**Verification of Active and Passive Groundwater Remediation Efforts**

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The verification of ground-water contamination remediation efforts requires thorough documentation of subsurface conditions before, during, and after cleanup efforts have ceased. The documentation includes proof of: reduction of risk to human or environmental health, achievement of regulatory cleanup concentration goals in soil, gas or liquid media, or verification of continued approach to background environmental quality conditions. Meeting any one or all of these requirements calls for a comprehensive approach to the design and operation of remediation efforts with an emphasis on the monitoring of environmental conditions. These tasks are most challenging for in-situ remediation efforts which employ active (i.e., pumping or vacuum application) rather than passive (i.e., natural water and vapor gradient) conditions.

VERIFICATION OF ACTIVE AND PASSIVE GROUND-WATER CONTAMINATION REMEDIATION EFFORTS

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ABSTRACT

The verification of ground-water contamination remediation efforts requires thorough documentation of subsurface conditions before, during and after cleanup efforts have ceased. The documentation include include proof of: reduction of risk to human or environmental health, achievement of regulatory cleanup concentrations goals in soil, gas or liquid media, or verification of continued approach to background environmental quality conditions. Meeting any one or all of these requirements calls for a comprehensive approach to the design and operation of remediation efforts with an emphasis on the monitoring of environmental conditions. These tasks are most challenging for in-situ remediation efforts which employ active (i.e., pumping or vacuum application) rather than passive (i.e., natural water and vapor gradient) conditions.
1. INTRODUCTION

The practice of site characterization for potential organic contaminants has evolved slowly in the past decade. Early guidelines [1,2,3], for minimal ground-water contamination detection monitoring (i.e., monitoring wells upgradient and downgradient) have been applied to many sites of potential concern from detection through remedial action selection phases.

This minimal approach has often been applied regardless of the physicochemical characteristics of contaminant mixtures or the complexity of the hydrogeologic setting. For soluble inorganic constituents, this approach may be adequate for detection. Assessment efforts require substantially more comprehensive approaches. For organic contaminant detection and assessment (i.e., determination of the nature and extent of contamination) efforts, wells alone have been found to be inadequate monitoring tools. This paper focuses on the monitoring needs for remediation principally by in-situ biological methods for volatile organic compounds present in hydrocarbon fuels and organic solvents. Recognition of the value of subsurface soil vapor surveys for volatile organic components of fuel and solvent mixtures have generated a flurry of modified, monitoring well-based site characterization approaches [4]. However, these approaches to site characterization and monitoring network design suffer from the failure to identify the total mass of contaminant in the subsurface for three main reasons.

First, although volatile organic compounds (VOCs) are mobile in ground-water and frequently early indicators of plume movement [5], their detection via vapor or well samples and apparent aqueous concentration distribution does not identify the total mass distribution of organic contaminant [6]. Secondly, efforts to correlate observed soil vapor or ground water VOC concentrations with those in subsurface core samples have often been unsuccessful. This is because current bulk jar collection/refrigeration at 4°C guidelines for solid core samples for VOC analyses lead to gross negative errors [7]. Thirdly, "snapshots" (i.e., one-time surveys) of background and disturbed ground-water chemistry conditions have been interpreted as "constant" ignoring temporal variability in subsurface geochemistry.

The result of the slow improvement in site-characterization and monitoring practices has often been the very low probability detection of the source of mobile organic contaminants. This outcome may be followed by the misapplication of risk-assessment and remediation models.

Nonetheless, there exist good reasons for a more optimistic view for the future reliability of site characterization and monitoring efforts.

2. ACTIVE AND PASSIVE REMEDIATION APPROACHES

Active in-situ remediation efforts generally involve the control of subsurface ground-water or vapor flow. Also they rely on the application of a suite of physical, chemical, and microbiological processes to destroy or transform contaminants to less harmful or less mobile chemical constituents. The most effective active remediation schemes sustain hydraulic (ground-water) or pneumatic (vapor) control within the zone of treatment. This facilitates contaminant removal or transformation but calls for careful design of an active remediation-based monitoring system. Such levels of control have most often been achieved in "closed-loop" treatment designs where extracted fluids are returned to the subsurface treatment zone. In these instances it is necessary to monitor both the process stream and in-situ environmental conditions for concentrations of parent compounds and transformation products. Linked to net flow and the volume of the treatment zone, these monitoring data provide the basis for estimates of the net removal/transformations of the original contaminants. The reliability of these data is critical to the verification of cleanup performances.

Passive remediation efforts rely on intrinsic biological and/or chemical processes to mediate the destruction or transformation of contaminants. Though they may take more time to achieve acceptable levels of contaminant removal than active methods, the existing monitoring design from detection or assessment phases of the project may need only slight modification as to sampling location, frequency and selection of monitoring parameters. This approach may significantly reduce the cost of remediation.

