

00-74

# Environment Canada

Water Science and  
Technology Directorate

---

Direction générale des sciences  
et de la technologie, eau

# Environnement Canada

Numerical Simulation of enhanced Diesel Fuel  
Dissolution and Biodegradation in Groundwater

By:

J. Molson, E. Frind, D. Van Stempvoort, S. Lesage

TD  
226  
N87  
no.  
00-74

00-74

## **Numerical Simulation of enhanced diesel fuel dissolution and biodegradation in groundwater**

### **MANAGEMENT PERSPECTIVE**

This modelling was conducted at University of Waterloo, funded in part by NSERC and CRESTech, in collaboration with Environment Canada, and PERD funds under the Clean Environment (Toxic) Issue.

This collaborative work is a component of an ongoing research project for the development of groundwater remediation technologies. This paper documents a successful modelling approach for simulation of the processes that occur when humic acids are used to remediate diesel fuel. The complex 3D modelling is based on laboratory work at the bench and pilot scale conducted over the past 5 years by NWRI in the AQUAREF.

The computer model generated at Waterloo will be marketed by Waterloo Hydrogeologic. A copy of this model will be available to research scientists at NWRI for future applications.

Keywords: diesel, humic, dissolution, modelling

## **Simulation numérique de processus améliorés de dissolution et de biodégradation du carburant diesel dans les eaux souterraines**

### **SOMMAIRE À L'INTENTION DE LA DIRECTION**

Cette étude de modélisation, financée en partie par le CRSNG et CRESTech, a été effectuée à l'Université de Waterloo, en collaboration avec Environnement Canada et grâce à des fonds du GRDE disponibles dans le cadre du secteur d'activité « Un environnement sain (substances toxiques) ».

Cette étude effectuée en collaboration est l'un des éléments d'un projet de recherche en cours pour le développement de technologies d'assainissement des eaux souterraines. Cet article documente une approche de modélisation qui a donné de bons résultats pour la simulation des processus qui surviennent lorsqu'on utilise des acides humiques pour l'assainissement de zones contaminées par le carburant diesel. La modélisation 3D complexe est basée sur des études en laboratoire et à l'échelle pilote effectuées au cours des cinq dernières années par l'INRE et compilées dans la base de données AQUAREF.

Le modèle informatique produit à Waterloo sera commercialisé par Waterloo Hydrogeologic. Un exemplaire de ce modèle sera mis à la disposition des chercheurs de l'INRE pour leurs applications futures.

Mots clés : diesel, humique, dissolution, modélisation

## NUMERICAL SIMULATION OF ENHANCED DIESEL FUEL DISSOLUTION AND BIODEGRADATION IN GROUNDWATER

J.W. Molson<sup>1</sup>, E.O. Frind<sup>1</sup>, D.R. Van Stempvoort<sup>2</sup>, and S. Lesage<sup>2</sup>

<sup>1</sup> Dept. of Earth Sciences, University of Waterloo, Waterloo, Canada N2L 3G1

<sup>2</sup> National Water Research Institute, Burlington, Ontario, L7R 4A6

**ABSTRACT** A three-dimensional numerical model (BIONAPL/3D) is applied to simulate a pilot-scale experiment in which humic acid is used to enhance the dissolution of a residual diesel fuel source. The 3D conceptual model includes 8 diesel components (BTEX, methyl-, dimethyl- and trimethylnaphthalene; and a relatively inert remaining fraction), as well as the humic acid carrier, dissolved oxygen and a microbial population. Parameters for modelling equilibrium and kinetic sorption of the humic acid to the aquifer material were based on lab batch and column experiments. Simulations confirmed the observed increases in effective solubilities, up to a factor of 10 for the trimethylnaphthalenes and on the order of 2-5 for the more soluble components. The model successfully reproduced the effluent concentrations, which were significantly reduced due to biodegradation. The model is well suited for quantifying enhanced dissolution behaviour of other organic contaminants and for application to larger and more complex field-scale systems.

