## APPLICATION OF AN INNOVATIVE VISUALIZATION METHOD FOR DEMONSTRATING INTRINSIC REMEDIATION AT A LANDFILL SUPERFUND SITE

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#### ABSTRACT

A visualization method is utilized as part of the assessment of intrinsic remediation for a landfill Superfund Site. Radial diagrams aligned in the same sequence as the preferentially-reduced electron acceptors are employed to depict spatial variations in redox potential relative to background conditions. Radial diagrams are also employed to simultaneously depict spatial and temporal variations for trichloroethane, 1,2-dichloroethane, 1,1-dichloroethane, and chloroethane. This visualization approach provides a more simple and illustrative demonstration of the effectiveness of intrinsic remediation than can be realized using contour maps or tabulated data. Guidance is provided for selecting the configurations of the axes for the radial diagrams.

#### **INTRODUCTION**

The utilization of intrinsic remediation requires that sound technical documentation, clearly illustrating the effectiveness of this measure, be presented to regulatory agencies and concerned citizens. Assessment of the distributions of multiple chemicals that are co-dependent on each other (such as redox indicators of biodegradation, or parent compounds and daughter products of biodegradation) can be complex and cumbersome to document. Scientific documentation of intrinsic remediation may also be difficult for a non-technical audience (e.g. the community) to understand. Incorporating visual aids as part of these assessments will provide a more convincing demonstration of the effectiveness of intrinsic remediation.

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A study was recently undertaken at a landfill Superfund Site in Michigan to support intrinsic remediation as a principal component of the final groundwater remedy. The natural attenuation of site-related contaminants (including chlorinated aliphatic hydrocarbons (CAHs) and metals) was evaluated to determine if intrinsic remediation was justified as an alternative to the groundwater pump-and-treat system specified in the Record of Decision. Multiple lines of evidence supporting the effectiveness of intrinsic remediation were previously documented. Complex conditions at the landfill site required that rigorous scientific documentation be prepared in order to present these lines of evidence to the regulatory agencies and concerned citizens.

An innovative visualization method was applied to the site data to more clearly illustrate the effectiveness of intrinsic remediation at the site. A visualization tool (SEQUENCE) was developed to facilitate the preparation of visual aids that may be used to supplement the scientific documentation. The visual analysis provided valuable insight into the complex and integrated processes governing intrinsic remediation at the site. The visual aids prepared using SEQUENCE provide clear and illustrative evidence supporting intrinsic remediation as an effective alternative to groundwater pump-and-treat. This paper summarizes the application of SEQUENCE for visually demonstrating the effectiveness of intrinsic remediation at the site.

#### BACKGROUND

The biodegradation of organic compounds is coupled with the reduction of electron acceptors. Typical electron acceptors available in groundwater, in the order of those that release the greatest energy to those that release the least energy, are as follows: dissolved oxygen, nitrate, manganese (IV) and iron (III) oxide and hydroxide coatings on soil sediments, dissolved sulfate, and carbon dioxide (Baedecker and Back, 1979; Lyngkilde and Christensen, 1992a). The step-wise, or sequential reduction of these electron acceptors occurs as the groundwater redox potential becomes increasingly more reducing during the biodegradation of organic compounds.

When groundwater becomes depleted of dissolved oxygen and nitrate, conditions are sufficiently reducing for the reduction and subsequent dissolution of the manganese and iron coatings to occur. These reactions will result in the mobilization of reduced manganese and iron in groundwater. As soon as iron-rich groundwater comes in contact with dissolved oxygen, either through aeration or mixing with oxygenated recharge water, the dissolved ferrous iron (Fe(II)) will immediately oxidize to ferric iron (Fe(III)) and subsequently precipitate in the form of ferric coatings on soil sediments (Appelo and Postma, 1993). Manganese will be slower to react than ferrous iron when exposed to dissolved oxygen (Hem, 1985). However, in time it will also oxidize to form manganese coatings on soil sediments.

