Twenty-Ninth Central Canadian Symposium on Water Pollution Research

February 9 & 10, 1994
Canada Centre for Inland Waters
Burlington, Ontario

Abstracts

Themes:
Water Pollution Control Technology
In-Situ Remediation of Contaminated Aquifers
The Impact of Pollutants on Aquatic Ecosystems
Indicators of Environmental Sustainability
The Contamination of Groundwater by Pesticides
Pulp and Paper Effluent Impacts II

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Canadian Association on Water Quality
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TWENTY-NINTH CENTRAL CANADIAN SYMPOSIUM ON WATER POLLUTION RESEARCH

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• FINAL PROGRAM •

FEBRUARY 9, 1994:

8:00-8:45 Registration

8:45-9:00 Opening Remarks, CCIW Auditorium
J. Norman, President - CAWQ and J. Barica, Symposium Chairman and Editor - WPRJC

Session 1: Water Pollution Control Technology
CCIW Auditorium, Chair: S. Nutt

9:00-9:30 **R. Gehr and J. Nicell**
A Comparison of UV and Ozone Disinfection: Issues Raised During a Study on a Physicochemically Treated Effluent

9:30-10:00 **E. Jowett and M. McMaster**
Landfill Leachate Treatment Using a New Single-Pass Biofilter-Preliminary Laboratory Results

10:00-10:30 **Y. Du, R. Tyagi and T. Sreekrishnan**
Effects of Diffusional Limitation Inside the Floc on Dynamics of Activated Sludge Process

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

11:00-11:30 **A. Vladars-Usas, T. Duever, R. Hudgins, P. Silveston and S. Akesson**
Improved Clarification Using Overflow Baffles

11:30-12:00 **A. Baker, P. Dold, R. Jones, T. Briggs**
Development of a Mechanistic Model for Activated Sludge Treatment of Petrochemical Industry Wastewater

12:00-12:30 **L. Lishman and K. Murphy**
Alternate Control Strategies for Effective Nitrification with the Activated Sludge Process

12:30-1:30 LUNCH - MAIN MALL AREA

1:30-2:00 **J. Copp and K. Murphy**
Nitrification Parameter and Biomass Evaluation for the Modelling of Nitrifying Activated Sludge Systems

Session 2: In-Situ Remediation of Contaminated Aquifers
CCIW Auditorium, Chair: S. Lesage

2:00-2:30 **S. Lesage and S. Brown**
In-Situ Biochemical Degradation of Perchloroethylene DNAPL

2:30-3:00 **S. Forsey, K. Hamilton and J. Barker**
Evaluation of Strong Chemical Oxidizing Agents for the Purpose of *In-Situ* Remediation of Creosote Residuals

3:00-3:30 **C. Ptacek, D. Blowes and K. Waybrant**
Removal of Metals from Contaminated Groundwater Using *In-Situ* Porous Reactive Walls

3:30-4:00 COFFEE BREAK - MAIN MALL AREA

4:00-4:30 **W. Robertson and J. Cherry**
In-Situ Denitrification of Septic System NO_3^- Using Reactive Porous Media Barriers: Field Trials

4:30-5:15 CAWQ GENERAL MEETING - CCIW AUDITORIUM

5:15-6:00 RECEPTION - CCIW CAFETERIA

Session 3: The Impact of Pollutants on Aquatic Ecosystems
North/South Seminar Rooms, Chair: K. Kaiser

9:00-9:30	**K. Kaiser and M. McKinnon** Preliminary Environmental Impact Predictions for Selected New Drug Type Chemicals
9:30-10:00	**S. Norris and A. Houston** The Effects of Temperature Regime on Nickel Toxicity in Goldfish (*Carassius auratus L.*)
10:00-10:30	**J. Kochany and R. Maguire** Abiotic Transformations of Quinoline in the Aquatic Environment
10:30-11:00	COFFEE BREAK - MAIN MALL AREA
11:00-11:30	**J. Buttle** Hydrological Controls on Field Exports of Metolachlor to Receiving Streams
11:30-12:00	**T. Mayer and E. Reyes** The Role of Sediments in the Tributary Transport of Phosphorus and Heavy Metals
12:00-12:30	**M. Comba, J. Metcalfe-Smith, M. McKinnon and K. Kaiser** Organochlorine and PCB Residue Levels in Zebra Mussels of the Lower Laurentian Great Lakes and the St. Lawrence River
12:30-1:30	LUNCH - MAIN MALL AREA
1:30-2:00	**C. Loh, S. Springthorpe and S. Sattar** Characterization of a Hollow Fibre System for Studies of Microbial Fate in Aquatic Ecosystems
2:00-2:30	**J. Triska, G. Garbai, B. Bourgoin and A. Mudroch** New Solid-Phase Extraction Materials in Studies of Contamination of Water by Pesticides
2:30-3:00	**T. Murphy, A. Moller, M. Fox and J. Babin** *In-Situ* Sediment Bioremediation in Hamilton Harbour
3:00-3:30	COFFEE BREAK - MAIN MALL AREA

Session 4: Indicators of Environmental Sustainability
North/South Seminar Rooms, Chair: J. Barica

3:30-3:50	**L. Smith and D. Shrubsole** Indicating Risk: Lessons from Elmira on the Inherent Limitations of Sustainability Indicators
3:50-4:10	**K. Brady, A. Brady, K. Grant and M. Wong** A Framework for Ecosystem-Based Management: Developing Ecosystem Goals, Objectives and Indicators
4:10-4:30	**G. Wichert** Fish as Indicators of Ecological Conditions: Historical Sequences in Some Subwatersheds of Toronto Area Streams
4:30-5:15	CAWQ GENERAL MEETING - CCIW AUDITORIUM
5:15-6:00	RECEPTION - CCIW CAFETERIA

Poster Session Displays
Main Mall Area

J. Fischer, B. Apedaile and L. Vanclief
Loadings of Agricultural Herbicides to a Southeastern Ontario River

J. Struger, C. Bishop, K. Pettit, H. Tse, P. Ng and G. Peat
Environmental Fate and Effects of Organophosphorus Insecticides on Amphibians in a Muck Crop Growing Area of Ontario, Canada

G. Prill, J. Headley and R. Smillie
Development of On-line QA/QC Techniques for Statistical Evaluation of GC/MS Environmental Analysis of Pesticides in Groundwater

S. Efler, P. Hodson, J. Wilson and A. El-Shaarawi
Protocol for Measuring Activity of Ethoxyresorufin-*o*-Deethylase in Fish Tissue with a Micro-Plate Fluorometer and Spectrophotometer

L. Hewitt, J. Carey, K. Munkittrick and D. Dixon
An Evaluation of GC Detectable Constituents in Treated Bleached Kraft Mill Effluent to Induce Mixed Function Oxygenase Activity in Rainbow Trout

FEBRUARY 10, 1994:

Session 5: The Contamination of Groundwater by Pesticides
North/South Seminar Rooms, Chair: A. Crowe and P. Milburn

8:30-8:40	**A. Crowe and P. Milburn** Introduction
8:40-9:00	**W. Lampman** Susceptibility of Groundwater to Pesticide and Nitrate Contamination in Predisposed Areas of Southwestern Ontario
9:00-9:20	**D. Briggins and D. Moerman** Pesticides and Farm Well Water Quality Studies in Nova Scotia
9:20-9:40	**R. Carter, P. Nalasco and W. Stiebel** Investigation and Interim Remediation of Pesticide Contamination at a Site in Cambridge, Ontario
9:40-10:00	**D. McNaughton** Investigations of Pesticides in Groundwater Beneath Three Irrigated Sites Near Outlook, Saskatchewan
10:00-10:30	COFFEE BREAK - MAIN MALL AREA
10:30-10:50	**J. Mutch, M. Priddle and R. Jackson** Long-term Persistence of Aldicarb Residues Beneath a Potato Field on Prince Edward Island
10:50-11:10	**J. Buttle, P. Morgan, C. Metcalfe and D. Ostrander** Laboratory Studies on the Leaching of Aldicarb Through a Tropical Soil from Belize, Central America
11:10-11:30	**A. Crowe** Computer Analysis of the Factors Controlling Pesticide Migration and Persistence in Agricultural Regions Across Canada
11:30-11:50	**P.-Y. Caux** Sustainable Agriculture and Canadian Water Quality Guidelines
11:50-12:10	**D. Alley and B. Kirschner** International Joint Commission Activities Related to Groundwater Contamination by Pesticides in the Great Lakes Basin
12:10-1:30	LUNCH - MAIN MALL AREA
1:00-1:30	PROFESSOR/STUDENT DISCUSSION - SOUTH ROOM CAFETERIA
1:30-1:50	**J. Lawrence and M. Hendry** Application of a Mesoscale Model to Examine the Fate of Pesticides
1:50-2:10	**B. Butler, F. Breen, R. Allen-King and J. Barker** Fate of the Herbicide Glufosinate-ammonium and Diclofop-methyl in Groundwater
2:10-2:30	**J. Gaynor, C. Tan, C. Drury, I. van Wesenbeeck and T. Welacky** Atrazine Concentration and Losses in Subsurface Runoff as Affected by Tillage, Band Application, Intercrop and Water Table Control
2:30-2:50	**P. Milburn, D. Leger, H. O'Neill, J. Richards and K. MacQuarrie** Pesticide Leaching Associated with Conventional Potato and Corn Production in Atlantic Canada
2:50-3:20	COFFEE BREAK - MAIN MALL AREA
3:20-3:40	**D. Bourgeois, P. Deveau and V. Mallet** Microextraction of Polychlorinated Biphenyls and Dichlorodiphenyltrichloroethanes from Tap (Environmental) Water and Analysis by Gas Chromatography-Electron Capture Detector
3:40-4:00	**I. van Wesenbeeck and W. Reynolds** Field Measurements of Water and Solute Transport Parameters
4:00-4:20	**R. Clemente and R. De Jong** A Comparison of LEACHM Simulations with Field Data

4:20-4:40	**R. De Jong, W. Reynolds, S. Vieira and R. Clemente** Prediction of Pesticide Migration on a Watershed Basis: Methodology
4:40-5:00	**W. Reynolds, R. De Jong and S. Vieira** Prediction of Pesticide Migration on a Watershed Basis: An Application

Session 6: Pulp and Paper Effluent Impacts II
CCIW Auditorium, Chair: P. Hodson and H. Vaughan

8:50-9:00	**P. Hodson** Introduction
9:00-9:30	**K. Lindsay and D. Smith** Factors Influencing Pulp Mill Effluent Treatment in Alberta
9:30-10:00	**H. Melcer, P. Steel, A. Schnell, A. McKinlay and R. Cook** The Removal of Toxic Contaminants from Bleached Kraft Mill Effluent with Enhanced Biological Treatment Methods
10:00-10:30	COFFEE BREAK - MAIN MALL AREA
10:30-11:00	**F. Archibald and L. Roy-Arcand** Photodegradation of High Molecular Weight Kraft Bleachery Organochlorine and Colour
11:00-11:30	**S. Rao, B. Burnison, D. Rokosk and C. Taylor** Mutagenicity/Toxicity Assessment in Bleached Kraft Mill Effluents
11:30-12:00	**R. Robinson, K. Solomon, G. Van Der Kraak, J. Carey, K. Munkittrick and P. Flett** The Effects of Pulp and Paper Mill Effluent on Fish Reproduction - A Laboratory Perspective
12:00-12:30	**A. Schnell, P. Hodson, P. Steel, H. Melcer and J. Carey** Characterization and Biotreatability of Bleached Kraft Mill In-Plant and Combined Process Effluents with Respect to Toxic Compounds and MFO Induction Potential
12:30-1:30	LUNCH - MAIN MALL AREA
1:00-1:30	PROFESSOR/STUDENT DISCUSSION - SOUTH ROOM CAFETERIA
1:30-2:00	**J. Parrott and P. Hodson** Polychlorinated Dibenzo-*p*-dioxins (PCDDs), Dibenzofurans (PCDFs) and Other Inducers of Mixed Function Oxygenase (MFO) in Rainbow Trout
2:00-2:30	**J. Wilson, J. Parrott and P. Hodson** Additivity of Polychlorinated Dibenzo-*p*-dioxin (PCDD) Mixtures for Inducing Ethoxyresorufin-*o*-deethylase (EROD) Activity in Rainbow Trout
2:30-3:00	**P. Hodson, J. Wilson, M. LeMay and S. Efler** Factors Affecting the Induction of Mixed Function Oxidase Enzymes in Rainbow Trout Exposed to Pulp Mill Effluents
3:00-3:30	COFFEE BREAK - MAIN MALL AREA
3:30-4:00	**B. Burnison, P. Hodson, D. Nuttley and S. Efler** Isolation and Characterization of a MFO-Inducing Substance
4:00-4:30	**D. Bennie, B. Burnison and P. Hodson** Characterization of Chemicals Associated with MFO-Inducing Fractions of BKME
4:30-5:00	**J. Carey, P. Hodson, K. Munkittrick and M. Servos** An Overview of Recent Canadian Federal Research on the Physiological Effects of Pulp Mill Effluents on Fish

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Session 1 — Water Pollution Control Technology

A COMPARISON OF UV AND OZONE DISINFECTION: ISSUES RAISED DURING A STUDY ON A PHYSICOCHEMICALLY TREATED EFFLUENT

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Disinfection of treated domestic wastewaters will become increasingly popular due to the need for direct wastewater recycling in arid areas, or the use of receiving water bodies for recreational purposes. The Montreal Urban Community (MUC) employs physicochemical processes for its domestic water treatment, the major goal being phosphorus removal. Long–range plans involve usage of the downstream receiving water body, the St. Lawrence River, for swimming and aquatic sports. Pilot studies were therefore conducted to assess the feasibility of using UV light or ozone for disinfection. Chlorination facilities already exist, but are not being used because of concerns with respect to by–product formation.

The UV system tested employed medium–pressure lamps, which have an intensity approximately ten times that of conventional low–pressure lamps. The use of the latter would be infeasible for the high flows at the MUC plant (up to an average flow of 44 m^3/s by 1996). Adequate disinfection was achieved at a dose of 50 $mW \cdot s/cm^2$. This dose was selected based on: a downstream requirement of 200 coliform forming units (CFU) per 100 mL as required by the Quebec Ministry of the Environment (MENVIQ) for swimming at a location 4 km downstream from the point of discharge; an assumed dilution factor of 75 based on the results of a tracer study conducted in 1983; and an overall photoreactivation and dark repair factor of 2.73 based on measurements in the plant and simplifying assumptions for the river. The repair factor would vary with the UV dose chosen, and other variables affecting the final performance would include the coagulant used (ferric chloride was used for this study, but some tests were also performed with alum), the effluent turbidity, and the particle size distribution.

The treated MUC wastewater is carried by a 4.4 km outfall tunnel which discharges into the river. It was anticipated that this tunnel could serve as the contact chamber for ozonation. In addition to disinfection, ozonation tends to increase the dissolved oxygen of the effluent, another desirable feature. Pilot studies were therefore conducted to assess the feasibility of ozonation. These were carried out between the months of July and October (1992) in order to have results which correspond to the season in which the need for disinfection is greatest. Ozone disinfection was capable of reducing the fecal coliform counts from typical 0.4 to 4 million CFU/100 mL to less than 100 CFU/100 mL depending on the dose applied. However, it became evident that the magnitude of the ozone dose itself had no direct relation to disinfection efficiency due to the influence of other variables, especially effluent COD. A probability plot showed that an ozone dose of 15 mg/L would be sufficient to reach the target disinfection level of 5000 CFU/mL (stipulated by MENVIQ) prior to discharge into the outfall tunnel in 90% of the cases. An ozone dose of 19 mg/L was sufficient in 99% of the cases. Results indicated that a residual was necessary before disinfection could be achieved. Integrated CT values (residual concentration × time) were well correlated to disinfection, and a value of 0.15 mg·min/L was sufficient to reach target values. The major interference to ozone disinfection was COD, which was poorly removed by the physicochemical treatment process, and which was partially oxidized by ozone. An increase in BOD_5 following ozonation was observed which can be attributed to an increase in biodegradability of contaminants following oxidation. Dose–response curves plotted as a function of COD indicated that COD was consuming a significant fraction of the applied ozone. Therefore, for this waste, ozonation would be inappropriate for disinfection. However, when ferric chloride coagulant was replaced by alum, disinfection performance improved dramatically. This may be due to the presence of ferric ions which can act as scavengers for the free radicals which play a major role in ozone disinfection.

Toxicity evaluations based on daphnia, Microtox, and Ames procedures demonstrated that no increase in toxicity of the wastewater could be attributed to ozonation and UV disinfection; thus supporting their use as alternatives to chlorination. However, both UV and ozone disinfection have inherent disadvantages when compared with chlorination in that a residual is not maintained following discharge. Microbes can regenerate following UV disinfection due to photoreactivation and repair mechanisms, and the oxygen-rich environment resulting from ozonation can provide favourable conditions for microbe proliferation. Therefore, the potential for effluent deterioration due to microbe regrowth in the long outfall tunnel prior to its dilution in the St. Lawrence River was of considerable concern. A study was initiated to measure regrowth in the tunnel (fecal coliform and enterococci bacteria) and to measure waste contaminant concentrations at the discharge point and downstream where swimming is likely to occur. Results were inconclusive but did yield the following observations: (1) in some instances, effluent microbe concentrations from the outfall tunnel were indeed higher than influent concentrations; and (2) measurements of contaminant concentrations indicated that the assumed dilution factor at a point 4 km downstream, which was used to select UV and ozone disinfection doses, is highly optimistic for the summer months. This would indicate that the design values chosen were not conservative.

Thus the choice of a disinfectant for wastewater is heavily dependent on issues including effluent wastewater quality, regrowth in the outfall tunnel, hydraulics of the receiving water body, and the type and quality of upstream treatment processes.

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Landfill Leachate Treatment Using a New Single-Pass Biofilter—Preliminary Laboratory Results

Domestic and municipal sewage wastewaters have been successfully renovated in laboratory and field trials over the past few years with the newly developed single-pass 'Waterloo Biofilter'. The special absorbent filter medium optimizes conditions for aerobic biological activity and allows for simultaneous loading and aeration. As a result, loading rates ten times greater than that with sand or soil media are achieved with no sacrifice in effluent quality and no apparent plugging difficulties. During 16 months of treating primary clarifier effluent at the Waterloo sewage treatment plant, average removal rates of 98% BOD (133 to 2.3 mg/L) and 96% TSS (80 to 2.8 mg/L) were attained at 55 cm/day loading rates. Total and fecal coliform removals were 99.3% and 99.5%, respectively. Nitrification was thorough at 5–15°C, with ~23 mg/L NO_3–N and ~1 mg/L NH_4–N in the treated water. A small ventilation fan improves nitrification.

Laboratory experiments with leachate from the Britannia landfill in Mississauga over a five-month period successfully demonstrate that the biofilter can be used for leachate renovation as well, including thorough nitrification and suspended solids removal. At loading rates of 25–28 cm/day, TSS removal rates averaged 90–95% (80–100 mg/L in leachate to 4–5 mg/L in treated water) and $CBOD_5$ removals ranged from 83% to 99% (185–324 mg/L to 4–25 mg/L). As yet, phenols and COD have not been analyzed. Thorough nitrification was obtained without additional acidification (170–250 mg/L NO_3–N in the treated water) even at high pH (7.5–8.0 in leachate to 9.3–9.5 in treated water). NH_4–N decreases from 250–313 mg/L in the leachate to <1 mg/L in the treated water, with the occasional anomaly. Coliform bacteria (total and fecal) decrease by 2 orders of magnitude. Heterotrophic bacteria are abundant (~6e6 CFU/100mL) and the leachate required no microbial seeding or addition of nutrients. The acclimatization period for full nitrification and BOD/TSS removal is 7–10 days using new filter medium; less with a used biofilter with existing biomat.

Very preliminary metals analyses from Britannia indicate significant removal of Al, Pb, and Hg (>97%), and partial removal of Zn (~80%) and Cu (~54%). No change was evident with B, Cr, Co, Ni, and V. The metals Be, Cd, and Mo were not detectable in the leachate or treated water. Higher removal rates coincide with metals associated with particulate matter, which are presumably retained in the biomat. It is speculated that the ferric iron hydroxides forming in the biofilter are mediated by the intense biological activity and facilitate metal removal by adsorption, analogous to metalliferous Fe-Mn nodules on the seafloor.

Although in the initial stages, similar renovation is indicated for a second leachate wastewater and a third is being tested shortly. Pilot demonstration units are being set up on-site to transfer the laboratory experiments to the field.

Effects of Diffusional Limitation inside the Floc on Dynamics of Activated Sludge Process

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A complete mechanistic model of suspended growth system such as activated sludge process must take into consideration the reaction kinetics in three levels: 1) the cell model, since the cell (though the cell here may be merely a functional term) is the most basic unit for reactions to take place; 2) the floc model, since the internal mass transfer resistance in floc will affect the reaction patterns within the floc in general; and 3) the reactor model. The model of activated sludge process developed by the IAWPRC task group is comprehensive in terms of the reaction kinetics on cell level. Nevertheless, it is less comprehensive on floc level because it was developed under the assumption that the variation of diffusional resistance within the floc due to the change of floc size was ignored. This assumption is true in cases where the liquid in aerator is well agitated and the flocs are small in size. However, it cannot be accepted in some other cases. A modification is thus required in this respect if a general case is to be concerned.

