
Modeling Intrinsic Remediation With Multiple Electron Acceptors: Results From Seven Sites

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ABSTRACT

Recent results from the Air Force Center for Environmental Excellence's (AFCEE) Natural Attenuation Initiative indicate that anaerobic processes dominate the biodegradation of dissolved petroleum hydrocarbons during intrinsic remediation (natural attenuation) of contaminated aquifers. In particular, sulfate reduction and methanogenesis appear to be the major sinks for BTEX compounds at seven AFCEE Natural Attenuation sites. Oxygen and nitrate serve as minor electron acceptors while ferric hydroxide utilization appears to be relatively insignificant.

Data from the seven AFCEE sites are currently being analyzed to determine the best method to simulate natural attenuation with multiple electron acceptors. The seven sites represent a variety of geographic locations (Alaska to Florida) and hydrogeologic settings (both high and low plume length/seepage velocity ratios). Two intrinsic remediation models are being developed, the BIOPLUME III numerical model and BIOSCREEN, a simple spreadsheet-based analytical modeling system. BIOSCREEN has been used to compare two different ways to simulate the kinetics of intrinsic remediation: 1) as a first-order decay expression and 2) as an instantaneous reaction between dissolved hydrocarbons and available electron acceptors.

The BIOSCREEN results indicate that both the first-order decay and instantaneous reaction models can be calibrated to simulate the observed BTEX concentrations in the field. The instantaneous reaction model provides a much closer match to the observed utilization of electron acceptors, however.

These results suggest that 1) the instantaneous reaction model is a better approach to simulating intrinsic remediation than a first-order decay model, and 2) the rate of actual BTEX dissolution from source zones may be much higher than the rate predicted by intrinsic remediation models that do not consider high biodegradation rates in the source zone. Methods for estimating plume lifetimes using the BIOSCREEN model will be presented.

INTRODUCTION

Review of Intrinsic Remediation

Naturally occurring contaminant attenuation processes such as biodegradation, adsorption, and dispersion can significantly enhance the rate of organic mass removal from contaminated ground water aquifers. Evaluating the effectiveness of these mechanisms is becoming recognized

as a cost-effective component of the remedial investigation for petroleum fuel spill sites. Data obtained from the intrinsic remediation investigation is used to characterize site conditions, to quantitatively assess the effectiveness of natural attenuation at the site, and to more accurately determine the actual risk to human health and the environment posed by site contaminants. Natural attenuation processes can, in some cases, contain the spread of ground water contaminant plumes, thereby preventing the completion of exposure pathways. The intrinsic remediation option, combined with long term monitoring, then becomes a cost-effective remedial approach. In cases where intrinsic remediation alone is not adequate to prevent the transport of hazardous constituents to receptor sites, cost savings can still be realized by limiting the degree of source zone remediation to a level which, in conjunction with downgradient natural degradation, will achieve risk-based clean-up standards.

Biodegradation in Groundwater Aquifers

Laboratory microcosm studies have confirmed the ability of naturally occurring (indigenous) microorganisms to degrade petroleum hydrocarbons in aquifer materials. The oxidation of organic contaminants, such as benzene, to carbon dioxide or simple organic acids can occur by alternative modes of metabolism possessed by individual species of soil bacteria. Each mode of metabolism requires a unique electron acceptor which becomes reduced during the oxidative degradation of the organic substrate. These electron acceptors include oxygen, nitrate, sulfate, ferric iron, and carbon dioxide. Site geochemical data can be used to demonstrate the depletion of electron acceptors (oxygen, nitrate, and sulfate) and the accumulation of degradation metabolites (methane and reduced iron) within the contaminant plume, thereby providing evidence of groundwater contaminant removal by indigenous bacteria.

The Air Force Natural Attenuation Initiative

Over the past several years, the high cost and poor performance of many pump and treat remediation systems has stimulated research to evaluate natural attenuation as an alternative technology for groundwater remediation. Researchers associated with the U.S. EPA R.S. Kerr Environmental Research Laboratory have suggested that anaerobic pathways could be a significant, or even the dominant, degradation mechanism at many petroleum fuel sites (Wilson, 1995). The natural attenuation initiative, developed by the Air Force Center for Environmental Excellence, is designed to evaluate anaerobic degradation at over 40 sites around the country and to develop modeling tools that simulate both aerobic and anaerobic biodegradation and accurately predict the rate of attenuation occurring at contaminated sites. Each site is being analyzed according to the technical protocol developed by the Air Force Center for Environmental Excellence (Weidemeier et al., 1995).

The following sections summarize some of the key research findings from one phase of the Air Force Natural Attenuation Initiative conducted by Groundwater Services, Inc. (GSI). Site data collected by GSI in addition to data reported by other Natural Attenuation Initiative researchers (Wiedemeier, 1994) confirm the importance of anaerobic biodegradation in groundwater at many sites. Preliminary results from the development of Intrinsic Remediation models are also discussed.

