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Development of Bioplume 4 Model for Fuels and Chlorinated Solvent Biodegradation

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ABSTRACT: The Bioplume model has been in development and use for modeling biodegradation and natural attenuation since the late 1980s. Bioplume 1 focused on aerobic biodegradation of BTEX. Bioplume II simulated oxygen and hydrocarbons and simulated biodegradation using an instantaneous reaction. Anaerobic biodegradation in Bioplume II was modeled as a first-order reaction. Bioplume III expanded the kinetic expressions for biodegradation available in Bioplume II and included first-order, instantaneous, and Monod kinetics. Additionally, Bioplume III simulated the anaerobic electron acceptors in the subsurface along with oxygen and hydrocarbon. In this fourth generation version, the conceptual model for biodegradation in Bioplume has been significantly changed. There is a growing appreciation for the role of Iron III minerals in the abiotic transformation of contaminants including *cis*-DCE and vinyl chloride and MTBE. Existing codes cannot simulate biodegradation by iron reducing microorganisms in a logical and straightforward manner. Bioplume 4 was developed to meet this need. The key changes include: (1) simulating both fuels and chlorinated solvents; (2) eliminating Monod kinetics due to the lack of kinetic rate data; (3) addition of zero-order kinetic expression for BTEX; (4) allowing iron reduction and methanogenesis to occur simultaneously for BTEX; and (5) incorporating biodegradation for vinyl chloride and *cis*-DCE using Iron III as an electron acceptor. Furthermore, the Bioplume 4 model incorporates a new interface for data entry and visualization that allows comparison to measured data in monitoring wells. This paper presents the new biodegradation conceptual model implemented in Bioplume 4 as well as illustrative examples.

INTRODUCTION

The Bioplume model has been in development and use for modeling biodegradation and natural attenuation since the late 1980s. Borden and Bedient (1986) presented a conceptual model for aerobic biodegradation and developed the first version (Bioplume 1). The main concept in Bioplume 1 involved neglecting the kinetics of the biodegradation reaction (Borden et al., 1986) and representing the aerobic biodegradation as an instantaneous reaction between the hydrocarbon and oxygen. Rifai et al. (1987, 1988, and 1990) implemented the instantaneous reaction assumption into the USGS Method of Characteristics fate and transport model (Konikow and Bredehoeft, 1978) to develop the second version of the Bioplume model or Bioplume II. Anaerobic biodegradation in Bioplume II was modeled as a first-order reaction since not much research had been done on the anaerobic biodegradation of fuel hydrocarbons at the time. Rifai et al. (2000) expanded the kinetic expressions for biodegradation available in Bioplume II and included first-order, instantaneous, and Monod kinetics in their development of Bioplume III. Additionally, Rifai et al. (2000) simulated the anaerobic electron acceptors and their

transport in the subsurface along with oxygen and hydrocarbon to model anaerobic biodegradation.

The interest in biodegradation and natural attenuation continues to increase with more emphasis on chlorinated solvents and alternate pathways for their biodegradation. For example, there is a growing appreciation for the role of Iron III minerals in the biotic transformation of contaminants including *cis*-DCE and vinyl chloride and MTBE. Existing codes cannot simulate biodegradation by iron reducing microorganisms in a logical and straightforward manner. Bioplume 4 was developed to meet this need. In this fourth generation version, the conceptual model for biodegradation in Bioplume has been significantly changed. The key changes include: (1) simulating both fuels and chlorinated solvents; (2) eliminating Monod kinetics due to the lack of kinetic rate data for fuels and chlorinated solvents; (3) addition of a zero-order kinetic expression for BTEX; (4) allowing iron reduction and methanogenesis to occur simultaneously for BTEX; and (5) incorporating biodegradation for vinyl chloride and *cis*-DCE using iron III as an electron acceptor. Furthermore, the Bioplume 4 model incorporates a new interface for data entry and visualization that allows comparison to measured data in monitoring wells.