**RÉSUMÉ** Un modèle numérique tri-dimensionnel (BIONAPL/3D) est utilisé afin de modéliser une expérimentation à l'échelle pilote, dans laquelle l'acide humique est employé afin d'augmenter la dissolution de diesel en phase résiduelle. Le modèle conceptuel 3-D inclut 8 composantes du diesel (BTEX, méthyl-, diméthyl-, triméthyl-naphtalène et une autre fraction représentant la fraction résiduelle), de même que le transporteur d'acide humique, l'oxygène dissout et une population microbienne. Les paramètres utilisés, afin de modéliser les cinétiques de sorption de l'acide humique, ont été évalués par des essais d'adsorption et des essais en colonnes. Les simulations effectuées confirment une augmentation de la solubilité, d'un facteur allant jusqu'à 10 dans le cas du triméthyl-naphtalène et d'un facteur allant de 2 à 5 pour le composé le plus soluble. Le modèle a su reproduire avec succès la concentration de l'effluent, qui fut significativement réduite par la biodégradation. Le modèle semble bien adapté pour simuler des sites plus complexes et de plus grande échelle.

### 1. INTRODUCTION

Under natural conditions, multicomponent nonaqueous phase liquids (NAPL's) trapped within an aquifer typically dissolve very slowly, taking several decades or longer to completely dissolve. Conventional pump-and-treat technology is often not a practical option under these conditions. Much of the current NAPL remediation research is therefore focussing on enhanced dissolution processes in which the effective source dissolution rate is increased by introducing a flushing agent to which aqueous hydrophobic organic contaminants (HOC's) can partition. Possible approaches, for example, include flushing a residual NAPL source with surfactants, cosolvents or dissolved organic carbon (DOC).

Dissolved organic carbon is now receiving increased attention as an alternative to surfactants and cosolvents for NAPL remediation. DOC is a naturally occurring product of organic matter decay which is relatively inexpensive, non-toxic to microbes and has shown strong sorbing potential for HOC's (McCarthy & Jimenez, 1985; Chiou et al. 1986; Johnson & John 1999). In contrast to surfactants, solubilization by humic acid does not depend on reaching a critical micelle (aggregate phase) concentration (Lesage et al. 1997; Guetzloff & Rice, 1994). Furthermore, in cases where NAPL mobilization would risk further contamination, for example to an underlying aquifer, DOC may be preferred because it

tends to decrease the interfacial tension to a lesser extent than surfactants or alcohol cosolvents (Johnson & John, 1999).

A significant fraction of DOC is often composed of dissolved humic substances (DHS), or humic acid (HA), a mixture of complex macromolecular compounds to which dissolved organic contaminants are readily bound (McCarthy & Zachara, 1989). Humic substances have been studied in great detail over the past decade, primarily with respect to their potential use as a carrier for contaminant remediation (Abdul et al. 1990; Gauthier et al., 1987; Johnson & John, 1999).

Sorption processes play critical roles in determining whether the carrier will enhance or reduce contaminant mobilization. Sorption of mobile organics to the mobile humic acid, for example, will enhance mobilization, however sorption of organic-laden humic acid to aquifer solids will tend to reduce mobilization. Furthermore, these sorption processes often show nonlinear behaviour (Carter & Weber, 1994). Johnson and John (1999) highlight the need to more accurately define the sorption behaviour of both HA and surfactants before choosing the most suitable remediation option.

In this paper, we develop an advanced 3D numerical model to help interpret a pilot-scale experiment involving humic acid flushing of a residual diesel fuel source. Details of the experiment are provided by Van Stempvoort et al., 2000). The model is calibrated with respect to dissolution and biodegradation rates; however, most simulation parameters were obtained from independent sources. We show that laboratory-derived sorption parameters can be applied at larger scales and that nonlinear and kinetic sorption behaviour of the humic acid must be considered to reproduce the observed trends. Predictive simulations are made to assess remediation efficiency (to drinking water limits) with and without the humic acid carrier.

