TABS ON CONTAMINATED SITES

Contaminated Sites Program - Federal Sites

This is one in a series of Technical Assistance Bulletins (TABs) prepared by
Environment Canada-Ontario Region for Federal Facilities operating in Ontario.

TAB #19

Intrinsic Remediation- An Introduction

DESCRIPTION:
Intrinsic Remediation is a potential remedial option for the contaminant and reduction of the mass and concentration of petroleum hydrocarbons at contaminated sites, with no significant risk to environmental and/or human receptors. It is an innovative remedial approach that relies on natural attenuation processes to remediate contaminants in the subsurface. This approach contrasts with active (engineered) remedial methods which require that contaminants be removed from impacted media or be destroyed *in situ* using external means to achieve the desired clean-up level.

1. INTRINSIC REMEDIATION AS A REMEDIAL OPTION

1.1 Introduction

Intrinsic remediation (IR) relies on naturally occurring processes to reduce contaminant concentrations in hydrocarbon-impacted soil and groundwater. IR has also been referred to as Remediation by Natural Attenuation (RNA). Natural processes occur continuously in the subsurface even during active remedial work. Evidence presented in two comprehensive studies by NRC (1994) and Lawrence Livermore National Laboratory (1995) suggests that natural bioremediation was often the dominant process in attenuating petroleum hydrocarbons in groundwater at impacted sites both with and without active forms of remediation in place. The goal of an IR assessment is to evaluate whether these natural processes ***alone*** are sufficient to meet applicable criteria prior to impact upon potential on-site and off-site receptors (e.g. water wells, streams and lakes). In some instances, IR may be applied in conjunction with a conventional remedial technology such as source removal, or could be used as part of a risk assessment. Intrinsic remediation of groundwater is typically the primary focus, considering that groundwater is the most significant pathway to potential receptors.

IR is most commonly applied at hydrocarbon-contaminated sites, because petroleum hydrocarbons tend to degrade more readily than many other contaminants (e.g. chlorinated solvents). At such sites, the primary parameters of concern from the perspective of mobility and toxicity are the monoaromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes (BTEX)). These compounds are also relatively soluble and susceptible to biodegradation in the subsurface. As a result, the primary focus of IR assessments has been to determine the natural attenuation of the BTEX compounds. Other hydrocarbons, which are generally less mobile and less toxic, however, also undergo biodegradation, resulting in the consumption of electron acceptors. The presence of liquid petroleum hydrocarbons at a site does not necessarily preclude the use of IR.

Biodegradation of BTEX/petroleum hydrocarbon constituents by indigenous subsurface microbes appears to be the primary mechanism for intrinsic remediation. During biodegradation, microbes transform available nutrients, including hydrocarbons, into forms useful for energy and cell production. Microbes obtain this energy by facilitating the transfer of electrons from electron donors to electron acceptors. Electron donors include natural organic material and petroleum hydrocarbons.

Electron acceptors in groundwater include dissolved oxygen, nitrate, iron (III), sulphate and carbon dioxide. The use of electron donors by microbes begins with dissolved oxygen (aerobic conditions). Aromatic hydrocarbons undergo both aerobic and anaerobic biodegradation. The field parameters which indicate the presence of aerobic and anaerobic conditions are dissolved oxygen (D.O.) and the oxidation-reduction (or REDOX) potential.

IR has also been applied successfully to sites impacted with chlorinated solvents and other organic contaminants (e.g. dinitrotoluene, Bradley *et al*., 1997). The focus of this Technical Assistance Bulletin (TAB) is on petroleum hydrocarbons in groundwater; however, similar procedures can be used for other contaminants if the same lines of supporting evidence of natural attenuation are obtained.

This TAB presents a recommended course of action to enable proponents to scientifically apply the case for intrinsic remediation as a viable remedial option at hydrocarbon-contaminated sites, typically associated with fuel leaks or spills. It is recommended that the IR approach be evaluated in advance of engineered approaches because of the potentially significant savings in remedial efforts at low-risk sites. There are limitations to the IR approach (discussed in Section 5) and it must be applied on a site-by-site basis. This TAB is not designed to be a comprehensive document outlining every procedure and rationale required for an IR assessment to be undertaken. The reader is referred to the 'references and sources' section for further detailed information.

