Recommendations are made on the use and applicability of the various approaches to modelling persistent organic compounds.

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**FIELD VALIDATION OF THE ENVIRONMENT CANADA 7-DAY FATHEAD  
AND CERIODAPHNIA SHORT-TERM CHRONIC TOXICITY PROTOCOLS  
FOR PREDICTING RECEIVING WATER IMPACTS OF PULP MILL EFFLUENTS.**

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P.E. Kapteyn<sup>1</sup>, and P.V. Hodson<sup>4</sup>

In July, 1991, new national regulations to restrict effluent discharge by Canadian pulp and paper operations will come into effect under authority of the Fisheries Act and the Canadian Environmental Protection Act. The regulations will require routine monitoring of effluent sublethal toxicity. In support of the proposed regulations, the Canadian government initiated a program in 1988 to develop standardized biological test methods (i.e., aquatic bioassays) to predict the sublethal toxicity of pulp and paper effluents to receiving water species. At present, the Canadian versions of the "Test of larval growth and survival using fathead minnows" and the "Test of survival and fecundity using *Ceriodaphnia*" are in final draft form. Both of these protocols were modelled after similar tests developed by the US EPA.

This paper will discuss the preliminary results of a field validation study relating results from effluent and receiving water toxicity tests to measurements of the physiological impacts on indigenous fish populations in rivers receiving effluent from pulp and paper mills. In the initial stages of the study, the focus has been on two bleached kraft pulp and paper mills. The first mill (A) is characterized by older process technology, and utilizes primary effluent treatment. The second mill (B) represents a modern mill, with oxygen pre-bleaching, high chlorine dioxide substitution, and secondary effluent treatment. In the fall of 1990, final effluent collected from these two mills was used in effluent toxicity tests with fathead minnows. Effluent toxicity tests and dilution factors predicted no downstream toxicity of receiving water samples. Final effluent from mill A was toxic to fathead larva with a Chronic Value of 18% v/v. Final effluent from mill B was non toxic at 100% v/v, and fathead larval growth was positively correlated to effluent concentration. In receiving water toxicity tests, water samples were collected from the two rivers at sites upstream and downstream of the mill discharges. In both rivers, larval fathead growth was largest in water samples taken immediately downstream of the mill discharge. Larval growth was positively correlated to AOX and chloroguaiacol levels in receiving water samples, and to male liver somatic index and serum glucose levels in white suckers collected from both rivers. Larval growth was negatively correlated to white sucker gonad somatic index and testosterone levels. Future plans include the incorporation of the *Ceriodaphnia* test into the study, and expansion of the project to include a larger number of pulp and paper mills.

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## PREDICTING ORGANOCHLORINE CONTAMINANT CONCENTRATIONS IN LAKE ONTARIO FISH

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It is generally accepted that "food chain biomagnification" is responsible for the elevated concentrations of organochlorine contaminants. This view is reexamined using data from the Ontario Ministry of the Environment sport fish contaminant monitoring program and additional data obtained by our laboratory.

A regression model was recently developed (Rasmussen et al. Can. J. Fish, Aquat. Sci. Oct. 1990) which predicts PCB concentrations in Lake Trout found in inland lakes in Ontario. In this model, trophic structure is the most significant variable. If planktivorous fish (smelt, alewives and coregonids) as well as the freshwater shrimp Mysis relicta are present, elevated PCB concentrations are found in Lake Trout. Other predictors of bioaccumulation were latitude and percent lipid. A lack of correlation is a means to identify lakes where point source inputs of organochlorine compounds are significant. In this presentation, we use the data for lakes north of Lake Ontario to predict the PCB concentration in Lake Ontario Trout and other fish. At the same time the contaminant signature found in Mysis relicta from two northern lakes is compared with that for Lake Ontario.

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# EFFECTS OF EROSIVITY BY RAINFALL ON AGRICULTURAL RUNOFF WATER QUALITY

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The characteristics of rainfall with respect to its effects on soil erosion is its erosivity which is defined as the product of rainfall intensity and rainfall kinetic energy. And the soil erosion during rainfall determines the agricultural runoff water quality which in turn influences the water body quality in which the agricultural runoff water joins. The impact brought about by the agricultural runoff is the eutrophication of surface water (i.e., lakes, streams and rivers) because the nutritive substances transported into surface water body by agricultural runoff that mostly results from relatively important rainfall events over fertilize the aquatic plants and thus lead to the eutrophication. Of nutritive substances carried in runoff, the phosphorus (P) has been found as the major determinant of eutrophication of surface water. Furthermore, only a fraction of phosphorus in runoff is biological available (BP) and this fraction of phosphorus is found composed of dissolved P (DP) in runoff water and of partial particulate phosphorus (PP) associated with eroded sediment which becomes bio-available when DP is depleted.

The agricultural runoff water quality at different erosivity has been examined by our study, which includes the runoff volume, soil loss, phosphorus loss, and the concentration and load of biological available phosphorus in runoff. The experimentation was undertaken in soil plots which were subjected to a regular cultivation by means of natural rainfalls during 6 months. After each significant rainfall event, the runoff volume was measured and a certain amount of runoff was brought back and then analyzed in our laboratory. The concentration of suspended eroded soil in runoff, total phosphorus concentration and the concentration of bio-available phosphorus in runoff have been determined. The erosivity of each rainfall was calculated according to the rainfall amount with time and finally all data were statistically analyzed by the SAS programme (version 6.02).

Our results indicate a increase of runoff volume with erosivity. On the other hand, the increase of erosivity conducts higher soil erosion and subsequently more soil loss by runoff and at the same time results also in higher phosphorus concentration in runoff and thus causes more P loss. Our data showed that 90% total BP (TBP) is contributed by particulate phosphorus (PP) and 45-60% TP in runoff is bio-available. Moreover, the principal P source in runoff is the eroded soil with which more than 90% P is associated. TBP concentration and load in runoff are subsequently affected by erosivity. Namely, a increase of erosivity raises the content of eroded soil, phosphorus, bio-available phosphorus and thus worsens the water quality. Although, the amount and intensity of natural rainfall can not be controlled, its erosivity could be reduced through the attenuation of rainfall impact on soil, e.g., by mulch cover, which then results in less impact of agricultural runoff on the environment.

**Keywords:** runoff water quality, eutrophication, erosivity, total phosphorus, particulate phosphorus, biological available phosphorus.

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## FEASIBILITY OF RETROFITTING FOR BIOLOGICAL PHOSPHATE REMOVAL IN QUEBEC

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The objective of this project was to determine the feasibility of retrofitting existing wastewater treatment plants in Quebec for biological phosphate removal. In comparison with chemical phosphorus precipitation this technology offers the advantages of not needing any chemicals, of reduced sludge production, and of offering the possibility to achieve phosphate removal throughout the year.

For retrofitting, it was desired to expose the biomass to a plug flow sequence of anaerobic-aerobic conditions, to ferment primary sludge when possible, and to treat wasted sludge rapidly to prevent phosphate release from the biomass into solution.

From a total of about 300 municipal treatment plants, a total of 41 suspended growth systems were retained (excluding lagoons). Data for these were obtained from the Quebec Ministry of the Environment (MENVIQ) and operators from the individual municipal treatment plants. A further selection based on population size and effluent guidelines reduced the number considered to 16 plants for which detailed design and operating data was collected about influent and effluent characteristics, amount and cost of chemicals, and process configuration. Of these plants, 9 were considered as offering an interesting potential to operate economically in a biological phosphate removal mode: 5 activated sludge plants, 2 oxidation ditches and 2 sequencing batch reactors.