RELATIVE IMPORTANCE OF ELECTRON ACCEPTORS

In the presence of organic substrate and dissolved oxygen, microorganisms capable of aerobic metabolism will predominate over anaerobic forms. However, dissolved oxygen is rapidly consumed in the interior of contaminant plumes, converting these areas into anoxic (low oxygen) zones. Under these conditions, anaerobic bacteria begin to utilize other electron acceptors to

metabolize dissolved hydrocarbons. The principle factors influencing the utilization of the various electron acceptors include: 1) the availability of specific electron acceptors at a particular site, and 2) the relative biochemical energy provided by the reaction.

Preferred Reactions by Energy Potential

Biologically mediated degradation reactions are oxidation/reduction (redox) reactions, involving the transfer of electrons from the organic contaminant compound to an electron acceptor. Oxygen is the electron acceptor for aerobic metabolism whereas nitrate, ferric iron, sulfate, and carbon dioxide serve as electron acceptors for alternative anaerobic pathways. This transfer of electrons releases energy which is utilized for microbial cell maintenance and growth. The biochemical energy associated with alternative degradation pathways can be represented by the redox potential of the alternative electron acceptors: the more positive the redox potential, the more energetically favorable is the reaction utilizing that electron acceptor. Organisms with more efficient modes of metabolism grow faster and therefore dominate over less efficient forms. The relative redox potential and reaction preference for each electron acceptor is shown below:

Electron Acceptor	Type of Reaction	Metabolic By-Product	Redox Potential (pH = 7, in volts)	Reaction Preference
Oxygen	Aerobic	CO ₂	+ 820	Most Preferred
Nitrate	Anaerobic	N ₂ , CO ₂	+ 740	↓
Ferric Iron (solid)	Anaerobic	Ferrous Iron (dissolved)	- 50	↓
Sulfate	Anaerobic	H ₂ S	- 220	↓
Carbon Dioxide	Anaerobic	Methane	- 240	Least Preferred

Based solely on thermodynamic considerations, the most energetically preferred reaction should proceed in the plume until all of the required electron acceptor is depleted. At that point, the next most-preferred reaction should begin and continue until that electron acceptor is gone, leading to a pattern where preferred electron acceptors are consumed one at a time, in sequence. Based on these principles, one would expect to observe monitoring well data with "no-detect" results for the more energetic electron acceptors, such as oxygen and nitrate, in locations where evidence of less energetic reactions is observed (e.g. monitoring well data indicating the presence of ferrous iron).

In practice, however, it is unusual to collect samples from natural attenuation monitoring wells that are completely depleted in one or more electron acceptors. Two processes are probably responsible for this observation:

- Alternative biochemical mechanisms having very similar energy potentials (such as aerobic oxidation and nitrate reduction) may occur concurrently when the preferred electron acceptor is reduced in concentration, rather than fully depleted. Facultative aerobes, for example, can shift from aerobic metabolism to nitrate reduction when oxygen is still present but in low concentrations (i.e. 1 mg/L oxygen; Snoeyink and Jenkins, 1980). Similarly, noting the nearly equivalent redox potentials for sulfate and carbon dioxide (-220 volts and -240 volts, respectively) sulfate reduction and methanogenic reactions may also occur together.
- Standard monitoring wells, having 5 to 10 foot screened intervals, mix waters from different vertical zones. If different biodegradation reactions are occurring at different

depths, then one would expect to find geochemical evidence of alternative degradation mechanisms occurring in the same well. If the dissolved hydrocarbon plume is thinner than the screened interval of a monitoring well, the geochemical evidence of electron acceptor depletion or metabolite accumulation will be diluted by mixing with clean water from zones where no degradation is occurring.

Therefore, most natural attenuation programs yield data that indicate a general pattern of electron acceptor depletion, but not complete depletion, and an overlapping of electron acceptor/metabolite isopleths into zones not predicted by thermodynamic principles. For example, a zone of methane accumulation may be larger than the apparent anoxic zone. Nevertheless, these general patterns of geochemical changes within the plume area provide strong evidence that multiple mechanisms of biodegradation are occurring at many sites.

Distribution of Electron Acceptors at Field Sites

The potential for alternative biodegradation reactions in groundwater plumes can be assessed by measuring: i) background (i.e., upgradient) concentrations of dissolved electron acceptors (oxygen, nitrate, and sulfate), and ii) in-plume concentrations of methane and reduced iron (i.e., the metabolic by-products of methanogenic and iron-reduction mechanisms). The Air Force Technical Protocol for Intrinsic Remediation prescribes measurement of these five geochemical indicators as part of the field investigation. A study of seven Air Force base sites yielded the following summary of available electron acceptors and metabolic by-products. From these data, the most significant accumulations of methane were observed at sites (e.g., Patrick AFB) having relatively low background concentrations of other electron acceptors (especially sulfate and oxygen).

