Twenty-Eighth Central Canadian Symposium on Water Pollution Research

February 10, 1993
Canada Centre for Inland Waters
Burlington, Ontario

Abstract Booklet

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**The Canadian Association on
Water Pollution Research and Control**

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Canada Centre for Inland Waters, Burlington, Ontario

Session 1: Water Pollution Control Technology
CCIW Auditorium, Presider: T.B.A.

9:00-9:30 **R.Anani, University of Western Ontario**
Effects of High Sulfate Concentration on the Performance of Granules in Upflow Anaerobic Sludge Blanket Reactors

9:30-10:00 **C.F.Shen, University of Western Ontario**
Toxicity of Sulfite and Cadium in Anaerobic Digestion

10:00-10:30 **J.J.Ganczarczyk, University of Toronto**
Fractal Dimensions and Shape Factors of Digested Sludge Particle Aggregates

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

11:00-11:30 **P.R.Berube, University of Toronto**
Organic Carbon Sources for Sulphate Reducing Bacteria in the Treatment of High Sulphate Waste Streams

11:30-12:00 **R.D.Tyagi, Universite du Quebec**
Biodegradation of Petroleum Refinery Wastewater: A Bioreactor Comparison

12:00-12:30 **J.Wu, University of Windsor**
Optimization of the Reaction Conditions for Enzymatic Removal of Phenol from Wastewater in the Presence of Polyetheylene Glycol

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

1:30-2:00 **I.W.Koster, Ecotechniek BV**
Ecowat - A New Technology for Treatment of Wastewater with a high Nitrogen Level

2:00-2:30 **L.A.Lishman, McMaster University**
Simulation of Long Term Performance Using the IAWPRC Model

2:30-3:00 **J.Shepherd, University of Guelph**
Pilot Studies of VOC Emissions from Drop Structures in Wastewater Collection Systems

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

3:30-4:00 **B.Scott, National Laboratory for Environmental Testing**

An Analytical Perspective on the Development of Automated Early Warning Systems for Wastewater Treatment Plants

4:00-4:30   **R.J.Mitchell, Queen's University**
Centrifuge Modelling of Solute Transport in Partly Saturated Sand

Session 2: The Impact of Pollutants on Aquatic Ecosystems
North/South Seminar Rooms, Presider: T.B.A.

9:00-9:30   **P.V.Hodson, Environment Canada**
Physiological Responses of Fish in "Control" and BKME-Polluted Rivers

9:30-10:00   **K.T.Shum, Dept. of Fisheries and Oceans**
Enhanced Rates of Pollutant Processing due to Wave-Induced Advective Transport Below a Rippled Sediment Bed

10:00-10:30   **M.A.Salah, T.U.N.S.**
Numerical Modeling of the Processing of Acidic Precipitation by Urbanized and Semi-Urbanized Ecosystems

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

11:00-11:30   **M.B.McKinnon, Environment Canada**
Maximizing your Spreadsheet's Potential: The COMPUTOX™ Database

11:30-12:00   **D.V.Ellis, University of Victoria**
Distribution of Infaunal Benthos after 20 Years of Submarine Tailings Disposal to a Fjord

12:00-12:30   **J.W.Moore, Alberta Environmental Centre**
Biological Control of Aquatic Vegetation Using Grass Carp

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

1:30-2:00   **S.Thompson, University of Toronto**
Impacts of Reducing Loadings of 8 Persistent Toxics on Concentrations in Lake Ontario

Session 3: Groundwater and Soil Remediation
North/South Seminar Rooms, Presider: T.B.A.

2:00-2:30   **S.D.Conrod, Groundwater Tech Canada**
In Situ Remediation of Hydrocarbon Impacted Soil and Groundwater

2:30-3:00   **B.Danesh, Acres International Ltd.**
Welland River Contaminated Sediment Treatment Demonstration

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

3:30-4:00   **M.R.Sick, G.F.S.**

Directed Soil Air Circular Flow for the Remediation of CHC-Contaminated Sites

4:00-4:30 **H.B.Lee, Wastewater Technology Centre**
In Situ Extraction and Derivatization of PCP and Related Compounds from Soils

4:30-5:00 **H.Xu, Environment Canada**

Identification of Petroleum Contamination Sources by Fingerprinting of Petroporphyrins in Soil and Crude Oil Samples

Poster Presentations
CCIW - Main Mall Area

Oxidation as a Pretreatment to Bioremediation of Coal Tar Contaminated Soils
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Pesticide Concentrations and Use Patterns in Urban Streams and Stormwater Detention Ponds
J. Struger[1], D. Boyter[1], Z.J. Licsko[2], B.D. Johnson[3]
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[2] 16 Wilfred Laurier, Guelph, Ontario, Canada N1G 4L9
[3] Department of Environmental Biology
University of Guelph
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A Continuous Monitoring Technique for Agricultural Herbicides
J.D. Fischer[1], J. Struger[1], L.C. Merkley[2], D.G. Hayman[2] and I.B. Wilcox[2]
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Photolytic Decomposition of the Herbicide, Triclopyr, in Terrestrial Environment
B. Danesh
Acres International Limited
5259 Dorchester Road, Niagara Falls, Ontario, Canada L2E 6W1

Groundwater Toxicity Aspects due to Nitrogen Compounds Transport in Soil-Water Medium
M. Elektorowicz and R.N. Young
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The Biological Remediation of Hydrocarbon Contaminated Soils

B.A. Lorenz[1], L.J. Lawlor[1] and N. Kosaric[2]
[1] Imperial Oil Limited Research Centre, Sarnia, Ontario, Canada
[2] University of Western Ontario, London, Ontario, Canada

A Techno-Economic Study of Processes for heavy Metal Leaching from Sewage Sludge

T.R. Sreekrishnan, R.D.Tyagi and P.G.C. Campbell
Institut National de la Recherche Scientifique
INRS-Eau, Complexe Scientifique
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Remediation of Municipal Incinerator's Bottom Ash

J. Hadjinicolaou, R.N. Yong and E. Bahout
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High Strength Nitrogen Removal from an Anaerobically Treated Waste by the IACM Process

Z.X. Yang[1] and K.C. Lin[2]
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Twenty-Eighth Central Canadian Symposium on Water Pollution Research

Water Pollution Control Technology

EFFECTS OF HIGH SULFATE CONCENTRATION ON THE PERFORMANCE OF GRANULES IN UPFLOW ANAEROBIC SLUDGE BLANKET REACTORS

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Abstract

This study aimed at evaluating the long-term effects of high sodium sulfate concentration in a medium on the performance of Granulated Anaerobic Bacteria (referred to simply as granules) placed in that medium. The effects on the performance of granules were expressed by the changes, as functions of time, in the capabilities of these granules to consume organic compounds dissolved in the medium and to produce gas, mainly methane and carbon dioxide. The long-term effects of high sulfate concentration on the settling properties, size distribution, and volatile suspended solids (VSS) content of the granules were also investigated.

This study was carried out in a water-jacketed 7.7 litre Upflow Anaerobic Sludge Blanket (UASB) Batch Reactor with circulation. The circulation rate was kept constant throughout the study giving, therefore, a constant upflow velocity at 1.52 m/h. In order to minimize possible mechanical stress on the granules by the upflow currents, a special design was introduced for deflecting the circulating medium stream at the point of entry into the reactor. A constant reactor temperature at 35°C was maintained by pumping and circulating warm water through the reactor jacket using a forced circulation water bath.

The study required acclimatizing 1400 mL of Biopaq Lavalin granules to the operating conditions including upflow velocity, temperature, and feed composition. The 1400 mL granules (containing a total of 46 grams VSS) were placed in the reactor occupying, therefore, 18.2 percent of the 7.7 litre volume of the reactor. The rest of the reactor was filled with 4.56 g/L COD synthetic medium which was replenished every other day, over a period of three months, with fresh feed containing acetic, propionic, and butyric acids, K_2HPO_4, Na_2SO_4, NH_4HCO_3, $NaHCO_3$, yeast extract, $CaCl_2.2H_2O$ and trace elements including $FeCl_2.4H_2O$, H_3PO_3, $ZnCl_2$, $CnCl_2.2H_2O$, $MnCl_2.4H_2O$, $(NH_4)_6MO_7O_{24}.2H_2O$, $AlCl_3$, $CoCl_2.6H_2O$, and $NiCl_2.6H_2O$. The sodium sulfate concentration in the synthetic feed was 21.5 mg/L. The acclimatization period was followed by two months of high sulfate period whereby the medium was regularly replenished with feed having similar composition as that used in the

acclimization period <u>except</u> for the sodium sulfate which was <u>shock increased</u> from 21.5 mg/L to 6455 mg/L.

Gas measurement was made by closing the reactor tightly after each feeding and allowing the gas formed to get out of the reactor, through a tube, to a graduated container in which water was lodged by suction. The gas coming from the reactor was bound to push against and displace an amount of water equivalent to the gas volume itself. The consumption of organic compounds was evaluated by determining the Chemical Oxygen Demand (COD) of the remaining organic compounds using the potassium dichromate oxidation method and subtracting the obtained value from the total COD of a sample representing the medium at time zero after feeding.

In order to obtain representative samples of the granules <u>without</u> subjecting such delicate particles to potentially destructive stirring, a novel sampling kit for sampling granules was introduced and abundantly proven.

Because a batch reactor was used, therefore, continuous feed with constant concentration, steady values for COD conversion and gas production were not to be expected in this study. Instead, two terms were introduced: COD_{24}, which related to the COD converted in the first 24 hours since the medium was replenished with fresh feed at a specific loading rate of 0.62 gCOD/(gVSS)(BATCH), and GAS_{24}, which relates to the volume of gas produced in the first 24 hours since the medium was replenished with fresh feed at specific loading rate of 0.62 gCOD/(gVSS)(BATCH). These two terms could be generalized as COD_t and GAS_t where t is any time passed since the replenishment of the medium. Therefore, COD_{24} was 64.6 percent just before high sulfate concentrations were administered. After 5 days of high sulfate, COD_{24} dropped to 48.2 percent and kept dropping slowly until it reached 33.2 percent after two months. Resuming feed containing low sulfate concentration resulted in only slow recovery which brought COD_{24} value back up to just 44 percent after two weeks. <u>This indicated that the granules suffered some slowly reversible damage.</u> Gas production followed a similar trend as COD conversion. Therefore, GAS_{24} started at 5724 ml before having high sulfate concentration in the medium. However, GAS_{24} dropped to 5225 ml after ten days of high sulfate and continued to drop slowly until GAS_{24} reached 3635 ml after two months of high sulfate. Afterwards, resuming low sulfate concentration in the medium resulted in the value of GAS_{24} to reach 5277 ml after two weeks. As for hydrogen sulfide, data from this study indicated that increasing sulfate concentration from 21.5 to 6455 ml/l (more than 300 times) increased hydrogen sulfide production by only <u>four</u> times.

Investigation of settling properties indicated that high sulfate concentration caused the granules to become slightly smaller but heavier; a phenomenon which started to reverse itself when sulfate concentration was returned back to low levels. Values of VSS decreased slightly at high sulfate concentration and tended to slowly increase again when low sulfate conditions were resumed.

TOXICITY OF SULFITE AND CADMIUM IN ANAEROBIC DIGESTION

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Abstract

Toxicity of sulfite and cadmium ions to anaerobic granular sludge was investigated in eight laboratory-scale anaerobic upflow sludge blanket reactors (UASBR) with volume of 1.2 litres each. The toxicity was studied during acclimation and shock load conditions with synthetic feed at temperature of 35°C. The COD loading rate was 14.3 gCOD/day/l for all reactors during the study period. Under process acclimation study, one reactor (R1) was used as control, 4 reactors (R2-R5) were used for the sulfite toxicity study. The toxicity of cadmium was studied in 3 reactors (R6-R8). Under shock load conditions, 4 reactors were used to the study of sulfite and cadmium toxicity, and two reactors were used for sulfite and cadmium respectively.

The toxicity of sulfite was studied using sulfite concentrations from 5 to 1000 mg S/l as added in the form of sodium sulfite to the feed. The bacteria in the reactors acclimated to new environment after they were fed with the feed containing sulfite. No inhibition of COD digestion rate was observed in the reactor with sulfite concentration up to 1000 mg S/l during process acclimation. Slight decrease in COD digestion rate in the reactors with sulfite was due to the high sulfide concentration in the effluent. This sulfide contributed additional chemical oxygen demand to the effluent and caused a decrease in COD digestion rate when compared with a controlled reactor. Under shock loading, the COD digestion rate was severely temporally inhibited in the reactors with sulfite concentration of 500 to 1000 mg S/l. However, the COD digestion rate was recovered in 5 days and 2 weeks respectively. No long term toxic effects were observed. Photographs from scanning electron microscopy indicate that Methanothrix-like rod shaped bacteria dominated. The bacterial composition did not shift to sulfur reducing bacteria.

The COD digestion rate in the reactors was inhibited at cadmium dosage of 2.4 g/load under both acclimation and shock load conditions although the studied dosages varied from 4 mg to 2.4 g/load. Under both conditions, the COD digestion rate in the reactor with cadmium dosage of 1.6 g/load was not disrupted during the study period and was higher than 95%. However, the toxic effect was shown immediately after the addition of cadmium when

its dosage was 2.4 g/load. Acclimation did not seem to improve the bacteria's ability to overcome the toxicity from cadmium. The experimental data indicate that there exists a certain critical value of cadmium loading rate which affects COD digestion rate in the reactor. Above this critical value, the reactor system was unable to withstand the cadmium toxicity and the toxicity to anaerobic bacteria increased rapidly. When the dosage of cadmium was lower than the critical value, cadmium was not toxic to the bacteria. The concentration of free cadmium was very low in the reactors under normal conditions, but increased rapidly when the COD digestion in the reactor failed. The bacteria could not be reactivated after they were poisoned by cadmium. The anaerobic granular sludge developed in UASBR showed a high tolerance to cadmium when compared to the results from other researchers.

Sulfite in the feed was converted into sulfide or sulfur in the reactors. No sulfite was detected in the effluent, while a sulfate concentration of 77 mg S/l was measured in the effluent. Sulfite seems to be a more energetically favourable oxidant than sulfate. When the sulfite concentration was 1000 mg S/l in the feed, the sulfide concentration resulting from sulfite reduction was 310 mg S/l, and did not inhibit the anaerobic digestion process.

The addition of sulfite in feed favoured the bacterial growth rate. Sulfur reduction processes produced more biomass than methane fermentation. The settling properties of granules were evaluated by fractioning the granules under certain upflow velocities. The density of granules is affected by the percentage of inorganic precipitates inside the granules. When reactors were operated at low specific COD loading rate, the bacterial growth rate was low, and more inorganic precipitates were formed inside the granules which consequently settled faster.

