AFIT/GEE/ENV/95D-04

VALIDATION TESTING A CONTAMINANT TRANSPORT AND NATURAL ATTENUATION SIMULATION MODEL USING FIELD DATA

THESIS

Steven J. Flier

AFIT/GEE/ENV/95D-04

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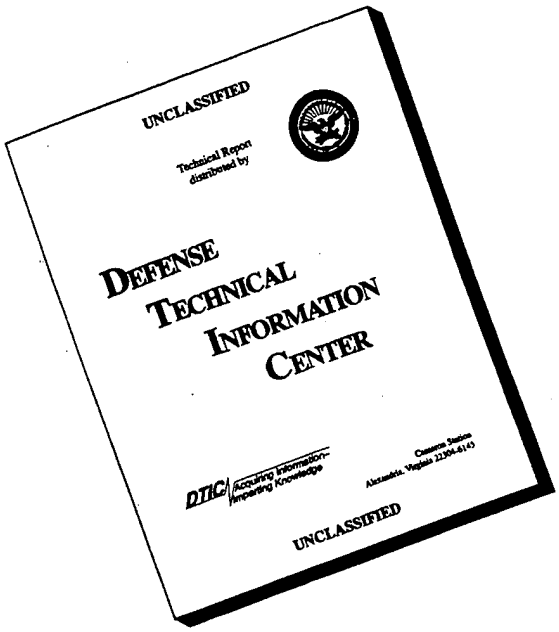

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Presented to the Faculty of the School of Engineering

of the Air Force institute of Technology

Air University

In Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Engineering and Environmental Management

Steven J. Flier, B.S., GS-11

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Edward Heyse

Member

Member

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Steven J. Flier

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Abstract

This research extends the work begun by Enyeart (1994) which evaluated the process of intrinsic bioremediation, and which developed a model for predicting the velocity of an aerobic degradation front, as it traverses the length of a JP-4 contaminant plume. It is assumed this aerobic front will traverse the contaminant plume as dissolved oxygen is carried by the ground water through the sorption-retarded contaminant.

The ultimate purpose of Enyeart's model is to use it to develop field guidance for assessing the feasibility of intrinsic bioremediation to restore petroleum-contaminated soils. After simulating intrinsic bioremediation many times with a spreadsheet model, results were used to develop a linear regression model to predict the velocity of the aerobic front, and thus the time it takes to propagate through from the rear to the front of the simulated plume. The time needed for the aerobic front to travel from the rear to the front of the plume is taken as the time to contaminant remediation.

In the present work, Enyeart's model was validity tested by comparing its output prediction with field measured values. A methodology was developed to compare the model output with field measured data. The results were analyzed, and the results of this first stage of validity testing show a reasonable basis for accepting the model. Further validity testing of the model will be required to assess its performance across a wide range of field conditions. It is hoped that contaminated-site managers will one day use the validated regression model to predict the time required to affect the complete remediation of a contaminated site via intrinsic bioremediation.

VALIDATION TESTING A CONTAMINANT TRANSPORT AND NATURAL ATTENUATION SIMULATION MODEL USING FIELD DATA

I. Introduction

General Issue

The Air Force today faces the cleanup of thousands of hazardous-substance contaminated sites at its installations, world-wide, as a result of past practices which were considered adequate by past standards but which, we have since learned, were not sufficiently adequate to protect the local environment of the soil and groundwater, in the affected areas.

It has been estimated that there are over 2,200 Air Force petroleum-contaminated sites. The majority of such sites are contaminated with fuel, especially jet fuel, but there are gasoline and diesel fuel contaminated sites, as well. The costs per site to install a pump-and-treat system typically range from $1 Million to $5 Million (Miller, 1992:3). The total cost to characterize and remediate such sites can be even substantially higher. In light of the budget realities facing the nation in this last half-decade of the century, it is incumbent upon the Air Force to investigate the range of other, less expensive, remediation techniques.

In light of the extensive costs involved, efforts to prioritize remediation projects according to human health and environmental risk considerations have been undertaken.

The goal is to identify, and clean up the worst-offending sites first; that is, those involving the most immediate, population-sensitive threat. Prioritization of sites requires a certain level of information obtained during site initial investigations. While the high priority sites go on to be addressed with full site characterization studies, lower-priority site cleanups have been postponed.

In demonstration of its commitment to cleaning up these sites, and to meet the stringent legal requirements set by federal, state, and local regulatory bodies, the Air Force created the Installation Restoration Program (IRP) to accomplish site cleanups. The issue then, in light of the aforementioned budget realities, is how the IRP manager is to manage the remediation of those sites deemed to be of relatively low priority.

Regardless of the priority given a site, the Air Force is committed to the remediation of all contamination. Those contaminant plumes which might eventually migrate to a receptor human population or which have potential to otherwise impact sensitive environmental areas may, nonetheless, be considered as lower in priority than more seriously situated or contaminated areas. Because of budgetary constraints, these sites may have their remediation activities indefinitely postponed.

Specific Problem

What is needed then is a low-cost remediation tool to deal with these lower priority sites. Specifically, there is one method particularly well suited to this task. Intrinsic bioremediation, also known as natural attenuation or natural bioremediation, involves monitoring the movement and deterioration of a contaminant plume which

result from the natural processes of contaminated groundwater migration and microbial degradation of petroleum substrate inherent to a particular site. With further research and understanding of intrinsic bioremediation, there is a strong prospect that it may gain wide acceptance by environmental regulators, and go on to be widely applied in the field. Simply stated, intrinsic bioremediation shows great promise as becoming the definitive method for remediation for many of our lower priority, and borderline priority sites.

Objective

This thesis will address the method of intrinsic bioremediation and prediction tools that will be needed if the IRP manager is to be able to select candidate sites for remediation by this method. Specifically, this thesis will begin the process of field verification of a prediction model previously developed (Enyeart, 1994). The method used will be to compare the model's predictions – using for model input the field measured data – with field measured values, to determine if the model adequately predicts petroleum hydrocarbon remediation in a real-world environment.

Knowing the desired spatial limitation of contaminant migration, and hence, the maximum allowable duration to cleanup, is key to determining the feasibility of this method. The previously developed intrinsic bioremediation simulation model, hereinafter referred to as the dynamic degradation model, relies on certain site parameters to predict the contaminant concentration distribution in time along the longitudinal centerline of the contaminant plume.

Site input parameters for this model include the combined concentration of the petroleum contaminant constituents benzene, toluene, ethylbenzene, and the methyl-, para, and ortho-xylenes (BTEX), the relative velocity of the groundwater to the contaminant plume, and the groundwater dissolved oxygen levels. The model has been kept straightforward in concept and easy to use for screening those sites which appear to be candidates for intrinsic bioremedaition. It has been developed in a quite conservative way, so that it tends to underestimate the potential for intrinsic bioremediation.

As envisioned, if the model would predict successful attenuation, then the IRP manager would be advised to pursue more, expensive characterization of the site for the purposes of proving the viability of intrinsic bioremediation. Furthermore, if the model were to predict success in this regard, it may be used to help persuade the regulatory community to allow additional time for characterization of the site. During the course of the actual, intrinsic bioremediation, the only costs would be those for monitoring, to ensure that the cleanup continued to progress as predicted. This could lead to substantial savings of resources.

However, if the model were to predict that intrinsic bioremediation would not work, since the model is of a highly conservative nature it is still possible that the method would indeed be effective. This is one of the more pressing problems within the field of intrinsic bioremediation modeling.

The present state of mathematical models, for example BIOPLUME II, is that in predicting the natural bioremediation of a contaminated aquifer they tend to be overly conservative, or else require very extensive field-data collection. The high cost of this

extensive site characterization, as well as the legal and administrative work that must be done in order to initiate the natural bioremediation option, has led too often to this method being viewed as a high risk alternative (Borden, 1994:192-193).

Notwithstanding the fact that many such models developed to date share this overly-conservative shortcoming, the proposed field version of the dynamic degradation model presently under consideration for field use has the practical benefit of being very quick and easy to use. With additional model development, the dynamic degradation model might be useful – in the case of a negative result – to perform a sensitivity analysis, perhaps allowing a better understanding of reasons for the unfavorable prediction. This may allow a deeper understanding of whether, with additional site information, natural bioremediation could be proved a viable option or, in any case, assist in determining the best available remediation method. Therefore, it is hoped that the model will be made practical through this, and any subsequent investigations and developments.

Scope and Limitations

The subject model's original development focused on the intrinsic bioremediation of the BTEX constituents of JP-4 contaminated soils. The model focuses on the BTEX components of the fuel because the BTEX components are found in virtually all petroleum-based fuels, and they are considered to be among the most toxic constituents of these fuels.

Although the model was developed specifically for addressing JP-4 contaminated sites, it could be tailored to accommodate other, common petroleum fuels, as well. The current thesis effort will focus on testing the model using contaminated aquifer field data for a controlled, standardized gasoline (PS-6) release.

The potential for contamination to migrate to a receptor population is usually low in the unsaturated soil above the groundwater (vadose) zone, and is highest in the dissolved contaminant plume. Therefore, as originally conceived, this model, the research on which it is based, and the current work will ignore contamination in the vadose zone.

II. Literature Review

Overview

The need to consider alternative methods for contaminated site cleanup, in particular the potential acceptance of promising intrinsic bioremediation techniques as an alternative to expensive, capital and maintenance intensive methods – such as pump and treat systems – highlights the importance of the development of reliable, numeric models for the prediction of contaminated-site remediation.

That there is a need to further exploit alternatives to expensive site remediation, especially through the expanded use of intrinsic bioremediation techniques, has been extensively promoted by the Chief of the Technology Transfer Division of the Air Force Center for Environmental Excellence. The fact that vast amounts of resources have already been spent remediating some ground water systems that may have otherwise been prime candidates for implementation of intrinsic bioremediation techniques tends to highlight the problem of increasing constraints and limitations placed on Air Force funding resources.

Obtaining adequate funding for remediation of sites posing a more immediate risk might be enhanced through the use of intrinsic bioremediation at sites posing less risk. In this way a better distribution of resources might be obtained between high risk, and low risk contaminated sites. For example, with intrinsic bioremediation the only substantial expenses are for site characterization and periodic monitoring. As mentioned earlier,

with more traditional techniques such as pump and treat systems, a typical capital investment alone could be between $1 M to $5 M (Miller, 1992:3).

In order to set forth the motivation of the current thesis effort it will be helpful first to review Enyeart's thesis, which led to the development of the model. The following sections, through BTEX - Electron Acceptor Biodegradation Reactions, reviews that work.

The physio-biochemical mechanisms involved in the chemical fate and transport of a contaminant plume will be reviewed in the following sections. The role of microorganisms as catalysts in the oxidation, and hence chemical conversion, of these contaminants, the stoichiometric relations which can be inferred for these reactions, and the transport of the contaminant plume through the soil matrix, also will be discussed and reviewed, with respect to their influence on model design.

Basis of Dynamic Degradation Model

The basis of Enyeart's dynamic degradation model are the processes most responsible for contaminant degradation, specifically the processes involved in the degradation of benzene, toluene, ethylbenzene, and xylenes (BTEX), which are the major contaminants of interest associated with fuel spills, and which may become dissolved in, and transported via, the ground water in the saturated zone of the soil. These processes will be reviewed in the following sections.

Fuel-Spill Plume Profile. The vertical and horizontal extent of fuel-hydrocarbon contamination resulting from a fuel spill is determined by the nature of the contaminant

and the prevailing hydrogeological regime of the underlying soils. Petroleum fuel is less dense than water (specific gravity < 1.0). It therefore "floats" as it accumulates at the surface of an aquifer's capillary fringe.

Although these fuels are considered to be not readily dissolved in water, nonetheless, some of the constituents of the fuel will go into solution in the ground water in significant amounts, at the "floating" contaminant-groundwater interface. A dissolved hydrocarbon plume will thus be created, moving away from the initial contaminant site in the direction of groundwater flow. The following illustrations (figures 1 and 2) show the major features of a typical fuel spill.

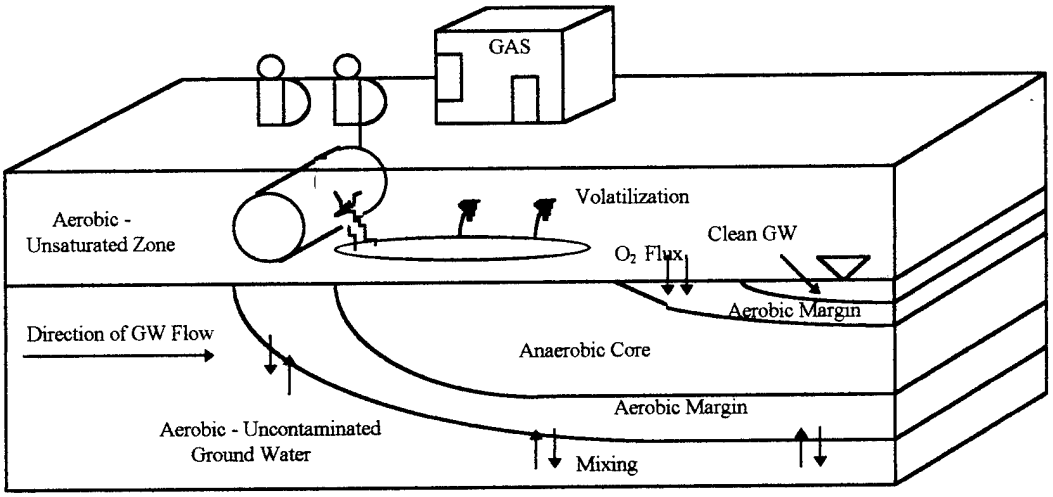

Figure 1. Basic View of a Hydrocarbon Plume from a Fuel Release (Borden, 1994: 184)

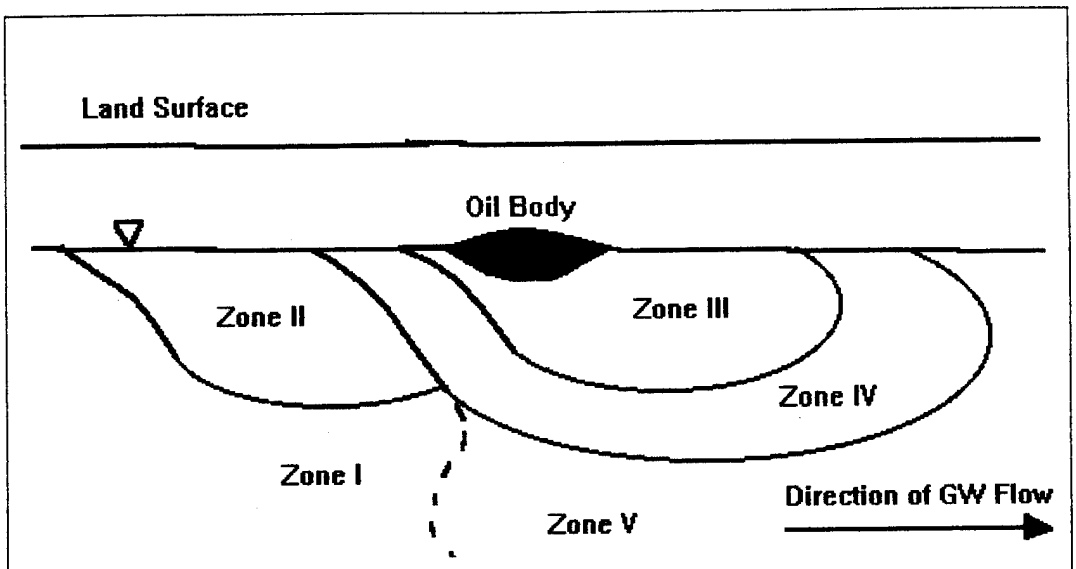

Figure 2. Detailed View of Intrinsic Bioremediation Zones Within Hydrocarbon Plume, Bemidji, Minnesota (Adapted From Baedecker, 1993: 573)

Zone I is the native groundwater (oxic: significant levels of dissolved oxygen). Zone II is contamination from additional crude oil release which may or may not exist at a site. Zone III is the concentrated dissolved contaminant plume (anoxic). Zone IV is a transition zone between the concentrated plume and the surrounding native water which is suboxic. Lastly, Zone V shows the oxic ground water down gradient of the plume (Enyeart, 1994:7-8).

From the above illustrations, the existence of zones of different processes can be seen. Most notable is the difference between the oxic, anoxic, and intermediate or transition zones, within the plume. In the oxic zones, it is aerobic microorganisms, whereas in the anoxic zones, it is the anaerobic microorganisms, which act as the predominant biological catalysts for bioremediation.

Hydrocarbon Biodegradation. The chemical transformation of hydrocarbons via biologically catalyzed reactions in the soil leads, generally, to the production of less

harmful compounds (Reinhard, 1994:131). The process requires an electron acceptor, to which a contaminant-substrate electron is transferred via the actions of the microbial catalyst, and through which it derives needed energy. The electron acceptors considered in this work have been observed to be effective. They are further discussed in the following sections.

Oxygen. Aerobic microbes use oxygen (O_2) as their sole electron acceptor. The aerobic reaction is generally preferred, and generally happens at a faster rate, and prior to, anaerobic reactions. Reaeration will occur as a result of oxygen infiltration from the overlying unsaturated (or vadose) zone, but the degree of infiltration into the core of the plume is believed to be small.

The overall degree to which this infiltration contributes to aerobic degradation is not certain (Wilson, 1994). The dynamic degradation model therefore assumes that no anaerobic degradation will occur in the presence of oxygen, and that no infiltration of oxygen will occur from the unsaturated zone.

The aerobic chemical transformation of fuel hydrocarbons may be described by a first-order exponential decay function (Domenico and Schwartz, 1990:476). The appropriate half-lives may vary greatly depending on the specific site conditions, and they are the least well known parameters in the model (Enyeart, 1994:36). The following table shows published values for unacclimated – that is, the lag time for microorganism adaptation to the contaminate substrate is included – half-lives of the BTEX compounds.

Table 1. Aerobic Biodegradation Half-Lives
(Mackay, 1993:64-82; Howard, 1991:111; Vashinav and Babeu, 1987:242)

Hydrocarbons	Half-lives (hours)
benzene	240-384, 672
toluene	168-672
ethylbenzene	144-240, 888
xylenes (ortho-, meta-, para-)	168-672

The model uses upper bound values for benzene and ethylbenzene. Literature suggests, however, that the half-lives for benzene and ethylbenzene are higher than those for toluene or xylene, given similar conditions. The upper-bound values given in the above table are the highest reported for each compound (Enyeart, 1994:10).

Anaerobic Electron Acceptors. Anaerobic microbes are inhibited in the presence of oxygen, so anaerobic electron acceptors become important only in the absence of oxygen. Similarly, a particular kind of anaerobic microorganism will be acclimated to use only one type of anaerobic electron acceptor, and the other electron acceptors present will tend not to be used until the one presently being utilized has been depleted.

The model accounts for this selectiveness through the assumption that the anaerobic electron acceptors contribute to biodegradation only after all oxygen has been depleted, and that the anaerobic electron acceptors are used in order of their redox potential, a less energetic electron acceptor coming into play only after all more energetic electron acceptors have been depleted.

Some of the anaerobic electron acceptors are, like oxygen, dissolved in the ground water (or dissolved-phase), whereas others are insoluble (or solid-phase), and tend to be bound to the soil matrix. The soluble anaerobic electron acceptors considered herein are nitrate, and sulfate, and the insoluble ones are manganese (IV), and iron (III).

Later, in the discussion of the model's development, it will be seen that the contaminant plume is replenished with dissolved-phase electron acceptors as they are carried into the trailing edge of the plume via ground water flow, because the contaminant plume is retarded in its movement compared to the ground water due to organic sorption effects. As the contaminant plume moves through the soil matrix, it encounters and is replenished from the leading edge of the plume by, solid-phase electron acceptors.

The anaerobic chemical transformation of fuel hydrocarbons may be described by a first-order exponential decay function, as well. Some observed values for anaerobic biodegradation are given in the following table.

Table 2. Anaerobic Biodegradation Half-Lives
(MacKay, 1993:46-82; Howard, 1991)

Hydrocarbons	Half-Lives: (hours)
benzene	2688-17280
toluene	1344-5040
ethylbenzene	4224-5472
o-xylene	4320-8640
m-xylene	672-12688
p-xylene	672-2688

The literature provides only a generic range for the anaerobic half-lives, and so the dynamic degradation model uses the same half-life value for all anaerobic degradation (Enyeart, 1994:11).

Redox Potential. The different energy potential of different electron acceptors affects their relative utilization by the microbial community in the metabolism of the (hydrocarbon) substrate for metabolic energy consumption and biomass production. The redox potential of an electron acceptor affects the order in which the electron acceptors are involved in the biodegradation reactions. The following figure shows the relationship of common electron acceptors with regard to their redox potential.

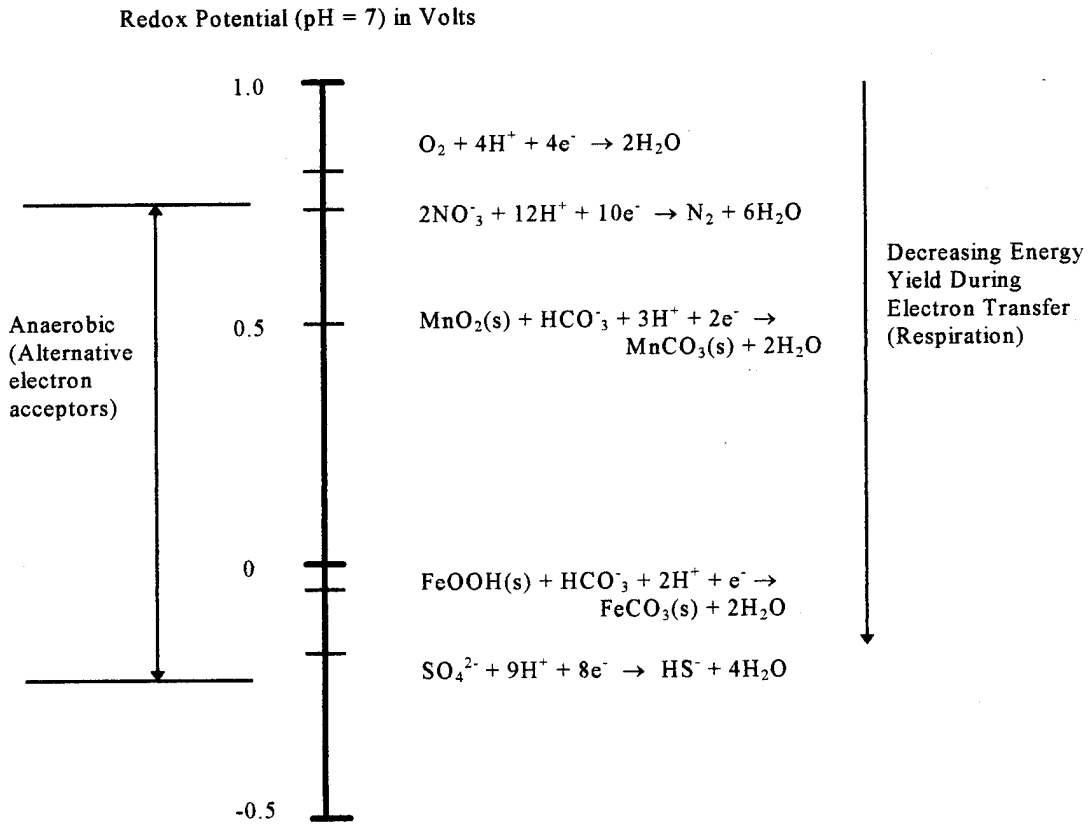

Figure 3. Key Electron Acceptors Involved in the Biochemical Transformation of Fuel Hydrocarbons. After Stumm and Morgan, in Bouwer (Bouwer, 1994:151).

Figure 3. graphically illustrates the electron acceptor hierarchy of energy yield. We see that the order in which the electron acceptors (considered in the model) are utilized is: oxygen, nitrate, manganese (IV), iron (III), and sulfate. This is also the order in which the dynamic degradation model accounts for hydrocarbon degradation reactions using these electron acceptors. The specific chemical reactions will be given in a later section of this chapter.

Contaminants of Interest. The fuel hydrocarbon contaminants which pose the greatest risk to human health and the environment are the aromatic compounds of benzene, toluene, ethylbenzene, and the ortho-, meta-, and para-xylenes, collectively known as BTEX. The BTEX compounds are common fuel constituents, and make up a significant portion of the dissolved hydrocarbon groundwater contaminants resulting from fuel spills. The contaminants considered in the dynamic degradation model are therefore limited to the BTEX compounds.

According to Blaisdell and Smallwood, the most common regulatory limit for BTEX concentration in ground water is 10 ppm (Blaisdell and Smallwood, 1993:90). This level will be used to determine that cleanup has occurred in validating the dynamic degradation model.

Degradation of BTEX. The theoretical basis of the intrinsic biodegradation of hydrocarbon (BTEX) contaminant in the subsurface is the presence of microorganisms which have been reported to be abundant (Lee and others, 1988: 30). These microbes

play the role of biological catalyst, without which, no significant contaminant degradation would occur.

Chemically, there are a number of likely pathways for the biological degradation of BTEX. The *Pseudomonas*, *Acinetobacter* and *Bacillus* bacteria are well documented as promoters of intrinsic biodegradation (Chapelle, 1993:336-337). In the development of the model, it was assumed that there are plenty of acclimated microorganisms present, for intrinsic bioremediation to occur.

Chemical Basis for the Biodegradation of BTEX. The theoretical chemical pathways by which biodegradation might occur have been described for both aerobic, and anaerobic processes (Chapelle, 1993:336-337). Figure 4, on the following page, illustrates a possible pathway for the aerobic degradation of benzene.

In order for benzene to degrade anaerobically, the oxidation, or reduction of the benzene ring must first occur. Pathways involving the biodegradation of toluene, with Fe(III) as the electron acceptor, and the biodegradation of all the BTEX with nitrate present, with significant biodegradation rates, have been reported (Chapelle, 1993:342-344).

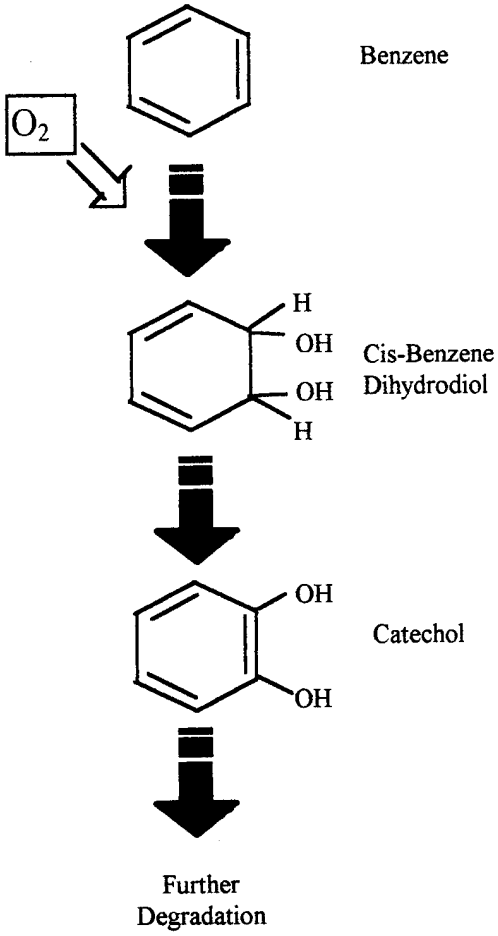

Figure 4. Example of aerobic biodegradation pathway of benzene to catechol (Chapelle, 1993: 337)

Field Observations of BTEX Biodegradation. In a 1981 experiment, aromatic compounds were found to undergo biodegradation (Tabak and others, 1981:1509). Measurable microbial growth was observed in the presence of benzene, toluene and ethylbenzene. Further studies have shown that the BTEX compounds are degraded under anoxic conditions (Chapelle, 1993:344).

A crude oil spill in Bemidji, Minnesota, was the site of an investigation into aerobic and anaerobic degradation, which found the presence of concentration gradients – between the contaminant plume and the surrounding, native water – of dissolved oxygen, and other electron acceptors. The loss of volatile organic compounds was observed after taking into consideration other possible losses, such as sorption and dispersion, indicated that biodegradation had taken place. The conclusion that aerobic and anaerobic biodegradation had taken place was further supported by the fact that less contaminant dispersion was observed than expected (Bennett and others, 1993; Eganhouse and others, 1993; Baedecker and others, 1993).