Measured Background Electron Acceptor Concentration or In-Plume By-Product Concentration (mg/L)					
Base Facility	Background Oxygen	Background Nitrate	Maximum Ferrous Iron	Background Sulfate	Maximum Methane
POL Site, Hill AFB, Utah*	6.0	17	50.5	98	2.0
Hangar 10 Site, Elmendorf AFB, Alaska*	0.8	15	9.0	23	9.1
Site ST-41, Elmendorf AFB, Alaska*	8.6	25	40.5	55	1.6
Site ST-29, Patrick AFB, Florida*	3.7	0.30	1.9	10	15
Bldg. 735, Grissom AFB, Indiana	11.0	0.9	2.8	80	1.8
SWMU 66 Site, Keesler AFB, Mississippi	2.05	0.7	36.6	26.2	7.4
POL B Site, Tyndall AFB, Florida	1.93	0.93	1.6	13.4	4.6

*Data collected by Wiedemeier; all other data collected by Groundwater Services, Inc.

Biodegradation Capacity

For a given background concentration of an individual electron acceptor, the potential contaminant mass removal or "biodegradation capacity" depends on the "utilization factor" for

that electron acceptor. The utilization factor, defined as the mass of electron acceptor required to degrade a given mass of dissolved hydrocarbon, can be estimated from the stoichiometric equation for the degradation reaction. Dividing the background concentration of an electron acceptor by its utilization factor provides an estimate (in concentration units) of the assimilative capacity of the aquifer by that mode of biodegradation. Wiedemeier et al. (1994) suggest the use of the following utilization factors:

Electron Acceptor	Utilization Factor: Mass Electron Acceptor Consumed per Mass Dissolved Hydrocarbon Degraded
Oxygen	3.14 gm/gm
Nitrate	4.9 gm/gm
Ferrous Iron	21.8 gm/gm
Sulfate	4.6 gm/gm
Methane	0.78 gm/gm

Note that while the utilization factors for oxygen, nitrate, and sulfate are very close in value, the background concentrations for nitrate and sulfate can be much greater than those seen for oxygen. Therefore, if not limited by kinetics, the combined assimilative capacity of an aquifer to degrade petroleum contaminants by anaerobic processes can far exceed the capacity due to aerobic mechanisms alone.

The following table presents the estimated biodegradation capacities for seven sites. To compute these biodegradation capacities, the change in electron acceptor concentration (or metabolite accumulation for methane and iron mechanisms) observed within the contaminant plume, relative to background values, were divided by the appropriate utilization factors.

Biodegradation Capacity (mg/L of Hydrocarbon)						
Base Facility	Aerobic Biodegradation	Nitrate Reduction	Iron Reduction	Sulfate Reduction	Methanogenesis	Total Biodegradation Capacity
POL Site, Hill AFB, Utah	1.9	3.5	2.3	21.3	2.6	31.6
Hangar 10 Site, Elmendorf AFB, Alaska	0.3	3.1	0.4	5.0	11.8	20.6
Site ST-41, Elmendorf AFB, Alaska	2.7	4.5	1.9	12.0	2.1	23.2
Site ST-29, Patrick AFB, Florida	1.2	0.1	0.1	2.2	19.5	23.1
Bldg. 735, Site, Grissom AFB, Indiana	2.9	0.2	0.1	13.0	1.23	17.4
POL B Site, Tyndall AFB, Florida	0.46	0.02	0.06	1.3	5.9	7.7
SWMU 66 Site, Keesler AFB, Mississippi	0.53	0.14	1.7	4.9	9.5	16.7

Note: Values in BOLD represent electron acceptor with highest biodegradation capacity.

Electron Acceptor Utilization at Seven Sites

Figure 1 depicts the relative biodegradation capacity for each electron acceptor at each site. In each case, either sulfate reduction or methanogenesis appears to provide the highest degradation capacity for intrinsic remediation. Geochemical data further indicate that the degradation capacities by anaerobic mechanisms were utilized at these sites. A significant percentage of sulfate was removed from the groundwater located inside the contaminant plume at all sites except Patrick AFB, indicating a very active sulfate reduction reaction. Above background concentrations of methane were measured at all sites, indicating active methanogenic reactions. While accumulations of reduced (ferrous) iron were observed at many sites, the high utilization factor for ferric iron (21.8 mg of ferrous iron by-product is associated with the degradation of 1 mg of dissolved hydrocarbon), results in relatively minor degradation capacities by iron reduction. It is possible, however, that ferrous iron becomes sorbed to the aquifer matrix (Lovely, 1995), thereby preventing an accurate assessment of potential contaminant degradation by iron reducing bacteria.

While oxygen depletion was observed at every site, the contribution of aerobic processes to contaminant mass removal is relatively small. This is explained by the typically low concentrations of dissolved oxygen, compared to other electron acceptors. This analysis did not, however, account for reaeration from the vadose zone, and, therefore, potentially underestimates the contribution of aerobic oxidation.

The geochemical data for the ST-29 site at Patrick AFB, indicate extremely low background levels of nitrate and sulfate (below 0.3 and 10 mg/L, respectively), and show no evidence of nitrate or sulfate utilization. The data from this site did demonstrate significant methane accumulation within the anoxic portion of the plume. Significant methane concentrations were also observed at Keesler AFB and the Hangar 10 Site at Elmendorf AFB within the anoxic and sulfate depleted portion of the plumes. Relatively minor accumulations of methane were observed at sites having high background levels of sulfate, even within the oxygen depleted portion of the plumes, indicating possible inhibition of methanogenic bacteria by sulfate (see electron acceptor data for Hill AFB, Grissom AFB, and Site ST-41 at Elmendorf AFB).

