

Coupled Biogeochemical Modeling of Ground Water Contamination at the Bemidji Minnesota Crude Oil Spill Site.

By Gary P. Curtis, Isabelle M. Cozzarelli, Mary Jo Baedecker, and Barbara A Bekins.

ABSTRACT

Fully-coupled multicomponent reactive solute transport simulations were performed for the groundwater contamination at the Bemidji, MN crude oil spill site. The simulations included the oxidation of the dissolved crude oil constituents by microorganisms using four different terminal electron acceptors: O_2 , MnO_2 , $Fe(OH)_3$ and CO_2 . The simulations also accounted for the dissolution of reactive phases resulting from the limited amount of each reactant, the formation of new phases containing Mn^{2+} and Fe^{2+} , and the outgassing of CO_2 and CH_4 . The simulations assumed that O_2 was used preferentially and that all other terminal electron acceptors were used in parallel. Simulation results are presented that reproduce many of the features illustrated by the field data including the disappearance of the O_2 , the appearance of Mn^{2+} , Fe^{2+} , and CH_4 , the pH values, the diminished concentrations of solid phases Fe^{+3} beneath the oil body as well as the increase in Fe^{+3} -containing solid phase concentrations in the dow

INTRODUCTION

The dissolution and biodegradation of crude oil in an unconfined aquifer near Bemidji, MN has caused a diverse range of geochemical changes. Baedecker and others (1993) identified five geochemical zones that have developed as a result of these biodegradation reactions. These zones are depicted in figure 1 as zones I-V. Briefly, these zones have been described as: (I) the background water which is a Ca-Mg- HCO_3 water with a pH 7.6 to 7.8, that is saturated with oxygen, (II) a mixed zone characterized by low O_2 and elevated dissolved organic carbon (DOC), (III) an anaerobic zone with high concentrations of DOC, Fe^{2+} , Mn^{2+} and CH_4 , and a pH of 6.8, (IV) a transition zone between highly reducing conditions and oxidized conditions, and (V) an impacted zone, that shows elevated concentrations of Ca and Mg.

There have been at least three previous reports on modeling the geochemical changes in the Bemidji aquifer but none have conducted fully coupled modeling. Bennett and others (1993) matched the water composition in the anoxic core

of the plume by conducting reaction path calculations that mixed water from a silty layer near zone II with water from the boundary between zones II and III followed by oxidation of DOC by goethite. Baedecker and others, (1993) reported on a reaction-path model along a flow path from the zone III toward zone IV. The simulations required outgassing of CO_2 and CH_4 even though the flow path was 2 meters below the water table surface. Although these mixing and reaction path calculations can account for some geochemical changes, they do not account for any limitations imposed on the hypothesized mixing by the flow system.

Essaid and others (1995) conducted two dimensional reactive transport simulations that accounted for the biodegradation of crude oil, the consumption of O_2 , solid phase Mn(IV) and solid phase Fe(III) and the production of dissolved Mn^{2+} , Fe^{2+} , and CH_4 . These rate-controlled simulations showed that many of the features of the plume could be reproduced including the disappearance of O_2 , the appearance of Mn^{2+} , Fe^{2+} , CH_4 and the disappearance of DOC, and volatile DOC, the two forms of dissolved crude oil considered. These simulations did not include

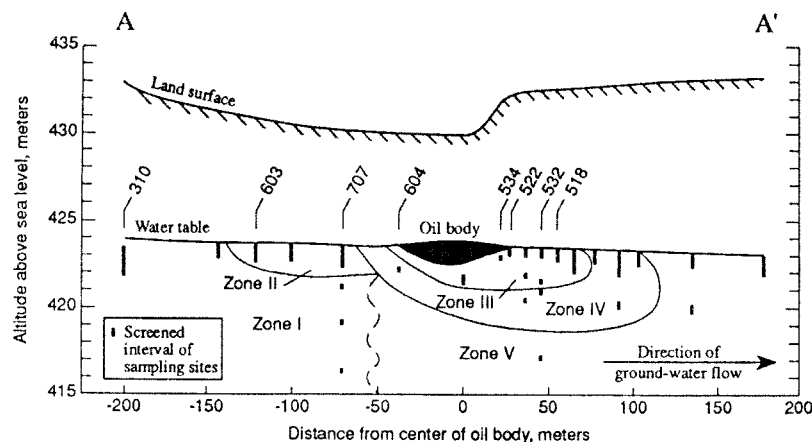


Figure 1. A cross section of the Bemidji aquifer (after Baedecker and others, 1993).