1.2 Advantages of IR

The major advantages of IR relative to conventional engineered technologies for remediation of hydrocarbon-fuel-contaminated media at low-risk sites (e.g. no exposure pathways completed to receptors) are:

1.2.1 Contaminants (petroleum hydrocarbons) are transformed to innocuous by-products (CO_2 and H_2O) and are not simply transferred elsewhere.

1.2.2 It is always non-intrusive and poses little or no disturbance to nearby surface activities or facilities.

1.2.3 Engineered technologies can result in the creation of additional contaminant pathways to potential receptors (e.g. air emissions, subsurface vapour migration).

1.2.4 It is typically more cost effective than engineered methods.

1.2.5 Limitations of mechanized remediation (e.g. equipment failure) are completely avoided.

1.2.6 Hydrocarbon compounds that are most toxic and mobile (e.g. BTEX) are also generally most susceptible to biodegradation.

1.2.7 Where IR is not suitable as the sole remedial method, it can be used readily in conjunction with other technologies at any time during the site's remediation life-cycle.

1.2.8 Data obtained during an IR assessment can be very useful in evaluating other remedial methods (e.g. oxygen requirements), contaminant fate, transport mechanisms and exposure pathways.

1.3 Supporting Evidence

In order to scientifically support intrinsic remediation, the proponent must demonstrate that natural degradation is occurring at rates sufficient enough to be protective of human health and the environment. Evidence to support IR can be derived from a documented loss or reduction in the mass of contaminants in the field. In addition, contaminant and geochemical analytical data, whether direct or conclusive indirect evidence of microbiological activity, groundwater flow, transport and degradation modelling, can be used to support IR.

These lines of evidence are discussed in the subsequent sections of this bulletin. The overall IR Assessment Procedure is presented in a flow chart in Appendix A.

2. SAMPLING PROTOCOLS AND SITE INSTRUMENTATION REQUIREMENTS

Prior to conducting any type of remedial action at a contaminated site, a comprehensive site assessment must be undertaken. This assessment identifies the particular characteristics of the site including the source(s), nature and extent of contamination. Site assessment procedures are outlined in **TAB #2**: *Site Assessment Procedures*.

During the Site Assessment phases, strict quality assurance/quality control procedures must be adhered to in order to produce reliable data for site characterization and remediation purposes. Such procedures are outlined in **TAB #4**: *Sampling and Analysis of Hydrocarbon Contaminated Soil*; **TAB #5**: *Sampling and Analysis of Hydrocarbon Contaminated Groundwater*); and documents such as *Subsurface Assessment Handbook (*Waterloo Centre for Groundwater Research-University of Waterloo, 1994).

One key aspect of the IR assessment procedure is the collection of high quality data from all areas of the site including background or upgradient conditions. At least one upgradient well and one or more wells located in unimpacted zones downgradient of the contaminated area are required to characterize background conditions. This information is essential for showing that natural attenuation processes are occurring and determining the future natural attenuation capacity of the groundwater flow system in the direction in which the dissolved hydrocarbon plume migrates. In addition, the front (leading edge) of the plume should be determined as precisely as reasonably possible.

One of the main goals of the Site Assessment procedure is to obtain enough information to determine whether the plume is shrinking, stable or expanding. The determination of the status of the plume is the primary line of evidence that is used to determine the potential effectiveness of IR. At most sites, either groundwater monitoring data over a period of years and/or precise information regarding when the contaminants were released are required to determine the status of a plume.

3. CHEMICAL ANALYSIS REQUIREMENTS

In addition to the key analytical parameters to be tested for at hydrocarbon-contaminated sites, several other chemical parameters must be defined across the site to aid in the IR assessment. Typical contaminant analyses at hydrocarbon sites are recommended in **TAB #4** and **#5** (BTEX, TPH [light and heavy], phenols, metals and polycyclic aromatic hydrocarbons [PAHs]). In order to assess the assimilative capacity of a natural system, the various parameters in the following sections must also be determined.