In a field investigation of aerobic degradation in a shallow aquifer at a naval air station in Maryland, two similar spills, but one recent and one which occurred some time before, were investigated. Samples revealed the presence of BTEX compounds in the area of the recent spill, whereas at the older spill, little of the original fuel constituents were found (Lee and Hoeppel, 1990). Intrinsic bioremediation was indicated by the absence of other remediative mechanisms.

Hinchee and Say compiled data which show a decrease in oxygen levels of 10%, over 80 hours, during in situ respiration tests at eight jet fuel contaminated sites. At nearby uncontaminated, background sites, the oxygen levels decreased by only 2%, maximum, over the same period. Aerobic degradation was the cause given for the excessive oxygen demand over the contaminated sites (Hinchee and Say, 1992:1309).

In a study of anaerobic decay, a site characterization of a gasoline contamination site near Empire, Michigan, revealed dissolved oxygen levels in the surrounding area

ground water so low as to be considered, essentially, anaerobic. First order biodegradation rates were measured for the BTEX compounds, with toluene showing the fastest rate, and then ethylbenzene, followed by the xylenes, with benzene showing no apparent degradation (Barlaz and others, 1992).

Biodegradation of the BTEX compounds has been demonstrated under both aerobic, and anaerobic conditions. The rate at which the biodegradation process occurs is highly dependent on the electron acceptor involved. All the BTEX species generally degrade more quickly under aerobic, than anaerobic conditions, and the anaerobic degradation of benzene is the slowest of all observed. However, the determination of anaerobic, exponential decay constants for different alternate electron acceptors is not well documented, and the difference in their decay constants is unknown.

Field Parameters and Their Effect on Bioremediation

The important parameters which may influence the biodegradation of BTEX are considered in the following sections. The parameters may, or may not have been included in the development of the dynamic degradation model. Either way, the rationale of the attendant assumptions, and the effects of whether or not the parameter has been included in the model, are discussed.

Electron Acceptors. The availability of electron acceptors is a primary consideration in the biodegradation of BTEX. The total quantity, and the relative amount of each electron acceptor may have a significant effect on the rate, and overall potential

for biodegradation to occur. The concentration of electron acceptors – those shown in figure 3 – are included as input parameters in the model.

Acclimation of Microorganisms. Acclimation is the process – which involves a lag time – within which the extant microbial community adjusts to a new substrate, or electron acceptor, through the synthesis of different enzyme systems. Measured lag times are not readily available, and probably are very case-sensitive. A 43 day acclimation lag time was found for sulfate reducing bacteria on a m-cresol substrate (Chapelle, 1993:346).

Although lag times may be significant, their inclusion was considered beyond the scope of the model. This constitutes a non-conservative assumption of the model, because the effect of ignoring the lag time is to increase the amount of contaminant that will be predicted by the model to have been degraded.

Hydrogeologic Considerations. Dispersion of the contaminant plume caused by the motion of groundwater through the porous aquifer media leads to a lowering of contaminant concentration levels. Alone, dispersion effects do not lead to the loss of contaminant mass; only chemical transformations can account for that. The model does not account for dispersion, which constitutes a conservative assumption.

Sorption-desorption effects of the organic contaminants to the organic carbon constituents of the aquifer, cause a retardation effect on the movement of the contaminant plume. This is an important aspect of the dynamic degradation model, being the basis for the movement of groundwater into the retarded contaminant plume

from the rear, thus supplying dissolved electron acceptors to the plume. Although the retardation factor may be calculated from other aquifer parameters – porosity, solids density, organic carbon content – it may be determined by dividing the groundwater velocity by the contaminant plume velocity. The retardation factor used in this work was determined in this way, as reported in the data set.

Lastly, water hardness and pH may have an adverse effect on the biodegradation of hydrocarbon contaminants. A range of 6.5 to 7.5 for pH, and a value of water hardness, alkalinity (as $CaCO_3$) = 100 mg/L have been reported as being the ideal range for hydrocarbon degradation (Wilson, 1994). The model does not account for these factors, but for the current data set from the Borden aquifer, the respective values (pH = 7.3 to 7.9; alkalinity (as $CaCO_3$) = 100 to 250 mg/L) are close to, or within these ranges.

BTEX - Electron Acceptor Biodegradation Reactions

Oxygen Reactions. The microbially catalyzed reactions involving oxygen release the greatest potential energy for metabolism and biomass growth than any other biodegradation reactions. Oxygen has been shown to be the preferred electron acceptor, and so it is utilized before any of the anaerobic electron acceptors. The following are stoichiometric reactions involving oxygen, for BTEX:

Benzene: $C_6H_6 + 7.5\ O_2 \rightarrow 6\ CO_2 + 3\ H_2O$

Toluene: $C_7H_8 + 9\ O_2 \rightarrow 7\ CO_2 + 4\ H_2O$

Ethylbenzene: $C_8H_{10} + 10.5\ O_2 \rightarrow 8\ CO_2 + 5\ H_2O$

Xylene: $C_8H_{10} + 10.5\ O_2 \rightarrow 8\ CO_2 + 5\ H_2O$

Nitrate. Nitrate reduction of hydrocarbons has been widely observed in the field. It is the anaerobic electron acceptor with the highest redox potential, and no other anaerobic electron acceptors will be utilized until the nitrate has been depleted. It is soluble in the ground water, and is modeled as introduced from the rear of the plume as the ground water overtakes the retarded contaminant plume. The concentration of nitrate ($[NO^-_3]$ = 0.6 mg/L), given by the field data and used in this work's model validation, is at the extreme low end of the expected range given by the literature (0 to 40 mg/L), (Enyeart, 1994:54).

Once the oxygen is depleted, the nitrate, at such low levels, should be depleted in a relatively short period of time. Nitrate oxidation of the BTEX is represented by the following, likely reactions:

Benzene: $C_6H_6 + 5\ NO_3 \rightarrow 6\ CO_2 + 3\ H_2O + 5/2\ N_2$

Toluene: $C_7H_8 + 6\ NO_3 \rightarrow 7\ CO_2 + 4\ H_2O + 3\ N_2$

Ethylbenz.: $C_8H_{10} + 7\ NO_3 \rightarrow 8\ CO_2 + 5\ H_2O + 7/2\ N_2$

Xylene: $C_8H_{10} + 7\ NO_3 \rightarrow 8\ CO_2 + 5\ H_2O + 7/2\ N_2$

Manganese (IV). The role of Mn(IV) in biodegradation reactions is uncertain, but recent evidence – the increase of Mn(II) over background levels within the plume – shows that it was involved in the remediation of a crude oil spill at Bemidji, Minnesota (Baedecker, 1993:576-584).

Mn(IV) is present as oxide coatings on the sand particles in the Borden aquifer material (the field site used in this study), at concentration of manganese (IV) of:

[Mn(IV)] = 44 mg/L (Nicholson and others, 1983:161-162). The only other reported value found from field studies was [Mn(IV)] = 10.4 mg/L (Baedecker, 1993:576).

The following stoichiometric relationships are proposed for Mn(IV), in the bioremediation of BTEX:

Benzene: $C_6H_6 + 15\ MnO_2 \rightarrow 6\ CO_2 + 15\ Mn^{2+} + 15\ O^{2-} + 3\ H_2O$

Toluene: $C_7H_8 + 18\ MnO_2 \rightarrow 7\ CO_2 + 18\ Mn^{2+} + 18\ O^{2-} + 4\ H_2O$

Ethylbenz.: $C_8H_{10} + 21\ MnO_2 \rightarrow 8\ CO_2 + 21\ Mn^{2+} + 21\ O^{2} + 5\ H_2O$

Xylene: $C_8H_{10} + 21\ MnO_2 \rightarrow 8\ CO_2 + 21\ Mn^{2+} + 21\ O^{2} + 5\ H_2O$

Iron (III). The role of Fe(III) in the biodegradation of hydrocarbon reactions is widely reported (Borden, 1994:181). The subsequent reduction of ferric iron, Fe(III) levels, with the increase of ferrous iron, Fe(II), indicate that this is a significant reaction.

The existence of extremely high levels of Fe(III), [Fe(III)] = 10,425 mg/L, present on the Borden aquifer sands as an oxide coating, is extremely high compared to the values cited by Baedecker, or Borden (Baedecker and others, 1993:576; Borden, 1994:182). However, the sensitivity analysis performed by Enyeart shows that, above certain levels, the degradation of BTEX is insensitive to greater levels of anaerobic electron acceptors (Enyeart, 1994:57).

Because model calculations involving the electron acceptors are concentration independent, as long as the electron acceptors are not depleted, it follows that their relative abundance will have no effect on the prediction of the amount of biodegradation

of BTEX, and hence, on the BTEX levels. The following stoichiometric relationships have been suggested in the cited literature:

Benzene: $C_6H_6 + 30\ Fe(OH)_3 \rightarrow 6\ CO_2 + 30\ Fe^{2+} + 60\ OH^- + 18\ H_2O$

Toluene: $C_7H_8 + 36\ Fe(OH)_3 \rightarrow 7\ CO_2 + 36\ Fe^{2+} + 72\ OH^- + 22\ H_2O$

Ethylbenz.: $C_8H_{10} + 42\ Fe(OH)_3 \rightarrow 8\ CO_2 + 42\ Fe^{2+} + 84\ OH^- + 26\ H_2O$

Xylene: $C_8H_{10} + 42\ Fe(OH)_3 \rightarrow 8\ CO_2 + 42\ Fe^{2+} + 84\ OH^- + 26\ H_2O$

Sulfate. The lowest on the redox potential diagram of the electron acceptors considered in this work, sulfate will not be utilized until all the other electron acceptors have been depleted. Given the high levels of Fe(III) present in the Borden aquifer, it is unlikely that the sulfate will ever be "seen" in the computations of BTEX levels, over the time period covered by the field study. However, evidence of sulfate involvement in biodegradation reactions is more widely reported than that for either manganese or iron.

The following theoretical chemical transformation reactions are given:

Benzene: $C_6H_6 + 4\ SO_4 + 2\ H_2O \rightarrow 6\ HCO_3 + 4\ HS$

Toluene: $C_7H_8 + 4.5\ SO_4 + 3\ H_2O \rightarrow$

$7\ HCO_3 + 2.25\ H_2S + 2.25\ HS + 0.25\ H$

Ethylbenz.: $C_8H_{10} + 5\ SO_4 + 3\ H_2O \rightarrow$

$8\ HCO_3 + 2.5\ H_2S + 2.5\ HS + 2.5\ H$

Xylene: $C_8H_{10} + 5\ SO_4 + 3\ H_2O \rightarrow$

$8\ HCO_3 + 2.5\ H_2S + 2.5\ HS + 2.5\ H$

Sulfate levels found in the Borden aquifer range from 10 to 30 mg/L. Although for this dissolved species, some non-conservative behavior has been observed – sulfate may display varying degrees of sorption when pH drops below 5 – the Borden aquifer pH is reported to be between 7.3 and 7.9, so no retardation is expected.

Basis of Intrinsic Bioremediation Model and Overview of Model Development

The intrinsic bioremediation model under consideration is based on the stoichiometric relationship between the petroleum-hydrocarbon contaminant substrate, and the electron acceptors available for introduction into the contaminant plume. The quantity of electron acceptors available for reduction in this relationship is a key rate limiting factor in the bioremediation of the substrate, as expressed by Dr. John Wilson, USEPA R.S. Kerr Environmental Research Laboratory, in an interview with Capt. John Enyeart (Enyeart, 1994).

Dynamic Degradation Model Basics. The dynamic degradation model is the spreadsheet simulation model, developed by Captain Enyeart. A graphical depiction of the model is given in figure 5. This model takes into account: the level of BTEX contaminants, dissolved oxygen, nitrate, Mn(IV), Fe(III), and sulfate; first-order decay rates, and the basic hydrologic parameters of conductivity, porosity, hydraulic gradient, and organic carbon content of the soil.

The dynamic degradation model accounts for the movement of dissolved and solid-phase electron acceptors in to the contaminant plume, the chemical transformation of the contaminants in the presence of these electron acceptors, and the continuous

replenishment of the dissolved electron acceptors with the movement of groundwater through the retarded contaminant plume, and of the solid-phase electron acceptors with the movement of the contaminant plume through the soil. See "Dynamic Degradation Model" section, below, for a more comprehensive discussion of this model.

Aerobic Front Velocity Predictor. A regression model developed by Enyeart (1994) – called the Aerobic Front Velocity Predictor, or AFV_{10} – is based on the dynamic degradation model results, and is used to predict intrinsic bioremediation considering only the aerobic electron acceptors. The fact that the dynamic degradation model was relatively insensitive to the presence of anaerobic electron acceptors – above a certain limit – and the fact that ignoring these electron acceptors amounts to, in effect, a conservative assumption, tends to emphasize the relative importance of the aerobic electron acceptors.

The physical process being modeled by the AFV_{10} is the movement through the contaminant plume of a "front" of low BTEX concentration, caused by the movement of dissolved oxygen with the ground water, through the sorption-retarded plume. A graphical description of this aerobic front movement is given in figure 6.

As oxygen becomes available for the bioremediation of contaminant, and contaminant concentrations are reduced – starting from the rear of the plume – it is able to penetrate progressively further into the rear of plume due to the ever decreasing level of the contaminant's oxygen demand, the contaminant having been degraded by earlier "doses" of oxygen-rich groundwater that moved through that same portion of the plume.

As already stated, the AFV_{10} is based on the dynamic degradation model. The velocity of the moving front of low BTEX concentration – moving from the rear to the front of the plume, and modeled by the dynamic degradation model – was compared to the input parameters of the model, and a step-wise regression analysis was performed using the STATISTIX™ software package. The following regression equation was the result of Enyeart's analysis.

$$AFV_{10} = 0.099 - 0.007 * BTEX + 0.010 * O_2 + 0.029 * V_{REL} + 8.1\text{ E-}5 * BTEX^2$$

However, this regression equation was later revised in this work because its development did not anticipate cases of low V_{REL} (the velocity of the ground water relative to the sorption-retarded contaminant plume) and low *BTEX* levels, as is the case with the Borden site field measured model input parameters (see chapter 4, "The AFV_{10} Regression Model: Aerobic Velocity").

The rationale for development of this model is to provide a simple "rule of thumb" method for installation restoration program (IRP) contaminated-site managers to predict the success of intrinsic bioremediation, given certain easily obtained site parameters. The application is simple: once the aerobic front velocity has been predicted, the time it takes to traverse the entire length of the plume can be determined.

Once the plume has been traversed in this way, it may be predicted to have been, effectively, remediated. If this remediation occurs before the plume has come into contact with environmentally sensitive receptors, then active remediation is not necessary.

For simplicity, and for incorporating a conservative approach, the regression model focuses on the role of aerobic degradation. This model might be combined with other analyses as required by the prediction of a near failure of intrinsic bioremediation in an aquifer rich in anaerobic electron acceptors.

For example, a static analysis of the degradation potential of the anaerobic electron acceptors might be done to show degradation at the front of the plume which might extend the time required for significant contaminant to reach a sensitive receptor. Further consideration of such other analyses which might be combined with the AFV_{10} to improve the reliability of predictions is beyond the scope of this work.

Dynamic Plume Model

The dissolved electron acceptors are introduced into the contaminant plume with the flow of groundwater. The rate of introduction from the rear of these dissolved electron acceptors (V_{REL}) is equal to the difference of the groundwater velocity (V_{GW}), and the retarded-contaminant plume-flow velocity (V_{CON}).

$$V_{REL} = V_{GW} - V_{CON}$$

where: $V_{CON} = V_{GW} / R$

R = Retardation Factor

and: $R = 1.29$

Benzene concentration field measurements at the Borden site were found to have a retardation factor of from 1.06 to 1.29 (Hubbard and others, 1994:10-1). The higher value was used because the R values reported by Hubbard were determined by comparing field measured velocities of the conservative tracer plume with those for the contaminant

plume. Skewed breakthrough curves due to rate limited sorption tends to result in understating R when using this technique.

The rate of introduction from the front into the contaminant plume of solid-phase electron acceptors in the soil is equal to the velocity of the contaminant plume, or

$$(V_{CON}) = (V_{SOIL}).$$

Since the model is Lagrangian – by this definition the observer moves with the contaminant plume – the apparent velocity of the contaminant plume is zero, and the apparent velocity of the soil containing the solid-phase electron acceptors is equal to the actual velocity of the contaminant plume that would be measured in the field. The basic concept of contaminant movement into the plume is illustrated by Fig. 5.

The model input includes the concentrations of the five electron acceptors with the highest redox energy: O_2, NO_3, Mn(IV), Fe(III), and SO_4. The contaminant-plume

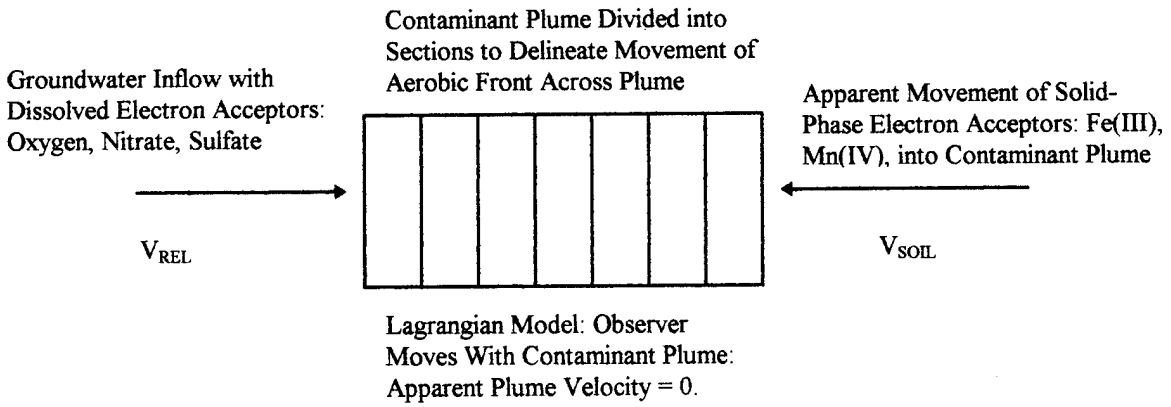

Figure 5. Intrinsic bioremediation model conceptual diagram.

model input includes the concentrations of the five electron acceptors with the highest redox energy: O_2, NO_3, Mn(IV), Fe(III), and SO_4. The contaminant-plume initial BTEX

concentrations are assumed to be representative of the plume width, and to be distributed uniformly throughout the length of the plume at time $t = t_0$. Although this may not be realistic, and tends to be conservative, in the present work this effect will be minimized by using the Borden investigation's contaminant injection mass, and geometry parameters, to determine an average contamination throughout the plume at time $t = 0$.

As the dynamic degradation model is run through a series of time steps, the movement of electron-acceptor carrying water, or soil, through equal portions of the plume is simulated. The degradation of the contaminant takes place in accordance with biodegradation kinetics and electron acceptor availability, in the order of their redox potential.

The kinetic, or dynamic degradation model is illustrated in Fig 6, below. The overall length of the plume is divided into sections so that accurate results are obtained for the degradation of all four BTEX, in accordance with the conditions within each section of the plume. This will allow the modeling of the complete aerobic degradation of BTEX, as it progresses from the rear of the plume (on the left) through to the leading edge of the plume.

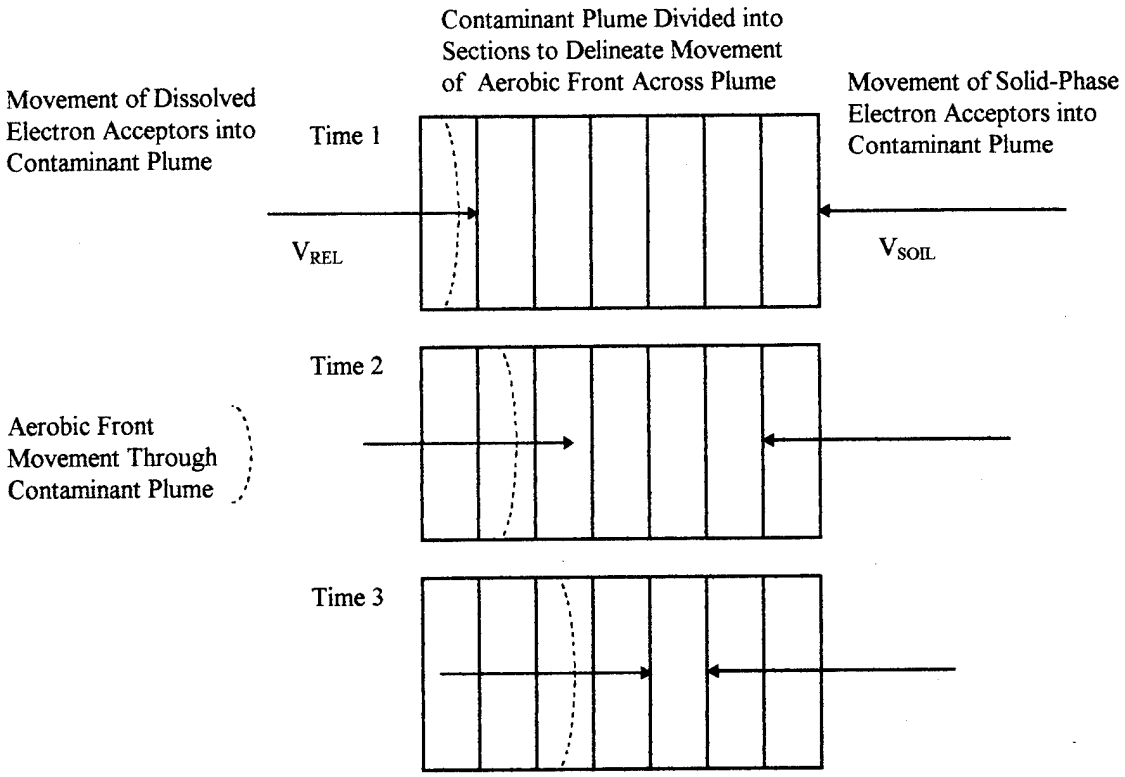

Figure 6. Diagram of electron acceptor movement into contaminant plume. The AFV_{10} is represented by the broken lines.

Since it is impractical to assume complete degradation, it was desirable to determine at what concentration the risk due to BTEX would be considered low enough to constitute a trivial, or *de-minimus* risk. In the thesis by Blaisdell and Smallwood (1993), it was determined through a survey of numerous state regulatory agencies that a total BTEX concentration of 10 ppm represented the appropriate level of acceptable risk in most instances. This fact, coupled with the concept of an advancing aerobic-degradation of BTEX, leads to the definition of the Aerobic Front Velocity

defined as the velocity of the BTEX = 10 ppm isopleth, subsequently referred to throughout as the AFV_{10}.

The AFV_{10} concept is further refined by the regression model developed to predict the velocity of the aerobic front until it has reached the leading edge of the contaminant plume. This would allow the manager to predict the time needed for the plume to degrade to safe levels, and hence, the distance traveled by harmful levels of contaminant. Thus, the AFV_{10} predictor has the potential to become a useful tool for predicting the success of intrinsic bioremediation.

Model Theoretical Considerations.

The dynamic-plume model, as illustrated in figures 5 and 6, computes the concentration of contaminants remaining after biodegradation within each plum section, as a function of the electron acceptors available for use in the biodegradation reaction. The electron acceptors are divided into two groups: dissolved and solid-phase. The dissolved electron acceptors are introduced into the contaminant plume from the rear, with the groundwater, whereas the solid-phase electron acceptors appear to move from the front of the plume, rearward, as the plume moves into the soils which contain them.

The computed value of remaining contaminants and electron acceptors in a plume-section after some time step, Δt, is affected by the amount of newly introduced electron acceptors within that section, during that time step. Furthermore, the accuracy of the computation is dependent on the size of Δt, and on the water input ratio (where V

= V_{REL}), or soil input ratio (where V = V_{SOIL}). The water in put ratio is described by :

$$V^*\Delta t/\Delta x \leq 1.$$

The condition imposed by this expression is that the movement of electron acceptors (with velocity, V) through the plume section (of length, Δx), will not penetrate past the far end of the section within the allotted time-step (of duration, Δt). Violating this would induce error in obvious ways, in the computation of electron acceptor levels intended for use in calculations for a particular plume section.

The larger the time step (Δt), the more it tends to induce error (Wood, 1993:42). The physical phenomenon being modeled is a continuous process; the movement of contaminant and electron acceptor species, and the biochemical reactions involving them, happen in a smooth, and unbroken continuum of essentially instantaneous events.

However, the model discretizes this process into Δx *unit-width blocks*, within which the continuous processes are described as, essentially, finite *clumps* of the reacting species in space and time. Therefore, the smaller both the Δt and the Δx are, the more closely they represent the continuum inherent in the natural processes being modeled.

Contaminant Degradation

The amount of degradation due to the electron acceptors is computed by one of two formulas. Whether the concentration of electron acceptors will be depleted in a given time step depends on their stoichiometric balance to the contaminants. If they are present in excess – that is, if $mass.EA < Ea_{avail}$, according to formula (3) – then the

formula used (2) is time dependent. Otherwise, they are calculated using a concentration-dependent formula (1).

$$P(EA) = P_0 - MB \times Ea_{avail} \quad (1)$$

$$P(EA) = P_0 \times \exp(-k_i \times t_{avail}) \quad (2)$$

$$mass.EA = [P_0 - P_0 \times \exp(-k_i \times t_{avail})] \times 1/MB \quad (3)$$

$P(EA)$ = Concentration of pollutant after degradation with a given electron acceptor – or "new" concentration of pollutant – (ppm or m/l^3)

P_0 = Initial concentration of pollutant – from the preceding step – (ppm or m/l^3)

MB = Mass balance factor: for each BTEX, the expected fraction of its mass to the total BTEX mass

Ea_{avail} = Expected electron acceptors available to pollutant P (ppm)

k_i = Exponential decay rate for pollutant P_i

$mass.EA$ = Mass of EAs needed in the time available (t_{avail}) for biodegradation

t_{avail} = time available to degrade pollutant P_i in a single time step, Δt

where: $t_{avail} = \Delta t$, if the required mass of electron acceptor is greater than the amount of electron acceptor *available* ($mass.EA > Ea_{avail}$)

otherwise: $t_{avail} = ts - [(\ln(P(EA_t)/P_O)) \times 1/(-k_1) + \ln(P(EA_{t-1})/P_O) \times 1/(-k_2)$

Model Validation Procedures and Criteria

Model validation is the comparison of simulated results generated by the model, with actual field, or laboratory measured data, which are indicative of the physical and chemical processes embodied by the model. In order to comprehensively validate a model, it is necessary to test it over the complete spectrum of the anticipated conditions.

This would involve completing an entire matrix of differing climate, soils, physio-chemical processes and the field-measured responses to them, covering the scope of the model user's needs.

Although a validation problem may only address a very narrowly defined (and scoped) model - e.g., limited to addressing a specific site or compound - the model validation process is inherently evolutionary: further refinements in the understanding of chemical fate and transport phenomenon will lead to improved model development, and validation protocols. Existing models will continue to be updated, and improved, by this process (Hern and others, 1986:61.)

The current work involves validating a model (the dynamic degradation model) intended to generate a prediction of contaminant concentrations in a soil matrix. This model's intended use is to provide a simulation of the selective contaminant degradation, from the rear of the contaminant plume, caused by the influx of oxygen (and other dissolved electron acceptors) with the groundwater, through to the front of the sorption-retarded plume. A so-called aerobic front velocity (designated as the AFV_{10}) is measured as the rate at which the *de minimus* (or trivial) concentration level of contaminant travels, with respect to the plume, from the rear to the front of the contaminant plume.

Using the results of the dynamic degradation model, a regression model has been developed, via stepwise regression, to predict the AFV_{10}. This derivative model is referred to as the AFV_{10} predictor, or regression model. The purpose of this work is to begin the task of field validation of the dynamic degradation model, on which the AFV_{10}

predictor model is based. The ultimate fruition of this and any subsequent work will be the development, and utilization, of a fully validated AFV_{10} predictor.

The AFV_{10} predictor model is intended to be used by IRP managers as a "rule of thumb," for the determination of whether, in a given case, intrinsic bioremediation is feasible. In predicting the time needed for contaminant levels throughout the plume to have biodegraded to *de minimus* levels, the IRP manager will then be able to compare this with the predicted distance traveled by the plume in that time. If contaminants have been biodegraded to below *de minimus* levels before the contaminant plume impacts on an environmentally significant receptor, then intrinsic bioremediation may be assumed, preliminarily, to be effective. At this point, further site characterization would be warranted to support the case for intrinsic bioremediation.