Iron and manganese coatings act as strong adsorbents for other metals. During the reduction and dissolution of these iron and manganese coatings (such as during the

biodegradation of landfill-related organic contaminants), the previously adsorbed metals are also mobilized into groundwater (Baedecker and Back, 1979). When the iron and manganese are later oxidized farther downgradient in the aquifer, they have the potential to co-precipitate or adsorb other metals, which makes these reactions of particular importance at landfill sites (Baedecker and Back, 1979).

Arsenic is a naturally-occurring element that is ubiquitous in the environment. Arsenic in soils and sediments is known to be tightly bound to soil constituents, especially iron (Hem, 1985). Naturally occurring arsenic in the soil may be mobilized into groundwater upon the reductive dissolution of iron coatings. Therefore, dissolved arsenic derived from naturally-occurring soil sediments may also be found in the ferrogenic zone. The mobilized arsenic may adsorb to oxidized iron upon downgradient mixing with oxygenated groundwater.

With the long-term migration of organic contaminants in groundwater, a sequence of redox zones of increasing redox potential will develop downgradient from the source area (Lyngkilde and Christensen, 1992a; Appelo and Postma, 1993). The sequence of these redox zones, in order of the closest to the farthest away from the landfill, will be as follows:

- 1. methanogenic zone;
- 2. sulfidogenic zone (sulfate-reducing);
- 3. ferrogenic zone (Fe(III)-reducing);
- 4. manganogenic zone (Mn(IV)-reducing);
- 5. nitrate-reducing zone; and
- 6. aerobic zone.

The extent of each individual redox zone is site-specific, and will depend on substrate migration pathways, kinetics of redox processes, hydraulic retention times, and the availability of various electron acceptors in groundwater. Ultimately, the site-specific distribution of redox zones downgradient from the source area will control the natural attenuation of organic contaminants in impacted groundwater (Lyngkilde and Christensen, 1992b).

## SITE SETTING

The site setting includes a 25-acre landfill in the northern portion of the site that received municipal and industrial waste from 1968 to 1980. The landfill does not have an engineered leachate collection system. Approximately 30,000 drums have been excavated from two drum disposal areas at the site. Volatile and semi-volatile organic contaminants, as well as organic-rich landfill leachate, have been transported with infiltrating water through the 75-foot thick unsaturated zone below the source areas to the unconfined, shallow aquifer underlying the site. Infiltration events and drum removal activities have resulted in the gradual depletion of contaminant mass within the source areas. Figure 1

illustrates the landfill and drum disposal area locations, shallow aquifer monitoring well locations, and groundwater elevation contours.

The site has been the subject of a number of environmental investigations. The site was added to the National Priorities List in 1984. This led to the initiation of one drum removal effort in 1988, and a second drum removal effort in 1994. A site-wide Remedial Investigation and Feasibility Study (RI/FS) was completed by the United States Environmental Protection Agency and the Michigan Department of Natural Resources in 1990. A site-wide remedy, which included the completion of drum removal activities, is currently being developed as part of the Remedial Design/Remedial Action (RD/RA) for the site.

## VISUAL ANALYSIS OF INTRINSIC REMEDIATION

A previous assessment of intrinsic remediation at the site (Carey et al., 1996) presented multiple lines of evidence that supported the effectiveness of this remedial measure, including:

- 1. reduced redox potential downgradient of the source areas, indicating that biodegradation of site-related organic compounds was occurring;
- 2. plume conditions at steady-state or receding conditions (based on historical trends in total chlorinated ethane and ethene concentrations); and
- 3. decreasing flow path concentrations of individual CAH compounds.

Tabulated data were previously utilized to demonstrate these lines of evidence. An additional analysis has since been conducted to visually demonstrate these lines of evidence in a clear and succinct manner. The innovative visualization method used for this analysis is described below. The visual aids demonstrating these lines of evidence are presented, advantages that can be realized by applying this visualization method to intrinsic remediation assessments are discussed, and guidelines for applying this visualization method are provided.