inorganic reactions including the carbonate system or the redox reactions involving O_2 and the reduced forms of Mn and Fe. In addition, precipitation of new phases containing reduced Fe and Mn was accounted for using a single constant for each metal and the formation of new phases containing oxidized Fe and Mn in the transition zone was ignored. Accurately accounting for these reactions may be important because they involve the electron acceptors for the biodegradation reactions which cause the geochemical changes in the aquifer.

The objectives of this work were to demonstrate the use of RATEQ (Curtis, in preparation), a fully coupled model for simulating biogeochemical transport, and to reproduce the field observations for multiple inorganic and organic species.

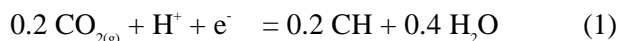
CONCEPTUAL MODEL

Geochemical Reactions

Modeling reactions involving the degradation of dissolved crude oil is difficult, in part, because crude oil is a complex mixture of many individual compounds. In view of this complexity, the dissolved crude oil is represented here as a generic hydrocarbon and denoted as CH (Baedecker and others, 1993; Bennett and others, 1993). This approach establishes the nominal redox-state of the crude oil and allows one to express the degradation reactions as

stoichiometrically balanced reactions.

Formulating these reactions is critical for both mathematically coupling the oxidation of the electron donors (CH) to the different terminal electron acceptors, and for formulating the fully-coupled, multicomponent mass balance model. The half-reaction for the formation of CH is



The logarithm of the equilibrium constant ($\log K$) for this reaction was found to be 2.1 using the approach of MacFarlane and Sims (1993).

In the aquifer at Bemidji, the dominant electron acceptors available for the oxidation of CH are O_2 , solid phase Mn(IV), solid phase Fe(III), and CO_2 . Neither NO_3^- nor SO_4^{2-} are significant electron acceptors in this system because the concentration is too small (Baedecker and others, 1993; Bennett and others, 1993). The half-reactions for the electron acceptors are coupled with that for the electron donor (eqn 1) to give the final, stoichiometrically balanced reaction for the oxidation of the hydrocarbon (table 1). Each reaction in table 1 is written for the oxidation of 0.2 moles of CH. Thus, the $\log K$ values illustrate the thermodynamic basis for the sequential use of electron acceptors that is often observed for microbial processes.

In addition to the reactions involving the biodegradation of the dissolved crude oil, many other geochemical reactions occur in the aquifer. The bulk mineralogy of the Bemidji aquifer consists primarily of quartz, feldspars, calcite and dolomite, (Bennett and others, 1993). For the

Table 1: Reactions for the oxidation of CH by various electron acceptors.

Reactions	log K
$.2 \text{ CH} + .25 \text{ O}_2(\text{g}) + .1 \text{ H}_2\text{O} = .2 \text{ HCO}_3^- + .2 \text{ H}^+$	18.6
$.2 \text{ CH} + .5 \text{ MnO}_{2(\text{s})} + .8 \text{ H}^+ = .2 \text{ HCO}_3^- + .5 \text{ Mn}^{2+} + .4 \text{ H}_2\text{O}$	18.6
$.2 \text{ CH} + \text{Fe}(\text{OH})_{3(\text{s})} + 1.8 \text{ H}^+ = 2 \text{ HCO}_3^- + \text{Fe}^{2+} + 2.4 \text{ H}_2\text{O}$	13.9
$.2\text{CH} + .225 \text{ H}_2\text{O} = .075 \text{ HCO}_3^- + .125 \text{ CH}_4 + .075 \text{ H}^+$.9

simulations presented here, calcite and dolomite were included in the simulations, as were the aqueous carbonate and hydroxide species. In addition, a number of other redox reactions, sometimes called secondary reactions (Hunter and others, 1998), such as the oxidation of Fe^{+2} by MnO_2 or O_2 have been included.