FRACTAL DIMENSIONS AND SHAPE FACTORS OF DIGESTED SLUDGE PARTICLE AGGREGATES

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Abstract

A multi-exposure photographic method and image analysis system were used to measure the terminal settling velocities and some geometric characteristics of digested sludge particle aggregates larger than 35 μm (>90%) of the sludge mass. It was found that the studied aggregates showed specific characteristics due to their origin and to the digestion process. Low shape factors of the aggregates reflected their highly irregular forms, especially for a range of characteristic length 300 to 400 μm. The morphological properties of digested sludge particle aggregates allowed to characterize them at least to a substantial extent, as statistically self-similar fractals.

The terminal settling velocities of digested sludge particle aggregates in the free settling regime ($0.01 < Re < 4.0$) may followed an equation incorporating the aggregate's fractual geometry. The observed settling velocities were from 0.14 to 2.47 mm.s^{-1} within the limits of the particle aggregates characteristic length from 35 to 1,660 μm.

The size-density fractal dimension D for these aggregates was estimated to be 1.9. This value is relatively high as compared with other particle aggregates, and that suggests that the digested sludge aggregates were more compact and contained more higher inorganic parts than non-stabilized microbial aggregates. The magnitude of the fractal dimension could be a useful reference for identifying the mechanism of aggregate formation. Most sludge particle aggregates may be generated by differential sedimentation whereas larger aggregates (over 1200 - 1400 μm) can be formed by shear coagulation. The larger fractal aggregates may permit advective flow during settling. This phenomenon will ensure increasing chances of collision between fractal aggregates.

ORGANIC CARBON SOURCES FOR SULPHATE REDUCING BACTERIA IN THE TREATMENT OF HIGH SULPHATE WASTE STREAMS

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Abstract

A series of tests was designed to attempt to evaluate the easily available and readily degradable (EARD) organic matter in different organic materials. Ethanol, animal feed (rabbit pellets), and various municipal wastes (leaf compost, raw sewage, activated sludge and digested sludge) were investigated.

A laboratory scale study was then conducted to investigate the correlation between the theoretical amount of sulphate to be removed (calculated from the EARD organic matter (e.g., 250 mg/L of EARD organic matter is required to reduce 1000 mg/L of sulphate)), and the amount of sulphate actually reduced by the Sulphate Reducing Bacteria (SRB).

Ethanol was found to be the most suitable substrate for the SRB about 2.13 mL of ethanol per litre of mixed liquor was needed to reduce the sulphate concentration from about 6600 mg/L to 5500 mg/L. Of the municipal wastes investigated, thickened activated sludge was found to be the most suitable organic material. About 58.5 g of activated sludge per litre of mixed liquor was utilized to reduce about 550 mg/L of sulphate. Rabbit pellets, digested sludge, raw sewage and leaf compost were less suitable as substrate sources. Of the EARD organic matter extracted from the different organic materials, only a fraction was utilized by the SRB. This utilizable fraction was found to decrease with the complexity of the organic material.

BIODEGRADATION OF PETROLEUM REFINERY WASTEWATER: A BIOREACTOR COMPARISON

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Abstract

Biological treatment of petroleum refinery wastewater was studied in four different type of bioreactors: activated sludge process, RBC coupled to a polyurethane foam (RBC-PUF), cage type RBC (RBC-cage) and airlift. The PUF was attached on both sides of biodisks. In the case of cage reactor, cube shape of polyurethane foam pieces ($1 \times 1 \times 1$ cm^3) were filled (1080 pieces) in each cage. RBC-PUF and cage reactors were operated at 25 litres working volume and airlift was operated at 66 litres whereas activated sludge unit had a working volume of 10 litres. The air flow rate in the airlift reactor was kept at 4 cfm or 0.113 m^3/min. (1.716 volume of air per unit volume of reactor per min.). The wastewater employed was collected from the effluent of an API separator and dissolved air flotation (DAF) process of a petroleum refinery. The wastewater composition varied widely, due to different operating conditions, shut-off of an API separator as well as refinery shut downs. The wastewater was collected once a week and stored in a cold room at 4°C to retard the biological activity. Domestic wastewater water in equal volume to refinery wastewater was used to start the experiments. Throughout the experimental study the reactors temperature varied between 27 and 30°C. All chemical analyses were performed according to "Standard Methods".

The biodegradation studies were carried out at varying hydraulic (0.79 m^3/m^3/d to 3.16 m^3/m^3/d or from 1.5 m^3/m^2/d to 6 m^3/m^2/d) and organic loading (0.6 to 3.0 kg COD/m^3/d or from 10 to 100 g COD/m^2/d). COD removal efficiency of up to 87% was achieved. The results obtained in terms of biodegradation of COD, NH$_3$-N, phenol, hydrocarbons and suspended solids in the four different reactor systems were compared. The RBC-PUF reactor gave almost similar results with that the RBC-Cage reactor. Airlift bioreactor was found to give a better performance in terms of COF biodegradation. However, an excessive air requirements in airlift reactor may be less attractive due to economic reasons. Therefore, optimization of air requirement is necessary. Nitrogen and phenols removal above 90% were

achieved in all the reactors. The RBC-PUF reactor and RBC-Cage reactor were found to have a better performance than a conventional RBC for the biodegradation of COD, phenol, hydrocarbons and suspended solids. This was attributed to a higher biomass concentration (70 gVS/m^2) achieved in these reactors than in a simple RBC.

A variation of phenol influent concentration in the range of 10 mg/L to 100 mg/L did not affect the reactor effluent phenol concentration. Similarly, influent COD (100 to 900 mg/L) and hydrocarbons (40 to 120 mg/L) did not affect the effluent quality. Therefore, these reactors (RBC-PUF and RBC-Cage) were found to have a very good shock absorbing characteristic. The results obtained in the four reactor systems shall be presented and discussed with respect to the biodegradation of COD, phenol, hydrocarbons, nitrogen and suspended solids in refinery wastewater.

OPTIMIZATION OF THE REACTION CONDITIONS FOR ENZYMATIC REMOVAL OF PHENOL FROM WASTEWATER IN THE PRESENCE OF POLYETHYLENE GLYCOL

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Abstract

Phenols and phenolic compounds are found in effluents of industrial operations such as coal conversion, pulp and paper manufacturing, wood preservation, metal casting, etc. Many of these phenolic compounds are considered to be hazardous pollutants. Therefore, development of proper technology for the removal of phenolic compounds from wastewater is becoming important.

Klibanov and co-workers first proposed a horseradish peroxidase (HRP) method to remove phenols from wastewater. In this method, HRP catalyzed the oxidation of phenols with hydrogen peroxide, generating phenoxy radicals. These radicals then react to form insoluble polymers which can be easily removed from wastewater. Nakamoto and Machida studied the addition of additives, such as gelatin and polyethylene glycol (PEG), to suppress the inactivation of HRP. In this way, the amount of peroxidase required was reduced to 1/200 of that required without these additives. However, they investigated the phenol concentrations between 10 and 30 g/L, whereas in practice the range between 0.1 and 1 g/L is more frequently encountered. No information is available on the effect of the additives over this range.

The purpose of this paper is to investigate the effect of the additive, polyethylene glycol (PEG), on the horseradish peroxidase (HRP) catalyzed dephenolization over the phenol concentration range of 1 to 10 mM (0.1 to 1.0 g/L). This information is very important in enzyme reactor design. The optimum pH, HRP concentration, PEG concentration and the molar ratio of hydrogen peroxide and phenol have been investigated in the presence of PEG at room temperature in order to achieve the maximum phenol removal efficiency with the minimum cost. The effect of concentrations of HRP and PEG on reaction time was also investigated. Experimental results show that the addition of PEG has significant protective effect on the activity of HRP. The amount of peroxidase required is reduced to 1/40 and 1/75 of that required without PEG for 1 and 10 mM phenol solutions, respectively. The higher the

phenol concentration, the more effective was the addition of PEG. In the presence of PEG, the optimum pH is 8.0 and the optimum molar ratio of hydrogen peroxide and phenol is around 1.0. The minimum doses of HRP and PEG required for at least 95% removal were determined for several phenol concentrations and two empirical models are proposed to predict the minimum HRP and PEG doses [$(HRP)_{min}$ and $(PEG)_{min}$] required for 95% removal over the entire phenol concentration range of 1 t0 10 mM:

$$(HRP)_{min} = 0.0435 + 0.0048\ C_{ph} + 0.0031_{ph}C^2 \tag{1}$$

$$(PEG)_{min} = 0.0065 + 0.0241\ C_{ph} \tag{2}$$

where C_{ph} is the phenol concentration. The validity of the two models has been proved by testing them with experimental data. Under the reaction conditions optimized as described above, the reaction times for at least 95% removal from 1 mM and 10 mM phenol solutions were 5 hours and 3 hours, respectively. An increase in HRP concentration significantly reduced the reaction time; however, an increase in PEG concentration showed negligible influence.
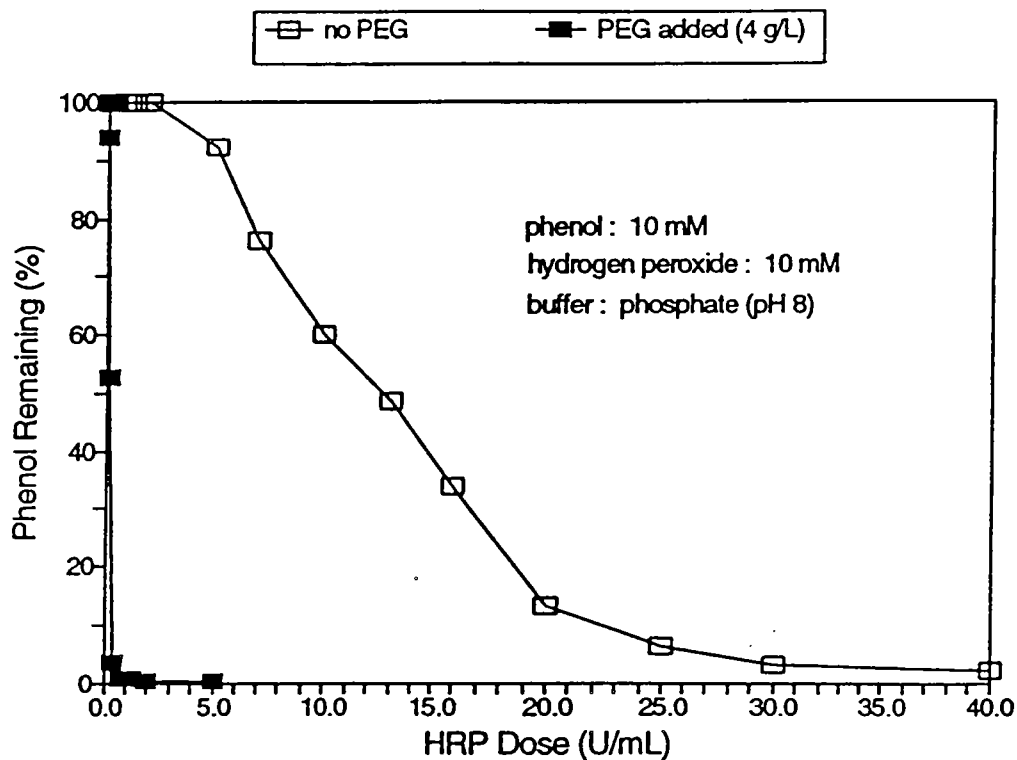
Comparison of Turnovers in the Cases with and without PEG

Phenol Conc. (mM)	Phenol Removal (%)	HRP Dose (U/mL)	Additive	Turnover
1	98.5	2.0	no	8,490
1	96.4	0.05	PEG	332,500
10	97.0	30.0	no	5,750
10	96.5	0.4	PEG	415,000

Turnover = moles of phenols removed/moles of HRP added.
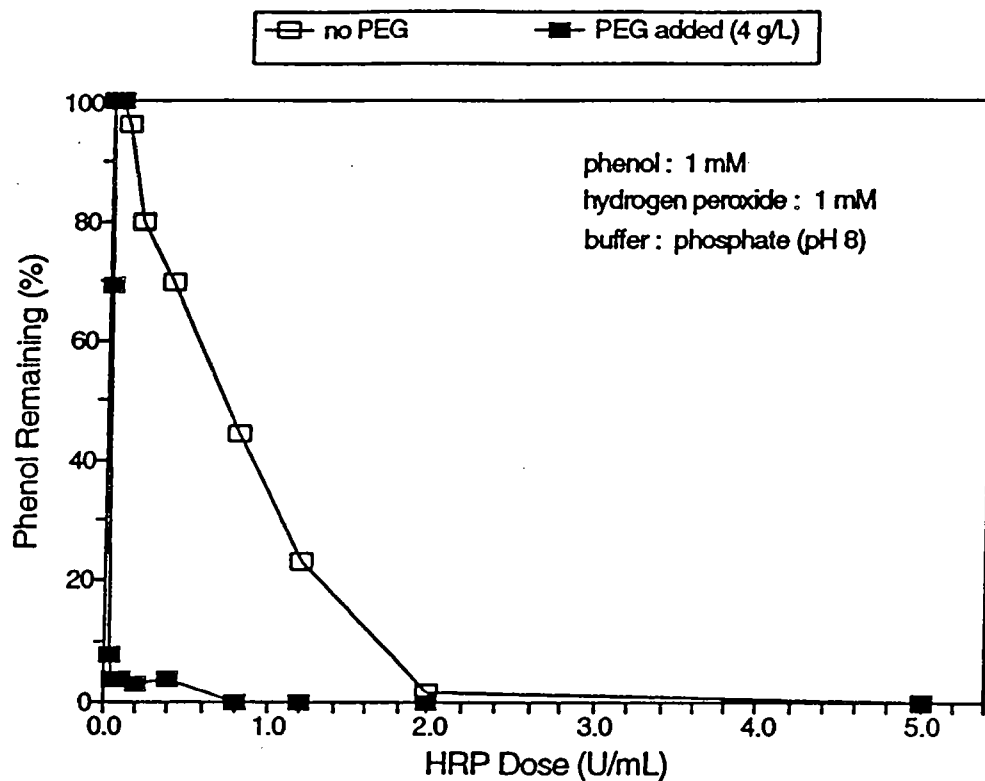
**Effect of Adding PEG on Phenol Removal Efficiency
in 1 mM Phenol Solution**

**Effect of Adding PEG on Phenol Removal Efficiency
in 10 mM Phenol Solution**

ECOWAT - A NEW TECHNOLOGY FOR TREATMENT OF WASTEWATER WITH A HIGH NITROGEN LEVEL

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Abstract

In conventional wastewater treatment suspended solids and BOD are sufficiently removed as result of gravitational settling and the action of aerated activated sludge biomass. Removal of phosphorus and nitrogen normally is very poor. Nutrient removal from wastewater becomes more important due to the need to prevent eutrophication of surface waters into which wastewater treatment installations discharge their effluent. Therefore at present conventional wastewater treatment systems are hardly sufficient for treatment of municipal wastewater, let alone stronger wastewaters. The Ecowat process has been developed by the Wageningen Agricultural University and the environmental technology company Ecotechniek as a system capable of treating very strong wastewaters which are characterized by a high level of COD as well as a high level of nitrogen, such as liquid manure, landfill leachate, airfield/aeroplanes de-icing fluids, slaughterhouse wastewaters, etcetera. The Ecowat process consists of separate biological reactors for nitrification and denitrification and a physical/chemical process for removal of phosphorus and humic substances.

