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Use of Humic Acids to Enhance the
Removal of Aromatic Hydrocarbons
From Contaminated Aquifers.

By:

S. Lesage, H. Wu, K.S. Novakowski, S. Brown

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MANAGEMENT PERSPECTIVE

Title: USE OF HUMIC ACIDS TO ENHANCE THE REMOVAL OF AROMATIC HYDROCARBONS FROM CONTAMINATED AQUIFERS.

Author(s): Suzanne Lesage, Hao Xu, Kent S. Novakowski and Susan Brown.

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This project was completed last year and received funding from GASReP. The report describes the initial laboratory studies on the potential use of humic acids as an alternative to surfactants and the initial phase of the pilot scale remediation experiments conducted in AQUEREF on the dissolution of diesel fuel by the humic acids. During the course of the experiment, it was noted that biodegradation was occurring in the tank. This led to a second project on the effect of humic acids on bioremediation.

Next Steps:

The effect of humic acids on bioremediation also received funding from GASReP under a new project number. This study continues and is funded for another year.

**USE OF HUMIC ACIDS TO ENHANCE THE REMOVAL OF AROMATIC
HYDROCARBONS FROM CONTAMINATED AQUIFERS.**

Suzanne Lesage, Hao Xu, Kent S. Novakowski and Susan Brown.

Groundwater Remediation Project, National Water Research Institute, Environment
Canada, Burlington, Ontario, L7R 4A6

Report to GASReP

February 19, 1997.

Executive Summary

An approach commonly used to clean up groundwater contaminated by petroleum hydrocarbons, such as the polycyclic aromatic hydrocarbons (PAHs) involves pumping the water to the surface and then treating it. The low solubility of petroleum hydrocarbons in water and unfavourable hydrogeological conditions, however, limit the efficiency of this "pump and treat" method. Addition of surfactants to the groundwater has been shown to enhance the dissolution of hydrocarbons. However, the surfactants can interfere with bioremediation and may be toxic to aquatic organisms in groundwater discharge areas. Humic acids, naturally occurring in soils and groundwater, have a surface activity similar to that of surfactants and were considered as a potential environmentally suitable alternative to synthetic surfactants.

The objective of the present study was to examine how humic acids influence the behaviour of petroleum products in the saturated zone and to determine the potential for humic acid amendments to enhance the dissolution of aromatic hydrocarbons from diesel fuel.

A three-stage approach was selected:

1. Static dissolution experiments, using phenanthrene as a pure standard, to determine the effect of concentration and contact time.
2. Dynamic dissolution experiments, using diesel and gasoline fuels in small laboratory columns, to simulate contact between a stationary volume of fuel and aqueous solution of increasing humic acid concentrations.
3. Model aquifer experiments, conducted in a large stainless steel tank containing sand contaminated with diesel fuel, to assess humic acid (at 1g/L) and contaminant transport, and the effectiveness of the source dissolution process.

This project differs from most published studies in that diesel fuel was used as the source of the aromatic hydrocarbons. The solubility of PAHs obtained by contact of water with diesel fuel or oil is very different from that potentially obtained by dissolving the pure

crystalline standards. The solubility depends on the proportion of each compound in the petroleum mixture and on the efficiency of the contact between water and the petroleum product in the soil.

As water contacts a petroleum contaminated soil, a significant portion of the aromatic hydrocarbons are initially removed as a non-aqueous phase liquid (NAPL). However, a significant portion remains behind, adsorbed onto the aquifer material, or trapped between particles. The purpose of the addition of humic acids was to help dissolve this residual.

The results of the study show that:

- humic acids, in increasing concentrations, significantly increase the dissolution of aromatic hydrocarbons from petroleum fuel;
- a ten-fold increase in effective solubility was observed for trimethylnaphthalene;
- the efficiency of the humic acids decreases with increasing ionic strength and pH;
- humic acid transport is not significantly retarded by low levels of organic carbon and, as a result, most of the humic acid solution was recirculated;
- in the column experiments, a two-stage removal process was observed: (1) an initial rapid phase as NAPL droplets; (2) a slower phase where dissolution was predominant;
- in the model aquifer experiment, no NAPL movement was observed, because the emplaced diesel source was designed not to exceed the sand holding capacity;
- unlike surfactants, humic acids were found to enhance dissolution even below their critical micelle concentration;
- the sodium humate used in the experiments cost \$860 for 10,000 L. The same amount of solution could be obtained for approximately \$50, by using peat moss as a source of humic acids; and
- evidence suggests that biodegradation of the PAHs occurred in the tank, thus alleviating the need for further treatment of the effluent.

The study concludes that humic acid amendments are a cost-effective method of enhancing the dissolution of PAHs from a diesel source. Humic acid can be recovered and recirculated for conservation and cost savings. The biodegradation observed required further assessment in order to be able to determine its limiting factors. Such a study has been initiated and is also funded by GASReP. These initial results are encouraging and it is recommended that the results be further validated by field testing.

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1.0 INTRODUCTION

Contamination of subsurface aquifers by gasoline and diesel fuels is a serious environmental problem in Canada. Polynuclear aromatic hydrocarbons (PAHs) in gasoline and diesel fuels are of particular concern because many of them are carcinogenic and they are persistent. Aromatic hydrocarbons can represent up to 60 % of diesel fuels (Block et al., 1991).

Despite the development of alternative approaches, pump and treat continues to be the leading method for the remediation of groundwater contaminated by gasoline and diesel fuels. The efficiency of this technique is however limited by the low solubility of the aromatic hydrocarbons, especially the PAHs. To improve the chemical dissolution process, surfactants, such as sodium dodecylsulfate, ethoxylated alcohols, alkylethoxylates, etc., are often injected into the contaminated aquifers. The use of synthetic surfactants, however, may have a negative impact on the aquifer (Lewis, 1991). For example, alkylethoxylates are toxic in the mg/L range to a variety of aquatic organisms. Surfactants may also interfere with the biodegradation of the petroleum hydrocarbons (Rouse et al., 1994). In addition, those surfactants that are biodegradable may cause excessive bacterial growth and clogging of the aquifer. Humic acids (HA), which are intrinsic to soil and groundwater and have surface activity similar to that of surfactants, may provide an environmentally suitable alternative to synthetic surfactants in the remediation of soil and groundwater contaminated by petroleum products.

The influence of humic substances on the solubility and mobility of aromatic hydrocarbons and other organic contaminants has been the subject of numerous studies. The aqueous solubility of hydrophobic organic contaminants has been observed to increase in the presence of the dissolved humic substances (Carter and Suffet, 1982; Chiou et al., 1987; Johnson-Logan et al., 1992; Johnson et al., 1993; McCarthy and Jimenez, 1985; Shinozuka et al., 1987; Webster et al., 1986). The binding of PAHs by humic substances increased with

the decrease of solution pH and ionic strength (Schlautman and Morgan, 1993) and the partitioning coefficients (K_{oc}) of the hydrophobic organic contaminants were strongly correlated with the degree of polarity and aromaticity of the humic substances (Chiou and Kile, 1994; Gauthier et al., 1987; Xing et al., 1994). Backhus and Gschwend (1990), concluded that the presence of humic substances (<40 mg C/L) would double the mobile load of hydrophobic pollutants such as benzo[a]pyrene or perylene, but will have little effect on the mobility of less hydrophobic pollutants.

The objective of this study was to investigate the influence of HA on the removal of aromatic hydrocarbons from petroleum products in groundwater aquifers and to evaluate the potential use of HA, as a cost effective additive, in groundwater and soil remediation. In contrast to most published studies, diesel fuel and gasoline were used as a source of the aromatic hydrocarbons and the experiments were conducted with a large concentration range of HA, different pH and ionic strengths. To simulate common remedial practice, the effects of HA were studied at two different stages: the initial flush and residue cleanup. The elution efficiency and mechanisms involved are also discussed.

In order to prove the feasibility of using HA in the field, a pilot scale experiment was conducted. One of the reasons that few field-scale experiments have been reported is that environmental authorities are increasingly reluctant to allow controlled spills followed by a treatment that is yet to be proven effective. In order to test new technologies at near field scale, a model aquifer with a very dense monitoring network was constructed, providing controlled conditions only possible in a semi-artificial system. The physical aquifer model was designed and installed at the National Water Research Institute of Environment Canada in Burlington in the newly created Aquatic Ecosystem Restoration Evaluation Facility.

2.0 LABORATORY EXPERIMENTS

2.1 Introduction

Before undertaking a large scale experiment, the behaviour of HA solutions of different concentrations and under various pH and ionic strength conditions was studied in laboratory columns. The influence of HA concentrations (0, 40, 400 and 800 mg/L), pH (5, 6, 7, 8, 9.5) and ionic strength (0, 0.01, 0.05, 0.1 M) were evaluated. Small scale columns have the advantage of allowing several different experiments with replicates to be conducted in a relatively short time. Preliminary results have been reported (Xu et al., 1994).

2.2 Materials And Methods

2.2.1 Materials

2.2.1.1 Aromatic compounds. Diesel fuel (provided by Imperial Oil of Canada Ltd.) and gasoline (unleaded) were used as sources of PAHs and BTEX (standing for benzene, toluene, ethylbenzene and o-, m- and p-xylenes) in most of the experiments. They were selected as more representative of real life situations, because the solubility of aromatic compounds obtained by contact of water with petroleum products is very different than that potentially obtained by dissolving the pure standards. The solubility of aromatic compounds depends on the mole fraction of each compound in the petroleum mixture and is therefore different for every fuel or gasoline. The concentration of aromatic hydrocarbons in the diesel fuel sample were measured by GC/MS and HPLC. The results are shown in Table 1, with their solubility as pure standards.

The aqueous solubility of pure phenanthrene (Supelco Canada, Oakville ON), as a function of HA concentration, was also studied.

2.2.1.2 Humic substances A soil HA (sodium humate; Aldrich, Milwaukee WI, USA) was dissolved in Milli-Q water (Waters/Millipore purification system, Mississauga, ON), centrifuged at 10,000 RPM for 30 minutes, further diluted to 40 to 4,000 mg/L and then filtered with 3.0 μm or 0.45 μm pore size of filters.

2.2.1.3 Solid phase Sep-Pak^R cartridges packed with silica (1.0 cm x 2 cm; Waters/Millipore, Mississauga ON) were selected as solid phase because quartz silica is one of the most common geological materials in groundwater aquifers. Silica is non-sorptive and the cartridges are relatively uniform, which is ideal for the study of the dissolution process. The same type of silica was also employed for column studies.

All other chemicals were analytical grade and used without further purification.

Table 1. The content of aromatic hydrocarbons in the diesel fuel sample and aqueous solubility for the pure standards.

Aromatics	%(Wt.) ^a	Mole % ^a	Solubility (mg/L) ^b
Benzene	0.00	0.00	1800*
Toluene	0.13	0.32	524*
Ethylbenzene	0.18	0.39	206*
m+p - Xylenes	0.89	1.90	173*
o - Xylene	0.30	0.64	200*
Trimethylbenzenes	0.93	1.76	48*
C ₁ - Naphthalenes ^c	2.89	3.92	25**
C ₂ - Naphthalenes ^c	10.96	13.53	2.5**
C ₃ - Naphthalenes ^c	5.85	6.64	2.1**
C ₄ - Naphthalenes ^c	1.71	1.79	? ^d
Phenanthrene	0.31	0.34	1.1**
C ₁ - Phenanthrenes ^c	0.60	0.60	0.3**
Total	24.75	31.83	-

^a Measured by GC/MS and HPLC;

^b From literature:

* Montgomery, J.H., 1990 and 1991;

** IUPAC, 1989.

^c C₁, C₂, C₃, and C₄ designate mono-, di-, tri-, and tetramethyl substituted PAH, respectively.

^d Solubility data are not available.

2.2.2 Experimental procedures

2.2.2.1 Batch experiments The apparent aqueous solubility of phenanthrene was studied in batch experiments. A solution of 20 µg of phenanthrene in 100 µL of dichloromethane was added to a test tube and the dichloromethane was evaporated in a fume hood. Solutions (4 mL) with different concentrations of HA were added to individual test tubes. This ensured that more phenanthrene (5 mg/L) was present than necessary to generate a saturated solution.

The tubes were then placed on a shaker at room temperature and sampled at 15 minutes, 3 hours, 1 day, 5 days and 36 days. The undissolved solute was separated by centrifugation (3,200 RPM x 30 minutes) or filtration (0.45 μ m) and the supernatant was analysed by HPLC.

2.2.2.2 Column studies Effects of HA on the removal of aromatic hydrocarbons were studied using a miniature column (Sep-Pak^R, silica) to simulate the contact between a stationary volume of diesel fuel or gasoline and a flow of water with different concentrations of HA (0, 40, 400, 600 and 800 mg/L), pH values (5 to 9.5) and ionic strengths (0.01 to 0.1 M). In each experiment, 40 μ L of diesel or 30 μ L of gasoline were injected into the cartridge and aqueous solutions were passed through the cartridge at a flow rate of 0.3 mL/min. Eighty milliliters (in 10 mL fractions) of effluent from the cartridge were collected for the analysis of PAHs and BTEX.

A similar experiment was also conducted using a glass column (1.8 cm x 7.0 cm). Silica (4 g) was soaked into 20 mL of dichloromethane containing 40 μ L of diesel fuel. After the evaporation of dichloromethane the silica coated with the diesel fuel was packed into the column (only about 2/3 of the column was filled) and the rest of the column was filled up with uncoated silica. The column was flushed initially with Milli-Q water (2.4 L) and the removal of PAHs in the diesel residue was studied under different pH values, ionic strengths and in the absence and presence of HA.

2.2.3 Analytical methods

2.2.3.1 PAHs The analysis was conducted using a high pressure liquid chromatograph (HPLC model 600E; Waters/Millipore, Milford, USA) equipped with a fluorescence detector (model 470) and a photodiode array detector (Waters). Different PAHs were separated on two C₁₈ columns (3.9 mm x 15 cm) connected in series, using a linear gradient

program. The mobile phase was initiated with a 60 % acetonitrile-water mixture that was changed to 80 % of acetonitrile over 5 minutes and maintained at this ratio for 28 minutes.

2.2.3.2 BTEX The column effluents were analysed for BTEX by purge-and-trap GC/MS. One to ten mL samples, were diluted to 40 mL with Milli-Q water and injected by a PTA autosampler (Dynatech) to a purge cell of an Unacon model 810 purge-and-trap (Envirochem, Unacon) which was interfaced to the GC/MS (Hewlett-Packard, 5890-5970). The BTEX were then separated by a DB-624 fused silica capillary column (J&W, 30 m, 0.32 mm i.d., 1.8 μ m film thickness). The oven temperature of the gas chromatograph was increased from -15 °C to 35 °C at a rate of 10 °C/min and to 135 °C at 4 °C/min.

2.3 Results and Discussion

2.3.1 Static Dissolution (Batch, Pure Standard)

Batch experiments were performed to supply information on the apparent aqueous solubility of phenanthrene in relation to contact time and the concentration of HA. Figure 1 shows that the solubility of phenanthrene increased with the increase in contact time and HA concentration. The solubility of phenanthrene from the present study was lower (0.45 mg/L) than that (1.1 mg/L) from literature (Table 1). This is because this experiment was conducted in a solution with higher pH and ionic strength (pH 8, I 0.05 M), which are more representative of groundwater conditions. The equilibrium was reached in one day in the absence of HA and with 40 mg/L HA. In the presence of increasing HA concentrations, the concentration kept increasing. This implies that several mechanisms may be involved in the dissolution of phenanthrene by HA. Slow sorption kinetics on soil have been observed and are attributed to diffusion (Pignatello and Xing, 1996).

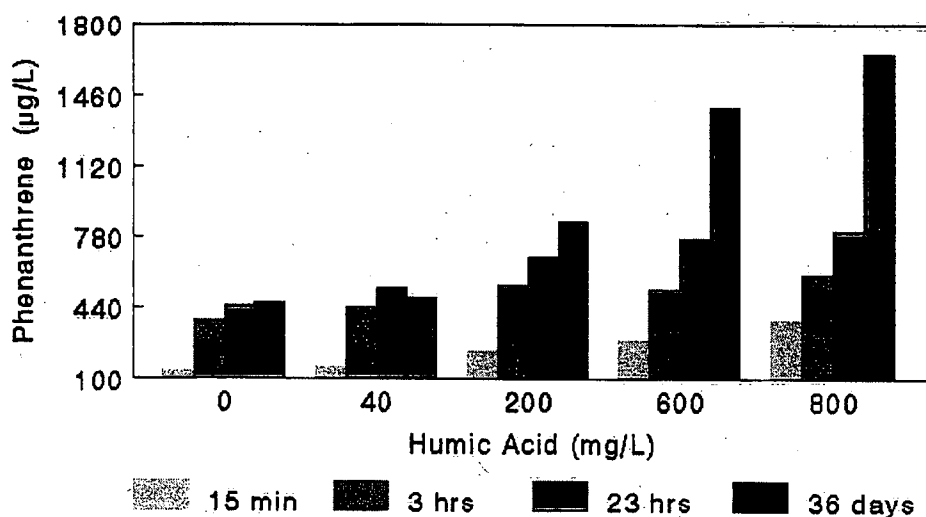


Figure 1. Apparent aqueous solubility of phenanthrene as a function of contact time and humic acid concentrations(pH = 8, I= 0.05).