Finally, a preliminary economic study was conducted on 7 of these promising plants. For four plants, the only modifications were in the mode of operation since the process of configuration provided enough flexibility to create a plug flow regime and that mixing could be achieved without aeration. In another case, very favourable influent characteristics (with a major contribution from a dairy industry) would also allow operation for biological phosphate removal at a negligible cost. Proper modifications of the aeration system would be required, however, should that industrial contribution be significantly reduced, as is expected. In the other two cases, modifications to the mixing system in the non-aerated zone, the use of a primary sludge fermenter, and precipitation of released phosphate in the anaerobic sludge digester was recommended. For these two plants, the actualized cost of retrofitting was similar to that of the yearly chemical cost.

Thus, depending on influent characteristics, existing plant configuration and equipment, the cost of retrofitting for biological phosphorus removal was found to range from important to negligible.

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# WASTEWATER CHARACTERIZATION FOR ACTIVATED SLUDGE MODELLING

J. Gibson<sup>1</sup> and P.L. Dold<sup>1</sup>

The expanded function of the activated sludge system has increased the level of complexity in design, operation and control. Increasingly, mathematical modelling of system behaviour is being used as a tool to facilitate the tasks of designers and operators. Application of activated sludge kinetic models such as the IAWPRC model requires specification of influent wastewater characteristics. Accurate estimates of the wastewater parameters are essential if the models are to provide satisfactory predictions of effluent quality, sludge production, oxygen utilization, and dynamic process behaviour.

The fundamental parameters utilized in current models are the influent concentrations of chemical oxygen demand (COD) [for the organic material] and the total Kjeldahl nitrogen (TKN) [for the nitrogenous material]. In applying the models the user is required to divide both the influent COD and TKN into a number of fractions.

## INFLUENT COD FRACTIONS

*Biodegradable and unbiodegradable fractions:* The first division of the influent COD is into biodegradable COD and unbiodegradable COD. Each of these fractions is subdivided further into two sub-fractions.

*Unbiodegradable sub-fractions:* The unbiodegradable material is divided into an unbiodegradable soluble fraction and an unbiodegradable particulate fraction.

*Biodegradable sub-fractions:* The biodegradable material is divided into a readily biodegradable fraction and a slowly biodegradable fraction.

## INFLUENT TKN FRACTIONS

*Ammonia and organically bound fractions:* The first subdivision of the influent TKN is into free/saline ammonia and organically bound TKN. The organically bound TKN is divided further into three sub-fractions.

*Organically bound TKN:* The organic nitrogen is divided into an unbiodegradable soluble fraction, an unbiodegradable particulate fraction and a biodegradable fraction.

*Biodegradable organic sub-fractions:* The biodegradable organic nitrogen is divided into a soluble fraction and a particulate fraction.

## MEASUREMENT METHODS FOR INFLUENT WASTEWATER CHARACTERISTICS

Methods for determining the parameters characterizing a domestic wastewater divide into three groups:

*Direct analysis of the wastewater:* The ammonia fraction and the division of the biodegradable organic nitrogen between soluble and particulate material is determined through analysis of the wastewater. For the determination a sample of the wastewater is taken and a portion filtered through a 0.45 mm membrane filter to remove particulate

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material. The unfiltered sample and the filtrate are then analyzed using standard techniques to determine the concentrations of TKN in the unfiltered sample and TKN and ammonia in the filtrate.

*Analysis of continuous flow activated sludge systems:* Accurate estimation of the unbiodegradable soluble and particulate COD fractions is achieved through analysis of data gathered in the operation of a laboratory scale single reactor aerobic activated sludge system operated under steady state conditions at a fixed sludge age. In fine-tuning the fit of predicted and observed effluent TKN, nitrate and oxygen utilization rate data it is possible to estimate the unbiodegradable soluble organic nitrogen content of the wastewater.

*Aerobic batch test:* The readily biodegradable COD content of a wastewater can be determined from analysis of the oxygen utilization rate response observed in an aerated batch test. A measured volume of wastewater of known total COD is combined with a measured volume of activated sludge mixed liquor. From immediately after the start of the test OUR measurements are made at intervals of a few minutes; measurement continues for a period of approximately 1 to 2 hours. The conditions in the test system allow the oxygen consumed in the utilization of the readily biodegradable COD to be measured, and hence the concentration.

Details of the various experimental methods are presented in the paper together with results obtained from analysis of the influent to a Canadian water pollution control plant treating a typical municipal wastewater.

## FACTORS AFFECTING DISPERSION OF ACTIVATED SLUDGE FLOCS

Dahong Li<sup>1</sup> and Jerzy J. Ganczarczyk<sup>2</sup>

Size distribution of flocs influences mass transfer and biomass separation in the activated sludge process. Therefore, it is of primary importance to establish the role of specific process operation factors on this distribution with a special emphasis on formation of primary particles (dispersed bacteria and very small flocs) which flocculate less effectively and may contribute to the level of residual suspended solids in final effluents.

Samples of mixed liquor from five, full-scale, conventional sewage treatment plants were analyzed for the floc size distribution during a period of two years. The results of these tests were presented in the form of the parameters of the previously developed power-law model for the floc sizes across of the whole spectrum, and of the log-normal model for flocs larger than 10  $\mu$ m. The parameters of these models were, in turn, correlated with the respective values of (1) sludge loading, (2) substrate removal rate, (3) dynamic sludge age, (4) mixed liquor suspended solids level, (5) mean velocity gradient in aeration tanks, (6) wastewater hydraulic retention time, (7) dissolved oxygen level, and (8) mixed liquor temperature. The stepwise regression using, when necessary, the linearized forms of the above relationships was applied to investigate the combined effects of operating factors on floc size distribution. The effects of the factors and interaction of selected factors on the frequency of occurrence of the primary particles were examined by logistic regression and stepwise regression.

It was found that the plants' operation factors of conventional activated sludge process affect the floc size distribution in a complex way. The scale and shape parameters of the power-law distribution model correlated well with sludge loading and mixed liquor suspended solids values. The scale parameter of this distribution was also affected by the dissolved oxygen levels and velocity gradients in the aeration tanks. The shape parameter was affected by the dynamic sludge age values. Both parameters of the log-normal distribution model correlated with mixed liquor suspended solids values. The mean log values were affected by velocity gradients and the logarithmic standard deviation values were affected by sludge loading values.

The scale or the shape parameters of the power-law floc size distribution model were influenced in a statistically significant way by the ratio of dissolved oxygen level to the substrate removal rate, the level of dissolved oxygen raised to the power of -0.64, the sludge loading raised to the power of 0.065, and the product of the mean velocity gradient and the hydraulic retention time. For the flocs larger than 10  $\mu$ m, the log-normal distribution model was affected significantly by the product of the mean velocity gradient and the hydraulic retention time, the dynamic sludge age, and the level of mixed liquor suspended solids. The sludge loading was the most important and statistically significant factor influencing the frequency of occurrence of the primary particles (< 2  $\mu$ m).

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It is expected that an extension of this study over the range of operation factors of the conventional activated sludge, would help to generalize the obtained results in a more substantial way.

## SELECTION CRITERIA OF APPROPRIATE SITES FOR ELIMINATION OF MUNICIPAL SOLID WASTES IN METROPOLITAN AREAS

Elecktorowicz M.<sup>1</sup>, Hadjinicolaou J.<sup>1</sup>, Yong, R.N.<sup>1</sup>

According to information from Environment Quebec, 40% of the contaminated sites in the Montreal area are situated in old landfill territories, and consequently carrying important impact on groundwater quality.

