Evaluating the Progress of Natural Attenuation in Groundwater

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Module 1: Introduction

Learning Objectives

By the end of this section, you will be able to:

- **Identify** the key performance monitoring objectives for Monitored Natural Attenuation (MNA) remedies.
- **Evaluate** the appropriateness of a monitoring well network for statistical analysis based on geohydrological stability.
- **Select** the correct phase of statistical analysis (Phase 1 or Phase 2) based on the current stage of the remedial process.

Executive Summary: Monitored Natural Attenuation (MNA) is a formal CERCLA remedy that requires objective, statistical demonstration to verify that natural processes will attain cleanup goals within a reasonable timeframe. This manual provides a two-phase statistical framework to forecast cleanup dates and evaluate ongoing remedy performance during five-year reviews.

Overview of MNA in Groundwater Remediation

Monitored Natural Attenuation (MNA) has been a significant component of remedies at National Priority List (NPL) sites, utilized in over 20% of groundwater remedies between 1982 and 2005, and 18% from 2005 to 2008. Its use is expected to increase as primary source areas are depleted by aggressive treatments, leaving MNA to address residual contamination.

Remedial Action Objectives

EPA expectations for MNA are defined by its ability to reach cleanup levels in a **reasonable timeframe** compared to other alternatives. Performance monitoring is critical to:

- **Demonstrate** that attenuation is occurring according to expectations.
- **Detect** changes in environmental conditions that may reduce efficacy.
- **Verify** that the contaminant plume is not expanding.
- **Ensure** no unacceptable impact to downgradient receptors.
- **Confirm** attainment of final remediation objectives.

⚠️ **Safety Constraint:** MNA is considered a remedy like any other in CERCLA enforcement. Cleanup goals specified in the **Record of Decision (ROD)** must be met throughout the entire plume, not just at selected wells.

Framework for Statistical Evaluation

The methodology presented in this report is divided into two distinct phases:

Phase 1: Pre-Selection Analysis

- **Timing:** Best undertaken during site characterization before MNA is formally selected.
- **Purpose:** Determines if natural processes are capable of reaching goals in a reasonable period.
- **Technique:** Uses **regression analysis** to extract rate constants and estimate cleanup dates.

Phase 2: Performance Monitoring

- **Timing:** Conducted after MNA selection, specifically during five-year review cycles.
- **Purpose:** Verifies ongoing performance and determines if recent attenuation is adequate to meet the ROD date.
- **Technique:** Compares actual concentrations to **interim goals** to estimate the probability of meeting the final deadline.

Geohydrological Prerequisites

Before applying statistical methods, the engineer must verify the integrity of the data source:

- **Well Representativeness:** Wells must adequately characterize the plume both vertically and horizontally.
- **Flow Stability:** Directions of groundwater flow must be stable; shifts can be falsely interpreted as "attenuation".
- **Well Condition:** Deterioration of the monitoring well can lead to unreliable data.

💡 **Design Tip:** Statistical analysis is only as reliable as the data subjected to it. If the monitoring network is insufficient, the resulting forecasts will be technically indefensible.

Data Analysis Prior to MNA Selection

Phase 1 analysis aligns with the **OSWER Directive** three-tiered approach. It provides the "first line of evidence" by demonstrating a clear and meaningful trend of decreasing concentration over time.

- **Rate Constants:** Regression provides a precise definition of trends.
- **Target Dates:** If the ROD does not specify a date, Phase 1 can be used to select one by extrapolating the historical record.

🧮 **Calculation Note:** When using regression to select a target date, engineers must account for uncertainty. If the rate of attenuation continues as in the past, half the time the true cleanup date will be further in the future than the average predicted date.

Data Analysis After MNA Selection

Phase 2 accounts for the fact that attenuation rates are not static. Changes can occur due to:

- **Water Table Fluctuations:** High water can inundate residual contamination in the unsaturated zone.
- **Substrate Depletion:** Bacteria may exhaust necessary substrates like molecular hydrogen or sulfate.
- **Active Measures:** Source control, biostimulation, or bioaugmentation will interfere with natural attenuation trends.

⚠️ **Safety Constraint:** Evaluation of MNA should be restricted to periods before active remediation begins or after its benefits have been fully realized to avoid skewed results.

Checkpoint Quiz

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1. **When is Phase 1 data analysis most appropriately conducted?**
   a) Only after the cleanup goal has been exceeded.
   b) During performance monitoring after the ROD is signed.
   c) During site characterization before MNA is selected as the remedy.
   d) Only when a site has no active source areas.

Answer: (c). Phase 1 is best undertaken before MNA is selected as part of the remedy.

2. **According to the OSWER Directive, what is considered the "first line of evidence" for MNA?**
   a) Documented institutional controls.
   b) Microcosm studies showing biodegradation.
   c) Historical data demonstrating a clear trend of decreasing contaminant concentration.
   d) Verification that the plume is expanding laterally.