Research To Be Presented. During 16 months a testing factory with a biological reactor wet volume of approximately 70 m^3 was operated continuously. The nitrification reactor was operated in a feed-batch mode. The denitrification step consisted of a group of parallel operated fixed sludge up-flow anoxic reactors. The physical/chemical step for phosphorus and humic substances removal consisted of a pipe flocculator and a decanter centrifuge. The influent of the testing factory was the liquid fraction of anaerobically digested pig manure. This influent was characterized by a COD concentration of 21000 mg/l and a Kjeldahl-nitrogen concentration of 6500 mg/l, 5500 mg/l of which was present as ammonium-nitrogen. The phosphorus content was 200 mg/l.

Results. The COD removal efficiency exceeded 97.7% and the nitrogen removal efficiency exceeded 99.8 and 99.9% for Kjeldahl-nitrogen and ammonium-nitrogen respectively. The phosphorus removal exceeded 99.5%.

The effluent contained less than 500 mg/l COD, less than 20 mg/l BOD, less than 15 mg/l Kjeldahl-nitrogen (3 of which being ammonium-nitrogen) and less than 1 mg/l phosphorus. The sludge quality will also be presented. The heavy metal content of the sludge, which was produced as a pasteous slurry of 14% total solids, was well within the standards set for agricultural use.

The nitrification capacity of the biomass present in the Ecowat process was much higher than in activated sludge from conventional wastewater treatment systems. The Ecowat process worked at a nitrification rate of 1 kgN (m^3.d) which is 5 to 10 times faster than in conventional wastewater treatment systems loaded with liquid veal manure and more than 20 times faster than in sewage treatment installations.

SIMULATION OF LONG TERM PERFORMANCE USING THE IAWPRC MODEL

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Abstract

A validated mathematical model is a powerful tool. Models of activated sludge plants can be used to predict effluent nitrogenous and carbonaceous species or alternately it can be used to determine the reactor solids required to achieve specified effluent limits. With such capabilities it can be used for the design of new plants or the expansion and optimization of existing facilities. The IAWPRC model has been shown to be reliable in predicting plant performance under both steady-state and dynamic conditions. The IAWPRC has forty input parameters classified into three broad categories: influent characteristics, kinetics and stoichiometry. Protocols for determining the coefficients involve mathematical estimation techniques or running lab scale biological reactors under a number of different conditions. The applicability of the model is dependent on the variability of its constants. If a large proportion of the constants change are dependent on the wastewater and plant configuration, then the model will be of limited use as a design tool and as a source of information for decision making.

Data from three Canadian sewage treatment plants suggest the characteristics of the influent COD (soluble or particulate) are a function of the wastewater strength. Data sets for influent raw wastewater (Dundas STP and the Burlington Skyway STP) were examined. The soluble COD in the raw wastewater remains relatively constant with a mean of 78 mgCOD/l. The particulate COD varies linearly as the influent COD strength. The pooled data for primary effluent wastewater (Dundas STP and Hamilton Woodward STP) confirmed the dependency of fractions on wastewater strength. The physical characteristics of Canadian wastewater changing as a function of wastewater strength make it seem improbable that the COD fractions used in the IAWPRC model would remain constant with changing wastewater strength; however, the filterability of the influent wastewater changing in a predictable and consistent fashion indicates wastewaters similar in physical and perhaps biological nature.

A comprehensive pilot plant study on nitrification was undertaken at the Wastewater Technology Centre in Burlington, Ontario. Biosim (©Envirosim Associates) a variant of the

IAWPRC model (Lishman and Murphy, 1992) was calibrated using data originating from this study. The calibrated model was validated using data from a bench scale treatability study undertaken by Matthews and Melcer (1991) at Hamilton Woodward Sewage Treatment Plant. This pseudo steady state experimental program was approximately a year in duration. In its first phase, the SRT of the plant was operated at 8 days while the HRT was varied between 2-6 hours. In phase two, the system was stressed by operating at SRT setpoints of 4 and 6 days while the HRT setpoints were varied from 2 to 4 hours. During phase 2 the reactor temperature was maintained close to full-scale aeration tank temperatures which range between 9 and 25°C. To accommodate the transitionary periods after changes in either temperature, SRT, or HRT, a FORTRAN version of the IAWPRC, was written to allow wastage, flow, temperature and influent loadings to be input on a daily basis. Statistical methods were used to approximate the data on days where analytical values were not available. Simulation of 444 days of data gave good agreement between the experimental and simulated values. Typical agreement for MLVSS, effluent $NH_3N.NO3-N$ is illustrated in Figures 1 and 2. Comparisons between predicted and measured effluent CODs are not meaningful as essential all biodegradable soluble COD is removed. It is not possible to compare oxygen utilization rates (OURs) as the influent utilized in the simulation is a 24 h composite. There is good agreement between the actual and simulated values for both MLVSS and nitrogenous species. This suggests that the model can adequately simulate plant performance without a large number of model coefficients being changed for each wastewater treatment plant. If this is verified by future studies then a powerful tool is available that can be used for the design of new wastewater treatment plants or the optimization of existing facilities.
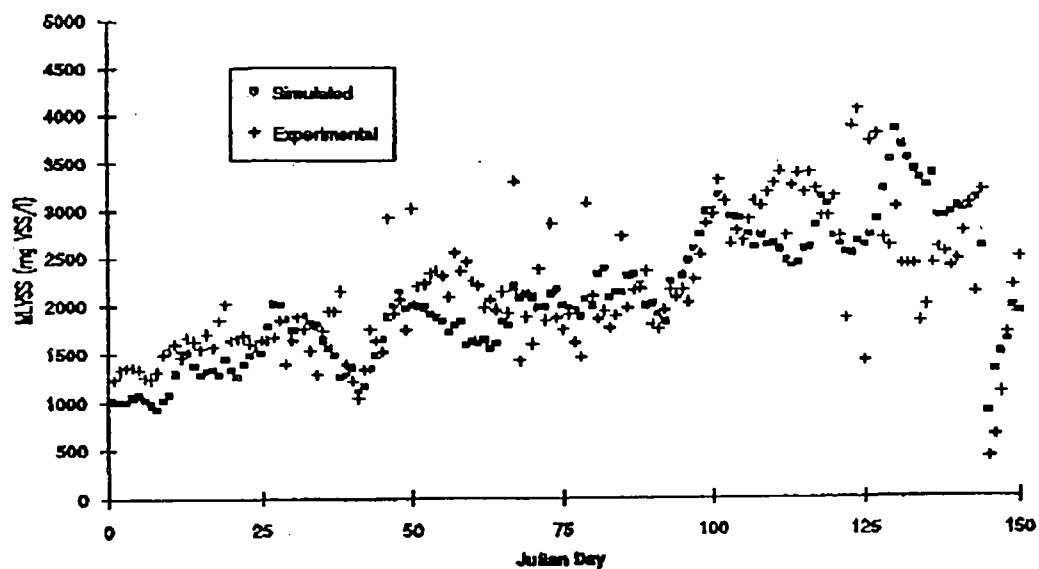
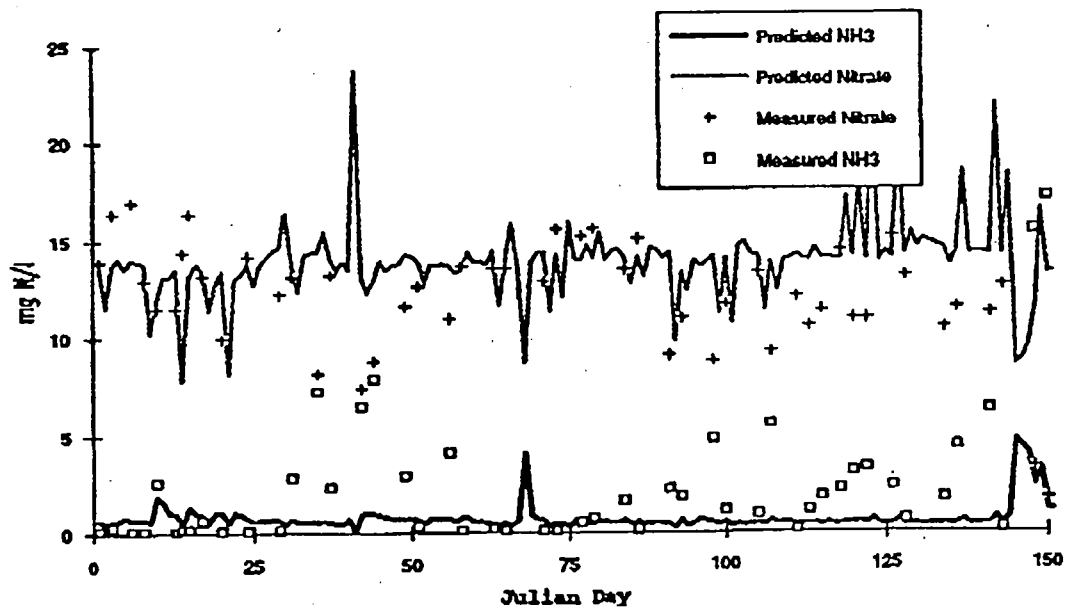Figure 1- Comparison between Actual and Simulated MLVSS

Figure 2- Comparisons between Actual and Simulated Nitrate and Ammonia Values

PILOT STUDIES OF VOC EMISSIONS FROM DROP STRUCTURES IN WASTEWATER COLLECTION SYSTEMS

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Abstract

A wide range of volatile organic compounds (VOCs) have been observed in municipal and industrial wastewaters. If released to the atmosphere, some VOCs are considered to be toxic air contaminants, and many are highly reactive and contribute to the formation of photochemical oxidants. For these reasons, municipal and industrial wastewater collection and treatment facilities have come under increasing regulatory scrutiny as sources of VOC emissions. Fugitive emissions of VOCs can occur during wastewater collection, with gas-liquid mass transfer occurring at areas of high turbulent mixing, e.g., sewer drop structures. However, little is known regarding VOC stripping efficiencies at sewer drop structures, and the sensitivity of emissions to system variables such as drop height, tailwater depth, liquid flowrate, headspace ventilation rate, and compound properties such as Henry's law constant. This paper describes a series of 10 pilot experiments to determine stripping efficiencies and system mass transfer coefficients (K_s) for drop structures consistent with small municipal sewers and on-site industrial sewers.

An enclosed pilot-scale drop structure was constructed at the Wastewater Technology Centre, where experiments may be carried out using either tap water or raw wastewater. If so desired, tap water may be heated to a specified temperature and stored for use during an experiment. The structure itself is cylindrical, with a height of 2 m and diameter of 1.5 m. Several flanged inlet ports allow for variation of drop height and of influent pipe diameter. Tailwater depth is controlled by an external standpipe at the system's liquid outlet. Headspace ventilation is achieved with compressed air which exits the structure through a vertical exhaust stack.

Four volatile tracers (1,1,1-trichloroethane, toluene, deuterated chloroform, ethylene dibromide) were continuously injected into the pilot system through a stainless steel injection port on the influent pipe, and into water flowing upstream of the drop. Steady-state liquid samples were collected immediately upstream of the drop, and in a discharge pipe flowing

out of the drop wet well. Steady-state gas samples were collected on multi-stages adsorbent tubes from the exhaust vent.

Results indicate a high positive correlation between system mass transfer coefficients and Henry's law constant. This was observed at both low and high headspace ventilation rates (high and low gaseous accumulation in headspace) suggesting that air entrainment and subsequent stripping by diffused air bubbles in tailwater accounts for a large fraction of emissions from drop structures. Furthermore, lower volatility compounds (ethylene dibromide and chloroform) were the most sensitive to changes in headspace ventilation rate, indicating the importance of gas-phase mass transfer resistance in enclosed headspace systems. Over all experiments, stripping efficiencies ranged from as low as 0.10% (ethylene dibromide) to as high as 18% (1,1,1-trichloroethane), with K_a varying from 0.005 m/hr (ethylene dibromide) to 0.95 m/hr (1,1,1-trichloroethane).

Additional analysis of system mass transfer coefficients has indicated a positive correlation between VOC stripping and the rate of potential energy dissipation of water as it plunges over the drop, subsequently increasing turbulent mixing of the tailwater. There is abundant data in related literature describing this phenomenon at wastewater treatment processes which use mechanical surface aerators. Comparisons are drawn between drop structures and surface aerators to aid in the quantification of emissions from the former.

To date, results suggest that sewer drop structures are a major mechanism for VOC emissions from small sewers. Mass transfer due to entrained air bubbles appears to be a dominant mechanism for such transfer, and headspace ventilation conditions can have a significant impact on the degree of gas-liquid mass transfer at such structures. Experiments are continuing to supplement existing data for a wider range of VOCs and semi-VOCs, as well as system operating conditions.

AN ANALYTICAL PERSPECTIVE ON THE DEVELOPMENT
OF AUTOMATED EARLY WARNING SYSTEMS
FOR WASTEWATER TREATMENT PLANTS

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Abstract

Wastewater treatment plants are faced with the problem of treating water than may contain a continuously changing array of organic and inorganic compounds. These compounds may be present as a result of naturally occurring processes or from the industrial, agricultural or recreational activities of humans. Advanced information on the quality of water approaching a treatment plant would provide operators with both time and opportunity to take necessary actions to adequately treat water. The level of corrective action taken by treatment personnel will be a function of the information available about the condition and quality of water approaching a treatment plant. In general, the more specific and timely the information, the more exact the corrective action which can be taken.