The presently used criteria seemed to be insufficient and ineffective. In the effort to find optimal landfill sites as well as appropriate areas for other types of solid wastes eliminations, recent research in geoenvironmental field showed the necessity of changing the existing criteria.

This paper presents a new methodology and new criteria for the selection of landfill alternative sites. The new criteria are developed in conjunction with the American, Canadian and European experiences considering many aspects of environmental protection priorities.

The above criteria have been developed as results of a case study concerning solid wastes management, treatment and elimination for the Metropolitan area of Montreal.

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## USE OF THE AERIS MODEL TO ASSESS RISKS ASSOCIATED WITH THE DECOMMISSIONING OF INDUSTRIAL SITES

K.R. Hosler<sup>1</sup>, T.L. Bulman<sup>2</sup> and T.W. Constable<sup>1</sup>

After operations at an industrial site have ceased, the site must be decommissioned to make it suitable for a future land use. The decommissioning of any industrial site is a complex problem involving a range of activities including: site characterization, an initial monitoring program for on-site contamination, removal of surface and subsurface structures, determination of acceptable levels of contamination or clean-up criteria, implementation of the clean-up strategy, and long-term monitoring to ensure that criteria have been met. One of the most difficult of these activities is the selection of the clean-up criteria that are to be applied to the site. Historically, the process used to determine these criteria often varied considerably among jurisdictions, resulting in widely variable clean-up levels between similar sites, poor correlations between clean-up levels and human health considerations, and other serious shortcomings.

In response to the need for establishing a standard approach for selecting site-specific clean-up criteria that took into account both human health considerations and on-site conditions, a computer model entitled AERIS (Aid for Evaluating the Redevelopment of Industrial Sites) was developed. AERIS performs risk assessment on chemical pollutants by combining multi-media fate and transport pathways analysis with exposure assessment. The results can be used to assist in the selection of environmental clean-up criteria by identifying the major contributing exposure factors and concerns at a particular site, those aspects of a site redevelopment scenario with the greatest need for site-specific information, and the extent to which on-site remedial action may be required.

AERIS provides a cost-effective method for performing site-specific toxicological risk assessment with associated risk characterization. A major benefit to be derived from its use is the ability to efficiently evaluate a particular site for many different scenarios (such as differing land uses, receptor characteristics, climate zones, soil types, etc.) by running the model several times in succession while changing one variable at a time. In this way, the assessment of clean-up criteria for a decommissioned site becomes a standardized practice that is less labour-intensive than most other methods and provides site-specific information that is often unavailable with other approaches. This capability should make AERIS a valuable aid for evaluating the redevelopment of industrial sites.

This paper describes the AERIS model, how it uses exposure assessment in conjunction with toxicity evaluation data to determine contaminant clean-up levels at decommissioned industrial sites, the basis for its decision-making processes, and how it could serve as an industry standard for selecting clean-up criteria for industrial site redevelopment.

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## WASTE REDUCTION PLANNING IN INDUSTRY

Hélène Roberge<sup>1</sup> and Brian Baetz<sup>2</sup>

Due to new government regulations, industrial waste disposal and treatment costs are increasing rapidly, and waste reduction is becoming an economically attractive alternative. A mathematical model was developed to assist in the long and short term planning of waste reduction, treatment and disposal strategies for industry.

The problem was first modelled as a mixed integer linear program (MILP), comprising an objective function, which is subject to a number of constraints. The objective function is minimized and includes capital and operating costs for waste reduction, treatment and disposal. The constraints include binary decision variables, mass balances, technical constraints, and dimensions of the problem. The MILP model is meant to be general and flexible, so that it can be adapted to describe a particular facility.

The MILP was adapted to a case study problem in the petrochemical industry, and was solved on a VAX using LINDO, a well-tested, commercial software package. The problem was also modelled as a forwards recursion dynamic program, which was coded in FORTRAN and run on a SUN workstation.

The modelling approach was validated by identifying assumptions, performing a sensitivity analysis on the case study and with input from an industrial contact. The computer code was verified by comparison with results obtained from LINDO.

The model is a potentially useful tool in planning for the implementation of industrial waste reduction, treatment and disposal strategies, when the results are reviewed and interpreted by people who have experience and a good understanding of the facility being studied.

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## COAL TAR CONTAMINATION NEAR RANDLE REEF, HAMILTON HARBOUR

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To support the remedial action plan of Hamilton Harbour, and to determine the extent of coal tar contamination in a toxic area of the harbour, 81 sediment cores were collected for chemical and biological study. Approximately 55,500 m<sup>3</sup> of sediments bounded by Randle Reef, pier 15, and Stelco are contaminated with coal tar. The coal tar distribution is variable but the highest concentrations are near the Stelco outfall pipes and the Hamilton-Wentworth combined sewer outfall pipe. The total concentration of near-surface sediments exceeds 200 µg/g. The concentration of PAHs that results in the death of 50% Daphnia magna and Hexagenia is less than 244 µg/g and 329 µg/g, respectively. Sediments containing more than 89 µg/g of PAHs suppress at least half of the photoactivity of Photobacterium phosphoreum. The acute toxicity of the sediments of all of Hamilton Harbour is significantly correlated to the PAH concentration.

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## HAMILTON HARBOUR WATER CLARITY RESPONSE TO NUTRIENT ABATEMENT

S. Painter<sup>1</sup>, L. Hampson<sup>1</sup>, and E.S. Millard<sup>2</sup>

Hamilton Harbour is one of 42 areas of concern in the Great Lakes Basin. The Provincial and Federal governments are committed to the development of a Remedial Action Plan (RAP) to restore the beneficial uses of the Harbour. Swimming and fish habitat are two of the beneficial uses identified by the Hamilton Harbour Stakeholders. Both uses require improvements in the Harbour's water clarity. Beginning in 1988, the addition of a pickle liquor step at the Hamilton Sewage Treatment Plant (STP) successfully reduced the total phosphorus loading into the Harbour from 515 kg.day<sup>-1</sup> to 364 kg.day<sup>-1</sup> in 1990. A comparison of the 1987 and 89/90 Harbour data showed that chlorophyll decreased 15 g.L<sup>-1</sup> and seston decreased 2.8 mg.L<sup>-1</sup>, which improved Secchi disc transparency 42 cm from 148 cm to a two year summer average of 190 cm. Secchi disc transparencies in the 3 metre range appear to be attainable when chlorophyll concentrations are below 7 g.L<sup>-1</sup>.

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## SPATIAL VARIATION IN WATER QUALITY AND CONTAMINANTS IN HAMILTON HARBOUR

Murray N. Charlton<sup>1</sup>

Water quality parameters were measured at 24 stations in Hamilton Harbour in 1988, 89, 90. Parameters such as phosphorus, ammonia, and chlorophyll were measured in water samples at two depths representing the epilimnion and hypolimnion. Temperature, oxygen, pH, turbidity, and conductivity were measured with an in-situ electronic profiling apparatus. The profiles were stored on computer media in the field and transmitted to a mainframe database. A suite of programs were then run to display time-depth diagrams, time trends, and spatial patterns. In some surveys, 10:1 ratio of high to low surface ammonia concentrations reflected the interaction of load location, metabolism, and horizontal mixing. A similar ratio is present vertically for some parameters. The surveys reveal loading of ammonia to the bottom waters after stratification that exacerbate the oxygen depletion problem. Rapid deoxygenation of bottom waters following stratification is consistent with ammonia metabolism. Fluctuations of oxygen isopleths are consistent with large inflows of Lake Ontario water as evidenced by conductivity fluctuations in profile displays. Anoxia did not occur and is in fact rare in historic data. Near anoxic water moves according to thermocline tilt into shallow fish habitat areas.

