Remediation of Petroleum-Contaminated Ground Water by Natural Attenuation:

Guidance & Analysis Tool Package

Hun Seak Park

Toxics Cleanup Program; Washington State Department of Ecology

June 18, 2004

Natural Attenuation Processes

Non-Destructive	Destructive
– Dispersion	– Biodegradation
– Sorption $K_d = (K_{oc})*(f_{oc})$	– Abiotic Reactions (hydrolysis)
– Dilution by recharge	
– Volatilization	

Adapted from ASTM

Why Natural Attenuation?

- Perceptions of Cost Savings as compared with more conventional (engineered) remedial alternatives;
- Lessen the problems dealing with the complexities of subsurface system; and
- Illusion of "Nature will take care of it?" and "Do nothing and walk away?"

Core Publications used to develop Natural Attenuation Policy

- ***USEPA, May 2001***, Monitored Natural Attenuation: USEPA Research Program- an EPA Science Advisory Board Review. EPA-SAB-EEC-01-004;
- ***USEPA, April 1999***, Use of monitored Natural Attenuation at superfund, RCRA Corrective Action, and Underground Storage Tank Sites;
- ***National Research Council***, March 2000, "Natural Attenuation for Groundwater Remediation", by National Risk Management Research Laboratory Committee on Intrinsic Remediation;
- ***ASTM E1943-98***, Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites;
- ***US Air force*** Center for Environmental Excellence, 1995, "Technical Protocol for Implementing Intrinsic Remediation with Long-term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater;
- All 50 US states, federal, industries' policies; most current articles, and
- Dr. Matthew Small: (UA EPA R9) critical peer-review/help!

US EPA and National Research Council's Most Recent View

USEPA, May 2001, Natural Attenuation: USEPA Research Program- an EPA Science Advisory Board Review. EPA-SAB-EEC-01-004

1. Natural Attenuation is **not a "do-nothing" alternative**
2. Natural Attenuation is an effective **knowledge-based** remedy where a proper and thorough engineering analysis informs the **understanding, monitoring, predicting, and documenting** of the natural processes that reduce risks of exposure to acceptable levels

The Primary Challenge in Natural Attenuation Evaluation at petroleum-contaminated ground water

Not in demonstrating that degradation (or natural attenuation) is occurring;

But in demonstrating that (bio)degradation is a primary mechanism and at an acceptable rate to protect human health and the environment, and will continue to do so for an acceptable period of restoration time.

Three Basic Questions that the Guidance will guide to:

- What is threshold requirements for the use of Natural Attenuation: how to analyze, interpret, integrate, and evaluate the process?
- How to implement and monitor processes?
- Condition of Site closure?

Three Parts of Guide

Either one page policy, or most extensive handbook style…

- ✓ Written Guidance: threshold criteria for feasibility & performance monitoring plan
- ✓ Analysis Tool Package (MS Excel): *easy and hands-on application of all calculations necessary; enter data ->click ->and interpret/evaluate the results*
- ✓ Written User's Manual *and Workflow and calculation module charts*

The Guide provides....

- ✓ The advantages and limitations,
- ✓ Conducting a remedial investigation: what data must be collected to adequately characterize the site and evaluate the feasibility,
- ✓ Evaluating the feasibility of natural attenuation, threshold criteria; evaluation methodologies recommended; and hands-on analysis tool packages,
- ✓ Performance monitoring plan,
- ✓ Contingency plan,
- ✓ Comparative analysis of feasible cleanup action alternatives,
- ✓ Selecting a cleanup action (s), and
- ✓ Implementing the selected cleanup action.

Threshold Criteria (MTCA 173-340-370(7))

✓currently able to reduce contaminant concentrations;

✓able to reduce contaminant mass;

✓able to achieve cleanup standards within a reasonable restoration time frame;

✓adequately protective of human health and the environment during the restoration time frame;

✓source control is conducted to the maximum extent practicable; and

✓provides adequate compliance monitoring.