- **Summary Point:** Data from seven sites strongly indicate that anaerobic processes are much more important than aerobic processes in achieving contaminant mass removal in groundwater. Calculations based on electron acceptor utilization indicate that oxygen was responsible for 1% to 17% of total biodegradation capacity at the seven sites. Taken together, sulfate reducers and methanogenic bacteria were responsible for 61% to 94% of total biodegradation capacity.

SIMULATING INTRINSIC REMEDIATION

Modeling Natural Attenuation with Aerobic and Anaerobic Reactions

Two natural attenuation models are currently being developed which will simulate both aerobic and anaerobic biodegradation reactions observed at field sites. The first model, BIOPLUME III (an extension of the BIOPLUME II in-situ biodegradation model), is being developed by Dr. Hanadi Rifai of Rice University. A simplified natural attenuation spreadsheet model, BIOSCREEN, is being now being tested by Groundwater Services, Inc. (GSI) and the Air Force.

Both models will be validated against twelve datasets from natural attenuation sites around the country.

BIOPLUME II, developed in 1989 by Hanadi Rifai, simulates natural attenuation due to adsorption, dispersion, and aerobic biodegradation, but does not simulate anaerobic degradation processes directly. The BIOPLUME III model will be expanded to simulate the transport and uptake of anaerobic electron acceptors. In essence, the multiple electron acceptor model will track the utilization of six components: contaminants, oxygen, nitrate, sulfate, ferrous iron, and methane. The BIOPLUME III model will allow the user to choose among three kinetic expressions: (1) first-order decay; (2) Monod dual-substrate kinetics (Rifai and Bedient, 1990); and (3) instantaneous reaction between organic contaminants and electron acceptors. To simulate biodegradation with the instantaneous reaction assumption, site-specific background electron acceptor data for oxygen, nitrate, and sulfate will be utilized. The degradative capacity due to iron reduction and methanogenic mechanisms will be estimated from the observed concentrations of ferrous iron and methane within the plume.

BIOSCREEN Intrinsic Remediation Screening Model

BIOSCREEN is designed to be an easy-to-use screening tool for simulating natural attenuation of dissolved hydrocarbons at petroleum fuel release sites. The software, programmed in the Microsoft Excel spreadsheet environment and based on the Domenico analytical solute transport model, has the ability to simulate advection, dispersion, adsorption, and biodegradation by both aerobic decay and anaerobic reactions. BIOSCREEN includes three model options: 1) solute transport without decay, 2) solute transport with first-order decay, and 3) solute transport with biodegradation assuming an "instantaneous" biodegradation reaction. Attachment 1 shows the input screen and one of two output screens for the model.

The first model option (transport without decay) is appropriate for predicting the movement of conservative (non-degrading) solutes. The only attenuation mechanisms are dispersion in the longitudinal, transverse, and vertical directions, and adsorption of contaminants to the soil matrix. The second option allows the user to simulate the combined effects of alternative mechanisms of biodegradation by inputting a single first-order decay coefficient. The third option (transport with an "instantaneous" biodegradation reaction) allows the user to input site specific geochemical data (i.e., background concentrations for individual electron acceptors and metabolic by-products) to simulate both aerobic and anaerobic biodegradation.

The instantaneous reaction is incorporated into the spreadsheet-based analytical model by applying the principle of superposition. Accordingly, the effects of the instantaneous biodegradation reaction are superimposed on the predicted plume following transport without decay. Contaminant concentrations at any location and time within the flow field are corrected by subtracting 1 mg/L organic mass for each mg/L of degradation capacity provided by each of the available electron acceptors. This approach was first developed to simulate aerobic biodegradation, and is discussed in detail by Borden et al. (1986). Application of the instantaneous reaction model to spreadsheet systems is described by Connor et al., (1994).

BIOSCREEN output includes: i) plume centerline graphs, ii) 3-D color plots of plume concentrations, and iii) mass balance data showing the contaminant mass removal by each electron acceptor (instantaneous reaction option). See Attachment 1 for examples.

COMPARISON OF FIRST-ORDER VS. INSTANTANEOUS KINETICS

The first-order decay and instantaneous reaction models were evaluated in detail as part of the model development work performed for AFCEE. The goal was to determine the best kinetic model for each electron acceptor, or to combine the electron acceptors in some fashion to simulate the natural attenuation observed at field sites.

- **First-order decay:** This widely used model assumes the biodegradation rate is proportional to the concentration of dissolved hydrocarbon and is often described as a lumped model where several biological and other attenuation mechanisms are lumped together in one overall decay factor. Some site specific factors, such as the amount of available electron acceptors, are not considered. In addition, the first-order decay model does not assume there is any biodegradation of dissolved constituents in the source zone. In other words, this model assumes that biodegradation starts immediately downgradient of the source, and biodegradation does not depress the concentrations of dissolved organics in the source zone itself.