## 2. THE CONCEPTUAL MODEL

The conceptual model for the diesel fuel simulations assumes a three-dimensional (3D), 3-phase system (Figure 1) consisting of a non-aqueous phase (the residual multicomponent diesel source), an aqueous phase (containing the dissolved diesel components and mobile carrier), and a sorbed phase (including the sorbed diesel components and sorbed carrier). The humic acid carrier (Aldrich HA) is assumed here to behave as a single compound, although in reality it is a mixture of various components with similar structure but different molecular weights (Stevenson & Goh, 1971). Our results will show that this approach is reasonable.

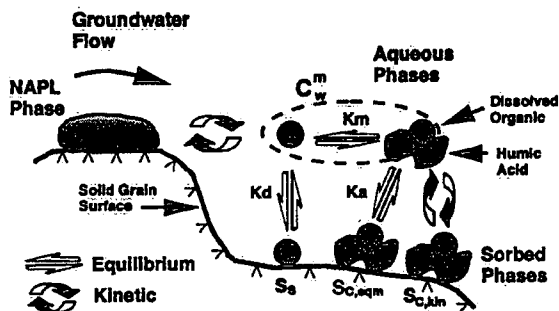


Figure 1. Conceptual model for enhanced dissolution showing the NAPL, aqueous and sorbed phases.

Sorption of the carrier to the aquifer solids is represented by a mixed equilibrium/kinetic two-site conceptual model using a Langmuir isotherm for the equilibrium component. In this model, a fraction of the solid sorption sites for the carrier is assumed to be in equilibrium with the carrier while sorption to the remaining fraction is kinetically limited. The approach combines the 2-site sorption model used by Haggerty & Gorelick (1995) (extended here to include Langmuir isotherms) with the dissolution enhancement approach as presented by Ji & Brusseau (1998).

## 3. THE NUMERICAL MODEL

To simulate the pilot-scale test, several coupled processes must be considered in the model. These processes include dissolution of the residual diesel source, transport and sorption of the aqueous diesel components, transport and sorption of the humic acid carrier, and electron acceptor-limited organic biodegradation.

The numerical model BIONAPL/3D is based on a finite element Galerkin solution of the advection-dispersion equation for each of the aqueous organic components, the humic acid carrier, and the dissolved oxygen (Molson, 2000a,b). Diesel fuel dissolution is simulated using a kinetic mass-transfer rate assuming validity of Raoult's Law (Frind et al., 1999). Biodegradation is simulated using an oxygen-limited dual-Monod approach (Frind et al., 1989). A mixed kinetic/equilibrium approach is adopted for sorption of the humic acid carrier to the aquifer solids. Equilibrium sorption is assumed for binding of the organics to the humic acid (defined by  $K_m$  in Figure 1).

The model assumes fully saturated conditions and accounts for relative permeability increases due to NAPL dissolution. The nonlinear equations are coupled using Picard iteration with a conjugate gradient matrix solver.

## 4. THE PILOT-SCALE EXPERIMENT

The pilot-scale experiment was performed at the Canada Centre for Inland Waters (CCIW), Burlington, Ontario (Lesage et al., 1997; Van Stempvoort et al., 2000). A model sand aquifer, shown in Figure 2, was constructed within a stainless steel tank measuring 5.5 x 1.2 x 2 m in the longitudinal, transverse horizontal and vertical directions respectively and was filled with winter sand of porosity 0.30 and bulk density 1860 kg/m<sup>3</sup>. Approximately 500 mL of diesel fuel was mixed with 25 kg of water-wet sand, creating an initial residual source with a NAPL saturation of approximately 0.09. Water and the humic acid solution enters from the left face of the domain (corresponding to the head tank) while effluent is withdrawn from a fully-screened well located just inside the right boundary near the end of the tank.