This work deals with the dynamic modelling and simulation investigation of activated sludge process by incorporating intraparticle mass transport in floc to account for the effects of the diffusional limitation on the process dynamics. In process model development, the following assumptions and principle were followed:

1) The kinetic model developed by the IAWPRC task group is employed in this work since it is believed to represent the state of the art in terms of the kinetics on cell level for the activated sludge process;
2) The floc model is assumed to concern only the aerobic growth of heterotrophic bacteria and the nitrification that involves the activity of autotrophic bacteria. Accordingly, the intraparticle diffusional limitation inside the floc is restricted to the terms of dissolved oxygen, soluble organic substrate and ammonium nitrogen. The diffusion of other substrates or materials within the floc, however, is ignored due to the fact that it is much faster compared to that of organic substrate;
3) The activated sludge process considered in this study is assumed to consist of an aerator and a clarifier. The hydraulic characteristics of the aerator take the form of a continuously stirred tank reactor (CSTR);
4) To raise simulation efficiency, the 'separation principle' is adopted i.e., the floc model is arranged to link up with the system model by using the parameter of effectiveness factors. An index is also defined specifically so that the process dynamics with the IAWPRC task model can be viewed as a special case in this study when the index is equal to 1.0.

To develop floc model, some assumptions were made that include pseudo-steady state, uniform density of the biomass and spherical biofloc with average size. The floc model with three material balance equations and boundary conditions on the floc level were then proposed in this study for describing the diffusional resistances of dissolved oxygen (S_{DO}), readily biodegradable substrate (Ss) and ammonium nitrogen (S_{NH3}) inside the floc, respectively. The diffusion coefficients of the considered substrates were taken from literature. The floc model was applied to evaluate η_1 and η_3 as a function of the biofloc's diameter (r) at different level of dissolved oxygen concentration (S_{DO} is from 1.0 to 3.0 g (-COD) m-3), soluble substrate concentration (Ss is from 0.6 to 6.0 g COD m-3), ammonium nitrogen concentration (S_{NH3} is from 0.1 to 2.4 g NH3-N m-3) in bulk phase as well as the concentration of heterotrophs (X_{BH} is from 600 to 2400 g COD m-3) and autotrophic bacteria (X_{BA} is from 30 to 160 g COD m-3) in aerator. The floc model developed was connected with the system model by the two effectiveness factors $\eta_1$and η_2 i.e., the ratio between the actual rate and the intrinsic rate for the aerobic growth process of heterotrophs and for the aerobic growth process of autotrophs, respectively.

To work out a solution for the floc model equations mentioned above is a time consuming computing task since this is actually a two-point boundary problem. To facilitate process simulation for process control, an important concern in this study is to build a separate model that is able to relate the effectiveness factors with the operating condition at different level as described above. The artificial neural network technique was employed in this work for this modelling task. First, the floc model equations were solved off-line, by using the orthogonal collocation numerical technique in this study due to its computing efficiency, corresponding to more than one thousand different conditions. A data base concerning the two effectiveness factors and other six process variables was then established. With the data base available, an artificial neural network model was finally formed with six input variables (r, Ss, S_{DO}, S_{NH}, X_{BH} and X_{BA}) and two output variables (η_1 and η_3). The neural model developed has one hidden layer with ten neural nodes and it was shown to have an excellent predicting capability with the average error as low as 0.03.

An extensive simulation investigation of the activated sludge process was finally carried out with the neural model incorporated into the system model to evaluate the process dynamics under different environmental and operating conditions.

Floc radius cm	Ss g COD m-3	SDO g -COD m-3	SNH3 g N m-3	XBH g COD m-3	XBA g COD m-3	Effect. factor 1	Effect. factor 3
0.001	0.6	1	0.1	600	90.39	0.985	0.991
0.001	0.6	1	0.1	1450.3	90.39	0.985	0.996
0.001	0.6	1	0.1	2400	30	0.986	0.998
0.004	2.62	3	2.4	1450.3	90.39	0.841	0.994
0.004	2.62	3	2.4	1450.3	160	0.84	0.99
0.004	2.62	3	2.4	2400	90.39	0.841	0.996
0.004	2.62	3	2.4	2400	160	0.841	0.994
0.004	6	1	0.1	600	30	0.881	0.873
0.004	6	1	0.1	1450.3	90.39	0.881	0.865
0.004	6	1	0.1	1450.3	160	0.88	0.838
0.004	6	1	0.1	2400	30	0.881	0.896
0.004	6	1	0.41	600	30	0.88	0.956
0.004	6	1	0.41	600	90.39	0.875	0.915
0.004	6	1	0.41	600	160	0.871	0.873
0.004	6	1	0.41	1450.3	30	0.881	0.969
0.008	0.6	1	0.1	1450.3	30	0.607	0.917
0.008	0.6	1	0.41	2400	30	0.607	0.972
0.008	0.6	1	0.41	2400	90.39	0.605	0.93
0.008	0.6	1	2.4	600	90.39	0.583	0.871
0.008	0.6	1	2.4	600	160	0.56	0.771
0.008	0.6	1	2.4	1450.3	30	0.605	0.983
0.008	0.6	1	2.4	1450.3	90.39	0.598	0.949
0.008	0.6	1	2.4	2400	90.39	0.602	0.969
0.008	0.6	1	2.4	2400	160	0.598	0.946
0.008	0.6	2	0.41	2400	160	0.586	0.886
0.008	0.6	2	2.4	600	30	0.585	0.979
0.008	0.6	2	2.4	600	90.39	0.581	0.934
0.008	0.6	2	2.4	600	160	0.575	0.878
0.008	0.6	2	2.4	1450.3	30	0.587	0.991
0.008	0.6	2	2.4	1450.3	90.39	0.585	0.974
0.008	0.6	2	2.4	1450.3	160	0.583	0.953
0.008	0.6	2	2.4	2400	30	0.587	0.994
0.008	0.6	2	2.4	2400	90.39	0.586	0.984
0.008	0.6	2	2.4	2400	160	0.585	0.972
0.008	0.6	3	0.1	600	30	0.58	0.838
0.008	0.6	3	0.1	600	90.39	0.58	0.675
0.008	0.6	3	0.1	600	160	0.58	0.569
0.008	6	1	0.41	600	30	0.669	0.862
0.008	6	1	0.41	600	90.39	0.662	0.744
0.008	6	1	0.41	600	160	0.657	0.652
0.008	6	1	0.41	1450.3	30	0.671	0.907
0.008	6	1	0.41	1450.3	90.39	0.668	0.845
0.008	6	1	0.41	1450.3	160	0.665	0.786
0.008	6	1	0.41	2400	30	0.672	0.92
0.008	6	3	0.41	2400	30	0.65	0.929
0.008	6	3	2.4	600	160	0.643	0.895
0.008	6	3	2.4	1450.3	30	0.65	0.988

0.011	0.6	3	0.1	2400	90.39	0.426	0.761
0.011	0.6	3	0.1	2400	160	0.426	0.669
0.011	0.6	3	0.41	1450.3	30	0.426	0.913
0.011	0.6	3	0.41	1450.3	90.39	0.425	0.786
0.011	2.62	1	0.1	600	90.39	0.475	0.485
0.011	2.62	1	0.1	600	160	0.475	0.396
0.011	2.62	1	0.1	1450.3	30	0.477	0.742
0.011	2.62	1	0.1	1450.3	90.39	0.476	0.619
0.011	2.62	1	0.1	1450.3	160	0.476	0.534
0.011	2.62	1	0.1	2400	30	0.477	0.776
0.011	2.62	1	0.1	2400	90.39	0.476	0.684
0.011	2.62	1	0.1	2400	160	0.476	0.61
0.011	2.62	1	2.4	1450.3	160	0.454	0.768
0.011	2.62	1	2.4	2400	30	0.475	0.965
0.011	2.62	1	2.4	2400	90.39	0.47	0.916
0.011	2.62	1	2.4	2400	160	0.464	0.855
0.011	2.62	2	0.1	600	30	0.459	0.635
0.011	2.62	2	0.1	600	90.39	0.458	0.469
0.011	2.62	2	0.1	600	160	0.458	0.38
0.011	2.62	2	0.1	1450.3	30	0.459	0.733
0.011	2.62	2	0.1	1450.3	90.39	0.459	0.604
0.011	2.62	2	0.1	1450.3	160	0.458	0.518
0.011	2.62	2	0.1	2400	30	0.459	0.77
0.011	2.62	2	0.1	2400	90.39	0.459	0.671
0.011	2.62	2	0.1	2400	160	0.459	0.595
0.011	2.62	2	0.41	600	30	0.458	0.801
0.011	2.62	2	0.41	600	90.39	0.457	0.614
0.011	2.62	2	0.41	600	160	0.456	0.506
0.011	2.62	2	0.41	1450.3	30	0.458	0.891
0.011	2.62	2	0.41	1450.3	90.39	0.458	0.769
0.011	2.62	2	0.41	1450.3	160	0.457	0.672
0.011	2.62	2	0.41	2400	30	0.459	0.92
0.011	2.62	2	0.41	2400	90.39	0.458	0.836
0.011	2.62	2	0.41	2400	160	0.458	0.758
0.011	2.62	2	2.4	600	30	0.456	0.947
0.011	2.62	2	2.4	600	90.39	0.45	0.835
0.011	2.62	2	2.4	1450.3	160	0.453	0.88
0.011	2.62	2	2.4	2400	30	0.458	0.984
0.011	2.62	2	2.4	2400	90.39	0.457	0.959
0.011	2.62	2	2.4	2400	160	0.455	0.929
0.011	2.62	3	0.1	600	30	0.452	0.629
0.011	2.62	3	0.1	600	90.39	0.452	0.462
0.011	2.62	3	0.1	600	160	0.452	0.374
0.011	2.62	3	0.1	1450.3	30	0.452	0.729
0.011	2.62	3	0.1	1450.3	90.39	0.452	0.598
0.011	2.62	3	0.1	1450.3	160	0.452	0.511
0.011	2.62	3	0.1	2400	30	0.452	0.767
0.011	2.62	3	0.1	2400	90.39	0.452	0.666
0.011	2.62	3	0.1	2400	160	0.452	0.588

IMPROVED CLARIFICATION USING OVERFLOW BAFFLES

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Abstract

Clarifier studies in our laboratory have been concerned for several years with mechanical ways to improve the efficiency of solids removal by adding baffles near the overflow weir. The purpose of this study was to collect data as a basis from which to design a full-scale trial for this potentially useful technology. As a working hypothesis, it was assumed that the solids removal efficiency from any suspension could be significantly improved by adding a baffle (lip) of known width, angle, and depth below the surface. Experiments were conducted in a rectangular laboratory clarifier to establish the influence of these variables on the solids removal efficiency. Thus, the specific objectives of this study were:

- to outfit an existing rectangular clarifier with computer-controlled concentration measuring equipment to reduce or avoid the labour of grab-sampling as well as to manage the necessarily large volume of data,
- to determine the clarifier performance in the absence of overflow baffles,
- to extend experiments carried out in the laboratory clarifier to verify the choice of baffle angle (including a zero angle to provide a lip), and baffle width and compare these as a function of overflow rate, and
- to examine the dependence of clarifier behaviour on baffle angle, baffle width, and overflow rate.

The laboratory-scale clarifier used in this set of experiments was fabricated from Plexiglas™. Overflow baffles to fit across the tank were also of Plexiglas™ and positioned near the effluent trough. The clarifier was fed from a head tank supplied by a feed reservoir whose volume

totalled approximately 2000 L. A Moyno positive displacement pump was used to pump the suspension from the reservoir to the head tank. In the first set of tests, Celite™ 545 (Johns-Manville), diatomaceous silica, was used to create the settling suspensions; in the second and third sets, a thermo-mechanical pulp derived from black spruce wood was used. The latter material was provided by Abitibi-Price Inc., Mississauga, Ontario.

From the head tank, the flow rate of the suspension was recorded electronically by means of a flow meter, after which the feed entered the clarifier. In the clarifier, the concentration was measured by a calibrated, computer-controlled Claritek Suspended Solids Monitor™. This equipment recorded a moving average (at a rate of about once per second) of many concentration readings of a suspension in view of the high variability that is typical of gravity clarifiers. Removal data from each experimental run were filed in the computer's hard drive.

Two-level factorial-design experiments were performed. With an inlet concentration of 550 mg/L of Celite suspended in water, the influence of four factors (flow rate, depth of baffle, width of baffle, and baffle angle) was tested using a full 2^4 factorial design. The response variable recorded in all of these measurements was the percent removal, i.e., the per cent increase in solids removal resulting from using a baffle in the clarifier tank.

Results indicated that although flow rate (overflow rate) is the key variable, under some conditions, baffle angle (horizontal = 0 degrees), depth (below the surface) and width (dimension of the baffle between its attached side and its free side) may be significant. Yet, the pattern under which improvements can be expected is still not clear. This result implies that improvements in removal from clarifiers must be sought by a process of "fine-tuning." This implies a need for baffles of alterable dimensions to suit a particular flow condition.

DEVELOPMENT OF A MECHANISTIC MODEL FOR ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL INDUSTRY WASTEWATER

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More stringent legislation governing water quality standards for industrial effluent discharges has resulted in a thorough evaluation of activated sludge systems treating these wastewaters in order to optimize system performance. One approach that has been applied successfully to the optimization of systems treating *municipal* wastewaters is utilization of a dynamic mechanistic model; for example, the IAWPRC model.

This paper outlines the development of a comprehensive dynamic mechanistic mathematical model for predicting the behaviour of an activated sludge system treating a petrochemical plant wastewater at the Polysar Rubber Corporation installation in Sarnia, Ontario. Influent to this system consists of five separate streams which differ substantially in chemical composition.

Model development involved a number of key stages:

- Identification of the key components to be monitored in the system.
- Determination of the key biochemical processes and removal mechanisms occurring within the system.
- Formulation of the components and processes into a mathematical model.
- Once the mathematical framework is in place the stoichiometric and kinetic coefficients in the model were calibrated using experimental data.
- The final stage of model development involved verification of the calibrated model with an alternate set of data to ensure the model is capable of predicting system behaviour under a set of operating conditions different from those used in the calibration stage.

A number of aerobic activated sludge batch tests were conducted on each of the five influent streams by mixing proportions of each stream with activated sludge from the full-scale system (examples overleaf). The changes in COD, TKN, and oxygen utilization rate (OUR) were monitored during the tests to obtain information on the kinetics of the removal processes. Additional batch tests were designed to quantify aspects such as rates of stripping of volatile organics and activated sludge decay rates. The responses in the batch tests, together with data from the full-scale plant, enabled the model to be calibrated. This involved matching model predictions to observed behaviour.

The paper describes the stages in development of the dynamic model. Subsequently the calibrated and verified model was incorporated in a process simulator (GPS-X™). This provided a tool for evaluating strategies for optimizing performance of the Polysar treatment system. That part of the study is described in a separate paper.

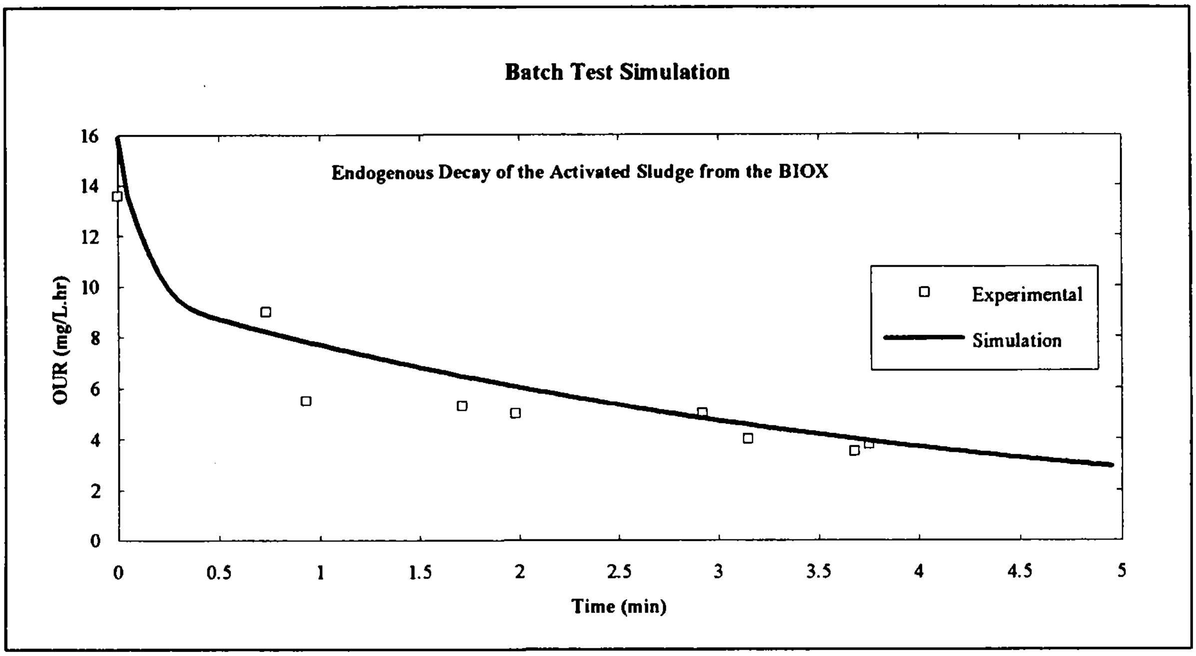

Figure 1 : The experimental results of an endogenous decay rate test are presented above along with the simulated results of the test conducted using the GPS-X™ . The model was able to predict the observed values of OUR measured in the experiment with reasonable accuracy.

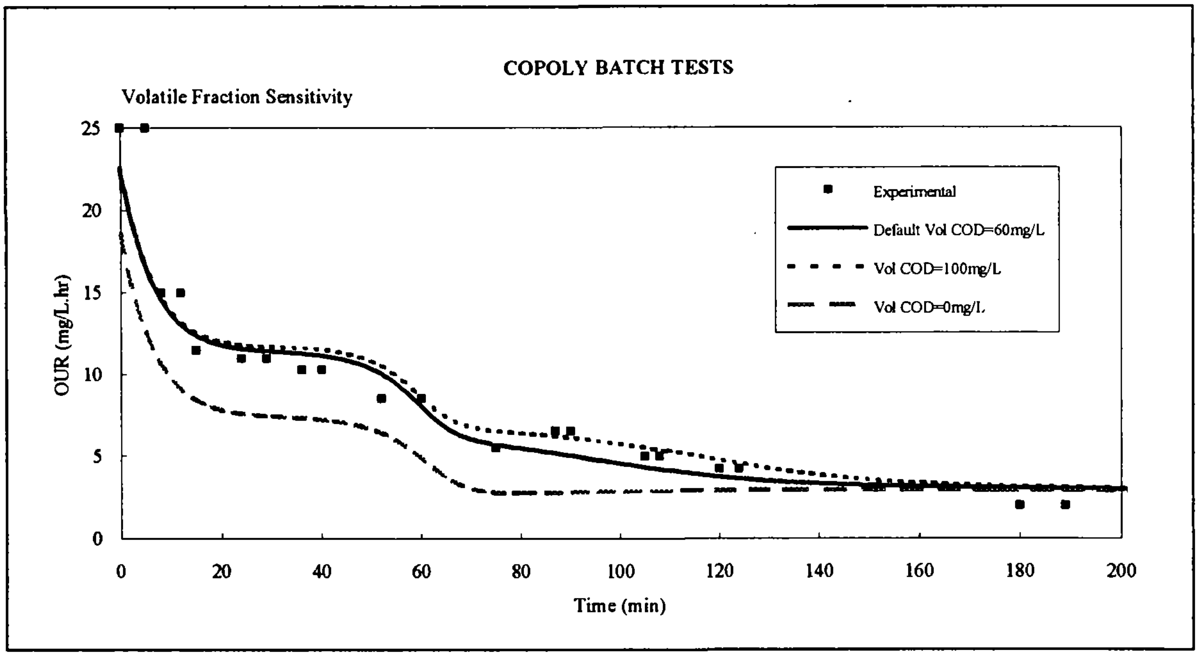

Figure 2: Impact of the volatile organic compound fraction in the COPOLY stream on the behaviour of the batch test OUR.

Alternate Control Strategies for Effective Nitrification with the Activated Sludge Process

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Nitrification can proceed under cold temperatures if sufficiently long solids retention times are maintained. Long retention times imply higher mixed liquor suspended solids (MLVSS) concentrations and thus increased solids loading to the secondary clarifier. These constraints imply that upgrading existing activated sludge plants to achieve year round nitrification could require the construction of additional secondary clarifiers in addition to increases in aeration capacity. If additional clarifier capacity is required it would be the major cost factor. An effective control strategy providing consistent nitrification yet minimizing the solids loading to the clarifier would substantially reduce the costs associated with nitrifying at cold temperatures. It would also be beneficial if the chosen control strategy was easy to implement from an operational viewpoint.