The shortcomings of previous contaminant detection and assessment monitoring efforts have been recognized. New guidelines and recommendations on network design and operations will lead to more comprehensive, cost-effective site characterization [7,9] in general. Also, excellent reviews of characterization and long term monitoring needs and approaches in support of in-situ remediation efforts should guide us in this regard [10,11]. Site characterization efforts provide a basis for long term monitoring design and actually continue throughout the life of a remediation project.
Active and passive in-situ bioremediation approaches have been applied frequently to subsurface cleanups of organic contaminants (e.g., fuels, solvents, pesticides, etc.). The monitoring measures for verification of bioremediation performances have been identified as: the documented decline of contaminant concentrations, identification of favorable conditions (e.g., substrate, nutrient, pH, electron-acceptors) for microbial activity, demonstration of an active microbial population capable of transforming the major contaminants, and the identification of intermediate break-down or end-products in the subsurface. The supply of suitable electron acceptors (e.g., O₂, NO₃⁻, FeIII, SO₄²⁻, etc.) may be the crucial element in successful in-situ remediation efforts.

While these measures are necessary, they are not sufficient to establish the remedial effectiveness or performance of in-situ methods. The minimal measures noted above must be integrated into a mass-balance for contaminants and transformation products. A number of inorganic and organic indicators of subsurface transformation can be used to permit the approach to mass balance for specific organic contaminants. Table 1 shows various example monitoring indicators appropriate for solvent and fuel contamination situations where transformations occur under known limits of oxidation-reduction conditions.

<table>
<thead>
<tr>
<th>General Conditions</th>
<th>Contaminant Mixture</th>
<th>Inorganic</th>
<th>Organic General</th>
<th>Organic Specific</th>
</tr>
</thead>
<tbody>
<tr>
<td>aerobic (oxic)</td>
<td>Gasoline, Benzene, Toluene, Xylene, Alkylbenzenes</td>
<td>CO₂, O₂, NO₃⁻, NO₂⁻, FeII</td>
<td>low-molecular wt. aromatic acids, organic acids</td>
<td>Trichloroethylene, CH₄-methane, Dichloroethylene, Vinyl chloride, C₂H₄-ethylene, C₂H₂-methane</td>
</tr>
<tr>
<td>anaerobic (anoxic)</td>
<td>Tetrachloroethylene, Trichloroethylene</td>
<td>NH₃, FeII</td>
<td>low-molecular wt. organic acids, Trichloroethylene</td>
<td>Dichloroethylene, Vinyl chloride, C₂H₄-ethylene, C₂H₂-methane</td>
</tr>
</tbody>
</table>

TABLE 1 General Monitoring Indicators for Organic Contaminant Mixtures

It should be noted that subsurface redox conditions are not in chemical equilibrium and that transitional environments exist where intermediate transformation product stability may be significant [8].

The use of these indicators along with monitoring the concentration of the original compounds provides a more comprehensive approach to verifying remediation performance. There are relatively few examples of the mass balance approach, since there may be multiple pathways for field microbial transformation and the reaction products may be unknown. The pathways for microbial transformation are being delimited by a combination of field and laboratory experiments. Also the suite of reaction products are being determined by advanced analytical methods which will support the mass balance approach.

3. ADVANCED SITE CHARACTERIZATION AND MONITORING

How do we proceed to estimate the potential for subsurface intrinsic bioremediation success and track its performance into the future? Clearly, we should seek to design technically-defensible characterization and monitoring networks which will provide reasonable estimates of the in-place contaminant distribution over time. A dynamic, ongoing site characterization effort therefore includes objectives to:

1) identify the spatial distribution of contaminants, particularly their relative fractionation in subsurface solids, water, and vapor, along potential exposure pathways recognizing that the mass of contaminants frequently resides in the solids;
2) determine the corresponding spatial distribution of total organic matter since overall microbial activity and disruptions in subsurface geochemical conditions (and bioremediation indicators) are due to the total mass of reactive organic carbon;
3) estimate the temporal stability of hydrogeologic and geochemical conditions which may favor microbial transformations in background, source and downgradient zones during the first year of characterization and monitoring;
4) derive initial estimates of net microbial transformations of contaminant-related organic matter over time which may be built into the long-term monitoring network design.

The first three objectives establish the environment of major contamination and the conditions under which bioremediation may occur; the latter two objectives are vitally important since the evaluation of the progress of intrinsic bioremediation processes depends on distinguishing...
compound "losses" due to dilution, sorption and chemical reactions from microbial transformations. This approach has been suggested emphatically by Wilson [10] and was recently developed into a technical U.S. Air Force (USAF) protocol by Wiedemeier, et al. [11].