The development of Bioplume 4, as in Bioplume III, was based on the 1989 version of the MOC model (Goode and Konikow, 1989). The key differences between Bioplume III and Bioplume 4 include:

1. Iron reduction and methanogenesis modeling approach for fuel hydrocarbons has changed. In Bioplume 4, iron reduction and fermentation are allowed to occur simultaneously. Fermentation is a first-order decay reaction that is not limited by an electron acceptor while iron reduction is limited by the concentration of bioavailable iron in the matrix. Iron reduction may be zero-order or first-order;
2. Chlorinated solvent reductive dechlorination is modeled using a first-order reaction; and
3. Biodegradation and chemical degradation of lower chlorinated solvents via iron minerals is also modeled using a first-order reaction.

The following sections describe in more detail the conceptual model for biodegradation used in Bioplume 4 and provide examples of its newly developed interface.

CONCEPTUAL MODEL FOR FUEL BIODEGRADATION

The conceptual model used in Bioplume 4 to simulate the aerobic and anaerobic biodegradation processes involved tracks four plumes simultaneously: hydrocarbon, oxygen, nitrate, and sulfate. Biodegradation using these three electron acceptors occurs sequentially and each of the three reactions proceeds until all the available electron acceptor is consumed. Furthermore, nitrate reduction is not allowed to occur in the presence of oxygen, and sulfate reduction cannot occur in the presence of oxygen or nitrate. The model then simulates the biodegradation of the hydrocarbons using bioavailable iron as an electron acceptor and via fermentation. These last two reactions can occur concurrently. However, iron reduction cannot begin until all the oxygen, nitrate and sulfate have been consumed. Thus, biodegradation occurs sequentially in the following order:

$$\text{Oxygen} \rightarrow \text{Nitrate} \rightarrow \text{Sulfate} \rightarrow \text{Iron (III) and Fermentation}$$

Biodegradation of the hydrocarbons using oxygen, nitrate and sulfate can be modeled as a zero-order, first-order or as an instantaneous reaction. Biodegradation via iron reduction, however, can only be modeled as a zero-order or first-order reaction while fermentation is modeled strictly as a first-order reaction. The zero-order and first-order reactions for oxygen, nitrate, sulfate and bioavailable iron are simulated as limited reactions, i.e., limited by the electron acceptor concentration: once the electron acceptor is consumed, the reaction stops. This conceptual model for fuel hydrocarbon biodegradation is summarized in Table 1:

TABLE 1. Summary conceptual model for hydrocarbon biodegradation

REACTION PATHWAY	USER OPTIONS FOR REACTION KINETICS	SEQUENCE IN REACTION	LIMITED BY ELECTRON ACCEPTOR?
Dissolved oxygen as electron acceptor	• First-Order Decay or • Zero-Order Decay or • Instantaneous Reaction	First	YES
Nitrate as electron acceptor		Second (after oxygen gone)	YES
Sulfate as electron acceptor		Third (after nitrate gone)	YES
Bioavailable Iron as electron acceptor	• First-Order Decay or • Zero-Order Decay	Fourth (after sulfate gone) (both these pathways happen simultaneously	YES
Fermentation	• First-Order Decay		NO

CONCEPTUAL MODEL FOR HIGHER CHLORINATED SOLVENT BIODEGRADATION

The Bioplume 4 model simulates the biodegradation of the highly chlorinated solvents (three or more chlorine atoms in the molecule, e.g., tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1 trichlorethane (1,1,1 TCA), 1,1,2 trichloroethane (1,1,2 TCA), carbon tetrachloride, chloroform, or methylene chloride) as a first-order reaction (Table 2). Electron acceptors do not limit the reductive dechlorination of these chlorinated solvents.