The relationship between the apparent solubility of phenanthrene and the concentrations of HA is shown on the same figure. Evidently, HA increased the solubility and this effect was linear at HA concentrations from 40 to 800 mg/L. The presence of 800 mg/L of HA, resulted in a 3-fold increase in apparent solubility. This agrees with a previous study by Chiou and coauthors (1987), in which a linear relationship between HA (0 to 100 mg/L) and the solubility of DDT and PCBs was reported.

2.3.2 Dynamic Dissolution (Columns, Petroleum)

Unlike crude oil or other petroleum products, gasoline and diesel fuels are light and have low viscosity. In the absence of sorption by soil organic carbon, only a fraction of the oil remained trapped as residual. Therefore, the results are discussed as two stages: the initial flush and the residue cleanup. In the first stage, more than half of the gasoline and diesel fuels are eluted as a non-aqueous phase, possibly as emulsions or micelles, where the aromatic hydrocarbons can be removed either with the non-aqueous phase or dissolved in the

aqueous phase. After several pore volumes, only one phase (the aqueous phase) is present in the effluent and the aromatics are removed solely by dissolution.

2.3.2.1 Initial flush. During the initial flush, three groups of PAHs were detected. They were monomethylnaphthalenes, dimethylnaphthalenes and trimethylnaphthalenes. The concentration of naphthalenes from diesel fuel as a function of the volume of water eluting the column is shown on Figure 2. In general, the concentration of naphthalenes decreased as the volume of water increase. Higher concentrations of methylnaphthalene than di- and

trimethylnaphthalenes were observed in spite to the fact that it was present in lower concentration in the diesel (Table 1). The theoretical concentration of a given solute dissolved from a mixture is proportional to its mole fraction in the mixture and its aqueous solubility.

The higher aqueous solubility of methyl

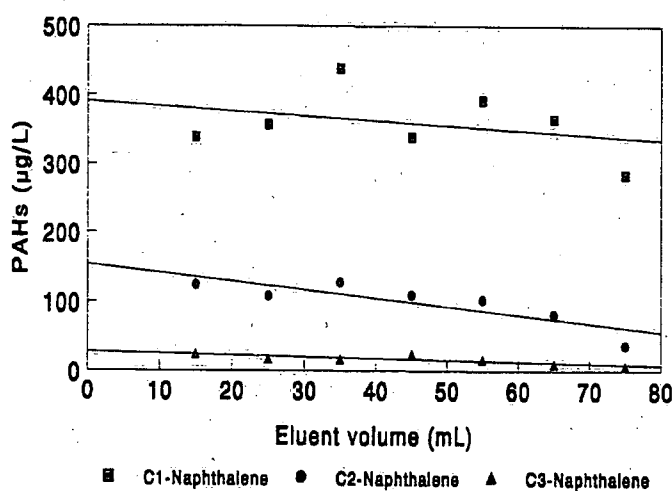


Figure 2. Dissolution of PAHs from diesel fuel ($HA = 0$, $pH = 8$, $I = 0.05$).

naphthalene (25 mg/L compared to 2.5 and 2.1 mg/L; Table 1) results in a relatively higher concentration. No reliable measurement could be obtained in the first 10 mLs of eluent because of the presence of an emulsion. This initial phase was very short and it would seem that from 15 mLs onward, while still in initial phase, the aromatic compounds were mainly present as dissolved components.

The effect of HA concentrations on the dissolution of PAHs is shown on Figure 3. The HA increased the removal of methylnaphthalenes from the diesel fuel sample. The

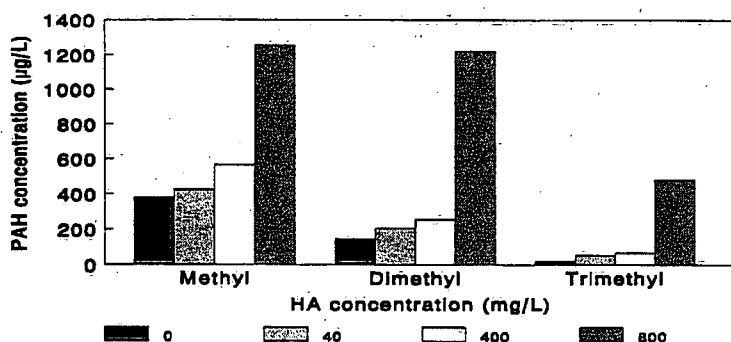


Figure 3. Effect of humic acids on dissolution of methylnaphthalenes from diesel.

to occur at at least ten times the concentration (7.4 g/L, Guetzloff and Rice, 1994). A possible explanation is that the dissolution in this case is not a true dissolution but a partitioning between two phases, the diesel and the HA.

The effect of solution pH on the dissolution of the methylnaphthalenes is illustrated on Figure 4. At a constant ionic strength (0.05 M) and in the presence of 400 mg/L of HA, the removal of the methylnaphthalenes decreased with increasing pH. The concentration of the monomethylnaphthalenes in the effluent was about twice as high at pH 5 than at pH 9.5.

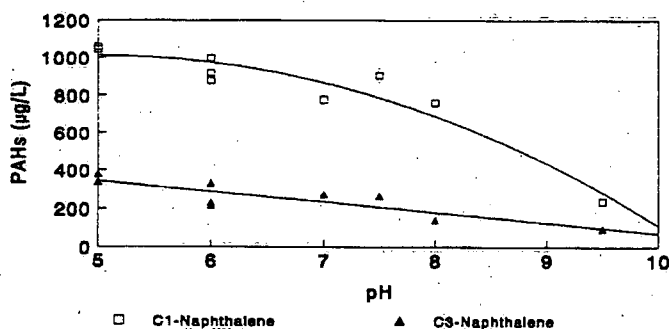


Figure 4. Dissolution of PAHs from diesel as a function of pH (HA = 400 mg/L, I = 0.05 M).

concentration of naphthalenes was found to increase with increasing HA concentrations, but the correlation was not linear. This cannot be attributed to the presence of a micellar phase, because it is known

This is because an increase in pH progressively deprotonates HA molecules but has little effect on the aqueous activity coefficient of nonpolar, non-ionizable PAH molecules. Deprotonation increases the polarity of HA, alters

its structure, decreases its ability to bind the PAHs, and thereby reduces its solubilization power. The result is consistent with an earlier study on fulvic and HA from Suwannee River using pure PAH standards (Schlautman and Morgan, 1993).

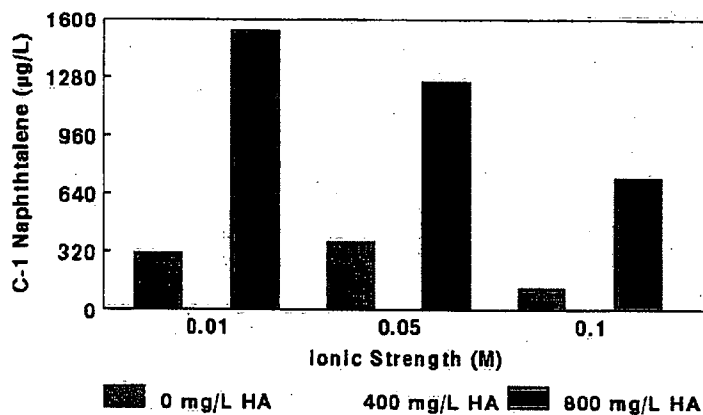


Figure 5. Elution of PAHs as a function of ionic strength and humic acid concentration (C-1 naphthalenes, pH = 8).

As shown on Figure 5, the dissolution of methylnaphthalenes decreased with increasing ionic strength from 0.01M to 0.1M at pH 8. At fixed pH values, increase in electrolyte concentrations are expected to increase the activity coefficient of PAHs and to salt them out of solution. A more pronounced effect was observed at higher HA concentration (800 mg/L), implying that the electrolyte concentration not only affects the activity coefficients for PAHs, but also affects the behaviour of HA in solution.

The effect of HA on the dissolution of BTEX from gasoline was also studied (results not shown). Enhancement of the aqueous solubility by HA was different for different aromatic compounds. HA had little effect on the dissolution of benzene and toluene, some effect on ethylbenzene and o-xylene but a more substantial effect on trimethylbenzene and diethylbenzene. This follows the trend observed with surfactants, whereby the most soluble compounds are the least affected.

3.2.2 Residue cleanup

It is usually more difficult to clean the residue than the initial contamination of petroleum because the residue contains the components that the least water soluble and have been strongly adsorbed by soil. Figure 6 illustrates the elution of PAHs

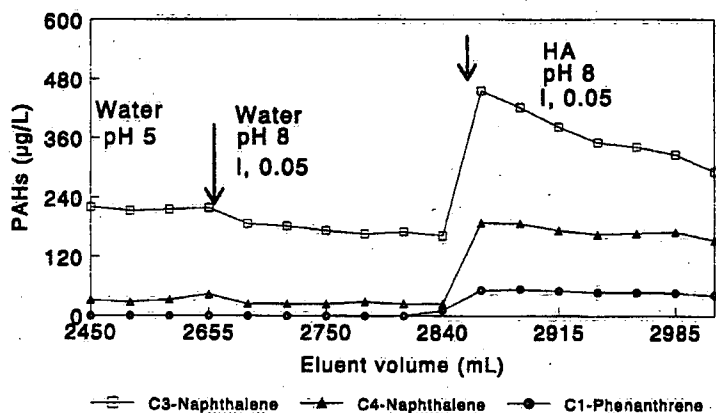


Figure 6. Dissolution of PAHs from diesel residue.

from the diesel residue after several hundred pore volumes of water were passed through the column. After 2500 mLs of water had passed, trimethylnaphthalenes were the dominant species in the effluent, because the source was depleted of the more soluble methylnaphthalenes and dimethylnaphthalenes. Changes of the eluent pH (from 5 to 8) and ionic strength (from 0 to 0.05 M) after 2650 mLs, slightly reduced the elution of the methylnaphthalenes. HA (800 mg/L) markedly enhanced the dissolution of tri-(C3) and tetramethyl-(C4)-naphthalenes. Methylphenanthrenes, that have very low aqueous solubilities (0.3 mg/L for 1-methylphenanthrene; Montgomery, 1991) and which were below detection limit in the aqueous effluent, were dissolved by the addition of HA.

2.4 Conclusion

HA can enhance the removal of aromatic hydrocarbons from diesel fuel and gasoline. This process can be divided into two stages, i.e., the initial flush and the residue cleanup. In the first stage, the aromatic hydrocarbons are flushed out with the non-aqueous phase or

dissolved in the aqueous phase. HA can increase the flush efficiency by increasing the aqueous solubility of aromatic hydrocarbons, or by other mechanisms, such as formation of emulsions. The efficiency of removal of the aromatic hydrocarbons from diesel fuel is positively related to the concentration of HA. It is also influenced by the solution ionic strength and pH. When only residual fuel is left, the dissolution of aromatic hydrocarbons in the aqueous phase is the only important process. The concentration of HA is a more important factor in the dissolution of aromatic hydrocarbons than solution ionic strength and pH.

It is interesting to note that HA can increase the removal of PAHs at a concentration level as low as 40 mg/L. In the initial flush stage, the presence of 800 mg/L HA tripled the amount of PAHs removed compared to water only. In the residue cleanup stage, the enhanced dissolution depends on the individual compounds and the effect is largest for the least soluble compounds.

3.0 MODEL AQUIFER

3.1 Introduction

Although most injection/withdrawal technologies involving the addition of surfactants can be made to work in the laboratory, this does not guarantee success in the field. Many field failures are attributed to aquifer heterogeneity, but because field sites are difficult to control, the reasons for failure often cannot be investigated in detail. For this reason, a model aquifer of moderate scale with a dense monitoring network was built, providing field-scale, yet controlled, conditions, only possible in a semi-artificial system. Few studies have been published on the movement of dissolved humic material in aquifers (McCarthy et al., 1993; Rutherford et al., 1992), and these were dealing with low concentrations of naturally occurring HA. It was therefore important to study the movement of the HA in the sand in the presence and absence of the contaminants.

3.2 Methods

3.2.1 Tank Design

Some model aquifers are in fact large scale columns where vertical transport of contaminants are measured (Facility for Indoor Aquifer Testing - FIAT-, National Hydrology Research

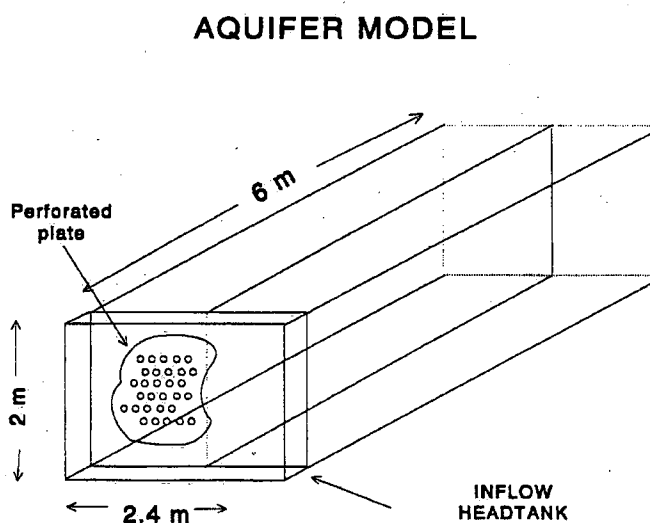


Figure 8. Schematic outline of the tank.

		1	2	3	4	5	6	7	8	9	10	
C	A	■	■	■	■	■	■	■	■	■		
	B	■	■	■	■	■	■	■	■	■	■	W
	C	■	■	■	■	■	■	■	■	■	■	●
	D	■	■	■	■	■	■	■	■	■		
T	D	■	■	■	■	■	■	■	■	■		
	C	■	■	■	■	■	■	■	■	■	■	W
	M	■	■	■	■	■	■	■	■	■	■	●
	B	■	■	■	■	■	■	■	■	■	■	
	A	■	■	■	■	■	■	■	■	■		

Figure 8. Monitoring well numbering (top view). Control (C), Treatment (T), Source (S) and Withdrawal Wells (W).

indoor contained alternative to the isolated cells which have been used in the field at Canadian Forces Base Borden by the University of Waterloo to assess contaminant transport and novel remedial technologies. Similar physical models exist at the US EPA R.S. Kerr Laboratory in Ada, Oklahoma. Theirs are made of glass and are mostly dedicated to groundwater transport and geophysics.

The tank was made entirely of 1/4" industrial grade stainless steel (rectangular 2.4 m x 6 m x 2 m deep) with an external support structure made of steel beams. Water was introduced in a head tank separated from the soil filled portion by a perforated plate such as not to impede water flow (Figure 7). Further technical details about the design are provided in Appendix (7.1) and in proceedings (Lesage et al., 1995).

3.2.2 Setup

The monitoring wells, consisting of 79 bundles of five tubes (3 mm; nominal 1/8" o.d.) terminating at different depths, with a stainless steel porous cup at the end, were suspended from a wooden grid at the preset intervals of 30 cm, (depth and length) and 25 cm

Institute,
Environment
Canada,
Saskatoon). For
this study, it was
decided to build
a rectangular
column to
measure
horizontal
transport. This
design is an

suspended from a wooden grid at the preset intervals of 30 cm, (depth and length) and 25 cm (width). In addition, withdrawal wells (5 cm i.d., 10 cm o.d. with their own packing and screened over their whole length) were installed in each side of the tank . Details of the monitoring system are shown on Figure 8. A medium to coarse mixed sand was obtained from a local sand and gravel supplier (particle size 0.6 μm - 2.4 mm). Further details on filling the tank can be found in Appendix 7.2.

3.2.3 Tracer tests

The hydraulic properties of the tank were determined by conducting a tracer test using lissamine, as a fluorescent tracer, and sodium bromide as a conservative tracer. Over 5,000 samples were collected and analysed for lissamine (by fluorescence) and for bromide (by conductivity). The details can be found in Appendix 7.3.

3.2.4 Emplacement of the Source

The results of the tracer test were used to decide on the optimal placement of the source. Because the main goal of this experiment was to cleanup petroleum present at residual saturation in the saturated zone, it was necessary to devise a method of introduction that would provide a well defined source in terms of both mass and geometry. Indeed, it would be difficult to monitor the movement and the changes of petroleum concentration if the concentration was not even across the monitoring well. Based on the results of the tracer test, it was decided to place a rectangular source centered at depth 4, facing rows B and C. Five additional monitoring wells (labelled M) were added in the center of rows B and C (Figure 8). The holding capacity of the sand was determined in a column experiment and it was found that 500 mL of diesel could be held by 20 kg of sand. Technical detail on the emplacement of the source can be found in Appendix 7.4.