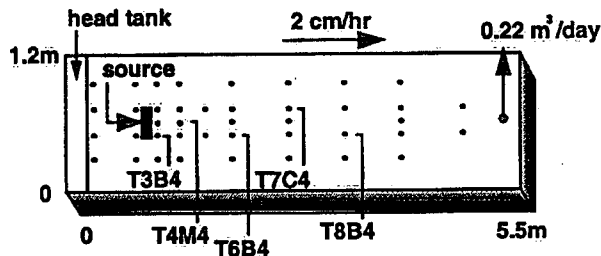


Figure 2. Plan-view layout of the pilot-scale experiment.

Initial flow velocities were maintained at approximately 2 cm/hr but may have decreased later in time due to bacterial pore clogging. The source was allowed to dissolve for 50 days under ambient conditions (water flush) after which humic acid at a continuous concentration of 0.83 g/L was added at the head tank and re-circulated using the extraction well. Throughout the 5-year experiment, the dense 3D multilevel sampling array was monitored for humic acid concentrations and several diesel fuel components.

### 5. SIMULATION OF THE PILOT-SCALE EXPERIMENT

Following the fitting of the batch sorption data, the 3D model was applied to simulate the enhanced dissolution of the residual diesel fuel source at the pilot scale. The domain consisted of a three-dimensional grid measuring 5.5 m x 1.2 m x 1.25 m, resolved using 57 x 20 x 15 (= 17,100) elements in the longitudinal, transverse horizontal and vertical dimensions, respectively (Figure 3). Grid spacing varied along the flow direction from 0.016 m within the source to 0.2 m towards the downgradient boundary. Spatial resolution was based on the grid Peclet criterion and by reaction stability and convergence constraints.

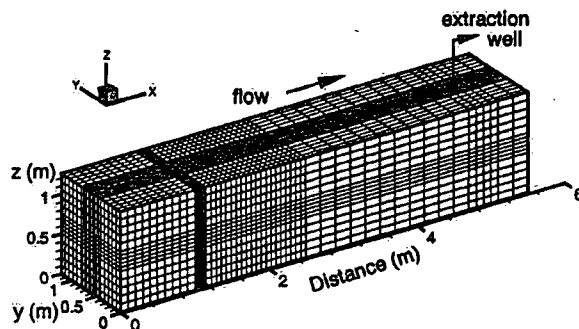


Figure 3. The 3D finite element numerical grid.

Material properties and flow gradients were obtained from the experimental data (Table 1). A fixed head was assigned at the left inflow face (corresponding to the head tank) while all remaining boundaries were impermeable. The withdrawal well was assigned a total flux of 0.216 m<sup>3</sup>/day. Dispersivities of 0.025, 0.005 and 0.005 m were assigned for the respective x, y and z dimensions based on model calibration to a conservative bromide tracer. Simulation time steps varied from 0.2 days at early time and during initial HA flushing, to 1.0 days at later times.

The simulated source consisted of 500 mL of diesel fuel placed within the fine-mesh area 1m from the left inflow

boundary. Seven unique diesel fuel compounds were considered in the model: benzene, toluene, ethylbenzene and the xylene isomers (BTEX), as well as methyl-naphthalene, dimethylnaphthalene and trimethylnaphthalene. An eighth "pseudo-component" was used to represent the remaining, relatively less soluble, diesel fuel compounds.

Organic properties, including aqueous solubilities and partition coefficients were obtained from laboratory batch tests or published data. Oxygen was considered as the single electron acceptor with a single microbial population. Including the humic acid carrier, the concentration of 11 "species" are simulated at each time step over the 19,488-node grid. The computational effort decreases over time as the more soluble components dissolve and are removed from the model.

The simulated breakthrough curves of the naphthalene components at a point immediately downgradient from the source (monitor T3B4) are compared to the observed data in Figure 4. Three distinct trends characterize both the simulated and observed concentration profiles: an early-time plateau, a sharp increase, and a slow decline.