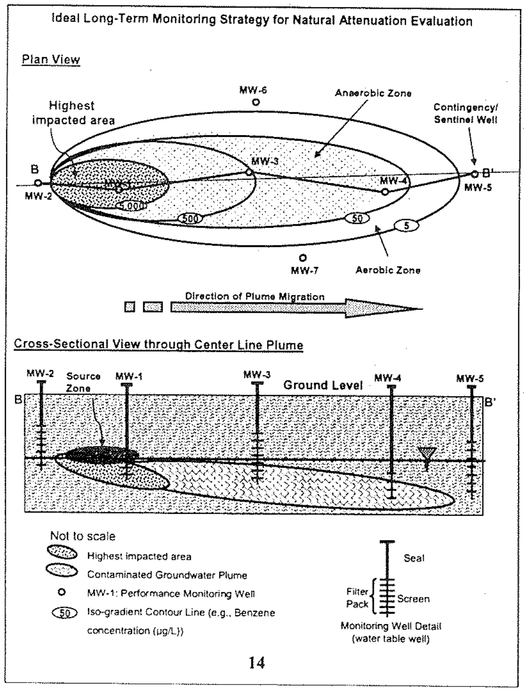
Format of Threshold Requirements

Issue:	Is natural attenuation currently able to reduce contaminant concentrations?
Action:	Evaluate plume status and status of contaminant concentrations within the plume.
Decision:	If plume stable or shrinking, then CONTINUE. If plume expanding, then conduct MORE SOURCE CONTROL or STOP.

1. Criterion:
2. Evaluation Methods: *recommended*
3. Decision:

Minimum Monitoring Plan for Assessing Feasibility of Natural Attenuation

Task	Duration and Frequency of Monitoring	Number and Location of Monitoring Wells
Contaminants of Concern & Ground Water Table Elevation	Four sampling events (quarterly) over one (1) year sampling period in order to define seasonal fluctuations in concentrations of contaminants	• One (1) well in up-gradient (not impacted) background area • One (1) well within source (most impacted) area • Two (2) wells within contaminated dissolved portion of plume • One (1) well in down-gradient "sentinel" area
Geochemical Indicators	Any two sampling events (semi-annually) over one (1) year sampling period in order to define seasonal fluctuations in concentrations of contaminants	



14

Six Calculation Modules

Tier I: without Ground Water Flow Model (well-to-well analysis); Module 1-3

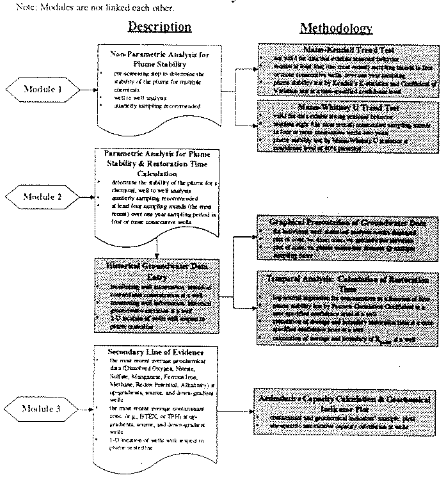
Tier II: with Ground Water Flow; Module 4-6

- Types of questions to be answered
- Types and minimum number of data required
- Types of Analysis and evaluation to be conducted

Calculation Modules

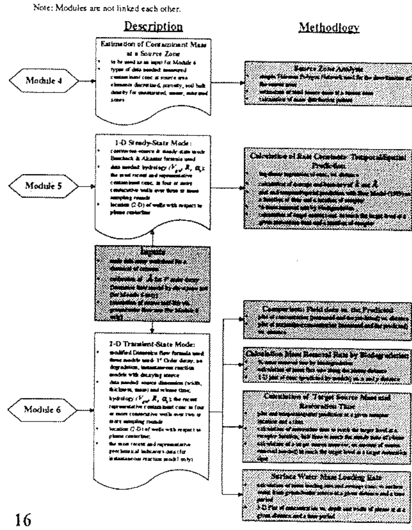
Calculation Module for Natural Attenuation Analysis
Tier I Analysis

Note: Modules are not linked each other.



Calculation Module for Natural Attenuation Analysis
Tier II Analysis

Note: Modules are not linked each other.