The latter reference focuses directly on the implementation of intrinsic remediation for dissolved fuel contamination in ground water. The general approach is shown in Figure 1 which has been modified from the original work. The USAF Protocol [11] has as its goals the collection of data necessary to support:

1.) Documented loss of contaminants of the field scale,
2.) The use of chemical analytical data in mass balance calculations, and
3.) Laboratory microcosm studies using aquifer samples collected from the site.

These data, if collected in three dimensions for an extended period time should be sufficient to successfully implement intrinsic remediation [12]. The data collected in the initial site characterization effort (Figure 1) support the development of a site-specific conceptual model. This model is a three-dimensional representation of the ground water flow and transport fields based on geologic, hydrologic, climatologic, and geochemical data for a site. The conceptual model, in turn, can be tested, refined and used to determine the suitability of intrinsic remediation as a risk-management strategy. The validity of the conceptual model as a decision tool depends on the complexity of the actual hydrogeologic setting and contaminant distributions relative to the completeness of the characterization database. The USAF Protocol is quite comprehensive in identifying important parameters, inputs and procedures for data collection and analysis. The major categories of necessary data are listed in Table 2 from the USAF Protocol [11]. Detective monitoring datasets available prior to in-depth site characterization are more likely to contain contaminant-related information rather than the three-dimensional aquifer property, hydrogeologic or geochemical data needed to formulate a conceptual model. A recognition of the variability inherent in these parameter distributions is critical to site-characterization efforts.

![FIGURE 1 Intrinsic Remediation Flow Chart](image-url)
FRACTIONATION AND SPATIAL EXTENT OF CONTAMINATION

1. Extent and type of soil and ground water contamination
2. Location and extent of contaminant source area(s) (i.e., areas containing free- or residual-phase product)
3. The potential for a continuing source due to leaking tanks or pipelines

HYDROGEOLOGIC AND GEOCHEMICAL FRAMEWORK

4. Ground water geochemical parameter distributions (Table 3)
5. Regional hydrogeology including:
   - Drinking water aquifers and
   - Regional confining units.
6. Local and site-specific hydrogeology, including:
   - Local drinking water aquifers;
   - Location of industrial, agricultural, and domestic water wells;
   - Patterns of aquifer use;
   - Lithology;
   - Site stratigraphy, including identification of transmissive and nontransmissive units;
   - Grain-size distribution (sand vs. silt vs. clay);
   - Aquifer hydraulic conductivity determination and estimates from grain-size distributions;
   - Ground water hydraulic information;
   - Preferential flow paths;
   - Location and type of surface water bodies; and
   - Areas of local ground water recharge and discharge.
7. Definition of potential exposure pathways and receptors.

TABLE 2
Site Specific Parameters to be Determined during Site Characterization (modified from Reference 11)

3.1 SAMPLING IN SPACE

The initial site characterization phase should be designed to provide spatially dense coverage of critical data over volumes corresponding to ten to one-hundred year travel times along ground water flow paths. The "volume-averaged" values of the contaminants, hydrogeologic and geochemical parameters within zones along the flow path(s) should be derived from large enough datasets to permit estimation of statistical properties (e.g., mean, median, correlation distance, variance, etc.). Specifically, this means that the datasets for derived mass loadings of contaminants, aquifer properties, and geochemical constituents (Table 3) derived from spatial averages of data points must include approximately 30 or more data points [13,14,15]. Indeed, this minimum dataset size strictly applies to points in a plane. Two major decisions which must be made with regard to how spatially averaged masses of contaminants, electron donors (e.g., organic carbon, Fe²⁺, S⁰, NH₃, etc.) and electron acceptors (e.g., O₂, NO₃⁻, NO₂⁻, Fe and Mn oxides, SO₄²⁻, etc.) are to be estimated.

The first question deals with identification of the media in which the bulk of the constituent's mass resides. For aquifer properties (e.g., grain size, laboratory estimates of hydraulic conductivity, etc.) the answer is simple. In this case, the solids are clearly the media of interest. For constituents particularly VOC's which are sparingly water soluble, the bulk of the contaminant mass may in fact reside in the solids though both solids and water samples must be collected carefully.