Hern, Melancon, and Pollard have outlined a stepwise approach to model validation, which is intended as a generic guideline for conducting a model validation test. These guidelines are not intended as a rigid set of rules to be carried out in sequence, but, depending on the particular data requirements and validation scenario involved, may involve different sequencing, or overlap between the steps. The following table (table 3) outlines the steps for validating contaminant fate and transport models.

Table 3. Steps in Field Validation of Soil Fate and Transport Models.
(Hern and others, 1986:62)

Step 1. Identify Model User's Need -- The first step in field validation is to obtain a clear understanding of the model user's need, i.e., how will the model be used.

Step 2. Examine the Model --

Step 2a. Detailed examination of the model: The user must precisely define model input data requirements, output predictions, and model assumptions.

Step 2b. Collect Preliminary Data and Performance of Sensitivity Analysis: Preliminary data are required to conduct a sensitivity analysis and determine the most important input variables.

Step 3. Evaluate the Feasibility of Field Validation -- Some models cannot be validated in the field, and the validator should consider this possibility.

Step 4. Develop Acceptance Criteria for Validations -- The model user must provide criteria against which the model is to be judged.

Step 5. Determine Field Validation Scenario -- Many different approaches to field validation are possible. A scenario should be identified and approved by the model user.

Step 6. Plan and Conduct Field Validations Which Should Include the Following Steps --

Step 6a. Select a Site and Compound(s): Consideration of model input requirements, analytical methods, sources of contamination, and site soil characteristics, etc. are among the many factors to consider in selecting a site and compound(s).

Step 6b. Develop a Field Study Design: Development of a detailed field sampling plan for the specific model compound and site.

Step 6c. Conduct Field Study: Implementation of the field plan is not addressed in these guidelines.

Step 6d. Sample Analysis and Quality Assurance: Many analytical procedures are available depending on the chemical and the matrix. Standardized methods should be used together with a sound quality assurance program.

Step 6e. Compare Model Performance with Acceptance Criteria: A comparison must be made between the performance of the model and the user's acceptance criteria using either graphical or statistical techniques (Hern and others, 1986:62).

Further development of the steps outlined in the above table, are given in the following sections.

Step 1: Identify Model User's Need. The modeler needs an in-depth understanding of the problem, from the user's point of view. All intended purposes must be understood, a priori, for the modeler to fully assess the utility of the model. The limitations of the model may thus be discovered to preclude appropriate further development, saving the user much expense by avoiding unnecessary validation work.

Step 2: Examine the Model. A determination of the assumptions used in constructing the model, the required model inputs and outputs, and obtaining appropriate test data for performing sensitivity analysis is necessary in order to properly examine the model. Input data must be defined as to the proper units, and whether the input data are spatially or temporarily averaged in some way, or represent an isolated point in space or time.

Model output needs to be defined in terms of model input. Furthermore, the sensitivity of model outputs to changes in the model's inputs must be determined. A large variation of outputs caused by a relatively small change in a particular parameter-input value would indicate a relatively large degree of model sensitivity to that parameter. Understanding sensitivity enables the better allocation of resources for subsequent data collection (Hern and others, 1986:64).

In his thesis, Enyeart (1994) performed a sensitivity analysis for the dynamic degradation model. In that work, Enyeart (1994) employed a simple, high and low

screening regime which was the only available, practical approach, given the model requirement for manual parameter change for each model run. With the exception of additional time-step-size (Δt) validation – confirming that the smaller time steps used in the version of the dynamic degradation model, developed for the current effort, is consistent with the output of the original model – the current effort relies solely on the sensitivity analysis performed in Enyeart's (1994) thesis.

Step 3: Evaluate the Feasibility of Field Validation. "Field validation is probably the most credible test of a model." However, field validation results may be inappropriately applied, and may therefore be of questionable value. For instance, a model which assumes a steady state or the existence of a dynamic equilibrium, may be problematic, since these conditions do not exist for long in nature. Large input sampling error for relatively sensitive parameters can lead to large output errors. Input parameters may not be readily available or quantifiable, and model output parameters may not be easily collected in the field, for comparison.

Although obtaining conclusive results from validation efforts is not always practical, and the process involved must be approached with caution, still, the value of field validation is apparent when considered with the alternative of relying on an unvalidated model, for which the user has no sense whatsoever for the behavior of the model under real-world conditions.

Step 4: Develop Acceptance Criteria for Validations. The user must determine the criteria used to accept or reject the model. This criteria must be determined prior to

validity testing the model, so that the propensity to "design the criteria to the model" is reduced. In other words, we do not wish to see how well the model predicts the field measured data, and then determine that the results are "close enough" (possibly introducing bias), but rather, more objectively determine the user's needs, and only then determine whether the model results are able to meet those needs.

The sensitivity analysis component of validity testing provides a measure of the required accuracy and precision for the model. The acceptance criteria should reflect the predictive ability of other available predictive methods, and the relative limits of their accuracy and precision requirements. Furthermore, the acceptance criteria should be stated in these same terms, and in terms of a confidence interval, if possible.

Step 5: Determine Field Validation Scenario (Natural Conditions). The "natural field condition" may be characterized by any combination of different soil types, climate, chemical and pollutant conditions, occurring simultaneously in the field test site. These "real world" conditions may constitute the key element for the ultimate model validation scenario.

Step 6: Plan and Conduct Field Validations. The field design of sampling and analysis was provided in the Borden field experiment and data set (Hubbard and others, 1994). Further discussion is provided in chapter 3 of this work.

Step 6e: Compare Model Performance with Field Observations. A number of different comparison schemes may be used to compare the model predictions with the

field observations; choosing among these will depend on the characteristics of the respective data. Rigorous statistical methods may be inappropriate, depending on whether the underlying statistical distributions are known, and on the comparability of the magnitudes of the data sets to be considered (Hern and Others, 1986:64).

Borden Site: Present and Past Investigations

Site Characteristics. The field investigation serving as the source of the data used for this comparative study, was performed at Canadian Forces Base Borden (CFB Borden). This site is located in Alliston, Ontario, Canada, in an inactive sand quarry, the base of which is about 100 by 250 meters, and which is relatively flat with little vegetative growth. The investigated sand aquifer is typical of ones used for public drinking water in the glaciated northeast. Up gradient of the quarry is an abandoned landfill, which is the source of a contaminant plume running underneath the test site, but having no effect on the upper part of the aquifer where the data for the current work were obtained.

The Borden test site has been studied extensively. The site was instrumented to study fate and transport of inorganic and halogenated organic compounds (Mackay, 1986), in addition to later, tracer tests being conducted using other gasoline components. The hydrology of the site is therefore well understood (Hubbard and others, 1994:2-1).

Original Purpose of Field Study. The Borden experiment was designed to investigated the behavior of solute plumes – some containing oxygenates – after they

have migrated some distance from the contaminant source. The object was to determine whether there was a co-solvency effect of the oxygenates on the gasoline plume, possibly making the gasoline constituents more soluble in the ground water, and to determine whether there was an effect on the overall degradation of the contaminants due to the presence of the oxygenates.

The present thesis work focused on the BTEX constituents of the American Petroleum Industry standard, regular unleaded PS-6 gasoline plume, without oxygenates. Target concentration for total BTEX for the experiment was set at 15 mg/L – about one tenth of saturation concentration – a level considered typical under such circumstance (Hubbard and others, 1994:3-2).

Site Physical and Chemical Hydrogeology

The Borden site, test aquifer, which is unconfined and extends down to about nine meters from the surface, is formed by glaciofluvial deposits with horizontal discontinuities consisting of medium to fine sands, as well as lenses of coarse sands, to silty clays (Macfarlane, 1983). What is believed to be an amorphous oxyhydroxide coating covers many of the mineral surfaces in this aquifer (Ball and others : 1990) (Hubbard and others, 1994:2-3).

Freyberg (1986), measured the spread of the concentration distribution about the plume center of mass by the spatial covariance structure. Temporal changes in this structure indicate the aquifer heterogeneity-induced changes in concentration distribution across the contaminant plume. Since the vertical thickness of the tracers remained

essentially unchanged, only the horizontal component of the spatial covariance tensor needs to be considered.

The sampling variability involved in measuring the vertical components of the covariance tensor were large, and the temporal variation in estimates of these could not be distinguished from sampling noise. The transverse dispersivity in the aquifer was determined to be an order of magnitude less than the advective dispersivity (Freyberg, 1986:77-78).

The low vertical and transverse dispersivity which exists in the Borden aquifer make it potentially ideal for making comparisons of the kind envisioned in this work. The centerline concentrations which are the major focus of the model output (see chapter 3, "Model Accommodation of Field Data") are well accommodated by the field data. These subjects will be treated in depth in the following chapters.

III. Methodology

Overview

The original thesis work covered the development of a static-plume model, a dynamic-plume model, and an aerobic-front velocity predictor, which is a regression model based on the dynamic-plume model output. This work is limited to validation testing the dynamic-plume model using the field data, and comparing the prediction of the Aerobic Front Velocity regression model with the field results.

The input parameters for the model are intended to be data that are readily available from a standard remedial investigation. However, obtaining values for the solid-phase electron acceptors for the Canadian Forces Base Borden aquifer was difficult. It is surprising that these numbers should be difficult to obtain for the Borden aquifer, as it is one of the most heavily studied sites in the literature.

The only reference found for solid-phase electron acceptors for this site was an article related to the detailed assessment of landfill leachates which included a reference to sand samples taken from the CFB Borden aquifer, which "contained 10-35 mmol/kg of leachable Fe, and 0.04-0.15 mmol/kg leachable Mn as oxide coatings (Dicken (unpublished), 1980, as *cited* by Nicholson)." The higher numbers correspond to the uncontaminated sands.

With the exception of the manganese and iron concentrations which were obtained from earlier investigations at CFB Borden, all required input values for the

model are included in the American Petroleum Industry (API) data set used in this work, and described more fully below.

The calculation for the necessary conversions from molar concentration given by Nicholson, to the model-required mass per volume concentration (mg/L) for Fe(III) and Mn(IV) is as follows. Using the larger number given for the (clean) soil, the concentration of solid-phase Iron(III) is

$$[Fe(III)] = \frac{\rho_{BS} * [Fe(III)_{MD}] * AW_{Fe}}{\eta} = 10{,}425 \text{ mg/L}.$$

Similarly, the appropriate calculation for Manganese(IV) is:

$$[Mn(IV)] = \frac{\rho_{BS} * [Mn(IV)_{MD}] * AW_{Mn}}{\eta} = 43.95 \text{ mg/L}.$$

where:

ρ_{BS} = Bulk Soil Density[a] = 1.76 kg/L

AW_{Fe} = Atomic Weight of Iron = 55.85 amu

AW_{Mn} = Atomic Weight of Manganese = 54.94 amu

$[Fe_{MD}]$ = Molar Density of Iron(III) in Bulk Solids[a] = 35 mMol/kg

$[Mn_{MD}]$ = Molar Density of Mn(IV) in Bulk Solids[a] = 0.15 mMol/kg

η = Aquifer Porosity[b] = 0.33

[a](Nicholson, 1982 : 161-62), [b](Hubbard, et.al., 1994 : 3-3), [b](Freyberg, 1986 : 52)

The values obtained above for the solid-phase electron acceptors are not likely to be depleted significantly from the biodegradation of the contaminant plume considered in this study. These are high levels and could lead to substantial levels of the reduced species of Fe and Mn, which are very mobile under the slightly acidic and moderately reducing conditions in the CFB Borden aquifer (Nicholson and others, 1983 : 161-162).

Furthermore, the results of Enyeart's (1994) study showed that, above a certain minimum concentration, the ultimate degradation of contaminants was relatively insensitive to higher concentrations of Fe(III) and Mn(IV), and to the other anaerobic electron acceptors, as well.

This result is not surprising, given the contact time and amount of contaminant coming into contact with these solid electron acceptors, their relatively slow reaction rates, and given other conditions conducive to their reduction. Specifically, if there are plenty of other, preferred electron acceptors, or if the contaminant plume is not too large, or if it is moving so rapidly that contact time is minimized, for example, then the amount of solid-phase electron acceptors is not likely to be significantly depleted.

In the present work, the Fe(III) and Mn(IV) levels were kept at 1000 and 100 ppm, respectively, in order to fit the spreadsheet model's cell, numeric formatting settings (larger values caused a numeric overflow condition, and could not be easily fixed). Because of the model's insensitivity to the level of the anaerobic electron acceptors present (particularly at such high levels), the results are identical to those that would be obtained using the values as calculated in the equations, above. Simulations

eventually confirmed that anaerobic electron acceptors were never depleted to levels sufficient to affect degradation rates.

Other than the manganese and iron values, as previously noted, above, the source of all data is American Petroleum Industry (API) Publication Number 4601 (Hubbard and others, 1994).

Analysis of Pollution Source

The original model was developed assuming JP-4 as the contaminant. The current work will instead use a standard gasoline (PS-6), as supplied by the American Petroleum Institute (API). The field investigation on which the test of the subject model will be based, was performed by injecting a gasoline-contacted water into the shallow sand aquifer at CFB Borden (Barker, 1990) (Hubbard and others, API 4601).

The model must account for the portion of the electron acceptors reduced by the other-than-BTEX portion of the petroleum hydrocarbon contaminant. The reduction of electron acceptors by the other contaminant constituents makes them unavailable for oxidation of the BTEX.

API publication #4601 references a possible value for the BTEX mass factor for this investigation. Although BTEX comprises only about 15% of PS-6 gasoline, it makes up as much as 60% of the mass of the PS-6 constituents going into solution. (Hubbard and others, 1994: 3-2). The computation of this reported value did not exclude the non-degradable hydrocarbons, and so it is considered to be *low* as a basis for mass stoichiometry relationships. Therefore, a higher value will be used.

Enyeart (1994) found that some components of JP-4 are essentially non-degradable. That is, they are unlikely to degrade at significant rates compared with those for BTEX. The current work will assume that the BTEX mass fraction for the PS-6 gasoline are comparable to those for JP-4. Therefore, the BTEX fraction of total biodegradable hydrocarbons found by Enyeart for JP-4 (81%), will be used for the PS-6 gasoline. This assumption may be somewhat non-conservative in its effect, since it implies that there will be more electron acceptors available to degrade the BTEX constituents of the PS-6 fuel.

However, a portion of the hydrocarbon contaminant will be sorbed onto the organic material in the soil, and this will cause an electron acceptor demand not measured in sampling only the ground-water dissolved BTEX. This is conservative in effect, and tends to counter the effect caused by the assumption of a non-conservative, non-degradable hydrocarbon fraction.

Model Verification and Consistency of Results

In the analysis performed to ensure consistency of model results done by Enyeart (1994), it was found that the model achieved consistent results when both the Δt and the Δx are kept below certain values. Furthermore, implied in this analysis is that the water input ratio, or $V_{rel}*\Delta t/\Delta x$, should be kept within a certain range. Also, by reasoning similar to that above for the water input ratio, the input ratio of the solid electron acceptors (or soil input ratio: $V_{soil}*\Delta t/\Delta x$) into the plume must not exceed one. For the Borden aquifer data, where the solid input ratio is 3.448 times as great as the water input

ratio, this puts an upper limit on the water input ratio of about 0.29, in order to keep the ratio less than 1.

In Enyeart's work, conservative values were used for both Δt and Δx. For example, Δt was tested and proved to be small enough at 2.4 days – that is, simulation results were consistent throughout a range of Δt, from 0.05 to 2.4 days – but a value of 0.5 day was used to be conservative (Enyeart, 1994:48). For Δx, a value of 1.0 feet was deemed small enough, and in the present work a value of $\Delta x = 0.1004$ foot was used. The water input ratio used in Enyeart's model testing was: $V^*\Delta t/\Delta x = 0.258$, which compares with the ratio of $V^*\Delta t/\Delta x = 0.287$ used in the present work.

As already mentioned, in the current effort it was necessary to increase the *resolution* of the model because the relative velocity (V_{REL}) found in the field was low compared to Enyeart's test data, and so the number of plume sections was increased, and hence Δx was reduced. The Δt was kept at 0.5 day, in order to maintain nearly the same water input ratio as used in Enyeart's test data, which was prudent to avoid the introduction of possible *averaging errors*, which could be introduced if the water input ratio was allowed to be set too low.

Because the water input ratio affects the amount of averaging used to model the *mixing* of the continuously introduced, electron-acceptor carrying ground water, if it is set too small then unrealistically small average values of electron acceptor concentration might be obtained in plume sections, resulting in an apparent loss of electron acceptor, and accumulating error, as the model is run. This is shown in the analysis performed by

Enyeart (1994). When the Δx was increased to 1.2 foot – thus decreasing the water input ratio – inconsistently high values of contaminant were observed, due to the apparent lowered electron-acceptor concentration caused by the averaging effect (Enyeart, 1994 : 53).

Because of the nature of the Borden site field input data parameters – the retardation factor and, hence, the water input ratio was low, leading to undesirable averaging effects compared to the test data set used to develop the original dynamic degradation model – the present work involved modifying the original dynamic degradation model to increase its resolution. This was done by increasing the number of plume sections from 10 to 98 (reducing the Δx from .9843 to 0.1004) – and using the highest retardation value found in the field. Keeping the Δt and the Δx below the limits found in the sensitivity analysis, and keeping the water input ratio close to the conservative ratio used in the test case of Enyeart's thesis, should ensure results from the present model (with 98 sections) are consistent with Enyeart's model (with 10 sections) when run with the same data set.

This was tested by resetting the current model (98 sections) with the original (test) data set and running it forward to several points in time, and comparing the results with the original model (10 sections), run the same way. The results are shown in fig 7. The analysis performed by Enyeart, together with efforts to keep both the time step Δt, the section length Δx, and the water input ratio well within conservative parameters, as well as the check on model consistency as charted in figure 7, show that the current model can be expected to produce results consistent with the original model.

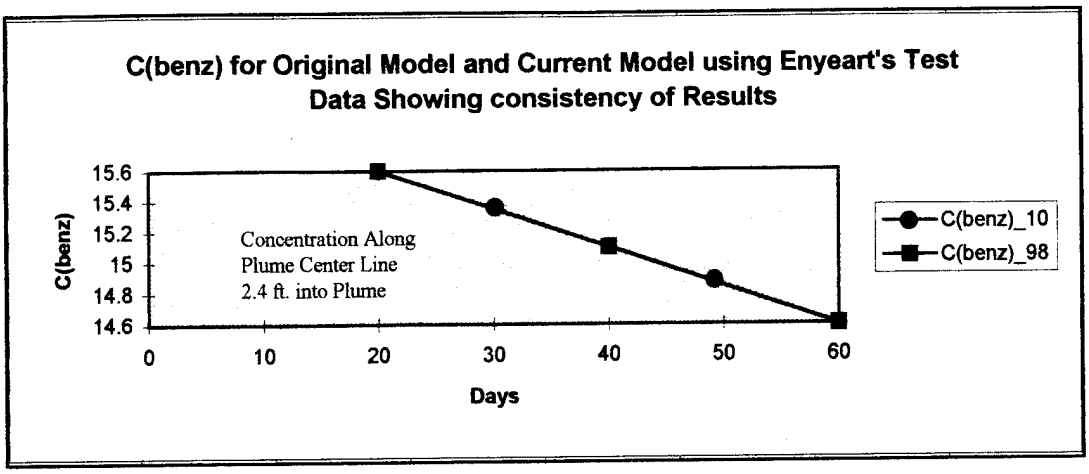

Fig. 7. Comparison of Model Results: Original Model (10 plume sections) with Currently Developed Model (98 plume sections). Model Consistency is Maintained.

There are plenty of solid-phase electron acceptors present in the Borden aquifer, the anaerobic-degradation rate is relatively low, and the contaminant-plume velocity (V_{SOIL}) (i.e., the velocity of introduction, with the soil, of solid-phase electron acceptors into the front of the plume) is high compared to the relative ground-water/contaminant-plume velocity (V_{REL}) (i.e., the velocity of introduction of dissolved electron acceptors into the rear of the plume). The overall impact of these conditions to the dynamic degradation model's output (prediction) should be a relatively flat distribution of contaminant concentration in the parts of the plume away from the aerobic front. That is, the model should be expected to predict that degradation of contaminant will occur evenly, across the plume, as a result of the high level of anaerobic electron acceptors,

which will not be significantly depleted due to their high rate of replenishment (high V_{SOIL}).

The aerobic electron acceptor (and the other dissolved electron acceptors), carried into the plume with the ground water, will result in preferential degradation from the rear of the plume, forward. An illustration of these results is given in the following figure (figure 8).

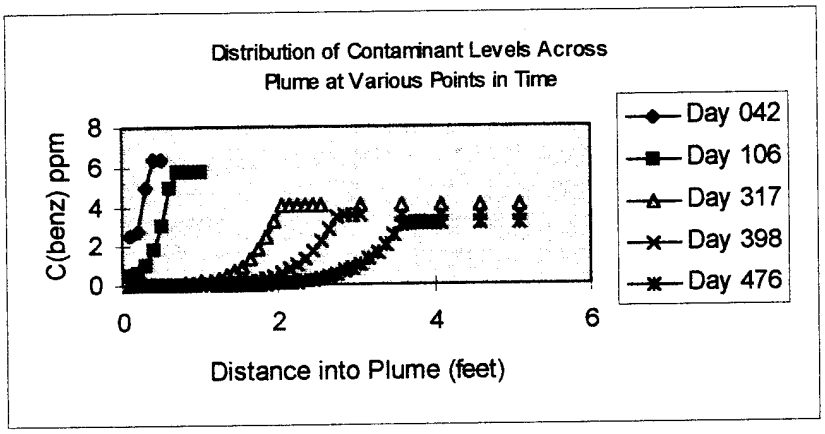

Figure 8. Contaminant Distribution Across Model Plume in Time

Model Accommodation of Field Data

In order to successfully run and test the model, a proper interpretation of the input parameters, as represented by the field data, must be made. Several approaches were considered for the initial BTEX concentrations. It was determined that the known mass of BTEX injected into the aquifer be considered as the basis for a uniform concentration

calculation over the volume, based on the injection time and geometry. This better fits the model assumption that the initial concentration is evenly distributed throughout the plume, and establishes a mass basis for the calculation.

The model assumes a zero width to the plume, but may accommodate mass calculations through the use of a width-representative centerline-concentration. Therefore, it was decided to use such a representative concentration for the initial BTEX concentrations. These will be based on the known concentrations of the injected contaminants, the time over which the injection occurred, and the groundwater velocity in the vicinity of the injection well.

Once the initial conditions have been entered into the model, and the model is run to a predetermined point in time, comparison of the model's predicted results with the measured field results can be accomplished.

A proper interpretation of the results, as they compare to the field data, must be determined. In order to compare the spatial distribution of contaminant mass in the field-measured plume, it must be divided in some way analogous to the model, which displays the predicted contaminant concentrations within each plume segment. In this way the predicted concentrations, and the changing distribution of those concentrations, can be compared to their analogous field-measured values.

Aerobic Front Analysis

The Aerobic Front Velocity, or AFV_{10}, is the velocity of the front delineated by the bioremediation of BTEX to below the 10 ppm level, corresponding to a 4 ppm

Benzene level (Enyeart, 1994: 40), as it occurs from the rear to the front of the plume. This velocity will be measured by mapping the spatial movement of the benzene concentration as it is reduced to 4 ppm, or lower, relative to the predicted center of mass of the contaminant plume, based on the velocity retardation factor, a function of the organic content of the soil. The concentration measurements are taken over each of the model's plume segments at specific points in time for this calculation.

Comparison of the AFV_{10} predicted by the model with the AFV_{10} measured in the field is an important focus of this work. A primary consideration is how the model output is to be spatially aligned with the field measurements to facilitate this comparison. The model is one-dimensional and does not account for dispersion of the contaminant plume, and so the plume is modeled as a centerline concentration characteristic of the width of the plume, and with a constant plume length. It is this constant-length center-line concentration model that must be spatially aligned with the field measured plume.

The position of the contaminant plume center of mass at any particular time, in general, is not that predicted by the retarded velocity of the plume alone. The rate at which contaminant mass is being degraded at any particular area of the plume depends on the distribution within the plume of conditions favorable for biodegradation, leading to a change in mass distribution. Therefore, the center of mass of the plume may appear to move at a different rate than the velocity predicted by considering groundwater and sorption affects alone.

Put simply, the model measures the AFV_{10} as the speed at which the 4 ppm benzene front moves across the constant length centerline of the model, which is divided

into sections allowing delineation of this effect. There is no such constant reference relative to the plume as it is delineated by the field investigations. Therefore, such a reference needs to be defined.

The field measurements include the center of mass of the plume for each contaminant, as well as the center of mass of the conservative tracer (chloride). The chloride tracer thereby gives an indication of the groundwater velocity, and the comparison of this with the contaminant plume center of mass gives the retardation factor.

The length of the conservative plume changes in time (because of dispersion during flow over a given period). The conservative plume's length at any given time, divided by the retardation factor, is used as the standard, or *ruler* for the expected length of the contaminant plume at that time, without consideration for losses from the back of the plume due to biodegradation (Heyse, 1995).

Figure 9 illustrates some of these basic concepts. Three snapshots in time are shown of one plume as it is transported via advection, spread out through dispersion-diffusion, and, in this hypothetical case, selectively bioremediated from the rear of the plume forward – caused by the introduction of dissolved electron acceptors from the rear – as groundwater overtakes the sorption-retarded contaminant plume. This loss of mass – selectively from the rear of the plume – causes the center of mass to be shifted progressively forward compared to the hypothetical point where the center of mass would otherwise be, based on contaminant velocity alone.

In this scheme, the center of the model's plume length, or ruler – divided into sections depicting a dynamic contaminant gradient – is positioned over this hypothetical, velocity-predicted, center of mass (note: the ruler *grows* with the hypothetical size of the plume, based on the size of the conservative tracer plume). In this way, the AFV_{10} may be measured as the dissolved electron acceptors (most notably O_2) reduce the contaminant concentration from the left to the right along the plume-length ruler. Note in figure 9, for example, that the 4 ppm isopleth moves from the left, along the ruler in time, providing the basis of the AFV_{10}.

The illustration at time $t = t_2$, shows how the values measured in the field might be *fitted* to the length of the model's set-length ruler. In this way, an indication of the mass along the centerline of the plume is captured for direct comparison with the model.

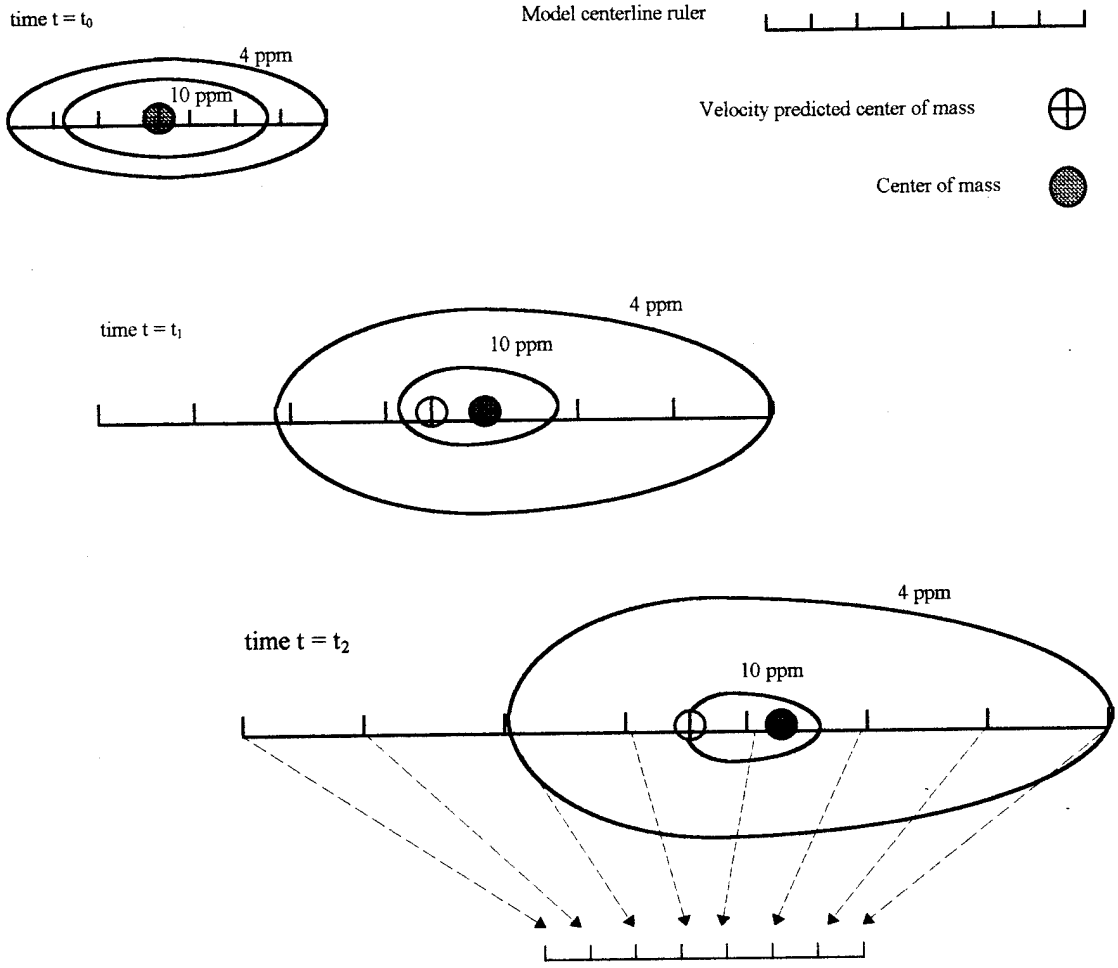

Fig. 9. Representation of a scheme to fit the model to field data.