The effectiveness of three control strategies: conventional SRT control, mixed liquor (MLVSS) control and a Modified Fixed Mass Wastage (MFW) control based upon control chart strategy, were investigated using actual data from Hamilton Woodward Avenue Sewage Treatment Plant (Woodward STP) and a calibrated variant of the IAWPRC model. The data from a "pseudo steady" state (constant flows) bench study conducted by the Wastewater Technology Center at Woodward STP was simulated successfully over 440 days by the model. Actual STP flow variations were superimposed on the pilot plant data to create a data base simulating actual daily loadings to the full scale STP for the period of study. Using the estimated flow weighted loadings the model predicted that at a SRT of 4 days and temperatures ranging from 17 - 25 °C, consistent nitrification could be achieved. Using either MLVSS or MFW control, nitrification equivalent to that obtained under SRT control was achieved. Operation under any of the three control scenarios gave equivalent loadings to the clarifier. Simulations run at 8 °C indicated again that both MLVSS and MFW control performed as effectively as SRT control. Use of either MLVSS control or the preliminary MFW, even with control settings that have not been optimized, is preferential to SRT control due to the ease of operation.

Nitrification Parameter and Biomass Evaluation for the Modelling of Nitrifying Activated Sludge Systems

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Recent changes enacted by Ontario's Ministry of the Environment and Energy - Municipal Industrial Strategy for Abatement program call for non-toxic effluent wastewater discharges. Although ammonia has not been identified for elimination, it is toxic to aquatic life at concentrations typical of treated municipal discharges. This has renewed interest in nitrification as a means to eliminate ammonia from wastewater.

This study examined a number of nitrification parameters that are required for the simulation of a nitrifying activated sludge system. By studying dominant cultures of nitrifying organisms several parameter estimates (Y_g, d, b, K_{NH}, μ_{max}) were evaluated.

An *in-situ* nitrifier mass estimation technique was developed to estimate the nitrifier population within an activated sludge sample through the addition of dominant culture. This technique was applied to activated sludge samples from the Milton Wastewater Treatment Plant and the results were compared to population estimates calculated using the IAWPRC wastewater model equations. Several sets of parameter estimates were used, including the values developed in this investigation and the IAWPRC default estimates.

Session 2 — In-Situ Remediation of Contaminated Aquifers

IN-SITU BIOCHEMICAL DEGRADATION OF PERCHLOROETHYLENE DNAPL.

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Solvents present as dense non-aqueous phase liquids (DNAPL) are a severe problem in groundwater. They act as a constant source of contamination of groundwater flowing through it. Therefore any site remediation where DNAPL is present must start with the removal of the source. When the contamination is shallow, excavation or soil venting of the dewatered area are possible solutions. At depth, current technologies attempt to remove the DNAPL by pump-and-treat, sometimes using surfactants to enhance dissolution. The removal of the dissolved volatiles is accomplished by air stripping, where the off gases must be treated, followed by charcoal adsorption. These treatments are merely phase transfer and concentration steps. The solvents remain unchanged. No method exists whereby the DNAPL can be destroyed *in-situ*. *In-situ* biodegradation of dense chlorinated solvents such as perchloroethylene has been observed, but occurs within the dissolved plume only. The proposed methodology attacks the DNAPL in-situ and starts degrading it immediately, as it comes in contact with the remedial solution.

Vitamin B12 (B12), in the absence of a cell and even of a protein structure, which is often thought essential for the correct alignment of the substrate with the catalytic centre of the enzyme, is capable of reductively dechlorinating chlorofluorohydrocarbons, chlorinated aliphatic and aromatic hydrocarbons. Vitamin B12 is highly water soluble. It was therefore a good potential candidate for delivery into the subsurface as an *in-situ* treatment. In this paper, a series of column experiments were conducted to verify whether B12 would be effective in the treatment of PERC present as a residual DNAPL phase. The effect of the concentration of B12 on the rates of transformation and the product distribution was measured. The effect of sorption by organic carbon was studied using columns containing varying amounts of C18 silica.

The column experiments were designed to simulate a remedial solution passing through an area of the saturated zone where DNAPL was present at residual saturation. At 0.1 mg/L B12, TCE, the first product of dechlorination accounts for approximately 10% of the eluent and trans-DCE approximately 2%. Cis-DCE was only observed initially and did not amount to more than 1% of the products. At the 1 mg/L B12 concentration the percentage of TCE increased to 35% of the total. Trans-DCE and unreacted PERC acccounted for approximately 5% and 60% respectively. Cis-DCE was produced in concentrations ranging from 1 up to 5% of the total. The 10 mg/L concentration of B12 produced an effluent with more than 80% TCE, 13%unreacted PERC, and all the other compounds in the 1-3 % range. More than 90% of the material had eluted before 30 pore volumes. The product distribution remained the most constant of all three experiments.

The next group of experiments were aimed at studying the effect of the presence of organic carbon on the transformation of B12 catalysed transformation of PERC. Organic carbon was added to the column as particles of C18 bonded to silica. With the 0.1 % C18 column, no significant difference was observed in the retardation factors between PERC and its degradation products, but the removal of the solvents was somewhat slower than without any organic carbon. At 1% C18 sorption is beginning to be significant. The transformation products TCE and C- and T-DCE formed a much larger proportion of the effluent than would be expected based on the rate of reaction at 1 mg/L B12. The breakthrough curve for PERC lagged behind as would be predicted by its larger log K_{ow}. However, at this moderate concentration of organic carbon (0.11%), the reductive dechlorination of PERC by B12 is not significantly affected by the presence of a sorptive phase, and the reaction still occurs at the same rate. At 10% C18 (equivalent to 1% TOC), the retardation effect was qualitatively as predicted, but sorption was much stronger than anticipated. After 190 pore volumes, the column was eluted with surfactants and methanol, where most of the material that had not been accounted for, was eluted. It seems that PERC was simply strongly sorbed on the organic carbon.

Conclusion

The use of Vitamin B12 offers many advantages over current practice. The same reactions that are catalyzed by anaerobic bacteria using cometabolism can be effected using stable, non-toxic reagents. Because there are no living organisms to feed or destroy, the technology is applicable to concentrations ranging from saturation to low ppb level. The level of treatment obtained depends on the concentration of B12, the nature of the solvent to be degraded and the hydraulic retention time.

Evaluation of Strong Chemical Oxidizing Agents for the Purpose of *in situ* Remediation of Creosote Residuals.

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Abstract

Creosote is a dense nonaqueous liquid that may contain as many as 200 different chemicals. The composition of creosote depends on the coal tar from which it was produced but generally it contains 85% polynuclear aromatic hydrocarbons (PAHs), 10% phenolics and 5% heterocyclic compounds (nitrogen, sulfur and oxygen containing aromatics).

Creosote and coal tar are associated with manufactured gas plants, tar distillation works and wood preservative plants. Presently creosote is used in approximately 415 to 550 wood treatment sites within the United States. More than 40 of these sites are on the US EPA Superfund list and many more are being monitored.

Creosote liquids can migrate below the water table leaving a widely distributed residual source of contaminants leaching to the groundwater. Removal of deep creosote residuals especially below the water table by excavation, steam flushing, surfactants or by pump and treat technologies are generally not feasible. The chemical oxidation process would involve flushing the oxidizing agent through the contaminated zone to achieve the mineralization of wastes or in the case of the larger, more refractory, less soluble constituents their break down to more soluble and biodegradable acids and alcohols.

In conjunction with these experiments is an on going study of the fate and mobility of creosote compounds under natural condition at Canadian Forces Base Borden. If using an oxidizing agent is considered a suitable remedial technology the creosote source at CFB Borden will be used as a field test site.

The oxidizing agents selected for laboratory studies were potassium permanganate, hydrogen peroxide with ferrous ion (Fenton's Reagent) and potassium persulfate with ferrous ion. Batch laboratory experiments were conducted on representative creosote compounds and on creosote itself. Since the CFB Borden aquifer is buffered by carbonate minerals the batch experiments were buffered to a pH of 7.

Oxidation of phenolic wastes with Fenton's reagent has been reported by a number of researchers. Optimal pH's of these reactions were found to be between 2 and 4 with a molar ratio of 1:3:1 (organic : H_2O_2 : Fe^{2+}).

Using the molar ratio of 1:3:1 the oxidation of p-cresol at pH 7 was attempted. The reaction was slow but by increasing the ferrous ion and peroxide molar ratios to 1:30:8 (p-cresol : H_2O_2 : Fe^{2+}) rapid decomposition of p-cresol was observed. Similarly, the oxidation of p-cresol with persulfate required a large molar ratio of persulfate and iron (1:10:8, p-cresol : S_2O_8 : Fe^{2+}). Permanganate decomposed p-cresol within 5 minutes using the molar ratio of 1:1 (p-cresol : permanganate) .

At a pH of 7 the two iron catalyzed reagents suffer from a decrease in Fe^{2+} catalyst over time which impedes the oxidation capability of the reagents. The decrease in catalyst

can be attributed to the precipitation of iron oxyhydroxides and from the inability of the organic radicals to reduce Fe^{3+} back to Fe^{2+}.

Using the above molar ratios the oxidation of 1-methylnaphthalene, pyrene, and indole was conducted. Permanganate was able to decompose the three compounds. Fenton's and persulfate reagents decomposed 1-methylnaphthalene and indole but not pyrene at a pH of 7.

For the oxidation of creosote, 0.1 mL was added to one litre of buffered organic free water and was stirred for 2 days. The oxidizing agents were then added regularly according to the molar ratios found from the individual batch reactions with p-cresol.

All three reagents reduced the mass of the solubilized creosote compounds. The more soluble, easily oxidized compounds such as phenol, p-cresol, m-xylene and indole were decomposed readily. The more recalcitrant compounds such as fluorene, dibenzofuran, pyrene, naphthalene and phenanthrene were gradually oxidized to very small aqueous concentrations over the 27 day experiment (15 additions of oxidizing agents). At the end of the experiment creosote globules could still be seen in each of the reaction mixtures. Extraction of the reaction flasks with dichloromethane showed that the mass of the creosote was reduced and contained only the less water soluble compounds. The three reagents were able to reduce the mass of monitored compounds in the creosote phase by more than 90%.

During the creosote batch experiments with Fenton's and persulfate reagents a decrease in pH was observed after approximately 3 additions of reagents. Thus the ability of the reagents to decompose creosote at pH 7 was not assessed. The experiments did however, demonstrate the effectiveness of these reagents at lower pHs.

Fenton's and persulfate reagents could be used in acidic systems or those that are allowed to become acidic. At neutral pHs large molar ratios of iron and peroxide must be used since precipitation of iron oxyhydroxides continually removes the catalyst, Fe^{2+}.

Permanganate would be the preferred oxidizing agent for pH neutral, carbonate buffered aquifers, since it is capable of decomposing creosote compounds and the reagent's oxidizing ability is not adversely affected at a pH of 7.

Current research is focusing on column experiments in which the oxidizing agent is flushed through a column of sand containing creosote at residual concentrations.

Removal of Metals from Contaminated Groundwater Using *In-Situ* Porous Reactive Walls

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Porous reactive walls for remediating contaminated groundwater present a promising alternative to conventional remediation techniques. These walls are installed *in-situ* in the path of migrating contaminated groundwater by excavating subsurface materials and replacing these materials with a porous, permeable reactive media. Contaminants are passively removed from the groundwater upon contact with the reactive materials in the wall. Porous reactive walls potentially can save energy, save water, and avoid the need for construction of above-ground facilities. Rates of removal of Cr(VI) and metals contained in acid-mine drainage waters by porous reactive materials were assessed through bench-scale batch and column style tests. The rate of removal of dissolved Cr(VI) (20 mg/L initial concentration) by reaction with FeS_2, $FeCO_3$ and elemental Fe using batch tests indicate the removal rates were most rapid using elemental Fe as a reductant, with Cr(VI) concentrations lowered to less than 0.05 mg/L (the recommended drinking water limit) within 20 min. Duplicate experiments conducted at 4°C showed that Cr(VI) was also removed rapidly at low temperature. These results suggest that Cr(VI) removal using elemental Fe is possible at normal groundwater temperatures. A column test monitored for 22 months indicates Cr(VI) has been removed effectively to less than 0.05 mg/L by elemental Fe at a flow rate typical of those observed at sites of groundwater contamination. Removal of Cr(VI) has been successful for more than 120 pore volumes of contaminated water with no apparent clogging of the porous media. Batch tests were conducted to assess the rate of removal of SO_4, Fe, Zn, Ni, and Cd contained in simulated acid mine-drainage water. Different mixtures of organic carbon sources, including composted leaf mulch, composted sheep manure, wood chips, saw dust and sewage sludge, were added to promote bacterial sulfate reduction and precipitation of SO_4 and the metals as insoluble sulfides. The batch mixtures resulted in rapid (within days) and sustained removal of SO_4 and dissolved metals (Fe, Zn, Ni, and Cd) after sulfate-reducing conditions were established. Column tests conducted to assess the rate of sulfate removal by bacterial reduction also showed rapid and sustained removal of SO_4 after sulfate-reducing conditions were established. These tests were conducted at flow rates typical of those observed at mine-waste sites. The rate of Cr(VI) removal by elemental Fe and the rate of removal of metals and SO_4 by sulfate reduction achieved in the bench-scale tests are sufficiently rapid for successful application to field flow conditions. A field-scale trial of the sulfate-reduction system was initiated in October, 1993. Monitoring of this experiment will continue through 1994 and 1995.

In Situ Denitrification of Septic System NO_3^- Using Reactive Porous Media Barriers; Field Trials

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A new alternative septic system design is presented utilizing reactive porous media barriers for passive in situ attenuation of NO_3^-. The reactive material consists of solid organic carbon (sawdust) which promotes NO_3^- attenuation by heterotrophic denitrification. Four field trials are presented demonstrating two barrier configurations; as a horizontal layer positioned below a conventional septic system tile bed and as a vertical wall intercepting a horizontally-flowing downgradient plume. During one year of operation both barrier configurations have been successful in substantial attenuation (72 to 100%) of input NO_3^- levels of up to 125 mg/L as N.

Advantages of the barrier system are that it is simple to construct, no surface structures or additional plumbing is necessary and treatment is passive requiring no energy consumption and little or no maintenance. Mass balance calculations and preliminary results suggest that conveniently sized barriers have the potential to last for a long period of time without replenishment of the reactive material.

Session 3 — The Impact of Pollutants on Aquatic Ecosystems

Preliminary Environmental Impact Predictions for Selected New Drug Type Chemicals

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A selection of newly approved or pending chemicals shows a wide range of chemical structures. As there is a potential for larger scale manufacturing and release into the environment of these compounds, there is a need to assess their potential impacts. In the absence of available test data on the toxicity, persistence and bioaccumulation potential, some of those effects must be estimated from measured data on other chemicals of a similar nature.

This paper provides several examples of such new structures and gives some preliminary predictions on their potential environmental, particularly aquatic system impacts.

The Effects of Temperature Regime on Nickel Toxicity in Goldfish (*Carassius auratus L.*)

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Although it is widely assumed that temperature affects pollutant toxicity, few studies have investigated this relationship. Research which has been done has involved constant temperatures which are rarely if ever, actually experienced by north temperate, littoral zone, cyprinid species. To investigate the effects of temperature regime on nickel toxicity, 96- and 240-hr LC50 values for the heavy metal pollutant, nickel ($NiCl_2.6H_20$), were initially determined at 20°C (22.8 mg/L and 14.7 mg/L in artificially softened water). Constant temperature bioassays at 10, 20 and 30°C were conducted at each of 0, 240-h and 96-h LC50 nickel concentrations for 240 hours.

In order to determine the effects of various temperature changes it was imperative that the effects of a single temperature change be investigated before addressing more complex regimes. A single temperature change was imposed during nickel exposure in a series of tanks in which the exposure time varied between 24 hours and 216 hours before the change occurred. The tanks were initially set up at 20°C and altered ± 10°C at 2°C/hour to final temperatures of 10° or 30°C. The effects of single temperature change on mortality, and time duration at a high and low temperature during exposure could be evaluated.

Fluctuating temperatures during nickel exposure were investigated through two separate regimes. The first set of bioassays imposed diurnally cycling temperature changes (20±10°C) throughout the 10 day exposure to 240-h Ni. The second set of investigations approximated cyprinid movement through the littoral zone by imposing directionally random temperature changes (±2°C at 2-h intervals) again at 240-h Ni. Total length, fork length, weight, and exposure time were recorded for any mortalities.

Accumulative mortality curves under constant temperature regimes reported significantly higher mortality with increasing temperature and nickel concentration. At 10 and 30°C no significant differences in mortality curves were reported between low and high nickel concentration (240-h and 96-h exposure), however at 20°C significantly higher mortality was experienced in 96-h exposure groups. Constant 10°C mortality was significantly lower than 30°C at 240-h and each of 20 and 30° tanks at 96-h Ni exposure. A single temperature drop from 20° to 10°C resulted in a significant decrease in mortality rate. A single temperature rise from 20° to 30°C resulted in an significant increase in the morality rate. The rates of mortality during these experiments at the constant 10°, 20° and 30° surrounding the temperature change did not significantly differ from the constant temperature bioassays. Increased duration at higher temperatures during nickel exposure resulted in highest mortality. Cycling temperature bioassays produced accumulative mortality curves approximating constant 20°C curves with mortalities reported after peaks in the temperature cycle (20+10°C). Fluctuating temperature regime mortality curves also resembled constant 20°C tanks again recording mortalities after high temperature exposure (25-30°C).

Temperature significantly and marked affects acute nickel toxicity under both stable and fluctuating temperature regimes. With such varied environmental temperature conditions experienced by poikilotherms caution is advised when determining acceptable exposure limits.

ABIOTIC TRANSFORMATIONS OF QUINOLINE IN THE AQUATIC ENVIRONMENT

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The persistence and fate of quinoline and its derivatives in the aquatic environment are of particular interest for recent years. Those compounds occur widely in the natural products, coal, tar and mineral oil and have become widespread in the environment. Quinoline is a known carcinogen and mutagen, and is a common contaminant of soil and groundwater in the vicinity of wood preservation and fossil fuel facilities.

The most important degradation pathways of quinolines appear to be photooxidation and biological transformation by aquatic bacteria, fungi and animals. However, there is a shortage of data about the influence of naturally-occurring consituents on quinoline transformation in water.

This study was undertaken to determine the kinetics of quinoline degradation in natural waters and the effects of pH as well as certain naturally-occurring ions such as chloride, sulfate, nitrate, iron and natural dissolved organic matter (DOM). The studies were focused on the photochemical stability of quinoline under artificial light (Rayonet photoreactor $\lambda = 313$ nm) and in sunlight. The half-life of sunlight photodegradation of quinoline in lake water at 40° N latitude was calculated to be 14 calendar days in summer and 123 calendar days in winter. The photodegradation of quinoline, under both artificial light and sunlight, was significantly accelerated by nitrates and dissolved organic matter, two effective producers of hydroxyl radicals in aquatic environments. The presence of ferric ions also increased the photodegradation rate but the effect was more pronounced under sunlight. The rate was also faster at pH 4.5 than at pH 7.0. No significant effects of chloride and sulfate on quinoline photodegradation was found. Two photoproducts were identified in low yield, 2-hydroxyquinoline and 8-hydroxyquinoline.

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HYDROLOGICAL CONTROLS ON FIELD EXPORTS OF METOLACHLOR TO RECEIVING STREAMS

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Hydrological pathways of metolachlor transport from a 5.5 ha corn field to a small receiving stream in southern Ontario were examined over two successive growing seasons. Metolachlor was applied as an early post-emergence surface broadcast treatment in 1986 at a rate of 334.1 mg active ingredient m^{-2}. The following year, metolachlor was applied at 264 mg a.i. m^{-2} in two separate areas - as a pre-emergence surface spray with cross-contour plowing and as a pre-plant incorporated treatment with contour plowing. Metolachlor concentrations and loads in soils, surface runoff and tile drain discharge were monitored throughout the growing season, and were compared to total metolachlor export from the field. Surface runoff from the field is generated as Horton overland flow on upslope areas and saturation overland flow in the near-stream zone, and runoff plots were sited in order to examinine the influence of these two processes upon metolachlor concentrations and yields.