3.2.5 Addition of Humic Acid

HA was obtained as the sodium salt (Aldrich Chemicals, Milwaukee, WI) and prepared as a solution using tap water at a concentration of 1 g/L. The resulting pH was 8.5. Initially a concentrate was added to the head tank to the same concentration such as to provide a well-defined concentration gradient. The effluent was discharged to the bay (through a charcoal filter for the treatment side) until a constant concentration of HA was obtained at the withdrawal wells. The effluent was then collected and recirculated. A HA concentrate was added through a metering pump to make up for losses on the charcoal filter.

3.3. Results

3.3.1 Tracer Test

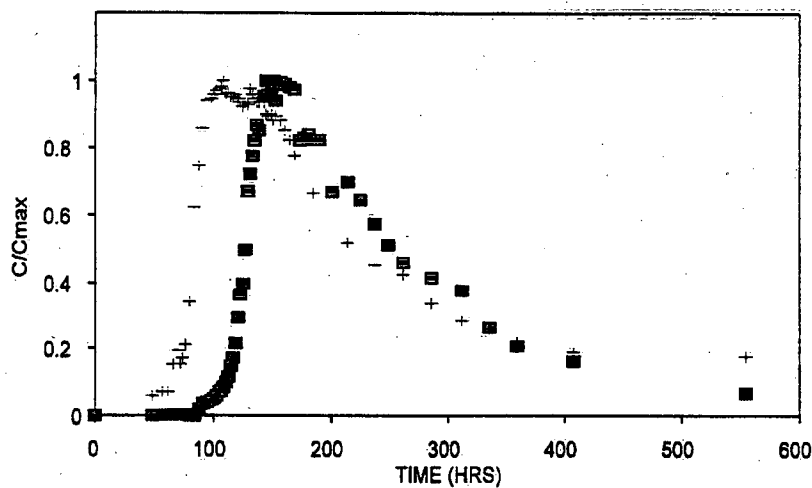


Figure 9. Example of the tracer test at C6B4. Elution curves for bromide (+) and lissamine (■).

interactions with particles of sand or clay. Only inorganic salts such as bromide are truly conservative, but electrode measurement, either with an ion selective electrode or by measuring conductivity are much more time consuming. The sand that was used here has a

Lissamine is often used as a tracer in hydrogeology because it is a highly fluorescent compound which can be measured rapidly. It is not entirely conservative and will sorb to organic carbon. It can also form some ionic

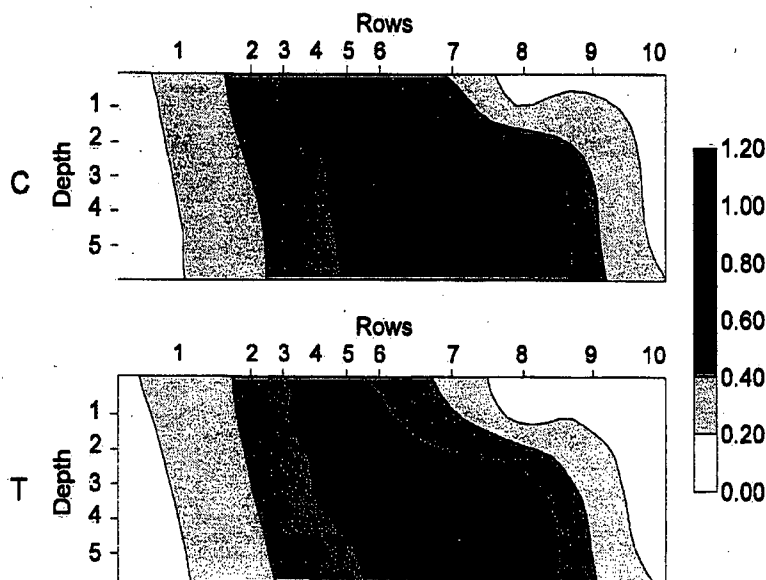


Figure 10. Contour plots of lissamine concentration (mg/L) at 310 hours for the control (C) and treatment side (T), at row B.

relatively low percentage of organic carbon, but nonetheless some sorption could be seen. From comparative breakthrough curves, a retardation factor of 1.3 was measured for lissamine with

respect to bromide (Figure 9). Knowing that the sand that was used has less than 0.1% or organic carbon, this retardation is most likely due to ionic interactions.

Interpretation of the tracer experiment yielded estimates of the transport properties of the aquifer material. As can be seen in a vertical contour (adjacent to the centre line) of the concentration of lissamine at 310 hours (Figure 10), the groundwater velocity was slower in the upper part of the tank. This effect is probably attributable to the presence of the capillary fringe and the free-surface at the head tank end. There were also differences between the breakthrough of the tracer between the control and treatment sides, but this difference was not as significant as that between different levels.

3.3.2 Modelling

Estimates of the longitudinal dispersivity and porosity of the sand were obtained by interpreting breakthrough concentrations of bromide from selected sampling points. This was

accomplished using a one-dimensional transport model (Novakowski, 1992) which accounts for an exponentially decaying source in the head tank and assumes the aquifer to be of semi-infinite extent. The governing equation is based on simple advection-dispersion and a third type boundary condition (decaying source) is employed at the interface between the head tank and the aquifer material. The model was formulated using dimensionless variables which incorporate the retardation factor directly. Interpretation of the breakthrough curves was conducted under the further assumption that the bromide tracer behaved conservatively during transport. To reduce the potential for boundary influences, the breakthrough curves selected for modelling were chosen from sampling points located close to the centre line of the tank and away from the withdrawal well and the head tank. The concentration profiles were then corrected for background and normalized to the initial bromide concentration in the head tank. Modelled fits to the concentration data were obtained by adjusting the independent parameters, longitudinal dispersion and porosity, and determining the average linear velocity from the pumping rate and specified porosity.

Modelling of the concentration profiles for bromide at four sampling locations indicated a longitudinal dispersivity of 0.005-0.015 m, a porosity of 28-32% and an average

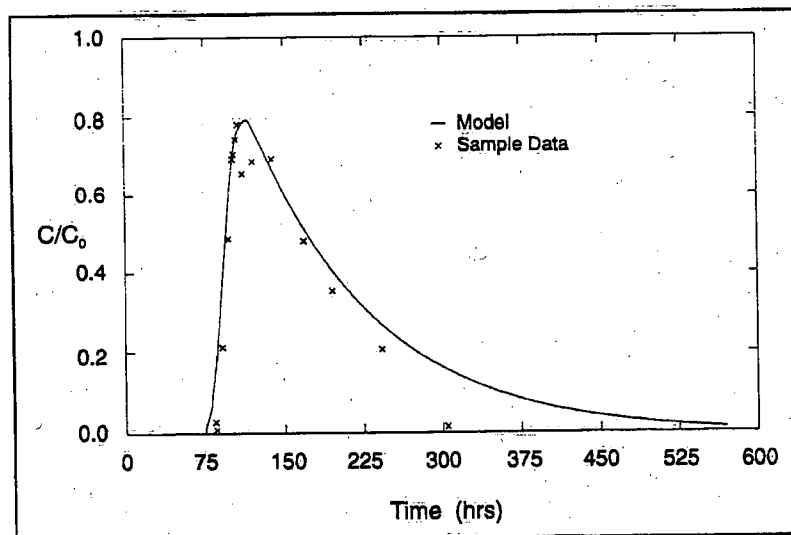


Figure 11. Model fit to a bromide breakthrough curve obtained at C6B4 (depth of 1.2 m, 2.0 m down-gradient from the head tank).

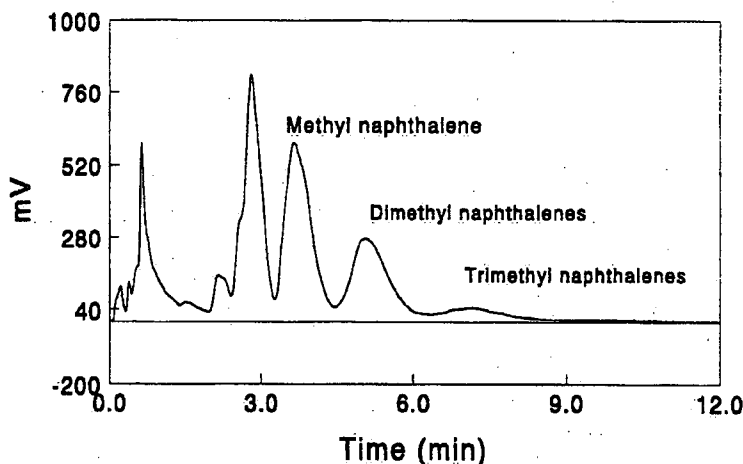
linear-velocity of 0.020-0.022 m/hr. A typical modelled fit is presented in Figure 11 for a sampling point at a depth of 1.2 m, 2.0 m down-gradient from the head tank. The porosity values determined from the modelling results are consistent with

independent determinations. Also the values for the longitudinal dispersivity suggest that the influence of macroscopic dispersion is negligible for this material.

It was necessary to determine the transport properties of the aquifer material prior to conducting the first experiment with petroleum, so that the differences in transport rate would not be attributed to changes in porosity due to the presence of the petroleum. The results were also used to direct the placement of the contaminated source. Although more difficult to achieve, it was determined that the source should be placed at 1.45 m, so that an even velocity field would be experienced.

3.3.3 Chemical Analysis

Monitoring the tank required a very large number (>1000) of analyses. It was initially thought that Total Petroleum Hydrocarbon (TPH, U.S. EPA Method 418.1) analysis with an Infra-Red (IR) detector would be a suitable surrogate parameter and that selected samples would be analysed by HPLC for PAHs. Preliminary tests showed that because TPH requires the extraction of the sample in a solvent such as CFC-113 it would be in fact more labour intensive than direct injection into the HPLC. Also, the fluorescence detector is orders



of magnitude more **Figure 12.** HPLC chromatogram of the diesel plume at T5B4.

sensitive than the infra-red detector commonly used for TPH, allowing the analyses to be done without sample pre-concentration.

The analysis for the full range of PAHs typically require solvent programming and approximately 45 minutes per sample. Because diesel fuel contains mostly methyl naphthalenes and phenanthrenes, they could be grouped together by using a much shorter column and an isocratic system, allowing us to get an analysis in 15 minutes. The other advantage of the system is that it allows for the simultaneous monitoring of the HA. A typical chromatogram is shown on Figure 12.

3.3.4 Diesel Plume

During the emplacement of the source, there was concern that some residual diesel fuel might float as an undissolved phase as the water table rose. To determine whether this occurred, the wells in the vadose zone were monitored for BTEX using headspace analysis and for PAHs by HPLC. BTEX and PAHs were found only in level four monitoring points, none above or below, clearly indicating that NAPL movement did not occur (Figure 13). A similarly-shaped plume of BTEX was also found moving ahead of the PAHs. This is further evidence that the aromatic hydrocarbons were only transported in the dissolved phase. Had

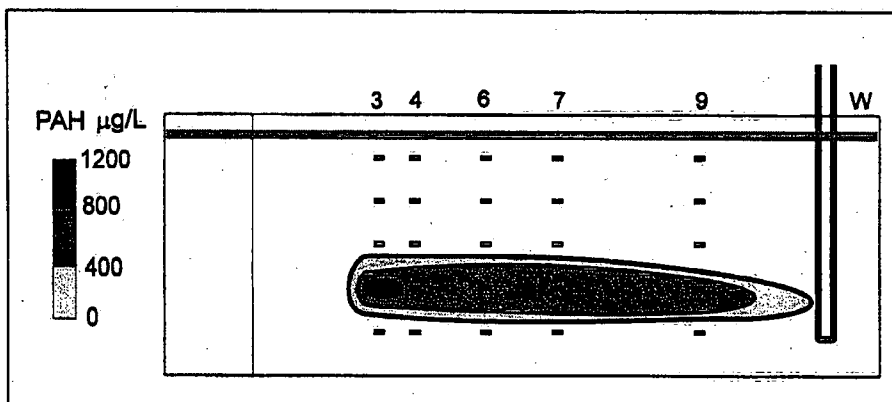


Figure 13. Cross-section of the PAH plume at 141 days.

t h e
c o m p o u n d s
b e e n
t r a n s p o r t e d
a s
N A P L
d r o p l e t s ,
t h e
v o l a t i l e
h y d r o c a r b o n s
a n d
P A H s

would not have been separated spatially with time. The proportion of individual components in the mixture would be identical at T4M, T7M and T8M (Figure 14).

There was also evidence of biodegradation of the volatile hydrocarbons. In spite of all the efforts to remove oxygen by sparging the incoming water with nitrogen and the fact that no nutrients were added, the concentration of volatiles decreased in

the aqueous samples. No bacteria were added, but natural soils are never sterile. These losses could not be attributed to sorption, because, as can be seen in Figure 14, toluene and ethylbenzene, the more water soluble compounds, disappeared the fastest. Volatilization was unlikely because the samples were all from the saturated zone at a depth of 1.2 m, where no gas phase was present. It also seems that o-xylene was depleted preferentially compared to the meta and para isomers.

3.3.5 Humic Acid Transport

One of the crucial parameters for the success of the application of HA as a treatment is its mobility in the subsurface in a variety of geologic media. Sorption of an organic solute to soil is related to the fraction of organic carbon in the soil. In the presence of soil organic carbon, organic contaminants partition themselves between water and the carbon on the soil particles. The retardation factor R_f is a measure of how much slower a solute is transported compared to groundwater:

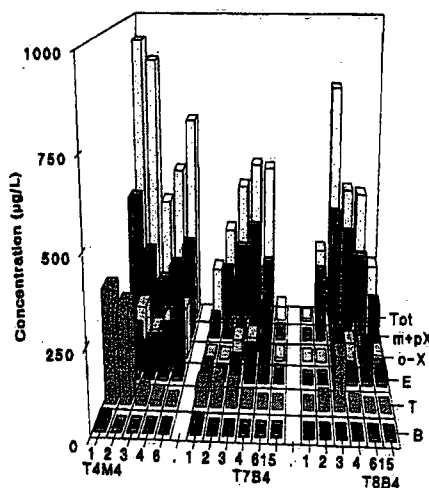


Figure 14 Change in the concentration of BTEX with time (weeks) at three monitoring points.

$$V_c = \frac{V_{GW}}{R_f} = \frac{V_{GW}}{1 + (\rho_b K_p / n)} \quad (1)$$

where V_c is the velocity of the solute and V_{GW} the groundwater velocity, ρ_b is the bulk density of the granular medium (g/mL), K_p is the partition coefficient (mL/g) and n is the porosity (dimensionless) (Freeze and Cherry, 1979). The partition coefficient K_p is the ratio of the mass of solute per unit mass of the soil to which it is sorbed, to the mass of solute per volume of solution (units reduce to mL/g). It can be related to the octanol/water partition coefficient (K_{ow}) and the fraction of organic carbon (f_{oc}) (Schwarzenbach and Westall, 1981):

$$\log K_p = 0.72 \log K_{ow} + \log f_{oc} + 0.49 \quad (2)$$

Therefore, at a known organic carbon content, if the $\log K_{ow}$ of a compound is known, its retardation factor can be estimated using a combination of equations 1 and 2.

In the case of HA, the octanol water partition coefficient isn't known. Also, because it is a mixture of compounds, a range of values rather than a single value would be obtained. In this case, estimating the retardation factor could entail a very large error. It was therefore more appropriate to obtain experimental data in a few types of soils from which expected behaviour could be predicted. To mimic organic carbon, an organic shale was ground and placed in a column with glass beads to a concentration of 0.5 and 1%. No retardation was observed with respect to bromide. This would support the hypothesis that little sorption of HA to organic carbon occurs at a pH of 8. Approximately 10% was lost by sorption onto the granular activated carbon that was used to treat the effluent.

An alternate technique was therefore used to estimate the organic content of the sand. Because diesel had been traveling through the tank for several weeks and the octanol-water partition coefficient for toluene and xylenes are well known, their retardation factors were used to estimate the organic content of the sand, using equations 1 and 2 above. It was estimated that the sand contained less than 0.002% organic carbon and hence HA would not be significantly retarded if hydrophobic interactions prevailed.

flow rates were controlled by individual peristaltic pumps which were adjusted everyday. In spite of that, small differences in



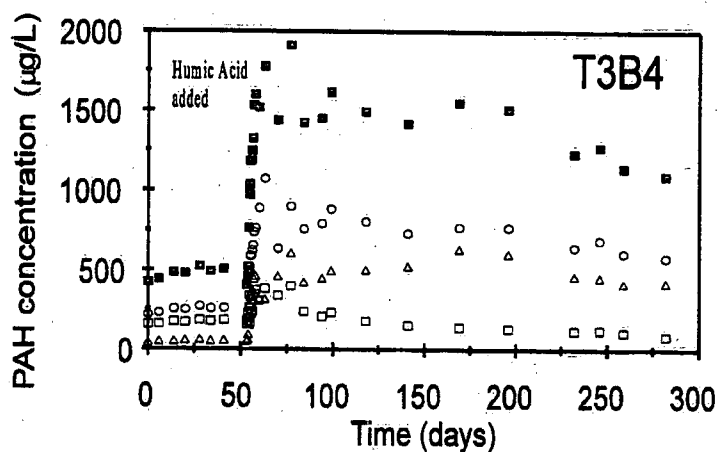


Figure 16. Effect of humic acid on methyl \square , dimethyl \circ and trimethyl \triangle naphthalene concentrations (\blacksquare total).

faster than any of the components of diesel. Using the breakthrough curve at a single monitoring well on each side for comparison (C6B4 and T6B4), retardation factors of 2.8 and 2.2 were calculated for the control and the treatment side respectively. It is also interesting to note that the presence of the diesel residual source did not seem to have any negative impact in the transport of HA. This would imply that the measured retardation factor is due to ionic rather than hydrophobic interactions with the sand.