This model is typically used by applying a rate constant obtained from the literature or by calibrating a rate constant against the observed concentration of dissolved hydrocarbon in the field. For example, literature values for the half-life of readily biodegradable dissolved hydrocarbons such as benzene ranges from 10 to 730 days while the half-life of less biodegradable constituents such as dissolved TCE is 10.7 months to 4.5 years (Howard et al., 1991). Note that first-order decay rates obtained from laboratory microcosm studies are usually not applicable to field sites because the amount of available electron acceptor that can be transported into the plume area is not the same as the amount of electron acceptor in the microcosm.

- **Instantaneous reaction:** The instantaneous reaction expression is a simplification of the Monod model that assumes the biodegradation rate is dependent on the transport of electron acceptors to the plume area, and not on the maximum utilization rate of the biomass. In other words, because the mixing of hydrocarbon and electron acceptors (by dispersive mixing, for example) is generally so slow, the maximum utilization rate in the biomass is never reached (Rifai, 1989). Nevertheless, the long residence times of contaminant plumes permits the assumption of an "instantaneous" reaction between electron acceptor and contaminant, leaving the availability of electron acceptor as the limiting condition.

To compare the two models, three lines of evidence were evaluated:

- **Available Reaction Time:** The maximum utilization rates observed in the laboratory were compared to the "reaction time" available for natural attenuation in the contaminant plumes. The results of a microcosm study conducted by Davis et al. (1994) indicate that dissolved benzene is almost completely consumed in about 8 days for low concentrations of benzene (1 mg/L) under aerobic conditions. Anaerobic reactions were slower: approximately 40 days were required to consume most of the benzene for both sulfate reducers and methanogens after an acclimatization period.

Result: These microcosm data support the conclusion that microbial kinetics are very fast compared to the typical residence time of dissolved hydrocarbons in the subsurface (i.e., as calculated from the plume length divided by the seepage velocity after adjusting for retardation). Most plumes have hydraulic residence times on the order of years or tens of years, which is much longer than the time required for the biomass to complete the

biological reaction. Therefore, for modeling purposes, the biological reaction can be considered to be instantaneous.

- **Prediction of Dissolved Hydrocarbon Concentrations:** A comparison of the two kinetic expressions was performed by calibrating BIOSCREEN model simulations to match the observed hydrocarbon concentrations for three sites. The predictive capability of both kinetic expressions were evaluated on their ability to reproduce the observed hydrocarbon concentration along the centerline of the plume.

Result: In general, both models were able to approximate the centerline plume concentrations by manipulating the input source concentration (see Figure 2). Both models simulated the Hill AFB site equally well, while the instantaneous reaction appeared to be a better fit for the Elmendorf AFB site and first-order decay a better fit for the Patrick AFB site.

- **Depletion of Electron Acceptors:** The second comparison utilized 1) a qualitative evaluation of electron acceptor utilization that conformed to an instantaneous or more kinetically constrained (first-order) reaction, and 2) a quantitative evaluation of the mass of biodegraded hydrocarbon as indicated by a mass balance of consumed electron acceptors. Using data from three sites, the areas between concentration contours were integrated to quantify the depletion of individual electron acceptors (oxygen, nitrate, and sulfate), and the accumulation of anaerobic metabolites (ferrous iron and methane) relative to background concentrations. These values were then divided by the appropriate electron acceptor utilization factor to estimate the contaminant mass destruction resulting from in-situ biodegradation. A mass balance was then performed as part of the modeling to compute the total mass removal (as predicted by the model) resulting from first-order decay versus that resulting from each individual electron acceptor in the instantaneous reaction simulations.

Result: The qualitative assessment indicated that available electron acceptors appear to be highly utilized in the source zones in all of the plumes studied. Kinetic constraints do not appear to limit the utilization of electron acceptors even at sites with relatively fast transport rates, supporting use of the instantaneous reaction model.

Mass balance results indicate that the first-order decay model under predicts the observed contaminant mass removal by a factor of 2 to 3. The instantaneous reaction model performs much better in predicting the mass removal by alternative electron acceptors (see Figure 2). Note that the mass balance computed the total mass (in kilograms) of contaminant consumed per ft of saturated aquifer in the contaminated area.

- **Summary Point:** The instantaneous reaction model simulates intrinsic remediation (natural attenuation) processes more accurately than a first-order decay model. The comparison between the two kinetic expressions was based on an evaluation of reaction and plume residence times, the ability to match observed hydrocarbon concentrations, and the ability to account for observed losses in electron acceptors.

IMPLICATIONS FOR ESTIMATING PLUME LIFETIMES

Application of the Intrinsic Remediation approach at field sites involves trying to answer two basic questions: 1) how large will the plume get if no engineered controls are installed, and 2)

how long will the plume persist in the subsurface. BIOSCREEN and BIOPLUME III are designed primarily to answer the first question of "how far will the plume extend from the source area?" The selection of the appropriate kinetic expression, however, has considerable effect on the resolution of the second question of "how long will the plume persist?"