## **Visualization Method**

Contour maps and tabulated data are typically used for presenting spatial and temporal variations in chemical distributions. However, site contour maps are difficult to interpret because of the large extent and variability of the multiple source areas, combined with the relatively low density of the site monitoring network that is typical for non-research sites. It is difficult to demonstrate the co-dependent fate and transport of redox parameters, or CAH parent compounds and daughter products, based on individual contour maps. An analysis of spatial and temporal trends based on tabulated data is a tedious undertaking, and does not easily illustrate trends that support intrinsic remediation.

As an alternative to conventional methods, an innovative visualization program (SEQUENCE) was developed. SEQUENCE was used to prepare visual aids that clearly illustrate spatial variations in redox conditions relative to background conditions at the site. SEQUENCE was also used to prepare visual aids that simultaneously illustrate spatial and temporal trends for multiple CAH compounds detected in the shallow aquifer at the site.

SEQUENCE was designed to plot radial diagrams representing measured concentrations, or calculated molarity values, for three or more chemicals. Each radial diagram consists of multiple axes (one for each chemical) extending radially around a uniform origin. SEQUENCE can be used to plot multiple values (concentrations or molarities) on each axis, so that one radial diagram can represent data for multiple monitoring wells, or data for one monitoring well corresponding to multiple sampling events. The individual axes for each radial diagram are aligned at user-specified angles around the origin.

SEQUENCE requires the specification of a configuration for each axis, including definition of the following: axis scale (log or normal); data range (minimum and maximum values); and the direction of increasing concentration or molarity (i.e. radially inward toward the origin, or radially outward away from the origin). SEQUENCE also requires specification of the origin coordinates for each radial diagram, to facilitate the plotting of multiple radial diagrams (each representing one monitoring well) directly onto a site map.

## **Redox Zone Evaluation**

The previous redox zone evaluation (Carey et al., 1996) was based on an analysis of the average oxygen concentrations and redox potential for background, boundary, and downgradient monitoring wells. The findings of this general evaluation were that the redox potential is:

- aerobic (oxidizing) upgradient of the potential source areas;
- anaerobic (reducing) directly downgradient of the source areas; and
- increasingly more oxidizing with increasing distance from the source areas.

The measured reduction in redox potential downgradient from the source areas (relative to background conditions) provided an important line of evidence which indicated that site-related organic compounds are undergoing biodegradation downgradient from the source areas.

SEQUENCE was used to prepare visual aids that clearly illustrate the above findings. These visual aids were also used to present additional insight into the spatial variation in redox conditions at the site, and to visually demonstrate the correlation between arsenic and iron mobility in groundwater at the site.

The redox radial diagrams prepared using SEQUENCE represent the co-dependent concentrations of oxygen, nitrate, manganese, iron, arsenic, and sulfate (i.e. redox

parameters) at individual monitoring wells. The axes of the redox radial diagrams were aligned in the same sequence as the electron acceptors that are preferentially reduced during biodegradation. To illustrate the correlation between iron and arsenic occurrence in the ferrogenic zone at the site, the axis representing arsenic was specified to lie adjacent to the axis representing iron.

The direction of increasing concentration for each axis was selected so that the background concentration for each redox parameter was plotted towards the outer extent of each axis. Oxygen, nitrate, and sulfate are detected at relatively high concentrations under background conditions; therefore, the axes representing these redox parameters are increasing in concentration in a radially outward direction from the origin of the diagram. Manganese, iron, and arsenic are at relatively low to non-detectable concentrations in groundwater under background conditions; therefore, the axes representing these parameters are increasing radially inward towards the origin of the diagram.