3.3.6 Humic Acid Effect on PAHs

Water was pumped through for a period of seven weeks prior to initiating the HA treatment. As the water passed through, a plume of PAH developed throughout the tank. A total PAH concentration of approximately 500 $\mu\text{g/L}$ was observed in the monitoring wells just beyond the source.

When after 51 days, HA was added to the head tank, an average three-fold increase in PAHs was observed which was well correlated with the increase in HA (Figure 16). A ten-fold increase in solubilization was observed for trimethyl naphthalene. This is consistent with what had been observed in the column studies above and is generally the case with

pumping rates may have occurred. When compared to the lissamine contour (Figure 10) which was taken after 13 days, it is evident that some retardation of HA did occur, but that movement was still

surfactants, where the least soluble compounds benefit the most from the addition of a solubilization agent.

These results were virtually identical to those observed in the laboratory for the enhanced dissolution of the residual phase (Section 2.3, Figure 7). In small columns where the amount of oil exceeded the holding capacity of the solid phase, a two-stage removal of the hydrocarbons had been observed: one where the oil was removed as droplets followed by a slower phase where dissolution was the predominant mechanism for removal. In the larger model, because the emplaced diesel source was designed such as not to exceed the holding capacity of the sand, only dissolution was observed. Unlike what is generally observed with surfactants (Thangamani and Shreve, 1994), the increase in solubility occurred below the critical micelle concentration for HA, (7.4 g/L for Aldrich HA, Guetzloff and Rice, 1994).

The sand used in the tank had a very low carbon content thus any interaction between the sand and the HA were expected to be ionic. Initially the HA had a pH of 8.5, but this was buffered down to 8.0 by the contact with the sand. At that pH sorption was not expected to be significant and indeed most of the HA was recuperated at the withdrawal wells. This allowed for recirculation of the treatment in a closed loop system, resulting in significant cost savings. The effluent was collected in a reservoir which was assayed for HA concentration and replenished as necessary by the addition of a concentrate through a metering pump.

The evolution of the PAH plume with time, in the presence of HA, is depicted in Figure 17. The plume labeled *51 days* was just before the addition of HA, 51 days after the emplacement of the source. As was shown above, a much higher concentration of PAHs was

achieved after the addition of HA. The depression on the longitudinal direction of the contour is attributable to the lower permeability in the source zone. From the tracer test, it was determined that one pore volume would take ten days to travel through the tank.

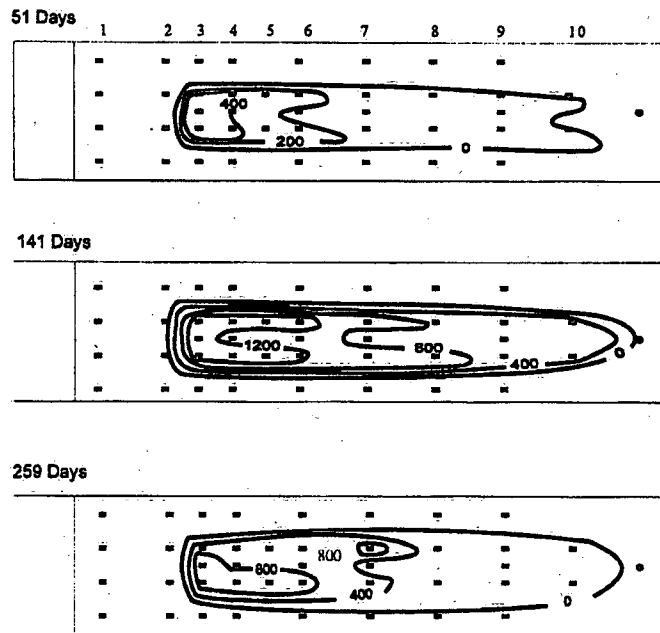


Figure 17. Distribution of PAH's (total, $\mu\text{g/L}$) before (51 days) and after the addition of humic acids.

After a period of 10 weeks, it was expected that more or less uniform

concentrations would be observed throughout the tank. While the concentrations of PAHs

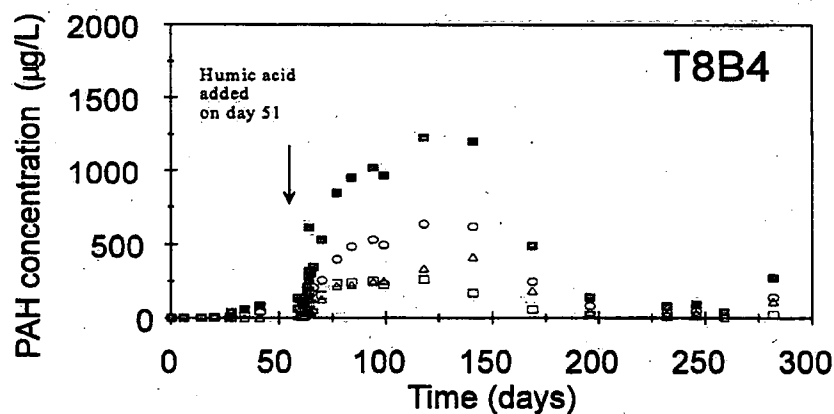


Figure 18. Disappearance of PAHs at T8B4, 2 m from the source. Methyl \square , dimethyl \circ and trimethyl \triangle naphthalenes (\blacksquare total).

nearest the source decreased only slightly (Figure 16), the concentrations of PAHs some distance away from the source began to be depleted (Figure 18), in spite of the fact that HA concentrations remained the same.

These losses were attributed to biodegradation. After a few weeks the PAH concentrations began to rise again. Aeration of the head tank reestablished the downward trend, thus supporting the biodegradation hypothesis. This finding is very interesting because no additional nutrients or sources of carbon were added to the system. The effect of HA on bioremediation is the subject of a new project (GASReP 9420).

4.0 COST ESTIMATES

The usefulness of a remedial treatment is not only related to its effectiveness and its relative innocuity to the environment, but the cost /benefit ratio must be considered. The use of HA in a recirculating system can help reduce costs. The cost of sodium humate used in these experiments was \$86 per kg. When used at 1g/L, the cost was \$860 for 10,000 L of solution. In order to reduce this cost further, peat moss was considered as a source of HA. From batch tests, it was found that peat moss contains approximately 10% extractable HA by weight using dilute sodium hydroxide as a base. The same amount of solution (10,000 L) could be generated on site for less than \$50.

5.0 CONCLUSIONS

Soluble HA were found to increase the dissolution of PAHs present in diesel fuel. Laboratory scale experiments were used to study the effect of pH and ionic strength as well as determine the optimal concentration of HA. A large scale aquifer model to study groundwater remediation technologies was successfully designed and constructed. The transport characteristics of the model aquifer were measured using a tracer experiment. A residual diesel source was emplaced and dissolved slowly such as would occur in a typical pump and treat scenario. The addition of HA was found to increase the concentration of PAHs dissolving from diesel by as much as ten-fold for trimethyl naphthalenes. Humic acids are therefore a potential sustainable alternative to the use of surfactants in the treatment of

petroleum fuel spills. Some biodegradation was evident in the tank. Future plans include a systematic laboratory study of the effect of humic acid on the degradation of more recalcitrant PAHs present in heavier fuels.

5.1 Acknowledgements

The authors wish to thank the Groundwater and Soil Remediation Program (GASReP), the National Energy Board and Environment Canada for their financial support. Thanks also to Imperial Oil of Canada Ltd. for the initial diesel fuel samples. The advice of Dr. Carl Enfield from the R.S. Kerr Laboratory in Ada, OK, on the design of the tank and the monitoring wells, is gratefully acknowledged. The technical assistance of Jerry Ford, John Voralek, Rob Hoag, Louise Durham, Kelly Millar, Mark Flumiani, Bryan Helfenbaum, Charlie Talbot, John Fitzgerald, Greg Bickerton, Dianne Thompson and Bryan Taylor has made this project possible.

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7.0 APPENDIX

7.1 Tank Design

The large scale model aquifer was designed, built and finally installed in October 1994. The tank was made entirely of 1/4" industrial grade stainless steel (rectangular 2.4 m x 6m x 2m deep) with an external support structure made of steel beams. While most physical aquifer models rely on a combination of injection/withdrawal wells to induce water flow, in this case it was decided to provide a head tank separated from the soil filled portion by a perforated plate. The plate was also made of 1/4" stainless steel plate, but perforated with 1" hole in quincunx such as not to impede water flow and provide a porosity greater than 0.3, a porosity characteristic of the most porous sands. The sand was retained by a polyester geotextile, a material compatible with most organic solvents. The purpose of using a head tank instead of injection wells was to provide an even flow field across the whole width and depth of the tank, a situation more closely resembling a natural groundwater flow system. A walkway was attached all around the tank to provide for a working area and minimize walking on the sand to prevent uneven compaction.

The tank, when filled with sand and water, constitutes a very heavy load that is beyond the support capacity of ordinary concrete floors. Also, because the Canada Centre for Inland Waters is built on reclaimed land, the bearing capacity of the subfloor had to be considered when placing such a heavy object. In addition, environmental regulations require that secondary containment be provided for the tank. For these reasons, the tank was located in the existing hydraulic laboratory where a large sump existed as a catchment basin. The sump area provided an already reinforced area below grade for the tank. A concrete pad was poured to level the bottom of the tank and spread the load over several pillars.

7.2 Setup

In order to provide for simultaneously studying the interaction of HA with the sand and its effect on a petroleum spill, the main part of the tank was divided longitudinally with a series of stainless steel plates sealed and bolted together. The bottom of the plates were secured with bentonite clay before starting to fill the tank with sand. The monitoring wells, consisting of 79 bundles of five tubes (3 mm nominal 1/8" o.d.) terminating at different depths, with a stainless steel porous cup at the end, were suspended from a wooden grid at the preset intervals of 30 cm, (depth and length) and 25 cm (width). In addition, withdrawal wells (5 cm i.d., 10 cm o.d. with their own packing and screened over their whole length) were installed in each side of the tank. Details of the monitoring system are shown on Figure 8. A medium to coarse mixed sand was obtained from a local sand and gravel supplier (Aggregate Analysis of Winter sand shown in Table 7-1; 32% carbonate by loss on ignition). The tank was filled with dry sand, from a moving conveyor belt. In order to prevent layering, the sand was mixed manually around the monitoring tubes, with edge cutters at every six inches. The sand was flushed for 24 h with helium to prevent any air entrapment. The tank was filled over a period of one week with tap water that was constantly purged with helium, to remove residual chlorinated compounds and dissolved air. The sand was allowed to settle in the latter part of December. A final settling was induced by forcing vibration of the tank by hitting it with a large rubber mallet. The first two hydraulic tests were conducted in January.

Table 7-1. Aggregate Analysis - Winter Sand

Sieve size	Weight % Retained	Weight % of Fraction
#4 - 4.75 mm	0	0
#8 - 2.36 mm	25.3	25.3
#16 - 1.18 mm	60.0	34.7
#30 - 600 μ m	90.0	30.0
#50 - 300 μ m	99.0	9.0
#100 - 150 μ m	99.5	0.5
#200 - 75 μ m	99.7	0.2

7.3 Tracer tests

The first hydraulic test was initiated by adding a concentrated solution of lissamine, as a fluorescent tracer, in the two injection wells while constantly pumping from the two withdrawal wells at the rate of 200 mL/min. The head tank was kept at a constant level. It became rapidly apparent that the gradient induced from the withdrawal wells combined with the higher level head tank were not sufficient to prevent flow in the opposite direction (towards the head). Computer modelling showed that it would not be possible to recirculate the treatment solution to more than 40%. Also, in spite of the fact that a wider injection well was used, the tracer distributed itself in a narrow band, not more than 60 cm wide. The delivery of the remedial solution would therefore not be very effective using this system. Adding more injection wells could alleviate the width coverage problem, but not the recirculation problem. It was therefore decided to use the head tank as the source of treatment, and recirculation would therefore occur from the two withdrawal wells into the head tank.

A second tracer test was initiated on January 31st. This time, a mixture of lissamine (2 mg/L) and sodium bromide (100mg/L) were introduced simultaneously into the head tank (total volume 3,120 L). A series of three gas diffusers were placed at the bottom of the tank to provide constant mixing. In addition, at the onset of the experiment, canoe paddles were used to help with the mixing. As the tracer was being depleted by pumping from the withdrawal wells (total pumping rate 400mL/min), the level in the head tank was kept constant by the addition of water through a float valve. This provided for a constantly decaying source, that is, the concentration of the tracers in the head decreased by dilution over the whole period of the experiment. Monitoring of the head tank began immediately. Over the course of the following two weeks, samples at rows two, six and nine were taken around the clock, and the breakthrough curve analysed at all points. Over 5,000 samples in all were collected and analysed for lissamine (by fluorescence) and for bromide (by conductivity). Horizontal contours of lissamine concentrations are shown in Figures 7-1 to 7-4. The relative movement of the control and the treatment side were very even at level 5 (Figures 7-2 and 7-4), but some edge effects were seen at the shallower depth. This is more evident in cross-section (Figure 7-5). The effect has been attributed to the capillary fringe.

The results of the tracer tests were grouped by rows, for each side of the tank in the next 20 figures (7-6 to 7-25). In the first figure of the set (7-6), the decaying concentration in the source and the breakthrough at both withdrawal wells are shown. The excellence of the match of flows on both sides can be seen by comparing the tracer test in both withdrawal wells. Both lissamine and chloride are shown on these figures. It is very obvious that lissamine is slightly retarded in the sand compared to chloride. It is still useful as a tracer however, because the lissamine measurements are much easier than the chloride and can be used as a guide for the frequency of taking the samples and many more samples can be analysed.

7.4 Emplacement of the Source

The results of the tracer test were used to decide on the optimal placement of the source. Because the main goal of this experiment was to cleanup petroleum present at residual saturation in the saturated zone, it was necessary to devise a method of introduction that would provide a well defined source in terms of both mass and geometry. Indeed, it would be difficult to monitor the movement and the changes of petroleum concentration if the concentration was not even across the monitoring well. Based on the results of the tracer test, it was decided to place a rectangular source centered at depth 4, facing rows B and C. Five additional monitoring wells were added in the center of rows B and C. The holding capacity of the sand was determined in a column experiment by adding diesel to a dry sand column until it dripped. It was found that 500 mL of diesel could be held by 20 kg of sand.

To emplace the source, first the water table was lowered to a depth of 1.60 m. A rectangle of the appropriate dimension was excavated to the same depth. In order to prevent disruption of the sand in the tank, a wood frame (20 cm X 40 cm X 2m) was lowered into the tank while the sand was removed by vacuuming using a ShopVacTM and temporarily placed on a clean tarp. A 25 kg portion was weighed and 500 mL of diesel (Esso, local supplier- not the same sample as for the laboratory test) was mixed with it. It was placed back into the bottom of the hole and covered with a layer of clean sand. A small core was taken from the source to measure potential losses by volatilization. The mixture was placed back into the bottom of the hole and covered with a layer of clean sand while the wooden form was pulled upwards using an overhead pulley. The water table was gradually reestablished by refilling the head tank while pumping at the withdrawal wells. This insured that flow proceeded in the desired direction.