To estimate plume lifetime, a mass balance approach can be applied. First, an estimate for the total mass of dissolvable hydrocarbons in the source area ("DMS") is developed by evaluating the mass of contaminants in soil samples and/or using estimates of the amount of free product and residual NAPL in the source zone. This is usually an order-of-magnitude estimate, yielding an order-of-magnitude estimate for plume lifetime. Next the mass flux from the source zone can be estimated by multiplying the average source concentration "Cs" by the groundwater flowrate Q through the source zone (assuming there is no flow or source contribution from the unsaturated zone). If the source concentration is assumed to remain constant during the entire lifetime of the source, the source lifetime (an approximation for plume lifetime) can be calculated as:

$$t = \text{DMS} / (Q * C_s) \quad \text{where}$$

- t = Source lifetime (years)
- DMS = Dissolvable mass in source (mg)
- Q = Groundwater flowrate through source zone (L/year)
- Cs = Actual source concentration if no biodegradation (mg/L)

Similar calculations can be performed for other dissolution models (such as an exponential decay model for the source concentration), but the fundamental mass balance relationship is dependent on three terms: DMS, Q, and Cs. Therefore, a correct assessment of these terms is required.

Application of the first-order and instantaneous reaction expressions in the BIOSCREEN model requires use of different input values for Cs. The first-order decay model assumes that the biodegradation occurs after the dissolved constituents leave the source zone and, therefore, the average source concentration observed in the source area monitoring wells is used for Cs. The instantaneous reaction model, on the other hand, assumes that vigorous aerobic and anaerobic reactions occur directly in the source zone and that monitoring well data from the source zone indicate field concentrations after biodegradation has occurred. Therefore, if the instantaneous reaction model is used, the Cs term is approximated as the measured source concentration plus the biodegradation capacity.

The impact of these two different assumptions about the Cs term is significant. At the Hill AFB site, for example, the observed source concentration in the field is approximately 15 mg/L total BTEX. If one uses the first-order decay model, the Cs term used to estimate source lifetime is 15 mg/L. With the instantaneous reaction model, however, the Cs term is 15 mg/L plus the biodegradation capacity of 31.6 mg/L, or a total of 46.6 mg/L for Cs. Therefore, the instantaneous reaction model implies that the source is dissolving away three times faster than the dissolution rate predicted by the first-order decay model. Further, the plume lifetime predicted by the instantaneous reaction model is three times shorter.

Similar results are observed when using more sophisticated numerical models such as BIOPLUME III. With this model, much more mass injection into source cells is required to calibrate the model when using the instantaneous reaction assumption as compared to first-order decay.

The assumption of biodegradation in the source term also explains why the first-order and instantaneous reaction model give different predictions for electron acceptor utilization shown on Figure 2. The instantaneous model yields higher total electron acceptor consumption because it assumes biodegradation occurs in the source zone, and as shown, more closely predicts the measured data than the first-order decay model. Work is continuing on refining these simple mass-balance dissolution models at sites undergoing biodegradation.

- **Summary Point:** The lifetime of the plume source zone can be estimated using a mass balance on 1) dissolvable hydrocarbons in the source zone, 2) flowrate through the source zone, and 3) an estimate for the source zone concentration assuming no biodegradation. Use of the instantaneous reaction model, which assumes vigorous biodegradation in the source zone, results in higher predicted dissolution rates from the source zone and, therefore, shorter lifetimes for the source and plume.

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REFERENCES:

Bedient, P. B., Rifai, H. S., and Newell, C. J., *Groundwater Contamination: Transport, and Remediation*, Prentice-Hall, Englewood Cliffs, New Jersey, 1994.

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- Borden, R. C., and Bedient, P. B., "Transport of Dissolved Hydrocarbons Influenced by Oxygen-limited Biodegradation: 1. Theoretical Development, 2. Field Application" *Water Resources Res.* 13:1973-1990, 1986a.
- Connor, John A., Newell, C. J., Nevin, J. P., "Guidelines for Use of Groundwater Spreadsheet Models in Risk-Based Corrective Action Design", in *Proceedings of The National Ground Water Association Petroleum Hydrocarbons Conference*, November, 1994.
- Domenico, P. A., and Robbins, G. A., "A New Method of Contaminant Plume Analysis," *Ground Water*, Vol. 23, No. 4, p. 476-485, 1985.
- Domenico, P. A., "An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species," *J. Hydrol.*, Vol. 91, p. 49-58, 1987.
- Howard, P. H., Boethling, R. S., Jarvis, W. F., Meylan, W. M., and Michalenko, E. M., *Handbook of Environmental Degradation Rates*, Lewis Publishers, Inc., Chelsea, Michigan, 1991.
- Lovely, D. Personal Communication, 1995.
- Newell, C. J., Bowers, R. L., and Rifai, H. S., "Impact of Non-Aqueous Phase Liquids (NAPLs) on Groundwater Remediation," Presented at Summer National AICHE Meeting, Symposium 23, "Multimedia Pollutant Transport Models", Denver, Colorado, August 16, 1994.
- Rifai, H. S., Bedient, P. B., Borden, R. C., and Haasbeek, J. F., *BIOPLUME II - Computer Model of Two-Dimensional Transport Under the Influence of Oxygen Limited Biodegradation in Groundwater, User's Manual, Version 1.0*, Rice University, Houston, Texas, 1987.
- Rifai, H. S., Bedient, P. B., Wilson, J. T., Miller, K. M., and Armstrong, J. M., "Biodegradation Modeling at Aviation Fuel Spill Site," *J. Environ. Engineering* 114(5):1007-1029, 1988.
- Rifai, H. S., Bedient, P. B., "Comparison of Biodegradation Kinetics With an Instantaneous Reaction Model for Groundwater," *Water Resources Research*, Vol. 26, No. 4, pp. 637-645, April 1990.
- Rifai, H.S., personal communication, 1994.
- Wiedemeier, T. H., Wilson, J. T., Kampbell, D. H, Miller, R. N., and Hansen, J.E., "Technical Protocol for Implementing Intrinsic Remediation With Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater (Draft)", *Air Force Center for Environmental Excellence*, April, 1995.
- Wiedemeier, T. H., Wilson, J. T., Miller, R. N., and Kampbell, D. H., "United States Guidelines for Successfully Supporting Intrinsic Remediation with An Example From Hill Air Force Base", *Proceedings of The National Ground Water Association Petroleum Hydrocarbons Conference*, p. 317-333, November 1994.
- Wilson, J.T. "Intrinsic Bioremediation-Methodologies," Presentation at the R.S. Kerr Groundwater Research Seminar, Oklahoma city, OK. June 1994.
- Wilson, J. T., McNabb, J. F., Wilson, B. H., and Noonan, M. J., "Biotransformation of Selected Organic Pollutants in Ground Water," *Develop. Industrial Microbiology* 24:225-233, 1983.
-