Specific analytical instrumentation combined with appropriate chemical methods are one way to provide early warning information to water treatment personnel on the quality of water approaching a treatment plant. Purge and trap devices interfaced with gas chromatographs offer one system of on-line sampling and analysis of water. Analytical data from these instruments in the form of chromatograms provide an historical record of water quality and can be used to indicate the need to issue warnings or advisories to water treatment personnel. However, the interpretation of analytical data from these systems has generally depended on an analyst's ability to observe and interpret subtle differences in the chromatographic patterns. This has limited the ability of automated systems to provide useful environmental information.

For these reasons, automated systems must be developed in conjunction with laboratory-based analyses. Laboratory studies allow quality control aspects of automation and data interpretation to be developed. This includes varying the environmental and chemical conditions that these automated systems will encounter to insure analytical ruggedization and reliability. Further, software capable of making "intelligent" decisions as to the importance of specific chromatographic patterns can be designed.

This paper describes work currently being undertaken at the National Laboratory for Environmental Testing which can be directly applied to the development of automated systems to supply early warning capabilities to treatment personnel. This work involved the development of chromatographic peak recognition software as well as quality assurance protocols. Within this context, the use of expert systems to act as advisors for these systems will be discussed.

CENTRIFUGE MODELLING OF SOLUTE TRANSPORT IN PARTLY SATURATED SANDS

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Abstract

Computer solutions to the problem of dissolved contaminant movements in partially saturated soils suffer from extreme nonlinearity of some variables and difficulties in determining values for other variables. Physical modelling in a geotechnical centrifuge is an independent viable alternative to numerical modelling but is promoted as a method of producing reliable data sets for validation of numerical predictions. Scaling laws for physical modelling are presented and dimensional analysis is used to identify applications of model test results to prototype situations.

Centrifuge modelling of the lateral spread of a conservative solute in a partly saturated fine sand has been accomplished at gravitational accelerations of 25 g and 50 g. The distributions of the contaminant after two months, six months and one year of prototype times was found experimentally by dissection of the models. The results support the contention that centrifuge modelling does correctly recreate prototype transport phenomenon, including transport due to matrix suction, in partly saturated fine sand. For the conditions modelled, it was found that all of the contaminant introduced at the soil surface became immobilized, for at least one year, in the upper two to three meters of the six meter deep soil profile.

Twenty-Eighth Central Canadian Symposium on Water Pollution Research

The Impact of Pollutants on Aquatic Ecosystems

PHYSIOLOGICAL RESPONSES OF FISH IN "CONTROL" AND BKME-POLLUTED RIVERS

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Abstract

Compared to control white sucker (*Catostomus commersoni*), suckers downstream of a bleached kraft pulp mill at LaTuque, Que., on the St. Maurice R., showed MFO induction, elevated levels of hematocrit, hemoglobin, serum glucose, serum protein, tissue lipid, and growth, and significant reductions in serum sex hormones during sexual maturation. Since MFO induction suggests exposure to xenobiotics, these responses may be indicative of toxicity and effects on the population. If so, physiological responses could be useful and inexpensive markers of important ecological effects. To verify whether these effects were consistent and due to effluent exposure or simply due to ecological gradients, we repeated this study during three seasons and in a second "control" river, i.e. a river having simlar ecological characteristics, but no pulp mill effluent. We found that the MFO response and increased glycogen liver and muscle storage showed consistent pulp mill related responses, regardless of season, and that the patterns of response between the two rivers were consistent with effluent exposure and not ecological gradients. Absolute levels of response were modulated by season, due either to the effects of temperature and feeding or to interactions with sexual maturation. In contrast, the response patterns of hematological parameters such a hematocrit and blood glucose, and condition indices such as liver somatic index or condition factor were either inconsistent among seasons, or showed a similar pattern of response in both rivers. For these parameters, the effects of pulp mill exposure chould not be separated from the effects of ecological gradients. Therefore, measures of fish energetics and detoxification enzymes appear to be more reliable indicators of exposure to pulp mill effluents, and perhaps to other toxic effects on fish populations.

ENHANCED RATES OF POLLUTANT PROCESSING DUE TO WAVE-INDUCED ADVECTIVE TRANSPORT BELOW A RIPPLED SEDIMENT BED

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Abstract

A quantitative understanding of the transport processes inside a sediment bed in the coastal or estuarine environment is necessary in estimating the rates of dispersion and degradation of pollutants. In most transport models to date the advection of pore water has been ignored. It has recently been shown (*Shum* [1992], *JGR 97*: 798) that, below a ripplied sediment bed in water of small to medium depth, gravity waves induce a time-averaged net circulation pattern which can be of a significant magnitude. The exchange of pore water with the overlying water can also be considerably higher than that in the corresponding case of a flat sediment bed.

In this study we shall examine how such advective transport of pore water affects the breakdown of marine-discharged pollutants settled onto a rippled sediment bed. The breakdown of pollutants can be due to bacterial or microbial actions and the ripples are assumed spatially periodic. The two-dimensional transport equation based on a continuum model, with a velocity field deduced in *Shum* [1992] and a consumption (processing) term governed by first-order kinetics, is solved numerically. The boundary concentration at the sediment-water interface is assumed constant whereas the flux of solute at the bottom of the sediment layer is assumed zero.

When advective transport is of a magnitude comparable to or greater than diffusive transport, significant variations along the ripple profile are found and the concentration below ripple troughs can be appreciably higher than that below the crests. The concentration gradient in the horizontal becomes of the same order of magnitude as that in the vertical. Further, when advective transport dominates over both diffusive transport and consumption, a region of uniform concentration is found immediately below the sediment surface away from the ripple crests. The thickness of this layer increases with the magnitude of advective transport relative to diffusive transport and rate of consumption, and is limited by the vertical extent of the circulation pattern of pore water.

The rate of processing over the sediment layer is compared with the corresponding case in the absence of advective transport. This ratio increases monotonously with the ripple slope and the ratio of the magnitudes of advective and diffusive transport, but attains a maximum as the rate constant of the first-order kinetics increases. Despite the much higher pore water flow below a rippled bed, this ratio is less than six for ripple slopes of 0.05 and 0.10.

These results suggest that one-dimensional diffusion models commonly assumed in transport/reaction models in a marine sediment bed may not be appropriate under field conditions applicable to our present model.

NUMERICAL MODELING OF THE PROCESSING OF ACIDIC PRECIPITATION BY URBANIZED AND SEMI-URBANIZED ECOSYSTEMS

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Abstract

A numerical model was developed to simulate the acid neutralization processes and the ion fluxes to urbanized and urbanizing ecosystems. The model was based on empirical relations that simulate the involved processes in the considered system. The simulated processes were accumulation and dissolution of dry deposition, diffusion or release of constituents in the liquid phase, chemical uptake and absorption, and washoff and leaching of chemical constituents.

The ecosystem was represented by a series of homogenous compartments (or stages). Each compartment was depicted and conceptualized as a continuous stirred tank reactor (CSTR). In the CSTR, empirical formulations were used to represent the simultaneous reactions occurring at that particular stage. These formulations provide a quantitative linkage between bulk deposition and the processing of incident precipitation by the contacted surface.

The model predicts changes in bulk precipitation chemistry in an urban environment, given the changes in the deposited chemical constituents. The simulated constituents included the major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, and NH_4^+) and anions (So_4^{2-}, NO_3^-, and Cl^-). The urban surfaces that can be simulated were confined to tree canopies and roof surfaces. The model simulates the major ion producing and consuming reactions occurring when rainfall strikes those urban surfaces. It can also answer some management questions pertaining to the predictability of the changes to urban stormwater ion fluxes. The model is also capable of demonstrating how large amounts of bulk deposition data can be handled systematically to anticipate water quality changes when it flows over those urban surfaces.

At the development and calibration stage, the model was used to simulate the processing of incident precipitation by the considered ecosystem surfaces. When validated (by more extensive use of the model), the model may also be used to evaluate the consequences of bulk deposition loading and to perform a reliable predictive analysis with respect to system properties.

Input data for the model were collected from field studies conducted in downtown Halifax and at the Halifax Urban Watersheds (HUW) for one year from May 1988 to June 1989. Bulk and wet precipitation, throughfall, stemflow, and roof runoff samples were collected from an urban treed site, a roof of a building and a Halifax Urban Watersheds hardwood site.

The model was calibrated and verified using two different sets of data for urban throughfall and roof runoff. Then, the model was applied to simulate and predict HUW observed data. Good calibration and verification results were achieved for both sites. The model performance in predicting HUW throughfall was also satisfactory.

The analysis of results indicated that the acidity of bulk precipitation was neutralized by the tree canopies and the roof surface. The roof surface showed higher acid neutralizing capacity than urban tree canopies. Hardwood trees in both sites showed similar impacts on bulk precipitation. Seasonal variations were observed in both treed sites as well as the roof site.

MAXIMIZING YOUR SPREADSHEET'S POTENTIAL: THE COMPUTOX™ DATABASE; CONTENTS, APPLICATIONS AND RESULTS

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Abstract

With the recent evolution of "386", "486" and the upcoming "586" (P5) microprocessors, microcomputing power has unleashed a new wave of computer software development previously not available. Such advancements are particularly noticed in the development of computer spreadsheets. Microsoft® Windows™ has virtually removed memory barriers which in the past have prevented spreadsheets to store and manipulate large amounts of data. This new generation of Window's specific spreadsheets can store more data, perform more functions and operate much faster.

We use the spreadsheet Quattro® Pro for Windows to store, track and manipulate large amounts of data in the form of COMPUTOX™, a toxicity database containing a list of approximately 1500 organic chemicals for which one or several aquatic and terrestrial toxicity endpoints for a selected number of species has been measured. This presentation provides for easy sharing with other Window's applications such as statistical packages, graphical software, expert system programs, and yes, database applications such as Dbase® IV and Paradox®.

The COMPUTOX™ database contains published and unpublished data in a common format [-log(BE)], where BE is the concentration needed to reach the toxicological enddpoint, such as LC50, EC50, LD50, and so forth. At present, the majority of data are acute toxicity values for aquatic species, i.e. 30-min Microtox, 48-hr *Daphnia magna*, and 96-hr fathead minnow LC50 concentrations with a few exceptions, such as 32-day fathead minnow LC50 values. For the terrestrial species, 96-hr LD50 values for oral, intravenous, and intraperitoneal exposure routes for rat and mouse are given. At present, 35 toxicity endpoints are covered for 30 species.

In the database, chemicals are identified by name, CAS registry number, RTECS number, chemical formula and molecular weight. In addition to the biological data described above, physico-chemical data, including the octanol/water partition coefficient, the Henry coefficient, aqueous solubility, and at present 27 topology indicators are provided. Any part

or the entire spreadsheet can be sorted by values or entries, in either ascending or descending order, in any combination or physico-chemical, toxicological or topological parameters. The user has the opportunity to add new, replace or delete individual data, entire lines or columns and to perform other typical spreadsheet functions, including printing, plotting and computing regressions. The database is available in QuattroPro™ (Borland International), Lotus 1-2-3™ (Lotus Development Corporation), or Excel™ (Microsoft Corporation) spreadsheet formats and can also be imported into databases and various statistical packages such as SPSS (SPSS Inc.) and Statgraphics (Statistical Graphics Corp.).

The database is being used to generate plots and regressions of the toxicological data in several ways. First inter-species correlations within and between aquatic and terrestrial species and endpoints clearly demonstrate the existence of highly significant quantitative relationships. The influence of certain chemical substituents, such as halogen or nitro groups, is explored as well as any correlations of the physico-chemical parameters and toxicological and topological parameters. Some of the results are highly significant and indicate the possibility for significant savings in experimental data needs in favour of simple computational predictions. This presentation provides overviews on the data, spreadsheet manipulations and results of regression analyses.

DISTRIBUTION OF INFAUNAL BENTHOS AFTER TWENTY YEARS OF SUBMARINE TAILINGS DISPOSAL TO A FJORD

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Abstract

Island Copper Mine in British Columbia has discharged its tailings (amounts up to about 50,000 tons per day) at depth (40 metres) to a fjord since 1971. The outfall is engineered to entrain a 1:2 mix with sea-water, and thereby create a tailings density current descending to fjord bottom by gravity flow. The outfall design has come to be the basis for Submarine Tailings Disposal systems (STD) used elsewhere in Canada, in Papua New Guinea, and with designs formulated for Alaska, Peru and Turkey. This paper described the infaunal benthos that has colonised stabilised and unstable tailings deposits, and compares the benthos with that present on adjacent sediments free of tailings.

In 1991 the infaunal benthos on thickest tailings (ranging from 46+ cms to many metres) was distinctive in species, with low density and low diversity populations. Numbers ranged from 160 - 9673 organisms/m^2, representing 3 - 49 species in three 0.05m^2 grab samples from each sampling station. The polychaete worm Cossura pygodactylata numerically dominated the fauna. Under cluster analysis, an impoverished benthos in the central fjord trough with active tailings flow could be separated from a richer benthos on surrounding thick but stabilized tailings. However, the two clusters were not significantly different, according to a bootstrap procedure, indicating an overlap in population characteristics on stable and unstable deposits.

Benthos on lesser tailings (23 cms or less in 1991), remote from the outfall or in shallow water, graded indistinguishably into benthos associations on seabeds without visible tailings. Organism abundance ranged from 3353 - 51113/m^2, and diversity from 27 - 132 taxa in 3 grab samples from each sampling station. In these light and no-tailings faunas a small bivalve mollusc Axinopsida serricata was usually numerically dominant, but one or more of a variety of 10 other species, mostly polychaete worms, were abundant at different sampling stations. One location was almost 50% nematode worms. There were two major clusters with light and no-tailings stations intermixed. There were significant differences between

a few individual sampling stations, mostly on light tailings, and with distinctive species, abundance or diversity.

The pattern of impact on the infaunal benthos in 1991 after 20 years of tailings discharge is that in the area destabilised by actively flowing tailings, benthos is smothered. After the tailings stabilise, the benthos recolonises to a self-maintaining, moderately abundant and diverse community within one or two years. These tailings beds support a commercially fished, benthic-feeding crab population free of trace metal contamination. Under light tailings deposition with stable deposits (e.g. up to 23 cms over 21 years) there is no detectable difference of the benthic populations from those present on adjacent similar habitats free of tailings. The 1991 data and analyses extend and confirm previous results and conclusions.