Data Set Characteristics

Applicability of Current Data Set. For the current study, the API Publication 4601 data set (Hubbard and others, 1994), from a study performed at Canadian Forces Base Borden was chosen. These data were collected in order to study the co-solvency effects of gasoline oxygenates on chemical fate and transport. The data were considered well suited for this work because of the similarity of pollutant compounds studied, to

those for which the dynamic degradation model was developed. In addition, the collected data are compatible with the required input parameters of the model, the Borden site is relatively homogeneous with respect to its hydrogeology, the aquifer exhibits low dispersivity in the transverse and vertical directions (Freyberg, 1986 : 77-78), and the overall data quality is high.

Additionally, the compounds of interest (BTEX) were present at high-enough levels to enable long-term tracking of their fate and transport; a single, uniform application of the compounds was done (the simplest situation), and a known mass of pollutants was released.

The data was determined to be particularly suitable due to the dense piezometer sampling network covering the extent of the plume for the entire time period of the intrinsic degradation of the plume. The quality of the data is known, and although not used directly in the statistical comparison of data in this work, it may be used in later efforts to extend this work, and lends credibility to the results obtained (Freyberg, 1986 : 77-78).

Model Acceptance Criteria

Following the guidelines laid out in Table 3., to the extent possible, the model user's needs are identified as the ability to predict the aerobic front velocity, or AFV_{10}, given certain easily obtained site hydrogeologic and chemical parameters. These model requirements, the most important predictor variables, have been determined previously through sensitivity analysis (Enyeart, 1994).

Furthermore, the underlying assumption of this thesis is that the model is amenable to field validation. The AFV_{10} model requires as input the readily obtained field parameters of dissolved oxygen, BTEX concentration, and the relative velocity of the ground water to the contaminant plume. The scope of this thesis effort made it mandatory to find a pre-existing data set.

The Borden site data set (Hubbard and others, 1994), as described above, not only fit the input data requirements, but included a body of analysis of spatial moments for determining the remaining contaminant mass in time, and vertically-integrated plume contaminant isopleth maps, for determining the AFV_{10}, for each sampling event in time.

In addition, this data set provided the other input parameters (site hydrogeologic parameters, anaerobic electron acceptor levels, sorption-desorption retardation factor) needed to run the underlying dynamic degradation model. This data set was therefore quite suitable to the task at hand, and might have served as a suitable template for developing a field study for this model's validation purposes.

The most important step in the current validation work is to develop the criteria for accepting or rejecting whether the model has passed the current round of validity testing. The rationale for this step is crucial to the set up of the comparison scenario.

The AFV_{10} Model. Eneyart (1994) originally tested the AFV_{10} regression model by using it to predict output values for the underlying dynamic degradation simulation model, on which the regression model was based. This was done by choosing for the input to the dynamic degradation model, values near the upper and lower limits of the

range of test input values (Table 4) used in the simulation model for the development of the AFV_{10} regression model, and then comparing the resulting output with that predicted by the AFV_{10} model, at the 95% prediction interval.

The significance of the prediction-interval analysis is that it provides a measure of the range around the regression-model predicted value, within which the value for a newly derived and independent single observation of the underlying process generating the data is expected to fall a certain percentage of the time.

AFV_{10} Model Validation Criteria. In the current work, in addition to using the 95% prediction interval to test individual observations, the 95% confidence interval will be used to compare both the dynamic degradation model, and the field measured value of the aerobic front velocity. The confidence interval will be used to compare the average of several AFV_{10} values with the predicted mean AFV_{10} from the regression model. If the resulting values fall within the 95% prediction, or the 95% confidence interval, respectively, then the validation will be accepted, and this step of the validation of the AFV_{10} regression model will be considered successful.

The Dynamic Degradation Model. Another check of the validity of the AFV_{10} model may be performed by testing the underlying dynamic degradation simulation model. If this model is found to be deficient, it would not reflect well on the derivative AFV_{10} predictor. If this underlying foundation of the AFV_{10} model is found to be performing satisfactorily, it should bolster the perceived usefulness of the AFV_{10} model.

In order to test the dynamic degradation simulation model, it was determined to use the single most valid determinant of whether intrinsic bioremediation has occurred. The loss of contaminant mass in the plume over time is the key consideration in determining whether bioremediation has occurred. In order to compute the predicted mass of contaminant remaining in the plume at a given time, the concentration of contaminant is summed across all plume sections, and then averaged across the plume by dividing by the number of sections in the plume.

The data set contains the mass (grams) calculated by the method of spatial moments, using the zeroth moment, for each of the data subsets. These masses are to be compared to the total remaining mass predicted by the simulation model. The model output is in units of concentration, and parts-per-million had to be converted to mass (grams) by scaling according to the fraction left of the original, time zero concentration, and the corresponding mass (grams) measurement at the time of the injection. This being done, the masses remaining in the plume may be compared at different points in time for the dynamic model, and the field measured data.

Dynamic Degradation Model Validation Criteria. As a measurement of how well the two mass values so obtained may compare, it has been determined that, given the assumptions and limitations of the dynamic degradation model, and the limitations inherent in the field data, a simple fractional comparison is all that is warranted.

Following this line of reasoning, and with a pragmatic, common-sense management approach, it was determined that a ratio of model predicted to field

measured rate of mass loss should equal at least 50%, and be no more than 150%. The reasoning is as follows.

First, "one-half" is an easily and widely understood numerical concept. It is easy to communicate, visualize, remember, and to grasp its relative significance. The proposed acceptance criteria range of 50% to 150% amounts to the model predicted value falling within "plus-or-minus one-half" of the field measured value.

Second, the assumptions incorporated into the model are somewhat conservative, overall. Therefore the ratio of the model to the field mass-loss rates is likely to be less than one: a conservative overestimation of the time to cleanup. On the conservative side, this amounts to a safety factor of two (i.e., 1/2). It is potentially less damaging to overestimate the time to cleanup (i.e., a small "rate" of contaminant mass loss) and so a factor of two, given the level of uncertainty and the conservative assumptions, is not excessive.

On the non-conservative end of the acceptance criteria range, because of the possibly serious repercussions associated with overestimating the rate of contaminant mass loss, and the large degree of uncertainty involved, a smaller safety factor of 1.5 (i.e., 1 + 1/2) will be used. Although consistent with the safety factor used in the non-conservative case – they are both based on one-half the field mass-loss rate – it is smaller safety factor relative to the base value than the safety factor used on the conservative side of the acceptance criteria range, because a non-conservative error is more serious than a conservative error.

Although this "safety factor" compounds the factors of safety inherent in most of the assumptions of the model, it is not excessive since the magnitude of the other factors may be unknown, and there are a few assumptions in the model which may accumulate in the non-conservative direction, as well (Enyeart, 1994 : 43). Among these non-conservative assumptions are that the microbes present will degrade the substrate, and that no acclimation lag time will occur before microorganisms begin their degradation work.

IV. Data Analysis: Model Predictions Versus Field Measurements

Analysis of Data

The AFV_{10} Regression Model: Aerobic Velocity. The criteria for acceptance of the AFV_{10} predictor regression model, in the context of the current validation scenario (limited to the current data set), has been set at the 95% prediction interval. This prediction interval was previously used by Enyeart to determine whether or not the dynamic degradation model's results were consistent with the regression model.

This regression model was derived from analysis of several data output sets – covering the spectrum of expected combinations of input parameters – from the dynamic degradation model. The results thus compared using the prediction interval were those obtained from running the dynamic degradation model for input parameter values at or near the upper and lower limits for the relative velocity (V_{REL}), and BTEX concentration (C(btex)), expected to be encountered under field conditions.

The significance of the prediction-interval analysis is that it provides a measure of the range around the regression-model predicted value, within which the value for a newly derived and independent observation of the underlying process generating the data is expected to fall a certain percentage of the time. When applied to the field data, the significance of this test is that it allows a measurement of how well the field data compare with the regression model's predicted value.

Table 4. Dynamic Degradation Cases used in AFV_{10} Regression Model Development. *Cases Added to Extend Valid Range of AFV_{10} Model.

Case	V_{REL} (ft/day)	O_2 (ppm)	BTEX (ppm)	AFV_{10} (ft/day)
1	1.0	4.0	20	0.068
2	1.0	4.0	33	0.04
3	1.0	4.0	40	0.04
4	1.0	4.0	50	0.025
5	0.05	4.0	33	0.0015
6	0.11	4.0	33	0.005
7	0.5	4.0	33	0.025
8	0.76	4.0	33	0.0325
9	1.0	4.0	33	0.035
10	1.5	4.0	33	0.053
11	0.5	2	33	0.01
12	0.5	2.5	33	0.012
13	0.5	3	33	0.015
14	0.5	3.5	33	0.02
15	0.5	5	33	0.025
16*	0.044	2.5	20	0.00215
17*	0.051	3	15	0.0350
18*	0.07	4	15	0.00603
19*	0.091	4.5	15	0.0134

Table 4 Cont. Dynamic Degradation Cases used in AFV_{10} Regression Model Development. *Cases Added to Extend Valid Range of AFV_{10} Model.

20*	0.141	4.5	15	0.0118
21*	.229	3.5	20	0.0123

The underlying chemical and hydrogeologic processes represented by the model are assumed to be the ones most responsible for BTEX degradation in the field. Although the regression model was developed based on dynamic degradation model input and output variable sets, and these were amended to include cases similar to the presently considered field data set, the newly observed field values for deriving the dependent variable (the AFV_{10}) are considered to be independent of the regression model. Table 4, above, shows the dynamic degradation model input (independent) and output (dependent) parameters used in the development of the AFV_{10} regression model.

The first 15 cases shown in the above table are the original ones used by Enyeart to develop the AFV10 regression model. In addressing the test site's data used for validity checking the model (the "Borden"data set), the regression data set was amended to 21 cases. The resulting regression model will be discussed in later sections of this chapter. The results of the original regression (with 15 cases) are shown in the following Statistix™ table.

Table 5. Statistix™ v.4.1 Output for Stepwise Regression of Dynamic Degradation Model Input and Output Parameters; 15 Cases Included

```
STEPWISE REGRESSION OF AFV10

UNFORCED VARIABLES: BTEX BTEX2 O2 OSQ VREL VRELSQ
  F TO ENTER  4.00
  F TO EXIT   4.00
```

STEP	R SQ	MSE	T	BTEX	BTEX2	O2	OSQ	VREL	VRELSQ
1	0.7156	1.016E-04		.	.	.	.	E	.
2	0.8784	4.702E-05	-4.01 +	A	.	.	.	E	.
3	0.9309	2.917E-05	2.89 +	A	.	C	.	E	.
4	0.9646	1.646E-05	3.08 +	A	B	C	.	E	.

RESULTING STEPWISE MODEL

VARIABLE	COEFFICIENT	STD ERROR	STUDENT'S T	P	VIF
CONSTANT	0.08036	0.02113	3.80	0.0035	
BTEX	-0.00453	0.00108	-4.20	0.0018	35.3
BTEX2	4.621E-05	1.499E-05	3.08	0.0116	35.9
O2	0.00539	0.00153	3.53	0.0054	1.1
sVREL	0.03671	0.00301	12.18	0.0000	1.2

CASES INCLUDED	15	R SQUARED	0.9646	MSE	1.646E-05
MISSING CASES	0	ADJ R SQ	0.9504	SD	0.00406

VARIABLES NOT IN THE MODEL

	CORRELATIONS		
VARIABLE	MULTIPLE	PARTIAL	T
OSQ	0.9905	-0.1253	-0.38
VRELSQ	0.9566	-0.5139	-1.80

The resulting equation is

$$AFV_{10} = 0.08036 - 0.00453 * BTEX + 0.00539 * O_2 \ldots$$
$$+ 0.03671 * V_{REL} + 4.621\text{ E-}5 * BTEX^2.$$

Note that the coefficients given in this regression analysis differs somewhat from the original regression model developed by Enyeart, which is given by

$$AFV_{10} = 0.099 - 0.007 * BTEX + 0.010 * O_2 + 0.029 * V_{REL} + 8.1\text{ E-}5 * BTEX^2.$$

The reasons for this discrepancy are unknown. Perhaps the analysis Enyeart performed included a typographical error in the input data (no longer available as entered), or possibly, the algorithms used in Statistix™ v.4.0, used by Enyeart, are different than those used in the version (4.1) used in the present work. The predicted value of AFV_{10} for the Borden site field input parameters, and the 95% prediction interval based on this regression, are shown in table 6.

Table 6. Statistix™ v.4.1 Predicted Value of AFV_{10}
With 95% Prediction Interval; 15 Cases Included

```
PREDICTED/FITTED VALUES OF AFV10
LOWER PREDICTED BOUND      0.0237
PREDICTED VALUE            0.0404
UPPER PREDICTED BOUND      0.0570
SE (PREDICTED VALUE)    7.483E-03

UNUSUALNESS (LEVERAGE)     2.4026
PERCENT COVERAGE             95.0
CORRESPONDING T              2.23

PREDICTOR VALUES: BTEX = 16.980,
BTEX2= 288.32, O2 = 4.0000, VREL = 0.0580
```

The predicted bounds of the 95% range are 0.0237 to 0.0570 ft/day. This range encompasses the value predicted by Enyeart's regression model (0.0405 ft/day), but it does not contain the value of the AFV_{10} measured directly from the dynamic degradation

model (0.010 ft/day). The observed AFV_{10} from the field measurements (0.0155 ft/day; see Appendix II) is not contained at the 95% level, either.

The Borden site field data parameters lie well outside the range of dynamic degradation model input parameter values used in the development of the AFV_{10} regression model. For the present work, it was decided that new cases would need to be developed in order to extend the regression model to cases such as the Borden site; that is, to sites with low BTEX, and low V_{REL}. The last six cases in Table 4 were thus added, and the resulting regression of the amended data set are shown in the following table.

Table 7. Statistix™ v.4.1 Output for Stepwise Regression of Dynamic Degradation Model Input and Output Parameters; 21 Cases Included

```
STEPWISE REGRESSION OF AFV10
UNFORCED VARIABLES: BTEX BTEX2 O2 OSQ VREL VRELSQ
  F TO ENTER  4.00
  F TO EXIT   4.00
```

STEP	R SQ	MSE	T	BTEX	BTEX2	O2	OSQ	VREL	VRELSQ
1	0.7725	7.541E-05		.	.	.	.	E	.
2	0.8665	4.670E-05	-3.56 +	.	B	.	.	E	.
3	0.9031	3.590E-05	2.53 +	.	B	C	.	E	.
4	0.9246	2.967E-05	-2.14 +	.	B	C	.	E	F

RESULTING STEPWISE MODEL

VARIABLE	COEFFICIENT	STD ERROR	STUDENT'S T	P	VIF
CONSTANT	-0.01201	0.00679	-1.77	0.0963	
BTEX2	-1.366E-05	2.867E-06	-4.76	0.0002	1.7
O2	0.00513	0.00170	3.02	0.0081	1.0
VREL	0.06503	0.01059	6.14	0.0000	13.7
VRELSQ	-0.01562	0.00731	-2.14	0.0483	11.8

CASES INCLUDED	21	R SQUARED	0.9246	MSE	2.967E-05
MISSING CASES	0	ADJ R SQ	0.9058	SD	0.00545

The resulting equation is

$$AFV_{10} = -0.01201 - 1.366\text{ E-}5 * BTEX^2 + 0.0513 * O_2 \ldots + 0.06503 * V_{REL} - 0.01562 * V_{REL}^2.$$

Note that in the amended model, as developed using stepwise regression on the ammended data set, the BTEX term has fallen out, and instead a new term, V_{REL}^2 has been included. This is merely the result of the stepwise regression procedure, as performed on the ammended data set, using the Statistix™ v.4.1 software package. The resulting confidence interval for the Borden site, model validation parameters, is given in the following table.

Table 8. Statistix™ v.4.1 Fitted Value of AFV_{10}
With 95% Confidence Interval; 21 Cases Included

```
CONFIDENCE FITTED VALUES OF AFV10
PERCENT COVERAGE              95.0

LOWER FITTED BOUND   3.682E-03
FITTED VALUE         8.313E-03
UPPER FITTED BOUND     0.0129
SE (FITTED VALUE)    2.185E-03

PREDICTOR VALUES: BTEX2 = 288.32,
O2 = 4.0000, VREL = 0.0580,
VRELSQ = 3.364E-03
```

The amended regression model's confidence interval bounds (0.00368 to 0.0129 ft/day) now compare rather well at the 95% level with the AFV_{10} predicted by the dynamic degradation model (0.010 ft/day). The AFV_{10} measured in the field at the Borden site of 0.0155 ft/day (see Table 9 and Appendix II), however, falls outside of this

confidence interval. The amended model has therefore not met the criteria for acceptance (see chapter 3, "Model Acceptance Criteria"), according to this stage of the overall model validity testing scenario. These results do not compare well with the prediction of Enyeart's original regression model, either (see Table 6, and contiguous text).

Table 9. Field Measurement Summary for Computed Aerobic Front Velocities

AFV at Several Contaminant Levels Between Subsequent Time Step (ft/day)		Calculations end day: 42	106	317	398	476
Interpolate for 4 ppm	begin day: 6	0.028	0.0119	0.0155	0.0101	0.0118
Interpolate for 4 ppm	begin day: 42		0.00257	0.0157	0.00995	0.0112
Interpolate for 1.5 ppm	begin day: 106			0.0225	0.0131	-----
Interpolate for 1 ppm	begin day: 317				0.0056	0.022
Interpolate for .35 ppm	begin day: 398	Average AFV = 0.0155 ft/day = SUM (all values)/14 values				0.0374

Comparing the individual observations calculated for the aerobic front velocities in Table 9 with the prediction interval bounds given in Table 10 (-0.0041 to 0.0208 ft/day), of the 14 AFV values calculated, 10 of them are contained within the 95% prediction interval. This is a good indication that the regression model adequately predicts the bioremediation in the field, and the model therefore meets the criteria for acceptance according to this stage of the regression model validity testing. The AFV_{10} predicted by the dynamic degradation model (0.010 ft/day) also compares well with this prediction interval.

Table 10. Statistix™ v.4.1 Predicted Value of AFV_{10} With 95% Prediction Interval; 21 Cases Included

```
PREDICTED VALUES OF AFV10
PERCENT COVERAGE                95.0

LOWER PREDICTED BOUND     -4.127E-03
PREDICTED VALUE            8.313E-03
UPPER PREDICTED BOUND         0.0208
SE (PREDICTED VALUE)       5.869E-03

PREDICTOR VALUES: BTEX2 = 288.32,
O2 = 4.0000, VREL = 0.0580,
VRELSQ = 3.364E-03
```

The Dynamic Degradation Model: Measured Versus Predicted Mass. In addition to the comparison of the predicted and measured aerobic front velocity (AFV_{10}), the predicted and the measured mass of contaminant (benzene) remaining after various time periods were compared. These values are provided by the Borden site data set (Hubbard and others, 1994 : 7-1, 7-9), and by the average of the summation of benzene levels across all the plume sections of the dynamic degradation

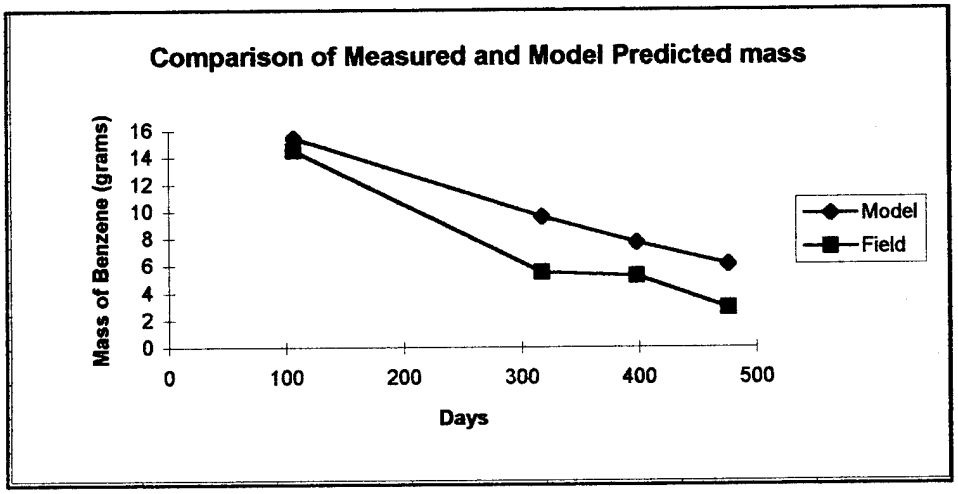

Figure 10. Mass of Benzene Remaining After Degradation as Predicted by the Dynamic Degradation Model and Measured at the Borden Site

model. Plots of the total benzene mass for the dynamic degradation model converted to mass units, and the field measured mass (obtained by spatial moment analysis) are shown in figure 10.

Visually, the two plots seem to compare well. The basis of the above chart is found in Table 11, below. This table also shows the comparison of the slopes for the two plots of the chart. Comparing the slopes provides a better indication of how well the dynamic degradation simulation model predicts overall intrinsic bioremediation.

Comparison of the slopes of the mass loss over time for the simulation model versus the field measurements – as shown in Table 11, model predicted mass loss is 81% of the field measured mass loss – shows that they are well within ± 50%, as specified in advance as the criteria for this comparison (see chapter 3, "Model Acceptance Criteria").

Table 11. Data for Comparison of Mass by Dynamic Degradation Model Simulation and Field Measured Values with Computation of Slope Ratios for Comparison of Trend

Comparison of Dynamic Degradation Model Predicted Benzene Mass Loss with Field Measured Mass Loss Computed Using Method of Spatial Moments						
Day	Model Mass	Measured Mass	Model Slope from day 106 to 476	Field Meas Slope: day 106 to 476	Slope Ratio: Mod/Field	Mass Loss: Model as % of Field
106	15.44	14.51				
317	9.58	5.50				
398	7.71	5.21				
476	6.10	2.89	-0.025	-0.031	0.81	81%

Benzene Concentration Value Measurements from Field Data. The basis of the model verification comparison conducted in this work is the determination of the field values (see Figure 9, and Chapter 3, "Aerobic Front Analysis"), as measured along the

plume centerline from the constant concentration isopleth maps from the depth integrated data (see Appc. II and III). The measurements performed to determine the aerobic front velocity from field values are shown on the isopleth maps in Appendix III.

The primary difficulty encountered when making these measurements was in determining the positions of the leading and trailing edges of the conservative tracer plume, which was the basis for laying the center line ruler along the corresponding contaminant plume in accordance with the scheme depicted in Figure 9. This center line ruler was used to divide the plume into sections along its center line, in order to lay out positions for determining contaminant levels in the contaminant plume, analogous to the way the simulation model plume is divided into sections. By comparing the position of contaminant levels in time – for different sampling dates – along the center line ruler, aerobic front velocities were determined in a similar way for both the model, and the field measured values, facilitating a direct comparison of the two.

It was more difficult to determine the leading and trailing plume edge positions for the later sampling dates (days 317, 398, and 476) than it was for those of the earlier sampling dates (days 6, 42, and 106). This is because the two plumes (conservative tracer and benzene contaminant) became more dispersed as they traversed longer distances, and they became more separated from one another as the benzene contaminant plume movement was retarded due to sorption effects. As the plumes became progressively more separated, the placement of the center line ruler on the contaminant plume relied more heavily on scaling based on the retardation factor. Additionally, the sampling network was much less dense for the later sampling dates. All these effects

combined resulted in less confidence in determining the position of the edges of the plume for the later sampling dates.

The principle of proportionality was used to *extrapolate* out away from the constant concentration isopleths of the conservative tracer plume, the zero level location used to determine the plume's leading and trailing edges. In other words, the position of the zero concentration level at the leading edge of the plume – which was not plotted directly – was determined relative to and proportional to the position of the existing, plotted contours. This method was supplemented by reliance on nearby point values, outside of the concentration contour plots, such as the 5 ppm value near the plume's leading-edge line for the day 398 plot (see App. III).

The results of the aerobic front velocity measurements are shown in Appendix II, Section A.1. The results have been calculated in several ways, as an average over all sampling dates, and for various combinations of earlier and later dates, in order to minimize the influence of the less reliable, later sampling dates. The overall average for the AFV_{10} of 0.0155 ft/day is shown to be in good agreement with those obtained using only earlier sampling dates, as well as various combinations of of data from earlier, and later sampling dates.

V. Conclusions and Recommendations

Conclusions

The dynamic degradation simulation model was shown to meet the criteria of the validation test. The AFV_{10} predictor regression model derived from it was shown to pass most of the limited validation tests, according to the criteria developed in chapter 3. The one criteria for which this model failed a validation test was for the comparison of the average of the field measured aerobic front velocity values to the 95% confidence interval for the AFV10 regression model fitted value. Although this average field value did not fall within the model's 95% confidence interval – it was 20% higher than the upper bound and therefore did not satisfy the criteria for this part of the validation test – it was off in the conservative direction and still met the ±50% management criteria developed for the dynamic degradation simulation model, a criteria which reasonably could be applied here, as well.

The model's 95% prediction interval was used to compare individual aerobic front velocity field values, and it was found that 10 out of 14 of the field measured values met this criteria. Based on this validation, plus the results of the confidence interval comparison described above, overall the validation of the AFV10 regression model was determined to be a success.

The significance of this validation is limited to the narrow scope of this work: the Borden site data set (Hubbard and others, 1994). More extensive validation of the AFV_{10}

regression model, and its underlying basis, the dynamic degradation model, will be necessary to fully validate the current models.

In this work it was found that the original AFV_{10} regression model equation was in error (this chapter, "The AFV_{10} Regression Model: Aerobic Velocity" section), and it was corrected. In addition, the AFV_{10} model was "extended" in its range of "coverage" of expected field conditions, by the addition of six cases with low relative velocity (V_{REL}), and low BTEX initial concentrations. These may be viewed as minor adjustments to the model to accommodate these previously unanticipated field conditions.

Recommendations for Further Research

Additional validation work using actual site data, such as that undertaken in this work, would be the most obvious follow-on research to this work. With the extension of the regression model to accommodate cases of low BTEX and low V_{REL}, such as found in the Borden site data, it is hoped that the regression model now will accommodate a wide range of site conditions.

Finding suitable data sets to compare with the model's output, it is anticipated, will continue to pose a challenge to the investigator. The Borden site data set used in the current work, was particularly well suited for the task of comparing site contaminant levels with those predicted from the model's output because of the relative hydrogeologic uniformity of the Borden site aquifer. The resulting, "well-behaved" contaminant plume constant-concentration isopleth contour mapping (see Appendix 2), allowed a relatively straightforward comparison of the AFV_{10}.

Ultimately, further validation testing of the AFV_{10} regression model will require comparing its results with a number of field data sets derived from a wide variety of sites, encompassing the full spectrum of likely field conditions. Only when this has been accomplished can the model be proposed for use in the field, for use by the IRP site manager as a screening tool for the initial determination of the feasibility of intrinsic bioremediation.