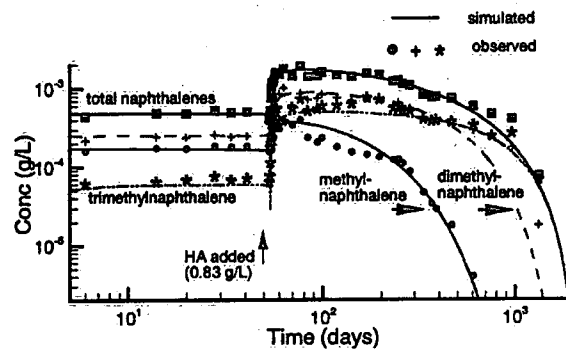


Figure 4. Simulated and observed concentrations of the naphthalenes at monitor T3B4.

During the initial 50-day period before humic acid was added, the diesel components dissolve from the source and reach their effective equilibrium saturations according to their aqueous solubilities, mole fractions and activities.

At 51 days, humic acid (0.83 g/L) was added to the head tank and reached the diesel source within two days. Partitioning of the organics onto the humic acid rapidly increases the effective solubilities of the naphthalene components with the steepest rise occurring within 5 days of the humic acid arrival. Peak enhanced solubilities are not reached until somewhat later.

Table 1. Physical and reactive properties of the diesel components assumed in the pilot-scale simulation model.

Diesel Component	Density kg/m <sup>3</sup>	MW kg/mol	Co <sup>(1)</sup> kg/m <sup>3</sup>	Mole fract. mol/(Σmol)	Kd <sup>(2)</sup> m <sup>3</sup> /kg	Km <sup>(3)</sup> m <sup>3</sup> /kg	D <sup>s(4)</sup> m <sup>2</sup> /s x 10 <sup>-10</sup>
Benzene	877.	.078	1.78	0.00003	0.0806	0.0	7.7
Toluene	870.	.092	0.52	0.0001	0.161	0.0	6.6
Ethylbenzene	870.	.106	0.15	0.0024	0.161	0.0	6.0
Xylenes	870.	.106	0.20	0.0048	0.161	0.0	5.6
Methylnap.	1000.	.142	0.035	0.0033	0.20	2.1	6.6
Dimethylnap.	1000.	.156	0.008	0.0152	0.40	3.7	6.6
Trimethylnap.	1000.	.170	0.0021	0.0138	1.3	10.	6.6
Other	862.	.230	0.001	0.9596	1.3	10.	5.0

(1) pure phase solubility, (2) distribution coefficient (organics - solids), (3) binding coefficient (organics - HA)  
(4) diffusion coefficient