The two growing seasons differed markedly in the timing and size of rainfall inputs to the field, and this was reflected in the pattern of metolachlor export from the field. Above-normal rainfalls during May 1986 resulted in elevated water table conditions and extensive surface saturation in the near-stream zone. Thus, four storms falling between 13 and 21 days after application transported ~ 95% of the total metolachlor export from the field over the growing season. Peak transport of metolachlor via tile drainage was also observed during this period. A drop in the near-stream water table level during the season resulted in decreased runoff generation and metolachlor export from the footslope area. At the same time, a portion of the metolachlor entrained on upslope portions of the field by Horton overland flow may have been deposited in footslope areas prior to entry to the channel. Persistence in upslope and footslope soils decreased exponentially after application over the growing season, although there was evidence of temporary accumulation and/or slower dissipation of metolachlor in footslope areas. Total export of metolachlor during the 1986 growing season was ~ 1% of applied a.i. 1987 experienced below-average rainfalls in May, leading to low water table elevations in footslope areas and no surface saturation. Thus, only Horton overland flow plots had significant responses to early season rainfalls. Little field runoff entered the stream during these events, suggesting that much of the metolachlor that was entrained upslope was deposited in footslope areas. This coincided with increased metolachlor levels in footslope soils throughout late-June and July. Heavy rainfall in early August resulted in rapid recharge of near-stream groundwater, elevated tile drain discharge, increased saturation overland flow, and conveyance of Horton overland flow from upslope areas to the stream channel. These storms produced the largest daily metolachlor export from the field during 1987 (233 mg); nevertheless, this was < 1% of the maximum daily export in 1986. Metolachlor levels in footslope soils dropped abruptly following this period, suggesting flushing of pesticide from near-stream soils.

Many workers have noted that the critical runoff events in terms of pesticide loss are those that occur shortly after application; however, it is the near-stream hydrologic conditions which determine whether field exports will enter receiving streams. Erosional and depositional processes must be considered when examining temporal trends in pesticide persistence in soils. In addition, differences between runoff generating mechanisms should be examined when monitoring and modelling pesticide transport.

Mayer, T. and Delos Reyes, E., National Water Research Institute, Burlington, Ontario, L7R 4A6. THE ROLE OF SEDIMENTS IN THE TRIBUTARY TRANSPORT OF PHOSPHORUS AND HEAVY METALS

Since nonpoint inputs enter the lakes via tributary inflow, better understanding of pollutant transport in rivers is required to reduce the loadings from nonpoint sources.

Tributary pollutant transport was studied through the field investigation of the role of sediments in transport of phosphorus and metals in two southern Ontario rivers, the Nith River and the Grand River. The two rivers selected for the study reflect different loading conditions, with the former one receiving largely agricultural runoff and the latter one receiving inputs from agricultural, urban and industrial sources. In both rivers, the loads of TP and heavy metals were controlled by suspended solids concentrations, which were, generally, elevated during the high flows (spring snowmelt and episodes of intensive rain events). Slight differences in the mode of P transport were observed between the two tributaries. Higher proportion (46%) of TP was transported in the soluble phase in the Nith River than in the Grand River, where only 40% of P was transported as soluble P. Investigation of the relationship between suspended matter, bank and bed material characteristics revealed that the river channel acts as a sediment sink during the low flow conditions. During the high flow conditions high current velocities cause streambed scouring and bank erosion, thus remobilizing the sediments and sediment associated contaminants, contributing so to total P and metals tributary load. Of the particulate P forms, it is the apatite-P, generally regarded as biologically inert, which contributes to the higher P loads during the high flows. No statistically significant upstream-downstream differences were found in water and suspended sediment chemistry, suggesting the absence of any significant sources and sinks of P and metals between the sampling sites, similarity of sediment sources and absence of any significant chemical and/or biological processing of particles during the transit. The only exception was the statistically significant inter-site difference in the Apatite-P concentrations in suspended sediments from the Grand River, showing the importance of the bank erosion to the Apatite-P contribution. Strong correlation of this particulate P form with the flow regime indicates the importance of differentiating the tributary P load, particularly during the wet years, when the P loads exceed the target loads stipulated by the Great Lakes Water Quality Agreement and the tributary loads constitute a significant portion of the total P load to the Great Lakes.

Organochlorine and PCB Residue Levels in Zebra Mussels of the Lower Laurentian Great Lakes and the St. Lawrence River.

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Abstract

Dreissena polymorpha or zebra mussels are bivalve relatives of the freshwater mussels, *Elliptio complanata* and *Lampsilis radiata*. In North America, zebra mussels were first observed during 1986 in Lake St. Clair, and later, found to inhabit Lake Erie, Lake Ontario, Lake Michigan as well as the Detroit, Niagara, Grand and St. Lawrence rivers. The infestation of the Laurentian Great Lakes with zebra mussels gradually displaced the native unionid populations, including E. *complanata* and L. *radiata*. The decline in numbers of these two popular biomonitoring species, now poses a significant problem to Great Lakes contaminant programs with the necessity to find a replacement organism. An obvious candidate given their physiological attributes, might be the zebra mussel. Adult zebra mussels can filter up to one litre of lake water per day in obtaining their basic diet of phytoplankton. Their filtering capacity is so effective, that noticeable reductions in phytoplankton density have been reported in certain areas of the Great Lakes, particularly in Lake Erie. Compared to other mussels, the zebra has a higher lipid to tissue ratio, therefore favouring bioaccumlation of lipophilic compounds. Zebra mussels are hardy, prolific and sedentary and can be

standardized for age. Zebra mussels may live in close contact to sediment, a major sink for organic contaminants, or be fixed in the water column, filtering suspended particulate matter and water. The latter two compartments are important components in the zebra mussel's foodchain and also in the mobilization of contaminants in large lakes and rivers. In Europe, preliminary investigations employing zebra mussels as bioindicators, found they strongly accumulated trace metals, organochlorines and radionuclides. In the present study, zebra mussels collected from the lower regions of the Laurentian Great Lakes were used as bioindicators and further evaluated for biomonitoring capabilities. The zebra mussels studied underwent rapid accumulation of some organochlorine compounds relative to centrifuged water concentrations, with concentration factors ranging between 10^5 and 10^8 for ΣDDT and PCB, in lipid of animals less than one year of age. Contaminant levels in zebra mussels from different drainage basins gave similar trends as data from herring gull (*Larus argentatus*) egg and spottail shiner (*Notropis hudsonius*), but not walleye *(Stizostedion vitreum)*. A strong correlation between PCB homologue distributions in zebra mussels, spottail shiner and native mussels (E. *complanata* and L. *radiata*) was found at a site where homologues differentiate a point source loading. The ability of contaminant concentrations in zebra mussels to rank sites to exposure from organochlorines was found to vary, depending upon the method used to express "concentration". Rankings were different based on the pesticide concentration when normalized to lipid, dry, wet, tissue or absolute weight.

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Characterization of a Hollow Fibre System for Studies of Microbial Fate in Aquatic Ecosystems

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The survival of microorganisms in the water environment is relevant to considerations of public health, toxicology and the assessment of risks associated with the release of genetically modified organisms. The fate of microorganisms exposed to constantly changing biotic and abiotic parameters in aquatic ecosystems cannot be studied accurately using closed batch samples. Dialysis sacs and diffusion chambers have been used as alternative *in situ* study systems to give more realistic microbial survival results. These systems theoretically allow for the exchange of solutes and dissolved gases across the semi-permeable membranes separating the reservoir containing the study organisms from the external environment. Organisms in these systems could then be retained within the study reservoir while being able to respond to any changes in the external environment. However, these systems are limited by the low rate of diffusion across their membranes and the tendency of the membrane pores to clog under certain field conditions. This results in a slow response time to changes in the external environment and a failure to respond to rapid but transient changes that might occur such as a plug-flow of nutrients down a river. In this study, a new system for studying microbial survival *in situ* was developed. This system employs a polysulfone hollow fibre exchange (HFE) system. The internal reservoir containing the study organisms is circulated by a peristaltic pump through the lumina of the hollow fibres where exchange of solutes and gases occurs. The hollow fibres allow for more rapid diffusion than the diffusion chamber system. due to a much larger surface area for exchange as well as differences in hydrostatic pressure along the length of the fibres. The surface area/volume ratio was 159 for the hollow fibres compared with a value of 1.6 for the diffusion chambers. In this study, the response time of the HFE system to changes in pH and redox values were characterized and compared with the response time of diffusion chambers. In the HFE system, pH equilibration between the internal reservoir and the external environment was acheived within seven minutes for even large initial

differences of six pH units. The diffusion rate of low molecular weight substrates were also determined and compared between the two systems. The T_{50} diffusion time for low molecular weight sugars was found to be within seven minutes. for the HFE system but was greater than one hour for diffusion chambers. The differential response rate of bacteria in the two systems to added nutrients in the external environment was also studied. In all cases, the HFE system demonstrated a much higher diffusion rate for solutes and responded more rapidly to changes in the external environment. The HFE system was also used to carry out *in situ* microbial survival studies in a number of locations, including a temperate river, an equatorial rainforest stream and the intake line of a water treatment plant. On a number of occassions, bacteria in the HFE system were observed to be rapidly affected by transient but significant changes in certain parameters such as biological oxygen demand and redox potential that occured in the body of water being studied. Therefore, the HFE system represents an improvement of available systems for the *in situ* study of microbial survival by allowing microbial interaction with real-time changes in the conditions of the aquatic environment

NEW SOLID-PHASE EXTRACTION MATERIALS IN STUDIES OF CONTAMINATION OF WATER BY PESTICIDES

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Solid-phase extraction (SPE) has been a widely used technique in preparation of samples for different analysis. For example, SPE has been applied in ion-exchange cleanup and concentration of contaminants for many years. However, after commercial introduction of Sep-Pak cartridges (Waters Associates, Milford, Massachusetts) around 1978, the method acquired additional potential in many analysis of organic contaminants in the environment. The emerging of the SPE method from the shadow of the liquid-liquid-extraction (LLE) as an important method in concentrating contaminants from environmental samples was recognized at the ACS National meeting in San Francisco in 1992. A new set of SPE devices has recently became available. By using the concept of membrane filters, the devices include flat disks with high cross-sectional areas that provide advantages not found in cartridges. These include decreased back pressure which enables greater flow rates, and a wider size of the bed which decreases the chance of plugging the discs by suspended matter. In addition, new technology for embedding the stationary phase into a disk format prevents channeling and improves mass transfer, particularly when using 8 μm particle size packings. Three basic disk configurations may be used in SPE:
- packing-impregnated PTFE;
- packing-impregnated polyvinyl chloride;
- derivatized membranes.

Only packing-impregnated PTFE devices are directly equivalent to typical SPE cartridges because the PTFE matrix contains the same stationary phases. The PTFE fibril network holds bonded silica particles in place. The 8 μm particles comprise about 90% and the PTFE about 10% of the weight of the device. The disks are available in sizes that fit a standard filter assembly. A 25 mm-diameter disk contains about 140 mg of the sorbent, and 47 mm-diameter and 90 mm-diameter disks contain about 500 mg and 2,000 mg of the sorbent, respectively. Most recent additions to the market are glass microfiber disks impregnated with chemically bonded sorbent, which are sufficiently rigid to eliminate external support. The glass microfiber disks have been evaluated for the isolation of abuse drugs from biological fluids including a direct derivatization procedure on the disk, and for the extraction of 46 organic compounds from water according the U.S. EPA Method number 525.1.

Contamination of both water and sediments by pesticides in Lake Erie is well documented. In the quantitative determination, the pesticides were extracted from water samples by the classical LLE technique using dichloromethane and the Goulden Large Scale Extractor. The advantages and disadvantages of LLE extractions are well known. The disadvantage is mainly the labor-intensive procedure and the use of relatively large volumes of solvents. The extraction solvents must be of high purity, as the impurities at the mg/L level generate significant backround interferences in the subsequent quantitative determination of contaminants in the water samples at the ug/L level. In addition, the solvents used in the extraction procedure must be disposed of which creates environmental problem. Consequently, it appears that there is growing interest in replacing the conventional LLE with SPE techniques. According to the recent ACS National Meeting, the SPE extraction may substitute the LLE in the near future. Recently, membrane extraction discs have been tested in different SPE techniques. The membrane extraction disks containing C8 or C18 reversed phase particles have been tested off-line for different groups of organic compounds, such as pesticides, phtalates, semi-volatile organic chemicals, organotin compounds, etc. Further, the extraction discs served as a component of an on-line system for the analysis of different types of pesticides and chlorophenols by liquid chromatography, and on-line system for the analysis of organophosphates by capillary gas chromatography. Membrane extraction disks were evaluated in detail for the analysis of pesticides in drinking water, simulated seawater, natural waters and soil samples.

In the present study, the performance of the Empore extraction disks was tested in the quantitative determination of eighteen pesticides of five different classes. The pesticides are of general concern for their extensive use in agricultural activities along the Canadian shoreline of Lake Erie. In the study, the type of pesticides was chosen regarding to their use in different mixtures for protecting crops as indicated by Agriculture Canada. Preliminary results of the study revealed that recoveries for most of the pesticides were within the U.S. EPA recommendation, i.e., from 70 to 130%, with the exception of metribuzin, cypermethrin and terbufos.

In Situ Sediment Bioremediation in Hamilton Harbour

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To enhance the biodegradation of organic contaminants, approximately 39 tonnes of oxidant and nutrients were injected into 2 hectares of sediments of Hamilton Harbour.

The effectiveness of the treatment is optimal in the laboratory with 78% and 68% of the oil (TPHs) and polynuclear aromatic hydrocarbons (PAHs), respectively biodegrading in 44 days. In the 1992 treatment in the Dofasco Boatslip, biodegradation of organic contaminants varied from 79% for low molecular weight compounds (BTXs), to 25% for TPHs, and 15% for 15 of the 16 priority pollutant PAHs. At first biodegradation of large molecular weight PAHs resulted in the production of naphthalene (mean from 280 μg/g to 549 μg/g). In the 1993 treatments, 94% of the naphthalene, and 57% of the TPHs biodegraded.

In the main basin of Hamilton Harbour one treatment was done in 1992 with less nitrate. About 80% of the hydrogen sulphide (293 μg/L to 53 μg/L at deep basin) was oxidized. Oxidation resulted in precipitation of about 98% of the porewater iron in the surface 15 cm of sediment but the concentration of most trace metals was unchanged. The high metal concentrations did not appear to limit bioremediation. In the first 4 months, 18% of the TPHs biodegraded, but a year later 40% of the TPH had biodegraded.

The in situ biotreatment of organic contamination takes time but for some sites the significantly lower cost relative to dredging and confinement makes in situ treatment a viable alternative.

Session 4 — Indicators of Environmental Sustainability

Abstract

Indicating Risk: Lessons from Elmira on the Inherent Limitations of Sustainability Indicators

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Sustainability represents a powerful unifying concept in resources management. It has been widely embraced both politically and intellectually. However, in many sectors, sustainability still awaits practical application. Often, the features of a sustainable future remain unclear and there are few examples that give practical expression to sustainability. Moreover, implementation of sustainability has been further curtailed by the absence of comprehensible sustainability indicators. Indeed, the identification and quantification of indicators signalling levels of sustainability remain poorly understood and largely undeveloped.

This paper addresses some of the inherent limitations of sustainability indicators. It uses a literature review to summarize the need for indicators of sustainability and the principles that should underpin their development. It then uses a case study of risk communication related to groundwater pollution in Elmira, Ontario to illustrate the problems involved in developing a robust, scientifically-valid indicator of sustainability that is both comprehensible and practical. In particular, the paper focuses upon the role of the media in the public communication of sustainability and the (non)utility of indicators in this respect.

Conventional economic and environmental indicators are inadequate to the task of measuring progress toward sustainability. Appropriate indicators of sustainability are desired to improve policy development, to re-focus political decision-making, to ensure accountability, to improve environmental monitoring and to foster improved dialogue among academics, politicians and the general public. Beyond an acknowledgement of basic principles, there is little consensus in the literature as to the design criteria for sustainability indicators. Much of the literature is concerned with the scientific validity and robustness of potential indicators. Relatively less attention has been placed on communication characteristics and requirements for sustainability indicators. Similarly, the role of the media in information dissemination has received scant regard thus far. A case study of groundwater pollution in Elmira, Ontario offers some insight on both

counts.

Groundwater contamination by N-nitrosodimethylamine (NDMA) in Elmira was first discovered by routine monitoring in the Fall of 1989. NDMA is carcinogenic and has been observed to cause cancer in animals even at low dosage. It is widely perceived as a health risk and its presence in Elmira's groundwater prompted considerable public concern and the imposition of water restrictions. The need to protect public health and the environment was evident to all stakeholders. However, the issue was enveloped in considerable controversy as a consequence of uncertainty (regarding the extent, sources and impact of the NDMA contamination of the groundwater), varying assessments of the risk posed by the contamination (between differing government agencies, various scientific experts, local industries and the public) and disagreements over the "correct" response to the situation.

A content analysis of newspaper coverage of the crisis between the Fall of 1989 and the Summer of 1992 was conducted. Data were collected on the source of information, the perception of risk, impacts, the effectiveness of actions, actions required and responsibility. These data were further supplemented by personal interviews with media representatives to provide insight into the media's coverage of the water contamination issue.

The study findings confirm the importance of media in information dissemination but indicate several reasons why public communication of environmental information is difficult. Environmental issues are hard for media to report. They are conditioned to reporting "news" and attempt to understand issues by focusing on events, impropriety and individuals. The scientific uncertainty inherent in environmental issues often is perplexing to the media and reinforces their desire for a single-window on information and for simple measures of environmental integrity (i.e. sustainability indicators). Concomitantly, the study found there was a pervasive lack of trust associated the credibility and provision of information provided by government agencies, industry and activist groups. In short, the media found credible information difficult to obtain, with sources perceived to be either tainted by bias or incapable of rendering a straightforward response.

The implications of the study for the development of sustainability indicators stem from the imperative for measures to be easily communicated to the public by the media. Environmental science lacks consensus on how best to tackle issues of uncertainty and complexity in understanding and communicating sustainability requirements. At the same time, legitimate academic disagreements between individual scholars and especially between disciplines, weaken the public credibility of information given to the media, further retarding public policy development.

Sustainability indicators can only be effective as public policy tools if they gain wide acceptance. Media scrutiny and ability to utilize indicators in communicating sustainability to the public are acid tests on the robustness and comprehensibility of those indicators. If science cannot communicate effectively through the media, it cannot hope to effectively redirect public policy. For many scientists, this corollary is antithetical to the very development of sound, scientific indicators of sustainability. It is an inherent limitation that must be overcome.

A Framework for Ecosystem-Based Management: Developing Ecosystem Goals, Objectives and Indicators

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Detailed Abstract

Introduction

The rise of environmental issues on public and hence political agendas has created an increased demand for succinct, understandable, and representative information about the environment. The challenge is to meet this demand for environmental information in a manner that suits decision-makers' needs for brevity, accuracy, and credibility. A national framework for ecosystem-based management which describes a method for identifying indicators for evaluating and reporting ecosystem health is one mechanism for meeting these information requirements. This paper advocates a framework which combines the scientific development of indicators with an objective-setting process which allows for input from stakeholders who utilize ecosystem resources (i.e., community groups, industry, local governments etc.).

Project Purpose and Scope

The overall aim of this initiative is to articulate a generic framework that has utility for both environmental managers and scientists who need to assess the "health" of ecosystems, whether it be for the purposes of environmental assessment, state of the environment reporting, internal reporting, or general environmental management. Elements of this framework have appeared in many ecosystem-based projects across North America, (e.g., the Great Lakes, the Northern River Basins Study, the Atlantic Coastal Action Program, the Fraser River Action Plan, etc.). The framework expresses successful elements of these different programs, and offers consistent terminology to describe these elements. Another primary aim of this project is to promote sound environmental decision-making through the use of ecosystem objectives and indicators. Increasing the development and use of ecosystem objectives and indicators will help redirect environmental monitoring and indicator selection from predominantly reactive processes to more anticipatory processes. The most significant challenges encountered in this work include identifying appropriate measures of ecosystem health, and effectively integrating community involvement.

Investigation and Results

Following a review of current approaches to indicator development and ecosystem based management, a four step process has been identified and described as a sound means to direct ecosystem management, and to report on its progress. The first step involves compiling a comprehensive review of information relating to the ecosystem in question. This knowledge should encompass ecosystem science, socio-economic information, historical resource use data, cultural information, and traditional knowledge.

The second step entails using this information as a basis from which to articulate ecosystem goals and objectives. Ecosystem *goals* have been defined as "broad based narrative statements which describe the desired state of an ecosystem" (Bertram and Reynoldson 1992). Ecosystem *objectives* are more specific narrative descriptions of desired conditions through a set of parameters, taking into account ecological characteristics and uses (Economic Commission for Europe 1991). To increase realism and cooperation in meeting the objectives, a wide array of stakeholders should be involved in the goal- and objectives-setting process (e.g., ecosystem scientists, industry, community groups, environmentalists, governments, Native groups, etc.).

Once ecosystem objectives have been articulated, the third step requires selection or development of indicators to gauge progress toward meeting the stated objectives. Indicators have been defined as "measurable features which singly or in combination provide managerially and scientifically useful evidence of ecosystem quality, or reliable evidence of trends in quality" (U.S. Intergovernmental Task Force on Monitoring Water Quality 1992). Since it is unlikely that a single indicator can provide sufficient insight into the health of an ecosystem, it is important to develop a comprehensive suite of indicators to adequately monitor progress towards ecosystem objectives. In most cases, indicators require quantitative endpoints or target values to provide a reference for healthy ecosystems, but in some cases, data trends may be as important as the actual values. The indicator selection process is predominantly a scientific exercise, with some community involvement to ensure that the indicators developed are meaningful to nonscientific decision-makers.