16

Module 1: Plume Status; non-parametric analysis

Non-Parametric Analysis for Plume Stability

- well to well analysis
- quarterly sampling recommended

Mann-Kendall Trend Test

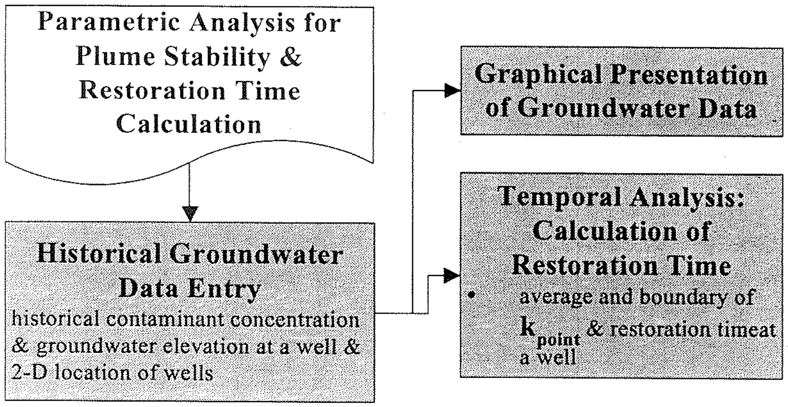
- not valid for seasonal behavior
- by Kendall's K-statistics and Coefficient of Variation test

Mann-Whitney U Trend Test

- for data exhibit strong seasonal behavior
- plume stability test by Mann-Whitney U statistics

User-specified confidence level as decision criteria

Module 2: Plume Status: parametric analysis



$$C_t = C_o * e^{-k_{point} t} \longrightarrow t_{Cleanup} = \frac{-\ln\left[\frac{C_{goal}}{C_o}\right]}{k_{point}}$$

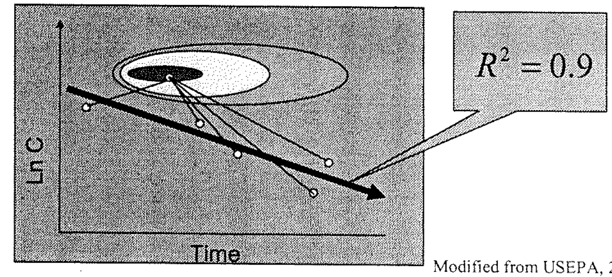
Typical Evaluation of Statistical Validity (well to well analysis)

*Pearson product moment correlation coefficient: $(R^2) > 0.9$?

*Problems

User cannot select/use level of confidence

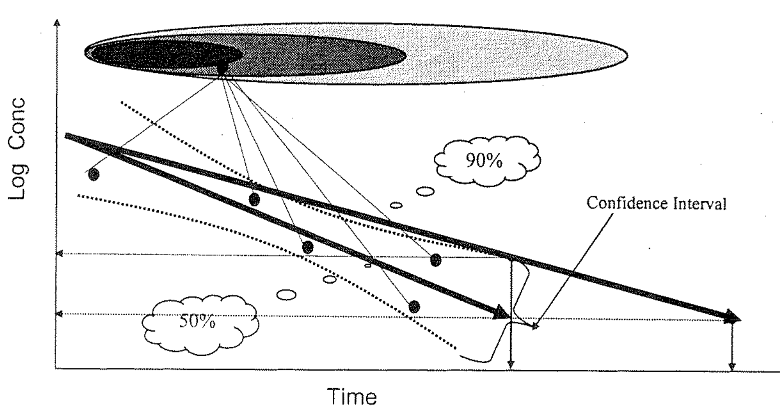
Number of data points and the degree of data scatter are not considered in the prediction and current plume status at a well.