A log scale was used for each axis of the redox radial diagrams because most redox parameter concentrations measured in the shallow aquifer at the site varied by 2 to 3 orders of magnitude (except oxygen, which varied by less than 1 order of magnitude). The range in axis concentrations was selected based on the range in measured concentrations at the site for each redox parameter. It was not necessary to utilize a uniform range in concentrations for each axis because a comparative analysis between the relative concentrations of each redox parameter was not required.

Figure 2 presents the radial redox diagram representing the average background concentrations for the redox parameters. The arrows on Figure 2 illustrate the direction of increasing concentration for each axis (i.e. radially outward or radially inward).

Figure 3 presents a conceptual illustration of the sequential reduction in redox potential that is expected to occur in the shallow aquifer during the biodegradation of organic compounds. The radial diagram in the upper left portion of Figure 3 (Step 1) represents the background redox state. The next radial diagram in the sequence (Step 2) illustrates the depletion of oxygen which occurs during the initial stages of biodegradation. The solid portion of the radial diagram in Step 2 represents the redox parameter concentrations that would occur once oxygen has been depleted. The outer boundary of the diagram in Step 2 represents the measured background concentrations, and is included to provide a simple visual illustration of the change in redox parameter concentrations relative to background conditions.

The remaining radial diagrams on Figure 3 (Steps 3 through 6) illustrate the continuing sequential reduction of electron acceptors that will occur during biodegradation. These steps represent the sequential development of the nitrate-reducing zone, the manganogenic zone, the ferrogenic zone, and the sulfidogenic zone, respectively. The radial diagrams presented in steps 5 and 6 were prepared based on the assumption that arsenic is co-dissolved during the reduction and dissolution of iron. This will occur only under certain

conditions. Evidence of the co-dependence between arsenic and iron at the site is discussed below.

Redox radial diagrams provide a fast and simple approach for identifying redox zones at monitoring wells, and for evaluating horizontal and vertical variations in redox conditions in an aquifer. As illustrated on Figure 3, the step-wise reduction in redox potential is easily identified by the step-wise reduction in size of the solid portion of each radial redox diagram following the reduction sequence.

Figure 4 presents redox radial diagrams for shallow aquifer monitoring wells at the site. These diagrams provide a very clear and visual demonstration of the variation in redox potential at the site. The redox radial diagrams for the three background wells (MW-9, MW-18, and MW-20) illustrate that background conditions are consistent and aerobic. The redox radial diagrams also illustrate that the redox potential is reduced below background conditions along the entire width of the landfill, and that the redox potential is generally increasing with distance downgradient from the site. These easily identified trends, which are based on the measured concentrations of all redox parameters, visually demonstrate the previously documented evidence that was based on tabulated concentrations of oxygen and redox potential at background, boundary, and downgradient monitoring wells.

Examination of the redox radial diagrams presented on Figure 4 indicates that the strongest reducing conditions occur downgradient from Drum Area 1 and the landfill at monitoring wells MW-31A-94 and MW-24. The strongly reducing conditions at these monitoring wells indicates that biodegradation has occurred more extensively downgradient from Drum Area 1 than the other source areas at the site, which is expected given the past disposal operations. Visual identification of the spatial variation in reducing conditions using redox radial diagrams provides additional insight that is otherwise obtained only after tedious examination of tabulated data and/or contour maps for each individual redox parameter.

As illustrated by the redox radial diagrams presented on Figure 4, the occurrence of arsenic in groundwater exhibits a strong correlation with the occurrence of iron. At all monitoring wells where iron was not present in groundwater, arsenic was also not present. Conversely, at all but one of the monitoring wells where iron was present in groundwater, arsenic was also present (MW35-94 being the exception). This trend suggests that arsenic is co-dissolved into groundwater during the reduction and dissolution of iron, and that arsenic adsorbs to oxidized iron coatings upon mixing with oxygenated groundwater downgradient from the site. The visual aids presented on Figures 3 and 4 can be particularly useful for illustrating this complex process to a non-technical audience.