3.1 Field analyses

The following groundwater analyses are essential to an IR assessment study and must be measured in the field:

- Dissolved oxygen (D.O.)
- REDOX potential (RP)
- Temperature
- pH
- Electrical Conductivity

Ideally these parameters should be measured using a flow-through cell and electrodes in the field. Other methods using down hole probes and field preservation techniques are also available for selected parameters.

3.2 Field and/or Laboratory Analyses

The following parameters are important to completing a comprehensive IR assessment study and, where possible, they should be measured in the field.

<u>Soil/Aquifer Material</u>

- Fraction of organic carbon (f_{oc}) sample(s) from background unimpacted area.
- Available nutrients: ammonia, total Kjeldahl nitrogen (TKN), and phosphorus.

<u>Groundwater</u>

- Nitrate (NO_3^-)
- Nitrite (NO_2^-)
- Sulphate (SO_4^{2-})
- Sulphide (HS^-)
- Iron (Fe [II] and total iron), dissolved
- Alkalinity, dissolved CO_2 (HCO_3^-)
- Methane (CH_4)
- Chloride (Cl^-)

Temperature, pH and conductivity are standard parameters which are measured when ground-water sampling is conducted. They provide an indication of well purging efficiency, and results from different wells can be used to determine whether or not wells are completed in the same groundwater zones.

Dissolved oxygen concentrations define aerobic and anaerobic conditions. REDOX potential identifies oxidizing and reducing conditions in groundwater. After dissolved oxygen is consumed, nitrate, iron (III) and sulphate may serve as alternative electron acceptors. Carbon dioxide is a product of aerobic hydrocarbon degradation whereas methane, sulphide and iron (II) are the products of anaerobic biodegradation of petroleum hydrocarbons. A detailed discussion of these processes is presented in **TAB # 20**: *Intrinsic Remediation - Contaminant Transport and Attenuation Mechanisms*. The analysis and application of these data in the IR approach is presented in Section 4.

4. DATA ANALYSIS REQUIREMENTS

As indicated earlier, studies of intrinsic remediation typically focus on groundwater because it is usually the most significant pathway that transports petroleum hydrocarbon releases to potential sensitive receptors. Based on the intrinsic remediation protocol developed for the U.S. Air Force (Wiedemeier *et al*., 1995 *Draft*), generic evidence that can be used to support intrinsic remediation includes the following:

1. *Documented loss of contaminants along a flowpath at the site:*
   Involves the use of changes in groundwater concentrations over time in conjunction with the hydrogeological setting to show that a reduction in the total mass of the contaminants has been occurring at the site.

2. *Data analysis and interpretation of chemical analytical data:*
   Involves the use of chemical data to show that a decrease in contaminant and electron acceptor (e.g. dissolved oxygen) concentrations over time can be correlated with increases in metabolic by-product concentrations (e.g. carbon dioxide). Chemical data can also be used to determine the future assimilative capacity of a groundwater system.

3. *Laboratory microcosm studies:*
   Involve the use of laboratory microcosms to show that indigenous microbes in the subsurface are capable of degrading site contaminants. Studies also provide information on degradation rates.

4. *Fate and transport modelling:*
   Involves the use of numerical models such as BIOPLUME III and Visual MODFLOW to support and predict the processes of natural attenuation.

Data analysis and interpretation are key components in developing evidence under each of these tasks.

4.1 IR Data Review and Processes

The IR process which should be implemented following a detailed site characterization is summarized below:

Step 1. Determine pathways and receptors; assess whether or not contaminant pathways to receptors are being completed.
Step 2. Assess physical and chemical data; develop conceptual model showing aerobic and anaerobic zones.
Step 3. Determine theoretical migration rates and loss of contaminant mass, and determine if actual rates are higher or lower than theoretical.
Step 4. Determine plume status: Is it shrinking, stable or expanding?
Step 5. If the plume is shrinking or stable, are there enough data to conclude that ***IR*** is a suitable method? If it is expanding, data on the rate of expansion should be obtained.
Step 6. Does comparison of background (low hydrocarbon concentrations) and plume (elevated hydrocarbon concentrations) data suggest that natural attenuation processes are active? See trends as described below (**Table 1**).