Answer: (c). The first line of evidence is historical data demonstrating a clear and meaningful trend of decreasing contaminant mass or concentration.

3. **Why is groundwater flow stability critical for statistical MNA evaluation?**
   a) Changes in flow direction can cause a plume to shift away from a well, creating a false impression of attenuation.
   b) Flow stability is required to calculate the water table height.
   c) Unstable flow prevents the use of biostimulation.
   d) Flow stability ensures that source remediation is 100% effective.

Answer: (a). Shifts in groundwater direction can be falsely interpreted as "attenuation" because the plume centerline moves away from the monitoring well.

Module 2: Illustration of the First Phase of Analysis

Learning Objectives

By the end of this section, you will be able to:

- **Evaluate** the spatial distribution of contaminants across a monitoring well transect to identify "hot spots".
- **Determine** the appropriate rate law (zero-order vs. first-order) for calculating natural attenuation based on historical monitoring data.
- **Calculate** the projected date to achieve cleanup goals using regression analysis and first-order rate constants.

Executive Summary: The First Phase of Analysis focuses on determining if natural attenuation processes can realistically achieve concentration-based cleanup goals within a required timeframe. This is accomplished by identifying the rate law, calculating rate constants via linear regression, and projecting future concentrations, provided that the geohydrological framework (groundwater flow and monitoring network) is verified as stable.

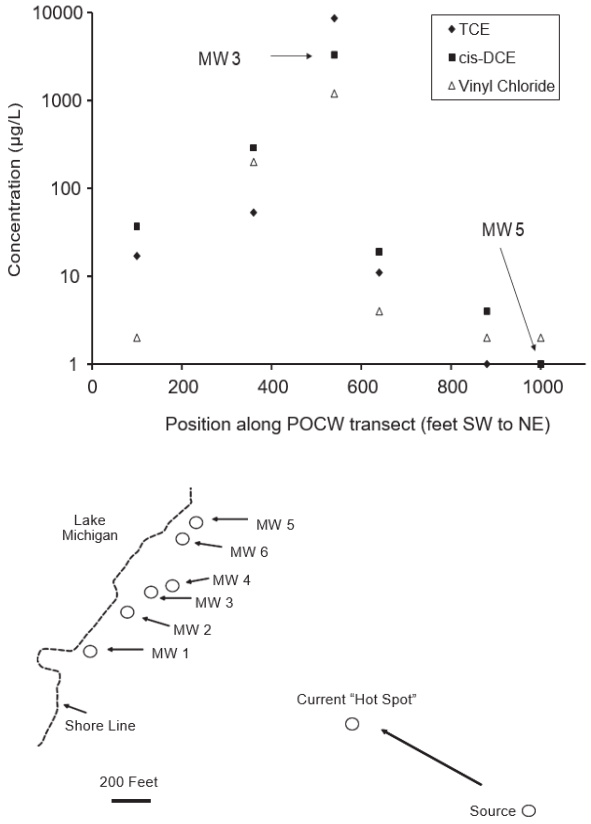

Figure 1. Distribution of TCE, cis-DCE and Vinyl Chloride in the most contaminated well in a transect of monitoring wells arranged between a source of contamination of TCE in ground water and Lake Michigan.

Table 1. Maximum concentrations of TCE, cis-DCE and Vinyl Chloride in a transect of monitoring wells (12/11/2000 to 10/03/2003).

Monitoring Well	Depth	TCE	*cis*-DCE	Vinyl Chloride
		fg/L	fg/L	fg/L
MW-1B	Shallow	18	4	2
MW-1A	Deep	17	37	2
MW-2B	Shallow	10	3	2
MW-2A	Deep	53	290	200
MW-3C	Shallow	8600	3300	1200
MW-3B	Intermediate	2300	3200	2200
MW-3A	Deep	20	1900	1500
MW-4C	Shallow	18	12	2
MW-4B	Intermediate	11	19	4
MW-4A	Deep	2	1	4
MW-5B	Shallow	1	1	2
MW-5A	Deep	1	1	2
MW-6		1	4	2

Identifying the Rate Law for Natural Attenuation

Attenuation typically follows a **first-order rate law**, meaning the rate of change is proportional to the current concentration.

Equation 1 (First-Order Rate):

$$r = \frac{dC}{dt} = k[C]$$

Where:

- **r** = Rate of change in concentration (fg/L per year)
- **C** = Concentration of contaminant (fg/L)
- **k** = First-order rate constant (1/year)

Equation 2 (Integrated First-Order):

$$ln[C] = kt + ln[C_0]$$

Where:

- **t** = Interval of time
- **C** = Final concentration
- **C0** = Initial concentration

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