One-dimensional reactive transport simulations were conducted along a 400m flow tube that extends from A to A' on figure 1. The initial conditions and the influent boundary condition were taken to match the average groundwater chemistry at well 310. The reactive phases and their relative amounts, expressed in units of moles of solid per liter of groundwater were; calcite (2M), dolomite (.25M), MnO_2 (0.001M) and $\text{Fe}(\text{OH})_3$ (0.12M). Given that the O_2 concentration in the aquifer was $2.5 \times 10^{-4}\text{M}$, $\text{Fe}(\text{OH})_3$ clearly has the potential to be one of the most important electron acceptors in the aquifer. Note that if all of $\text{Fe}(\text{OH})_3$ was reduced by CH, there would be a consumption of approximately 0.2 mole of H^+ per liter of aquifer (table 1). Extractions of cores taken from the site showed that after approximately 14 years half of the initial of $\text{Fe}(\text{OH})_3$ present beneath the oil body had been removed (Tuccillo and others, 1998) suggesting that there was a large consumption of H^+ . Because of this large consumption of H^+ , which tends to increase the pH, matching the observed decrease in the field pH was difficult.

REACTIVE TRANSPORT SIMULATIONS

The crude oil was assumed to dissolve into the groundwater according to a first order dissolution process:

$$\frac{\partial C}{\partial t} = k_{diss} (C_s - C) \quad (2)$$

where

- C is the concentration of CH
- C_s is the concentration of the CH in equilibrium with the crude oil, and
- k_{diss} is the first order dissolution constant.

The dissolution rate used in the simulations varied with distance along the flow path. The first order dissolution rate constant was zero except in Zone II (25 to 100 m upgradient from the center of the oil body) where the value was $5 \times 10^{-4} \text{ d}^{-1}$ and in Zone III (25 upgradient to 25m down gradient from the center of the oil body) where the value was $5 \times 10^{-2} \text{ d}^{-1}$. Outside of the zones where oil was assumed to be dissolving into the groundwater, the system was assumed to be in contact with atmospheric concentrations of O_2 . This was included downgradient of the oil body as an approximation to the annual water table fluctuations of approximately 0.5 m.

Degradation Rates

The reactive transport simulations presented here assumed that the microbial populations were constant in space and time. This assumption simplified the parameter estimation because it was difficult to obtain growth and decay parameters that gave acceptable simulation results. This difficulty may have been because of the autocatalytic nature of the reaction stoichiometry; if the biomass is allowed to vary, then the rate of the biodegradation reaction depends on the biomass produced by the reaction. A second difficulty encountered with simulating microbial growth was that the populations tended to grow

unbounded which contrasts with moderate populations observed in the field (Essaid and others 1995). The actual growth may be limited by nutrients such as phosphorous (Rodgers and others, 1999), or nitrogen (Essaid and others, 1995), although in the latter study it was found that it was still necessary to artificially limit growth. The assumption of a constant biomass is consistent with the approach used to simulate biodegradation with very low amounts of biomass produced per mole of carbon oxidized for methanogens at a creosote spill at Pensacola, FL (Bekins and others, 1993).

Although the biomass was assumed to be constant in time, a dual Monod kinetics formulation was used to simulate the reaction between the electron donor and the electron acceptor. For example, the oxidation of CH by Fe(OH)₃, has a rate law of the following form:

$$r = v_{\max} \left(\frac{C_{CH}}{C_{CH} + K_{CH}} \right) \left(\frac{C_{Fe}}{C_{Fe} + K_{Fe}} \right) \left(\frac{I_{O_2}}{C_{O_2} + I_{O_2}} \right)$$

where

- v_{\max} the maximum rate of substrate utilization,
- C_{CH} is the concentration of CH,
- K_{CH} is the half-velocity coefficient for the oxidation of CH by Fe(OH)₃,
- C_{Fe} is the concentration of Fe(OH)₃,
- K_{Fe} is the half-velocity coefficient for the reduction of Fe(OH)₃ by CH,
- I_{O_2} is the inhibition constant for the effect of O₂ on the Fe reduction rate, and
- C_{O_2} is the concentration of O₂.