## **Plume Conditions and Primary Flow Path Concentrations**

To present another application of this visualization method for intrinsic remediation assessments, SEQUENCE was utilized to simultaneously illustrate temporal and spatial

trends for individual chlorinated ethane compounds detected in the shallow aquifer at the site, including trichloroethane, 1,2-dichloroethane, 1,1-dichloroethane, and chloroethane.

SEQUENCE was used to prepare one CAH radial diagram for each monitoring well. Each CAH radial diagram consisted of four axes, each axis corresponding to one of the four chlorinated ethane compounds. Concentrations corresponding to 1988 and 1995 monitoring events were plotted on each axis. (Monitoring wells MW31A-94, MW32-94, MW33-94, and MW35-94 were installed in 1994; therefore, 1988 data was not available for these monitoring wells.)

Each axis of the CAH radial diagram was specified to have a log scale, with a uniform range in concentration from 1 to 100 micrograms per liter ( $\mu$ g/L). The axes were specified to have a uniform range in concentration in order to facilitate a comparison between the relative concentrations of each chlorinated ethane compound. (An analysis not presented in this paper found that the general shapes of the radial diagrams were similar regardless of whether concentration or molarity data were plotted. Therefore, concentration data were plotted for this analysis to allow for an easy comparison to groundwater criteria.)

Figure 5 presents the CAH radial diagrams for the shallow aquifer monitoring wells. Examination of these radial diagrams readily indicates that concentrations of all four chlorinated ethane compounds have decreased significantly between 1988 and 1995 at most monitoring wells, and have remained relatively stable at MW-8. Visual examination of the 1995 spatial distribution of chlorinated ethane compounds also indicates that concentrations of all four chlorinated ethane compounds are decreasing with distance downgradient from the site.

The simultaneous visualization of temporal and spatial trends for four chlorinated ethane compounds at the site provides a significantly more effective demonstration of intrinsic remediation than would be realized using multiple contour maps and tabulated data. Also, a comparison between redox radial diagrams (similar to those on Figure 4) and CAH radial diagrams (similar to those on Figure 5) would provide a convenient means of identifying whether the redox-dependent biodegradation of parent compounds to daughter products will occur.

#### SUMMARY

An innovative visualization method was applied to the intrinsic remediation assessment for a landfill Superfund Site. A visualization tool (SEQUENCE) was developed to facilitate the preparation of redox and CAH radial diagrams. The radial diagrams provide a clear and illustrative demonstration of the effectiveness of intrinsic remediation at the site. The visual analysis made it easier to present a thorough characterization of complex site conditions. The visual aids prepared using SEQUENCE provide a more convincing demonstration of the effectiveness of intrinsic remediation at the site, and provide a simple

means of explaining intrinsic remediation to a non-technical audience. Guidelines were presented for selecting axis configurations for redox and CAH radial diagrams.

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#### **Biographical Sketches**

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Figure 1 - SITE MAP

	LEGEND	Parameter	Average Concentration (mg/L)
٠	AVERAGE CONCENTRATION	0 <sub>2</sub>	6.8 9.6
0	METHOD DETECTION LIMIT (ANALYTE NOT DETECTED ABOVE METHOD DETECTION LIMIT)	Mn(I) Fe(I) As SO <sub>4</sub>	<0.02 <0.1 <0.001 39.7
NOTE	<ol> <li>ALL CONCENTRATIONS EXPRESSED IN mg/L.</li> <li>AVERAGE CONCENTRATIONS CALCULATED BASED ON MEASURED CONCENTRATIONS AT MONITORING WELLS MW-9, MW-18, AND MW-20.</li> </ol>		



# Figure 2 - BACKGROUND REDOX CONCENTRATIONS



Figure 3 - CONCEPTUAL REDUCTION SEQUENCE



Figure 4 - REDOX RADIAL DIAGRAMS



Figure 5 - CAH RADIAL DIAGRAMS