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## LOADINGS OF PCBs AND PAHS FROM HAMILTON HARBOUR TO LAKE ONTARIO

Michael E. Fox<sup>1</sup>, Raza M. Khan<sup>1</sup> and Lina A. Thiessen<sup>1</sup>

Hamilton Harbour has been identified by the International Joint Commission as an "area of concern" because of elevated levels of PCBs, PAHs and heavy metals. Reliable estimates of the potential for transport of these substances to Lake Ontario have significant influence on the creation of a remedial action plan. Several such loading estimates have been made in the past but none have made direct measurements of dissolved PCBs and PAHs in the water column. In this study, water movement in the connecting channel was measured in considerable spatial and temporal detail over a 10 day period in July 1990. Water samples were analyzed for PCBs and PAHs. The outflow of PCB was calculated to be 37 g/day. Because of a predominant thermally driven two layer system with return flow from Lake Ontario in the lower layer, an inflow of 34 g/day PCB was observed. The resultant net loading of PCB to Lake Ontario of 3 g/day is very small in comparison to the 5000 g/day estimated loading from the Niagara River. Extrapolation of these calculations to annual loadings is not warranted since the winter flow regime is predominantly plug flow. Winter measurements are in progress and should lead to estimates of annual loadings.

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## BIOLOGICAL SEDIMENT CRITERIA

Trefor B. Reynoldson<sup>1</sup>

Of the 42 designated Areas of Concern in the Great Lakes all but a few have been identified as having a problem with contaminated sediments. A key component of a management strategy for sediments are guidelines to determine when sediments can be left in place or when remediation is required. There has been a considerable effort over the past few years, particularly by the USEPA and Ontario Ministry of Environment, to develop numerical sediment criteria based upon chemical concentration. Two methods appear to be most widely used, first for chlorinated organic substances sediment criteria are being derived by equilibrium partitioning theory from water quality criteria; second the apparent effects threshold is being used. This technique requires large data bases and simply relates observed biological effects to distribution statistics for chemicals. The former is dependent on available water quality criteria, which are not always available, the latter presumes single chemicals are producing the observed biological responses.

It is suggested that the pursuit of chemical criteria is flawed. The purpose of sediment criteria is not regulatory but to provide a guideline for remediation, its need and success. As the concern with contaminated sediments is their biological implication it would seem far more logical to develop biological guidelines to determine the need for remediation. It is proposed that establishing target benthic communities and bioassay endpoints is a much more logical approach. An example of how such guidelines may work is illustrated by data from the Detroit River. Using benthic invertebrate distribution data from a series of clean sites it was possible to develop a predictive model for the type of organisms expected at new sites. This model was used to predict the species (guidelines) at a second set of sites. It was found that stations upstream of effluents met the guidelines and those downstream did not. This suggests that a workable set of biological targets can readily be identified and used as a practical management tool.

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## FISH AND FISH HABITAT IN HAMILTON HARBOUR

C.K. Minns<sup>1</sup> and V.W. Cairns<sup>1</sup>

This presentation provides a broad temporal overview of fishery issues in Hamilton Harbour, an IJC Area of Concern. The fishery issues relate to both development of a Remedial Action Plan (RAP) and implementation of federal fish habitat policy. Other talks in this session cover other aspects of the RAP process. Past, almost historical, conditions are reviewed giving a sense of the ecosystem that was lost and might be, to a degree, regained. In the 19th century, the Harbour's habitats were an essential ingredient in the production processes supporting much of the commercial fishery harvests of western Lake Ontario. Recent and current studies of fish and fish habitat provide a picture of the fish community and particular habitat needs as external pollutant loads are reduced and water quality improvements occur. Introduced and invading species like carp, alewife, and white perch dominate the fish community now but remnants of a preferred warmwater fish community persist providing a basis for fishery restoration. Future prospects for the Harbour are based on the stakeholder's stated RAP goals and objectives. A proposed, extensive, package of fish community manipulation and, fish habitat restoration and development is described. A package deemed essential for fishery restoration. An assessment of the potential for success completes the overview.

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## THE ANALYSIS OF N-NITROSODIMETHYLAMINE IN WATER BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY.

Robert L. Hong-You<sup>1</sup>, Piyouz S. Adeb<sup>1</sup> and Peter J.A. Fowlie<sup>1</sup>

N-Nitrosodimethylamine (NDMA or DMNA) a known and potent carcinogen is regulated by the Ontario Ministry of the Environment with a guideline level in water of 14 parts per trillion (ppt). The presence of this compound in several communities in Ontario necessitates the ability to analyze, detect and monitor for it at a very low level.

In conjunction with four laboratories, including the Wastewater Technology Centre Laboratory Division, a method for the determination of NDMA in water was developed. This was patterned after the U.S.EPA method 607 requiring the use of a liquid-liquid extraction followed by gas chromatography-mass spectrometry(GC-MS). By using d<sub>6</sub>-NDMA, isotope dilution GC-MS analysis was performed on all samples. The method detection limit based on a 1 litre sample was 10 ppt.

To ensure reliable and comparable data, especially with the required detection limits, a detailed quality control plan was adopted. Data generated from inter-laboratory studies showed good correlation and will be presented.

Several samples from a community which receives its source of water supply from the Grand River in Ontario were analyzed using this procedure. Due to the complex nature of this compound, the data illustrated some problems in interpreting the information. However the method was successfully implemented and was used to identify the source of NDMA contamination in this community.

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# SIMULATION OF PARTICLE GROWTH KINETICS IN A SUPERSATURATED IRON(III) COAGULATION / FLOCCULATION SYSTEM

George Eastwood<sup>1</sup> and W.J. Snodgrass<sup>1</sup>

The coagulation / flocculation process is widespread in the fields of water and wastewater treatment. Particle aggregation is instigated by the addition of metal salts or polymers. The aggregation rate is enhanced if the metal salt concentration is above the solubility limit of the metal hydroxide. Mechanisms include particle destabilization and sweep floc. The adsorption / coprecipitation of trace elements (e.g. As, Pb) onto iron floc, and the partitioning of hydrophobic organics (e.g. PCBs, PAHs) onto colloids, reinforce the potential of this process in contaminant removal. The removal of particles and associated contaminants in subsequent settling and filtration processes depends on the kinetics of particle growth and particle size distribution.

Attempts to model the flocculation observed in iron (III) - silica systems are hindered by the large number of potential interactions in a widely heterodisperse system, and by the uncertainty of the effects of nucleation and crystal growth under conditions of supersaturation. This research has simplified experimental conditions in order to differentiate between observations of perikinetic and orthokinetic transport rates, and a model has been developed which includes both flocculation and precipitation mechanisms of particle growth.

Classical nucleation theory and experimental observations of particle number concentrations were used to infer an initial bimodal particle size distribution immediately following coagulant addition. Diffusion controlled crystal growth of excess coagulant concentration onto the existing PSD and biparticle flocculation using Smoluchowski rate constants were simulated in parallel. The model was validated and calibrated with respect to the experimentally observed kinetics and extent of particle volume appearing above a lower detection size limit of 3.3 microns.

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## THE SOURCE OF NDMA IN A WATER SUPPLY

Dr. Peter Child<sup>1</sup>

In early 1990, N-Nitroso dimethylamine or NDMA, a known animal carcinogen and suspected human carcinogen, was detected in the drinking water supply of a community which draws its water from the Grand River. At a time when no NDMA was detected in the river itself, concentrations of 100-400 parts per trillion of the material were found at various points in the drinking water distribution system.