Rate expressions of this form are used for each of

Table 2: Reaction constants used for RATEQ simulation. Values not used in simulations are denoted by a ‘-’

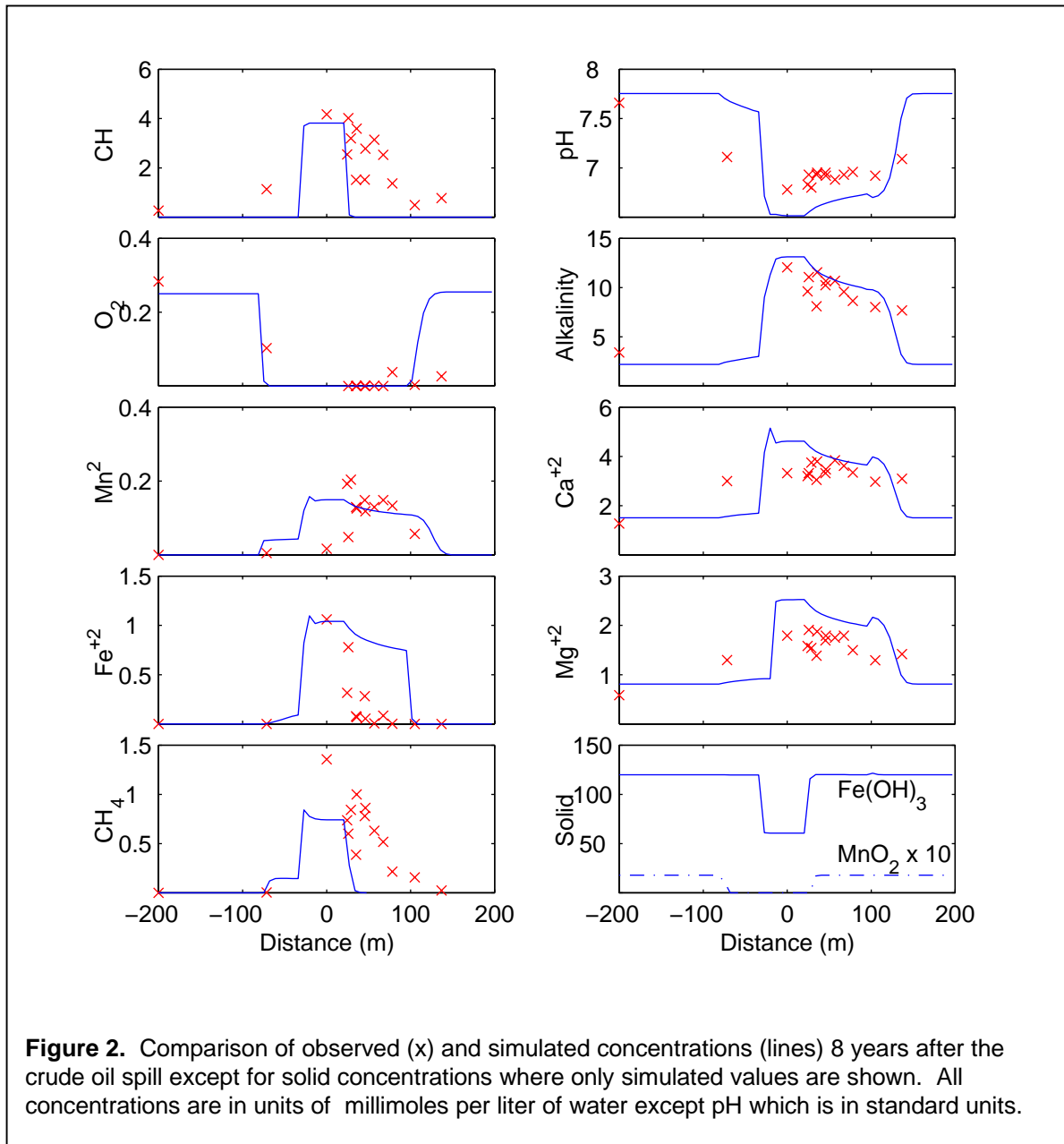
Acceptor	v_{\max} (d ⁻¹)	K_{CH} (M)	K_{Acc} (M)	I_{O_2} (M)
O ₂	1x10 ¹	1x10 ⁻³	1x10 ⁻⁴	-
MnO ₂	5x10 ⁻³	1x10 ⁻³	1x10 ⁻⁴	10 ⁻⁸
Fe(OH) ₃	4x10 ⁻⁵	1x10 ⁻³	6x10 ⁻²	10 ⁻⁸
CO ₂	2x10 ⁻⁴	1x10 ⁻³	-	10 ⁻⁸