The fourth step of the framework arises directly from the previous three steps -- during these activities, data gaps become apparent. These data gaps should be used to drive monitoring operations and direct research activities. This process will ensure that data is obtained to support the "best" indicators of ecosystem health, and that less effective indicators are not "settled for" because of lack of data.

The framework is envisioned as a dynamic process in which goals, objectives and indicators are continually updated as new information becomes available.

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Session 5 — The Contamination of Groundwater by Pesticides

Susceptibility of Groundwater to Pesticide and Nitrate Contamination in Predisposed Areas of Southwestern Ontario

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Agricultural practices today employ a vast array of chemicals in large volumes in order to improve both the quantity and quality of our agricultural products. While it has long been recognized that runoff from agricultural land has the potential to degrade surface water quality, only recently has attention been focused on the effect of agricultural chemical usage on groundwater. In order to study the effects of pesticides and nitrate usage on the quality of groundwater, in 1985, the Ontario Ministry of the Environment began operating a groundwater monitoring program in Southwestern Ontario.

Data generated from this program, which utilizes samples collected from both wells and piezometers, indicates that, in areas of heavy pesticide and nitrate usage, shallow groundwater is continuously testing positive for nitrate and a variety of pesticides. Factors which influence the number of positive incidents for pesticides are directly related to the persistence of the chemical, its method of application and the amounts utilized. Soil types, depth to groundwater and rainfall, although influencing the time of detection, do not govern the number of detection events.

Changes in agricultural practices were also monitored to see if pesticide reduction, a variation in the method of application, crop rotation and an increase in soil organic matter would influence the levels of pesticide contamination.

It was found that when chemicals of a low persistence were applied post emergent at the minimum recommended rate, pesticides were not detected in the groundwater. Crop rotation was also effective in reducing the level of pesticides in groundwater. Tillage practices and increases in organic matter in the soil appeared to reduce contamination events for pesticides but not for nitrates.

It was also found that elevated levels of potassium and/or nitrates in groundwater serve as reliable indicators of the groundwater's susceptibility to pesticide contamination.

Remedial action to alleviate the impact of pesticides and nitrates in groundwater must focus on the chemical usage patterns employed on the farm sites and a reduction of the overall quantities of pesticides and fertilizers utilized. These patterns must incorporate a well designed program of crop rotation with the appropriate application of these chemicals at the site.

Pesticides and Farm Well Water Quality Studies in Nova Scotia

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During the past five years, the Province of Nova Scotia has conducted two joint studies designed to address the concern over the possible impacts of pesticides and fertilizers on groundwater quality in agricultural regions. The study area, located in the Annapolis Valley of Nova Scotia, is the most intensively farmed region in the province and also contains some of the provinces's best surficial and bedrock aquifers. Over 90% of the mostly rural population rely on groundwater for household and farm water supplies.

The first study focused on an overview of water quality in the study area and included one-time testing of 102 farm wells for a variety of pesticides in the summer of 1989. A modified DRASTIC risk assessment model was used to evaluate the vulnerability of sub-areas within the study area to contamination with sample sites weighted towards those areas scoring the highest. The results showed that none of the wells contained pesticide concentrations above the Canadian drinking water guidelines, however, very low levels of pesticides were detected in 41% of the wells. Atrazine and its breakdown products accounted for 71% of the detections.

As a follow up to the overview study, case studies were carried out at selected sites in an attempt to identify sources and mechanisms of contamination. These results indicated that non-point sources accounted for 82% of well contamination by pesticides and that pesticide occurrence was independent of well construction method or well depth. Furthermore, indications are that atrazine contamination may be the result of historic rather than current agricultural practices.

The second study focused on seasonal variations in pesticide occurrences and included quarterly sampling of 20 wells known or suspected to contain pesticides between 1989 and 1992. These selected wells were not part of the 1989 overview study. The time-series data will be used to determine the between-season and within-season variation in pesticide concentrations. The data will also be used to examine des ethyl atrazine ratios as indicators of point versus non-point source contamination. Fluctuations in both mean atrazine levels and mean des ethyl atrazine to atrazine ratios occurred during the study period. The significance of these fluctuations, however, has not yet been determined.

Data collection is basically complete and both studies are in the report writing stages. Final reports are expected for the overview study by the end of 1993 and for the time study early in 1994.

Investigation and Interim Remediation of Pesticide Contamination at a Site in Cambridge, Ontario

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Investigations conducted from 1991 to 1993 at the Ciba-Geigy Canada Limited (Ciba) Cambridge Facility have determined that soil and groundwater at the site is contaminated with pesticides, volatile organic and nitrosoamine compounds.

Chemicals have been released to the soil from an underground process wastewater system; an above ground material transfer pump; storage areas; concrete-lined process waste pits; and infrequent single-event discharges. The Ciba site is in an environmentally sensitive location with eight municipal water supply wells radially located within 0.6 km to 2.2 km of the facility.

The distribution and movement of contaminants in the groundwater is complex and extremely variable beneath the site. Contaminants released to the soil have migrated to the water table, which occurs at a depth of approximately 10 metres below the ground surface. From the water table, contaminated groundwater has spread through the five overburden units westward (less than 200 metres) beyond the property boundary, and vertically downward to the bedrock which occurs at a depth of approximately 30 metres below the site.

The principal pesticides detected in the upper soil and groundwater zone include atrazine, dicamba, dinoseb, mecoprop, metolachlor, and 2,4-D. Dicamba, mecoprop, metolachlor, and 2,4-D have been measured above the analytical method detection limit in the bedrock groundwater beneath the site.

Aquifer tests conducted during the remedial investigation indicated that groundwater flow beneath the Ciba site is influenced by pumping of the municipal wells. Ongoing water quality monitoring of the municipal wells by the Regional Municipality of Waterloo has not detected any contaminants from the Ciba in the municipal water supply.

To halt further vertical and lateral spreading of groundwater contamination from the site, interim remedial actions are being implemented. A groundwater pump and treat system is being designed to capture and provide on-site treatment of contaminated groundwater. This interim system is scheduled for startup in early 1994. Work is ongoing to evaluate the fate, transport, and treatability of the pesticides occurring in the groundwater and soil at the site.

Investigations of Pesticides in Groundwater Beneath Three Irrigated Sites Near Outlook, Saskatchewan

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The contamination of groundwater by pesticides is a potential threat to the quality of drinking water on the Canadian Prairies, where geology, soils and land use practices favour the transport of contaminants through the unsaturated zone. The Outlook Pesticides Study was designed in 1986 as a joint research project between the National Hydrology Research Institute, the Regina Research Station of Agriculture Canada, and the Saskatchewan Research Council. In 1987, pesticides were investigated in groundwaters beneath three sites in the Outlook area of Saskatchewan. In 1988, work focused upon one of three sites, in order to obtain a more comprehensive data set.

All three sites were irrigated. There were detectable pesticide concentrations in groundwaters at all three sites, but the concentrations were very low. Pesticide concentrations were, as expected, not constant over time or space at any of the sites. Further and more detailed studies were undertaken to determine the physical and chemical reasons for the observed frequency and distribution of detections.

A more intensive study conducted in 1988 has shown a possible relationship between observation well hydrographs and pesticide detections. The observed relationship is apparently due to the presence of fractures in the unsaturated zone sediments. To overcome the data deficiencies, the type of research devoted to the fate of pesticides after application to farm land must evolve to a more careful inspection of the processes in the unsaturated zone. In order that the data arising from this study, and others like it, may be used to bring about the long-term protection of groundwater, the factors that effect downward transport of pesticides must be recognizable, quantifiable, and hence, applicable to models which will be of real use to scientists, regulators and farmers.

Long-term Persistence of Aldicarb Residues Beneath a Potato Field on Prince Edward Island

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Between 1978 and 1987, the pesticide aldicarb was used extensively on potatoes on Prince Edward Island (PEI) to control aphids and the Colorado Potato Beetle. A groundwater survey conducted in 1983/84 revealed that 19.4% (20 of 103) of domestic wells in high risk areas (near potato fields treated with aldicarb) contained low levels of aldicarb residues. Although the detection rate was high, all residue concentrations were less than the maximum acceptable concentration of 9 μg/L established by Health and Welfare Canada.

Aldicarb is an extremely toxic carbamate insecticide with an oral LD_{50} (rats) 0.9 mg/kg, and an aqueous solubility of 6000 mg/L. Aldicarb is manufactured in granular form, as Temik 10G® (10% aldicarb) and is applied with the seed potato at planting. Upon contact with soil moisture, the pesticide dissolves and is quickly oxidized to aldicarb sulfoxide, which in turn, may be further oxidized to aldicarb sulfone. Both daughter products (sulfoxide and sulfone) are also highly toxic, mobile and persistent, and represent an environmental risk. As a result, investigations of aldicarb contamination are concerned with the total aldicarb concentration (aldicarb + aldicarb sulfoxide + aldicarb sulfone). Each of the three aldicarb species may also degrade via chemical hydrolysis, forming relatively non-toxic oxime and nitrile species. It is at this stage that the pesticide is considered effectively degraded and is no longer an environmental concern.

Three field sites were established on PEI in 1985 and a four year study was conducted on the fate and migration of aldicarb beneath potato fields on PEI. The results of this work were discussed in previous papers (Priddle et al., 1989 and Jackson et al., 1990). However, at one site (Augustine Cove), long-term monitoring of aldicarb residues has continued. The objective of this presentation is to report the latest results of the study of the long-term persistence (and gradual disappearance) of aldicarb beneath a potato field on PEI.

The Augustine Cove field site is located in the main potato growing region of PEI (eastern Prince County). The overburden consists of approximately 2 to 3 metres of till, and is underlain by a unconfined, fractured, fine-grained sandstone aquifer. The site was instrumented with twenty-five 2-inch piezometers. The long-term monitoring phase of the project concentrates on the results from four piezometers which have been subjected to a more intensive sampling and analysis program. Aldicarb was applied to the field site at a rate of 2.0 kg a.i/ha in mid May in the years 1980, 1983 and 1986, and has not been applied since.

Previous field studies have found that aldicarb has persisted much longer than expected beneath the potato fields on PEI. It appears that the major phenomenon resulting in this long-term persistence of the pesticide is the storage of pesticide residues in the unsaturated portion of the overburden and the fractured sandstone. In combination with this storage mechanism, the cool temperatures found beneath potato fields on PEI has resulted in the prolonged persistence of aldicarb residues. The hydrolysis reactions which result in the degradation of the three aldicarb species are more sensitive to changes in temperature than are most chemical reactions. The rate of the reactions decrease by factors ranging from 3 to 5 for a reduction in temperature of 10°C (Lightfoot et al., 1987). Shallow groundwater temperatures tend to be cooler on PEI than in most other areas of North America where potatoes are produced. Temperatures range from approximately 5.5°C to 10°C at the Augustine Cove site, and this has contributed to the persistence of the pesticide in the unsaturated zone, and in the shallow groundwater, beneath the site.

The hydrolysis reactions for aldicarb are also pH dependent. However, observations on PEI suggest that the position of the residues in the unsaturated zone (in relation to the water table) has a more pronounced affect on the persistence of aldicarb than does variations in the pH level. Aldicarb residues appear to be stored in the unsaturated zone, with a portion of the pesticide residue being flushed to the water table with each recharge event. Aldicarb residue concentrations are generally higher in the spring (just after the spring snowmelt), or in the late fall, and tend to decline over the summer months as water levels decline.

Priddle et al. (1992) began the process of looking at the long-term persistence of aldicarb on PEI. On analyzing the results from 8 sampling periods (1985 to 1990), Priddle et al. (1992) found a relationship between the mean total aldicarb concentration in the four long-term monitoring piezometers, and the mean hydraulic head and time since the last pesticide application. Based on this analysis, with the minimum ($\sim$6.7 m) and maximum ($\sim$9.3 m) mean heads observed in the four piezometers, it was predicted that the total aldicarb concentration should decline to below detectable levels ($< 1\ \mu$g/L) between 6 and 8 years after the last pesticide application.

The long-term monitoring wells were sampled again in December 1993 to check the predictions made by Priddle et al. (1992). However, one of the long-term monitoring wells was dry at the time of sampling. As a result, in this paper the aldicarb data were reanalyzed using data from the three remaining long-term monitoring piezometers. The revised regression equation for the mean total aldicarb concentration (μg/L) is presented below:

$$\text{Total aldicarb conc.} = 0.989 * (\text{head}) - 0.0267 * (\text{time since last application}) \qquad r^2 = 0.922$$

This revised equation also predicts that the aldicarb residues should decline to non-detectable levels between 5.8 to 8.4 years after the last pesticide application. The results from the December 1993 sampling confirm this prediction. All samples collected had total aldicarb concentrations below the detection limit of 1.0 μg/L. Based on the equation given above, and on the range of mean heads in the three piezometers (6.70 to 9.30 m), the effective half-life of aldicarb residues beneath a potato field on Prince Edward Island ranges from approximately 2 to 3 years.

Laboratory Studies on the Leaching of Aldicarb Through a Tropical Soil from Belize, Central America

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Studies in temperate regions indicate that the carbamate insecticide aldicarb and its metabolites leach readily through agricultural soils into groundwater. However, little is known about the fate of this nematicide in tropical regions, where its leaching potential may be even greater because of high annual rainfall and the acidic nature and low organic content of many tropical soils. Examination of the leaching behaviour of aldicarb and its metabolites in columns containing soil from Belize, Central America, indicated that the total carbamate residues (TCR) could rapidly reach concentrations > 15 mg L^{-1} in porewater 1 m below the soil surface within 70 days of application. These values are well in excess of the US EPA Health Advisory level of 0.01 mg L^{-1}. TCR retention within a given depth interval in the soil columns relative to incoming TCR flux was greatest between 0 and 0.1 m, reflecting high organic matter contents in the upper soil. Retention below 0.1 m was relatively consistent with depth, while differences in relative retention between columns were due to a greater duration of leaching for the second column. Aldicarb was rapidly oxidized to aldicarb sulfoxide and aldicarb sulfone in these soils. The high concentration and mobility of TCR in this acidic soil is attributed to the transformation of the parent compound to the sulfoxide metabolite, which has a lower degradation rate and organic carbon partitioning coefficient than aldicarb.

Computer Analysis of the Factors Controlling Pesticide Migration and Persistence in Agricultural Regions Across Canada

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A major component of the regulatory process involves extensive field tests to assess the fate of a pesticide in the subsurface. Although these tests provide important information on the behaviour of the pesticide in the subsurface, they cannot assess every potential agricultural site, soil profile, or meteorological condition which may be encountered once the pesticide is approved for commercial use. Numerical models which simulate the transport and fate of pesticides within the subsurface offer a means of assessing the behaviour of pesticides under a variety of field conditions. The objective of this study is to undertake numerical analyses to provide insight into the factors which influence the mobility, retention and persistence of pesticides in the subsurface in various agricultural regions across Canada, and specifically assess (1) if significant differences in leaching rates and the depth of leaching of a pesticide occur among various agricultural regions, and (2) the relative importance of some physical factors that influence the leaching of a pesticide within an agricultural region.

Three important Canadian agricultural regions were examined; a wheat field in Saskatchewan, a corn field in Ontario and a potato field in New Brunswick (N.B.). The soil profile representing the most common soil for growing the given crop in a region was used (Dark Brown Soil, Brookston Soil and Holmesville Soil, respectively). Actual meteorological data recorded in each region was used for the simulations. The behaviour of two pesticides with very different properties, atrazine and metribuzin, were simulated. Although these pesticides are not the most commonly used pesticide in all or any of these three regions, they serve to illustrate how other pesticides having similar properties may behave.

The analyses are undertaken using the pesticide model LEACHM because it is able to simulate the actual physical, chemical and biological processes that occur within the subsurface. Sensitivity analyses were undertaken within each agricultural region and for each pesticide on three important parameters that influence the fate of a pesticide in the subsurface. Daily precipitation values were varied by $\pm 30\%$, fraction organic carbon (foc) varied from 0 to x3, and saturated hydraulic conductivity (Ksat) of all soil horizons varied by $x10^{\pm 2}$, from the control case. These ranges represent extreme variations that may be encountered in actual field settings. The depth to the water table was set at 3 m in all three regions.

The dominant factor controlling the leaching rate and depth of migration of the pesticides among the agricultural regions is the net amount of infiltration (actual precipitation and snowmelt - actual evaporation from the soil). The 20-year average infiltration rates for the agricultural regions representing Saskatchewan, Ontario and N.B. are 12, 52 and 86 cm/yr, respectively. In all simulations, where precipitation, Ksat and foc varied throughout the above range, both atrazine and metribuzin leached to a greater depth at a specified concentration, and the leaching rate or time for the pesticide to reach a given concentration at a specified depth, was greatest in the region with the highest infiltration rate. For example, in all simulations, atrazine leached to the water table in N.B. (>3 m), to a depth of 2-2.5 m in Ontario, and to a depth of 0.5-1 m in Saskatchewan. Increasing Ksat by 100x, or increasing precipitation by 30%, or decreasing foc to 0, was not sufficient to cause the pesticide to reach to the water table if the pesticide in the control case (Saskatchewan and Ontario) did not leach to the water table. Also, decreasing Ksat by 100x, increasing foc by 3x and decreasing precipitation by 30% still resulted in the pesticide leaching to the water table at a concentration of 0.01 mg/L in N.B. Although the relative depths of leaching and leaching rates were not as large for metribuzin as for atrazine, the above trend persisted. Implications from these analyses is that for a pesticide that has properties conducive for leaching, such as atrazine, the potential for groundwater contamination under most soil conditions and meteorological conditions is very high in N.B. and very low in Saskatchewan. Although the pesticide did not reach the water table in the Ontario scenario, the depth of leaching in all cases was sufficient to warrant concern that certain soil and meteorological conditions may favour groundwater contamination.

Analyses were also undertaken to determine the relative importance of Ksat, precipitation and foc in influencing the leaching rate and depth of leaching within each agricultural region; these parameters were varied as stated above. In all three regions, foc had a minor impact on the leaching rate and depth of leaching; decreasing foc to 0 led to an increase in the depth of leaching (at 0.01 mg/L) by a only few cm. A 30% increase or decrease in actual precipitation, increased or decreased, respectively, the maximum depth of leaching by approximately 20 cm in Saskatchewan, 50 cm in Ontario, and 60 cm in N.B., for atrazine, and approximately 15, 20 and 40 cm, respectively, for metribuzin. The leaching rate also increased or decreased as precipitation increased or decreased, respectively, but with a relatively much larger change due to an decrease in precipitation than to an increase in precipitation. For example, atrazine reached a depth of 1 m approximately 20 days faster in N.B., and 5 days faster in Ontario for a 30% increase in precipitation, versus 120 days slower in N.B. and 25 days slower in Ontario for a 30% decrease in precipitation. Similar results were obtained for the metribuzin simulations.

The largest change in the leaching rate and maximum depth of leaching of the pesticide occurred with changes in the saturated hydraulic conductivity of the soil profile. An increase or decrease in Ksat resulted in a corresponding increase or decrease in the leaching rate and depth of leaching. The maximum depth of leaching of the pesticide at a specific concentration ranged from 0.5 to 2 m for a change of Ksat by $10^{\pm 2}$. The time for the pesticide to reach a given depth at a specified concentration changed by almost a year in some cases. However, these changes in the leaching rate or depth did not vary as systematically as for the sensitivity analyses conducted with precipitation and foc. Further analysis of these results indicated that because the changes in Ksat resulted in largest changes in the leaching characteristics, the transport of pesticides in the soil profile becomes affected by the dramatic changes in infiltration rate due seasonal process (spring snowmelt and majors storms). The implications of these anaylses is that within an agricultural region, the foc of a soil profile has negligable impact of the depth and rate of leaching of a pesticide whereas Ksat has a significant influence on leaching rates and depth of leaching.

Sustainable Agriculture and Canadian Water Quality Guidelines

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Canadian Water Quality Guidelines (CWQG) are numerical concentrations designed to protect water use (e.g. raw water for drinking, aquatic life, livestock and irrigation). CWQGs follow nationally approved protocols specific to the water use. In Canada, they are used as scientifically defensible tools by managers to implement control measures under the Canadian Environmental Protection Act (CEPA) and the Pest Products Control Act (PCPA). They are based on the most sensitive species, preferably in chronic toxicity tests. Hence they serve the purpose of both (1) characterizing the receptor, and (2) determining the estimated environmental effects concentration (hazard assessment).

CWQG are developed under the auspices of the Canadian Council of Ministers of the Environment (CCME). They must obtain national approval prior to publishing. Pesticide guidelines are based on public documents or registrant data (with permission) and contain a detailed review of all the published information currently available regarding: production and registered uses, physical and chemical properties, sources and pathways for entering the aquatic environment, environmental concentrations, fate and persistence, bioaccumulation, toxicity to aquatic biota, non-target crops, livestock and related biota, and a review of available guidelines/objectives/criteria from other jurisdictions. When sufficient information is available, maximum numerical concentrations or narrative statements which will protect and maintain water use in Canada are recommended.