Table 1: IR Indicator Parameters Trends

BTEX/ Dissolved hydrocarbons	D.O.	NITRATE	Fe (II)	SULPHATE	SULPHIDE	METHANE	TEMP/pH	ORP
low	high	high	low	high	low	low	difference	high
elevated	low	low	high	low	high	high		low

Step 7. In the absence of sufficient information or to provide stronger supporting evidence conduct one or more of the following:
a) Assimilative capacity calculations.
b) Microcosm studies.
c) Groundwater modelling.

Step 8. Compare ***IR*** with other options.

Step 9. Select ***IR*** as the preferred option.

Step 10. As required, develop and implement the Long-Term Monitoring (LTM) program.

Step 11. No further action once objectives are met.

5. LIMITATIONS TO THE *IR* APPROACH

Intrinsic remediation is subject to natural and anthropogenic changes in conditions (changes in local hydrogeologic conditions, gradients, velocities, groundwater chemistry, electron acceptors, future releases, etc.). Aquifer and contaminant heterogeneity may complicate site characterization and affect the outcome of the IR assessment. The time frame for completion may be relatively long, because of the nature of subsurface reactions, microbial acclimation and growth and groundwater flow rates. Engineered remedial methods can generally be modified to account for changing conditions but IR relies mainly on natural attenuation, which is not controlled by human intervention. However, IR can be implemented alongside, or following, the use of engineered methods to achieve the desired cleanup level.

Several situations exist for which the IR approach is not recommended. These include:

1. Exposure pathways that are, or will be completed to receptors and thus present an unacceptable risk.
2. Presence of hydrocarbons in water supplies for human consumption or high risk sites (e.g. plume within capture zone of municipal well).
3. Sites where future development is likely within the attenuation zone (changes in land use or activities to include potentially more sensitive receptors) and such development cannot be prevented by institutional controls.
4. Sites that cannot be adequately characterized.
5. The presence of recalcitrant contaminants.

It may also be determined that IR is only acceptable if an additional remedial method is also applied. Changes in site conditions, whether institutional or natural, can drastically affect the outcome of an IR assessment. Examples of such changes include changes in groundwater gradients, flow directions, water levels and chemistry brought on by pumping, land-use or climate changes. Additional releases of contaminants can constitute a serious threat to the short-term effectiveness of IR.

SOURCES

Bradley, P.M., Chapelle, F.H., Landmeyer, J.E. and J.G. Schumacher. (1997) *Potential for intrinsic bioremediation of a DNT-contaminated aquifer*. Ground Water. Vol. 35, No. 1, pp. 12-17.

Lawrence Livermore National Laboratory (D.W. Rice, B.P. Dooher, S.J. Cullen, L.G. Everett, W.E. Kastenberg, R.D. Grose and M.A. Marino) (1995). *Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs)*, Lawrence Livermore National Laboratory, University of California, Livermore, CA, Submitted to the California State Water Resources Control Board and the Senate Bill 1764 Leaking Underground Fuel Tank Advisory Committee on October 16, 1995 (UCRL-AR-121762).

National Research Council (NRC) (1994). *Alternatives for Groundwater Clean-up*. National Academy Press, Washington, DC.

Waterloo Centre for Groundwater Research, University of Waterloo (WCGR-UW) (1994). *Subsurface Assessment Handbook for Contaminated Sites*. The National Contaminated Sites Remediation Program, Canadian Council of Ministers of the Environment Report CCME-EPC-NCSRP-48E, p.293.

Wiedemeier, T., Wilson, J.T., Kampbell, D.H., Miller, R.N. and J.E. Hansen (1995). *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring of Natural Attenuation of Fuel Contamination Dissolved in Groundwater (Volume 1)*, U.S. Air Force Centre for Environmental Excellence, Technology Transfer Division, Brooks Air Force Base, San Antonio, TX.

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Intrinsic Remediation Assessment Procedure