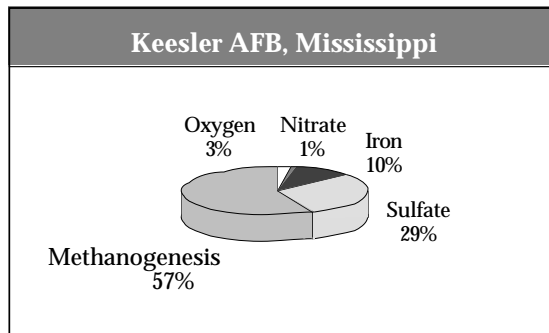
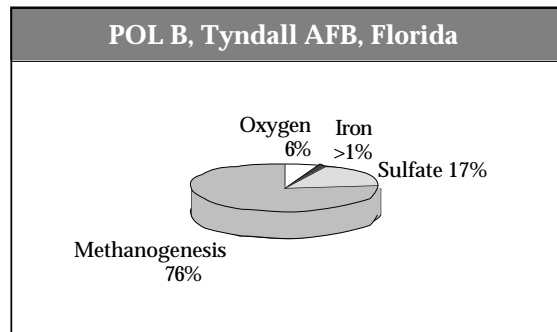
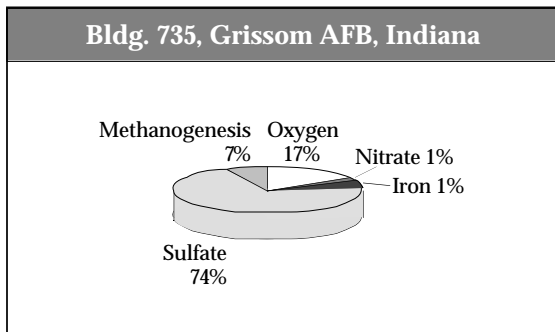
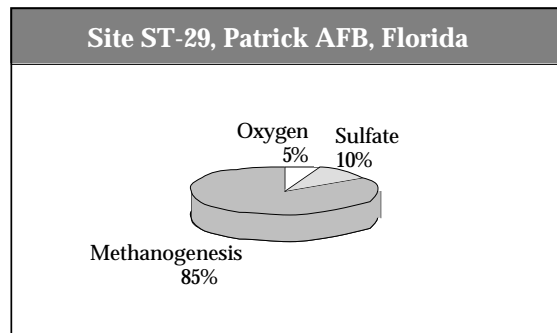
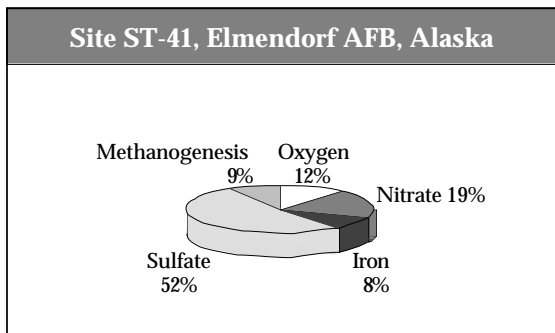
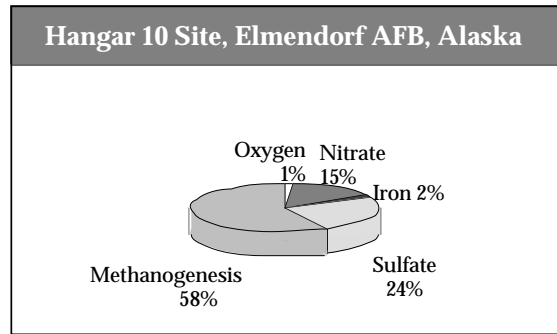
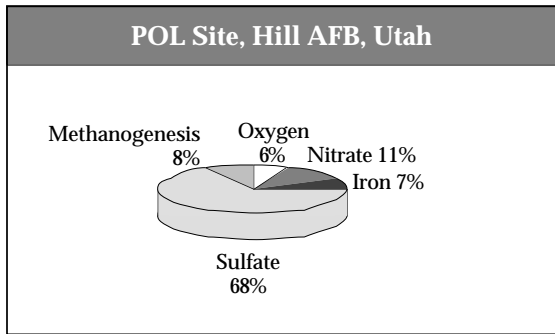
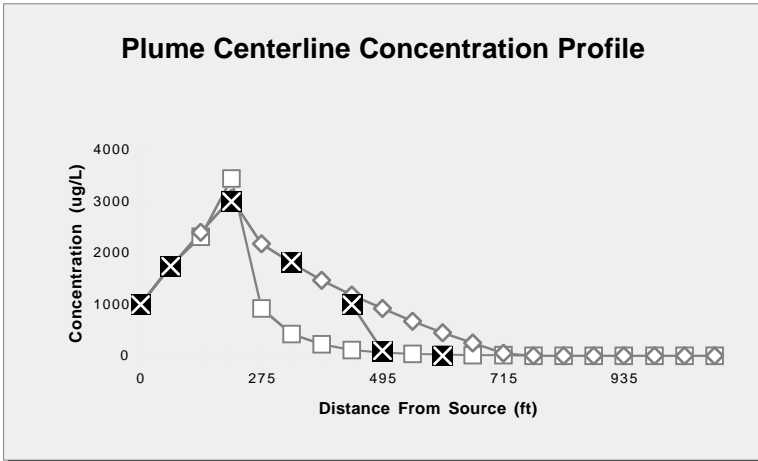