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Appendix I. Sample of Dynamic Degradation Simulation Model

A. Simulation Model Parameter Input Region

	DYNAMIC CASE OF JP-4 DEGRADATION						
Initial Values at Site:(mg/l)					Calc: GW/Petrl Velocity		
Benzene	7.19952		Hyd Conductivity		V.w	BTEX: R	V.rel
Toluene	5.010798		(ft/day)=	19.69		1.290	0.058
EthylB=	0.799758		Hy Grad=	0.0043	0.256567	1.149	0.033
Xylenes'=	4.019166	16.98	Porosity=	0.33	ft/d	1.175	0.038
E acceptors (*81%)			organic			1.392	0.072
Oxygen=	3.24		content=	0.0002	V.c		(ft/day)
Nitrate=	0.6		Plm sec=	98	0.198889	Use:	0.058
MnO2=	100		Sec Lth=	0.100408			
Fe(OH)3=	1000	1123.84	Plume Length			Time stp:	0.500
Sulfate=	20		(in ft)=	9.84		(days)	
			Water input ratio:		0.287217	Soil I.R.	0.990402

Deg Rate:	Aerobic	EA	Anaerob.	EA		Time Elapsed	
(-k in /days)		balance		balance			
B	-0.025	1.0003	-0.00167	0.8974		2.50	
T	-0.040	1.1459	-0.00521	1.0921		397.50	
E	-0.012	0.8294	-0.00343	1.0116		400.00	Days
X	-0.033	1.0847	-0.00357	1.0189		init:	0
	Contam/EA ratio					cir ref:	400.00
Cont	O	N	Mn	Fe	S		
B	0.325	0.252	0.060	0.024	0.203		
T	0.319	0.247	0.059	0.024	0.213		
E	0.315	0.244	0.058	0.024	0.221		
X	0.315	0.244	0.058	0.024	0.221		

Dynamic Degradation EXCEL Spreadsheet Model Run for T = 398 Days

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1		DYNAMIC CASE OF JP-4 DEGRADATION															
2																	
3	Initial Values at Site (mg/l)					Calc: GW/Petrl Velocity			Deg Rate:	Aerobic	EA	Anaerob.	EA			Time Elapsed	
4	Benzene	7.19952		Hyd Conductivity		V.w	BTEX: R	V.rel	(-k ln /days)		balance		balance				
5	Toluene	5.010798		(ft/day)=	19.69		1.290	0.058	B	-0.025	1.0003	-0.00167	0.8974			2.50	
6	EthylB=	0.799758		Hy Grad=	0.0043	0.256567	1.149	0.033	T	-0.040	1.1459	-0.00521	1.0921			397.50	
7	Xylenes'=	4.019166	16.98	Porosity=	0.33	ft/d	1.175	0.038	E	-0.012	0.8294	-0.00343	1.0116			400.00	Days
8	E acceptors (*81%)			organic			1.392	0.072	X	-0.033	1.0847	-0.00357	1.0189			init:	0
9	Oxygen=	3.24		content=	0.0002	V.c		(ft/day)		Contam/EA ratio						cir ref:	400.00
10	Nitrate=	0.6		Plm sec=	98	0.198889	Use:	0.058	Cont	O	N	Mn	Fe	S			
11	MnO2=	100		Sec Lth=	0.100408				B	0.325	0.252	0.060	0.024	0.203			
12	Fe(OH)3=	1000	1123.84	Plume Length			Time stp:	0.500	T	0.319	0.247	0.059	0.024	0.213			
13	Sulfate=	20		(in ft)=	9.84		(days)		E	0.315	0.244	0.058	0.024	0.221			
14				Water input ratio:		0.287217	Soil I.R.	0.990402	X	0.315	0.244	0.058	0.024	0.221			
15	Time Blk:	1	Section	1			C-First	Section	2			C	Section	3			C
16			P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
17	C(Benz):	0.000383	0.000379	0.000379	0.000379	0.000379	0.000379	0.000413	0.000413	0.000413	0.0004	0.000413	0.000738	0.000738	0.000738	0.0007	0.000738
18	C(Tol):	7.28E-07	7.14E-07	7.14E-07	7.14E-07	7.14E-07	7.14E-07	9.21E-07	9.21E-07	9.21E-07	9E-07	9.21E-07	2.19E-06	2.19E-06	2.19E-06	2E-06	2.19E-06
19	C(Ethl):	0.008103	0.008056	0.008056	0.008056	0.008056	0.008056	0.008077	0.008077	0.008077	0.0081	0.008077	0.00982	0.00982	0.00982	0.0098	0.00982
20	C(Xyl):	8.06E-06	7.92E-06	7.92E-06	7.92E-06	7.92E-06	7.92E-06	9.49E-06	9.49E-06	9.49E-06	9E-06	9.49E-06	1.99E-05	1.99E-05	1.99E-05	2E-05	1.99E-05
21	EAs remaining:		3.239606	0.6	87.013	998.67	20	3.238914	0.6	86.10356	998.63	20.00013	3.238168	0.6	85.18197	998.61	20.00349
22	Time Blk:	2	Section	1				Section	2				Section	3			
23			P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
24	C(Benz):	0.000379	0.000374	0.000374	0.000374	0.000374	0.000374	0.000408	0.000408	0.000408	0.000408	0.000408	0.000729	0.000729	0.000729	0.000729	0.000729
25	C(Tol):	7.14E-07	0.00	7E-07	7E-07	7E-07	7E-07	9.03E-07	9.03E-07	9.03E-07	9.03E-07	9.03E-07	2.15E-06	2.15E-06	2.15E-06	2.15E-06	2.15E-06
26	C(Ethl):	0.008056	0.00801	0.00801	0.00801	0.00801	0.00801	0.008031	0.008031	0.008031	0.008031	0.008031	0.009763	0.009763	0.009763	0.009763	0.009763
27	C(Xyl):	7.92E-06	7.79E-06	7.79E-06	7.79E-06	7.79E-06	7.79E-06	9.34E-06	9.34E-06	9.34E-06	9.34E-06	9.34E-06	1.96E-05	1.96E-05	1.96E-05	1.96E-05	1.96E-05
28	EAs remaining:		3.239557	0.6	86.11229	998.6281	20	3.238949	0.6	85.19082	998.6096	20	3.238174	0.6	85.55201	998.644	20.00013
29	Time Blk:	3	Section	1				Section	2				Section	3			
30			P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
31	C(Benz):	0.000374	0.00037	0.00037	0.00037	0.00037	0.00037	0.000403	0.000403	0.0004	0.0004	0.000403	0.00072	0.00072	0.000691	0.000691	0.00072
32	C(Tol):	7E-07	0.00	6.86E-07	6.86E-07	6.86E-07	6.86E-07	8.85E-07	8.85E-07	8.54E-07	8.54E-07	8.85E-07	2.1E-06	2.1E-06	1.87E-06	1.87E-06	2.1E-06
33	C(Ethl):	0.00801	0.007964	0.007964	0.007964	0.007964	0.007964	0.007984	0.007984	0.007965	0.007965	0.007984	0.009707	0.009707	0.009144	0.009144	0.009707
34	C(Xyl):	7.79E-06	7.67E-06	7.67E-06	7.67E-06	7.67E-06	7.67E-06	9.18E-06	9.18E-06	8.99E-06	8.99E-06	9.18E-06	1.93E-05	1.93E-05	1.78E-05	1.78E-05	1.93E-05
35	EAs remaining:		3.239524	0.6	85.19966	998.6097	20	3.238961	0.6	85.54815	998.6437	20.0001	3.238189	0.6	86.42971	998.6762	20.0027
36	Time Blk:	4	Section	1				Section	2			1	Section	3			1
37			P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
38	C(Benz):	0.00037	0.000365	0.000365	0.000365	0.000365	0.000365	0.000398	0.000398	0.000395	0.000395	0.000398	0.000711	0.000711	0.000683	0.000683	0.000711
39	C(Tol):	6.86E-07	0.00	6.73E-07	6.73E-07	6.73E-07	6.73E-07	8.68E-07	8.68E-07	8.37E-07	8.37E-07	8.68E-07	2.06E-06	2.06E-06	1.84E-06	1.84E-06	2.06E-06
40	C(Ethl):	0.007964	0.007918	0.007918	0.007918	0.007918	0.007918	0.007938	0.007938	0.007919	0.007919	0.007938	0.009651	0.009651	0.009091	0.009091	0.009651
41	C(Xyl):	7.67E-06	7.54E-06	7.54E-06	7.54E-06	7.54E-06	7.54E-06	9.03E-06	9.03E-06	8.84E-06	8.84E-06	9.03E-06	1.9E-05	1.9E-05	1.75E-05	1.75E-05	1.9E-05
42	EAs remaining:		3.239501	0.6	85.54481	998.6434	20	3.238961	0.6	86.42086	998.6759	20.0001	3.238205	0.6	87.21264	998.6866	20.00278
43	Time Blk:	5	Section	1				Section	2				Section	3			
44			P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
45	C(Benz):	0.000365	0.00036	0.00036	0.00036	0.00036	0.00036	0.000393	0.000393	0.00039	0.00039	0.000393	0.000702	0.000702	0.000675	0.000675	0.000702
46	C(Tol):	6.73E-07	0.00	6.6E-07	6.6E-07	6.6E-07	6.6E-07	8.51E-07	8.51E-07	8.21E-07	8.21E-07	8.51E-07	2.02E-06	2.02E-06	1.8E-06	1.8E-06	2.02E-06
47	C(Ethl):	0.007918	0.007872	0.007872	0.007872	0.007872	0.007872	0.007893	0.007893	0.007873	0.007873	0.007893	0.009595	0.009595	0.009039	0.009039	0.009595
48	C(Xyl):	7.54E-06	7.42E-06	7.42E-06	7.42E-06	7.42E-06	7.42E-06	8.89E-06	8.89E-06	8.7E-06	8.7E-06	8.89E-06	1.87E-05	1.87E-05	1.72E-05	1.72E-05	1.87E-05
49	EAs remaining:		3.239485	0.6	86.41245	998.6756	20	3.238956	0.6	87.20465	998.6865	20.00018	3.238218	0.6	86.52072	998.6539	20.00468
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Dynamic Degradation EXCEL Spreadsheet Model Run for T = 398 Days

	IB	IC	ID	IE	IF	IG	IH	II	IJ	IK	IL	IM	IN	IO	IP	IQ	IR
1																	
2																	
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14																	
15		C	Section	48			C	Section	49			C					
16	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)					
17	3.535	3.534962	3.537908	3.537908	3.534962	3.535	3.534962	3.537908	3.537908	3.534962	3.535	3.534962	3.552676	3.552676	3.549717	3.549717	3.549717
18	0.5866	0.58658	0.58811	0.58811	0.58658	0.5866	0.58658	0.58811	0.58811	0.58658	0.5866	0.58658	0.595823	0.595823	0.594272	0.594272	0.594272
19	0.2006	0.20057	0.200914	0.200914	0.20057	0.2006	0.20057	0.200914	0.200914	0.20057	0.2006	0.20057	0.202645	0.202645	0.202298	0.202298	0.202298
20	0.9123	0.91228	0.913911	0.913911	0.91228	0.9123	0.91228	0.913911	0.913911	0.91228	0.9123	0.91228	0.922111	0.922111	0.920465	0.920465	0.920465
21	999.14	22.52819	0	3.2E-16	94.08206	999.14	22.53572	0	3.24E-16	94.17552	999.19	22.54439	0	3.43E-16	94.28914	999.2212	22.57331
22			Section	48				Section	49								
23	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)					
24	3.532018	3.532018	3.534962	3.534962	3.532018	3.532018	3.532018	3.534962	3.534962	3.532018	3.532018	3.532018	3.549717	3.549717	3.546761	3.546761	3.546761
25	0.585053	0.585053	0.58658	0.58658	0.586091	0.585053	0.585053	0.58658	0.58658	0.586091	0.585053	0.585053	0.594272	0.594272	0.593777	0.592726	0.592726
26	0.200226	0.200226	0.20057	0.20057	0.200226	0.200226	0.200226	0.20057	0.20057	0.200226	0.200226	0.200226	0.202298	0.202298	0.201951	0.201951	0.201951
27	0.910651	0.910651	0.91228	0.91228	0.91152	0.910651	0.910651	0.91228	0.91228	0.91152	0.910651	0.910651	0.920465	0.920465	0.919698	0.918822	0.918822
28	999.0577	22.51893	0	3.18E-16	94.09813	999.1137	22.52819	0	3.23E-16	94.21155	999.1408	22.53572	0	3.39E-16	94.33934	999.1463	22.56406
29			Section	48				Section	49								
30	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)					
31	3.528879	3.529077	3.532018	3.532018	3.528879	3.528879	3.529077	3.532018	3.532018	3.528879	3.528879	3.529077	3.546761	3.546761	3.543609	3.543609	3.543808
32	0.583331	0.583531	0.585053	0.585053	0.583331	0.583331	0.583531	0.585053	0.585053	0.583331	0.583331	0.583531	0.592726	0.592726	0.590981	0.590981	0.591183
33	0.199781	0.199883	0.200226	0.200226	0.199781	0.199781	0.199883	0.200226	0.200226	0.199781	0.199781	0.199883	0.201951	0.201951	0.201502	0.201502	0.201605
34	0.90885	0.909026	0.910651	0.910651	0.90885	0.90885	0.909026	0.910651	0.910651	0.90885	0.90885	0.909026	0.918822	0.918822	0.917005	0.917005	0.917182
35	999.1131	22.51349	0	3.17E-16	94.09004	999.1405	22.5221	0	3.21E-16	94.21769	999.1463	22.53136	0	3.36E-16	94.34853	999.1473	22.55889
36		1	Section	48			1	Section	49			1					
37	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)					
38	3.52594	3.526138	3.529077	3.529077	3.52594	3.52594	3.526138	3.529077	3.529077	3.52594	3.52594	3.526138	3.543808	3.543808	3.540658	3.540658	3.540857
39	0.581812	0.582012	0.583531	0.583531	0.581812	0.581812	0.582012	0.583531	0.583531	0.581812	0.581812	0.582012	0.591183	0.591183	0.589443	0.589443	0.589645
40	0.199438	0.19954	0.199883	0.199883	0.199438	0.199438	0.19954	0.199883	0.199883	0.199438	0.199438	0.19954	0.201605	0.201605	0.201156	0.201156	0.201259
41	0.907228	0.907404	0.909026	0.909026	0.907228	0.907228	0.907404	0.909026	0.909026	0.907228	0.907228	0.907404	0.917182	0.917182	0.915368	0.915368	0.915545
42	999.1403	22.51029	0	3.15E-16	94.09624	999.1462	22.51666	0	3.2E-16	94.22704	999.1473	22.52527	0	3.33E-16	94.3583	999.1474	22.55576
43			Section	48				Section	49								
44	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)					
45	3.523004	3.523201	3.526138	3.526138	3.523004	3.523004	3.523201	3.526138	3.526138	3.523004	3.523004	3.523201	3.540857	3.540857	3.537709	3.537709	3.537908
46	0.580298	0.580497	0.582012	0.582012	0.580298	0.580298	0.580497	0.582012	0.582012	0.580298	0.580298	0.580497	0.589645	0.589645	0.587909	0.587909	0.58811
47	0.199096	0.199198	0.19954	0.19954	0.199096	0.199096	0.199198	0.19954	0.19954	0.199096	0.199096	0.199198	0.201259	0.201259	0.200812	0.200812	0.200914
48	0.905609	0.905784	0.907404	0.907404	0.905609	0.905609	0.905784	0.907404	0.907404	0.905609	0.905609	0.905784	0.915545	0.915545	0.913734	0.913734	0.913911
49	999.1461	22.51037	0	3.14E-16	94.10574	999.1473	22.51799	0	3.19E-16	94.237	999.1474	22.52595	0	3.31E-16	94.32943	999.2038	22.55641
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Dynamic Degradation EXCEL Spreadsheet Model Run for T = 398 Days

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1		DYNAMIC CASE OF JP-4 DEGRADATION								Initial inputs initial values only; Initial++ puts in inital and circular values See day counter below (A54							
2																	
3	Initial Values at Site:(mg/l)					Calc: GW/Petrl Velocity			Deg Rate:	Aerobic	EA	Anaerob.	EA				
4	Benzene	7.19952		Hyd Conductivity		V.w	BTEX: R	V.rel	(-k in /days)		balance		balance				
5	Toluene	5.010798		(ft/day)=	19.69		1.290	0.058	B	-0.025	1.0003	-0.00167	0.8974				
6	EthylB=	0.799758		Hy Grad=	0.0043	0.256567	1.149	0.033	T	-0.040	1.1459	-0.00521	1.0921				
7	Xylenes'=	4.019166	16.98	Porosity=	0.33	ft/d	1.175	0.038	E	-0.012	0.8294	-0.00343	1.0116				
8	E acceptors (*81%)			organic			1.392	0.072	X	-0.033	1.0847	-0.00357	1.0189				
9	Oxygen=	3.24		content=	0.0002	V.c		(ft/day)		Contam/EA ratio							
10	Nitrate=	0.6		Plm sec=	98	0.198889	Use:	0.057678	Cont	O	N	Mn	Fe	S			
11	MnO2=	100		Sec Lth=	0.100408				B	0.325	0.252	0.060	0.024	0.203			
12	Fe(OH)3=	1000	1123.84	Plume Length			Time stp:	0.500	T	0.319	0.247	0.059	0.024	0.213			
13	Sulfate=	20		(in ft)=	9.84		(days)		E	0.315	0.244	0.058	0.024	0.221			
14				Water input ratio:		0.287217			X	0.315	0.244	0.058	0.024	0.221			
15				49				Section	50			C	Section	51			C
16		C						P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
17		3.537908	3.537908	3.537908	3.534962	3.534962	3.534962	3.537908	3.537908	3.534962	3.535	3.534962	3.537907855	3.537908	3.534962	3.535	3.534962
18		0.58811	0.58811	0.58811	0.58658	0.58658	0.58658	0.58811	0.58811	0.58658	0.5866	0.58658	0.588110204	0.58811	0.58658	0.5866	0.58658
19		0.200914	0.200914	0.200914	0.20057	0.20057	0.20057	0.200914	0.200914	0.20057	0.2006	0.20057	0.200914007	0.200914	0.20057	0.2006	0.20057
20		0.913911	0.913911	0.913911	0.91228	0.91228	0.91228	0.913911	0.913911	0.91228	0.9123	0.91228	0.913910904	0.913911	0.91228	0.9123	0.91228
21			0	3.24E-16	94.17552	999.1943	22.54439	0	3.29E-16	94.33287	999.23	22.55373	0	3.39E-16	94.46028	999.24	22.56143
22				49				Section	50				Section	51			
23	I	C						P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
24	7.19952	3.537908	3.534962	3.534962	3.532018	3.532018	3.532018	3.534962	3.534962	3.532018	3.532018	3.532018	3.534961618	3.534962	3.532018	3.532018	3.532018
25	5.010798	0.58811	0.58658	0.58658	0.586091	0.585053	0.585053	0.58658	0.58658	0.586091	0.585053	0.585053	0.586579692	0.58658	0.586091	0.585053	0.585053
26	0.799758	0.200914	0.20057	0.20057	0.200226	0.200226	0.200226	0.20057	0.20057	0.200226	0.200226	0.200226	0.200569592	0.20057	0.200226	0.200226	0.200226
27	4.019166	0.913911	0.91228	0.91228	0.91152	0.910651	0.910651	0.91228	0.91228	0.91152	0.910651	0.910651	0.912279695	0.91228	0.91152	0.910651	0.910651
28			0	3.23E-16	94.21155	999.1408	22.53572	0	3.28E-16	94.38256	999.1558	22.54439	0	3.36E-16	94.51333	999.1568	22.55373
29				49				Section	50				Section	51			
30								P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
31			3.532018	3.528879	3.528879	3.528879	3.529077	3.532018	3.532018	3.528879	3.528879	3.529077	3.532017834	3.532018	3.528879	3.528879	3.529077
32			0.585053	0.585053	0.583331	0.583331	0.583531	0.585053	0.585053	0.583331	0.583331	0.583531	0.585053163	0.585053	0.583331	0.583331	0.583531
33			0.200226	0.200226	0.199781	0.199781	0.199883	0.200226	0.200226	0.199781	0.199781	0.199883	0.200225768	0.200226	0.199781	0.199781	0.199883
34			0.910651	0.910651	0.90885	0.90885	0.909026	0.910651	0.910651	0.90885	0.90885	0.909026	0.910651397	0.910651	0.90885	0.90885	0.909026
35			0	3.21E-16	94.21769	999.1463	22.53136	0	3.26E-16	94.39166	999.1568	22.53889	0	3.34E-16	94.52283	999.1569	22.54756
36				49				Section	50			1	Section	51			1
37								P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
38			3.529077	3.529077	3.52594	3.52594	3.526138	3.529077	3.529077	3.52594	3.52594	3.526138	3.529076501	3.529077	3.52594	3.52594	3.526138
39			0.583531	0.583531	0.581812	0.581812	0.582012	0.583531	0.583531	0.581812	0.581812	0.582012	0.583530606	0.583531	0.581812	0.581812	0.582012
40			0.199883	0.199883	0.199438	0.199438	0.19954	0.199883	0.199883	0.199438	0.199438	0.19954	0.199882533	0.199883	0.199438	0.199438	0.19954
41			0.909026	0.909026	0.907228	0.907228	0.907404	0.909026	0.909026	0.907228	0.907228	0.907404	0.909026005	0.909026	0.907228	0.907228	0.907404
42			0	3.2E-16	94.22704	999.1473	22.52527	0	3.25E-16	94.40134	999.1569	22.53452	0	3.32E-16	94.4937	999.2132	22.54205
43				49				Section	50				Section	51			
44								P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
45			3.526138	3.526138	3.523004	3.523004	3.523201	3.526138	3.526138	3.523004	3.523004	3.523201	3.526137618	3.526138	3.523004	3.523004	3.523201
46			0.582012	0.582012	0.580298	0.580298	0.580497	0.582012	0.582012	0.580298	0.580298	0.580497	0.582012012	0.582012	0.580298	0.580298	0.580497
47			0.19954	0.19954	0.199096	0.199096	0.199198	0.19954	0.19954	0.199096	0.199096	0.199198	0.199539886	0.19954	0.199096	0.199096	0.199198
48			0.907404	0.907404	0.905609	0.905609	0.905784	0.907404	0.907404	0.905609	0.905609	0.905784	0.907403514	0.907404	0.905609	0.905609	0.905784
49			0	3.19E-16	94.237	999.1474	22.52595	0	3.24E-16	94.37277	999.2127	22.53503	0	3.3E-16	94.48571	999.2386	22.54305
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Dynamic Degradation EXCEL Spreadsheet Model Run for T = 398 Days

	IB	IC	ID	IE	IF	IG	IH	II	IJ	IK	IL	IM	IN	IO	IP	IQ	IR
1																	
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12																	
13																	
14																	
15		C	Section	96			C	Section	97			C	Section	98			C-Last
16	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
17	3.535	3.534962	3.537908	3.537908	3.534962	3.535	3.534962	3.537908	3.537908	3.534962	3.535	3.534962	3.537908	3.537908	3.534962	3.535	3.534962
18	0.5866	0.58658	0.58811	0.58811	0.58658	0.5866	0.58658	0.58811	0.58811	0.58658	0.5866	0.58658	0.58811	0.58811	0.58658	0.5866	0.58658
19	0.2006	0.20057	0.200914	0.200914	0.20057	0.2006	0.20057	0.200914	0.200914	0.20057	0.2006	0.20057	0.200914	0.200914	0.20057	0.2006	0.20057
20	0.9123	0.91228	0.913911	0.913911	0.91228	0.9123	0.91228	0.913911	0.913911	0.91228	0.9123	0.91228	0.913911	0.913911	0.91228	0.9123	0.91228
21	1000	22.94751	0	1.16E-15	99.64504	1000	22.95685	0	1.17E-15	99.76739	1000	22.96611	0	4.33E-16	99.88956	1000	22.97065
22			Section	96				Section	97				Section	98			
23	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
24	3.532018	3.532018	3.534962	3.534962	3.532018	3.532018	3.532018	3.534962	3.534962	3.532018	3.532018	3.532018	3.534962	3.534962	3.53182	3.53182	3.532018
25	0.585053	0.585053	0.58658	0.58658	0.586091	0.585053	0.585053	0.58658	0.58658	0.586091	0.585053	0.585053	0.58658	0.58658	0.584853	0.584853	0.585053
26	0.200226	0.200226	0.20057	0.20057	0.200226	0.200226	0.200226	0.20057	0.20057	0.200226	0.200226	0.200226	0.20057	0.20057	0.200124	0.200124	0.200226
27	0.910651	0.910651	0.91228	0.91228	0.91152	0.910651	0.910651	0.91228	0.91228	0.91152	0.910651	0.910651	0.91228	0.91228	0.910475	0.910475	0.910651
28	999.9199	22.93809	0	1.16E-15	99.68972	999.9199	22.94751	0	1.17E-15	99.81189	999.9199	22.95685	0	1.9E-16	99.87833	1000	22.96928
29			Section	96				Section	97				Section	98			
30	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
31	3.528879	3.529077	3.532018	3.532018	3.528879	3.528879	3.529077	3.532018	3.532018	3.528879	3.528879	3.529077	3.532018	3.532018	3.528879	3.528879	3.529077
32	0.583331	0.583531	0.585053	0.585053	0.583331	0.583331	0.583531	0.585053	0.585053	0.583331	0.583331	0.583531	0.585053	0.585053	0.583331	0.583331	0.583531
33	0.199781	0.199883	0.200226	0.200226	0.199781	0.199781	0.199883	0.200226	0.200226	0.199781	0.199781	0.199883	0.200226	0.200226	0.199781	0.199781	0.199883
34	0.90885	0.909026	0.910651	0.910651	0.90885	0.90885	0.909026	0.910651	0.910651	0.90885	0.90885	0.909026	0.910651	0.910651	0.90885	0.90885	0.909026
35	999.9199	22.93179	0	1.16E-15	99.69029	999.9199	22.94126	0	1.16E-15	99.75727	999.9992	22.95068	0	1.59E-17	99.87841	1000	22.96002
36		1	Section	96			1	Section	97			1	Section	98			
37	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
38	3.52594	3.526138	3.529077	3.529077	3.52594	3.52594	3.526138	3.529077	3.529077	3.52594	3.52594	3.526138	3.529077	3.529077	3.52594	3.52594	3.526138
39	0.581812	0.582012	0.583531	0.583531	0.581812	0.581812	0.582012	0.583531	0.583531	0.581812	0.581812	0.582012	0.583531	0.583531	0.581812	0.581812	0.582012
40	0.199438	0.19954	0.199883	0.199883	0.199438	0.199438	0.19954	0.199883	0.199883	0.199438	0.199438	0.19954	0.199883	0.199883	0.199438	0.199438	0.19954
41	0.907228	0.907404	0.909026	0.909026	0.907228	0.907228	0.907404	0.909026	0.909026	0.907228	0.907228	0.907404	0.909026	0.909026	0.907228	0.907228	0.907404
42	999.9199	22.92545	0	1.15E-15	99.6364	999.9985	22.93495	0	1.16E-15	99.75702	1000	22.94443	0	3.46E-16	99.8786	1000	22.95384
43			Section	96				Section	97				Section	98			
44	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
45	3.523004	3.523201	3.526138	3.526138	3.523004	3.523004	3.523201	3.526138	3.526138	3.523004	3.523004	3.523201	3.526138	3.526138	3.523004	3.523004	3.523201
46	0.580298	0.580497	0.582012	0.582012	0.580298	0.580298	0.580497	0.582012	0.582012	0.580298	0.580298	0.580497	0.582012	0.582012	0.580298	0.580298	0.580497
47	0.199096	0.199198	0.19954	0.19954	0.199096	0.199096	0.199198	0.19954	0.19954	0.199096	0.199096	0.199198	0.19954	0.19954	0.199096	0.199096	0.199198
48	0.905609	0.905784	0.907404	0.907404	0.905609	0.905609	0.905784	0.907404	0.907404	0.905609	0.905609	0.905784	0.907404	0.907404	0.905609	0.905609	0.905784
49	999.9977	22.92589	0	1.15E-15	99.63582	1000	22.93538	0	1.16E-15	99.75739	1000	22.94486	0	1.26E-16	99.87879	1000	22.94759
50																	