BIOLOGICAL CONTROL OF AQUATIC VEGETATION USING GRASS CARP

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Abstract

In 1987 the Government of Alberta embarked upon a major program aimed at the use of grass carp (*Ctenopharyngodon idella*) as agents in the control of aquatic weeds in irrigation canals and dugouts. At present, a highly toxic herbicide (acrolein) is used to control weeds. Although this herbicide is acutely toxic to fish at a concentration of 0.1 mgL^{-1}, the usual application dose in canals is 5 - 8 mgL^{-1}, resulting in the large-scale loss of native fish.

Grass carp is a large, herbivorous cyprinid, originating from eastern China. The fish has been introduced to more than 50 countries and much of the USA. Grass carp has appeal for two reasons: (i) under ideal conditions, it can consume 2 - 3 times its weight per day in vegetation, and (ii) it is important in fisheries in many countries because of its size, production and palatability. Prior to the implementation of the current program, grass carp had not been used for aquatic weed control in Canada.

The first five-year phase of this program consisted of a series of seven studies:

i)   Acquisition of larval carp from a hatchery in Florida, transport to Alberta, and laboratory culture.

ii) Triploid induction and screening.

iii) Presence of pathogens, including parasites, viruses and bacteria.

iv) Winter survival in dugouts.

v)   Control of weeds, stocking rates, and carp growth.

vi) Acoustic and mechanical barriers to carp movement.

vii) Bird and fish predation.

Overall, it was found that grass carp can be easily transported and cultured, both indoors and outdoors. A number of commercial feeds were used for maintenance, along with grass cuttings and lettuce. Vitamin C supplements were needed to prevent scoliosis in young fish.

The method used to induce triploidy (giving a triploid number of chromosomes) was 98.0% successful. Triploids, with 72 chromosomes, are considered functionally sterile, and cannot reproduce. Ploidy was determined using Coulter Channelyzer instrumentation and chromosome analysis. No diploids (with 48 chromosomes and able to reproduce) were used in any test.

During the last five years, no pathogens that are listed in the Fish Health Protection Regulations (Fisheries and Oceans Canada) were found in any laboratory, dugout or canal population of grass carp. However, fish overwintering in some dugouts were susceptible to the protozoan parasite *Chilodonella cyprini*. This parasite infects the gills, causing massive necrosis and death. Fish were treated with sodium chloride to reduce or eliminate the infection.

During the summer, the rate of growth of fish in both dugouts and canals was fast, with fish increasing in weight by 59.6% (mean) during three months. The percentage of weed control ranged from 16 to 77, depending mainly on species of plant, stocking rate, and temperature.

Several bird species and northern pike (*Esox lucius*) preyed on small grass carp. Hence, the minimum stocking size was increased to approximately 25 cm.

The second phase of the program, scheduled for completion in 1996, will deal with the following subjects:

i)   Development of a hatchery in Alberta, with capability for triploid induction, incubation and rearing.

ii) Planting of grass carp in long reaches of canals, with studies emphasizing post-treatment recovery rates of vegetation, environmental risk assessment, and economic feasibility.

iii) Planting of grass carp in dugouts, with emphasis on stocking rates, interactions with other fish, environmental risk assessment and economic feasibility.

At the end of this phase of the program, a decision should be made on the use of grass carp as a replacement for aquatic herbicides.

IMPACTS OF REDUCING LOADINGS OF EIGHT PERSISTENT TOXICS ON CONCENTRATIONS IN THE WATER, SEDIMENT AND BIOTA OF LAKE ONTARIO

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Abstract

This study examines the impacts of reducing loadings of eight persistent toxics on concentrations in the water, sediment and biota of Lake Ontario, by applying the Rate Constant model[1].

These eight persistent toxics (lead, arsenic, PCBs and five polyaromatic hydrocarbons) have been identified as exceeding levels considered safe (i.e., standards, criteria and guidelines) in the water column or fish tissue in Lake Ontario and/or the Niagara River. The Lake Ontario Toxics Management Plan recognized that toxics in Lake Ontario must be reduced if fish are to be safe for unlimited human consumption and for sensitive , native species (e.g., the bald eagle, osprey, mink and river otter) to reproduce in the Lake ecosystem. To determine the toxic loading reductions required for obtaining acceptable concentrations the mass balance Rate Constant model is used to relate concentrations in water, sediment and biota with loadings. As well, the model estimates the time period required to achieve acceptable levels.

To reduce loadings both site-specific and general reduction strategies are prescribed based on knowledge of loadings by specific sources in the basin and general use of specific chemicals in industry and consumer products. The source of loadings for each chemical are shown concisely in a table in the study. Since the origin of loadings from the majority of sources (e.g., upstream of the Niagara River, runoff, the atmosphere and sewage treatment plants) are not specifically itemized the principal uses of the chemical (i.e., industries, consumer products) are also cited.

Recent loading estimates, in Thompson (1992), show that Lake Ontario receives approximately 1,500 kg (1,496 kg) of these eight toxics every day from the Niagara River, the atmosphere and Canadian sources. The Niagara River dominates all other sources

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[1] The Rate Constant model, a simple mass balance model, was developed by Professor Donald Mackay and Dr. R. Miriam Diamond in association with the International Joint Commission's Virtual Elimination Task Force.

constituting two-thirds of the total loadings. Other important sources are urban runoff, atmospheric deposition and municipal sewage treatment plants: rendering, respectively, 13, 9 and 6 percent of the total loadings. Lead loadings are the largest, representing roughly two-thirds of the total loadings, followed by: arsenic; the five PAHs; and then, PCBs.

Through reduction efforts, based on pollution prevention and phase-out approaches, in the Lake Ontario Basin it is estimated that loadings can be reduced by one-third to one-tenth (varying with the chemical) of present-day loadings. Additional efforts, outside of the basin, curtail the loadings further and quite dramatically.

The Rate Constant model consists of a whole lake model and a food chain model. This model has been demonstrated to be of value in setting attainable virtual elimination targets (Mackay et al.,1992). Essentially the model combines input loadings with the properties of Lake Ontario and the chemical of interest to calculate concentrations in water and sediment. These concentrations are then applied to the food chain model to compute concentrations in various organisms.

The processes computed by the "Rate Constant" model include:

- evaporation from water to the atmosphere
- outflow of chemical from the lake
- transformation of chemical to other chemical species in the water
- transfer from water to sediment
- transformation of chemical in the sediment
- burial to deep, inaccessible sediments
- bioaccumulation and removal (by egestion, respiration, growth dilution and metabolism) of chemicals in organisms in a six biotic (benthos, zooplankton, alewife, sculpin, smelt and lake trout) component food chain model.

Generally concentrations in water and sediment are found to fall fairly rapidly when loadings are severely curtailed. When modest reductions in loadings are modelled the rate of reduction in concentration is slow, because of continued loadings. The results of the modelling exercise are presented in simple and easily understood form, generally as graphics or histograms.

Twenty-Eighth Central
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Groundwater and Soil
Remediation

IN SITU REMEDIATION OF HYDROCARBON IMPACTED SOIL AND GROUNDWATER

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Abstract

The removal of volatile hydrocarbons from soils can be effectively accomplished by the application of soil vapour extraction. However, this technology requires that the soils be unsaturated. In areas where the contaminated soils are below the water table, application of soil vapor extraction requires that the soils be artificially dewatered. Coordinating the dewatering and vapor extraction designs is, however, difficult because of the different dynamics involved - air versus water movement. The following case history illustrates that such coordination can be accomplished and that a combined system of water and vapor extraction can be effectively utilized in treating soil and groundwater contamination.

The retail petroleum facility is located in an urban commercial area in Newfoundland. A gasoline leak in a buried product transfer line was the source of elevated gasoline vapors in many retail and commercial business basements located downgradient of the site. As a result of the leak, an entire block was evacuated by the city Fire Marshall and Provincial Department of the Environment and Lands Petroleum Division.

The site geology consists of a variable thickness of glacial till (2.0 to 5.0 meters thick) mostly of medium grained sands to gravels overlying a metamorphosed shale (slates). The bedrock contours of this rock unit can change elevation quite dramatically over short distance. Groundwater levels were detected 3.5 meters to 5.0 meters from surface across the site.

Separate phase hydrocarbon, absorbed and dissolved petroleum hydrocarbons were detected across the entire site and downgradient of the site.

A series of detailed shallow soil gas surveys, soil vapor extraction testing and hydraulic aquifer testing were performed during the fall of 1990 and early 1991. All data was compiled with in-house computer software programs as to model optimal radius of influence for the conceptual soil vapor extraction systems and aquifer pumping systems. The separate and dissolved phase hydrocarbon recovery system was designed using a simplified two-dimensional analytical groundwater flow modelling technique. The modelling approach

that was used enables multiple recovery points to be evaluated at varying flow rates within heterogeneous media, of the type found at the site. In addition to optimizing separate and dissolved phase recovery, the modelling analysis was also used to design a system that would allow for maximum dewatering of the soils to enhance the effectiveness of the soil vapor extraction components incorporated in the site remediation strategy. The costs for this type of analytical modelling for system design is much less than conventional numerical modelling approaches.

The detailed design studies indicated that five (5) recovery wells were needed to provide suitable hydraulic control and dewatering of the contaminated soils with two (2) water treatment systems consisting of one air stripper tower off-site and one low pro air stripper at the station. The testing also indicated four (4) soil vapor extraction units (four-2hp rotrons) would be manifolded to nine vapor points.

The conceptual remediation design was approved by the Newfoundland Department of the Environment and Lands Petroleum Division in early 1991 and construction started in May 1991. The systems were commissioned in August 1991. Monthly monitoring of the soil vapor extraction systems off-gas volatile organic compounds (VOC's) was performed along with sampling of the influent and effluent from the groundwater treatment system.

In August 1992 the remediation system located east (downgradient) of the service station was approved for closure by the Newfoundland Department of the Environment and Lands and city Fire Marshall based on low to non-detectable levels of petroleum hydrocarbons which had been attained over a four (4) month period in both the soil vapor extraction and groundwater treatment systems. Presently the service station remediation system is being monitored monthly, with an expected approval for site closure in early 1993.

EVALUATION OF CONTAMINATED SEDIMENT TREATMENT TECHNOLOGY FOR RIVER CLEANUP

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Abstract

In October and November 1992, Atlas Specialty Steels, Environment Canada, and Wastewater Technology Centre carried out the Welland River Dredging and Treatment Demonstration project. The demonstration involved the dredging and treatment of approximately 230 m^3 of industrial mill scale and contaminated clayey silt sediments from a section of the Welland River, Ontario. The industrial deposits and the sediments contain elevated concentrations of several metals, phosphorus, and oil and grease exceeding the Ontario Ministry of the Environment sediment quality guidelines.

The sediment treatment demonstration involved the design and construction of temporary facility, including a temporary storage basin, at the Atlas Steels North Filtration Plant. The facility was an innovative application of existing technologies comprising a coarse screen, screw classifier, fine screens, thickener, centrifuges, settling basin, and filtration plant designed to provide efficient separation of solid/liquid phases and size factors.

The temporary treatment facility operated successfully during the demonstration without any major problems. Greater than 99% of suspended solids in the dredged slurry were removed by the treatment technology. Metal removal efficiency for the overall treatment ranged from 93% for nickel to 99% for iron. Concentrations of volatile organics in the effluent from the treatment facility were below levels of concern.

The solids generated and separated by the treatment process are disposal ready and can be classified as nonregisterable, nonhazardous solid industrial waste according to Ontario Ministry of the Environment Regulation 309 leachate and slump tests. Some of the solids contain high nutrient levels and may qualify for spreading on agricultural land provided the application rates are adjusted to meet heavy metal concentrations in the applicable guidelines. The separated mill scale solids are being considered for recycling by Atlas.

This paper will present the result of the sediment treatment demonstration project.

Legend

- Sampling Location
- Influent Sampling Port
- Magnetic Fraction Sampling
- Non-Magnetic Fraction Sampling
- SP Slurry Pump
- FP Chemical Feed Pump
- PAC Powdered Activated Carbon
- VF Vacuum Filter
- SW Spray Water
- OS Oil Skimmer
- OC Odor Counteractant

- Contingency Measure for Odor Control
- Solid Discharge
- Slurry
- Thickener Sludge
- Water
- Filter Backwash Water
- Valve
- Pump
- Solid Stock Pile

Fig. 7.1

Wetland River Dredging and Treatment Demonstration
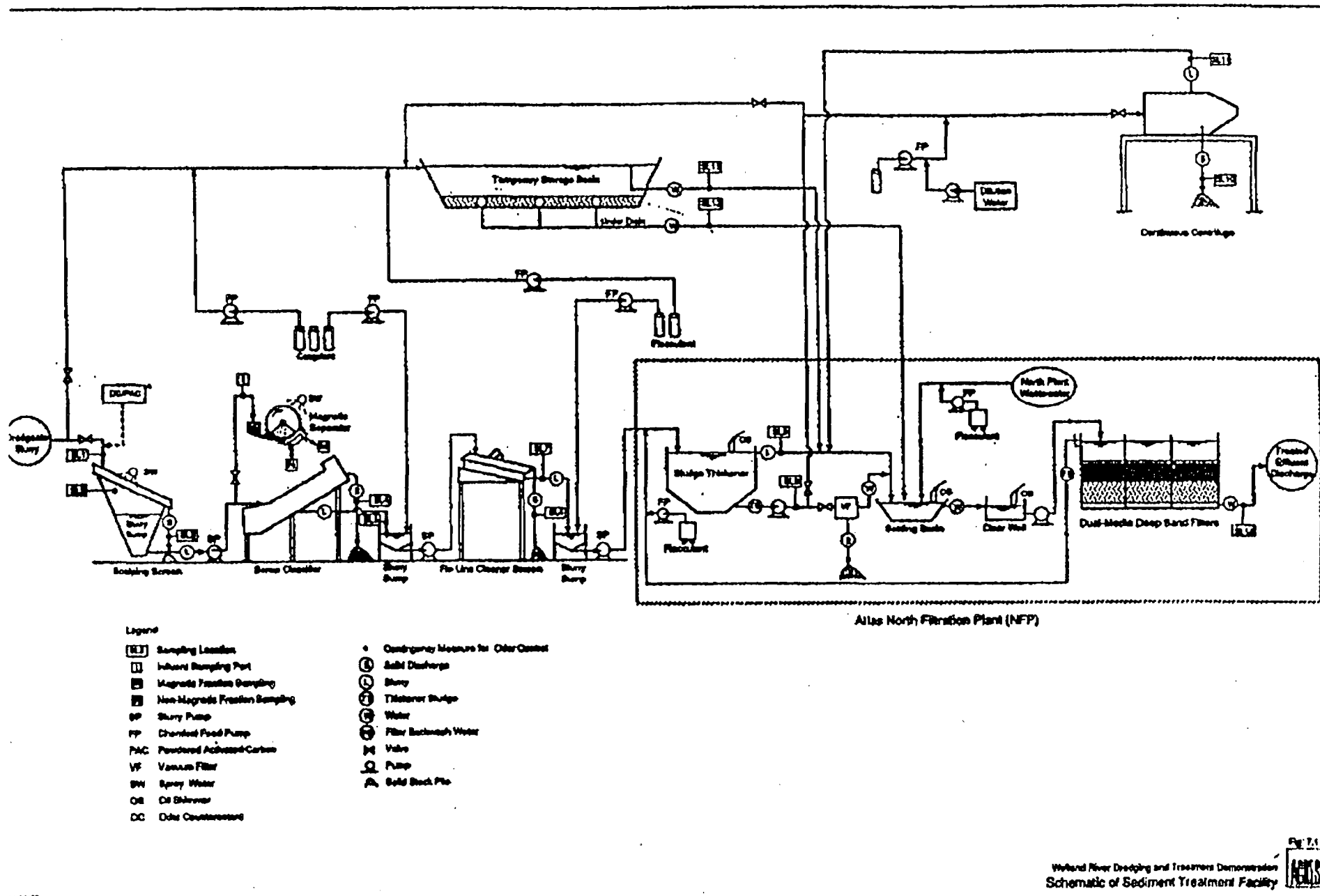Schematic of Sediment Treatment Facility