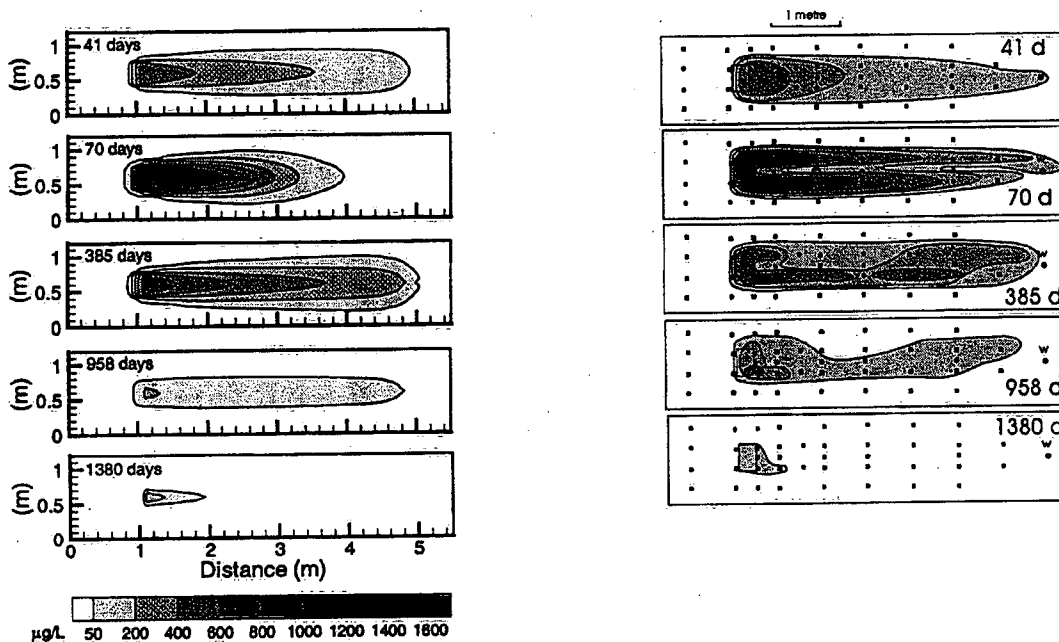


Figure 5. Plan-view sections (through the source) of the total naphthalene plumes showing simulated (left) and observed (right) concentrations.

The solubilities increased by up to a factor of 10 for the trimethylnaphthalenes. Afterwards, concentrations slowly decline due to source mass depletion, dispersion and biodegradation. The simulations suggest that the source was dissolving at equilibrium or near-equilibrium conditions throughout the experiment. The predicted dissolution times to reduce aqueous concentrations to 10 µg/L were 500, 1200 and 1700 days for the methyl-, dimethyl- and trimethylnaphthalenes, respectively.

The (total) naphthalene plumes are shown in plan view (through the source centre) at 41, 70, 385, 958 and 1380

days in Figure 5 for the simulated and observed systems. At 41 days (10 days before adding humic acid), the simulated plume has attained a steady state configuration with source concentrations of about 400 µg/L. Also, the 50 µg/L contour has just reached the extraction well which is in good agreement with the observed plume. Although the observed plume appears somewhat wider than the simulated plume, this is possibly an artifact due to the monitor well spacing and contour interpolation between monitors.

At 70 days (19 days after adding humic acid), the source concentration has increased to 1700 µg/L due to humic acid-enhanced dissolution of the residual diesel. The simulated 50 µg/L contour, however, has somewhat receded relative to its location at 41 days (Figure 5). The apparent shortening of the plume is caused by sorption of the aqueous organics to the sorbed carrier (enhanced sorption), immediately after humic acid flushing. This effect is not as apparent in the observed data, suggesting the effect of enhanced sorption may have been somewhat overpredicted. The origin of the narrow gap down the centreline of the observed plume at 70 days is uncertain but may be related to microbial growth or bypassing of flow around the source. The simulated plumes clearly do not match the observed small-scale irregularities, however the general concentration levels are maintained.

Once the carrier reaches higher concentrations along the plateau of the Langmuir isotherm, the sorption sites become saturated and the organics, which are sorbed to the carrier, become fully mobilized. The plume then begins to re-advance.

By 385 days, the total naphthalene plume has re-advanced although concentrations have already begun to decrease due to source depletion and biodegradation (Figure 5). By 958 days, the plume has receded to the extent that the 50 µg/L contour no longer reaches the extraction well. After 1380 days, the source concentration has decreased to approximately 200 µg/L and the plume extends less than a metre from the source.

Throughout the experiment, active biodegradation of the source and dissolved organics was occurring, as revealed by dissolved oxygen concentrations which decreased from a background of about 6.5 mg/L to less than 0.5 mg/L within the organic plumes (Van Stempvoort et al., 2000). Oxygen was clearly being depleted, however the spatial and temporal variation was unknown.

The simulated oxygen depletion plumes are provided in Figure 6, which show oxygen concentrations ranging from a background of 6 mg/L to essentially zero within the plume-impacted zone of the tank. The oxygen depletion plumes grow in size from 41 to 385 days after which they essentially reach a steady state configuration, maintained by biodegradation of the remaining diesel fraction.