In response to the need for a nationally consistent approach to the derivation of water quality guidelines, Environment Canada has undertaken a number of initiatives on behalf of the CCME Water Quality Task Force. Recently, in 1991, "A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life" was published to provide comprehensive guidance on the development of Canadian Water Quality Guidelines for the protection of aquatic life. This approach has now been endorsed by the Task Force.

Consistent protocols for the derivation of agricultural guidelines are also required in Canada. To date, no formalized protocol has been established for guidelines for irrigation water. Further, for livestock water, guidelines have generally used the Health and Welfare Canada guidelines for drinking water as surrogates. To address these needs, Environment Canada commissioned the present study to determine if scientifically defensible protocols could be established for agricultural water uses. The protocols are designed to provide a consistent scientifically defensible approach to the derivatives of guidelines for irrigation and livestock water.

In support of the Green Plan initiatives with regard to agricultural issues, this presentation will focus on the development of Water Quality Guidelines in providing concise and credible environmental information through which the agricultural sector's environmental performance can be evaluated objectively.

International Joint Commission Activities Related to Groundwater Contamination by Pesticides in the Great Lakes Basin

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The International Joint Commission (Commission) has long had an interest in the possible effects of groundwater quality on the Great Lakes Basin Ecosystem. Recently, the Commission's attention has been directed towards pesticide usage in the Great Lakes basin, subsequent groundwater contamination and potential human and ecosystem health implications. The extensive use of atrazine, its persistence in the environment and the susceptibility of groundwater systems to pesticide contamination throughout the basin, as indicated by DRASTIC scores, is a growing concern. Research has shown that persistent toxic chemicals, including atrazine are implicated in the disruption of endocrine systems in laboratory animals and in wildlife. Mirex levels in some Lake Ontario fish species appear to be escalating, possibly due to groundwater-borne leachate from waste disposal sites in the Niagara region.

The Commission tabulated several research needs in its Seventh Biennial Report. Among these are: the need to examine the location and role of groundwater conduits to the Great Lakes; the need to examine the cumulative impact of human activities on groundwater; the need to examine the persistence, transport and fate of pathogens and contaminants in and through groundwater; and the need to determine the impacts of land use practices, including pesticide application. The Commission's Report also recommends that, "governments improve the understanding of groundwater pollution and its impact on the Great Lakes, and act to eliminate its causes.".

Application of a Mesoscale Model to Examine the Fate of Pesticides

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A mesoscale model 4.6 m in height, 2.4 m in diameter, containing 65 tonnes of soil and geologic materials was constructed to investigate subsurface processes. The column was a repacked system with 11 cm (Ap), 20 cm (B), 3 m of glaciolacustrine sand (C) and the water table was 3.3 m from the surface. The model was designed to be a homogeneous isotropic system. Major ions, metals, pH, alkalinity, CO_2, N_2, O_2, CH_4, microbial numbers, biomass and heterotrophic potential were all monitored over time and depth. Analysis of spatial and temporal changes with respect water flux and gas concentrations in the model indicated that steady-state conditions were achieved within 130 days. Microbial analyses showed trends and levels typical of those reported for field studies of shallow vadose zones. Although microbial activity declined >100 fold below the soil horizons, activity in the vadose zone was substantial and accounted for 60% of total CO_2 production. The highest CO_2 concentrations and activity were measured in the A ($x=4.0\%$, $n=42$) and lowest in the B ($x=2.6\%$, $n=44$). The CO_2 concentrations in the C exhibited no significant differences with depth (3.3%, $n=176$). Measured microbial respiration rates suggested that between 50 and 70% of the respired CO_2 was produced in the unsaturated geologic medium beneath the Ap and B, and that there was sufficient CO_2 production potential by bacteria to account for the respired CO_2 determined from the flux calculations. The data suggested microbial activity in the C was the dominant source of CO_2. These preliminary studies indicated that the mesoscale model approximated field conditions and could be used to provide insight into soil and subsurface processes such as the fate of pesticides.

Assuming piston flow, the estimated transit time for water through the unsaturated zone at steady-state was 20-25 days. The herbicide diclofop-methyl (Hoe-Grass) was applied at 2X the agricultural rate and leaching of the herbicide through soil profile was monitored at intervals using suction lysimeters to collect pore water samples. Samples were analyzed for the presence of diclofop using solvent extraction with GC-ECD analyses, samples were also subjected to MS and MS-MS characterization. Diclofop was detected at the 0.08 m, 0.22 m, 0.36 m, and 0.54 meter samplers. However, the timing of detection, at 0.08 m immediately after application, 0.54 m sampler after 4 days and the 0.22 and 0.36 m samplers after 12 days indicated the presence of preferential flow paths. In contrast, chloride tracer tests had indicated that the system exhibited piston flow. Examination of the water chemistry and gas analyses from the 0.54 m sampling depth supported the existence of preferential flow. After completion of all herbicide transport and dissipation studies the model system was stained with fluorescein and then systematically sampled, excavated, and photographed under ultra violet illumination, to further examine flow patterns and flow paths within the model. Mapping of the distribution of fluorescein and examination of vertical sections confirmed that several pathways existed along inhomogeneities in the model's A and B horizons. These observations explained the distribution of diclofop-methyl and diclofop acid within the system. The diclofop dissipated at all sample depths within 35 days of application. Additional studies determined the fate of ^{14}C labelled diclofop-methyl in A, B and C horizon materials derived from the model system. The results of these studies indicated that the maximum conversion rate of diclofop to CO_2 in each of the horizons A, B and C was 1, 59 and 75%, respectively. These studies indicated that random inhomogeneities in the reconstructed soil profile were the major path for penetration of diclofop below the soil surface. Further, that the diclofop rapidly dissipated and degraded at all depths in the vadose zone. In addition, the results showed that these large scale physical models can exhibit variability similar to that observed at field scale.

Fate of the Herbicide Glufosinate-ammonium and Diclofop-methyl in Groundwater

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The fate of two herbicides, glufosinate-ammonium and diclofop-methyl, in aerobic groundwater environments was studied in laboratory and field experiments. The compounds are the active ingredients in two post-emergence herbicides used for control of certain grasses and broad-leaved weeds. Glufosinate (3-amino-3-carboxypropyl)-methylphosphinate), a glutamate analogue, irreversibly inhibits glutamine synthetase activity causing phytotoxic ammonium accumulation and eventually plant depth. Diclofop-methyl (2-(4-(2',4'-dichlorophenoxy)-phenoxy-methylpropanoate) hydrolyzes readily to diclofop-acid, the active form, which interferes with lipid synthesis in target plants.

In surface soil systems, both herbicides are known to biodegrade readily via a series of daughter products to eventually produce CO_2. However, their fate in the subsurface environment is unknown. The shallow sand and gravel aquifers that often serve as potable water sources are relatively nutrient-poor and microbially sparse, and have little capacity to retard organic contaminants, when compared with many surface soils. The leaching of herbicides from surface soils into groundwater has become a topic of concern in agricultural areas. Accidental introduction of herbicide directly into the groundwater is also a possibility, albeit relatively remote. Based on physical and chemical properties such as sorption coefficients and water solubilities, both compounds of interest and/or their daughter products have the potential to be relatively mobile in groundwater. An assessment of their transport and potential for degradation in the subsurface is critical to avoid situations that could result in inadvertent contamination of large volumes of groundwater.

In laboratory microcosms comprised of aerobic, saturated zone material from the CFB Borden aquifer, diclofop-methyl hydrolysis to diclofop-acid occurred rapidly ($t_{1/2}$ = 14 h to 32 h) at natural groundwater pH. Experiments indicated that diclofop-methyl and diclofop-phenol (a product of diclofop-acid degradation) were strongly sorbed by aquifer solids whereas the acid form was not. Diclofop-acid was recalcitrant in the static laboratory microcosms although evidence of its biodegradation was obtained in the field. Diclofop-phenol biodegradation, at a rate of about $3\mu g/L/d$, was observed in the laboratory.

The distribution pattern of diclofop-methyl and daughter products during a natural gradient field test conducted at Borden was complex but could be interpreted with the aid of laboratory results. Areas in which the diclofop-acid concentrations exceeded "expected" concentrations (based on levels of diclofop-methyl injected) developed in the aquifer. This occurred because the parent diclofop-methyl was strongly retarded but rapidly hydrolyzed, so the injected mass occupied a smaller volume than anticipated, whereas the acid form was transported at approximately groundwater velocity and degraded more slowly than its parent. Indirect evidence suggested some diclofop-phenol was degraded during the 148 d field test.

Glufosinate persisted for more than 90 d in the laboratory microcosms and *in situ* testers installed within the aerobic Borden aquifer, when added at concentrations of 50 to 400 μg/L. However, addition of an organic carbon source to glufosinate-ammonium-containing microcosms resulted in subsequent herbicide biotransformation and accumulation of the metabolite 3-methylphosphinyl-propionate. Experiments with enriched cultures derived from Borden sand showed that glufosinate-ammonium and sodium glufosinate were metabolized for nitrogen, in the presence of organic carbon. Ammonium appeared to be preferred over the glufosinate moiety as a nitrogen source. The indigenous Borden microbiota were able to use glufosinate for phosphorus or as a sole carbon and energy source.

The results of these studies suggest that diclofop will degrade in aerobic groundwater. On the other hand, glufosinate-ammonium attenuation in the subsurface will likely depend upon the availability of labile organic carbon and will be affected by the presence of other, preferred nitrogen sources.

Atrazine Concentration and Losses in Subsurface Runoff as Affected by Tillage, Band Application, Intercrop and Water Table Control

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Much of the nation's rural population is dependent upon groundwater to meet domestic and culinary needs. These groundwater resources underlie soil utilized for agricultural production. Recent surveys of groundwater quality have detected the presence of trace levels of herbicides used to enhance crop production by control of unwanted vegetation. Concern about preserving our soil resource against wind and water erosion has led to the adoption of conservation tillage. Some form of conservation tillage is being increasingly adopted as a management tool to preserve agricultural land from water and wind deterioration and to restore organic matter reserves. Conservation tillage involves crop residue management which alters surface runoff characteristics. On coarse textured soils conservation tillage has reduced surface runoff, increased deep percolation of water and increased the occurrence of herbicides in groundwater. Fewer results are available reporting the effects of reduced tillage on hydrologic characteristics, herbicide dissipation and occurrence in groundwater from fine textured soils. Ongoing studies at Harrow with a fine textured soil have provided data on the effects of tillage, intercrop, water table control and band application of herbicide on surface and subsurface runoff losses. Two conservation tillage treatments (ridge and zero tillage) were compared with conventional tillage for water quality. Herbicide loss was most related to incidence of a runoff producing event to herbicide application and depth of runoff than to tillage. Multiple regression analysis found 60% more atrazine was lost in surface runoff from conservation than conventional tillage but that loss through drain discharge was unaffected by tillage. No significant differences were detected in the total quantity of herbicide transported. Herbicide concentration of surface runoff was higher from conservation than conventional tillage probably because of herbicide washoff from the crop residue. These results contrasted with those reported from coarse textured soils where conservation tillage decreased herbicide loss in surface runoff and increased detection in groundwater. Tillage had little consistent effect on herbicide dissipation in the soil. Herbicide dissipation in soil was more related to soil moisture content and temperature than tillage. Atrazine residues were 74% higher on the tops than in the valleys of the ridge treatment because of differences in moisture content between the two environments. Herbicide residues were similar in soil from zero, ridge valleys and conventional tillage. In another study on the same soil type, tillage, a regress intercrop and controlled drain discharge were monitored for their effect on water quality. Soil saver tillage and the regress intercrop reduced atrazine loss in surface runoff compared to conventional tillage in one of two years. Tillage and intercrop effects were detected because a subsurface event preceded the surface event which allowed increased vertical movement of the herbicide and reduced surface transport. No controlled drain discharge, tillage or regress intercrop effects were detected when a surface and subsurface event occurred within 14 days of herbicide application. Herbicide loss amounted to 3% of that applied which was similar to losses from previous year's application. Herbicide was band applied over seeded row reducing input 50%. It was estimated atrazine loss would have been double that found had the application been made to the whole area. Application of atrazine in a band reduced atrazine loss in surface runoff in direct proportion to the quantity of herbicide applied ie application to half the area reduced transport 50%. Tile discharge contributed about 50% of the combined surface and surface atrazine lost by aqueous transport. Tile drains effectively reduce atrazine load to groundwater but will contribute to surface load. No atrazine was detected in groundwater at the 3 m depth. Introduction of banded herbicide application technology will allow reduced herbicide input and a subsequent improvement in surface and subsurface water quality.

Pesticide Leaching Associated with Conventional Potato and Corn Production in Atlantic Canada

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An objective of recent studies in Atlantic Canada has been to detect movement of in-use pesticides from their point of field application to entry into the shallow groundwater regime. This is accomplished through analysis of tile drainage water or shallow groundwater from farm fields of known crop management history. Under this scenario, pesticide detections above background levels are attributed to normal non point source application rather than spills or contamination by surface water. These studies indicate typical concentrations that could be carried via recharge to deeper groundwater supplies. In addition, they provide direct evidence of "leachability" under typical field conditions. To date, pesticides specific to potato (metribuzin, dinoseb, chlorothalonil) and corn (atrazine) production have been investigated. In the case of potato production, these studies have been complemented by sampling strategically located private and/or research wells for metribuzin and chlorothalonil. Based on pesticide properties, the fungicide chlorothalonil is considered a "non leacher". Herbicides metribuzin, atrazine and dinoseb are classed as "leachers".

Between 1987 and 1989, dinoseb and metribuzin were detected in farm scale tile drainage systems underlying commercial potato fields in northwest New Brunswick, both during the year of application and the following spring. Of the 232 samples collected, 126 had concentrations greater than the minimum detection limit. Ninety-five percent of the positive samples were less than 2 $\mu g\ L^{-1}$, substantially less than maximum acceptable concentrations (MAC) suggested by Health and Welfare Canada. Average dinoseb concentrations 12 months after application ranged from less than detection to 0.21 $\mu g\ L^{-1}$ (five site years); metribuzin concentration ten months after application averaged 0.22 $\mu g\ L^{-1}$ (one site year). Metribuzin was not detected in groundwater samples collected in fall '92 and spring '93 from multilevel research wells in northwest NB. These wells are located at the edge of commercial potato fields within a watershed dominated by potato production, and are in the vicinity of some tile drainage sites referred above.

Chlorothalonil residues at detection level concentrations (approx. 0.00 $\mu g\ L^{-1}$) were found in four of 66 samples collected from replicated tile drainage plots in Prince Edward Island seven months after application. No chlorothalonil residues were detected in a 1990 fall sampling of 19 private wells in northwest NB, even though these wells were in an area of intense potato production and were already affected by elevated nitrate concentrations. Concentrations were also less than detection during a September 1992 sampling of one of the multilevel research wells mentioned above.

Water samples from replicated drainage plots within a commercial corn field in southern NB were collected approximately every two weeks following post emergent atrazine application during 1989 and 1990. With the exception of an extreme event in 1990 (described below), atrazine concentrations ranged from 0.1 to 29 μg L^{-1}. For both crop years, concentrations declined with time after application to less than 1.0 μg L^{-1} just prior to spraying activities the following year.

In July 1990, during routine atrazine application, damage was sustained by the tractor mounted sprayer as the tractor became stuck in a localized wet spot. Approximately 70 g of active ingredient were accidently discharged at the site of the incident. Subsequent auto sampling every 4 hours of the drainage outlet, which served the area of the accidental atrazine discharge, revealed atrazine + desethyl atrazine concentrations to 140 μg L^{-1}. Atrazine concentrations were less than the MAC (60 μg L^{-1}) within two days of the initiation of tile flow. As a result of the 70 mm rainfall that caused the drainage event, approximately 18 g of active ingredient were discharged in the drainage water over a three day period.

Microextraction of Polychlorinated Biphenyls and Dichlorodiphenyltrichloroethanes from Tap (Environmental) Water and Analysis by Gas Chromatography-Electron Capture Detector

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The largescale use of polychlorinated biphenyl (PCBs) and dichlorodiphenyltrichloroethanes (DDTs) in North America has been curtailed in recent years. However, they are still found in many applications across the world and in many instances they find their way into the environment. Routine checks of environmental substrates reveal that DDTs and PCBs are still present although concentrations seem to be diminishing. Nevertheless, environmental substrates are continuously monitored for these contaminants because their great persistence leads to bioaccumulation which in turn may have a negative impact on the health of living species.

The techniques of choice for the analysis of PCBs and DDTs still remains GC-ECD because of its great sensitivity. However, in recent years, the technique of GC-MS has become more popular particularly with the advent of new mass selective detectors which offer comparable sensitivity to the ECD with added confirmation of species via mass spectral data.

Since the early seventies, one method for the quantitation of PCBs has been to compare the chromatogram with that of a mixture of commercial PCBs, commonly referred to as AROCHLORs. One or several peaks of the sample may then be quantified by comparing peak heights or areas and the result is often expressed as total PCBs. With recent advances in capillary column technology, greater specificity may be achieved and quantitation is then obtained on the basis of several specific congeners representing those most likely to be found in nature.

For this study, one group (STD-1) of PCBs comprising the following congeners: 10(dichloro-), 21 and 26(trichloro-), 49(tetrachloro-), 86 and 116(pentachloro-) and 136(hexachloro-) and some DDT analogs were selected on the basis of their longtime use as a group in our laboratory for their quantitation in water. A second group (STD-2) of PCBs, namely, 28(tri-), 52(tetra-), 101(penta-), 118(penta-), 153(hexa-), 137(hexa-), 138(hexa-), 153(hexa-) and 180(hepta-) congeners were selected because they are currently being used in Canada to compare various analytical procedures used by different laboratories in a check sample program.

PCBs and DDTs are usually extracted from water by solid phase absorbent columns or by liquid-liquid extraction. Solid phase extraction requires 20-30 mL of solvent while liquid-liquid extraction may require several hundred mL. A common solvent used is n-hexane because it removes many co-extractives that would otherwise interfere with the analysis. The use of a large volume of solvent is in itself a major drawback due to cost of purchase, handling and disposal. The time required for evaporation and the equipment needed are also major disadvantages.

The microextraction of chlorinated insecticides has previously been studied with a special home-made extraction apparatus using only 200 μL of solvent. However, the percentage recoveries varied between 48-62% which is not quite acceptable unless the relative error is very small. The need for special apparatus coupled with low recoveries and high variability probably explains why this particular method was never largely adopted.

In this study, a simple method is described for the liquid-liquid microextraction of some polychlorinated biphenyls, DDT and some related compounds, from tap (environmental) water. The water sample is extracted with 1 mL of n-hexane for 10 minutes; the extraction is repeated and an aliquot of the combined extracts is injected directly into a capillary gas chromatograph equipped with an electron capture detector.

The results indicate that the microextraction technique may be used for the quantitative recovery of PCBs and DDTs at their limits of quantitation. At 10 ng/L, an average recovery greater than 90% may be expected. The method is particularly useful in view of the relatively low cost of operation in terms of chemicals, apparatus and time with a minimum of organic solvent to be discarded or recycled.

Field Measurements of Water and Solute Transport Parameters

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Effective calibration and validation of physically based solute transport models requires in-situ measurement of several water and solute transport parameters, including the soil water characteristic, $\Theta(P)$, the hydraulic conductivity function, $K(P)$, the average linear pore water velocity, V, and the soil dispersivity, α. Obtaining reliable field scale estimates of these transport parameters is complicated by soil variability, and consequently many replicate measurements are usually required. As part of a study to model and predict the fate of non-point source agricultural pesticides on a watershed scale, a series of field experiments were conducted to measure water and solute transport parameters at 6 sites distributed through Southern Ontario (located near Ottawa, Alliston, Crediton, Brantford, Thamesville and Woodslee), all of which were in areas of intensive agriculture. The soil types represented at these sites are "typical" for the Southern Ontario region, and include a highly structured Rideau silty clay (Ottawa site), a structureless Tioga fine sand (Alliston), a well structured Brookston clay loam (Crediton), a moderately structured Guelph loam (Brantford), a poorly structured Brady sandy loam (Thamesville), and a Brookston clay loam that exhibits extensive shrinkage cracking in the plough layer (Woodslee).