Table 11.6

Welland River Dredging and Treatment Demonstration
Average of Daily Concentrations in Solids

Conventional Parameters

Process	MC (%)	LOI (%)	TOC (mg/kg)	TP (mg/kg)	TKN (mg/kg)	Oil&Grease (mg/kg)
Coarse Screen Solids	19.02	9.6	78581	NA	NA	7550
Classifier Solids	19.11	1.78	22000	1888	780	1148
Vibrating Screen Solids	67.64	23.8	179909	7147	17445	12991
Thickener (Centrifuge) Solids	64.36	9.16	75957	4366	8434	7817
Thickener Overflow	NA	NA	6614	123	6173	12345

Metals of Concern

Process	Cr (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Fe (mg/kg)
Coarse Screen Solids	NA	NA	NA	NA	NA	NA	NA
Classifier Solids	607	3463	1021	119	240	1342	298250
Vibrating Screen Solids	668	1706	1361	558	819	3896	167345
Thickener (Centrifuge) Solids	701	2128	1374	269	577	1912	153225
Thickener Overflow	247	2489	309	247	494	617	16667

Table 11.8

Welland River Dredging and Treatment Demonstration
Solids Composite Samples Results

Conventional Parameters

Sample	Oil&Grease (mg/kg)	LOI (%)	Mois (%)	TP (mg/kg)	TKN (mg/kg)	TOC (mg/kg)
Coarse Screen	5700	11.5	19.2	NA	NA	NA
Classifier	1200	1.5	8.6	1600	870	25000
Vibrating Screen	11200	18.9	45.7	6600	12100	250000
Centrifuge	7200	8.4	44.2	6200	6950	80000

Metals of concern

Sample	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Mo (mg/kg)
Coarse Screen	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Classifier	460	2100	916	121	306	1130	203000	1	79	527
Vibrating Screen	594	1760	1460	294	811	2930	158000	2	114	1020
Centrifuge	743	2280	1400	267	519	2140	183000	2	163	1350
OGSSUAL [1]	1700	NA	420	1100	4200	2800	NA	34	340	94

MOE Reg 309 Leach Test

Sample	PCB [2] (mg/L)	As (mg/L)	B (mg/L)	Ba (mg/L)	Cd (mg/L)	Cr (mg/L)	Pb (mg/L)	Se (mg/L)
Coarse Screen	<0.003	<0.005	<0.2	<0.5	<0.005	<0.05	<0.05	<0.002
Classifier	<0.003	0.007	<0.2	<0.5	<0.005	<0.05	<0.05	<0.002
Vibrating Screen	<0.003	0.006	0.3	<0.5	<0.005	<0.05	<0.05	<0.002
Centrifuge	<0.003	0.019	0.2	0.6	0.022	<0.05	0.1	0.005
Reg. 309 [3]	0.003	0.05	5	1	0.005	0.05	0.05	0.01

Notes:

[1] Ontario's Guidelines for Sewage Sludge Utilization on Agricultural Lands, 1986.
[2] Values were converted from mg/kg to mg/l considering 20 times dilution factor.
[3] MOE Regulation 309 Schedule 4 Criteria, 1989.
NA = Not Applicable

DIRECTED SOIL AIR CIRCULAR FLOW (BLK) FOR THE REMEDIATION OF CHC-CONTAMINATED INDUSTRIAL SITES

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Abstract

Directed soil air circular flow (BLK) is employed for the remediation of soils polluted with volatile contaminants. In addition, it can be used to inject reactive gases into the soil for the stimulation of biological or chemical degradation. BLK is a process patented by IEG mbH, Reutlingen, Germany.

Two screen sections built into the bore hole are separated into an upper and a lower section, each of which is connected to an above-ground ventilator (Fig. 1). This allows for the withdrawal of air from either segment individually or from both simultaneously. The extracted air, after passing through a suitable remediation unit (e.g. activated carbon filter), is reinfiltrated back into the soil.

Additionally, clean compressed air can be pumped into a pressurized air distributor located between the capillary fringe and the aquifer base according to the vertical distribution of the pollutants. The air bubbles rise within the well, causing the water inside the well casing to flow upward (air-lift effect). Consequently, a continuous circulation of groundwater is created in the area surrounding the remediation well, delivering new contaminants to the stripping site. Volatile contaminants dissolved in the groundwater and the capillary fringe are transferred from the liquid to the gas phase in an amount relative to their gas-liquid distribution coefficient and are extracted via the BLK-system.

The BLK, in contrast to conventional venting methods, is capable of generating a directed circulation through the center of the contamination. The circulation direction is reversible and can be adjusted according to the pollutant distribution in the soil. Air passing through the ventilator is heated, thereby enhancing desorption of contaminants adsorbed onto soil particles. This leads to a faster and more effective remediation of the site.
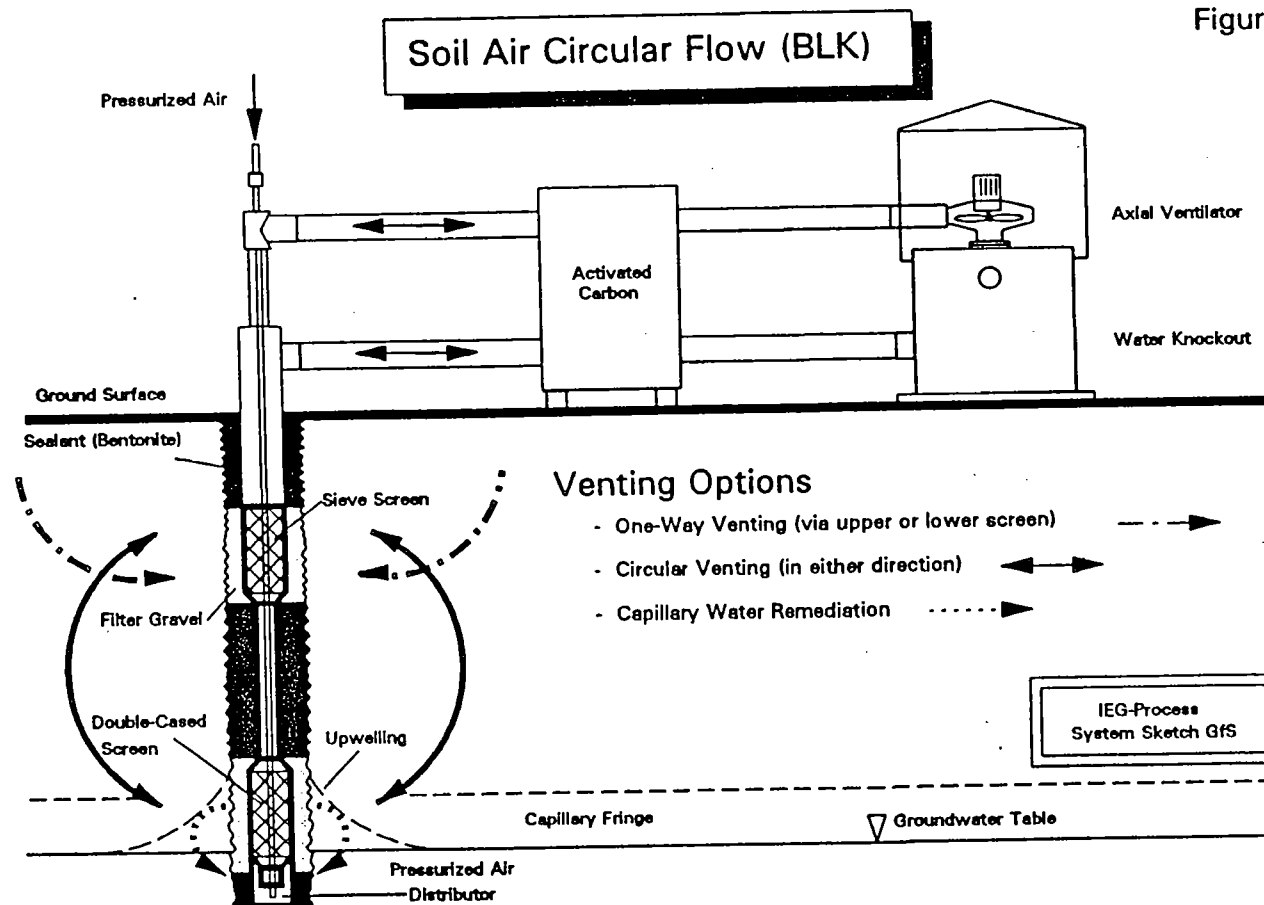
Nutrients in liquid or gas form can be introduced into the circulation to stimulate the biological degradation of contaminants. Chemical conversion of toxic substances into harmless and/or immobile material can be achieved in situ by introducing, for example, strongly reactive gases into the subsurface.

Results of two case studies in which BLK-systems were implemented are presented. One study compares performance data gathered over several years from a conventional one-way vapor extraction system to results from a BLK-system after one year of operation at the same site. The results show that the CHC-removal rate from the subsurface increased considerably after the BLK-system was installed. Higher removal rates are partly due to an increase in temperature in the subsoil (as a result of the circulating air), resulting in the following advantages:

1. If CHC in the form of dense non-aqueous phase liquids (NAPLs) are present in the subsoil, the liquid to gas transition is accelerated therefore CHC are extracted at a faster rate.

2. In contaminated soils where no NAPLS are present, the contaminants are found in the subsoil according to their distribution coefficients - soil (solid phase) - water (liquid phase) - and air (gas phase). With an increase in temperature the entire distribution shifts towards the gas phase causing a higher percentage of the contamination to be present in the soil air, which can be removed more readily.

3. Warming up of the subsoil also has a positive influence on poorly or non-permeable zones (e.g. clay lenses etc.). Removal of pollutants from such low permeability zones is mainly controlled by molecular diffusion. Apart from the soil parameters, the molecular constant of a given soil depends primarily on the temperature. A temperature increase thus leads to a faster removal of pollutants from those low permeability zones since the adsorbed CHC are transformed into the gas phase at a faster rate.

4. Creation of a laminar flow pattern in the vicinity of the well results in smaller negative pressures thus leaving the moisture in the subsoil and not in the off-air. The air-lift velocity to move contaminated air vertically from the well is attained.

5. By using double-cased screens (stainless steel, 65% of open screen/foot) with hydrophobic material between the two casings, a more effective phase separation of air, water, and/or free product can be achieved.

The two case studies presented demonstrate the efficiency of the BLK-systems and show detailed data on the horizontal and vertical distribution of the soil parameters (TOC, diffusion constants, sorption and retardation analysis, soil mechanical characteristics, CHC-concentrations, etc.). The distribution of the respective pollutants in the 3-phase system of the subsoil can be calculated.

Figure 1

Soil Air Circular Flow (BLK)

Pressurized Air

Axial Ventilator

Activated Carbon

Water Knockout

Ground Surface

Sealant (Bentonite)

Sieve Screen

Filter Gravel

Double-Cased Screen

Upwelling

Pressurized Air
Distributor

Capillary Fringe

Groundwater Table

Venting Options

- One-Way Venting (via upper or lower screen)
- Circular Venting (in either direction)
- Capillary Water Remediation

IEG-Process
System Sketch GfS

ON-LINE EXTRACTION AND DERIVATIZATION OF PENTACHLOROPHENOL AND RELATED COMPOUNDS FROM SOILS USING A SUPERCRITICAL FLUID EXTRACTION SYSTEM

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Abstract

Abnormal discoloration of wood, commonly referred as sapstain, is caused by fungi which derive nourishment from wood cells. Other than by kiln-drying, sapstain and mold on the surface of lumber can be prevented by treatment of wood with anti-sapstain chemicals. Due to their effectiveness, pentachlorophenol (PCP) and its derivatives are the most widely used anti-sapstain chemicals in Western Canada in the last 50 years. Recently, the application of PCP by the sawmilling and forestry industries has become an environmental concern since PCP is toxic to fish and mammals and technical grades of PCP are known to contain the highly toxic chlorinated dibenzo-p-dioxins and furans. In response to these concerns, the use of PCP as a wood preservative in British Columbia has mostly been phased out. However, this chemical is still being used in wood treatment plants in other parts of Canada for special applications.

PCP in soils or sediments can be traditionally determined by solvent extraction techniques (e.g. Soxhlet) or by a steam distillation approach. In both cases, the extraction process takes a few hours or longer. In the case of solvent extraction, a large amount of solvent must be used and a great deal of coextractives are produced. The latter often create a problem in the subsequent cleanup and chromatography analysis. If the extracted PCP is to be analyzed by gas chromatography in the form of an acetyl, methyl or pentafluorobenzyl derivative, extra time is required for the additional derivatization step.

Supercritical fluid extraction (SFE) has been proven to be a more efficient alternative than existing solvent extraction techniques for most solid samples. It has been successfully applied to the determination of PCBs, chlorobenzenes, PAHs, dioxins, resin and fatty acids in sediment and other matrices and the list is growing rapidly. Because of the non-polar nature of supercritical carbon dioxide, extraction recovery of polar parameters is low unless a modifier such as methanol is added to the system. Supercritical fluid extraction of free

pentachlorophenol from a soil sample has also been reported. More recently, the possibility of combined supercritical fluid extraction and derivatization of polar compounds has been explored. This latter approach further reduces sample preparation time and at the same time enhances the extractability of polar compounds since derivatives are in general less polar than their parent compounds. Previous work on resin and fatty acids demonstrated that this one-step technique can be applied to the rapid screening of the acids in sediment samples.