The source of the NDMA was traced to a reaction occurring between treatment chemicals used in the water plant. In this presentation the chemistry of the reaction, the steps taken to correct the problem, and the results of the ongoing monitoring of the water supply will be described. The special problems associated with confirming the absence of a chemical whose allowable drinking water limit equals the analytical method detection limit will also be discussed.

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# GROUNDWATER CONTAMINATION BY TOXIC ORGANICS: THE CASE STUDY OF VILLE MERCIER, QUEBEC, CANADA

Marc Halevy<sup>1</sup>, Robert Booth<sup>1</sup> and James W. Schmidt<sup>1</sup>

Extensive aquifer contamination in Ville Mercier, Québec, resulting in a groundwater with a high content of chlorinated and aromatic volatile organic compounds, prompted the Québec Ministry of the Environment to initiate Canada's first large scale aquifer remediation effort in 1984.

Rehabilitation of the aquifer and plume containment were initiated through the construction and operation of a 76 L/s pump-and-treat treatment facility, consisting of the following physical-chemical processes:

1. **Air Stripping** to remove volatile organic compounds and to aerate the groundwater for iron and manganese oxidation,
2. **Coagulation/Flocculation/Sedimentation/Filtration** to remove the precipitated metals, and
3. **Granular activated carbon filtration** to remove the remaining organics.

The SNC Group, responsible for the operation of the plant, was mandated by the Québec Ministry of the Environment (MENVIQ) to carry out bi-monthly collection and analysis of samples of groundwater taken along the treatment train. This resulted in a limited performance data compilation on the effectiveness of the train in treating the contaminated groundwater. Serious operational difficulties were encountered during the first year of operation. They were essentially resolved through the addition of hydrogen peroxide, chlorine and chlorine dioxide at critical locations along the treatment train. Moreover, no further hydrogeological assessment of the aquifer was conducted at any time during this five-year aquifer remediation exercise.

Given that this was the first large scale aquifer remediation project in Canada, a unique opportunity was afforded to evaluate the success of the remediation effort as well as the effectiveness of the contaminated groundwater treatment process. Consequently, a Canadian consortium consisting of The SNC Group, Laval University and the University of Sherbrooke was awarded, through the DSS unsolicited proposals program, a R,D&D contract to (1) assess the hydrogeological impact of the operating decontamination program on the aquifer and (2) to establish and, if appropriate, make recommendations to improve the performance of the treatment train in treating Ville Mercier's groundwater. This latter study is the focus of this paper.

The main objectives of the treatment study included:

1. an evaluation of the performance of the Ville Mercier Groundwater Treatment Plant through analyses of the historical data collected by its operator, The SNC Group, and from its owner, the MENVIQ,
2. a detailed performance evaluation of the treatment train through two (2) full-scale sampling monitoring campaigns, and

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3. the conduct of bench and pilot-scale studies in order to research, develop and demonstrate optimized alternative unit operations/treatment train for the treatment of Ville Mercier's contaminated groundwater and groundwaters of similar nature.

An analysis of the plant's historical data and the performance evaluation of the treatment train conducted in the context of the present study showed the inadequacy of the air stripping column and the two-step GAC filtration units to effectively remove the toxic organics from the groundwater.

Bench and pilot-scale studies demonstrated the need for a two-step process to treat the groundwater. The first step was the removal of inorganics, primarily iron, prone to precipitation, in order to minimize physical and biological fouling of downstream unit processes responsible for the ultimate goal, and the second step, the removal of organics.

An array of iron pretreatment technologies were evaluated at pilot-scale. Batch runs and subsequent performance evaluation of the recommended treatment train in a continuous mode of operation, determined that **aeration** conducted in a bubble column, followed by rapid **direct sand filtration** was a highly effective iron removal pretreatment technology.

The toxic organics in the groundwater were subsequently removed in an **air stripper**, designed to meet MENVIQ's drinking water objectives. Design and operational parameters will be presented. GAC filtration, as a polishing step, was evaluated as a process to remove the trace organics in the treated groundwater.

A biofouling control technology developed by F.J. Dart, from the Ontario Ministry of the Environment, which incorporates zinc granules in the sand filter bed to abate and control the growth of *Pseudomonas* in the sand filter, air stripper and GAC columns, was evaluated.

## BACTERIAL LEACHING OF SLUDGE INACTIVATED BY COPPER SULPHATE

Glynn Henry<sup>1</sup>, Durga Prasad<sup>2</sup>, Avtar Mavi<sup>3</sup>

Earlier studies have established that the bacterial leaching process extracts metals from anaerobically digested sludges, but does not reduce the indicator organisms nor perhaps, enteric pathogens. Land application of these 'metal free' sludges could be undesirable because of the possible presence of pathogens that are hazardous to humans and livestock. Of the sludge disinfection/stabilization processes available for commercial applications, none is suitable or ideal for most locations because of limited effectiveness or high cost. Copper sulphate, an effective algicide and bactericide (also toxic to other microflora and fauna), could be an ideal sludge disinfectant if used prior to and/or during the bacterial leaching process, since the added copper would then be removed subsequently along with other metals.

The purpose of this research was to: (1) assess the effect of copper sulphate on the bacterial leaching process, and (2) demonstrate that both sludge disinfection/stabilization and removal of metals, including copper, could be achieved during the bacterial leaching process.

A series of laboratory-scale bacterial leaching units was operated using anaerobically digested sludge treated with various dosages of copper sulphate.

Results showed that at a dosage of 30 mgCu/g dry mass, the performance of the bacterial leaching units deteriorated by 23 to 50%. However, in units with a lower dosage of 20 mg Cu/g dry mass (at pH 4.0, an aeration rate of 100 mL/min/L of sludge and a temperature of 20-25°C), metal removals increased to normal values (65 to 85%) and coliform reductions (total and faecal) were about 99.99%. These results were achieved at a detention time (DT) of 10 days but this time could be decreased to 5 days by increasing the concentrations of ferrous sulphate from 4 to 10 g FeSO<sub>4</sub>/L in the leaching units. In these units containing both the FeSO<sub>4</sub> and CuSO<sub>4</sub>, Thiobacillus ferrooxidans, the bacteria responsible for metal solubilization, appeared to be stimulated by relief from the copper inhibition and by the surplus of FeSO<sub>4</sub>, available as an energy source.

The possibility that both sludge disinfection and metal removals from sludge can be achieved during bacterial leaching, has been demonstrated. Further work is needed to establish the minimum copper dosage required for disinfection.

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# SIMULTANEOUS MUNICIPAL SLUDGE DIGESTION AND MICROBIAL METAL LEACHING

R.D. Tyagi<sup>1</sup>, J.F. Blais<sup>1</sup> and J.C. Auclair<sup>1</sup>

The high concentration of heavy metals in municipal sludges represent a major obstacle to the agricultural utilization of this biomass. Hyperactive bacterial strains have been developed in our laboratory which reduces the time of metal leaching from the conventional 10 days to 40 hours. Also, the sludge indigenous thiobacilli which can produce inorganic acids from sulphur compounds have been acclimated and their potential to solubilize heavy metals from sewage sludge has been investigated. The oxidation of sulphur compounds by indigenous thiobacilli of sludge accompanied with oxygen uptake causes sludge acidification, lowering Ph below 2.0. This Ph reduction solubilizes heavy metals to a level compatible with the recommended thiobacilli is not much influenced by the sludge type (secondary sludge, aerobically or anaerobically digested sludge) and by sludge total solids content.