TABLE 2. Summary conceptual model for biodegradation of higher chlorinated solvents

REACTION PATHWAY	USER OPTIONS FOR REACTION KINETICS	ORDER OF REACTION	LIMITED BY ELECTRON DONOR?
Reductive Dechlorination	• First-Order Decay	First (only reaction)	NO

CONCEPTUAL MODEL FOR LOWER CHLORINATED SOLVENT BIODEGRADATION AND CHEMICAL DEGRADATION

The Bioplume 4 model simulates the biodegradation of the lower chlorinated solvents (less than three chlorine atoms in the molecule, e.g., *cis* 1,2 dichloroethene (1,2-DCE) or vinyl chloride (VC)) using bioavailable iron as an electron acceptor. This reaction is modeled using first-order decay or second-order decay based on the chemical concentration of the chlorinated solvent and the amount of iron remaining on the matrix.

The Bioplume 4 model also simulates the abiotic degradation of these lower chlorinated solvents (using for example green rust or other iron minerals as a reactant) via a second-order decay reaction based on the chemical concentration of the chlorinated solvent and the amount of Iron II remaining on the matrix. Both of these degradation mechanisms for the lower chlorinated solvents are summarized in Table 3.

TABLE 3. Summary conceptual model for degradation of lower chlorinated solvents

REACTION PATHWAY	USER OPTIONS FOR REACTION KINETICS	ORDER OF REACTION	LIMITED BY IRON?
Direct biological oxidation using bioavailable iron as electron acceptors	• First-Order Decay or • Second-Order Decay based on COC concentration and amount of iron remaining on matrix	First (only reaction)	YES
Direct chemical reduction using green rust or other iron minerals as a chemical reactant	• Second-Order Decay based on COC concentration and amount of Iron II remaining on matrix	First (only reaction)	YES

BIOPLUME 4 INTERFACE

A new user interface has been developed for this fourth generation version of the Bioplume model. The interface relies on recent developments in computer-based technologies, particularly html programming and point-and-click functionality. Many of the interface features and functions that were incorporated in prior versions of Bioplume were maintained; however, some were eliminated due to their complexity and based on user feedback. As an example, drawing tools to "paint" spatially variable input for the model were incorporated into the new interface but "kriging" and "geostatistical" tools for generating these 2-D surfaces from point data were not. The new interface includes a *grid editor* (see Figure 1) that allows the user to paint in the values corresponding to a spatially distributed variable such as hydraulic conductivity, aquifer thickness and recharge. This eliminates the need for manual data entry. While "kriging" options were not included in the Bioplume 4 interface, the ability to import data from kriging software was maintained such that 2-D data for a grid can be imported directly into the input file for Bioplume 4 using the interface.

The new user interface was developed in the Windows environment, and is compatible with Windows versions 98 and higher. The user interface consists of two basic parts. The *preprocessor*, where the user enters in model values (see for example Figure 2), and the *postprocessor*, where the user can view the model output. Both are menu-driven and use pull-down menus to guide the user through the various steps and options within the model. Additionally, Bioplume 4 incorporates an electronic manual with help screens that is accessible throughout the interface.

The preprocessor includes eight basic steps for entering the Bioplume 4 input variables as shown in Table 4. Optional data entry steps include adding a base map to the model, and identifying the locations of existing monitoring points within the model grid. In addition to the grid editor for entering spatially variable data shown in Figure 1, the preprocessor incorporates other graphical tools for entering time-varying data such as source loading. Figure 3 illustrates the "slider" tool that allows the user to enter the