Depth 2 Time 146

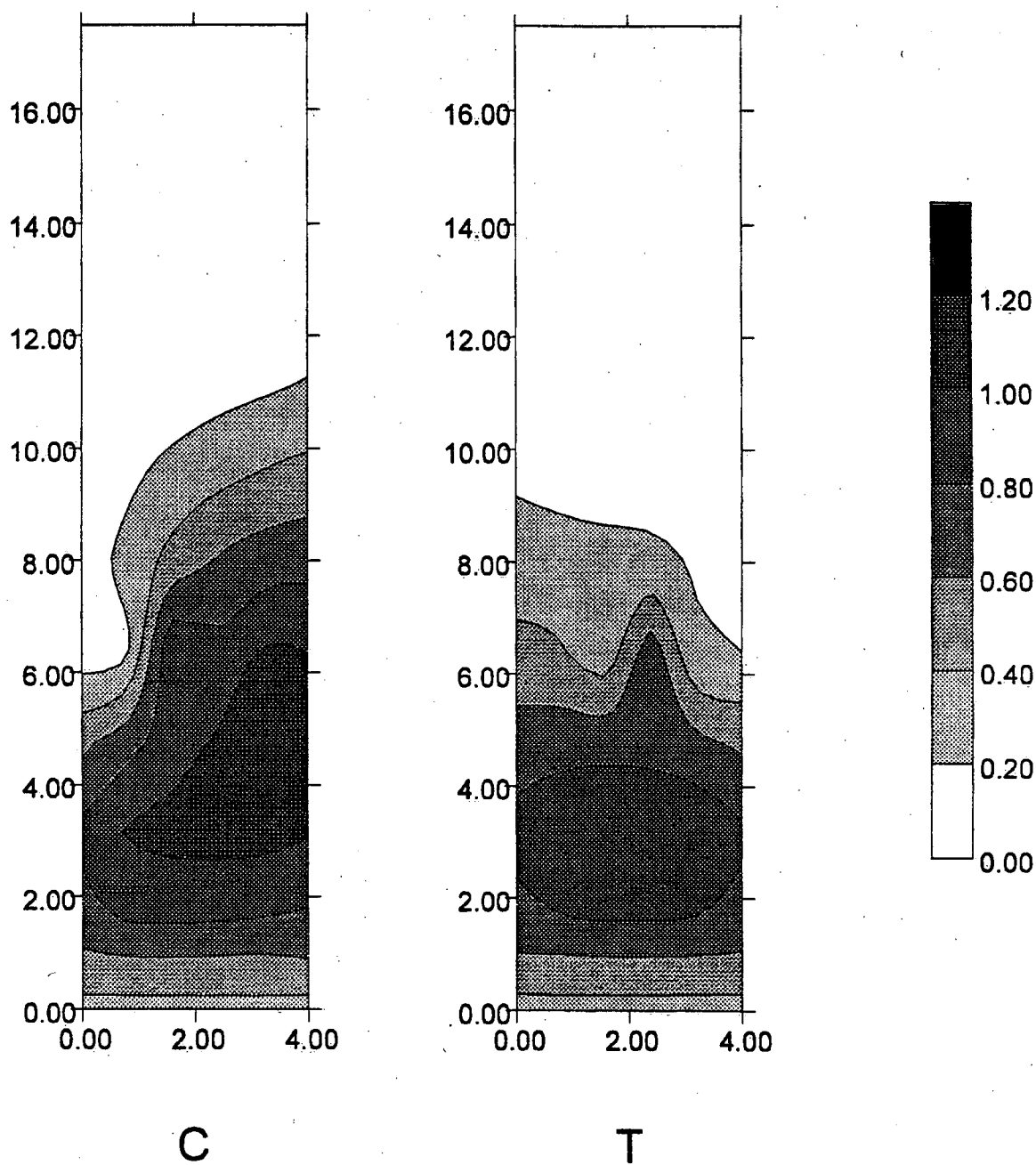


Figure 7-1 Horizontal contour plots of lissamine concentration (mg/L) at 146 hours for the control (C) and treatment side (T), at depth 2.

Depth 5 Time 146

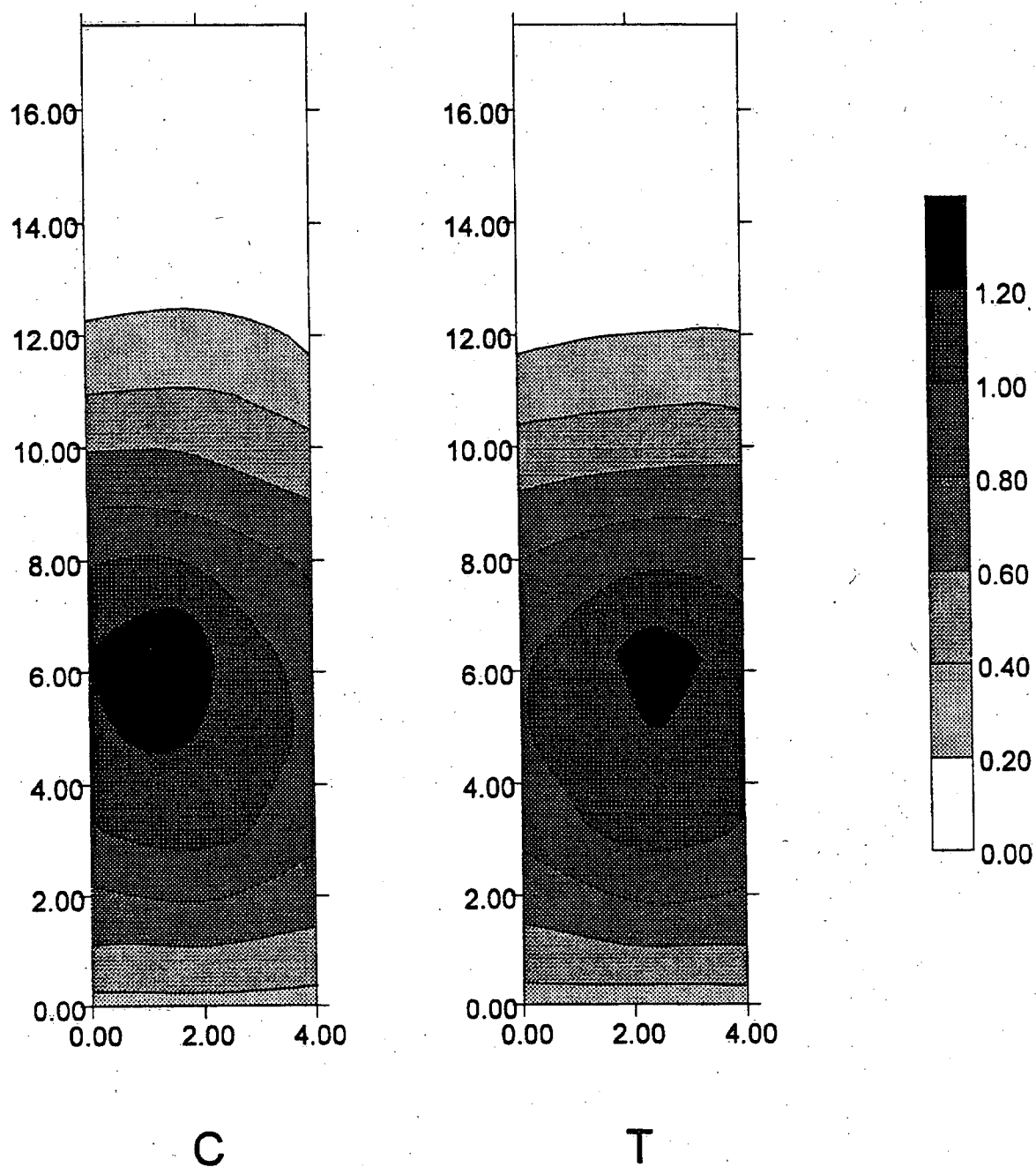


Figure 7-2

Horizontal contour plots of lissamine concentration (mg/L) at 146 hours for the control (C) and treatment side (T), at depth 5.

Depth 2 Time 300

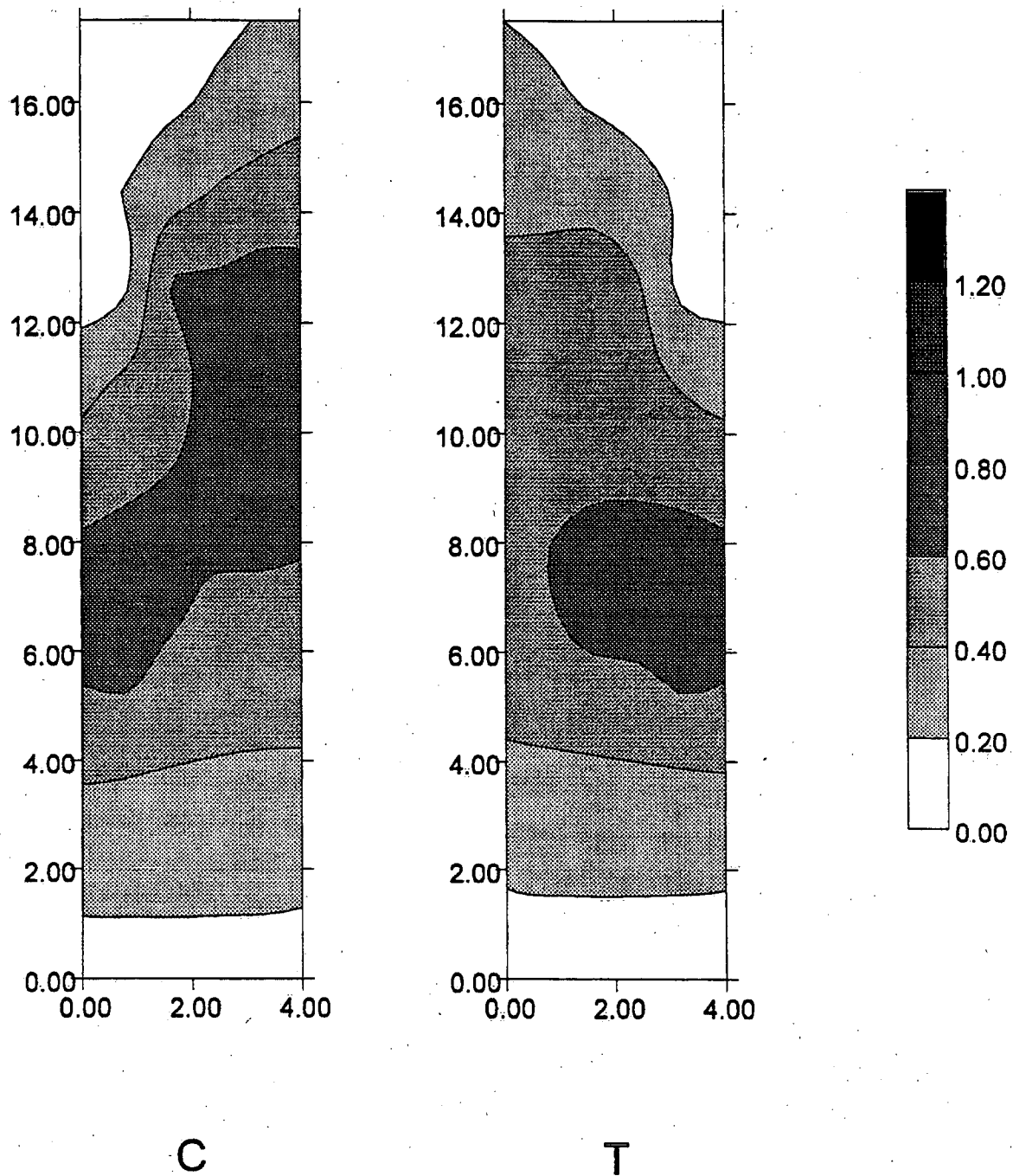


Figure 7-3 Horizontal contour plots of lissamine concentration (mg/L) at 310 hours for the control (C) and treatment side (T), at depth 2.

Depth 5 Time 300

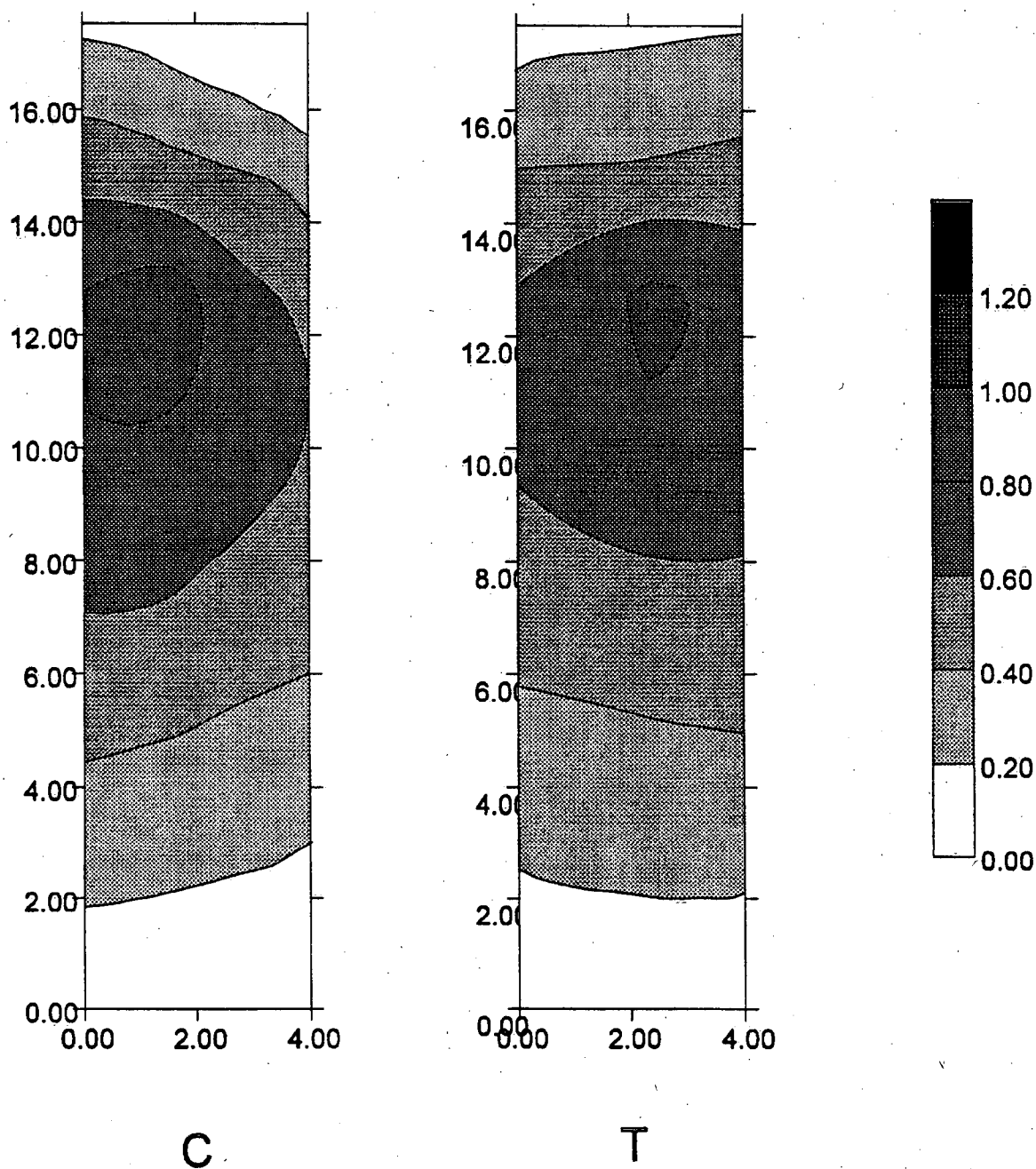


Figure 7-4 Horizontal contour plots of lissamine concentration (mg/L) at 310 hours for the control (C) and treatment side (T), at depth 5.