Modified from USEPA, 2002

Estimation of Restoration Time: @ a well

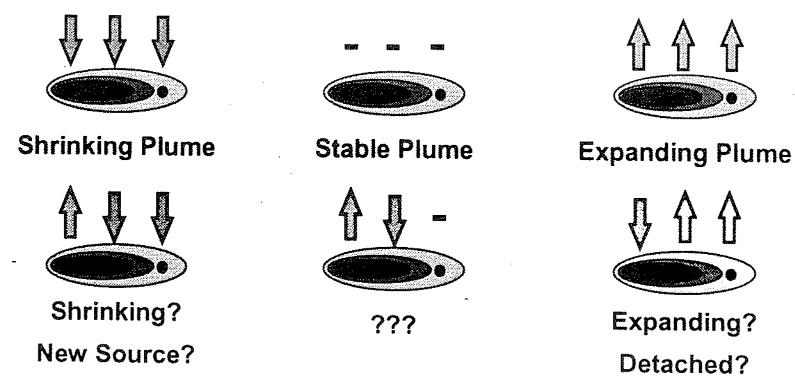
- Student t-test; **confidence interval** on the slope of log-linear regression: @ number of data and natural scatter in data points
- Restoration time @ one-tailed and user-specified confidence interval



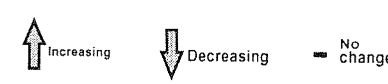
Modified from Matthew Small, 2002

Well Concentration vs. Time

Evaluating Concentration Trends at Multiple Wells:



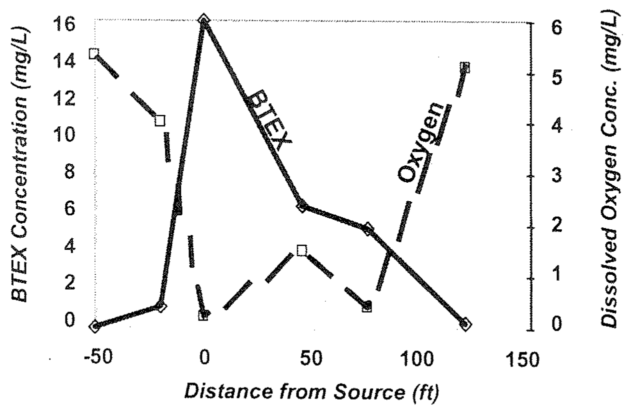
well locations and site-specific condition to define plume trend.



Module 3: Geochemical Indicator Evaluation

Geochemical Parameters Response

Dissolved Oxygen and BTEX Concentration vs. Distance)



Adapted from ASTM (1998)

Module 4: Estimation of Mass at a Source Zone

Estimation of Contaminant Mass at a Source Zone →

Source Zone Analysis
- Thiessen Polygon Network used
- estimation of total source mass mass distribution pattern at a source zone

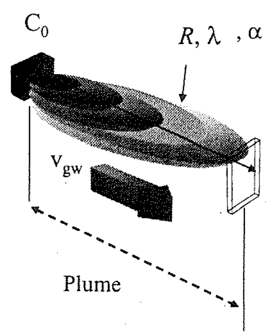
Thiessen Polygon Network

Module 5: Module 5: 1-D Steady State

1-D Steady-State Mode:
- Buscheck & Alcantar formula used
- V_{gw}, R, α_x
- location (2-D) of wells

Calculation of Rate Constants: Temporal/Spatial Prediction
- calculation of average and boundary of k and λ
- plot and temporal/spatial prediction
- % mass removal rate by biodegradation

Inputs
- calibration of λ for 1st order decay Domenico flow model by chi-square test (for Module 6 only)



Buscheck & Alcantar formula

$$\lambda = \frac{v_c}{4\alpha_x} * \left\{ \left[1 + 2\alpha_x \left(\frac{k}{v_{gw}} \right) \right]^2 - 1 \right\}$$

Module 6: 2 &3-D Transient State Mode

Inputs
- calibration of λ for 1st order decay Domenico flow model by chi-square test (for Module 6 only)

2-D Transient-State Mode:
- modified Domenico flow models with decaying source
- hydrology (V_{gw}, R, α_x)
- location (2-D) of wells with respect to plume centerline;

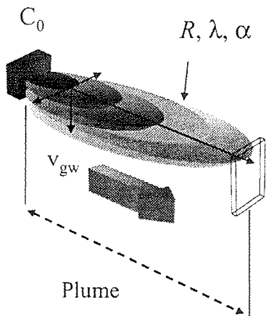
→ **Comparison: Field data vs. the Predicted**