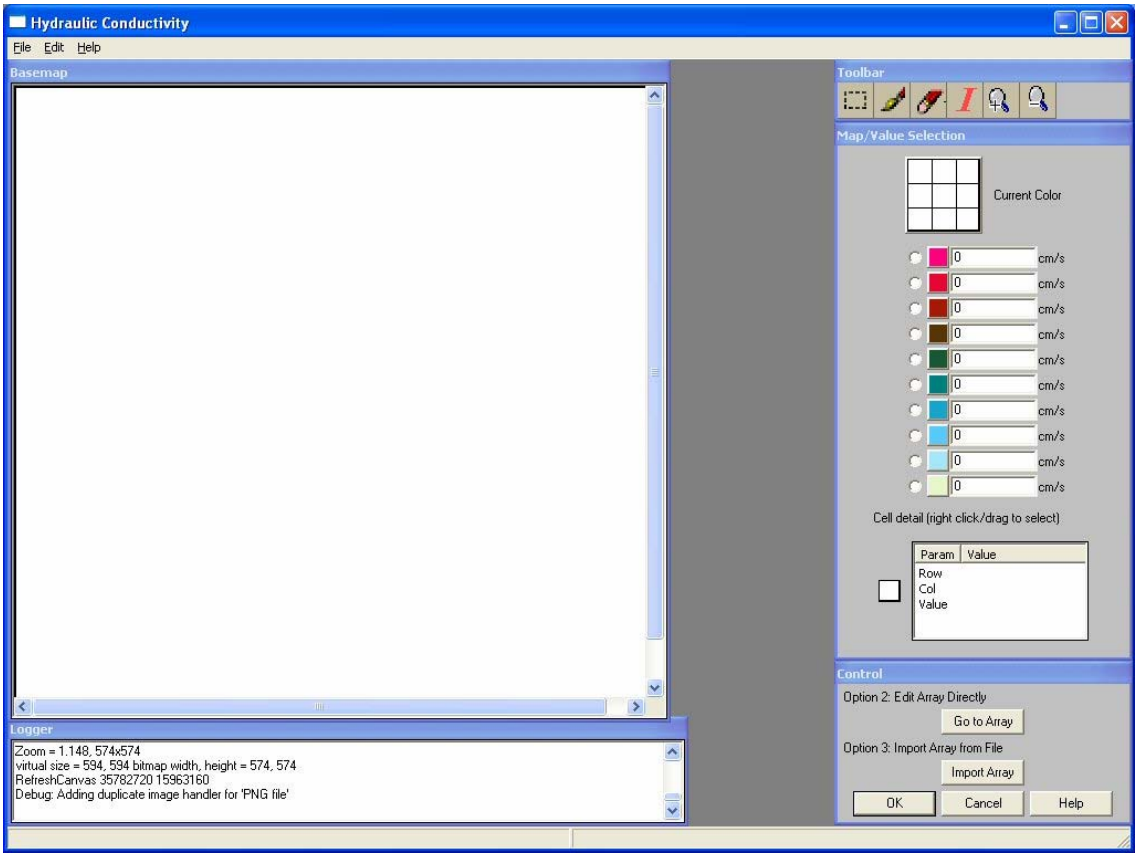

FIGURE 1. Grid editor for entering 2-D distributions for variables such as hydraulic conductivity, aquifer thickness, and recharge