Apart from heavy metals, another factor limiting the sewage sludge utilization in agriculture is the presence of pathogenic microorganisms. Therefore, the potential of the heavy metals bioleaching process for the elimination of pathogenic bacteria have been carried out by studies of indicator bacteria (total coliforms, fecal coliforms, fecal streptococci). The modification effected to some physical-chemical sludge characteristics (TS, VS, TSS, VSS, soluble carbon and sulphate) have equally been measured, as also the heavy metals solubilization. The results obtained revealed that the high sulphuric acid production (Ph < 2.5) by indigenous thiobacilli of sludge, allow a considerable reduction of bacterial indicators (> 98%) for all sludges (15 sludges) examined on a five day period, and heavy metal solubilization level compatible with the recommended norms for intensive sludge agricultural use. Moreover, this process allows a TSS and VSS reduction, but somewhat varied according to the sludge used. These results indicate that microbial leaching process utilizing indigenous bacteria can eventually replace the aerobic sludge stabilization or in other words microbial leaching of metals from sewage sludge digestion can be performed simultaneously in the same bioreactor. The results with respect to heavy metals removal and sludge digestion shall be presented and discussed.

**Keyword:** Municipal sludge, sewage sludge, heavy metals, pathogenic bacteria, sludge digestion, microbial leaching

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## MODELLING THE ENVIRONMENTAL FATE OF 2,3,7,8-T4CDD INTRODUCED TO RECEIVING WATERS VIA PULP MILL EFFLUENTS

A. Sardella<sup>1</sup>, M.E. Starodub<sup>1</sup>, and R.F. Willes<sup>1</sup>

The environmental fate of 2,3,7,8-T4CDD introduced via pulp mill effluents to two receiving waters was estimated using the Exposure Analysis Modelling System (abbreviated as EXAMS), version 2.92. The Rainy River in Western Ontario and the Athabasca River in Alberta were selected for assessment since they represent two different river systems receiving mill effluents. Steady-state environmental concentrations of 2,3,7,8-T4CDD in the water column and benthic sediments were estimated by EXAMS for a 130 km reach of the Rainy river under average (250 m<sup>3</sup>/s) and low flow (95 m<sup>3</sup>/s) conditions receiving pulp mill effluents containing 2,3,7,8-T4CDD at assumed concentrations between 0.1 to 1000 ppq with a mill effluent flow rate of 788 L/s. The environmental fate of 2,3,7,8-T4CDD discharged to the Athabasca river under average flow conditions four existing pulp mills and one proposed pulp mill on the Athabasca river located between Hinton and Fort McMurray was also modelled. A constant 2,3,7,8-T4CDD loading rate for the respective mills was calculated assuming a final effluent 2,3,7,8-T4CDD concentration of either 10 ppq or 100 ppq. Total environmental loading rates were calculated based on the discharge rates of the effluent from the mills.

All predicted dissolved 2,3,7,8-T4CDD concentrations at all loading rates assessed were below the present "best-available" detection limit of 10 ppq (10 pg/L) or 1.0 x 10<sup>-5</sup> ug/L for 2,3,7,8-T4CDD in aqueous solution.

The river flow rate was observed to act as a diluent of the introduced pulp mill effluents containing various levels of 2,3,7,8-T4CDD; estimated environmental concentrations of 2,3,7,8-T4CDD were inversely related to the river flow (i.e., the higher the river flow the lower the concentration of 2,3,7,8-T4CDD). The results of the model indicated that the predominant process governing the fate of 2,3,7,8-T4CDD in the aquatic environment was adsorption to suspended and benthic sediments. This process was described by the sediment partition coefficient (K<sub>ps</sub>) which is linearly related to the organic carbon partition coefficient (K<sub>oc</sub>) and the fraction organic carbon (f<sub>oc</sub>) of the sediment. Therefore, the following site specific environmental parameters were regarded as critical to the model: fraction of organic carbon in the water column, total suspended solids in the water column, bulk density of the benthic sediments, and percent water content in the benthic sediment. Phototransformation did not appear to represent a significant removal process in the river systems modeled and biotransformation was considered to be negligible. However, site specific measurements of phototransformation in the water column and biotransformation in the benthic sediments of 2,3,7,8-T4CDD may improve the accuracy of the environmental fate predictions.

The results of the Rainy and Athabasca rivers 2,3,7,8-T4CDD fate analysis predicted that approximately 94% of 2,3,7,8-T4CDD discharged to the river system would partition to the benthic sediment, the other 6% would remain in the water column. Validation of the model results focused on benthic sediment 2,3,7,8-T4CDD concentrations which should be measurable in the field. The predicted partitioning

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was supported by measurements of sediment 2,3,7,8-T4CDD concentrations in Rainy river system sediments, Lake Ontario sediments and results of WASP4 fate modelling of 2,3,7,8-T4CDD in Lake Ontario (EPA, 1990), and additional environmental fate studies of PCDD/PCDF reported in the literature.

**BIOACCUMULATION OF HEAVY METALS IN *GAMMARUS FASCIATUS*  
(CRUSTACEA: AMPHIPODA) IN RELATION TO CONTAMINATION OF  
SEDIMENTS AND WATER CHEMISTRY.**

Marc Amyot<sup>1</sup>, Bernadette Pinel-Alloul<sup>1</sup>  
and Peter G.C. Campbell<sup>2</sup>

The discharge of increasing amounts of pollutants into the environment due to various activities of man has contributed to the alteration of natural aquatic ecosystems. To detect and quantify such impacts on biota, one approach is to biomonitor the concentration of toxicants in organisms. Many factors influence the bioaccumulation of metals by benthic organisms, such as nutritional habits, distribution of metals in geochemical phases of sediments, bioavailability of metals (Tessier *et al.*, 1984; Campbell *et al.*, 1985; Campbell and Tessier, 1989) and environmental factors (organic matter, acidity,...) (Jackson, 1986, 1988; Campbell and Stokes, 1985; Stephenson and Mackie, 1988).

The goal of our study is to evaluate the value of benthic macrophytes-associated organisms as biomonitors of aquatic environments. In this perspective, we chose ten stations in submerged macrophytes communities (*Valisneria sp.*, *Myriophyllum sp.*, *Elodea sp.*) of St-Pierre Lake, a fluvial lake of St-Lawrence river. The chosen stations were representative of a heavy metal contamination gradient in sediments and of the organic matter concentrations in the water column. To take into consideration natural variations of environmental parameters such as conductivity (130-245 umhos), pH (6.77-8.50), turbidity (1.4-12.5 NTU), water colour (4.60-14.87 Hazen) and dissolved organic carbon (1.868-4.128 mg/L), stations were situated into two water masses, one coming from the St-Lawrence river (green waters) and the other, from northern tributaries (brown waters from Chicot and Yamachiche rivers).

We put into relation, using regression analysis and Kendall correlations, the concentrations of Pb, Cu, Mn, Zn, Cd and Fe found in *Gammarus fasciatus* (an epibenthic macrophytes-associated amphipod) with metal concentrations measured in sediments. The bioavailable fraction of metals in sediments was determined by sequential extraction procedures, the most easily extracted fraction being considered as the most bioavailable (Campbell and Tessier, 1989). On one hand, concentrations of Zn, Cu, Cd and Fe can be partly explain by their respective concentrations in various extractable phases of sediments. On the other hand, physico-chemical properties of water also seem important. Thus, variations of Ph are negatively correlated with amphipod concentrations of Mn, Fe, Cu and Zn, while turbidity is positively correlated with Fe, Cu and Zn.