Cross Section B Time 146

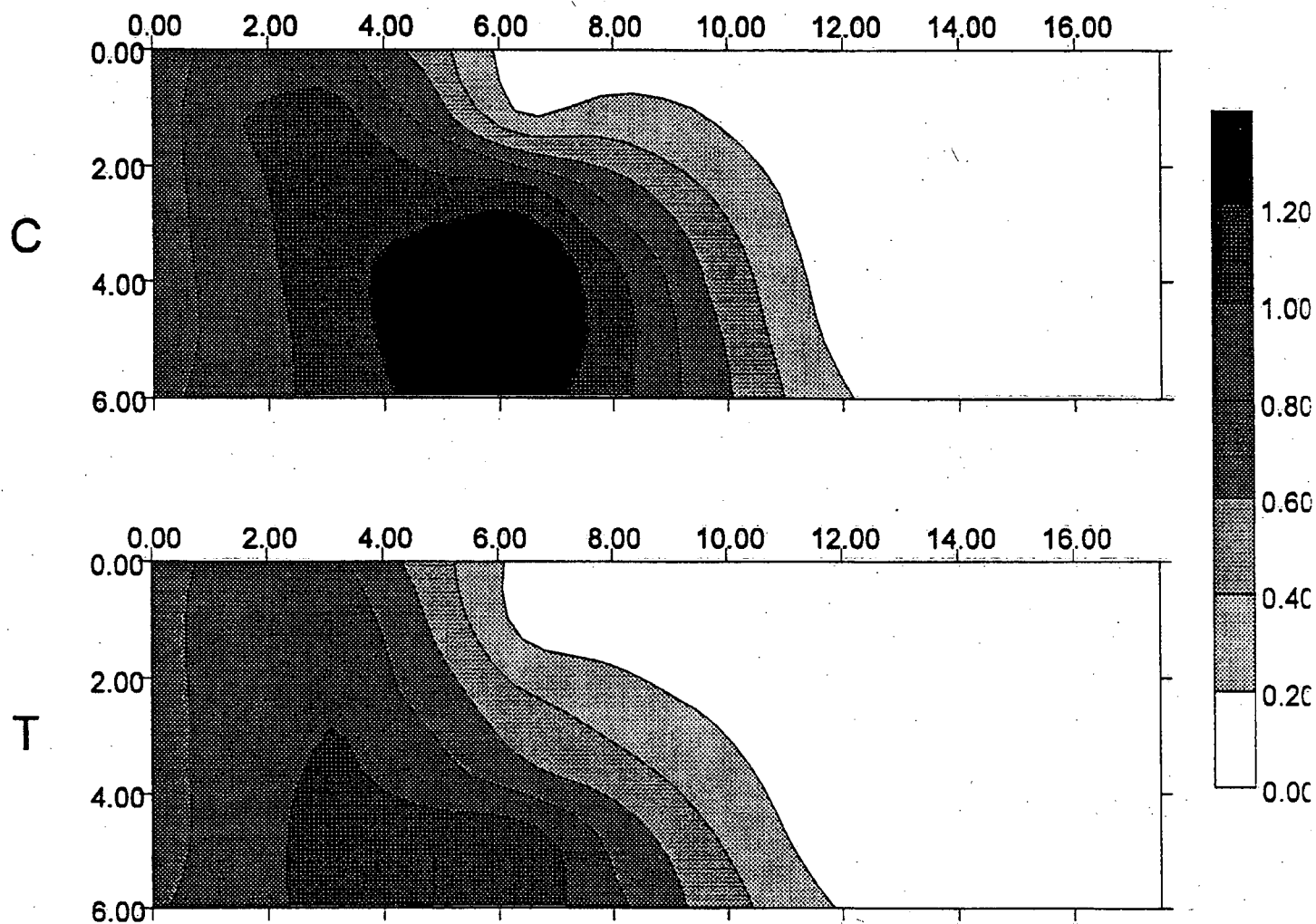


Figure 7-5 Vertical contour plots of lissamine concentration (mg/L) at 146 hours for the control (C) and treatment side (T), at row B

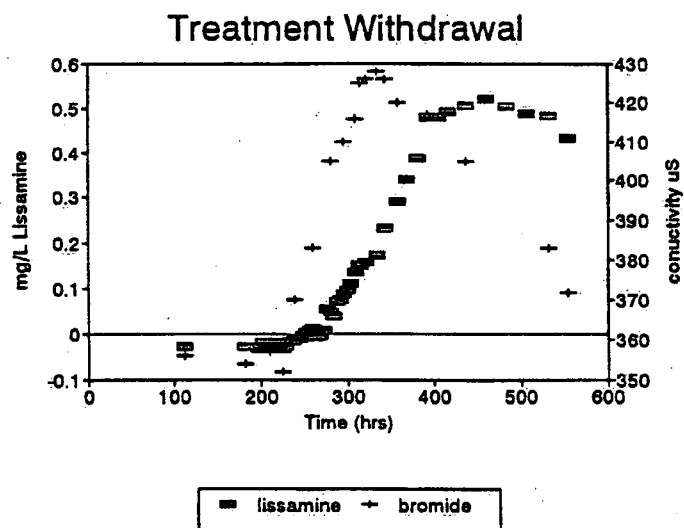
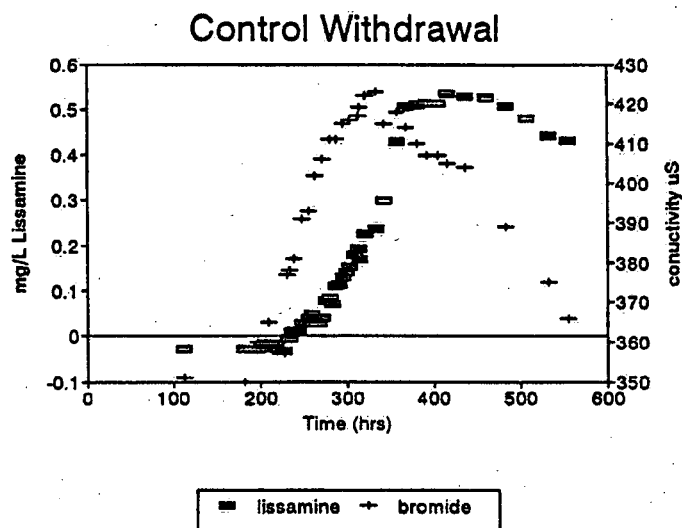
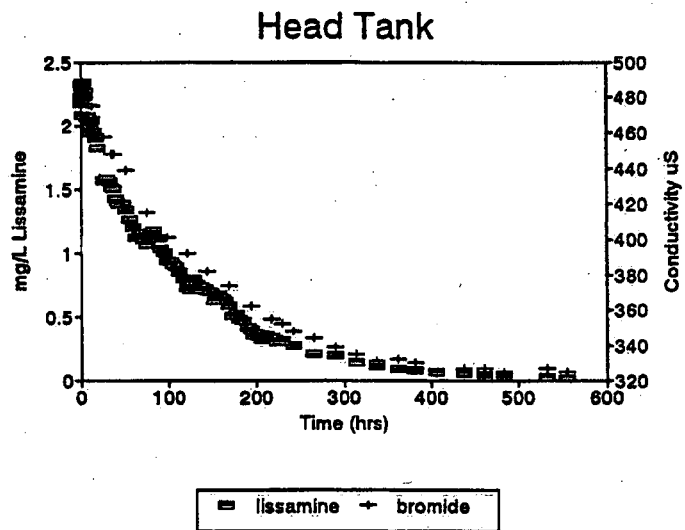


Figure 7-6 Tracer test in the head tank and the two withdrawal wells.

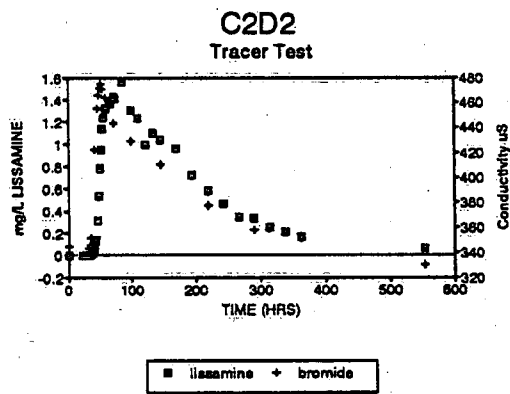
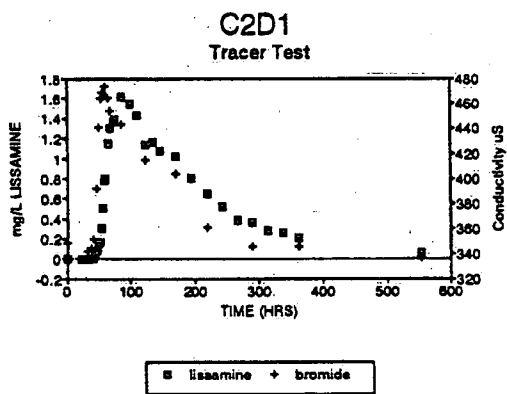
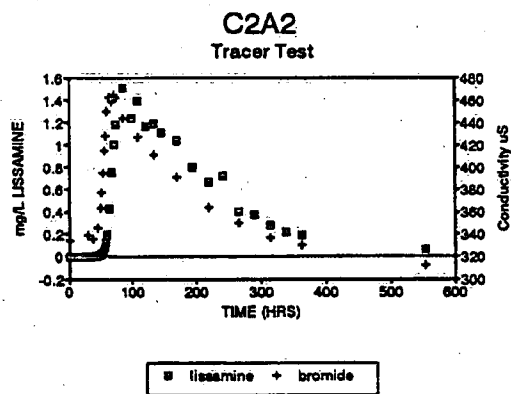
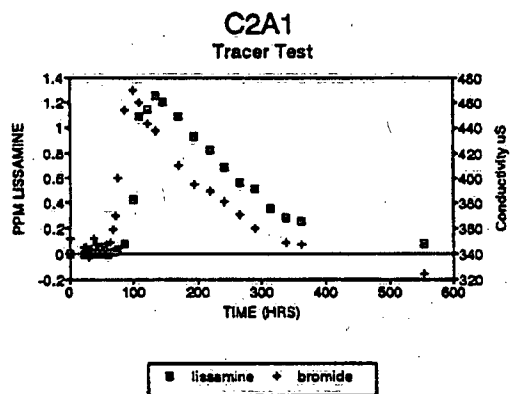


Figure 7-7 Tracer test at C2A1, C2A2, C2D1 and C2D2.

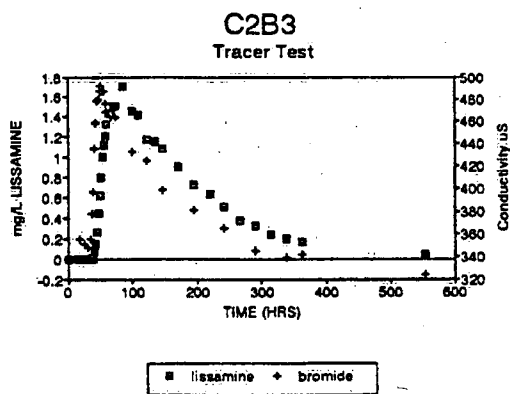
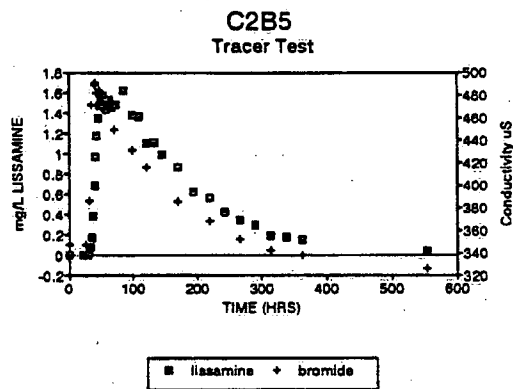
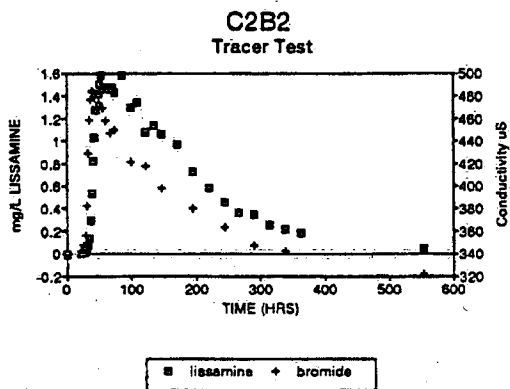
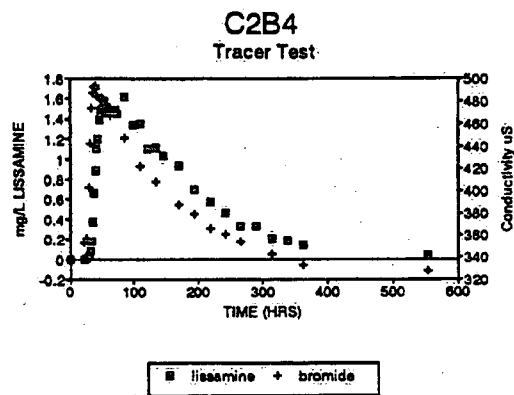
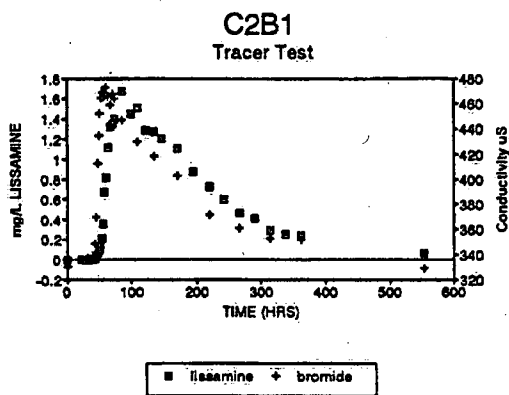


Figure 7-8 Tracer test at C2B1- C2B5.

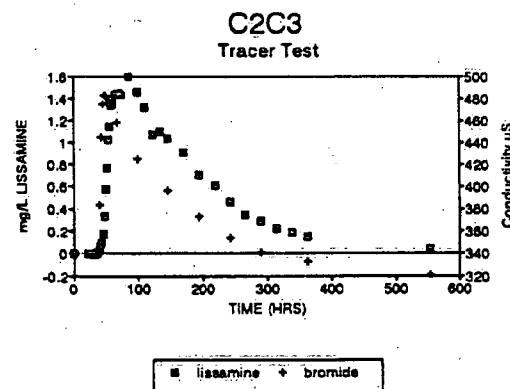
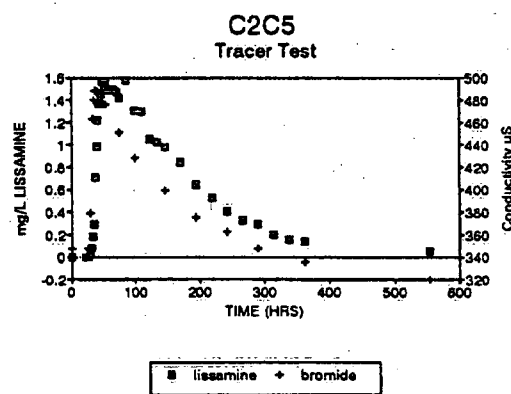
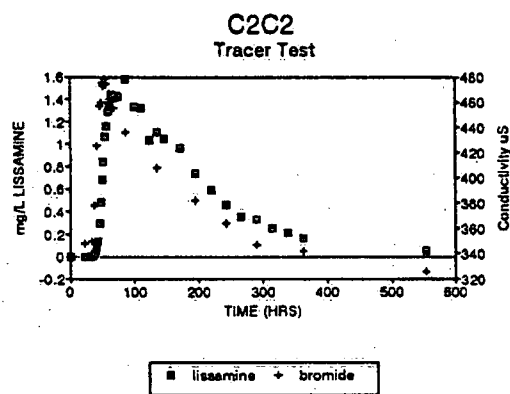
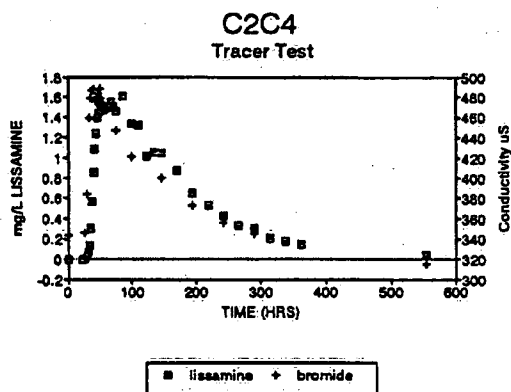
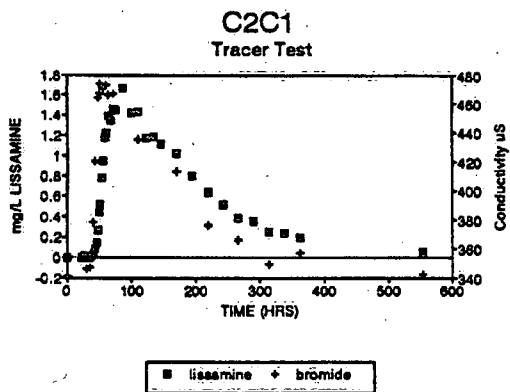


Figure 7-9 Tracer test at C2C1- C2C5.

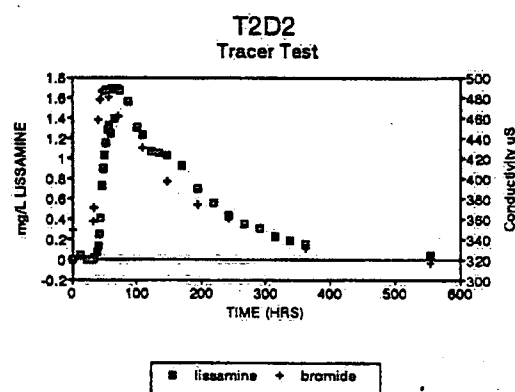
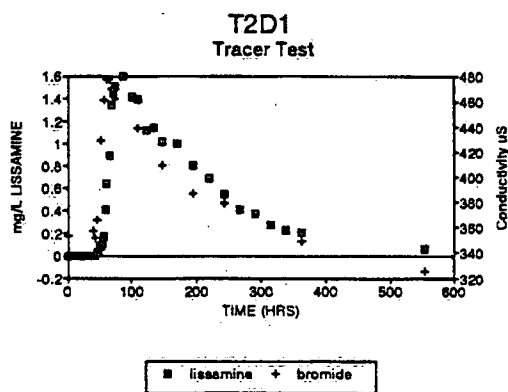
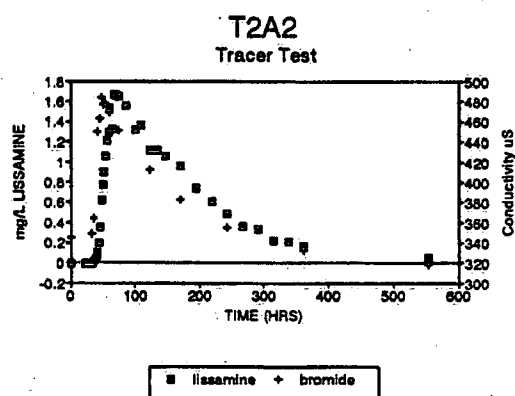
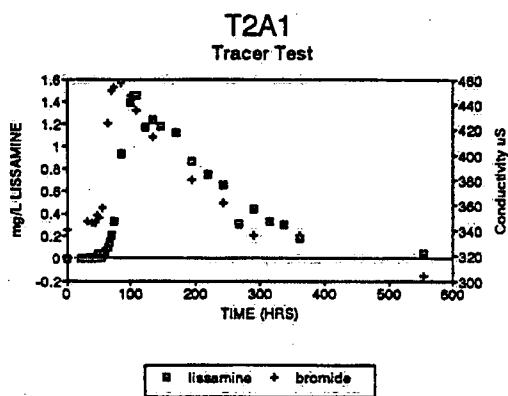


Figure 7-10 Tracer test at T2A1, T2A2, T2D1 and T2D2.