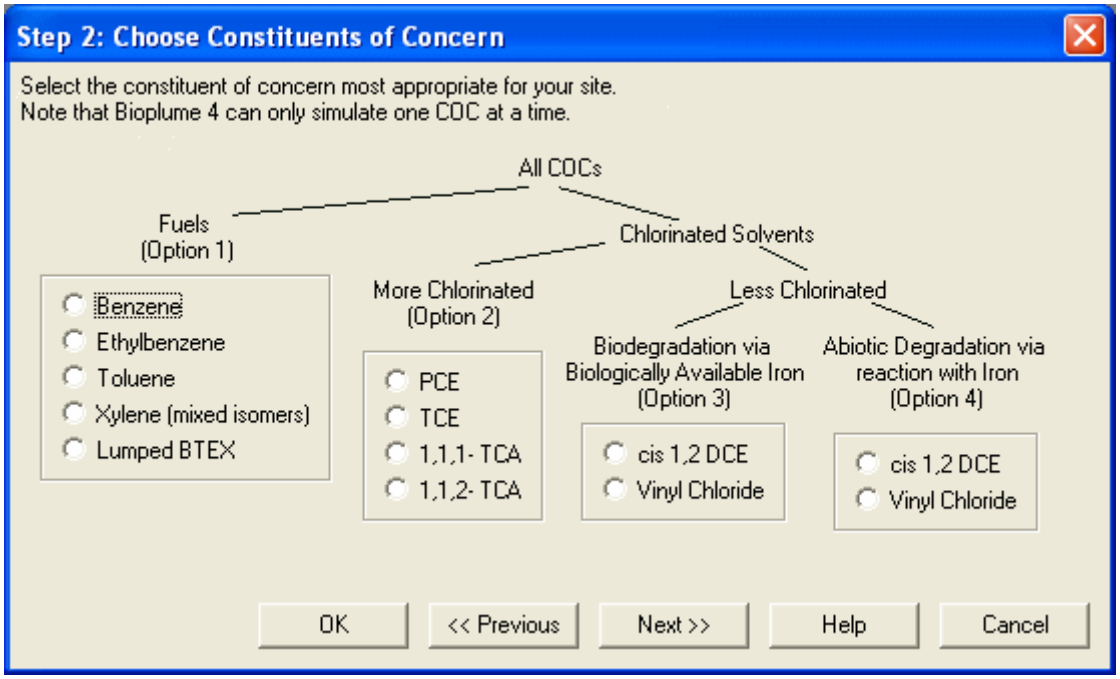

FIGURE 2. Example input screen for selecting compound of interest

TABLE 4. Data entry modules in Bioplume 4 preprocessor

General Site Description	This is general information about the run, including project name, description, current date, and notes.
Constituent of Concern	Select from the following: Benzene, Toluene, Ethylbenzene, Xylene, Lumped BTEX, PCE, TCE, 1,1,1-TCA, 1,1,2-TCA, *cis*-1,2-DCE, or Vinyl Chloride.
Grid Size	Select cell dimensions and the grid size (up to 100 x 100 cells).
Hydrogeologic Parameters	Enter Hydraulic conductivity, porosity, recharge, potentiometric surface, saturated thickness.
Transport Parameters	Enter Longitudinal dispersivity, ratio of longitudinal to transverse dispersivity, fraction of organic carbon on matrix, bulk density, distribution coefficient.
Source Zone	Enter source zone by either selecting an area or by placing "injection wells" and source zone decay parameters.
Biodegradation Parameters	Enter biodegradation decay rates for the chemical of concern for the aerobic and anaerobic pathways, as applicable.
Time Parameters	Enter the duration of the simulation.

source loading on an annual basis for a given site to represent a temporally variable source.

The postprocessor allows the user to view hydraulic heads, concentration maps for fuels or chlorinated compounds as well as the electron acceptors on an annual basis. The