Our results suggest that *Gammarus fasciatus*, being mainly detritivorous, could be a good biomonitor of concentrations of heavy metals in sediments. But, it appears that other factors, such as water chemistry, are involved. Further research will be needed in order to establish a complete bioaccumulation model involving this amphipod. In this perspective, we are currently analyzing other environmental parameters that have been collected at the same sites. Among these figure the concentrations of heavy metals in macrophytes, periphyton and plankton.

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The results of these experiments will help decision makers to elaborate pollution index that will include amphipods (which represent a basic link in the aquatic food chain being a major prey for a number of fish species) in a more proper manner. This study will also enhance the comprehension of the major route of entry of heavy metals in amphipods.

Key words: Heavy metals - Bioaccumulation - Amphipods - sediments.

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## A NEW METHOD FOR TESTING SOIL AND SEDIMENT SAMPLES

Anthony Bulich<sup>1</sup> and Grace Scheibner<sup>1</sup>

During the last 5 years Microtox, a Photobacterium based bioassay, has found increased application for measuring toxicity in sediments and solid waste samples. A unique modification of the Microtox protocol is described whereby test samples (sediments, soils, or solid wastes) can be assayed directly without the requirement to prepare sample extracts. The new test method also uses changes in bioluminescence as a measure of toxicity but takes advantage of direct contact between solid phase sample constituents and Microtox test organisms. Bound chemicals are able to interact with test organisms providing a realistic exposure route not always available with sample extracts. The proposed method has been developed using four EPA prepared spiked soil samples containing inorganic and organic chemicals. In addition, well characterized marine and fresh water sediments were included in the test sample set. Validation and comparative test data for this new method are presented along with a detailed test protocol. The ability to directly test a suspended particulate phase offers a potentially useful compliment to the standard Microtox Test procedure.

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## DEGRADATION OF PHENOLS BY ALGAE

V. Klekner<sup>1</sup> and N. Kosaric<sup>2</sup>

Strains of Chlorella sp., Scenedesmus obliquus and Spirulina maxima were tested for degradation of some phenolic compounds listed as EPA priority pollutants. Batch experiments were carried out in 250 ml shake flasks with 50 ml of liquid. Toxins were dissolved in a medium (pH 7 - 7.2) without a carbon source (except for testing Spirulina, in which case sodium bicarbonate was part of the medium at Ph 9 - 9.2) and algae prepared by a batch cultivation were added. For each experiment a control flask containing the same compounds without algae were run in parallel. The concentrations of phenols was determined in samples taken during shaking by GC and/or HPLC. The chloroform extracts of the cells were analyzed similarly.

Phenol in concentration of about 1000 mg/l was easily degraded by all tested algae in less than 5 days. Concentration of about 3000 mg/l resulted in both very slow degradation and algae turn brown. No product of degradation was found in the medium by GC.

2,4-dimethylphenol was found to be converted by Chlorella even at concentration of about 1000 mg/l to an isomer of dimethylbenzenediol that was in some cases accumulated in the medium. Depending upon biomass and toxin concentration the rate of degradation changed and an optimum of toxin concentration inducing degradation might exist. Complete degradation could be reached with high biomass concentration as no toxin or intermediate product was found in the media or in chloroform extract of the cells by GC.

2,4-dinitrophenol in low concentration (70 mg/l) was degraded by Chlorella very quickly after an adaptation period of about 20 days. Scenedesmus was found to degrade even higher (120 mg/l) concentration of toxin. The degradation was again very fast after an adaptation period of about 5 days. The higher concentration of toxin was not changed in the presence of Chlorella even if algae remained green and alive.

Biodegradation of 2,4-dichlorophenol was not proven but the condition under which algae can survive a higher concentration of toxin could be found.

Conclusion can be made that all algae tested, Chlorella, Scenedesmus, and Spirulina, have a mechanism for degradation of phenolic compounds. First step of degradation can be an oxidation of second carbon on the benzene ring to form a derivative of catechol. All used phenolic compounds were proven to be degraded except for 2,4-dichlorophenol. Substituent on benzene ring can increase toxicity of compounds and it may influence degradability. This is a well-known fact for bacterial degradation and our results indicate a similar relationship in case of algae.

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## USE OF FLY ASH IN THE REMOVAL OF COPPER, NICKEL AND ZINC FROM WASTEWATER

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The removal of copper, nickel and zinc from wastewater by fly ash was investigated to determine the effects of contact time, pH and temperature. The wastewater used in the study was raw wastewater collected from the City of Regina Municipal Wastewater Treatment Plant. The wastewater was spiked with stock solutions of copper, zinc and nickel to raise their concentrations to approximately between 0.5 and 1 mg/L. The fly ash used in the study was collected from the first bunker of Poplar Power Station's (Unit 2) electrostatic precipitators. Batch adsorption experiments were conducted at 5 °C, 10 °C and 21 °C.

The fly ash had a surface area of 1.5 to 1.7 m<sup>2</sup>/g and 50 to 60 percent of it was retained on a 325 mesh sieve. Removals of copper, zinc and nickel attained equilibrium in two hours. Removals of the three metals were found to be a maximum in the pH range of 3 to 3.5. It was found that the adsorption capacity of fly ash with respect to these three heavy metals generally decreased with an increase in temperature. Removals of copper, nickel, and zinc were approximately 73%, 33% and 99% respectively at 21 °C at a pH of 3.0 to 3.5.

Application of the Langmuir, Freundlich and BET isotherms to the batch adsorption data is also presented.

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**APPLICATION OF ROBOTICS AND DATA QUALITY MONITORING/  
CONTROL TO REDUCE OPERATOR INTERVENTION IN  
AUTOMATED ION TESTING OF  
DRINKING WATER**

Craig B. Ranger<sup>1</sup> and Jean Wong-Chong<sup>1</sup>

Increasing water quality monitoring regulations place an increased burden on municipalities to perform routine testing to ensure that their drinking water contains pollutants below the maximum limits allowed by regulations. The analyzer described in this paper automates the approved methods for determining inorganic ions in waters and minimizes the amount of time required for operation.

Automated chemistry analyzers have been used for years to decrease turnaround time for environmental testing laboratories. However, a severe limitation to overall productivity was the requirement of the operator to intervene frequently if (a) analyte concentrations in the sample exceeded the instrument's full scale setting and (b) quality control sets exceeded their control limits. Both of these issues have recently been addressed through the combination of a robotics-based sampler, a digital diluter and a sophisticated PC-based software program.

As a prerequisite to reaching our goal for minimizing operator intervention, we first had to design a sampling mechanism. After considering several approaches, we settled on an XYZ-type design because of its flexibility. Not only can this device enable complete random access to sample and standards and replicate sampling, but can also deliver a dilution probe to samples. In addition, it can accommodate bulk quantities of calibration standards and QC/QA sets which saves repeated pouring and placing of these items. The XYZ operates in a compact space with three axes of motion: radial (in and out); vertical (up and down) and horizontal (back and forth). It accommodates three 60 position sample rack, and one 60 position dilution tube rack and one 14 position bulk standards rack. It also has positions for a waste station for washout of the sample circuit between samples.

The next step was to identify a diluter which was reliable and could be interfaced with a PC. We settled on a single syringe unit with an RS232C interface to enable computer control to perform dilutions between 5:1 and 1000:1.

Finally, we had to write a software program to operate in conjunction with the robot, diluter and auto analyzer and to intelligently coordinate the operation of all three entities. This was written in Turbo Pascal, version 5.0.