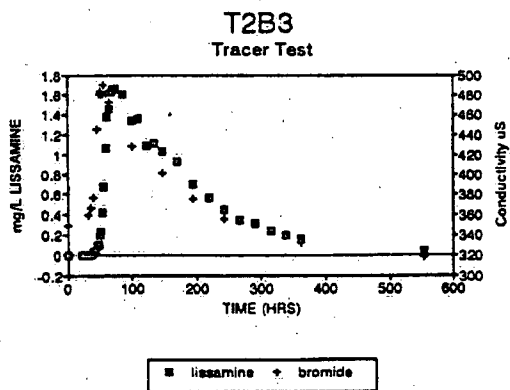
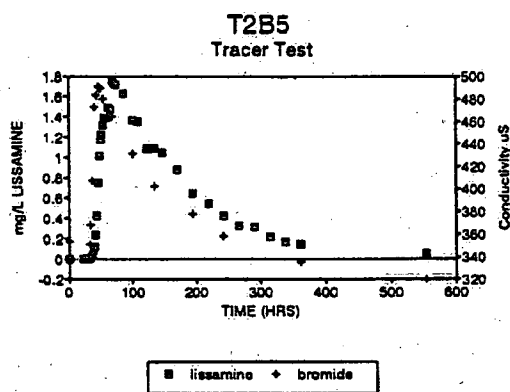
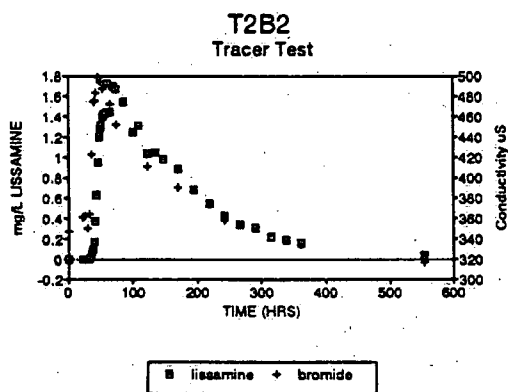
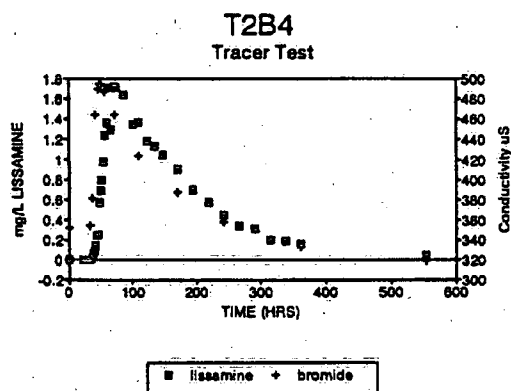
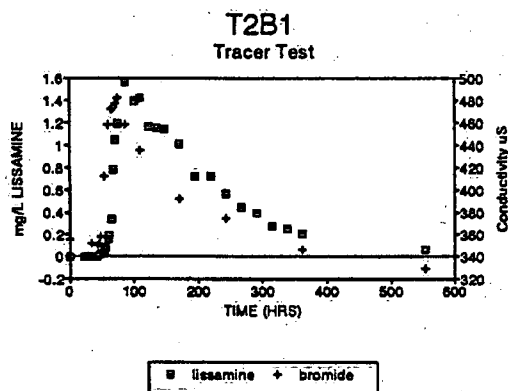


Figure 7-11 Tracer test at T2B1- T2B5.

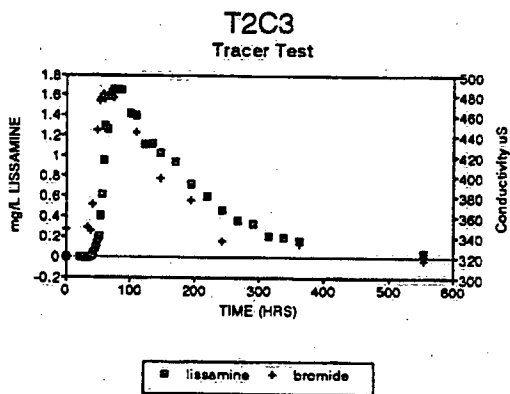
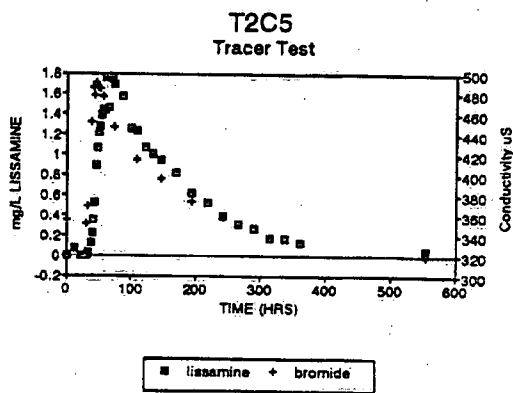
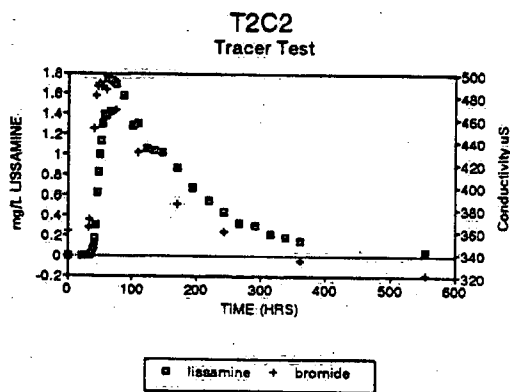
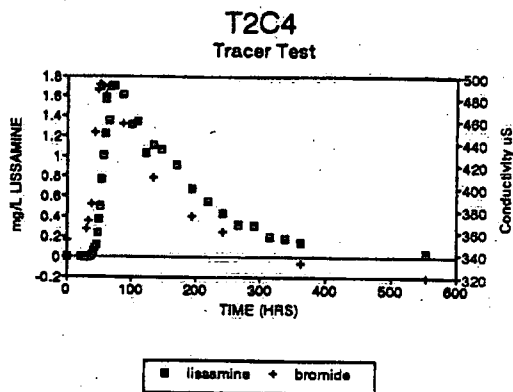
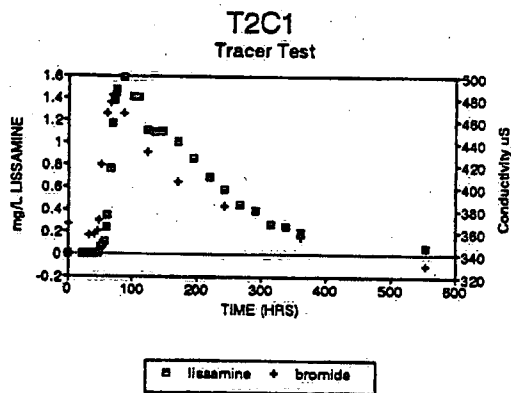


Figure 7-12 Tracer test at T2C1- T2C5.

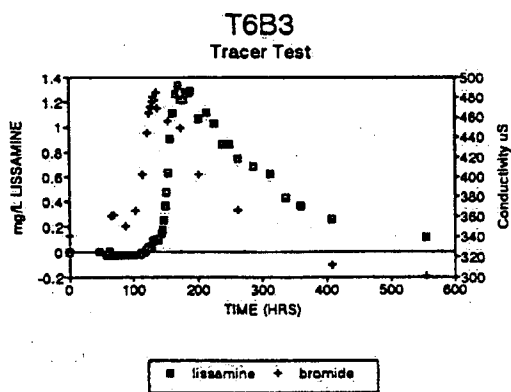
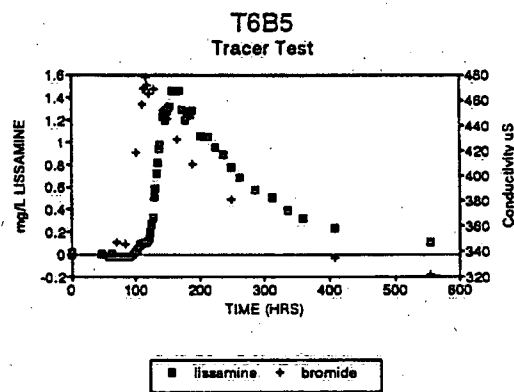
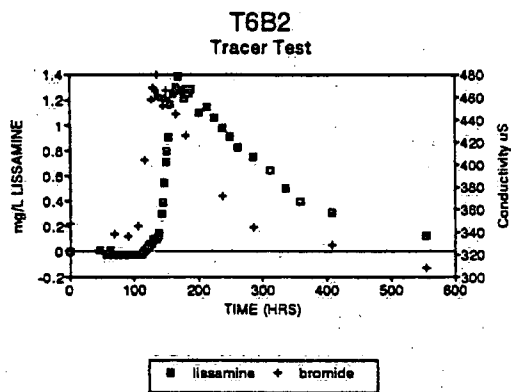
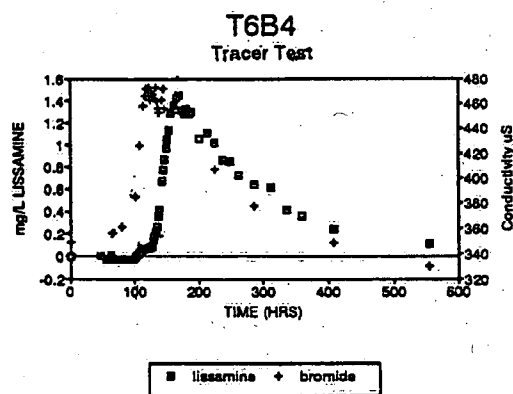
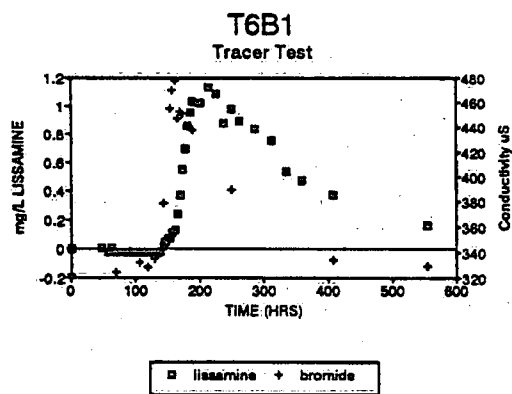


Figure 7-17 Tracer test at T6B1- T6B5.

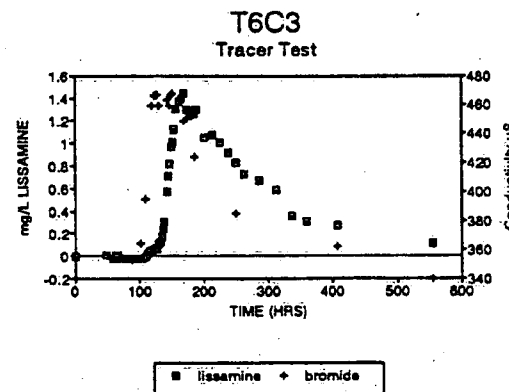
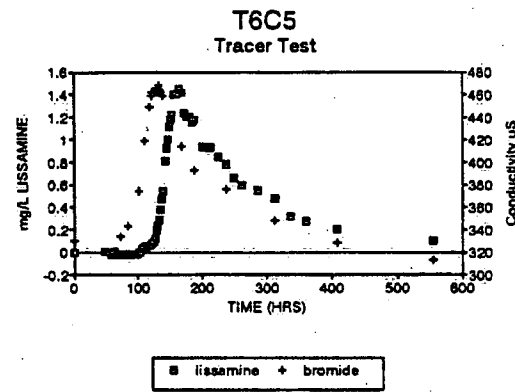
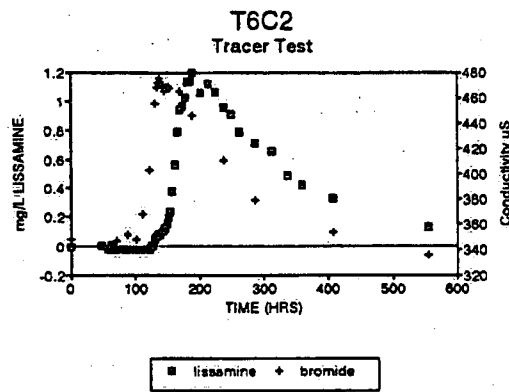
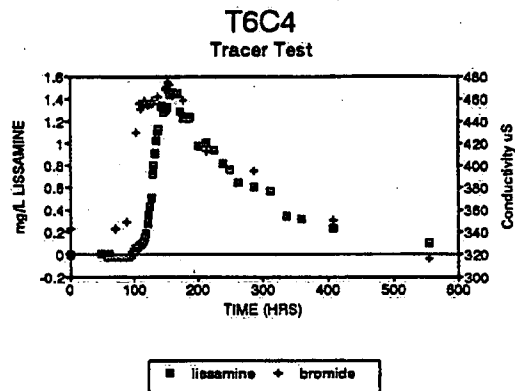
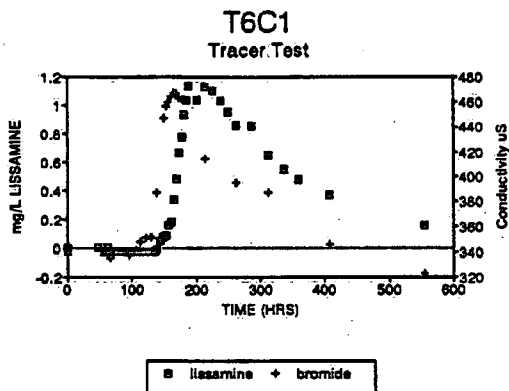


Figure 7-18 Tracer test at T6C1- T6C5.

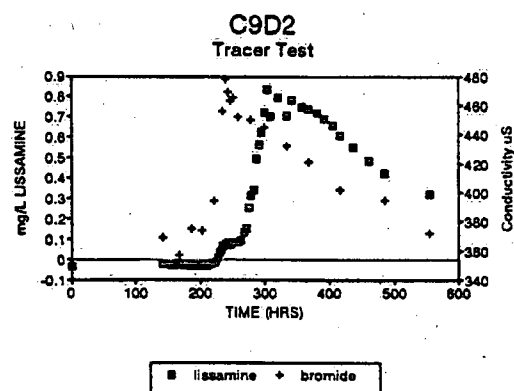
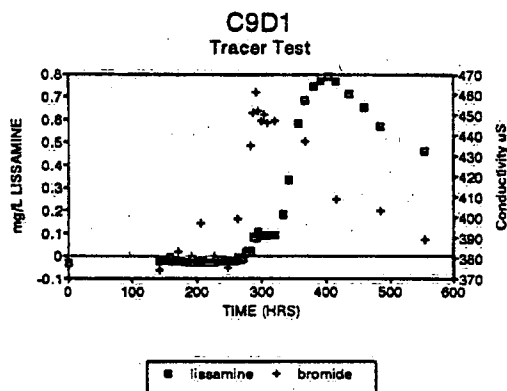
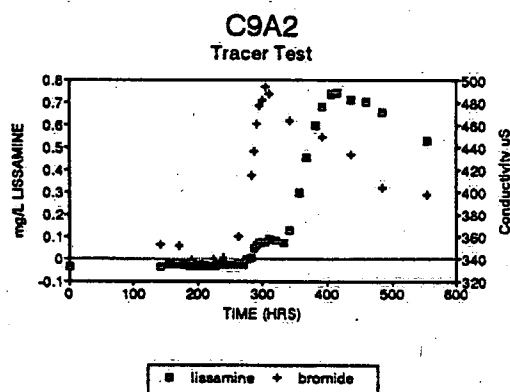
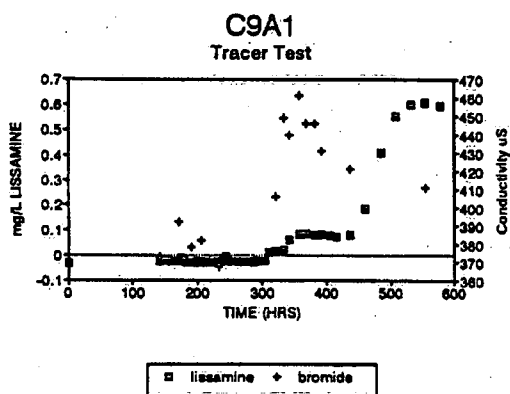


Figure 7-19 Tracer test at C9A1, C9A2, C9D1 and C9D2.