the reactions listed in table 1.

Results and Discussion

The simulation results are presented in figure 2 and are compared with data obtained in 1987 (Baedecker and others, 1993, Cozzarelli and others, 1999). The Monod parameters used in these simulations were obtained by setting the half velocity coefficient to the initial concentration of the electron acceptor, or the saturated concentration in the case of CH, and adjusting the value of v_{\max} to obtain an acceptable visual fit to the data. The values used in the final simulations are summarized in Table 2. Note that only anaerobic processes were inhibited by using an inhibition constant of 10⁻⁷ M O₂. Fe(OH)₃ reduction was not inhibited by MnO₂ because Fe²⁺ produced can be oxidized back to Fe⁺³ by an equilibrium controlled redox reaction with MnO₂. Methanogenesis was not inhibited by the presence of Fe(OH)₃ for reasons discussed below.

The simulations in figure 2 reproduce the observed trends illustrated by the data. These trends include the appearance of CH, Fe²⁺, Mn²⁺ and CH₄, and the disappearance of O₂. For CH₄, only about 10% of the quantity produced by methanogenesis is illustrated in figure 2. The balance of the methane was removed in the model as a gas. A gas phase containing both CH_{4(g)} and CO_{2(g)} in equilibrium with aqueous solution was assumed to form when the sum of the partial pressures of CH_{4(g)} and CO_{2(g)} exceeded 1 atmosphere. The simulations also reproduce the observed decrease in the field pH, as well as increases in Ca²⁺, Mg²⁺, and alkalinity. The simulated solid phase Fe(OH)₃ is not completely depleted which agrees with observations from sediments samples taken from cores obtained at the site (Tuccillo and others, 1999). For CH, the simulations show little migration downgradient from the source area probably because the crude oil has been approximated in these initial simulations by a single compound which is assumed to be completely biodegradable. It is known that even slight structural differences of individual compounds has a large impact on the extent of degradation (Eganhouse and others, 1993). Similarly, the O₂ concentration increased to saturated values 100 meters downgradient from the source to reflect reoxygenation of the



groundwater, possibly from fluctuations of the water table.

The simulations illustrated in figure 2 were obtained by assuming that iron reduction and methanogenesis occurred simultaneously. This approach contradicts the often assumed process of sequential use of electron acceptors by microorganisms, but is supported by the observed co-occurrence of iron reducing and methanogenic bacteria (Bekins and others, 1999). This was the only set of reaction constants that was found that matched the observed decrease in pH and gave relatively close agreement for dissolved Fe^{2+} and solid phase Fe^{+3} . The protons consumed in the

oxidation of $\text{Fe}(\text{OH})_3$ are balanced by protons produced simultaneously by methanogenesis.