## 6. LONG-TERM DISSOLUTION

Without a carrier, the diesel source will dissolve more slowly and the effective biodegradation rate will be reduced. This behaviour is shown in Figure 7 in which the long-term dissolution profile of the base case (calibration) scenario is compared to an otherwise equivalent simulation assuming no carrier.

The results show that the humic acid carrier has decreased the time required to reach drinking water limits by a factor of about 2 for methylnaphthalene, 2.5 for

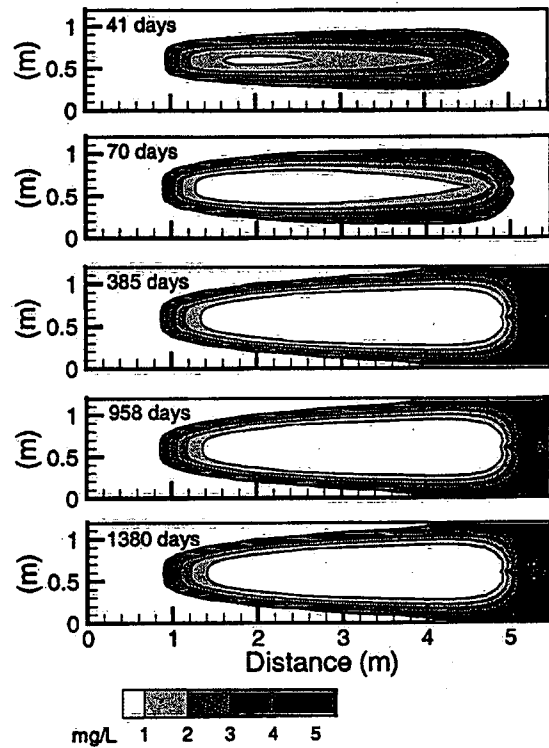


Figure 6. Simulated oxygen depletion plumes.

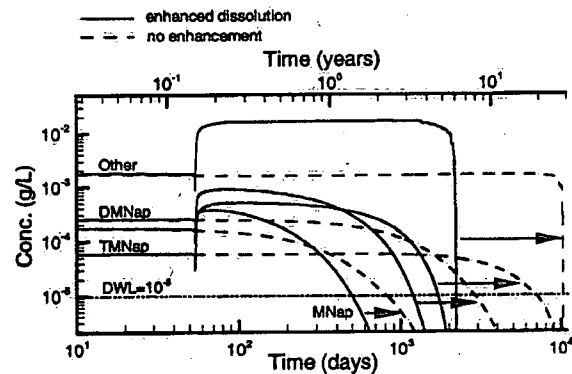


Figure 7. Simulated long-term dissolution of the diesel source comparing dissolution rates with and without a humic acid carrier. Arrows indicate increase in dissolution time assuming no carrier.

dimethylnaphthalene, 4 for trimethylnaphthalene, and 5 for the remaining components. Although the enhancement factors for the remaining components were unknown, both the observed and simulated sources were almost completely dissolved and degraded after 5 years, hence we can be fairly confident of the simulated bulk dissolution behaviour for the unmonitored fraction.



Environment Canada Library, Burlington



3 9055 1017 5568 3



Environment  
Canada

Environnement  
Canada

Canada

**Canada Centre for Inland Waters**

P.O. Box 5050  
867 Lakeshore Road  
Burlington, Ontario  
L7R 4A6 Canada

**National Hydrology Research Centre**

11 Innovation Boulevard  
Saskatoon, Saskatchewan  
S7N 3H5 Canada

**St. Lawrence Centre**

105 McGill Street  
Montreal, Quebec  
H2Y 2E7 Canada

**Place Vincent Massey**

351 St. Joseph Boulevard  
Gatineau, Quebec  
K1A 0H3 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

**Centre Saint-Laurent**

105, rue McGill  
Montréal (Québec)  
H2Y 2E7 Canada

**Place Vincent-Massey**

351 boul. St-Joseph  
Gatineau (Québec)  
K1A 0H3 Canada