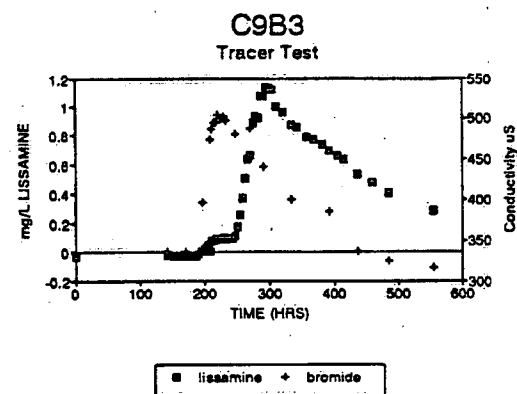
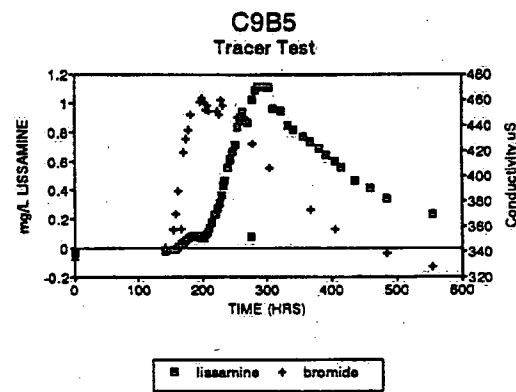
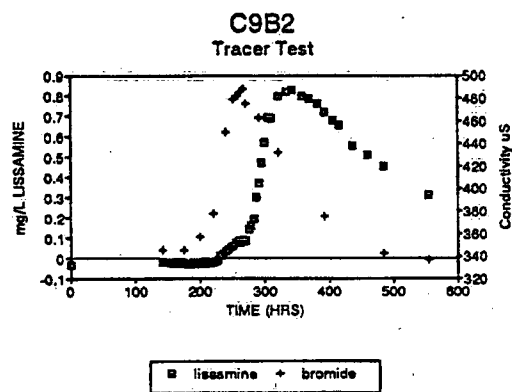
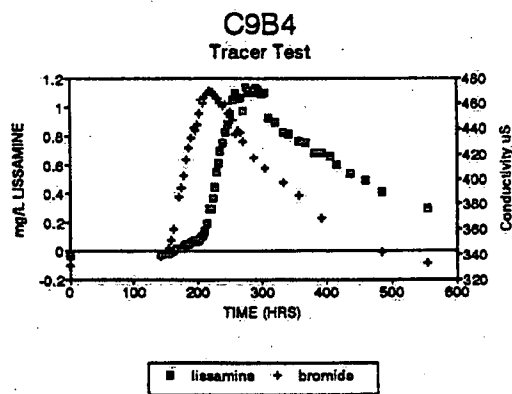
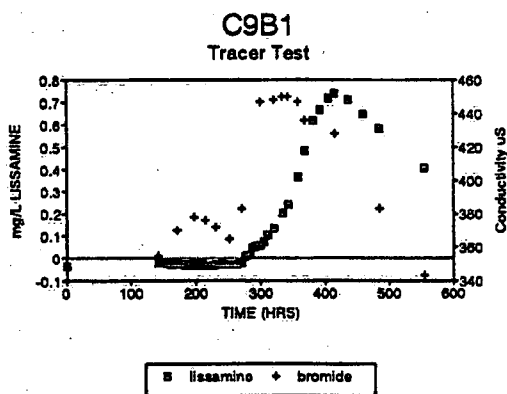


Figure 7-20 Tracer test at C9B1- C9B5.

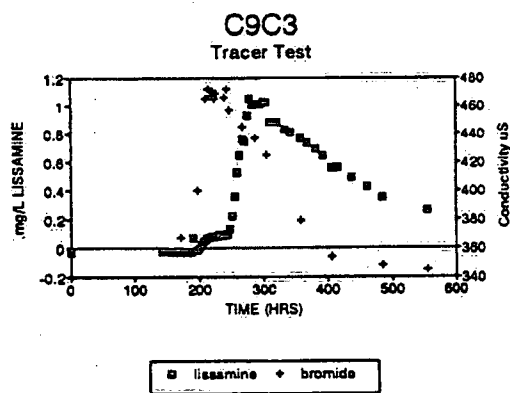
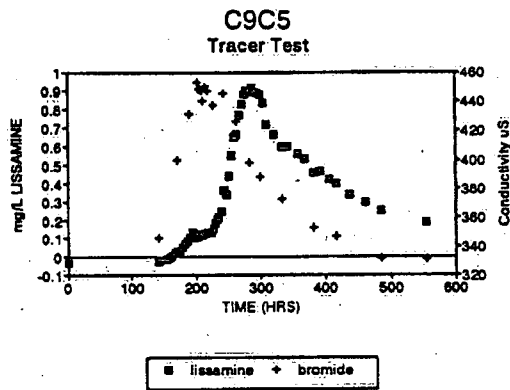
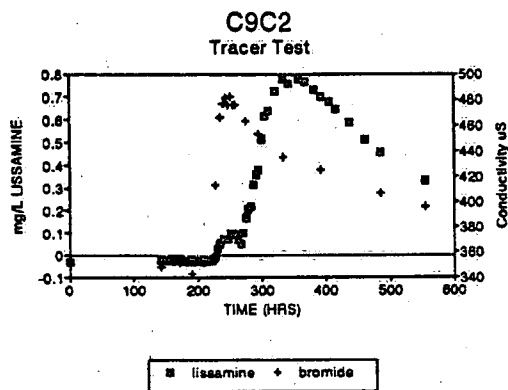
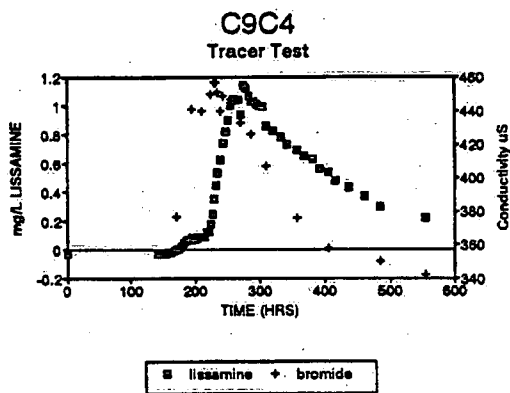
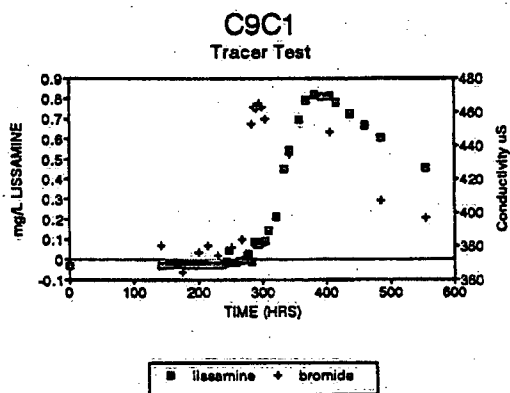


Figure 7-21 Tracer test at C9C1- C9C5.

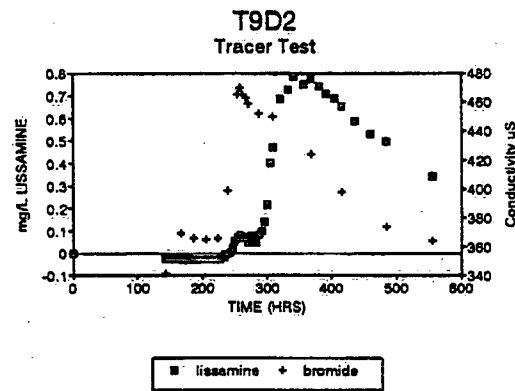
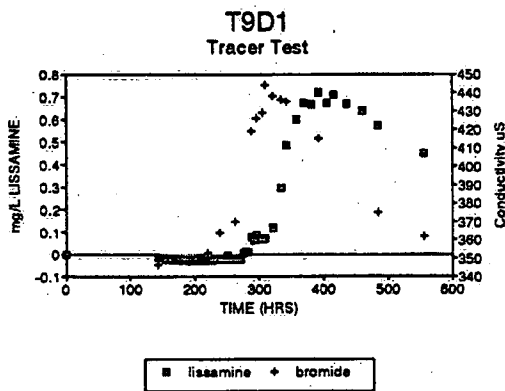
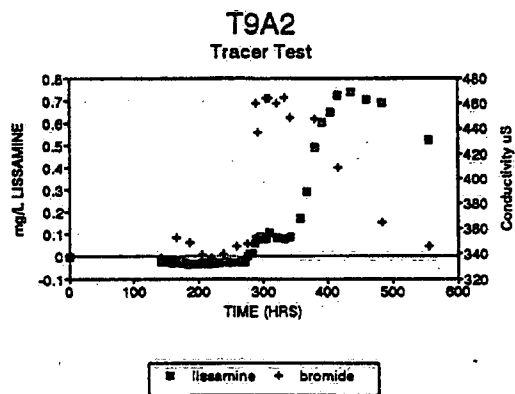
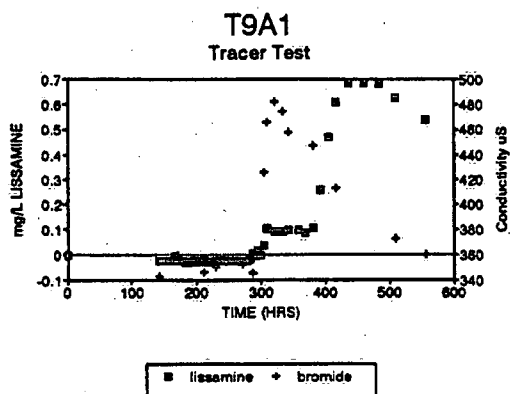


Figure 7-22 Tracer test at T9A1, T9A2, T9D1 and T9D2

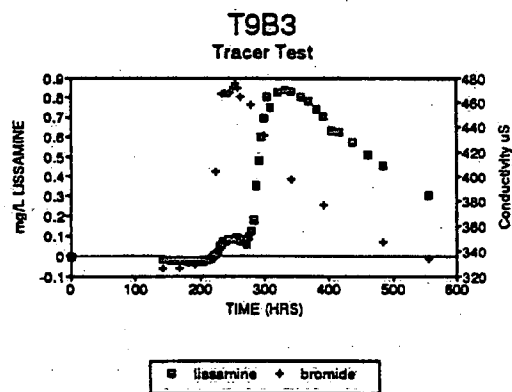
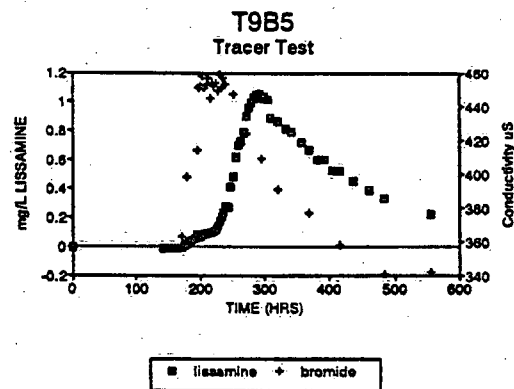
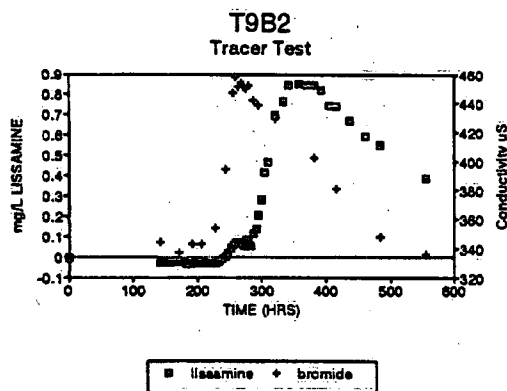
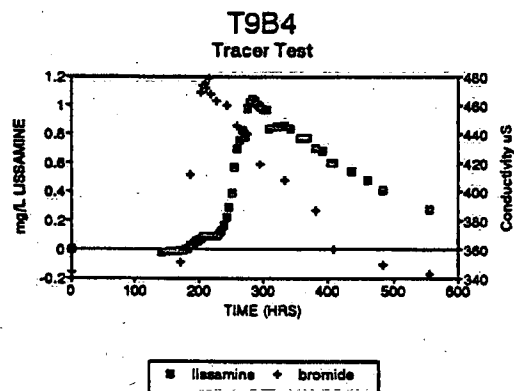
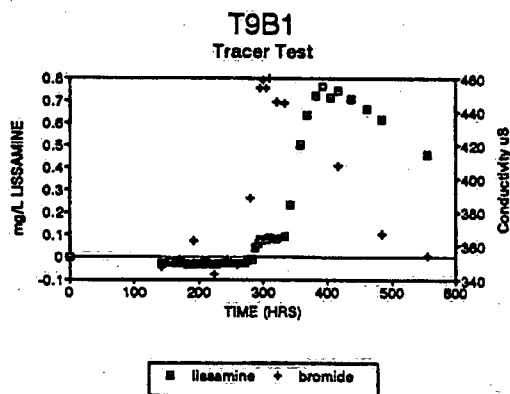


Figure 7-23 Tracer test at T9B1- T9B5.

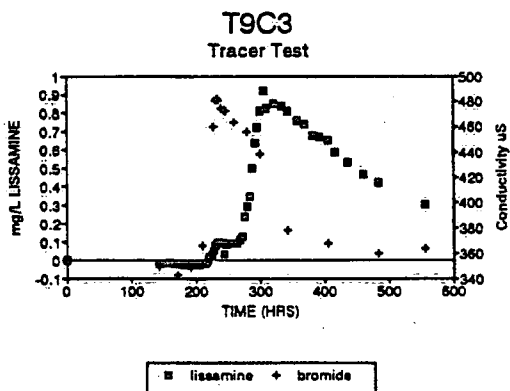
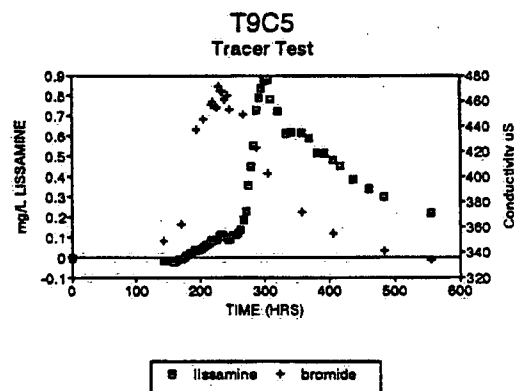
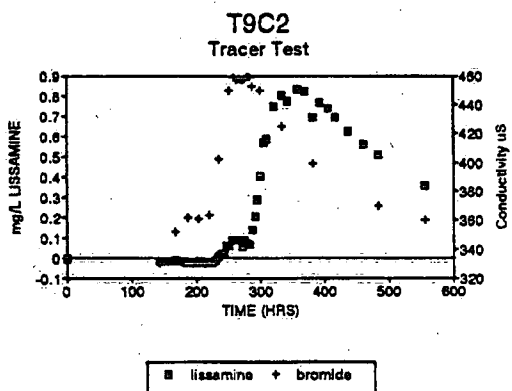
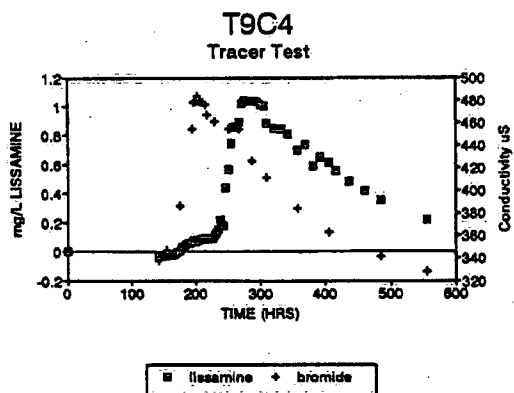
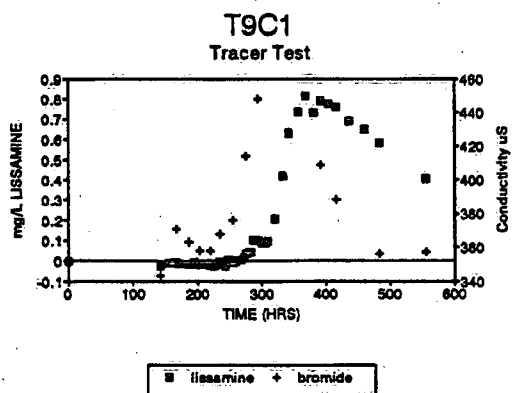


Figure 7-24 Tracer test at T9C1- T9C5.

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L7R 4A6 Canada



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**INSTITUT NATIONAL DE
RECHERCHE SUR LES EAUX**

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

Institut national de recherche sur les eaux
Environnement Canada
Centre canadien des eaux intérieures
Case postale 5050
867, chemin Lakeshore
Burlington, Ontario
L7R 4A6 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon, Saskatchewan
S7N 3H5 Canada



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