Dynamic Degradation EXCEL Spreadsheet Model Run for T = 398 Days

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1		DYNAMIC CASE OF JP-4 DEGRADATION								Initial inputs initial values only; Initial++ puts in inital and circular values						See day counter belov	
2																	
3	Initial Values at Site:(mg/l)					Calc: GW/Petrl Velocity			Deg Rate:	Aerobic	EA	Anaerob	EA				
4	Benzene	7.19952		Hyd Conductivity		V.w	BTEX: R	V.rel	(-k in /days)		balance		balance				
5	Toluene	5.010798		(ft/day)=	19.69		1.290	0.058	B	-0.025	1.0003	-0.00167	0.8974				
6	EthylB=	0.799758		Hy Grad=	0.0043	0.256567	1.149	0.033	T	-0.040	1.1459	-0.00521	1.0921				
7	Xylenes'=	4.019166	16.98	Porosity=	0.33	ft/d	1.175	0.038	E	-0.012	0.8294	-0.00343	1.0116				
8	E acceptors (*81%)			organic			1.392	0.072	X	-0.033	1.0847	-0.00357	1.0189				
9	Oxygen=	3.24		content=	0.0002	V.c		(ft/day)		Contam/EA ratio							
10	Nitrate=	0.6		Plm sec=	98	0.198889	Use:	0.057678	Cont	O	N	Mn	Fe	S			
11	MnO2=	100		Sec Lth=	0.100408				B	0.325	0.252	0.060	0.024	0.203			
12	Fe(OH)3=	1000	1123.84	Plume Length			Time stp:	0.500	T	0.319	0.247	0.059	0.024	0.213		INITIAL VALUE	
13	Sulfate=	20		(in ft)=	9.84		(days)		E	0.315	0.244	0.058	0.024	0.221			
14				Water input ratio:		0.287217			X	0.315	0.244	0.058	0.024	0.221			
15	Time Blk:	1	Section	1			I-First	Section	2			I	Section	3		I	
16			P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
17	C(Benz):	7.19952	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956	7.110956
18	C(Tol):	5.010798	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539	4.912539
19	C(Ethl):	0.799758	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152	0.795152
20	C(Xyl):	4.019166	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338	3.95338
21	EAs remaining:		2.436774	0.6	100	1000	20	2.436774	0.6	100	1000	20	2.436774	0.6	100	1000	20
22																	
23																	
24																	
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34																	

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1		DYNAMIC CASE OF JP-4 DEGRADATION								Initial Inputs Initial values only; Initial++ puts in inital and circular values						See day counter below	
2																	
3	Initial Values at Site:(mg/l)					Calc: GW/Petrl Velocity			Deg Rate:	Aerobic	EA	Anaerob.	EA				
4	Benzene	7.19952		Hyd Conductivity		V.w	BTEX: R	V.rel	(-k in /days)		balance		balance				
5	Toluene	5.010798		(ft/day)=	19.69		1.290	0.058	B	-0.025	1.0003	-0.00167	0.8974				
6	EthylB=	0.799758		Hy Grad=	0.0043	0.256567	1.149	0.033	T	-0.040	1.1459	-0.00521	1.0921				
7	Xylenes'=	4.019166	16.98	Porosity=	0.33	ft/d	1.175	0.038	E	-0.012	0.8294	-0.00343	1.0116				
8	E acceptors (*81%)			organic			1.392	0.072	X	-0.033	1.0847	-0.00357	1.0189				
9	Oxygen=	3.24		content=	0.0002	V.c		(ft/day)		Contam/EA ratio							
10	Nitrate=	0.6		Plm sec=	98	0.198889	Use:	0.057678	Cont	O	N	Mn	Fe	S			
11	MnO2=	100		Sec Lth=	0.100408				B	0.325	0.252	0.060	0.024	0.203			
12	Fe(OH)3=	1000	1123.84	Plume Length			Time stp:	0.500	T	0.319	0.247	0.059	0.024	0.213		CIRCULAR REF	
13	Sulfate=	20		(in ft)=	9.84		(days)		E	0.315	0.244	0.058	0.024	0.221			
14				Water Input ratio:		0.287217			X	0.315	0.244	0.058	0.024	0.221			
15	Time Blk:	1	Section	1			C-First	Section	2			C	Section	3			C
16			P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
17	C(Benz):	6.600911	6.519711	6.519711	6.519711	6.519711	6.519711	6.823213	6.823213	6.823213	6.8232	6.823213	6.823213	6.823213	6.823213	6.8232	6.823213
18	C(Tol):	4.469982	4.382329	4.382329	4.382329	4.382329	4.382329	4.639954	4.639954	4.639954	4.64	4.639954	4.639954	4.639954	4.639954	4.64	4.639954
19	C(Ethl):	0.758403	0.754035	0.754035	0.754035	0.754035	0.754035	0.778872	0.778872	0.778872	0.7789	0.778872	0.778872	0.778872	0.778872	0.7789	0.778872
20	C(Xyl):	3.617539	3.558327	3.558327	3.558327	3.558327	3.558327	3.74592	3.74592	3.74592	3.7459	3.74592	3.74592	3.74592	3.74592	3.7459	3.74592
21	EAs remaining:		0.673193	0.17233	0	0	5.744332	0	0	0	0	0	0	0	0	0	0
22																	
23																	
24																	
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35																	
36																	
37																	
38																	
39																	
40																	
41	Corner is at A43																
42																	
43	Time Blk:	5	Section	1				Section	2				Section	3			
44			P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
45	C(Benz):	6.657413	6.600911	6.600911	6.600911	7	6.600911	6.823213	6.823213	6.823213	6.823213	6.823213	6.823213	6.823213	6.823213	6.823213	6.823213
46	C(Tol):	4.513111	4.469982	4.469982	4.469982	4.469982	4.469982	4.639954	4.639954	4.639954	4.639954	4.639954	4.639954	4.639954	4.639954	4.639954	4.639954
47	C(Ethl):	0.763619	0.758403	0.758403	0.758403	0.758403	0.758403	0.778872	0.778872	0.778872	0.778872	0.778872	0.778872	0.778872	0.778872	0.778872	0.778872
48	C(Xyl):	3.650146	3.617539	3.617539	3.617539	3.617539	3.617539	3.74592	3.74592	3.74592	3.74592	3.74592	3.74592	3.74592	3.74592	3.74592	3.74592
49	EAs remaining:		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50																	

H. Algorithm Display for Dynamic Degradation Simulation Model:

Contaminant (benzene) degradation in **section 1, time block 1 (first section): Circular References** for using Excel's Iterative Calculation Feature under: Tools/ Options/ Calculation/ Iteration.

The circular references, placed in all plume sections of time block 1, use as their input values the plume sections in time block 5 (thus time block one effectively becomes time block 6, and so on). Because time block 5 uses as its input values from time block 4, and so on, this constitutes a circular formula reference in the spreadsheet (requiring use of the iterative function), allowing a potentially endless running of the model forward in time, without undue memory requirements.

The terms MOD_1! and MOD_2! refer to the sequential spreadsheet worksheets containing the model, and they are followed by the spreadsheet cell reference.

MOD_1!A17: C(Benz):

MOD_1!B17: =G45

MOD_1!C17: =IF((B17-B17*EXP($H$12*$J$5))/$J$11>($B$9*$F$14+(1-$F$14)*C49)*B17*$K$5/SUM($B17:$B20),B17-$J$11*($B$9*$F$14+(1-$F$14)*C49)*B17*$K$5/SUM($B17:$B20),B17*EXP($H$12*$J$5))

MOD_1!D17: =IF((C17-C17*EXP(($H$12-(LN(C17/B17)/$J$5))*$L$5))/$K$11>($B$10*$F$14+(1-$F$14)*D49)*C17*$M$5/SUM(C17:C20),C17-$K$11*($B$10*$F$14+(1-$F$14)*D49)*C17*$M$5/SUM(C17:C20),C17*EXP(($H$12-(LN(C17/B17)/$J$5))*$L$5))

MOD_1!E17: =IF((D17-D17*EXP(($H$12-(LN(C17/B17)/$J$5)-(LN(D17/C17)/$L$5))*$L$5))/$L$11>($F$10*$F$14*J49/$H$10+(1-$F$10*$F$14/$H$10)*E49)*D17*$M$5/SUM(D17:D20),D17-$L$11*($F$10*$F$14*J49/$H$10+(1-$F$10*$F$14/$H$10)*E49)*D17*$M$5/SUM(D17:D20),D17*EXP(($H$12-(LN(C17/B17)/$J$5)-(LN(D17/C17)/$L$5))*$L$5))

MOD_1!F17: =IF((E17-E17*EXP(($H$12-(LN(C17/B17)/$J$5)-(LN(E17/C17)/$L$5))*$L$5))/$M$11>($F$10*$F$14*K49/$H$10+(1-$F$10*$F$14/$H$10)*F49)*E17*$M$5/SUM(E17:E20),E17-$M$11*($F$10*$F$14*K49/$H$10+(1-$F$10*$F$14/$H$10)*F49)*E17*$M$5/SUM(E17:E20),E17*EXP(($H$12-(LN(C17/B17)/$J$5)-(LN(E17/C17)/$L$5))*$L$5))

MOD_1!G17: =IF((F17-F17*EXP(($H$12-(LN(C17/B17)/$J$5)-(LN(F17/C17)/$L$5))*$L$5))/$N$11>($B$13*$F$14+(1-$F$14)*G49)*F17*$M$5/SUM(F17:F20),F17-$N$11*($B$13*$F$14+(1-$F$14)*G49)*F17*$M$5/SUM(F17:F20),F17*EXP(($H$12-(LN(C17/B17)/$J$5)-(LN(F17/C17)/$L$5))*$L$5))

I. Algorithm Display for Dynamic Degradation Simulation Model:

Contaminant (benzene) degradation in **section 2 (middle section(s)), time block 1: Circular References** for using Excel's Iterative Calculation Feature under: Tools/Options/Calculation/Iteration.

MOD_1!H17: =IF((L45-L45*EXP($H$12*$J$5))/$J$11>(C49*$F$14+(1-$F$14)*H49)*L45*$K$5/SUM(L45:L48),L45-$J$11*(C49*$F$14+(1-$F$14)*H49)*L45*$K$5/SUM(L45:L48),L45*EXP($H$12*$J$5))

MOD_1!I17: =IF((H17-H17*EXP(($H$12-(LN(H17/L45)/$J$5))*$L$5))/$K$11>(D49*$F$14+(1-$F$14)*I49)*H17*$M$5/SUM(H17:H20),H17-$K$11*(D49*$F$14+(1-$F$14)*I49)*H17*$M$5/SUM(H17:H20),H17*EXP(($H$12-(LN(H17/L45)/$J$5))*$L$5))

MOD_1!J17: =IF((I17-I17*EXP(($H$12-(LN(H17/L45)/$J$5)-(LN(I17/H17)/$L$5))*$L$5))/$L$11>($F$10*$F$14*O49/$H$10+(1-$F$10*$F$14/$H$10)*J49)*I17*$M$5/SUM(I17:I20),I17-$L$11*($F$10*$F$14*O49/$H$10+(1-$F$10*$F$14/$H$10)*J49)*I17*$M$5/SUM(I17:I20),I17*EXP(($H$12-(LN(H17/L45)/$J$5)-(LN(I17/H17)/$L$5))*$L$5))

MOD_1!K17: =IF((J17-J17*EXP(($H$12-(LN(H17/L45)/$J$5)-(LN(J17/H17)/$L$5))*$L$5))/$M$11>($F$10*$F$14*P49/$H$10+(1-$F$10*$F$14/$H$10)*K49)*J17*$M$5/SUM(J17:J20),J17-$M$11*($F$10*$F$14*P49/$H$10+(1-$F$10*$F$14/$H$10)*K49)*J17*$M$5/SUM(J17:J20),J17*EXP(($H$12-(LN(H17/L45)/$J$5)-(LN(J17/H17)/$L$5))*$L$5))

MOD_1!L17: =IF((K17-K17*EXP(($H$12-(LN(H17/L45)/$J$5)-(LN(K17/H17)/$L$5))*$L$5))/$N$11>(G49*$F$14+(1-$F$14)*L49)*K17*$M$5/SUM(K17:K20),K17-$N$11*(G49*$F$14+(1-$F$14)*L49)*K17*$M$5/SUM(K17:K20),K17*EXP(($H$12-(LN(H17/L45)/$J$5)-(LN(K17/H17)/$L$5))*$L$5))

J. Algorithm Display for Dynamic Degradation Simulation Model:

Contaminant (benzene) degradation in **section 98 (last section), time block 1: Circular References** for using Excel's Iterative Calculation Feature under:Tools/Options/Calculation/Iteration.

MOD_2!IN17: =IF((IR45-IR45*EXP($H$12*$J$5))/$J$11>(II49*$F$14+(1-$F$14)*IN49)*IR45*$K$5/SUM(IR$45:IR$48),IR45-$J$11*(II49*$F$14+(1-$F$14)*IN49)*IR45*$K$5/SUM(IR$45:IR$48),IR45*EXP($H$12*$J$5))

MOD_2!IO17: =IF((IN17-IN17*EXP(($H$12-(LN(IN17/IR45)/$J$5))*$L$5))/$K$11>(IJ$49*$F$14+(1-$F$14)*IO$49)*IN17*$M$5/SUM(IN$17:IN$20),IN17-$K$11*(IJ$49*$F$14+(1-$F$14)*IO$49)*IN17*$M$5/SUM(IN$17:IN$20),IN17*EXP(($H$12-(LN(IN17/IR45)/$J$5))*$L$5))

MOD_2!IP17: =IF((IO17-IO17*EXP(($H$12-(LN(IN17/IR45)/$J$5)-(LN(IO17/IN17)/$L$5))*$L$5))/$L$11>($F$10*$F$14*$B$11/$H$10+(1-$F$10*$F$14/$H$10)*IP49)*IO17*$M$5/SUM(IO$17:IO$20),IO17-

$L$11*($F$10*$F$14*$B$11/$H$10+(1-
$F$10*$F$14/$H$10)*IP49)*IO17*$M$5/SUM(IO$17:IO$20),IO17*EXP(($H$12-
(LN(IN17/IR45)/$J$5)-(LN(IO17/IN17)/$L$5))*$L$5))

MOD_2!IQ17: =IF((IP17-IP17*EXP(($H$12-(LN(IN17/IR45)/$J$5)-
(LN(IP17/IN17)/$L$5))*$L$5))/$M$11>($F$10*$F$14*$B$12/$H$10+(1-
$F$10*$F$14/$H$10)*IQ49)*IP17*$M$5/SUM(IP$17:IP$20),IP17-
$M$11*($F$10*$F$14*$B$12/$H$10+(1-
$F$10*$F$14/$H$10)*IQ49)*IP17*$M$5/SUM(IP$17:IP$20),IP17*EXP(($H$12-
(LN(IN17/IR$45)/$J$5)-(LN(IP17/IN17)/$L$5))*$L$5))

MOD_2!IR17: =IF((IQ17-IQ17*EXP(($H$12-(LN(IN17/IR45)/$J$5)-
(LN(IQ17/IN17)/$L$5))*$L$5))/$N$11>(IM49*$F$14+(1-
$F$14)*IR49)*IQ17*$M$5/SUM(IQ$17:IQ$20),IQ17-$N$11*(IM49*$F$14+(1-
$F$14)*IR49)*IQ17*$M$5/SUM(IQ$17:IQ$20),IQ17*EXP(($H$12-(LN(IN17/IR45)/$J$5)-
(LN(IQ17/IN17)/$L$5))*$L$5))

K. Algorithm Display for Dynamic Degradation Simulation Model:

Contaminant (benzene) degradation in **section 1, time block 1 (first section): Initialization References** to set initial values – which rely on parameter input block values – throughout spreadsheet model, causing proper initial values to be calculated and displayed in plume sections in time blocks 2 through 4, in preparation for using circular (iterative) references – which rely on time block 5 values – for input into each subsequent time step or plume section for calculation.

MOD_1!A17: C(Benz):

MOD_1!B17: =B4

MOD_1!C17: =IF((B17-B17*EXP($H$12*$J$5))/$J$11>$B$9*B17*$K$5/SUM($B17:$B20),B17-
$J$11*$B$9*B17*$K$5/SUM($B17:$B20),B17*EXP($H$12*$J$5))

MOD_1!D17: =IF((C17-C17*EXP(($H$12-
(LN(C17/B17)/$J$5))*$L$5))/$K$11>$B$10*C17*$M$5/SUM(C17:C20),C17-
$K$11*$B$10*C17*$M$5/SUM(C17:C20),C17*EXP(($H$12-(LN(C17/B17)/$J$5))*$L$5))

MOD_1!E17: =IF((D17-D17*EXP(($H$12-(LN(C17/B17)/$J$5)-
(LN(D17/C17)/$L$5))*$L$5))/$L$11>$B$11*D17*$M$5/SUM(D17:D20),D17-
$L$11*$B$11*D17*$M$5/SUM(D17:D20),D17*EXP(($H$12-(LN(C17/B17)/$J$5)-
(LN(D17/C17)/$L$5))*$L$5))

MOD_1!F17: =IF((E17-E17*EXP(($H$12-(LN(C17/B17)/$J$5)-
(LN(E17/C17)/$L$5))*$L$5))/$M$11>$B$12*E17*$M$5/SUM(E17:E20),E17-
$M$11*$B$12*E17*$M$5/SUM(E17:E20),E17*EXP(($H$12-(LN(C17/B17)/$J$5)-
(LN(E17/C17)/$L$5))*$L$5))

MOD_1!G17: =IF((F17-F17*EXP(($H$12-(LN(C17/B17)/$J$5)-
(LN(F17/C17)/$L$5))*$L$5))/$N$11>$B$13*F17*$M$5/SUM(F17:F20),F17-

$N$11*$B$13*F17*$M$5/SUM(F17:F20),F17*EXP(($H$12-(LN(C17/B17)/$J$5)-(LN(F17/C17)/$L$5))*$L$5))

L. Algorithm Display for Dynamic Degradation Simulation Model:

Contaminant (benzene) degradation in **section 2, time block 1 (middle section): Initialization References** to set initial values – which rely on parameter input block values – throughout spreadsheet model, in preparation for using circular (iterative) references – which rely on time block 5 values – for input into each subsequent time step or plume section for calculation.

MOD_1!H17: =IF(($B17-$B17*EXP($H$12*$J$5))/$J$11>$B$9*$B17*$K$5/SUM($B$4:$B$7),$B17-$J$11*$B$9*$B17*$K$5/SUM($B$4:$B$7),$B17*EXP($H$12*$J$5))

MOD_1!I17: =IF((H17-H17*EXP(($H$12-(LN(H17/$B17)/$J$5))*$L$5))/$K$11>$B$10*H17*$M$5/SUM(H17:H20),H17-$K$11*$B$10*H17*$M$5/SUM(H17:H20),H17*EXP(($H$12-(LN(H17/$B17)/$J$5))*$L$5))

MOD_1!J17: =IF((I17-I17*EXP(($H$12-(LN(H17/$B17)/$J$5)-(LN(I17/H17)/$L$5))*$L$5))/$L$11>$B$11*I17*$M$5/SUM(I17:I20),I17-$L$11*$B$11*I17*$M$5/SUM(I17:I20),I17*EXP(($H$12-(LN(H17/$B17)/$J$5)-(LN(I17/H17)/$L$5))*$L$5))

MOD_1!K17: =IF((J17-J17*EXP(($H$12-(LN(H17/$B17)/$J$5)-(LN(J17/H17)/$L$5))*$L$5))/$M$11>$B$12*J17*$M$5/SUM(J17:J20),J17-$M$11*$B$12*J17*$M$5/SUM(J17:J20),J17*EXP(($H$12-(LN(H17/$B17)/$J$5)-(LN(J17/H17)/$L$5))*$L$5))

MOD_1!L17: =IF((K17-K17*EXP(($H$12-(LN(H17/$B17)/$J$5)-(LN(K17/H17)/$L$5))*$L$5))/$N$11>$B$13*K17*$M$5/SUM(K17:K20),K17-$N$11*$B$13*K17*$M$5/SUM(K17:K20),K17*EXP(($H$12-(LN(H17/$B17)/$J$5)-(LN(K17/H17)/$L$5))*$L$5))

M. Algorithm Display for Dynamic Degradation Simulation Model:

Contaminant (benzene) degradation in **section 98, time block 1 (end section): Initialization References** to set initial values – which rely on parameter input block values – throughout spreadsheet model, in preparation for using circular (iterative) references – which rely on time block 5 values – for input into each subsequent time step or plume section for calculation.

MOD_2!IN17: =IF(($B17-$B17*EXP($H$12*$J$5))/$J$11>$B$9*$B17*$K$5/SUM($B$4:$B$7),$B17-$J$11*$B$9*$B17*$K$5/SUM($B$4:$B$7),$B17*EXP($H$12*$J$5))

MOD_2!IO17: =IF((IN17-IN17*EXP(($H$12-(LN(IN17/$B17)/$J$5))*$L$5))/$K$11>$B$10*IN17*$M$5/SUM(IN17:IN20),IN17-$K$11*$B$10*IN17*$M$5/SUM(IN17:IN20),IN17*EXP(($H$12-(LN(IN17/$B17)/$J$5))*$L$5))

MOD_2!IP17: =IF((IO17-IO17*EXP(($H$12-(LN(IN17/$B17)/$J$5)-(LN(IO17/IN17)/$L$5))*$L$5))/$L$11>$B$11*IO17*$M$5/SUM(IO17:IO20),IO17-$L$11*$B$11*IO17*$M$5/SUM(IO17:IO20),IO17*EXP(($H$12-(LN(IN17/$B17)/$J$5)-(LN(IO17/IN17)/$L$5))*$L$5))

MOD_2!IQ17: =IF((IP17-IP17*EXP(($H$12-(LN(IN17/$B17)/$J$5)-(LN(IP17/IN17)/$L$5))*$L$5))/$M$11>$B$12*IP17*$M$5/SUM(IP17:IP20),IP17-$M$11*$B$12*IP17*$M$5/SUM(IP17:IP20),IP17*EXP(($H$12-(LN(IN17/$B17)/$J$5)-(LN(IP17/IN17)/$L$5))*$L$5))

MOD_2!IQ17: =IF((IQ17-IQ17*EXP(($H$12-(LN(IN17/$B17)/$J$5)-(LN(IQ17/IN17)/$L$5))*$L$5))/$N$11>$B$13*IQ17*$M$5/SUM(IQ17:IQ20),IQ17-$N$11*$B$13*IQ17*$M$5/SUM(IQ17:IQ20),IQ17*EXP(($H$12-(LN(IN17/$B17)/$J$5)-(LN(IQ17/IN17)/$L$5))*$L$5))

N. Algorithm Display for Dynamic Degradation Simulation Model:

Subsequent Time Steps: Section 1 (first section), time block 2. Plume section's formulas in time steps after the first time step are not affected by model initialization or circular reference setups. They are different from first time step formulas in that they reference plume sections in previous time steps.

MOD_1!A24: C(Benz):

MOD_1!B24: =G17

MOD_1!C24: =IF((B24-B24*EXP($H$12*$J$5))/$J$11>($B$9*$F$14+(1-$F$14)*C21)*B24*$K$5/SUM(B24:B27),B24-$J$11*($B$9*$F$14+(1-$F$14)*C21)*B24*$K$5/SUM(B24:B27),B24*EXP($H$12*$J$5))

MOD_1!D24: =IF((C24-C24*EXP(($H$12-(LN(C24/B24)/$J$5))*$L$5))/$K$11>($B$10*$F$14+(1-$F$14)*D21)*C24*$M$5/SUM(C24:C27),C24-$K$11*($B$10*$F$14+(1-$F$14)*D21)*C24*$M$5/SUM(C24:C27),C24*EXP(($H$12-(LN(C24/B24)/$J$5))*$L$5))

MOD_1!E24: =IF((D24-D24*EXP(($H$12-(LN(C24/B24)/$J$5)-(LN(D24/C24)/$L$5))*$L$5))/$L$11>($F$10*$F$14*J21/$H$10+(1-$F$10*$F$14/$H$10)*E21)*D24*$M$5/SUM(D24:D27),D24-$L$11*($F$10*$F$14*J21/$H$10+(1-$F$10*$F$14/$H$10)*E21)*D24*$M$5/SUM(D24:D27),D24*EXP(($H$12-(LN(C24/B24)/$J$5)-(LN(D24/C24)/$L$5))*$L$5))

MOD_1!F24: =IF((E24-E24*EXP(($H$12-(LN(C24/B24)/$J$5)-(LN(E24/C24)/$L$5))*$L$5))/$M$11>($F$10*$F$14*K21/$H$10+(1-$F$10*$F$14/$H$10)*F21)*E24*$M$5/SUM(E24:E27),E24-$M$11*($F$10*$F$14*K21/$H$10+(1-$F$10*$F$14/$H$10)*F21)*E24*$M$5/SUM(E24:E27),E24*EXP(($H$12-(LN(C24/B24)/$J$5)-(LN(E24/C24)/$L$5))*$L$5))

MOD_1!G24: =IF((F24-F24*EXP(($H$12-(LN(C24/B24)/$J$5)-(LN(F24/C24)/$L$5))*$L$5))/$N$11>($B$13*$F$14+(1-$F$14)*G21)*F24*$M$5/SUM(F24:F27),F24-$N$11*($B$13*$F$14+(1-$F$14)*G21)*F24*$M$5/SUM(F24:F27),F24*EXP(($H$12-(LN(C24/B24)/$J$5)-(LN(F24/C24)/$L$5))*$L$5))

O. Algorithm Display for Dynamic Degradation Simulation Model:

Subsequent Time Steps: Section 2 (middle section(s)), time block 2. Plume section's formulas in time steps after the first time step are not affected by model initialization or circular reference setups. They are different from first time step formulas in that they reference plume sections in previous time steps.

MOD_1!H24: =IF((L17-L17*EXP($H$12*$J$5))/$J$11>(C21*$F$14+(1-$F$14)*H21)*L17*$K$5/SUM(L17:L20),L17-$J$11*(C21*$F$14+(1-$F$14)*H21)*L17*$K$5/SUM(L17:L20),L17*EXP($H$12*$J$5))

MOD_1!I24: =IF((H24-H24*EXP(($H$12-(LN(H24/L17)/$J$5))*$L$5))/$K$11>(D21*$F$14+(1-$F$14)*I21)*H24*$M$5/SUM(H24:H27),H24-$K$11*(D21*$F$14+(1-$F$14)*I21)*H24*$M$5/SUM(H24:H27),H24*EXP(($H$12-(LN(H24/L17)/$J$5))*$L$5))

MOD_1!J24: =IF((I24-I24*EXP(($H$12-(LN(H24/L17)/$J$5)-(LN(I24/H24)/$L$5))*$L$5))/$L$11>($F$10*$F$14*O21/$H$10+(1-$F$10*$F$14/$H$10)*J21)*I24*$M$5/SUM(I24:I27),I24-$L$11*($F$10*$F$14*O21/$H$10+(1-$F$10*$F$14/$H$10)*J21)*I24*$M$5/SUM(I24:I27),I24*EXP(($H$12-(LN(H24/L17)/$J$5)-(LN(I24/H24)/$L$5))*$L$5))

MOD_1!K24: =IF((J24-J24*EXP(($H$12-(LN(H24/L17)/$J$5)-(LN(J24/H24)/$L$5))*$L$5))/$M$11>($F$10*$F$14*P21/$H$10+(1-$F$10*$F$14/$H$10)*K21)*J24*$M$5/SUM(J24:J27),J24-$M$11*($F$10*$F$14*P21/$H$10+(1-$F$10*$F$14/$H$10)*K21)*J24*$M$5/SUM(J24:J27),J24*EXP(($H$12-(LN(H24/L17)/$J$5)-(LN(J24/H24)/$L$5))*$L$5))

MOD_1!L24: =IF((K24-K24*EXP(($H$12-(LN(H24/L17)/$J$5)-(LN(K24/H24)/$L$5))*$L$5))/$N$11>(G21*$F$14+(1-$F$14)*L21)*K24*$M$5/SUM(K24:K27),K24-$N$11*(G21*$F$14+(1-$F$14)*L21)*K24*$M$5/SUM(K24:K27),K24*EXP(($H$12-(LN(H24/L17)/$J$5)-(LN(K24/H24)/$L$5))*$L$5))

P. Algorithm Display for Dynamic Degradation Simulation Model:

Subsequent Time Steps: Section 98 (end section), time block 2. Plume section's formulas in time steps after the first time step are not affected by model initialization or circular reference setups. They are different from first time step formulas in that they reference plume sections in previous time steps.