The final result has been a closed-loop automated chemical analyzer which can function unattended. The software detects any off-scale samples, estimates their values, determines the dilution ratio required to bring the analyte concentration into the working range of the chemistry and directs the XYZ sampler and diluter to perform the dilution. The sample is then rerun and integrated into the sampler report.

A QC/QA set can be specified for each run. This set can be determined repeatedly during a run and can consist of blanks, spikes, duplicates, and EPA knowns. Each

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member of the set can reside in a bulk vessel which the XYZ will automatically address when its introduction is required. The calibration standards can also be contained in bulk, available for injection as required during the run. Finally, one or more of the calibration standards can be specified to monitor system drift. If the drift exceeds the user-specified control limits, the software will direct the system to recalibrate, re-analyze all samples between the last check standard that passed and the most recent one that failed and continue on with the remaining samples.

In summary, an auto analyzer running approved methods has been enhanced to make it a closed-loop system which functions with no operator intervention.

# COMPARAISON ENTRE LA CAPACITÉ DE BIOACCUMULATION DU MERCURE DES GASTÉROPODES DE FAIBLE LONGÉVITÉ ET DES PÉLÉCYPODES DE L'ESTUAIRE D'EAU DOUCE DU SAINT-LAURENT

Louis Tessier<sup>1</sup>, Guy Vaillancourt<sup>1</sup>, and LeRoy Pazdernik<sup>1</sup>

La bioaccumulation du mercure chez les mollusques a fait l'objet de nombreux travaux, en particulier chez les moules (pélécy-podes) qui sont considérées comme de bons bioindicateurs des métaux lourds dans le milieu aquatique. Cependant, à notre connaissance, aucune étude n'a fait mention de la capacité des gastéropodes de faible longévité à accumuler le mercure. Le but de cette étude est de comparer la capacité de bioaccumulation du mercure chez deux espèces de gastéropodes (*Bithynia tentaculata* et *Viviparus georgianus*) et chez deux espèces de pélécy-podes (*Elliptio complanata* et *Lampsilis radiata siliquoides*). Les échantillons ont été récoltés entre Deschambault et la centrale Gentilly 2. Les échantillons ont été pris dans la zone littorale et sur la batture de Gentilly. La période d'échantillonnage s'est déroulée entre juin et août 1990. Le dosage du mercure a été effectué sur la chair, la coquille et l'ensemble chair-coquille pour différentes classes d'âges chez les gastéropodes et différents groupes chez les pélécy-podes. Le mercure a été dosé selon la méthode de la spectro-absorption atomique à vapeur froide après digestion et dissolution des échantillons par acide nitrique et perchlorique. Une analyse de variance, suivi d'un test de Scheffé a démontré des différences significatives ( $p < 0.05$ ) entre les espèces d'un même groupe (pélécy-podes, gastéropodes) et entre les deux groupes. Les valeurs minimums et maximums ont variées respectivement de 2,3 à 71,2 ng-g<sup>-1</sup> pour les pélécy-podes et de 7,1 à 109,9 ng-g<sup>-1</sup> pour les gastéropodes. Dans ce dernier cas on observe des variations importantes entre les différentes classes d'âge qui semblent indiquer la présence d'un patron de bioaccumulation qui leur est propre. Ainsi ces caractéristiques importantes pourraient privilégier l'utilisation des gastéropodes à titre de bioindicateur de mercure.

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## **EFFECT OF TILLAGE PRACTICES AND AGRICULTURAL IMPACTS ON WATER QUALITY IN EASTERN WASHINGTON**

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Conservation tillage practices have been advocated to reduce soil erosion and to protect water quality in surface waters subject to contaminants from agricultural runoff. Little quantitative research, other than on soil loss, is available. Research relating important water quality constituents and volumes in and of, agricultural runoff is vital in planning management practices best suited to a particular climate and soil type.

The results of this research provided information on how specific conservation tillage practices on Palouse area soils affected runoff volume and the concentrations of water quality constituents such as total solids, nutrients (nitrogen and phosphorus), and pesticides in the runoff, in comparison with conventional tillage. The information has direct application to much of the farmland in the United States, Canada and indeed in the Pacific Northwest region. These data are necessary for implementation of best management practices to reduce off-site impacts of agricultural runoff.

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**THE EFFECTS OF CONCENTRATED PULP MILL EFFLUENTS ON MIXED FUNCTION OXIDASE ACTIVITY (MFO) IN RAINBOW TROUT AS MEASURED BY 7-ETHOXYRESORUFIN-O-DEETHYLASE (EROD).**

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Pulp and paper mill effluents have been identified as being responsible for negative impacts in 14 of the 42 areas of concern surrounding the Great Lakes basin. A pressing need for further information about the impact of effluents from Canadian pulp mills has led to the use of mixed function oxidase enzymes as biological indicators of sublethal toxicity to fish. Induction of the 7-ethoxyresorufin-o-deethylase (EROD) enzyme has been shown to be one such indicator. During recent meetings in Winnipeg (Nov. 1 & 2, 1990) the incorporation of EROD into the new Canadian environmental guidelines for biological monitoring of fisheries was considered.

A high proportion of the chlorinated organic material (>80%) in biologically treated pulp mill effluent has a molecular weight greater than 1000 daltons. Because of its size this material has been thought to be biologically inert, however recent evidence has shown that under appropriate conditions some of this material can degrade to chlorinated guaiacols, catechols and veratroles. This degradation could contribute to the sublethal toxicity observed for fish in receiving environments. To date, little research has addressed this question. Various regulatory agencies in Canada and around the world are restricting pulp mill discharges of AOX (adsorbable organic halogen). The industry has questioned these regulations on the basis of the fact that the mix of compounds comprising AOX at any given mill is a function of operating parameters and effluent treatment. We suggest that it would be scientifically justifiable to regulate the industry based on the release of compounds with demonstrated toxicity. In this study we are attempting to characterize the components of treated and untreated effluents responsible for sublethal toxicity to fish.

EROD enzyme induction is being used as the indicator for the presence of biologically active compounds. Effluents in this study were concentrated using nanofiltration techniques from a mill on the St. Maurice River at La Tuque, Quebec. The La Tuque mill utilizes older technologies and only a primary treatment system. Extracts of suspended solids, receiving waters and effluents isolated during the concentration scheme were also prepared. These extracts and concentrates were intraperitoneally injected into rainbow trout and their EROD activity measured. The potential for these samples to induce EROD activity will be discussed.

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## ISOLATION OF HIGH MOLECULAR WEIGHT ORGANICS FROM KRAFT MILL EFFLUENT BY NANOFILTRATION

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Nanofiltration was used to concentrate the organic matter released into receiving waters by kraft mill effluents. Nominally, 1200 litres of effluent was concentrated 30-fold. The NF40 (Filmtec) membrane used had a molecular weight cutoff of 400 daltons and rejects 95% of the divalent and 40% of the monovalent ions. The performance of the membrane was monitored by flow rates at fixed pressure, recovery of dissolved organic carbon (DOC), chlorophenolics, conductivity and major ions. The flow rates decreased when the membrane became fouled as did DOC recoveries (normally *ca.* 70%). The most abundant chlorophenolics were chlorinated phenols and guaiacols. These compounds were not concentrated by nanofiltration, as expected. The concentrated organics were further fractionated into four molecular weight size classes by tangential flow ultrafiltration: > 30,000 daltons to < 10,000, > 10,000 to < 3,000, > 3,000 to < 1,000 and < 1,000 daltons. These fractions will be used for fish toxicity bioassays and biodegradation studies of the chlorinated high molecular weight organics.

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