Figure 1: Relative Biodegradation Capacity by Alternative Electron Acceptors

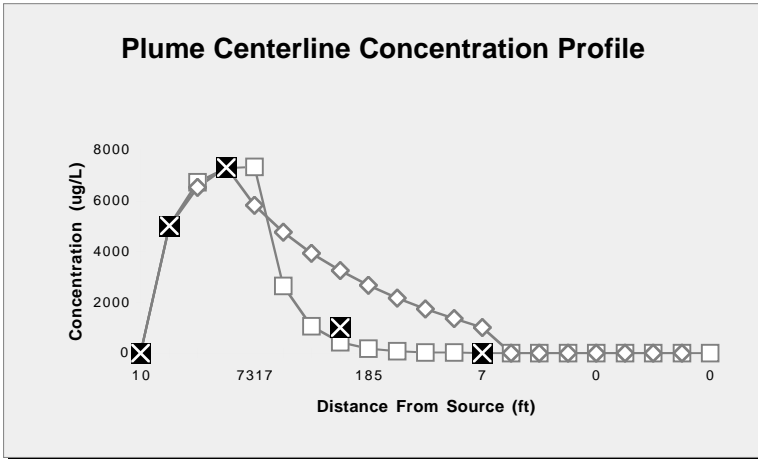
ST-41 Site/Elmendorf AFB



Total Mass Degraded (kg/ft):

Modeled		Observed
First-Order	Instantaneous	
9	260	277

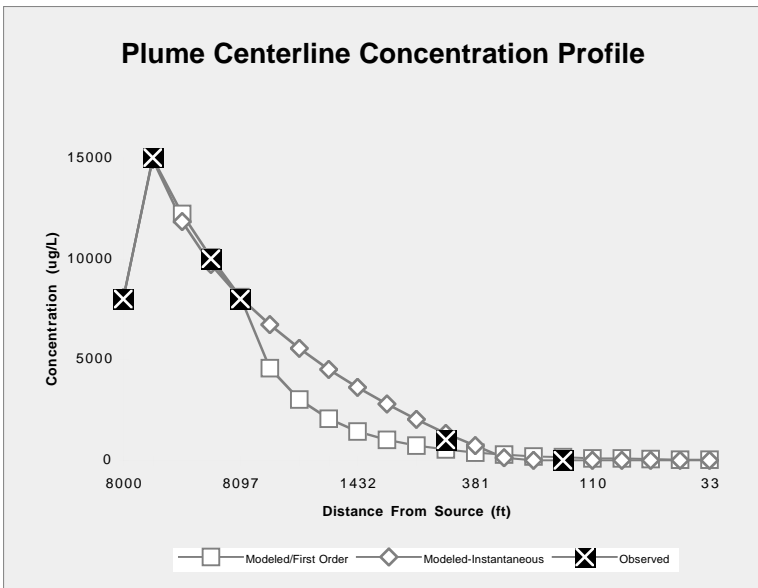
ST-29 Site/Patrick AFB



Total Mass Degraded (kg/ft):

Modeled		Observed
First-Order	Instantaneous	
17	27	30

POL Site/Hill AFB



Total Mass Degraded (kg/ft):

Modeled		Observed
First-Order	Instantaneous	
143	780	600

Figure 2: BIOSCREEN Modeling Results for Three USAF Sites