MOD_2!IN24: =IF((IR17-IR17*EXP($H$12*$J$5))/$J$11>(II21*$F$14+(1-$F$14)*IN21)*IR17*$K$5/SUM(IR17:IR20),IR17-$J$11*(II21*$F$14+(1-$F$14)*IN21)*IR17*$K$5/SUM(IR17:IR20),IR17*EXP($H$12*$J$5))

MOD_2!IO24: =IF((IN24-IN24*EXP(($H$12-(LN(IN24/IR17)/$J$5))*$L$5))/$K$11>(IJ21*$F$14+(1-$F$14)*IO21)*IN24*$M$5/SUM(IN24:IN27),IN24-$K$11*(IJ21*$F$14+(1-$F$14)*IO21)*IN24*$M$5/SUM(IN24:IN27),IN24*EXP(($H$12-(LN(IN24/IR17)/$J$5))*$L$5))

MOD_2!IP24: =IF((IO24-IO24*EXP(($H$12-(LN(IN24/IM24)/$J$5)-(LN(IO24/IN24)/$L$5))*$L$5))/$L$11>($F$10*$F$14*$B$11/$H$10+(1-$F$10*$F$14/$H$10)*IP21)*IO24*$M$5/SUM(IO24:IO27),IO24-$L$11*($F$10*$F$14*$B$11/$H$10+(1-$F$10*$F$14/$H$10)*IP21)*IO24*$M$5/SUM(IO24:IO27),IO24*EXP(($H$12-(LN(IN24/IM24)/$J$5)-(LN(IO24/IN24)/$L$5))*$L$5))

MOD_2!IQ24: =IF((IP24-IP24*EXP(($H$12-(LN(IN24/IM24)/$J$5)-(LN(IP24/IN24)/$L$5))*$L$5))/$M$11>($F$10*$F$14*$B$12/$H$10+(1-$F$10*$F$14/$H$10)*IQ21)*IP24*$M$5/SUM(IP24:IP27),IP24-$M$11*($F$10*$F$14*$B$12/$H$10+(1-$F$10*$F$14/$H$10)*IQ21)*IP24*$M$5/SUM(IP24:IP27),IP24*EXP(($H$12-(LN(IN24/IM24)/$J$5)-(LN(IP24/IN24)/$L$5))*$L$5))

MOD_2!IR24: =IF((IQ24-IQ24*EXP(($H$12-(LN(IN24/IR17)/$J$5)-(LN(IQ24/IN24)/$L$5))*$L$5))/$N$11>(IM21*$F$14+(1-$F$14)*IR21)*IQ24*$M$5/SUM(IQ24:IQ27),IQ24-$N$11*(IM21*$F$14+(1-$F$14)*IR21)*IQ24*$M$5/SUM(IQ24:IQ27),IQ24*EXP(($H$12-(LN(IN24/IR17)/$J$5)-(LN(IQ24/IN24)/$L$5))*$L$5))

Q. Algorithm Display for Dynamic Degradation Simulation Model:

Electron acceptor levels after degradation, section 1, time block 1. The relative logic for these blocks is the same for all plume sections.

MOD_1!A21: EAs remaining:

MOD_1!C21: =IF(($B$9*$F$14+(1-$F$14)*C49)-((B17-C17)/$J$11+(B18-C18)/$J$12+(B19-C19)/$J$13+(B20-C20)/$J$14)<0,0,($B$9*$F$14+(1-$F$14)*C49)-((B17-C17)/$J$14))

MOD_1!D21: =($B$10*$F$14+(1-$F$14)*D49)-((C17-D17)/$K$11+(C18-D18)/$K$12+(C19-D19)/$K$13+(C20-D20)/$K$14)

MOD_1!E21: =($F$10*$F$14*J49/$H$10+(1-$F$10*$F$14/$H$10)*E49)-((D17-E17)/$L$11+(D18-E18)/$L$12+(D19-E19)/$L$13+(D20-E20)/$L$14)

MOD_1!F21: =($F$10*$F$14*K49/$H$10+(1-$F$10*$F$14/$H$10)*F49)-((E17-F17)/$M$11+(E18-F18)/$M$12+(E19-F19)/$M$13+(E20-F20)/$M$14)

MOD_1!G21: =($B$13*$F$14+(1-$F$14)*G49)-((F17-G17)/$N$11+(F18-G18)/$N$12+(F19-G19)/$N$13+(F20-G20)/$N$14)

Appendix II. AFV_{10} Calculations

A. Calculation of AFV from Benzene Concentration Isopleth Values (see Appx III)

Table 12. Field Measurement Summary for Benzene Concentration Distributions Along Length of Contaminant Plume Center Line with Computed Aerobic Front Velocities

Table Shows Field-	C(benz) (ppm)				Day		
Measured Values at	Position (ft)	6	42	106	317	398	476
Positions Across	0	0	0	0.55	0.01	0	0.001
Contaminant Plume	1	0.75	0.01	0.75	0.1	0.1	0.005
(at right), and the	2	5	2.17	2.1	0.2	0.17	0.01
Resulting AFV	3	6	4.5	4.1	0.5	0.3	0.05
Obtained From Them	4	7	7	5.4	0.75	0.9	0.08
(below)	5	7	7	5.5	1.2	1	0.33
	6	7	7	6	1.5	1.1	0.35
	7					1.163	
	Plume Length = 9.84						
AFV at Several Contaminant Levels				Calculations end day:			
Between Subsequent Time Step (ft/day)		6	42	106	317	398	476
Interpolate for 4 ppm	begin day: 6		0.028	0.0119	0.0155	0.0101	0.0118
Interpolate for 4 ppm	begin day: 42			0.00257	0.0157	0.00995	0.0112
Interpolate for 1.5 ppm	begin day: 106				0.0225	0.0131	——
Interpolate for 1 ppm	begin day: 317					0.0056	0.022
		Overall Average AFV = 0.0155 ft/day					
Interpolate for .35 ppm	begin day: 398	= SUM(all values)/14 values					0.0374

1. Possible Alternative Average AFV Calculations:

   a. For 4 ppm only, days 6 and 42, and because the early measurements were taken over a denser sampling network, and are thus more accurate than later sampling events: 0.0142 ft/day

   b. Excluding day 398 because of discrepancy between "eyed" and proportional values: 0.0157 ft/day

   c. Excluding both days 398 and 317: 0.0131 ft/day

Because of the generally good agreement between these values, the overall average value of 0.0155 ft/day has been taken as the AFV_{10}.

B. Aerobic Front Velocity Measured from Dynamic Degradation Model Output

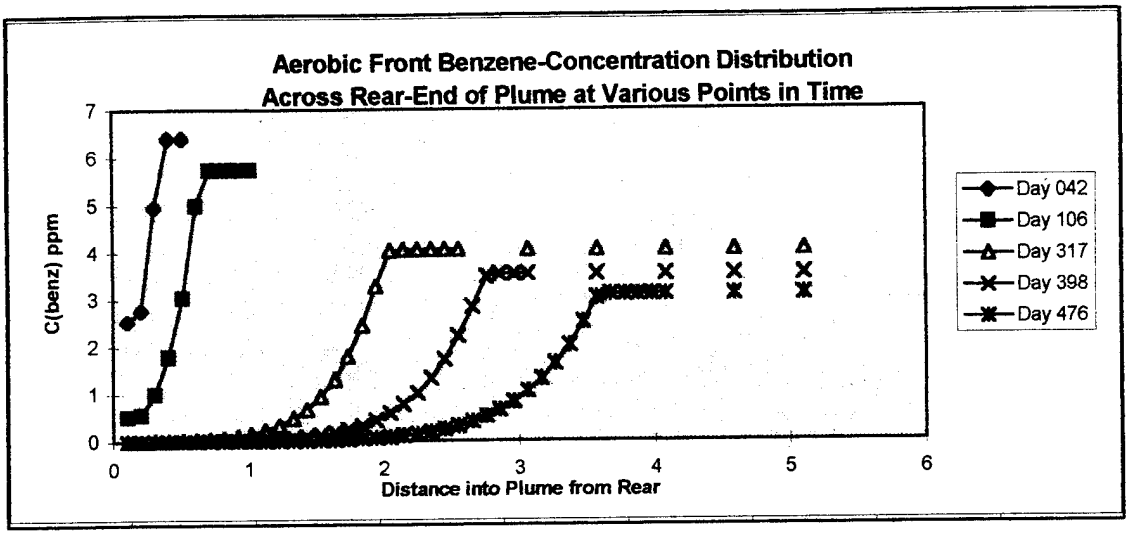
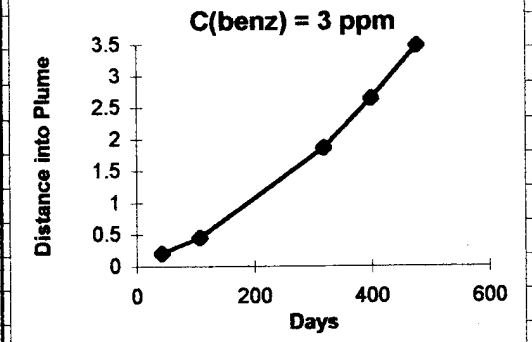
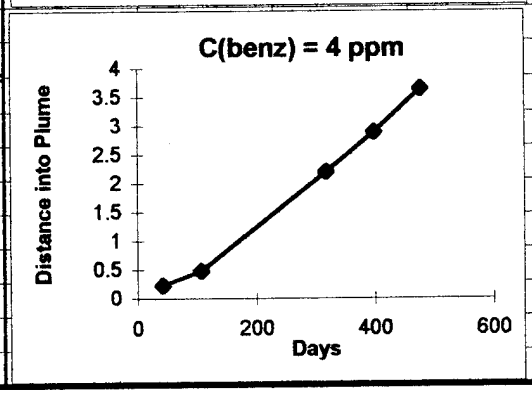


Figure 11. Aerobic Front Benzene-Concentration Distribution Across Rear-End of Plume at Various Points in Time

Table 13. Plots of Aerobic Front Movement From Dynamic Degradation Simulation Model Output With Computation of AFV

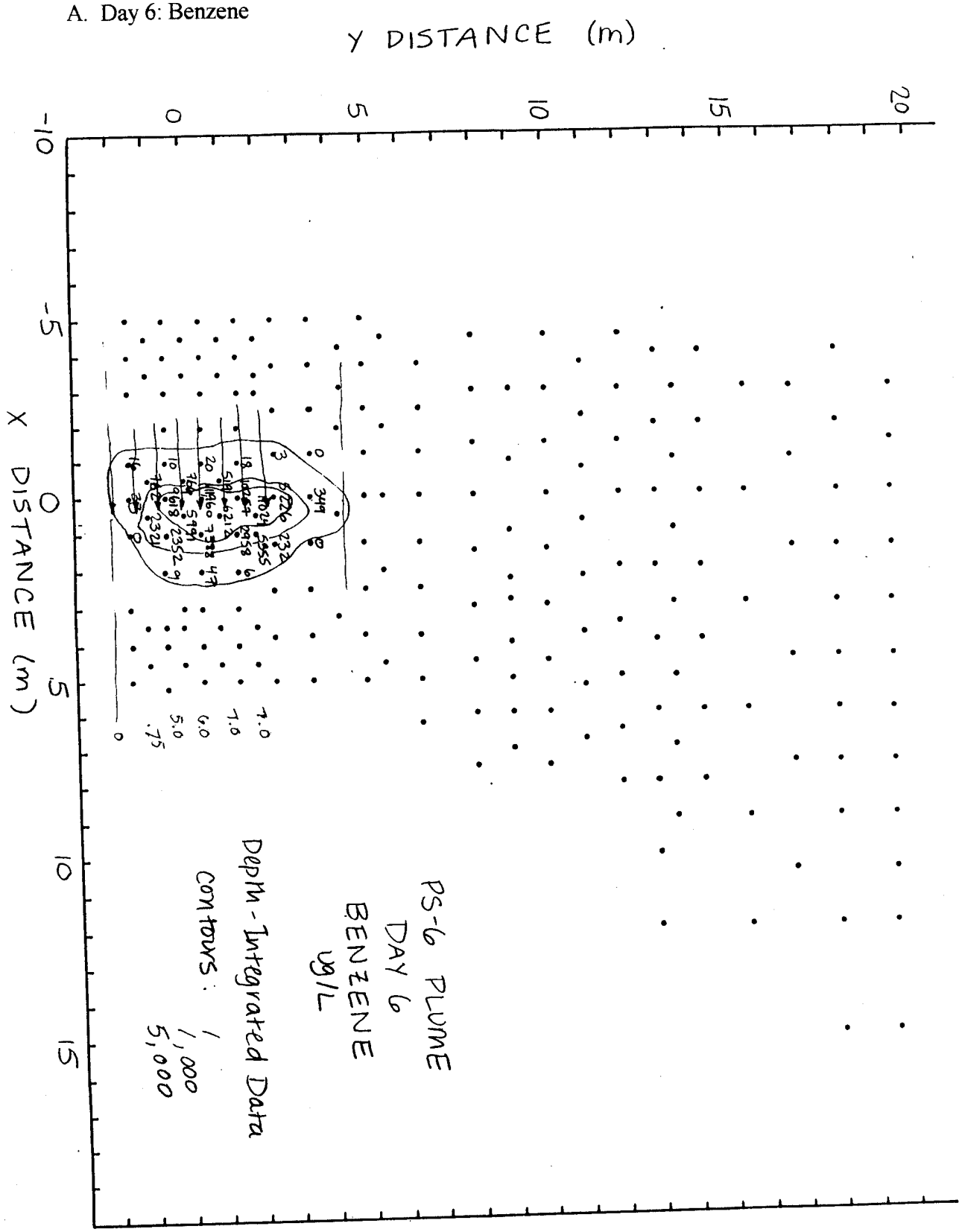
Plots of AFV from Dynamic Degradation Model Results		
Use: Avg AVF = 0.010 ft/day		
	C(benz) = 3 ppm	
	Days	x-Plume
	42	0.21
	106	0.45
	317	1.86
	398	2.64
	476	3.48
see multi-graph chart, below.		
AVF =	0.010769	
	C(benz) = 4 ppm	
	Days	x-Plume
	42	0.23
	106	0.48
	317	2.2
Extraplat'd	398	2.9
Extraplat'd	476	3.65
AVF =	0.009615	



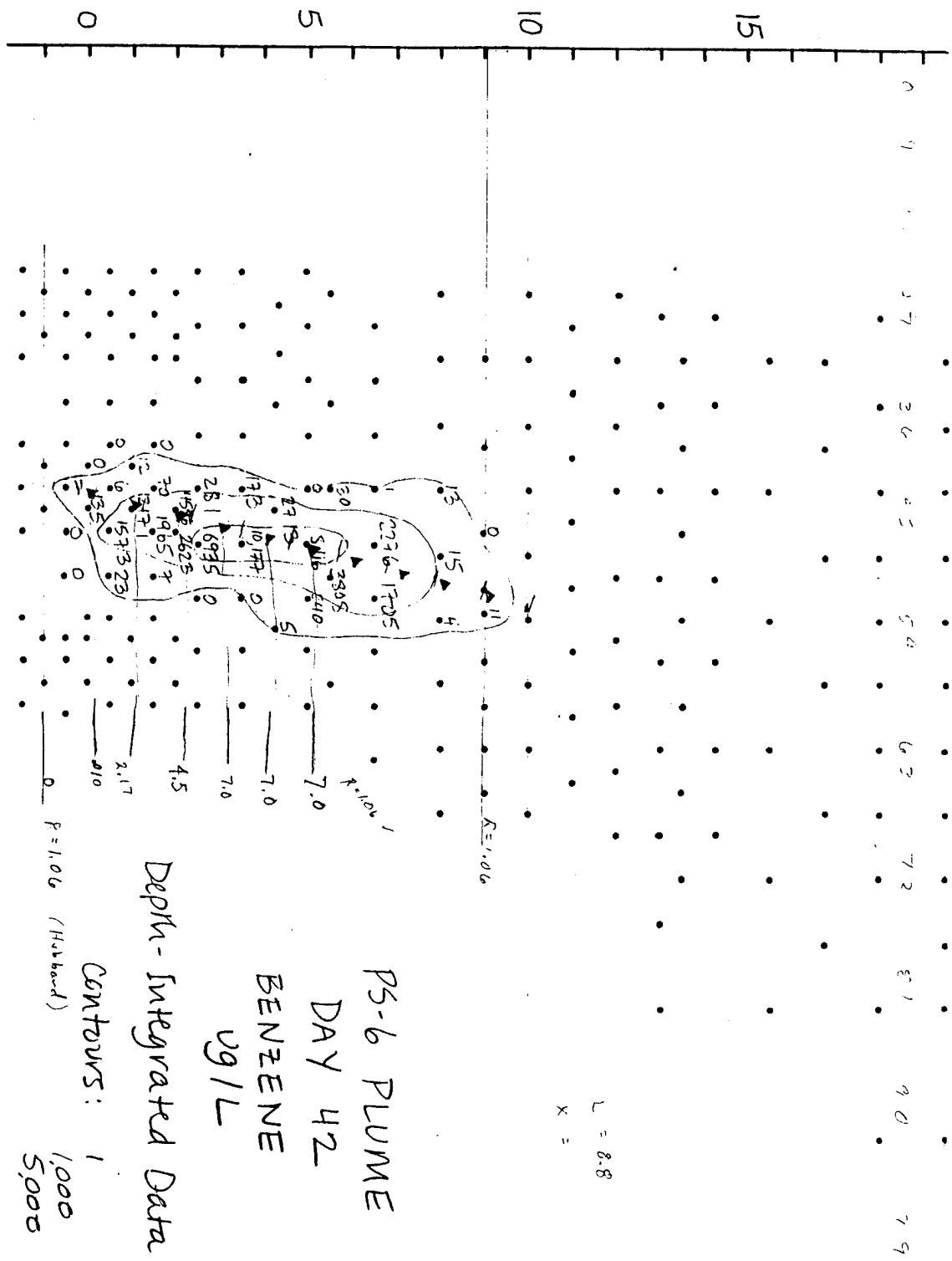


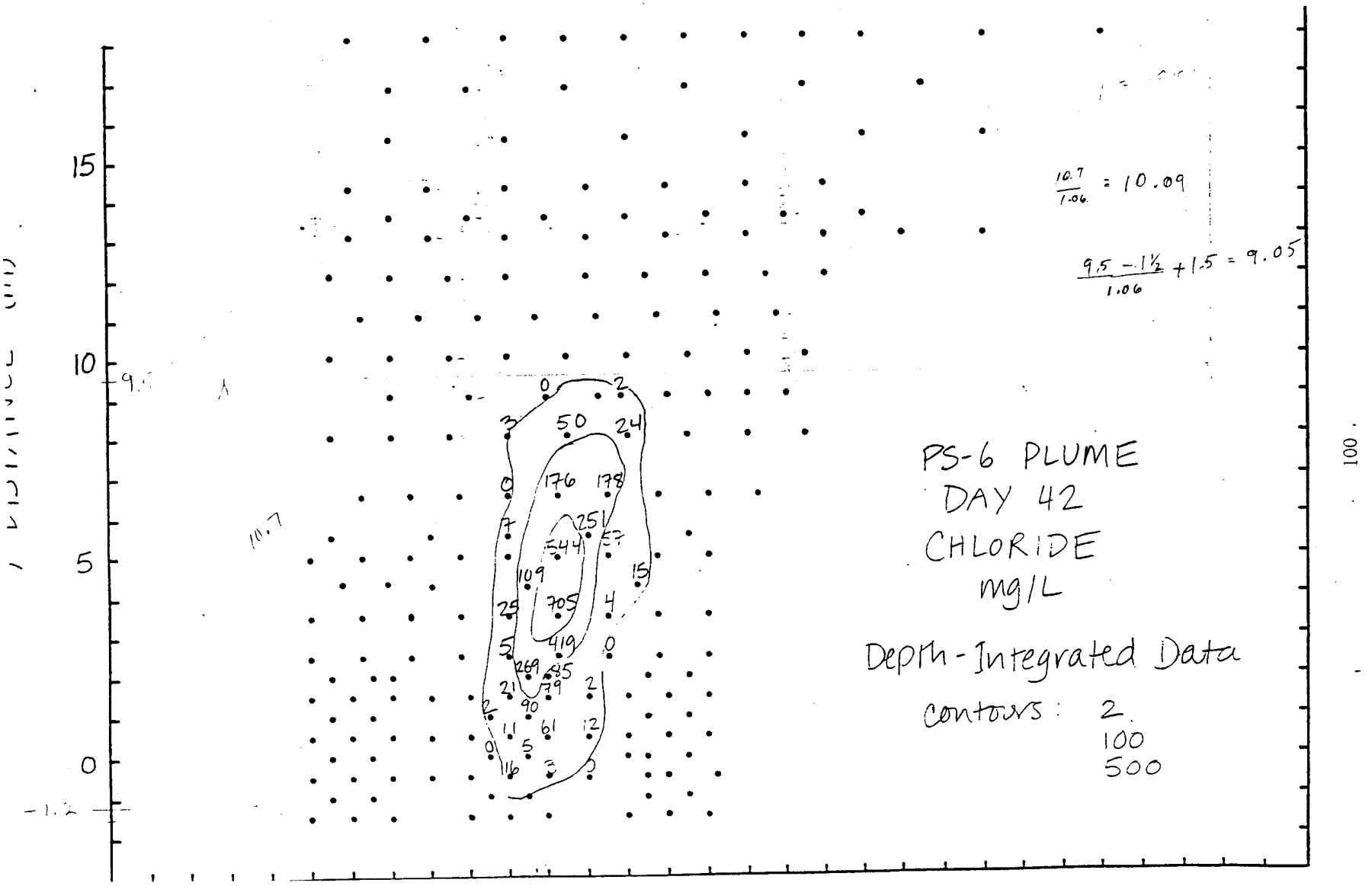
Appendix III. Contaminant and Tracer Isopleth Plot Field Measurements