At each study site, six replicate 1 m^2 plots were instrumented with time domain reflectometry (TDR) probes to simultaneously monitor volumetric water content (Θ) and the movement of chloride (CL^-) tracer. In each plot, the TDR probes were inserted vertically from the soil surface to 5 different depths, the depths at each site being customized to the soil profile characteristics (typically, the depths ranged from 10 cm to 80 cm). Each depth was replicated 5 times, which yielded a total of 30 replicated measurement points at each of the 5 depths for each of the 6 field sites. A rainfall simulator was used to uniformly apply a steady flux of water to each plot. When steady flow through the soil profile was reached (as indicated by steady water content with depth), a known mass (M_0) of CL^- was applied uniformly to the plot surface (typically, $M_0 = 80$ or 120 g m^{-2}) as a spike of concentrated potassium chloride solution, and subsequently leached through the profile using the rainfall simulator. Chloride "breakout curves" (BOCs), defined as relative mass of CL^- remaining above the TDR probe depth (M/M_0) versus pore volumes of soil solution leached (PV), were measured at each of the 5 probe depths. This was accomplished by using the TDR oscilloscope to monitor change in bulk soil electrical conductivity as the CL^- ion moved past the ends of the probes. The BOCs were obtained for field-saturated flow, where the full range of soil pore sizes can potentially participate in water and solute movement; and for near-saturated flow, where the soil macropores are largely empty of water and solute. Triplicate intact soil cores were collected at each of the 6 measurement sites for laboratory determination of Θ(P) and K(P). The V and α parameters were obtained from the CL^- BOCs by determining the rate of movement of the $M/M_0 = 0.5$ mass, and by least squares fitting the convection - dispersion equation to the BOC data.

The water and solute transport parameters exhibited considerable variability both within and among the 6 field sites, which demonstrates the need for extensive replication. At each field site, the CL^- tracer moved through the soil profiles with considerably greater average V for field-saturated flow than for near-saturated flow, reflecting the high permeability of the soil macropores. Although α varied substantially among field sites, it generally changed only moderately between field-saturated and near-saturated flow at any particular site. At the Ottawa and Brantford field sites, the BOCs were only moderately skewed and the $M/M_0 = 0.5$ mass occurred near 1 PV, indicating that the CL^- solute interacted with most of the water in these soil profiles regardless of texture or structure. At the Alliston, Crediton, Thamesville and Woodslee sites, however, the BOCs were strongly skewed and $M/M_0 = 0.5$ occurred at substantially less than 1 PV, indicating that a considerable proportion of the soil water in these profiles was by-passed by the CL^- solute. By-pass flow results in accelerated movement of solute through the soil profile, and must be accounted for in models if they are to accurately simulate and predict agrochemical movement.

A Comparison of LEACHM Simulations with Field Data

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Numerical simulation models, such as LEACHM (Leaching Estimation and CHemistry Model, Hutson and Wagenet, 1989) are now recognized as essential tools for analyzing the movement of water and solutes in the vadose (unsaturated) zone. LEACHM integrates the main mechanisms that control 1-D vertical movement of water and solutes in the soil profile, including: soil horizonation; saturated, unsaturated, steady and transient flow; crop growth and transpiration; solute sorption, degradation, advection, dispersion and by-pass of soil water; precipitation and evaporation; soil heat flow; and water table elevation. In this study, data measured in-situ in the soil profile are used to test and evaluate the LEACHM model for its ability to simulate and predict water and tracer movement under field conditions.

The water flow component of LEACHM was tested for its ability to predict in-situ measured soil water content profiles over the growing season in a poorly structured Caledon sandy loam soil planted to soybeans (located near Simcoe, Ontario); and in a well structured Rideau clay soil cropped to grass hay (located near Ottawa, Ontario). The weather data required by the model were obtained from nearby weather stations. The model was also evaluated for its ability to simulate in-situ constant flux chloride tracer breakout curve and water content data (i.e. results from short term miscible displacement experiments) collected at 6 field sites located in Southern Ontario near Ottawa, Alliston, Crediton, Brantford, Thamesville and Woodslee. Soil hydraulic property data required by the model were obtained from intact soil cores collected at each of the field sites.

The average prediction error (E), defined by

$$E = \sum_{i=1}^{n} (VP - VM)/n$$

where VP = predicted value, VM = measured value, and n = the number of observations, was used to measure the accuracy with which LEACHM can simulate the field data. In this work, VP and VM are, respectively, the predicted and measured water content or the predicted and measured relative mass of chloride tracer. The E value allows quantification of the over- and under- prediction by the model, as well as identification of systematic deviations between predicted and measured values.

For the prediction of water content profiles over a growing season, LEACHM yielded E values of -0.0091 $cm^3\ cm^{-3}$ to -0.0394 $cm^3\ cm^{-3}$ at the Simcoe site and E values of -0.0165 $cm^3\ cm^{-3}$ to + 0.0118 $cm^3\ cm^{-3}$ at the Ottawa site. For the prediction of water content profiles from the miscible displacement experiments, E values ranged from

+0.0004 to + 0.017 cm^3 cm^{-3}. The E values for the chloride breakout curves ranged from +0.006 to +0.0154. The discrepancies between model and data are attributed, for the most part, to errors and inadequacies in the input data, and/or to by-pass flow of the chloride tracer which was accounted for superficially in the model.

The E value results easily satisfied the criterion for model acceptance set by the Prediction Exposure Assessment Workshop (Hedden, 1986) which states that a model should be able to replicate field data within a factor of 2 for site-specific applications. It was therefore concluded that LEACHM performed satisfactorily for the simulation and prediction of vertical water and tracer movement through the soil profile under field conditions.

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Prediction of Pesticide Migration on a Watershed Basis: Methodology

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Although most pesticide contamination of ground water is below current Canadian drinking water guidelines, there is a growing public concern over potential health hazards related to long-term exposure to low levels of pesticides and their metabolites. Pesticide residues, e.g. atrazine, have been detected in surface, ground and tile drainage waters of agricultural watersheds, particularly where there is some combination of intensive agriculture with high pesticide usage, high rainfall, irrigation, coarse and other highly permeable soils, shallow water tables, and sloping topography. Consequently, there is a need to determine how important and widespread this type of contamination might be, what the controlling soil, land use and environmental factors are, and what agricultural practices are required to contain this type of pollution at acceptable levels. Essential steps in obtaining the above information include the identification of the primary mechanisms controlling pesticide movement through the soil profile, and the development of the capability to characterize and predict spatial and temporal variability in pesticide migration. To achieve these steps, a sophisticated solute transport simulation model is employed in combination with pedotransfer functions, geostatistical analyses and a geographic information system (GIS).

The solute transport model used is a modification of LEACHM (Leaching Estimation and CHemistry Model) (Hutson and Wagenet 1989), which integrates the major processes that occur in the soil profile, including: soil horizonation; saturated, unsaturated, steady and transient flow; crop growth and transpiration; solute sorption, degradation, advection and dispersion; precipitation and evaporation; soil heat flow; and water table elevation. Modifications to the model include:

(1) The Van Genuchten (Van Genuchten 1980) soil hydraulic properties (i.e. K-θ-h relationships) are incorporated to give more accurate representations of near-saturated water content and hydraulic conductivity.

(2) The transpiration model of Feddes et al. (1978) is used to obtain more realistic patterns of root water uptake.

(3) Soil and crop management data (planting, emergence, pesticide application, maturity and harvest dates) are modified to account for weather and soil texture.

(4) To run LEACHM continuously for a specified number of consecutive years, alterations are made to account for temperature, snow accumulation, spring runoff, and over-winter redistribution of water when the soil surface is frozen.

Soil and weather data required by the model are obtained from archived data bases (e.g. Canadian National Soil Database, Archived Weather Database), or estimated from soil survey data using pedotransfer functions. Pedotransfer functions are empirical regressions that estimate required, but unavailable (i.e. not measured) soil properties from the soil properties that are available. In this study, soil bulk density, soil water characteristic curves and hydraulic conductivity functions are estimated from available soil texture and organic carbon content data.

The LEACHM predictions of water and solute movement apply only to geo-referenced points because the model simulates vertical flow only. These predictions are extended to an areal basis by applying geostatistical analyses. First, semivariograms are calculated to establish and quantify the patterns of variability of the soil attributes, weather and LEACHM predictions across the area of interest. These patterns are then used in conjunction with kriging to interpolate the data from the original irregularly spaced point locations to a regular and finer grid. The kriging process provides interpolation estimates that i) formally account for the inherent spatial variability of the measured data within the area; and ii) are statistically unbiased with minimum possible estimation variance. The kriging interpolations provide the input for the GIS.

The GIS (we used the Integrated Land and Water Information System, "ILWIS", International Institute for Aerospace Survey and Earth Sciences, The Netherlands)is used mainly to produce map overlays of soil attributes, weather, land management practices, pesticide use and LEACHM predictions of pesticide loadings. The GIS provides an easy and effective means for quantifying map attributes, and for visualizing distributions and trends in the results.

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Prediction of Pesticide Migration on a Watershed Basis: an Application

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Transport model - geostatistics - geographical information system methodology was applied to predict atrazine migration through the soil profiles of the Grand River watershed in Southern Ontario. Soil and weather attributes required by the transport model (LEACHM-P) were obtained from the Canadian National Soil Database and the Archived Weather Database, and assigned to the geo-referenced centroids of the 37 soil landscape polygons (Soil Landscape Map of Canada) that fell within the watershed. The model simulated 10 consecutive years at each polygon centroid, assuming an initially atrazine-free soil profile. Corn (Zea maize L.) was grown each year over the entire watershed, with soil surface temperature, soil texture and accumulated corn heat units determining the planting and harvesting dates. Atrazine was applied every year at a rate of 150 mg m^{-2} (OMAF recommended rate), 3 weeks after planting. The predicted annual mass loading of atrazine to the 90 cm depth (average tile drain depth) at the end of the 10 year simulation was used as an indicator of atrazine contamination of ground water. Geostatistical kriging was used to interpolate the soil, weather and atrazine loading data from a point basis at each irregularly spaced polygon centroid, to a regular 2 km x 2 km grid covering the entire watershed (total of 1657 grid points with kriged interpolations). The interpolated data were input into the geographical information system (Integrated Land and Water Information System, "ILWIS", International Institute for Aerospace Survey and Earth Sciences, Netherlands) to produce maps of soil attributes, weather and atrazine loading for the Grand River watershed.

The LEACHM-P predictions of annual atrazine loading to the ground water (90 cm depth) were highly variable from point to point in the watershed (CV = 164 %), but became constant with time at any particular point after about 5-7 "simulation" years. The constant annual atrazine loadings (at the end of 10 simulation years) ranged from a low of zero to a high of 2.5 mg m^{-2}, the high value being less than 2 % of the annual application rate of 150 mg m^{-2}. The 60 ppb Canadian drinking water standard for atrazine was never exceeded at the 90 cm depth, however, the 3 ppb USEPA standard was exceeded on or before the 10'th simulation year in about 5 % of the watershed area. Generally speaking, the lowest atrazine loadings (0 - 0.1 mg m^{-2}) tended to correlate with heavy clay soils and low summer precipitation (June, July, August), whereas intermediate to high loadings (0.8 - 2.5 mg m^{-2}) tended to correlate with sandy to loamy soils and moderate to high summer precipitation. The correlations between atrazine loading and the soil and weather attributes were often statistically significant, but were generally not particularly high. This suggests that atrazine migration through the soil profiles in this

Session 6 — Pulp and Paper Effluent Impacts II

ABSTRACT

FACTORS INFLUENCING PULP MILL EFFLUENT TREATMENT IN ALBERTA

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This paper summarizes an investigation of the factors influencing the choice of in-plant and external effluent treatment systems in six Alberta pulp mills. The information was collected from a literature review and from interviews with involved government, industry and public officials.[3]

The pulping industry in Alberta employs state-of-the-art effluent treatment technology. The water licince parameter levels set by the provincial government are among the lowest in Canada and as low as any in the world. The Alberta pulp industry consistently discharges below these limits. The process of establishing the current advanced effluent treatment practices is an extremely intricate and complex system influenced by many factors in Alberta, and by other systems played out on the world level.

Factors influencing in-plant and external effluent treatment systems in six Alberta pulp mills were investigated. These factors included environmental impacts of pulp mill effluent, pulp mill technology development, government incentives and control of pulp mills, market influences, and public concerns. It was determined that public concern and awareness was instrumental in influencing government to approve mills with the best available technology and to implement high effluent discharge standards for the mills.

Between 1988-1991, four new pulp mills were constructed in Alberta, and the existing two pulp mills were upgraded as part of the provincial government's economic diversification program. This increased level of activity, especially the ALPAC hearing process, and global environmental concerns, enhanced public awareness of forestry development in the province. The public was concerned with harvesting practices and mill pollution as down-stream users of receiving waters. In the future, the controversy over pollution will not be about the impacts, but about whether or not the environment has been returned to its natural (original) state. Any effluent treatment system short of closed loop will not be acceptable to the public.

The process by which the pulp mill industry responded to the public concerns about the environment was complex. Described as a system, the process was defined by identifying basic pathways and interactions between the sector's influencing factors. Application of the scientific method is inadequate to resolve environmental disputes which are compounded by different paradigms. Defining the response process depends on the observer's point of view since environmental issues have become a matter of perception. Fully understanding these concepts is crucial for government to establish constructive policy and for industry to cost-effectively address public concerns.

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THE REMOVAL OF TOXIC CONTAMINANTS FROM BLEACHED KRAFT MILL EFFLUENT WITH ENHANCED BIOLOGICAL TREATMENT METHODS

ABSTRACT

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This investigation was conducted as a follow-up to a detailed laboratory-scale investigation conducted by the Wastewater Technology Centre (WTC) to evaluate the performance of activated sludge, aerobic stabilization basin and facultative stabilization basin systems for the treatment of effluents from a modernized bleached kraft mill. Based on the results of this work, pilot-scale activated sludge and aerated stabilization basin systems were constructed and located at E.B. Eddy's mill in Espanola, Ontario. Both units received combined effluent from the mill. The objective of this investigation was to demonstrate the potential of the enhanced activated sludge system to remove acute and chronic toxicity as well as a wide range of compounds known to exert toxic effects. The lagoon system was operated in parallel to compare the activated sludge system's performance with that of a traditional biological treatment technology. A limited amount of characterization data were also recorded to compare the pilot-scale lagoon's performance against that of E.B. Eddy's full-scale aerated lagoon system that was receiving the same wastewater.

Based upon the laboratory investigation results, the design of the activated sludge system was set at 1 day HRT and 25 - 30 day SRT, and operated at 30°C. The process design of the aeration cell was enhanced by the addition of a low residence time anoxic cell. Its performance was evaluated under actual mill operating conditions over an extended period. The lagoon operating conditions were changed periodically to evaluate two temperatures (10 & 20°C) and two HRTs (5 & 10 days).

The major observations that have been made may be summarized as follows. The raw wastewater was lacking in ammonia and phosphorus nutrients. Toxicity was observed in the feed as measured by the Rainbow trout LC_{50} and Microtox tests. The primary clarifier removed approximately 60% of the influent solids. The activated sludge effluent passed all acute and chronic toxicity tests as measured by Rainbow trout LC_{50}, Microtox and Ceriodaphnia LC_{50} & IC_{25} tests. A high level of effluent quality was achieved with low concentrations of AOX total (5-13 mg/L), AOX soluble (3-11 mg/L), total chlorophenolics (0.3-3.2 µg/L), toxicity equivalents (TEQ-PCP) (0.4-5.0 µg/L), total resin & fatty acids (0-<4 mg/L), BOD_5 (4-12 mg/L) and COD (142-274 mg/L) being recorded over the whole period of investigation. Similar but generally higher and more variable values were observed in lagoon effluents for all parameters, the higher values generally reflective of operation under low temperatures.

Measurements were also taken of the removal efficiency of hepatic MFO induction response, measured as 7-ethoxyresorufin-o-deethylase (EROD) enzyme activity. The highest removals were measured for the activated sludge system.

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PHOTODEGRADATION OF HIGH MOLECULAR WEIGHT KRAFT BLEACHERY ORGANOCHLORINE AND COLOR

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ABSTRACT

Previously it was shown that the high molecular weight (HMW) fractions of C and E-stage kraft bleachery effluents are very resistant to microbial degradation but are decolorized and dechlorinated by abiotic sunlight-dependent and sunlight-independent processes. In this work, to better understand the importance and mechanisms of this light-mediated effluent decolorization and AOX mineralization, two artificial light sources with defined outputs and spectra were used to irradiate hardwood and softwood HMW effluent fractions. Both longwave UV and blue-green visible light were effective in mineralizing a large fraction of the AOX to chloride ions, and in decolorizing the effluent over several days. Photo-decolorization showed a strong oxygen dependence while AOX mineralization did not. Visible light at an intensity comparable to the sun at the earth's surface in northern latitudes mineralized a substantial proportion of the "stable" HMW AOX, in both fresh and salt water, and at low and high effluent dilutions. Such light also mineralized an appreciable fraction of the HMW carbon to CO_2 by abiotic mechanisms. The hardwood HMW fraction showed insignificant toxicity as measured by a bacterial toxicity test, both before and after extensive photolysis.

MUTAGENICITY/TOXICITY ASSESSMENT IN BLEACHED KRAFT MILL EFFLUENTS

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The impact of pulp mill effluent discharges on receiving waters is one of great environmental concern. Effluents from pulp mills have been shown to contain mutagenic substances and fish in the vicinity of mill effluent discharges have shown signs of tumour development in addition to other physiological disorders. However, no direct or experimental evidence exists which attributes these observed incidences to mutagenic or carcinogenic substances in effluents. Equally important is information on the nature of such mutagenic substance/s present in such a complex mixture as BKME. The isolation of specific substances is difficult because of the profusion of chemicals dissolved in the effluent. In this study we measured mutagenic properties of both filtered effluent and several effluent fractions (obtained in non-polar and polar solvents using macroreticular resins, XAD-4 and XAD-8) and toxicity to a variety of bioassay organisms. While mutagenicity was measured using the Ames Test and SOS Chromotest, toxic properties were measured using the *Daphnia magna* and Microtox bioassays. Data indicate that bleached kraft mill effluent was found to be mutagenic with the majority of the activity associated with the polar compounds. Polar material adsorbed by XAD-4 and XAD-8 resins contained a mutagenic potency equivalent to that measured directly in the effluent. Whole effluent samples were non-toxic (Microtox bioassay), but the polar fractions were toxic (Microtox and *Daphnia magna* bioassays) while particulate associated materials were toxic just to Microtox bioassay. Our study has demonstrated that approximately 75% of the mutagenic substances from the filtered effluent were recovered with polar solvent elution from two resins suggesting that the mutagenic substances have properties similar to organic acids. This study has provided some insight with regard to specific fraction(s) which may contain the majority of direct-acting mutagenic compounds. The mutagenicity does not appear to be consistent with the well known "MX" mutagen, although "MX" was not measured directly. Further characterization of the mutagenic fractions from pulp mill effluents is currently underway.

The effects of pulp and paper mill effluent on fish reproduction -- A laboratory perspective. **R. D. Robinson**, Dept. of Environmental Biology, and Solomon, K. R., Centre for Toxicology, and Van Der Kraak, G. J., Dept. of Zoology, University of Guelph, Guelph, ON, Canada; Carey, J.H., NWRI, CCIW, Burlington, ON; and Munkittrick, K.R., and Flett, P. A., GLLFAS, CCIW, Burlington, ON. Fish collected near pulp mill sites have shown a range of biological responses, including a reduction in gonad size, delayed maturity, reduced expression of secondary sexual characteristics, and induction of liver detoxification enzymes (MFOs). Although MFO induction has been relatively easy to replicate in caged and laboratory exposures, steroid and reproductive effects have been more difficult to duplicate. This paper describes the development of a laboratory protocol for measuring the effects of pulp mill effluent on reproductive function in fathead minnows. Life cycle exposures of fathead minnows to secondary treated effluent from a bleached kraft pulp and paper mill have indicated delayed maturity, reduced secondary sex characteristics and reduced fecundity. In these life cycle tests, reduced steroid hormone synthetic capacity at lower effluent concentrations was predictive of whole organism effects at higher effluent concentrations. These effects on steroid biosynthesis have recently been measured in short duration (<30-d) exposures, and we are attempting to produce a short-term test for predicting the effects of effluent exposure on the reproductive potential of wild fish.

ABSTRACT

(Twenty-Ninth Central Canadian Symposium on Water Pollution Research)

CHARACTERIZATION AND BIOTREATABILITY OF BLEACHED KRAFT MILL IN-PLANT AND COMBINED PROCESS EFFLUENTS WITH RESPECT TO TOXIC COMPOUNDS AND MFO INDUCTION POTENTIAL

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Samples of various in-plant process waters obtained from a modernized bleached kraft mill, as well as a representative composite effluent blend (i.e., simulated combined mill effluent), were subjected to comprehensive chemical and biological characterizations and ultimate biotreatability assessments. The main objectives of this collaborative investigation between the Wastewater Technology Centre (WTC) and the National Water Research Institute (NWRI) were to identify the in-mill sources of effluent-associated mixed function oxygenase (MFO) inducing substances and to determine the maximum degree of biotreatability and corresponding levels of biorecalcitrant residual effects, if any. In addition to advancing the existing knowledge-base in this field, the results were intended to complement the promising findings of WTC laboratory and pilot scale studies on optimized biological treatment for the enhanced removal of persistent toxic compounds and MFO induction potency towards fish.