The second question pertains to the depth interval over which "planar" data points may be averaged. With fuel-related aromatic contaminants the depth interval above and below the capillary fringe/water table interface typically exhibits order of magnitude solid-associated concentration differences. This type of situation is typified by the BTEX data shown in Figure 2 for a fire training area at the recently decommissioned Wurtsmith AFB near Oscoda, MI. In this case the bulk of the contaminant mass along the axis of a dissolved BTEX plume with concentrations less than 1000 µg/L resides in aquifer solids below the water table. In this situation, averaging data points over depths of > 0.5 m could easily lead to order of magnitude errors in estimated masses for a site. Continuous coring of subsurface soils and close interval (i.e., < 1 m) sampling of water should be considered in many VOC investigations. In order to approach this level of depth detail in sampling, the use of "push" technologies and/or multilevel sampling devices present very useful tools for site characterization.
<table>
<thead>
<tr>
<th>CONTAMINATION AREA</th>
<th>APPARENT/ GEOCHEMICAL REDOX ZONE</th>
<th>CONTAMINANT MIXTURE</th>
<th>INORGANIC CONSTITUENTS</th>
<th>INTRINSIC CONSTITUENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOURCE</td>
<td>REDUCING ANOXIC</td>
<td>FUELS</td>
<td>O$_2$, CO$_2$, H$_2$S; pH, Fe$^{2+}$, HS$^-$/S$^0$, NO$_2^-$, NH$_3$, ALKALINITY</td>
<td>ORGANIC CARBONS, CH$_4$ ORGANIC ACIDS PHENOLS AS ABOVE AND CHLORINATED METABOLITES ETHYLENE, ETHANE</td>
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<tr>
<td></td>
<td></td>
<td>CHLORINATED</td>
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<tr>
<td></td>
<td></td>
<td>SOLVENTS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOWNGRADIENT</td>
<td>TRANSITIONAL/ SUBOXIC</td>
<td>* FUELS</td>
<td>O$_2$, CO$_2$, H$_2$S; pH, Fe$^{2+}$ ALKALINITY, NO$_2^-$, NO$_3^-$, NH$_3$, HS$^-$/S$^0$</td>
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<td></td>
<td></td>
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<tr>
<td>UPGRADENT/FAR-</td>
<td>OXIC</td>
<td>FUELS</td>
<td>O$_2$, CO$_2$, H$_2$S ALKALINITY, Fe$^{2+}$, NO$_3^-$, NO$_2^-$, NH$_3$</td>
<td>ORGANIC CARBON, CH$_4$ ORGANIC ACIDS PHENOLS AS ABOVE AND CHLORINATED METABOLITES ETHYLENE, ETHANE</td>
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<tr>
<td>FIELD DOWNGRADIENT</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SOLVENTS</td>
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<td></td>
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</tbody>
</table>

**TABLE 3**

Target Constituents for Site Characterization in Support of Intrinsic Bioremediation

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**FIGURE 2**

Fire Training Area - BTEX Plume (µg/kg)
The approach to site characterization for chlorinated hydrocarbons is significantly more difficult. There are very few models of site characterization for these contaminants which have estimated mass loadings in specific media. Many of the previously referenced methods may work satisfactorily. However, free-phase detection, assessment and quantitation may be expected to be more a matter of luck and exhaustive sampling rather than intuition based on experience.

3.3 SAMPLING OVER TIME

VOC compounds (e.g., aromatic hydrocarbons, chlorinated solvents) are among the target contaminants which have been considered as constituents of concern in remedial investigations. Their aqueous solubility and demonstrated association with aquifer solids requires sampling of these media during the site characterization phase. This suggestion also applies to organic metabolites of complex organic mixtures (e.g., ethylene, vinyl chloride, aromatic acids, phenols). Aqueous plumes which develop subsequent to the release of these organic mixtures and by-product compounds have received the most attention in the past. The fact that the mass of these contaminants frequently resides in the solids strongly suggests that the solids should receive the most attention in the initial site characterization effort. This should also be the case for the physical, geochemical, and microbial determinations.

Initially, conventional nested monitoring wells with screened lengths of 1 meter or more will be useful for estimating the spatial extent of the dissolved plume, for delineating apparent geochemical zones and to provide water level and aquifer property (e.g., slug and pump test derived hydraulic conductivity estimates). Semi-annual to annual sampling of wells, particularly multilevels appropriately designed and completed, should be quite useful over the course of the long term monitoring program. In this vein, their use should track the dowgradient progress of risk-associated target compounds and permit testing predictions of intrinsic bioremediation effects on risk reduction.

However, proof of the effects of the net removal of specific solid-associated contaminants due to intrinsic bioremediation will depend on solid sampling and analysis at annual intervals or greater. This is because solid-associated concentration may be expected to change slowly. Unless biotransformation can be shown to be a major loss mechanism for contaminants mainly in solids over extended periods of time it will remain an area of research rather than practice.

Since very few contamination situations have been monitored intensively for periods exceeding several years, it is difficult to define specific sampling frequencies for the range of hydrogeologic and contaminant combinations which may be encountered. Sufficient to say that the adoption and future refinement of technically defensible protocols which have been developed recently will improve intrinsic remediation approaches to risk management in subsurface contamination situations.

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REFERENCES