CONCLUSIONS

Coupled reactive transport simulations were performed to reproduce the observed geochemical trends in ground water at the Bemidji crude oil spill site. The simulations accounted for oxidation of CH, a dissolved crude oil constituent, by four electron acceptors: O_2 , MnO_2 , $\text{Fe}(\text{OH})_3$ and CO_2 . The simulations reproduced the general observed trends in CH, Fe^{+2} , Mn^{+2} , CH_4 , Ca^{+2} , Mg^{+2} , alkalinity, and pH. In this model, it was

necessary to allow Fe(OH)₃ reduction to occur simultaneously with methanogenesis to match the pH observed in the field. This approach contradicts the concept of sequential use of electron acceptors by micro-organisms, but it is supported by the coexisting iron-reducing and methanogenic microbial populations at the site (Bekins and others, 1999).

REFERENCES

- Baedecker, M.J., Cozzarelli, I.M., Eganhouse, R.P., Siegel, D.I., and Bennett, P.C., 1993, Crude oil in a shallow sand and gravel aquifer, III— Biogeochemical reactions and mass balance modeling in anoxic ground-water: *Applied Geochemistry*, v8, p529-549.
- Bekins, B.A. Cozzarelli, I.M., Godsy, E.M. Warren, E., Tuccillo, M.E., Essaid, H.I., and Paganelli, V.V., 1999, Chemical and Physical Controls on Microbial Populations in the Bemidji Toxics Site Cured-Oil Plume, in U.S. Geological Survey Toxic Substances Hydrology Program—Proceeding of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 3—Subsurface Contamination from Point Sources: U.S. Geological Survey Water Resources Investgations Report 99-4018C.
- Bekins, B.A., Godsy, E.M. and Goerlitz, D.F., 1993, Modeling Steady-State Methanogenic Degradation of Phenols in Groundwater: *Journal of Contaminant Hydrology*, v. 14, no. 3-4, p. 279-294.
- Bennett, P.C., Siegel, D.I., Baedecker, M.J. and Hult, M.F., 1993, Crude oil in a shallow sand and gravel aquifer, I – Hydrogeology and inorganic geochemistry; *Applied Geochemistry*, v8, p529-549.
- Cozzarelli, I.M., Baedecker, M.J., Eganhouse, R.P., Tuccillo, M.E., Aiken, G.R., Bekins, G.A., Jaeschke, J.B., 1999, Long-term geochemical evolution of the Bemidji Toxics site cured-oil plum, in U.S. Geological Survey Toxic Substances Hydrology Program—Proceeding of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 3—Subsurface Contamination from Point Sources: U.S. Geological Survey Water Resources Investgations Report 99-4018C.
- Eganhouse, R.P., Baedecker, M.J., Cozzarelli, I.M., Aiken, G.R., Thorn, K.A., and Dorsey, T.F., 1993, Crude oil in a shallow sand and gravel aquifer-II. *Organic geochemistry: Applied Geochemistry*, v. 8, p. 551-557.
- Essaid, H.I., Bekins, B.A., Godsy, E.M., Warren, E., Baedecker, M.J. and Cozzarelli, I.M., Simulation of aerobic and anaerobic biodegradation processes at a crude oil spill site, *Water Resources. Research.*, 31, p3309-3327.
- Hunter, K.S., Wang, Y, Van Cappellen, P., 1998, Kinetic modeling of microbially-driven redox chemistry of subsurface environments: coupling transport, microbial metabolism and geochemistry, *Journal of Hydrology*, v 209, p 53-80.
- McFarlane, M.J. and Sims, R.C., 1991, Thermodynamic framework for evaluating PAH degradation in the subsurface, *Ground Water*, 29, p 885-896.
- Rodgers, J.R., P.C. Bennett, and W.J. Choi, 1998, Feldspars as a source of nutrients for microorganisms, *American Mineralogist*, v. 83, 1532-1540.
- Tuccillo, M.E., Cozzarelli, I.M., and Herman, J.S., 1999, Iron reduction in the sediments of a hydrocarbon-contaminated aquifer: *Applied Geochemistry*, v. 4, no. 5, p. 71-83.

AUTHOR INFORMATION

Gary P. Curtis and Barbara A. Bekins, U.S. Geological Survey, Menlo Park, California

Isabelle M. Cozzarelli and Mary Jo Baedecker, U.S. Geological Survey, Reston, Virginia