In this report, we shall describe a rapid and quantitative method using an on-line extraction/derivatization technique for the determination of PCP and related compounds in soils contaminated by the wood preserving chemical. Phenols are extracted from soil and acetylated in-situ with supercritical carbon dioxide in the presence of triethylamine and acetic anhydride at a temperature of 80°C. Quantitative recovery of di-, tri-, tetra-, and penta-chlorophenols was obtained by a 10-minute extraction with carbon dioxide at 37.2 MPa (365 bar, 0.8 g/mL density) from soil samples fortified to 0.5 and 5 g/g levels. In a comparison study, the SFE and the steam distillation methods both produced very similar results for PCP and other chlorophenols in a reference sample. When this method is applied to some contaminated soil samples collected in a wood treatment plant, results for chlorophenols in a sample can be obtained in a short 90 minutes.

IDENTIFICATION OF PETROLEUM CONTAMINATION SOURCES BY FINGERPRINTING OF PETROPORPHYRINS IN SOIL AND CRUDE OIL SAMPLES

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Abstract

Petroleum is one of the major contaminants of soil and groundwater. It is very important for governments and responsible parties to identify the source of oil spills. Many studies have been conducted using GC fingerprints of hydrocarbons and PAHs. However, the patterns are very complex and subject to interferences. Also some of the components are more biodegradable hence the patterns are altered with weathering. An alternative chemical fingerprint indicator was sought.

Petroporphyrins (PPs) are a group of macrocyclic aromatic compounds found in petroleum. The composition of PPs is different for petroleum from different sources, depending on the origin and the diagenesis processes involved during the formation of the petroleum. Therefore, the PPs are ideal as fingerprint chemicals. The objective of the present study is to assess the use of this new chemical indicator, the PP fingerprint, to supplement other chemical indicators, i.e., BTEX (benzene, toluene, ethylbenzene and xylenes), polycyclic aromatic hydrocarbons (PAHs) and the total petroleum hydrocarbons (TPHs), for the identification of the petroleum contamination and verification of the contamination sources.

The separation of the PPs in soil and petroleum samples was achieved by HPLC. The BTEX, PAHs and TPHs were analyzed by GC-MS.

Three petroleum contaminated soil samples were collected from Ontario (Cambridge, Petrolia and Sarnia), two from Quebec and five from Alberta at pipeline transfer stations, oil mining operation and spill sites. Crude oil and diesel samples were also collected from the same sites.

The soil samples from Ontario show two different types of PP fingerprints. By comparison of the fingerprints of the crude oil samples, it could be concluded that the soil sample from Cambridge was contaminated by the crude oil from Alberta pipeline while the sample from Petrolia was contaminated by the Petrolia crude oil (Fig.1). On the other hand, the sample from Sarnia was contaminated by mixture of diesel from a refinery and the crude

oil from Alberta pipeline. The weathering process on these soils did not seem to affect the PP pattern. Coextractions from the soil do not interfere with. The result suggests that the PP fingerprint is a good chemical indicator for the identification of contaminant sources by crude oils.

However, because of the low volatility, the PPs are not present in some of the petroleum products, such as gasoline. Therefore, the BTEX is more useful to detect gasoline spills. The PAH and TPH analyses may also be needed because the volatility, solubility and biodegradability of the BTEX could cause difficulties to find the contamination source.

Fingerprinting of the PPs in the soil samples from Quebec and Alberta is in progress. In Quebec most petroleum crude is imported and, thus, to fully validate our method it is important to compare the behaviour of different sources of petroleum contamination. The petroporphyrin fingerprints and the other three chemical indicators are the backbone of a systematic protocol that is being developed to identify the sources of petroleum contamination in soil and groundwater.
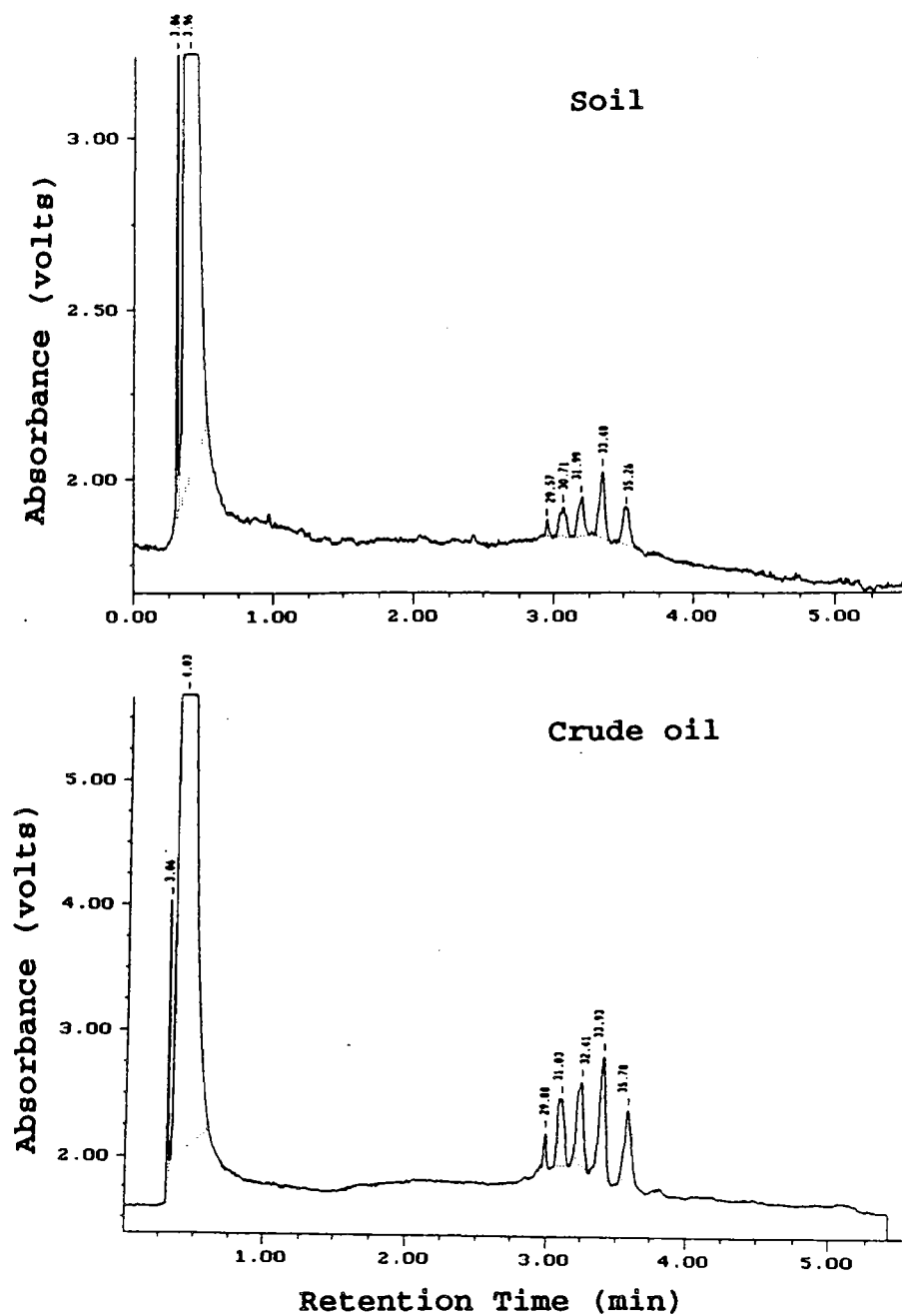
Figure 1. Fingerprints of petroporphyrins in the soil and crude oil samples from Petrolia, Ontario.

Twenty-Eighth Central Canadian Symposium on Water Pollution Research

Poster Presentations

OXIDATION AS A PRETREATMENT TO BIOREMEDIATION OF COAL TAR CONTAMINATED SOILS

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Abstract

Although manufactured gas plants are now obsolete, the residual environmental impacts on the former sites are presently of concern. Many of these plants disposed of the manufacture fuel gas wastes on-site in ponds, pits and storage tanks above or below the ground. Consequently, high levels of coal tar, known to contain carcinogenic polycyclic aromatic hydrocarbons (PAHs), have resulted in substantial soil contamination. Bioremediation is a promising approach to a solution since the organic portion of the coal tar has been found to be biodegradable. However, high molecular weight PAHs are tightly adsorbed to the organic component of the soil and thus require some form of pretreatment to facilitate sufficient bioavailability in a bioreactor.

The Wastewater Technology Centre (WTC) has conducted a preliminary investigation on chemical oxidation as a pretreatment to bioremediation of coal tar contaminated soils. The oxidant known as Fenton's Reagent (hydrogen peroxide and ferrous sulphate) was investigated as a potentially effective chemical pretreatment. Quantitative PAH removals as well as biological impacts on microbial toxicity and activity were monitored following the oxidation treatments.

The coal tar contaminated soil contained 256 ppm total PAHs bound to a sandy loam type matrix. The total organic carbon (TOC) for the untreated soil was 4.4% which accounts for the high degree of PAH adsorption. The Soil Microtox toxicity test was used to determine an EC_{50} of approximately 6800 ppm.

Batch screening oxidation experiments were performed to determine an effective dose for Fenton's Reagent in this application. Initially, 50 mM, 100 mM and 200 mM hydrogen peroxide was used in the oxidation reaction with an excess of ferrous sulphate catalyst. It was found that there was little difference between the low and high doses and thus further

work proceeded using the 50 mM hydrogen peroxide at an equal molar ratio with ferrous sulphate catalyst.

Two methods of investigation were performed to determine the effects of the oxidation at various pHs. The first was a radioactive tracer study where a known concentration of [14]Carbon labelled benzo(a)pyrene (^{14}C-BaP) was spiked onto the soil. The oxidation procedure involved addition of the Fenton's reagent to a 250 mL flask equipped with a volatile organics trap followed by 2 carbon dioxide traps in series. Following oxidation, the soil, liquid and gaseous phases of the slurry were monitored for radioactive products.

The second method involved direct measurement of changes in the concentration of the 16 EPA priority PAHs using GC/MS analyses. A similar oxidation procedure was followed, however, the soil was not radioactively spiked and no gas traps were used. Toxicity testing was performed on the treated soil and supernatant, while microbial activity testing was performed on the soil alone.

Preliminary results indicate that minimal ^{14}C-BaP was removed from the soil at slightly acidic pHs. However, a lower pH may increase the effectiveness of the reaction. There was some decrease in other PAHs but the mechanism of removal was inconclusive. Toxicity of the treated soils remained constant or decreased indicating that more toxic intermediates were not formed from the oxidation treatment. Microbial activity was not detected on any of the treated soils indicating that more severe treatments may be used without affecting the microbial integrity of the soil. Further experimental results will be presented and further research possibilities will be discussed.

PESTICIDE CONCENTRATIONS AND USE PATTERNS IN URBAN STREAMS AND STORMWATER DETENTION PONDS

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Abstract

A pilot study of two urban creeks in Hamilton and two urban stormwater detention ponds in Guelph was initiated in 1991 to determine possible urban pesticide contamination of aquatic systems. Water was analyzed for 2,4-D, mecoprop,dicamba, MCPA, diazinon, chlorpyrifos, dimethoate, atrazine, and metolachlor during base flow and precipitation events. Sediment was analyzed for organochlorine and selected pesticides. A pesticide/fertilizer use questionnaire was circulated to all residents of the two Guelph subdivisions in which the detention ponds were located.

Initial results indicate that 2,4-D concentrations exceeded guidelines for the protection of aquatic life in 20% of the samples. The majority of the exceedences occurred during run-off events after application. The maximum observed concentration was 14.6 µg/L which is 7 times greater than the guideline. Other compounds detected included the phenoxy acid herbicides mecoprop and dicamba and the organophosphorus (OP) insecticides diazinon, dimethoate and chlorpyrifos. Currently, there are no guidelines for the protection of aquatic life for the OPs. Results from the questionnaire suggest that pesticide use in the urban setting exceeds agricultural uses on an areal basis.

A CONTINUOUS MONITORING TECHNIQUE FOR AGRICULTURAL HERBICIDES

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Abstract

Paired subwatersheds undergoing conservation and conventional tillage, near Thamesford,Ontario, were continuously sampled for atrazine and metolachlor from May 5 to December 4, 1989. Modified Quality Environment Automatic Liquid Samplers were used to collect weekly flow proportional surface water samples. The samplers, which require no power supply, and have no moving parts, proved very reliable.

Concentrations were higher, during the growing season, for both compounds in the watershed undergoing conventional tillage. The guideline for the protection of freshwater aquatic life for atrazine (2 µg/L), was exceeded for six weeks in the conventional tilled subwatershed vs. one week in the conservation tilled subwatershed; the guideline for metolachlor (8 µg/L) was never exceeded. Discharge data were used to calculate weekly loadings in each watershed, and loadings were compared with the results of a pesticide usage questionnaire. Compared to the total amount of these pesticides applied during the 1989 growing season, 1.1% of the atrazine and 0.43% of the metolachlor in the conventional tilled subwatershed reached the creek by December 4th; 0.31% of the atrazine, and 0.07% of the metolachlor in the conservation tilled subwatershed reached the creek by that time. The usefulness of this sampling method for determining loadings, and pesticide impacts on aquatic ecosystems, will be discussed.

PHOTOLYTIC DECOMPOSITION OF THE HERBICIDE, TRICLOPYR, IN TERRESTRIAL ENVIRONMENT.
SESSION II: IMPACT OF POLLUTANTS ON AQUATIC ECOSYSTEMS

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Abstract

Triclopyr [(3,5,6-trichloro-2-pyridinyloxy) acetic acid] is a relatively new herbicide which was developed in the early 1970s as a replacement for the recently banned phenoxy herbicides. It is currently being considered in Canada and is used for vegetation control in the United States on right-of-way, industrial sites, managed forest and turf, range and pasture lands. Because of its effective plant and weed management triclopyr will undoubtedly receive increasing utilization in the terrestrial environment. As a result, the potential for environmental contamination may be greater.