A significant level of MFO induction potential was measured for untreated samples of diluted black liquor (softwood line, hardwood line), combined condensate (softwood plus hardwood lines), the D_C-, E_O-, H- and D-stage effluents from the softwood line bleach plant and the simulated mill effluent composite (SME). MFO induction levels were determined by 7-ethoxyresorufin-o-deethylase (EROD) activity measurements on liver samples following 4-6 day waterborne exposure (semi-static conditions; 24-hour renewals) of juvenile rainbow trout to effluent samples (10% v/v). The range of bioassay test concentrations with black liquor was 0.01-0.2% (v/v). Insignificant MFO induction responses were found with the "open" oxygen delignification stage effluent (SW), the dry woodroom (HW) effluent and the papermill effluent. There were no indications of hepatotoxicity effects during bioassay tests with the O_2-stage effluent at 2-10% (v/v). Interestingly, the apparent insignificant EROD induction potency of the O_2-stage effluent suggests that MFO inducing substances are generated in the subsequent stages of the softwood line bleach plant. It was also estimated that the D_C-stage effluent contribution to the induction potency of the SME sample was disproportionately high relative to the other constituent effluents.

Extensive 28-day batch aerobic biological treatment of the various effluent samples resulted in high degrees of contaminant removal (e.g., non-detectable levels of resin and fatty acids as well as base neutral and acid compounds and greater than 85% removal of chlorinated phenolics), complete detoxification (with respect to the Microtox bioassay) as well as substantial reductions in MFO induction potentials (10% v/v bioassays). Only the bleach plant effluents (SW line), in particular the D_C- and E_O-stage filtrates, exhibited residual EROD inductions of any biological significance, albeit at low levels, following ultimate aerobic biotreatment. The EROD induction potentials of black liquor (0.045% v/v) and combined condensate (10% v/v) were reduced to response levels that were considered biologically insignificant with this bioassay method. The results of this investigation indicate that conservative-mode biological treatment offers good potential for the enhanced treatment of bleached kraft mill effluents, as has been demonstrated in the continuous-flow WTC biotreatment studies.

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Polychlorinated Dibenzo-*p*-dioxins (PCDDs), Dibenzofurans (PCDFs) and Other Inducers of Mixed Function Oxygenase (MFO) in Rainbow Trout. J.L. Parrott and P.V. Hodson. National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, Canada. There are many known inducers of MFO activity in fish, such as PCDDs, PCDFs, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and polychlorinated diphenyl ethers (PCDEs). The chemical structure of the inducer determines its ability to induce MFO enzymes and its potency as an inducer. Specific structure of the inducer is required to fit into the Ah receptor which initiates mRNA production and enzyme protein synthesis. Elevated hepatic MFO activity common in fish downstream of pulp mill effluent discharges. The identity of the MFO-inducer(s) in effluents is, as yet, unknown, although initial theories linked PCDDs and PCDFs in effluents with induction. Naphthalenes and similar compounds have been detected in effluents from several pulp mills. The structures of these compounds suggests they may be MFO-inducers, especially when chlorinated in lateral positions. The ability of these compounds to induce MFO will be discussed, and compared to induction by tetrachlorodibenzo-*p*-dioxin (TCDD) and other PCDDs and PCDFs.

Additivity of Polychlorinated Dibenzo-*p*-dioxin (PCDD) Mixtures for Inducing Ethoxyresorufin-O-deethylase (EROD) Activity in Rainbow Trout. Wilson, J.Y.[1], Parrott, J.L.[2] and P.V. Hodson[2]. [1] Departments of Biology and Pharmacology, McMaster University, Hamilton, Ontario, Canada [2] National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, Canada.

Toxic equivalent factors (TEFs) are ratios expressing the relative potencies of two compounds causing the same effect. They estimate the risks of exposure to complex mixtures by expressing the concentrations of many components as the equivalent concentration of one reference component. For polychlorinated dibenzo-*p*-dioxins (PCDDs), the reference component is the most toxic, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The induction of ethoxyresorufin-O-deethylase (EROD), an enzyme of the mixed function oxygenase system in the liver, is a common indicator of PCDD exposure. TEFs can be calculated from the ratio of slopes of dose-response curves for EROD activity if the slopes for each compound are parallel. For fish, PCDDs applied singly have non-parallel slopes for the EROD versus liver concentration dose-response curves. Consequently, TEFs can vary depending on how they are calculated. There are three alternatives for evaluating effects of mixtures when slopes are non-parallel: 1) Compute TEFs based on specific liver concentrations, with a different TEF for each concentration chosen. The concentration most environmentally realistic is preferred for this method. This type of TEF can result in large errors when the concentrations deviate from the concentration range used for the TEF calculation; 2) Compute the combined effect of each measured congener by the regression equations from the single compound dose-response curves. These are more precise as they describe the relationship all along the dose-response curve. The dose can be related to the reference compound and the equivalent dose calculated. The summed equivalent doses are used to estimate the expected effect (<u>concentration-addition</u>); or 3) The effect of each individual congener is calculated from the individual dose-response relationship and the effect is summed to estimate the expected response (<u>response-addition</u>). We tested the hypothesis that effects of dioxin mixtures would show additivity in bioassays of EROD induction of fish exposed to defined mixtures. Mixtures of PCDDs were given in pairs of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) with either 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin (HxCDD) or 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HpCDD). After an eight-day exposure to a single oral dose, EROD activity and liver concentrations of PCDDs were measured in 100g rainbow trout. Mixtures were given in equi-potent and unequal (2/3 + 1/3) pairs. Doses of TCDD were in the range of 0 to 2.157 μg/kg. Doses of HxCDD and HpCDD were in the range of 0 to 4.962 and 0 to 57.876 μg/kg respectively. The concentration-addition model was used with the regression data of single PCDDs and compared with two types of TEFs and the response-addition model. Fish TEFs, calculated at threshold doses, most closely matched the concentrations found in environmental samples. Mammalian-based TEFs, calculated from

mammalian systems, were expected to underestimate the effects on fish. When predicted EROD activity was compared to actual EROD activity, the mixtures were less-than-additive. Use of the regression equations from the single compound data gave the best fit.

FACTORS AFFECTING THE INDUCTION OF MIXED FUNCTION OXIDASE ENZYMES IN RAINBOW TROUT EXPOSED TO PULP MILL EFFLUENTS

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As part of a program to identify compounds in pulp mill effluents that induce the mixed function oxidase (MFO) enzymes of fish, a protocol was developed for exposing rainbow trout fingerlings to effluent and for assaying liver MFO activity. The fractionation experiments required repeated testing of effluents and effluent extracts, so the protocol was developed for small volumes of test solutions made from effluent shipped to the laboratory in barrels. We have evaluated the importance of variations in testing procedures, in test organisms, in effluent handling and in exposure route on the response of fish to MFO inducers in effluent or to model compounds. Variables such as static vs static-renewal exposures, exposure time and fish size had a major impact on measured activity. The results demonstrated that quality control criteria developed for tests of lethality should also be applied to tests of MFO induction. Daily replacement of solutions, a standard exposure time of 4 d and loading rates of 0.5-1.0 g of fish per L per day are required to achieve reliable results. However, there is a lower size limit for fish of about 1.0 g each, using our current analytical protocol. Effluent storage was not particularly critical once the effluent was filtered to remove particulates. Potency for inducing MFO activity was unaffected by storage temperature (-4 to 13°C), or exposure time (1-3 weeks). However, storage in stainless steel containers caused a loss in potency, in contrast to storage in plastic or glass containers. Water chemistry was also important. Samples acidified to pH 6.0-7.0 were often acutely lethal, unless the sample was aerated for some time. For fish that survived, potency for MFO induction increased with pH, up to pH 8.5, the highest tested. Exposure via injection was also tried, and a routine exposure to ß-naphthoflavone (BNF), a model inducer, was used as a 'positive control' to ensure that fish were capable of responding to the accumulation of inducers from effluents. To dissolve materials for either aqueous or injection exposures, a variety of solvents were tried, many of which were acutely toxic. At a constant dose of BNF, many solvents caused reduced MFO activity or reduced induction. However a dose or concentration of each solvent could usually be identified that would not affect the induction caused by BNF exposure or an aqueous exposure to pulp mill effluent. Anesthetic (tricainemethane sulfonate) was found to have little impact on measured MFO activity. The result of these studies is a protocol that gives relatively consistent results and a sufficient statistical power to reliably identify fractions of effluent containing inducers.

ISOLATION AND CHARACTERIZATION OF A MFO-INDUCING SUBSTANCE

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Pulp mill effluents contain a myriad of chemicals which have the potential to cause deleterious effects on aquatic biota in a receiving waters. Some of these chemicals have an acute lethal impact on biota while others have a sublethal effect. One such sub-lethal effect is the induction of mixed function oxidases (MFO) in fish. The chemical(s) which cause this induction have been the subject of much scientific and media controversy. We initially followed the partitioning of the inducing activity in pulp mill effluent fractions by the Toxicity Identification Evaluation (TIE) or bioassay-driven chemical analysis approach. This procedure was eventually modified to a more direct technique. Final pulp mill effluent (Mill A and Mill B) was collected before its entry into the receiving water and centrifuged to remove suspended solids and the "fines" removed by glass fibre filtration. This filtrate was further filtered through a 0.2 µm filtration cassette housed in a Millipore® tangential flow apparatus. The filtrate was treated with DEAE cellulose to remove most of the coloured humic substances followed by filtration through either C_{18} resin or C_{18} Empore® disks. The centrifuged suspended solids (SS) and > 0.2 µm retentate (RET) were freeze-dried followed by methanol extraction. The DEAE cellulose and the C_{18} resin/disks were also extracted with methanol. The extracts of the four fractions were tested for MFO inducing activity (EROD) in a static four day rainbow trout bioassay. The removal of the suspended sediments and the > 0.2 µm retentate did not significantly decrease the MFO-inducing ability of the effluent. There was a slight decrease after DEAE cellulose treatment and a significant reduction after C_{18} treatment. The methanol extracts of SS, RET, and DEAE cellulose showed significant MFO-inducing capacity in Mill A effluent, but not in Mill B. The C_{18} resin/disk methanol extracts showed EROD activity in both effluents with extracts from Mill A being the most potent. Twenty litre equivalent of RET methanol extract from Mill A showed a 8-fold increase in the EROD activity over the whole effluent during a four-day static exposure of trout. An active fraction was isolated by solid phase extraction techniques and applied to further fractionation by reverse phase HPLC. The majority of the EROD activity was found in the relatively polar region of the chromatogram (K_{ow} = 2 to 4.5). While compounds such as phenanthrene and naphthalene are found in this fraction, they did not induce MFO activity when added to water.

Characterization of Chemicals Associated With MFO-Inducing Fractions of BKME

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Bleached kraft pulp mill effluents have been identified as significant sources of chlorinated and non-chlorinated organic contaminants, some of which have the potential to cause adverse effects, both lethal and sub-lethal, on aquatic biota. Of the sub-lethal effects, we have focused on the induction of mixed function oxidases (MFO) in fish using the Toxicity Identification and Evaluation (TIE) approach. The subject pulp mill effluent was centrifuged and filtered through 1 μm glass fibre filter. Filtration through a 0.2 μm filtration cassette in a tangential flow apparatus was the next separation step employed on the effluent. The resulting filtrate was treated with DEAE cellulose and then filtered through either C_{18} resin or C_{18} Empore disks. The centrifuged suspended solids and > 0.2 μm retentate (RET) were freeze-dried and extracted with methanol as were the C_{18} resin/disks. The fraction extracts were subsequently tested for MFO activity. The effluent fractions that were most successful in producing EROD activity were subjected to a variety of chromatographic techniques to identify the chemical constituents. Fractions were received as methanol or methanol/water extracts, evaporated to dryness using non-destructive techniques and reconstituted in ethyl acetate. The ethyl acetate extracts were subjected to electron impact gas chromatographic-mass spectrometric (EI-GC-MS) analysis using a Hewlett-Packard 5989A MS Engine. During the partitioning stage to ethyl acetate, a polar precipitate appeared and was separately reconstituted in methanol for particle beam high pressure liquid chromatography-mass spectrometric (PB-LC-MS) analysis using the H-P 5989A MS Engine. In some cases the detection limits of the PB-LC-MS were too high for our purposes. To overcome this problem, reverse phase high pressure liquid chromatography separations of the extracts were performed with the resulting peaks collected as distinct fractions. These relatively pure component fractions were then analyzed individually on the H-P 5989A MS Engine in the electron impact mode using the Direct Insertion Probe (DIP) attachment. Preliminary findings show that polycyclic aromatic hydrocarbons (PAH's), resin acids and fatty acids have been identified in these MFO-inducing fractions. The results of this analytical process should assist us in determining the identity/identities of the mill-related contaminants that are responsible for the MFO induction in fish.

Poster Session

Loadings of Agricultural Herbicides to a Southeastern Ontario River

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The Payne River, in the South Nation River basin, was continuously samples for atrazine and metolachlor throughout the period from April to October, during 1991 and 1992. The site, southeast of Ottawa, Ontario, represented a watershed area 152 km^2. Modified Quality Environment automatic samplers were used to collect weekly flow proportional surface water samples. The maximum concentration of atrazine were recorded for the weeks ending May 29, 1991 (0.83 μg/L), and July 30, 1992 (1.20 μg/L). These values were approximately half the Canadian Water Quality Guideline (CWQG) for the Protection of Freshwater Aquatic Life (2 μg/L). Maximum concentrations of metolachlor were also recorded for these dates; values were 0.43 μg/L and 0.25 μg/L respectively - well below the CWQG of 8 μg/L for the Protection of Freshwater Aquatic Life. Discharge data were used to calculate weekly loadings from the watershed, and seasonal loadings were compared with the results of a pesticide usage survey. Atrazine percent loading to the Payne River during both cropping seasons were the same (0.06%) despite different discharge patterns. Metolachlor percent loadings were similar for both years, and less than the value for atrazine. In 1991, 0.01% of the metolachlor applied to the study area reached the river during that cropping season. The corresponding value for 1992 was 0.02%. Atrazine loading associated with carry over from the previous cropping season were an important factor during the study period. Observed loadings, before application in a given year, exceeding the loading for the entire cropping season of that year.

Environmental Fate and Effects of Organophosphorus Insecticides on Amphibians in a Muck Crop Growing Area of Ontario, Canada

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Organophosphorus (OP) insecticides are used heavily in onion and carrot production in the Holland Marsh region of the Holland River watershed in southern Ontario. Surface water and sediment samples were collected at regular intervals and during application periods in the 1991-1993 growing seasons. Thirteen OPs were analyzed by a nitrogen/phosphorus detector and an electron capture detector. Trace concentrations (<2.2 µg/L) of terbufos, fonofos, malathion, diazinon, guthion, chlorpyrifos, ethion, dimethoate, parathion, phorate and disulfoton were observed in surface waters. Trace concentrations (<0.18 µg/L) of chlorpyrifos, ethion and fonofos were observed in sediments. Detectable concentrations in both surface water and sediments were observed more frequently adjacent to the application sites with little evidence of downstream transport.

In 1991-1993, hatching success and deformity rates of Leopard Frog (*Rana pipiens*), American Toad (*Bufo americanus*) and Green Frog (*Rana clamitans*) were assessed at four field sites in the watershed and in well water. Abnormality (rate of unhatched eggs and deformity) was higher in American Toad and Green Frog eggs exposed to field sites downstream of the control field site or well water. Leopard Frogs showed higher abnormality rates in the control area and in well water relative to downstream sites. These downstream sites had higher pesticide concentrations, particulate and nutrient levels relative to the control area indicating that increases in these stressors coincide with poorer development of amphibian eggs in two of three species tested.

In 1990 and 1992, species diversity and density of breeding amphibians was also assessed throughout the Holland River Watershed. Both diversity and density were lowest in the wetlands associated with the agricultural area.

Development of On-line QA/QC Techniques for Statistical Evaluation of GC/MS Environmental Analysis of Pesticides in Groundwater

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Laboratories equipped for high sample throughput and environmental analyses face the constant challenge of maintaining high quality of their data while sustaining high productivity. Failure to meet this challenge satisfactorily can result in serious consequences such as poor efficiency or even loss of credibility. To be cost effective, modern laboratories have become well equipped, using automation of environmental samples where appropriate. For example, hard copies of GC/MS analytical reports in a format suitable for a client, may be generated using autosamplers for data acquisition and subsequent automated data processing techniques. However, manual validation of the enormous volume of data generated by this process is slow and tedious.

The objective of this study was to develop on-line quality assurance and quality control procedures to expedite the monitoring and evaluation of pesticides in groundwater, specifically for (a) sample extractions, (b) instrumental data acquisition, and (c) computerized data reduction. Procedure files were developed for environmental analyses employing Hewlett Packard GC/MS systems. These files were complex sequences of executable commands which accessed on-lined computed data of: (1) the recoveries of surrogate standards; (2) the instrumental responses for multi-internal standards; (3) integration profiles of quantification ions; and (4) the laboratory performance for standard reference materials.

Application of items 1 - 4 are described for pesticides in groundwater, in which a "moving window" concept was supported using x-bar charts for evaluation of variable periods of a data set or composite data sets. Plots of the integrated areas of an internal standard determined for sequential analyses were very diagnostic. At a glance, problems arising from matrix effects or poorly spiked standards were readily flagged. Likewise, on-line plots of the laboratory performance for analyses of standard reference materials facilitated the evaluation of the quality of analytical data and prompted implementation of corrective action, where required. Hard copy summaries of quantification ion-profiles expedited the evaluation of problems arising from erroneous integration of extracted-ion profiles with poor peak shape.

PROTOCOL FOR MEASURING ACTIVITY OF ETHOXYRESORUFIN-O-DEETHYLASE IN FISH TISSUE WITH A MICRO-PLATE FLUOROMETER AND SPECTROPHOTOMETER

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Bioassays for induction of fish mixed function oxidase (MFO) activity have been developed as part of a program to identify inducing compounds in pulp mill effluents or their extracts. These bioassays test small fish (1-3 g) and apply experimental designs of up to 25 treatments, with five fish per treatment. We have developed a protocol for assaying the activity of one MFO enzyme, ethoxyresorufin-o-deethylase (EROD), that takes advantage of the analytical speed of micro-plate readers for measuring fluorescence and absorbance on large numbers of samples. Liver samples (0.01-0.05 g) are homogenized in 500 μL HEPES-KCl buffer immediately after fish have been sacrificed. Crude microsomal preparations are prepared by centrifugation at 9000xg for 20 min at 2°C. This 'S-9' fraction is stored in liquid nitrogen until analysis. The measurement of enzyme activity requires two steps. The first step is a kinetic assay of the conversion of the substrate ethoxyresorufin to resorufin in micro-titre plates. Since resorufin fluoresces at specific wavelengths, the progress of the reaction can be followed at one-minute intervals over a period of 12 minutes using a micro-plate fluorometer. The fluorometer data files are imported to spreadsheets where fluorescence is converted to concentrations of resorufin based on standards included with each plate. Slopes of lines relating concentration to time are calculated and crude activity is expressed as pmoles resorufin per minute. The second step is the measurement of total protein in the S-9 fraction using commercial protein kits and bovine serum albumin as a standard. The chemical reaction generates coloured products that are sufficiently stable to be measured on a micro-plate spectrophotometer, which automatically calculates protein concentrations from the standard included with each micro-plate. The protein data are imported into the same spreadsheets as the enzyme activities, and final activity is calculated by dividing crude activity by protein concentration, to give EROD activity as 'pmole resorufin per mg protein per minute'. These measurements demonstrate statistical properties of increasing variance with increasing average activity. However, non-homogenous variance can be corrected with log transformations. Treatments are compared by analyses of variance (ANOVA), or by linear regression of log-transformed values where a gradient of doses were used in a bioassay. Results are expressed as means and 95% confidence limits, calculated from pooled error variances, and all results are back-transformed to real numbers for graphical display.

An Evaluation of GC Detectable Constituents in Treated Bleached Kraft Mill Effluent to Induce Mixed Function Oxygenase Activity in Rainbow Trout.

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Abstract

The induction of mixed function oxygenase (MFO) enzymes coinciding with impaired reproductive performance in fish exposed to pulping effluents has been well documented but the compound(s) responsible is(are) unidentified. Juvenile rainbow trout were exposed to fractionated effluent samples from a bleached Kraft mill to evaluate effluent extractives for their potential to elevate MFO activity. Fish were exposed in static, nonrenewed, undiluted solutions for 4 d. MFO induction was measured as hepatic ethoxyresorufin-O-deethylase (EROD) activity. Exposures to whole and filtered (<1μm) effluent, resuspended solids and fractions generated from nanofiltration were conducted on samples of primary effluent, its effluent after secondary treatment, and effluent collected during a pulping shutdown. Exposure concentrations of constituents detected using gas chromatography (GC) with flame ionization (FID), electron capture (ECD) and mass spectrometer (MS) detection were compared with EROD profiles to evaluate their potential to cause induction. Several chlorinated phenolics correlated with the induction patterns observed while nearly all detectable extractives exhibited no correlation.