→ **Calculation Mass Removal Rate by Biodegradation**

→ **Calculation of Target Source Mass and Restoration Time**

→ **Surface Water Mass Loading Rate**

Modified from USEPA's BIOSCREEN 1.4



3-D Domenico (1987) model

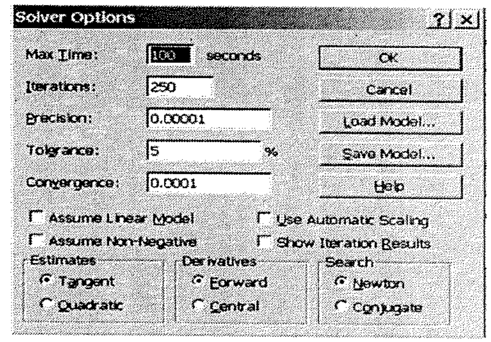
Analytical solute transport solution used as a model of "average" plume behavior: Planar and continuous/ decaying source.

$$C_{(x,y,z,t)} = \frac{1}{8} C_o * \exp\left[-k_s\left(t - \frac{x}{v_r}\right)\right] * \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \sqrt{\left(1 + \frac{4\lambda\alpha_x}{v_r}\right)}\right]\right\} * erfc\left\{\frac{\left[x - v_r t\sqrt{\left(1 + \frac{4\lambda\alpha_x}{v_r}\right)}\right]}{2\sqrt{\alpha_x v_r t}}\right\} *$$

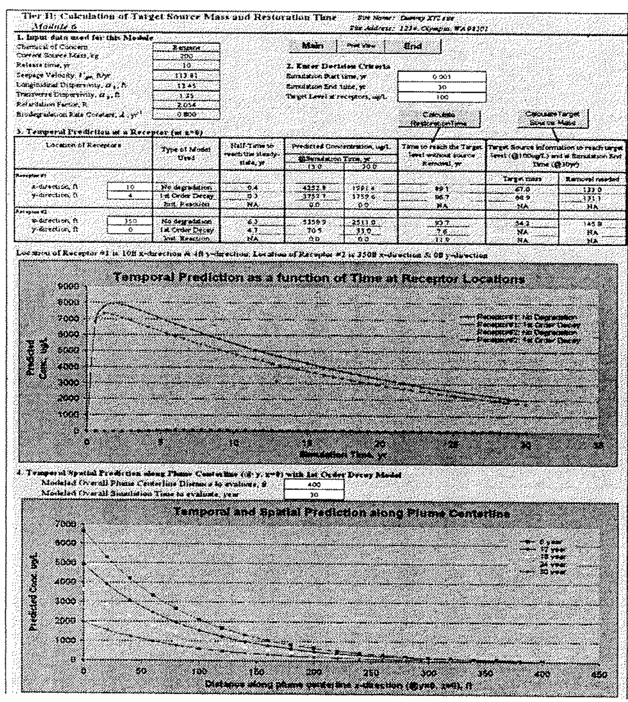
$$\left\{erf\left[\frac{\left(y + \frac{Y}{2}\right)}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{\left(y - \frac{Y}{2}\right)}{2\sqrt{\alpha_y x}}\right]\right\} * \left\{erf\left[\frac{\left(z + \frac{Z}{2}\right)}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{\left(z - \frac{Z}{2}\right)}{2\sqrt{\alpha_z x}}\right]\right\}$$

Calibration of "λ" biodegradation rate constant

- Normalized Concentration used
- Chi-Square statistics to test goodness-of-fit
- Iterative routine built-in-function MS Excel "Solver"



Example Worksheet Module 6



Seeking Board's advice on scientific defensibility on following technical aspects…

- Recommended methodologies for evaluating and determining the fasibility(§3.5);
- Other better evaluation methods reflective of current scientific understanding when evaluating the feasibility;
- Investigative monitoring plan (§3.4.2) for evaluating the feasibility;
- Long-term performance monitoring plan (Section 3.6.1).