In order to study the environmental fate of triclopyr and its metabolites following forest site preparation applications, a 2-yr. field monitoring study was conducted in a northern Idaho forest watershed. In this study, the dissipation in soil, distribution through the soil profile and residues in vegetation canopy following three herbicide application rates of 7.2, 9.6, and 19.2 kg/ha were evaluated. Regardless of the application rates, triclopyr concentration decreased to less than 90% of the initial concentration and was not detectable in the top 1 cm of soil (silt loam) within 230 and 690 days from the herbicide applications, respectively. Triclopyr dissipation from the soil surface was rapid immediately following application. Computer models were developed to predict the rate of photolytic and microbial decomposition of triclopyr in soil. The modelling results strongly supported the contention that photolytic decomposition was the primary mechanism of triclopyr dissipation in the study area.

The attached figure explains the diurnal variation of photolysis rate constant predicted for triclopyr as a function of time of day for selected days of the month of October at 47°N lattitude.

The importance of photolytic decomposition of organic chemicals in the terrestrial environment will be discussed.
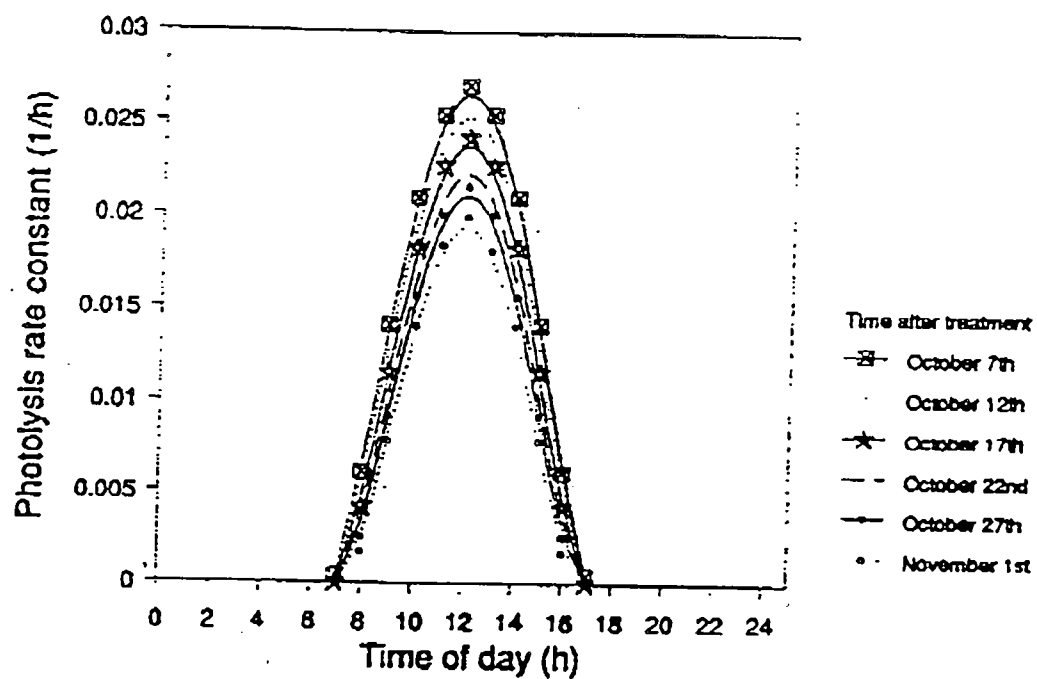
Figure 10. Diurnal variation of photolsis rate constant predicted for triclopyr as a function of time of day for selected days of the month of October at 47°N latitude.

GROUNDWATER TOXICITY ASPECTS DUE TO NITROGEN COMPOUNDS TRANSPORT
IN SOIL-WATER MEDIUM

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Abstract

In areas with very intensive production of cattle, the quality of groundwater is decreasing permanently. The management of animal wastes and its disposal without protection creates environmental hazards. The cattle manure pile, being rich in phosphorus, potassium and nitrogen, is subjected to leaching, runoff, infiltration and vaporization. The studies of the dynamics of nitrogen compound transport through the soil medium into groundwater in agricultural areas is the subject of studies.

Measurements of groundwater and soil have been performed on the territories of four dairy farms. The toxicity of groundwater has been tested there in sandy soil, as well in the clayey soil with various characteristics. The results show the impact of type of soil on nitrogen compounds transport through vadose and saturated zones in climate conditions of south Quebec. The potential of toxicity has been evaluated for every specific group of conditions: physico-chemical soil behaviour, precipitations, hydrography and waste management.

THE BIOLOGICAL REMEDIATION OF HYDROCARBON CONTAMINATED SOILS

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Abstract

Ever since the discovery of oil in the last century, we did, and still continue to, find more and more uses for this amazing product from the earth. It heats our home, powers our transportation vehicles, produces power, provides material for all types of plastics and serves us in many other ways.

However, along with all the benefits we have received from oil and its derivatives, one major drawback has been created - pollution. We have polluted our air with excess CO_2 from internal combustion engines. Precipitation absorbs the sulfur and nitrogen oxides which are produced in coal and heavy fuel burning power plants and falls to earth as acid rain. Oil refineries and petrochemical plants need water in their processes. This leads to pollution of the waterways when improperly treated process water enters the watercourse. Oil spills, like the Exxon Valdez, have led to direct contamination of the oceans and lakes.

The land has become polluted with hydrocarbons in many ways, as well. These include leaking underground and aboveground storage tanks, breaks in petroleum pipelines, spills of hydrocarbon during transit from storage to user and leaks at the refinery (Newton, 1990). These spills can be hazardous to the environment and to the human population in three ways: 1) migration of pollutant into the groundwater; 2) volatilization of lighter fractions into the atmosphere; and 3) direct contact with the contaminated soil particles, i.e., ingestion or skin absorption (Bauman, 1989). It is the potential of the contaminated soil at each unique site to become a source of pollutants in one of the above three pathways which dictates how it is treated.

With the heightening of environmental awareness and an increasing cost of running an industry, the unregulated and uncontrolled contamination and disposal of soil is becoming a very important issue in waste management. In the past, hydrocarbon contaminated soil was either ignored and taken out of service or excavated as a hazardous waste and sent to landfill. But now, the choice of leaving land for no distinct purpose, while land prices have been steadily increasing, is becoming financially unrealistic. Secure landfills for hazardous

waste are becoming full, the rules and regulations for using them have become tighter and the tipping charges for the landfills have skyrocketed.

As a result of public pressure, government regulations and industries' willingness to comply, alternatives are being sought to a static response to, or landfilling of, contaminated soil. The best solution is obviously prevention. However, unavoidable accidents do occur and the soil must be dealt with in a responsible manner. There is a wide range of chemical and physical methods which have been explored and are presently employed by industry. One option for clean-up which has become a viable option is biological remediation.

Bioremediation makes use of the natural degradation process. Microorganisms in all soils utilize organic compounds to provide for their growth and maintenance requirements. Petroleum products, containing primarily carbon and hydrogen, are aerobically oxidized by a wide variety of bacteria, molds and yeasts, found in the soil. With the addition of oxygen and nutrients, such as nitrogen and phosphorus, this naturally occurring process can be stimulated and used to the petroleum industry's advantage. Without enhancement, the degradation process will continue and most wastes will eventually degrade, but it will happen so slowly that it will be of little value to the industry.

In ex-situ bioremediation, the soil is excavated and treated in various ways. One method has been to adapt water treatment bio-units to create a soil/liquid slurry bioreactor. The soil is kept in suspension by mixing, shaking, or air infusion, in a mixture of pH adjusted, nutrient rich liquid. In this type of environment, the organisms have greater contact with the hydrocarbon, hence, reducing the time required to decrease the pollutant levels.

Another method of treating soils is the prepared bed technology. This method utilies concepts from composting and land farming to treat the soil. The soil is excavated, mixed with amendments and placed on an impermeable base, to eliminate possible contamination of groundwater with leachate.

In this project, the two methods described above for the biological remediation of soil were examined in a laboratory setup. Two types of soil were utilized using slurry bioreactors. One of these soils was used to simulate the prepared bed technology.

A TECHNO-ECONOMIC STUDY OF PROCESSES FOR HEAVY METAL LEACHING
FROM SEWAGE SLUDGE

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Abstract

Heavy metals present in sewage get concentrated in the sludge during the process of wastewater treatment. Disposal of this sewage sludge in agricultural land becomes a cause for concern due to the heavy metals present in them. A technologically sound and economically viable process is required to leach out the heavy metals from the sewage sludge.

Three processes are considered: (i) chemical leaching of the metals by addition of concentrated sulfuric acid to the sludge, (ii) sludge bioleaching using *Thiobacillus ferrooxidans*, (iii) sludge bioleaching by employing sulfur oxidizing bacterial strains, mainly *Thiobacillus thioparus* and *Thiobacillus thiooxidans*. Laboratory scale experiments were conducted for heavy metal leaching, using these three processes, on sewage sludges collected from various locations in Quebec and Ontario. The results indicate that metal solubilization efficiency varies with the metal to be solubilized as well as the type of sludge from which the metal has to be leached out. However, in most of the sludges and for all the metals studied (Cd, Cr, Cu, Ni, Pb and Zn), the process employing a consortium of sulfur oxidizing bacteria which oxidizes elemental sulfur to sulfuric acid was found to result in maximum metal removal. The acid addition process did have the advantage of simplicity and short process time, but lacked in terms of metal solubilization efficiency as well as the need for a considerable quantity of acid to be added to the sludge. Bioleaching using *Thiobacillus ferrooxidans* needed initial pH adjustment of the sludge and also lacked in terms of metal solubilization efficiency except in case of anaerobically digested sludges. A distinct advantage of the sulfur oxidation process was that it could achieve up to 35% reduction in sludge solids by aerobic sludge digestion proceeding parallel to the metal leaching operation.

Based on the experimental data the three processes were theoretically scaled to plant size units and the cost involved was computed. This study showed that sulfur oxidation process is the most attractive option at low plant capacities and with sludges having high solids concentration. Simultaneous metal leaching and sludge digestion by the sulfur

oxidation process compares well with aerobic digestion followed by acid addition. Sludge solids concentration and aeration rate were seen to be the most important parameters influencing the overall cost per tonne of dry sludge treated. Results from experimental as well as theoretical studies indicate that bioleaching by sulfur oxidizing bacteria is the most attractive among the three processes studied and that enhanced oxygen transfer methods can cut down the treatment cost further.

REMEDIATION OF MUNICIPAL INCINERATOR'S BOTTOM ASH

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Abstract

Since the bottom ash residues obtained from municipal solid waste incinerators contain considerable amounts of leachable heavy metals and organic/inorganic contaminants, problems have been encountered in deciding upon remediation and final disposal scenarios based on concerns about soil and groundwater contamination.

Several possibilities have been investigated for the ultimate disposal - other than landfilling of these residues such as; 1) structural fill for road subbases, 2) soil stabilizers, 3) concrete additives, and 4) building block materials. The basic factors influencing ash utilization scenarios include concerns of environmental impacts acceptability, technical and economical feasibility, and market availability.

Two treatment techniques have been initially considered, namely the metal recovery from the ash residues utilizing electro-chemical treatment techniques and a physical process which involves magnetic removal of metal and sieve analysis.

An optimization process has been established in the effort to define the amount of residues to be treated and the treatment techniques applied on the one hand and the economic factors that accompany such an action on the other.

HIGH STRENGTH NITROGEN REMOVAL FROM AN ANAEROBICALLY TREATED WASTE BY THE IACM PROCESS

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Abstract

This paper presents the results of a laboratory experiment on the removal of high strength nitrogen. The intermittently aerated completely mixed (IACM) process was used to remove nitrogen from a waste initially treated by an upflow anaerobic sludge blanket (UASB) reactor. Concentrations of ammonia nitrogen, organic nitrogen and BOD_5 in the waste are 150, 42 and 198 mg/L, respectively.

Nitrification and denitrification as well as carbon oxidation were achieved within a single-basin IACM reactor (with aeration on and off in cycles). A cycle time of 1 h was applied in the experiment. Methanol was used as a supplementary carbon source. Effects of F/M ratio, BOD_5/TKN ratio and aeration fractions (AF) on the removal efficiency of nitrogen were investigated.

The results show that two operating variables, F/M ratio and BOD_5/TKN ratio, are crucial to a successful removal of nitrogen by the IACM process. It was observed in the experiment that sludge could settle well only when low F/M ratios were applied. In order to supply adequate carbon for denitrification, the ratio of BOD_5/TKN in the influent should be high enough (at least 4.0) if the supplementary carbon source is to be added continuously. At the same time, however, the F/M ratio had to be low (around 0.1 g BOD_5/kg VSS.d) to maintain good settling of sludge. If the BOD_5/TKN ratio is too low, a poor nitrogen removal will occur even though the F/M ratio is low and sludge with good settling characteristics may develop. On the other hand, when a sufficient amount of carbon, i.e. high BOD_5/TKN ratio, is applied, bulky sludge may be experienced if the F/M ratio is not controlled to be low. The operation of the IACM process, therefore, should be designed in such a way that it not only provides adequate carbon source for denitrification but also keeps a low level of organic loading. For a waste with a high nitrogen concentration, such conditions imply that a long hydraulic retention (HRT), or a large volume of reactor is necessary.

A total of six AF values (1.0, 0.75, 0.50, 0.35, 0.20 and 0.10) were examined in the experiment. The maximum efficiency of nitrogen removal was achieved at AF's between 0.2 and 0.5. In general, more biomass could be maintained in the reactors at values of AF < 0.50. Under the condition that the values of BOD_5/TKN and F/M ratios were equal to 10 and 0.1, an efficiency of total nitrogen removal of 90% was achieved by the IACM reactors within the optimal range of AF values. Complete nitrification (NH_4-N $\approx$ 0 mg/L) could be accomplished even at low aeration fractions down to 0.2. This was attributable to the long HRT used in the operation. Under the condition of aeration fraction values higher than 0.5, a significant amount of NO_3-N was present in the effluent and denitrification was not well achieved.

Accompanying nitrification and denitrification in the IACM process was aerobic oxidation of organic carbon. Accounting for the external carbon loading attributed to the supplement of methanol, the IACM reactors were able to remove more than 98% of total BOD_5 and 82% of total COD at the optimal range of aeration fractions from 0.2 to 0.5. In general, COD and BOD_5 concentrations in the effluent tended to increase as the aeration fraction decreased below 0.5. Thus, less carbon was consumed at AF < 0.5 even though denitrification was more complete for 0.2 < AF < 0.5. This indicates that the aerobic oxidation of organics using oxygen as the electron acceptor was more dominant than anoxic oxidation of organics using nitrate as the electron acceptor. As a result, the effluent organics concentration would be lower if a longer period of aerobic environment is present in the process. Such observations are in line with the fact that oxygen has a higher oxidation potential than nitrate does.