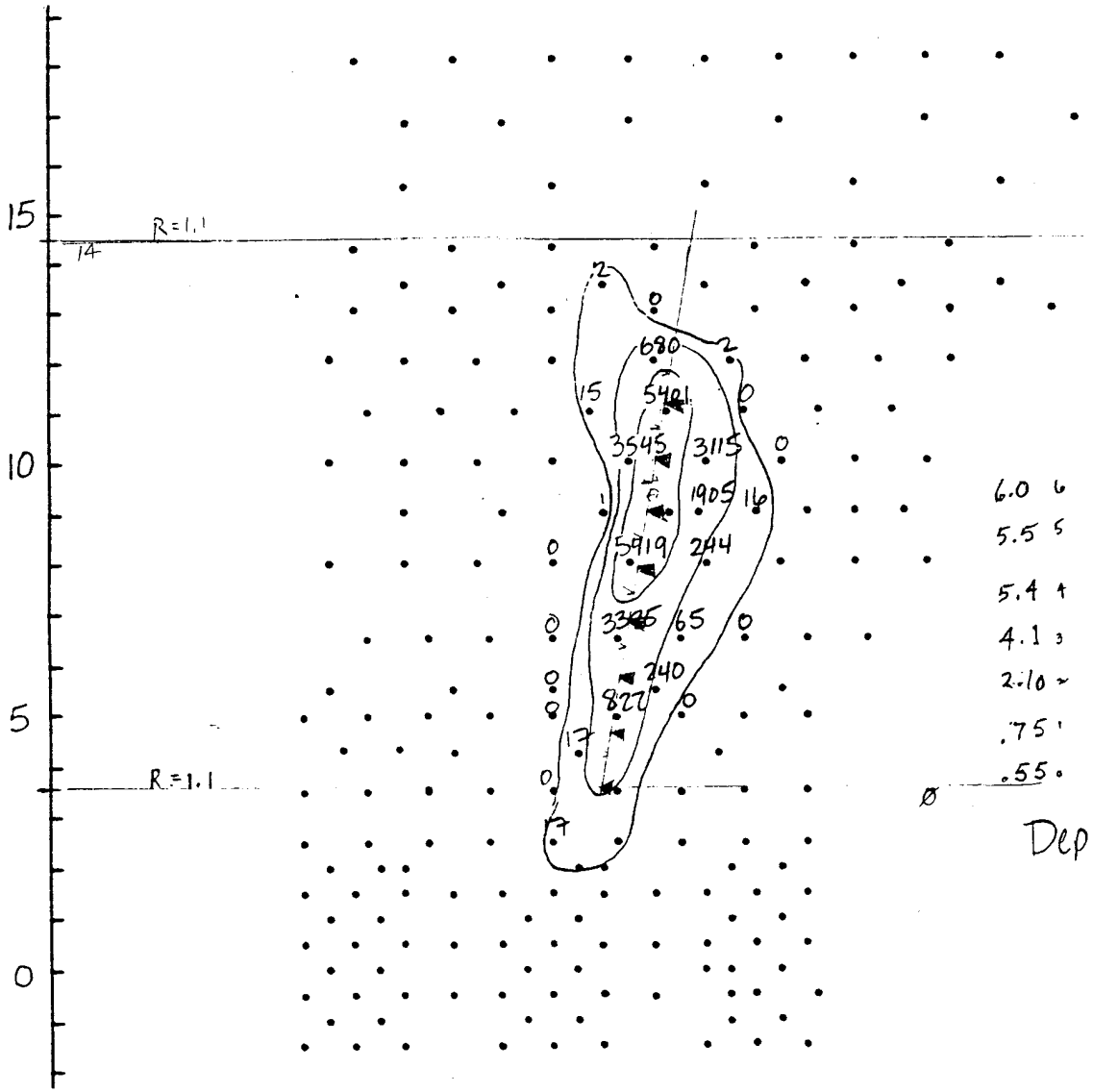
A. Day 6: Benzene

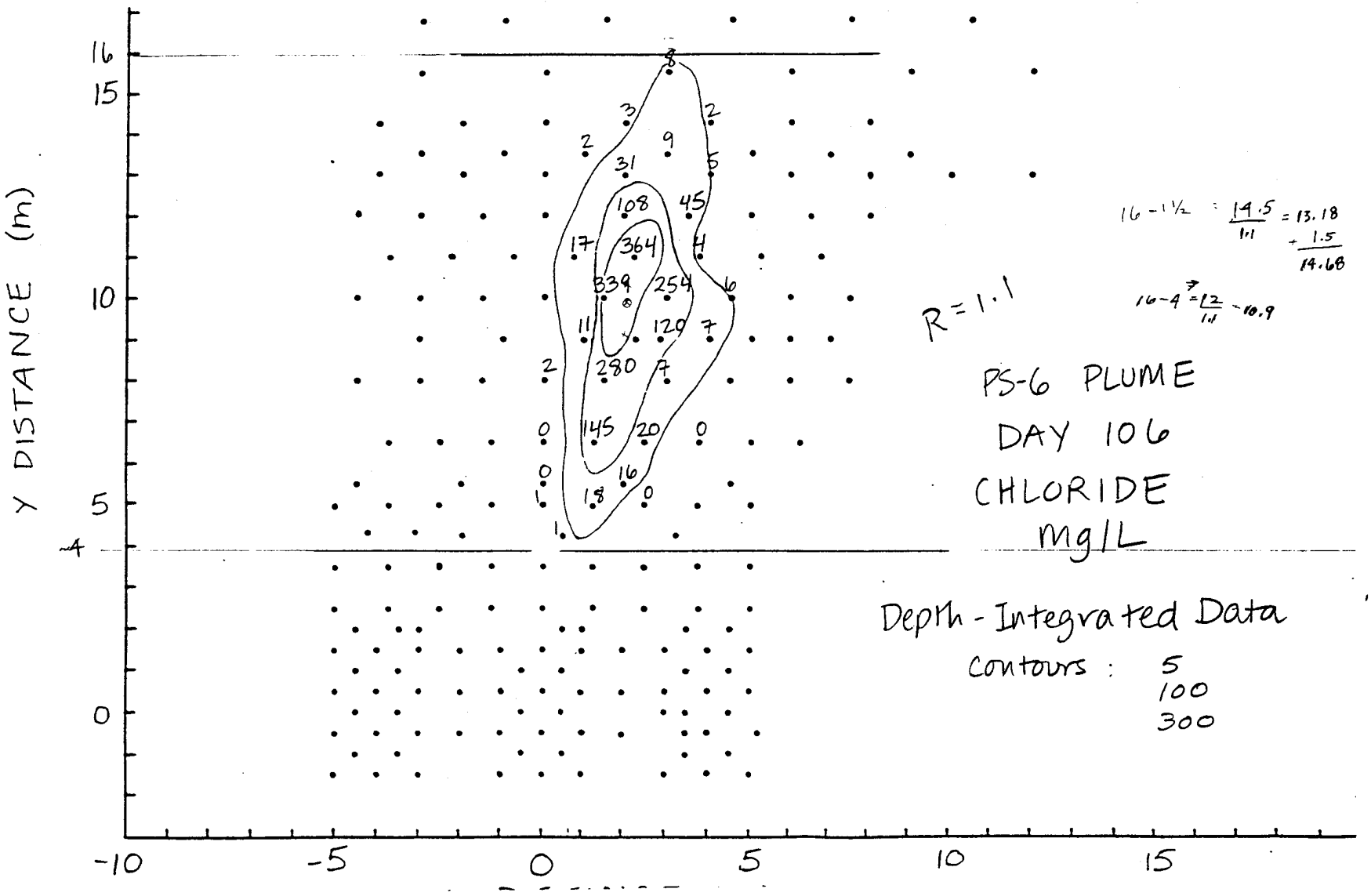


B. Day 42: Benzene and Chloride Tracer

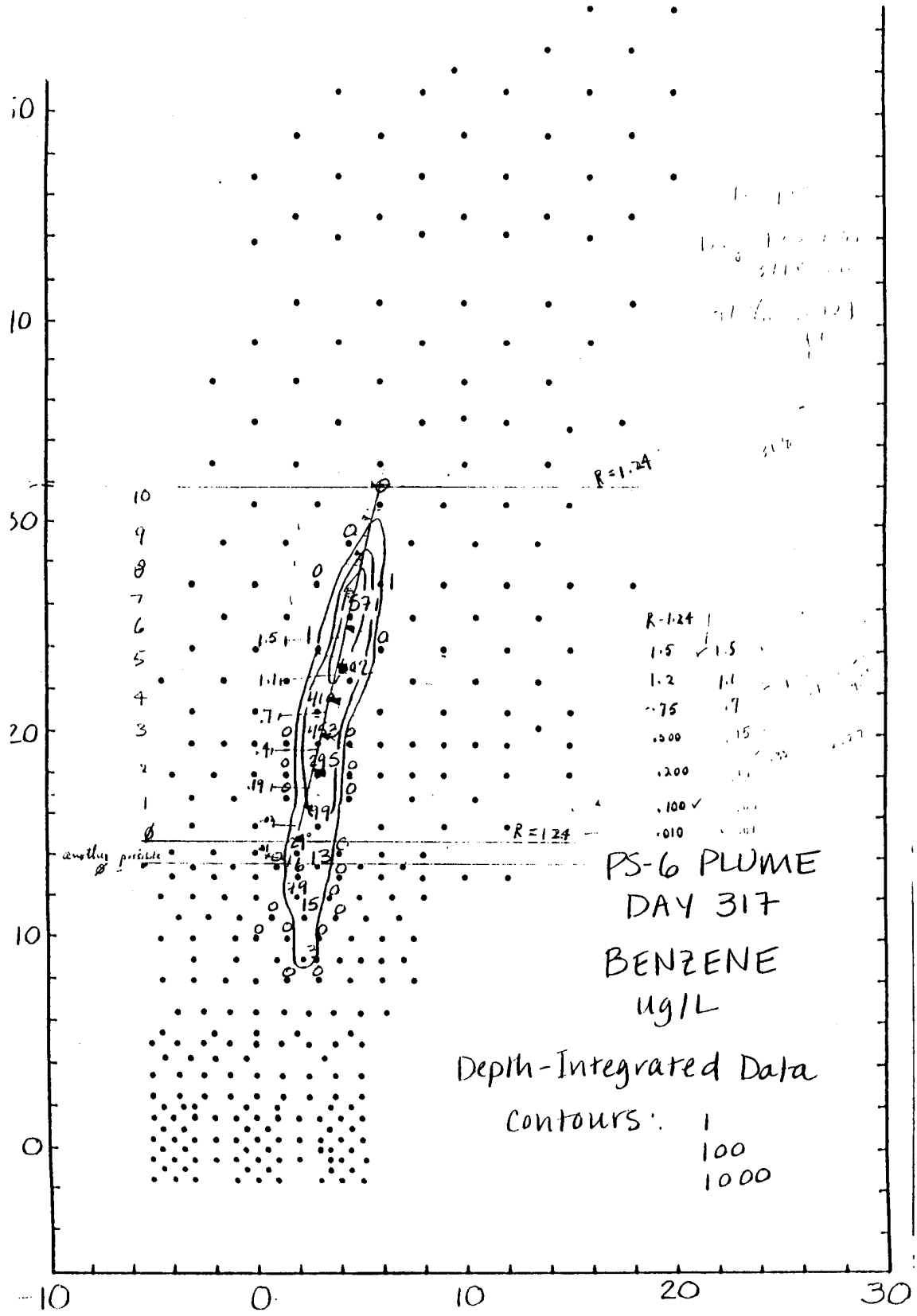


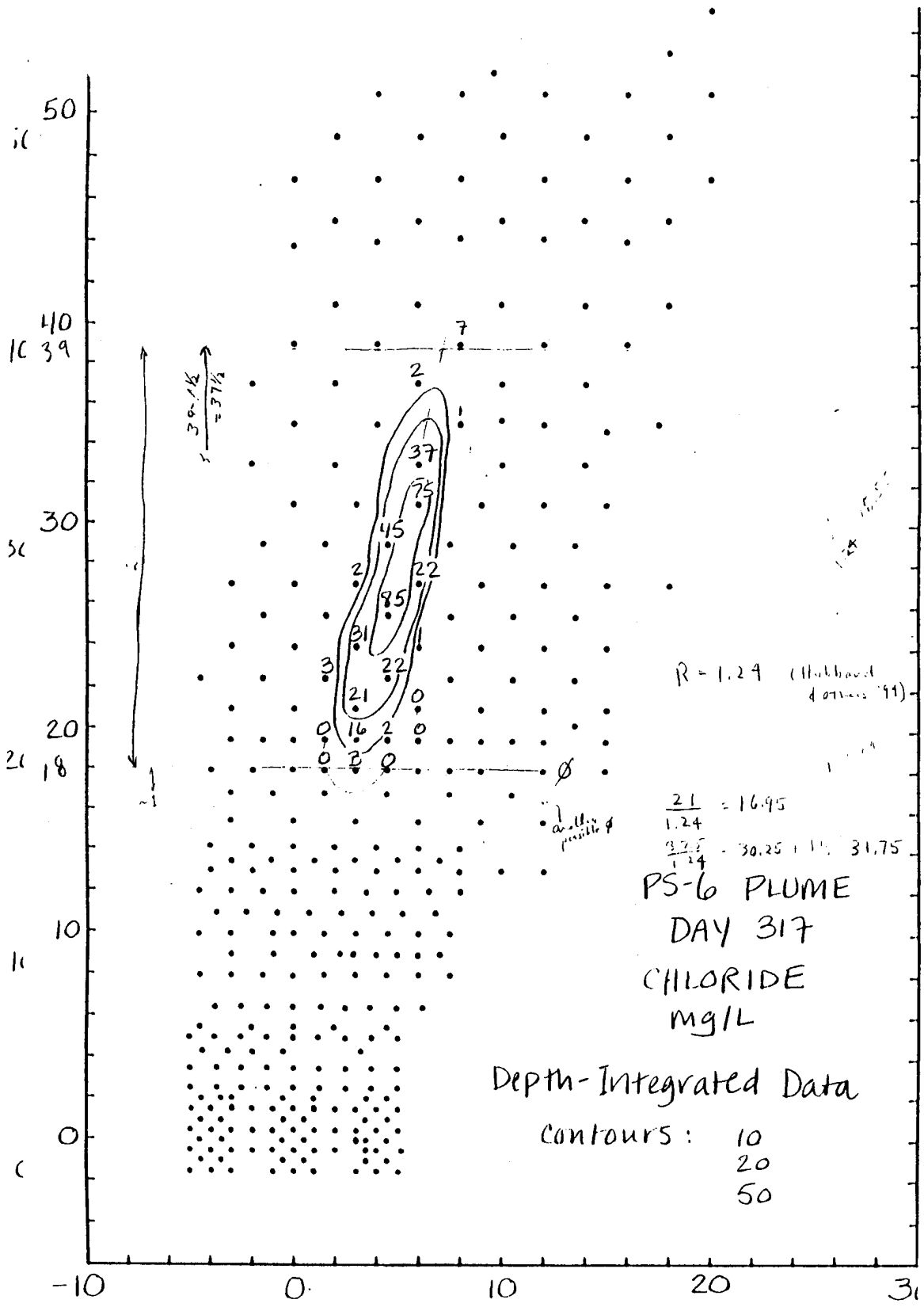

15
10
5
0
$\frac{10.7}{1.06} = 10.09$
$\frac{9.5 - 1\frac{1}{2}}{1.06} + 1.5 = 9.05$
PS-6 PLUME
DAY 42
CHLORIDE
mg/L
Depth-Integrated Data
contours: 2
100
500


15
10
5
0
R=1.1
14
R=1.1
680
5481
3545
3115
1905
5919
244
3385
65
240
827
6.0
5.5
5.4
4.1
2.10
.75
.55
PS-6 PLUME
DAY 106
BENZENE
UG/L
Depth-Integrated Data
Contours 1
500
5000

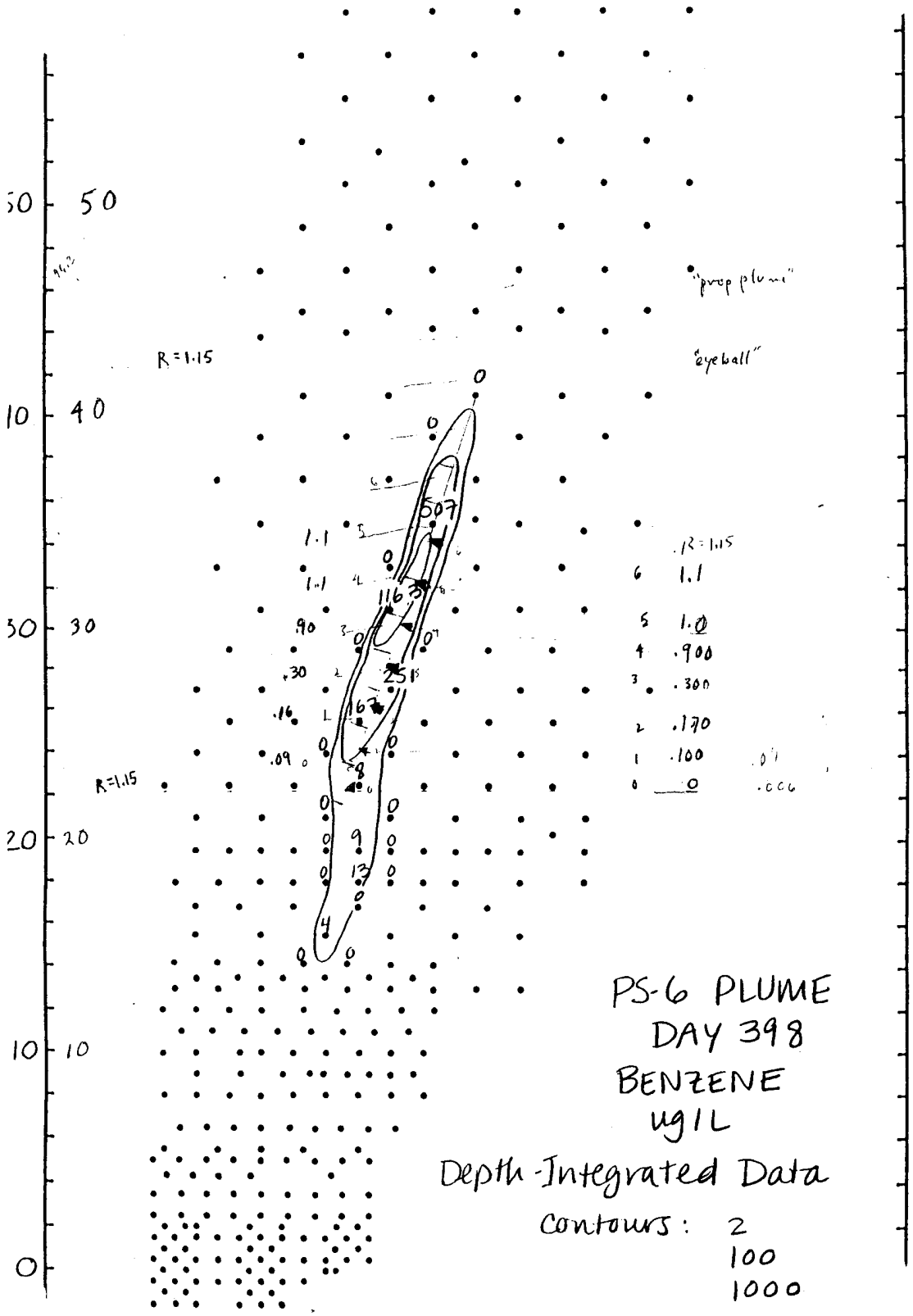

Y DISTANCE (m)
16
15
10
5
-4
0
-10
-5
0
5
10
15
8
3
2
2
9
5
31
108
45
17
364
4
839
254
6
11
129
7
2
280
7
0
145
20
0
0
16
1
18
0
1
R = 1.1
16 - 1½ : 14.5/1.1 = 13.18 + 1.5 = 14.68
16 - 4 = 12/1.1 = 10.9
PS-6 PLUME
DAY 106
CHLORIDE
mg/L
Depth - Integrated Data
Contours : 5
100
300

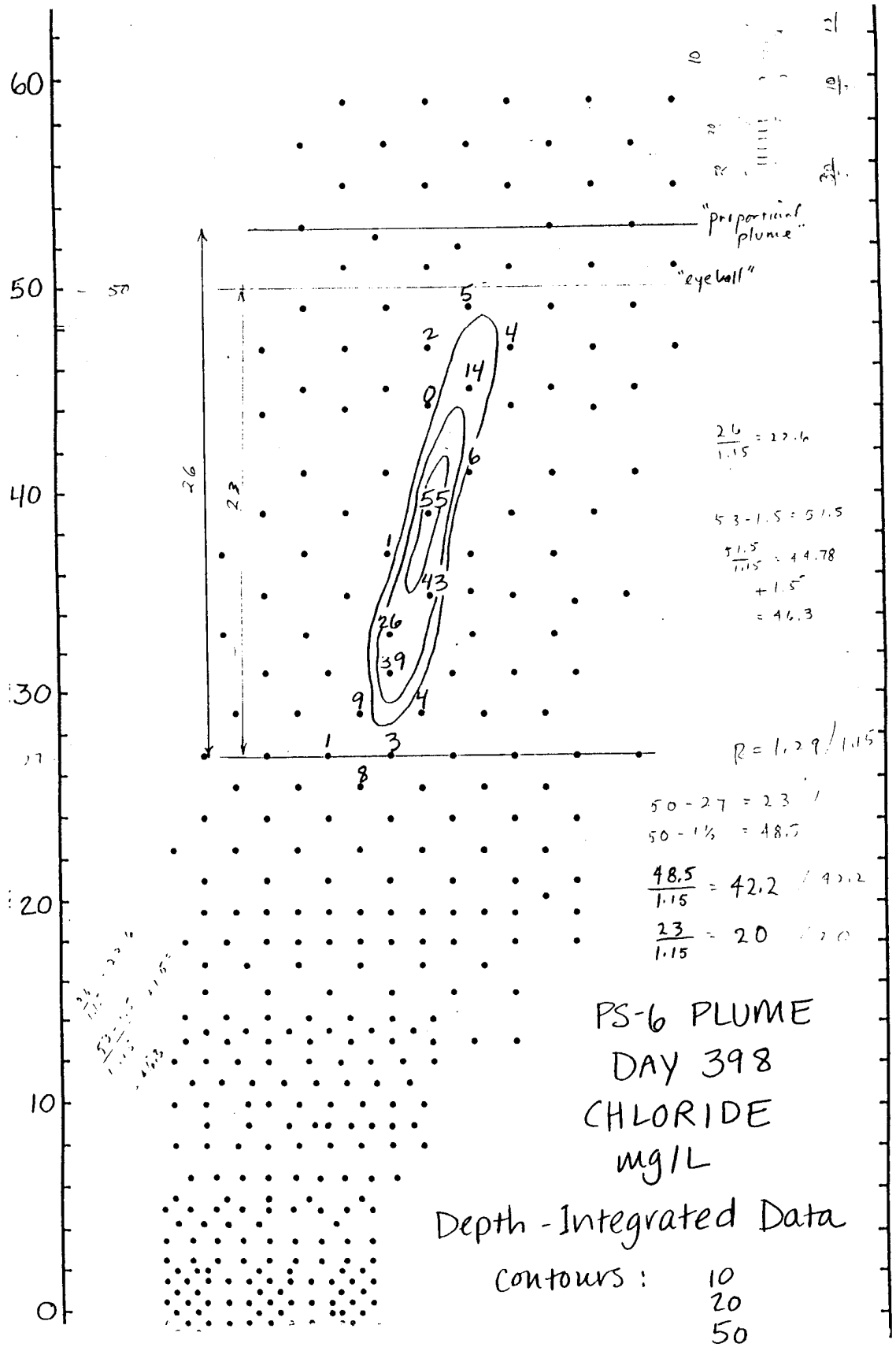
D. Day 317: Benzene and Chloride Tracer



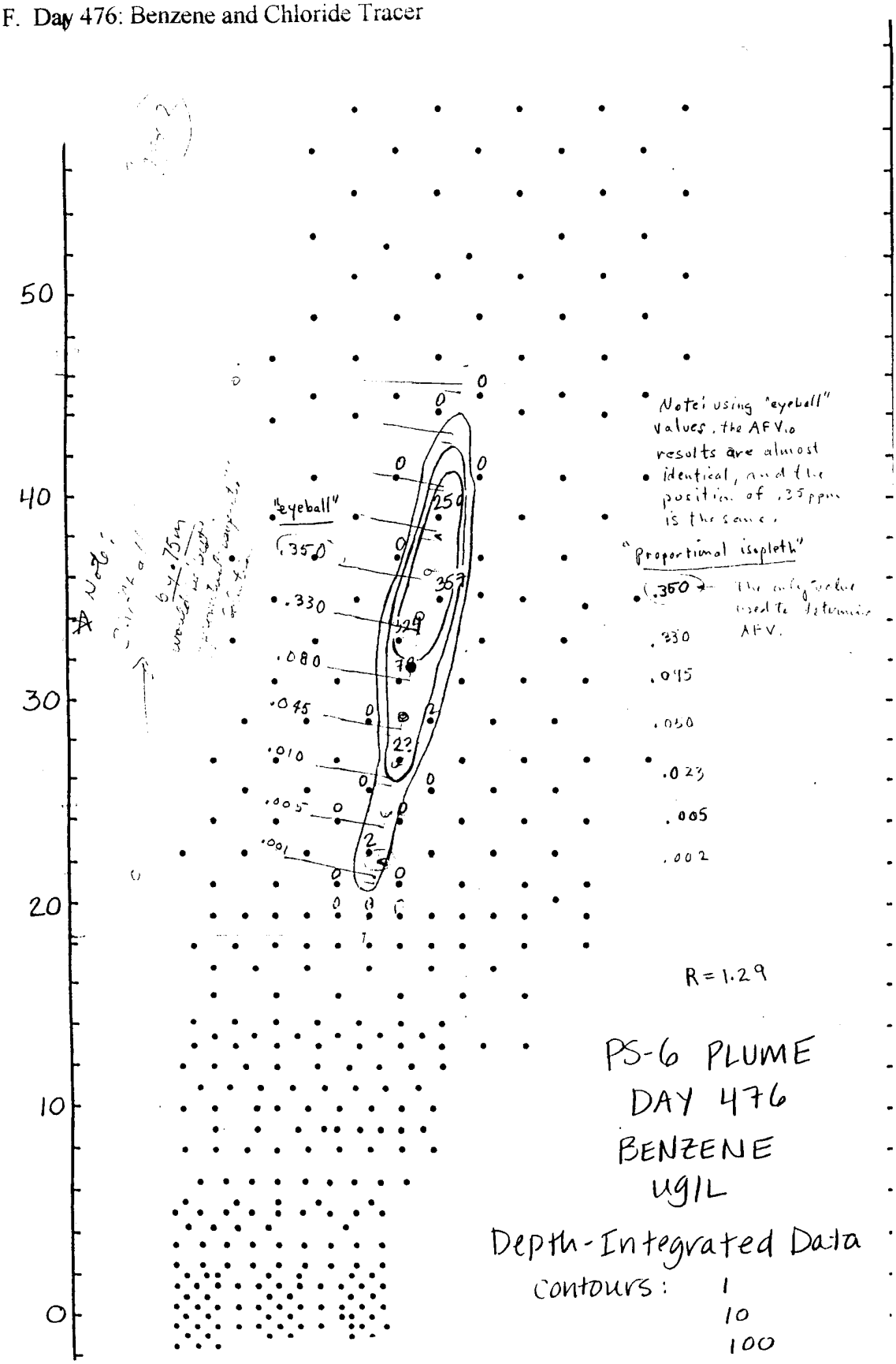

50
40
30
20
10
0
-10
0
10
20
7
2
1
37
75
45
22
85
81
22
3
21
0
16
2
0
0
2
0
Ø
R = 1.24
21/1.24 = 16.95
PS-6 PLUME
DAY 317
CHLORIDE
mg/L
Depth-Integrated Data
Contours: 10
20
50

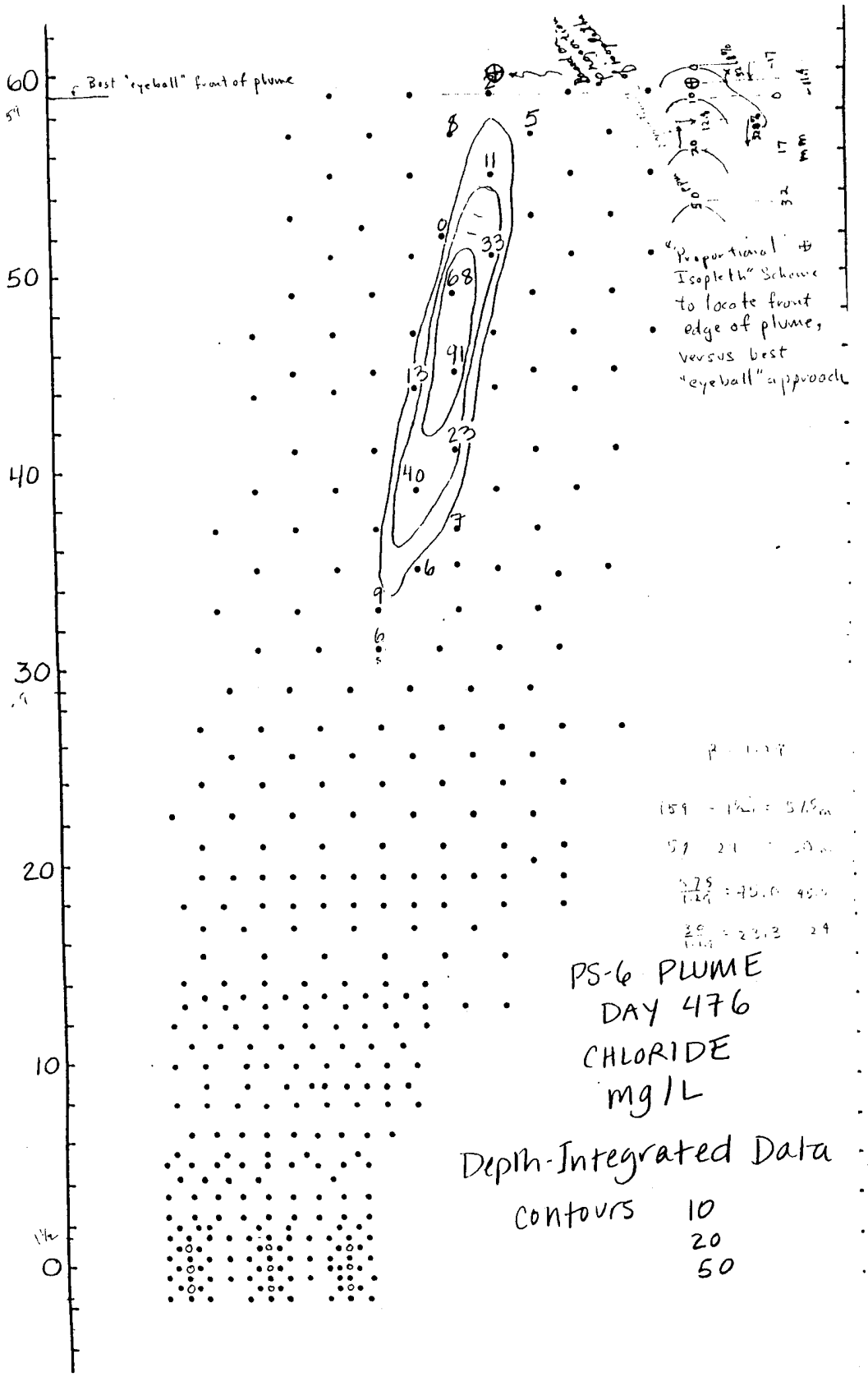
E. Day 398: Benzene and Chloride Tracer




60
50
40
30
20
10
0
"proportional plume"
"eyewall"
26
23
5
2
4
14
0
6
55
1
43
26
39
9
4
1
3
8
PS-6 PLUME
DAY 398
CHLORIDE
mg/L
Depth-Integrated Data
Contours: 10
20
50

F. Day 476: Benzene and Chloride Tracer




Best "eyeball" front of plume
"Proportional" Isopleth" Scheme to locate front edge of plume, versus best "eyeball" approach
PS-6 PLUME
DAY 476
CHLORIDE
mg/L
Depth-Integrated Data
Contours 10
20
50
60
50
40
30
20
10
0
8
5
11
33
68
91
13
23
40
7
6
9
6

Vita

Steven Flier was born on 24 April 1952 in St. Louis, Missouri. He attended Cleveland High School in St. Louis, and St. Louis Community College at Meramec. He attended The University of Texas at Austin, where he earned a Bachelor of Science degree in Civil Engineering in 1988. After graduation, he began working for the Air Force as a Palace Acquire Intern in the environmental engineering career field at the 12 CES, Randolph Air Force Base, Texas.

For 18 months, beginning in 1990, he worked for the 21 CES as the hazardous waste program director at Elmendorf Air Force Base, Alaska. From September 1991 until entering the Graduate Environmental Management program at the Air Force Institute of Technology in May 1994, he worked for the 11 CEOS, as the government – GOCO liaison on the Alaska Long Range Radar System, ensuring all facets of environmental compliance under the LRRS operations contract, for 15 remote radar stations, and 3 forward operating bases, all scattered over the most extreme reaches of "The Great Land."

Mr. Flier is married to the former Virginia Lee Trimble of St. Louis, Missouri, and has two children, Jessica and Peter, ages 11 and 8.

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REPORT DOCUMENTATION PAGE

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13. ABSTRACT *(Maximum 200 words)*

This research extends the work begun by Enyeart (1994) which evaluated the process of intrinsic bioremediation, and which developed a model for predicting the velocity of an aerobic degradation front, as it traverses the length of a JP-4 contaminant plume. It is assumed this aerobic front will traverse the contaminant plume as dissolved oxygen is carried by the ground water through the sorption-retarded contaminant. The ultimate purpose of Enyeart's model is to use it to develop field guidance for assessing the feasibility of intrinsic bioremediation to restore petroleum-contaminated soils. After simulating intrinsic bioremediation many times with a spreadsheet model, results were used to develop a linear regression model to predict the velocity of the aerobic front, and thus the time it takes to propagate through from the rear to the front of the simulated plume. The time needed for the aerobic front to travel from the rear to the front of the plume is taken as the time to contaminant remediation. In the present work, Enyeart's model was validity tested by comparing its output prediction with field measured values. A methodology was developed to compare the model output with field measured data. The results were analyzed, and the results of this first stage of validity testing show a reasonable basis for accepting the model. Further validity testing of the model will be required to assess its performance across a wide range of field conditions. It is hoped that contaminated-site managers will one day use the validated regression model to predict the time required to affect the complete remediation of a contaminated site via intrinsic bioremediation.

14. SUBJECT TERMS
Intrinsic Bioremediation, Natural Attenuation, Bioremediation
Biodegradation, BTEX, Ground Water Contamination

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