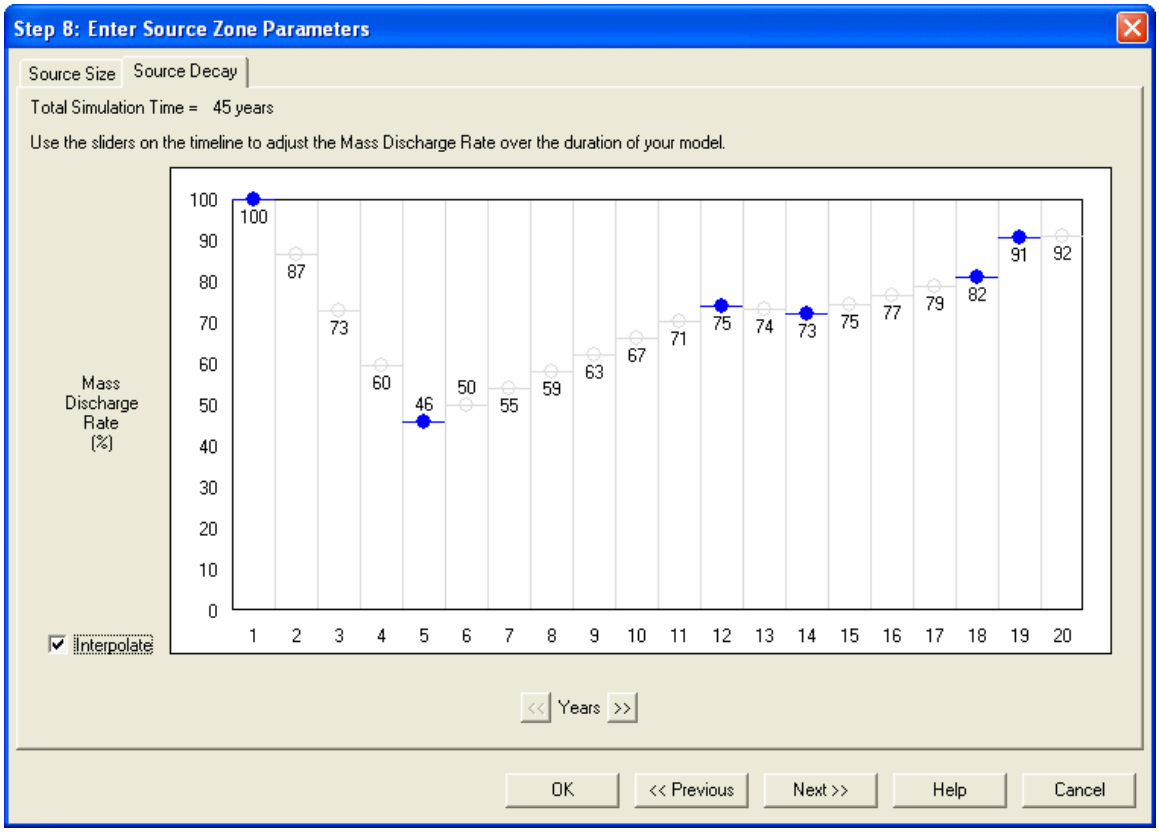

FIGURE 3. Input screen for entering variable source loading over time for Bioplume 4

user can also visually compare modeled results versus measured data at specific monitoring points or for the entire site using the tools in the postprocessor.

The Bioplume 4 interface additionally incorporates a set of tools designed to aid the user in modeling sites (see Table 5). The Wizard, for example, guides the user through the process of setting up a basic model while the Unit Converter allows users to enter model variables in metric or English units.

TABLE 5. Tools available within Bioplume 4 interface

Bioplume Model Wizard	Starts the model wizard, which will guide the user through the process of creating a very basic model
Unit Converter	A tool to help users convert units
Preferences	Edit the preferences for Bioplume
Grid Editor	Opens the grid editor, which allows the user to edit any of the grids in the model
Domenico Analysis	Opens a calculator for the Domenico equation, a common analytical model for groundwater transport
Mann Kendall trend Analysis	Opens a calculator to perform Mann Kendall trend analysis on imported site data.
Create AVI movie	Allows the user to create an AVI movie for the model output
Multipliers	Opens a table for multipliers for the model, which can be useful for performing sensitivity analyses on the model.

SUMMARY AND CONCLUSIONS

This paper describes the development of the fourth generation version of the Bioplume model for aerobic and anaerobic biodegradation of fuels and chlorinated solvents. The model varies significantly from its predecessors in its conceptual approach to modeling biodegradation. Fermentation and methanogenesis are allowed to occur simultaneously for hydrocarbons while chlorinated solvents are biodegraded using first-order and second-order reaction kinetics depending on their level of chlorination and the presence of bioavailable iron. A new interface that relies on commonly used computer technologies was also developed to facilitate data entry and model set-up for specific sites.

NOTICE

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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