Environment Canada
Ontario Region
Environmental Protection Branch

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 #20

Intrinsic Remediation-Biodegradation

DESCRIPTION:
The concept of ‘Intrinsic Remediation’ as a remedial method allows a proponent to definitively show that natural degradation processes are sufficient to reduce the concentrations of target contaminants to below applicable regulatory criteria levels before exposure pathways to potential receptors are completed.

1. TRANSPORT AND BIODEGRADATION MECHANISMS

The environmental fate and transport of a contaminant is controlled by the compound's physical and chemical properties, the properties of the subsurface media and geochemical and biological conditions in the zone through which the compound is migrating. The *in situ* processes which determine the rate of groundwater contaminant migration and natural attenuation are:

- Physical: advection, dilution, diffusion, dispersion and volatilization.
- Chemical: chemical (abiotic) degradation reactions, sorption and desorption.
- Biological: aerobic and anaerobic bio-degradation.

These processes are discussed in detail in **TAB # 21**. All processes except advection and desorption can reduce contaminant concentrations in groundwater and therefore contribute to intrinsic remediation. The evaluation of the biodegradation processes through calculation of the assimilative capacity of a system is presented in Section 2. The hydrocarbon plume (usually defined by the BTEX compounds) should be delineated for all available monitoring episodes. It is also useful to delineate zones for the various indicator parameters noted in Sections 3.1 and 3.2 of **TAB #19**. Dissolved Oxygen (DO) and REDOX Potential (RP) data can be used to define the aerobic and anaerobic degradation zones.

In order to compare theoretical and actual contaminant transport, physical data such as hydraulic conductivity, porosity and hydraulic gradients are used to determine the average linear groundwater velocity (see **TAB #21**, Page 1). Retardation of the hydrocarbon compounds due to sorption can be estimated using the measured fraction of organic carbon. These data can then be compared to the actual migration rates determined from field data.

2. DETERMINATION OF PLUME STATUS

The status of a plume can readily be determined if sufficient historical data for a particular site are available. Detailed discussions of various techniques are presented by Wiedemeier *et al.* In general terms, the status of a plume can be determined by comparing its size at various dates, assessing the movement of the leading edge of the plume or examining historical concentration trends at individual wells. The status of the hydrocarbon source (e.g. leaking tank still in place, residual soil contamination, etc.) must be considered because it will affect the status of the plume.

Sufficient data should be available in order for one or more of these techniques to determine if the plume is shrinking, stable or expanding. In the absence of sufficient data, the proponent/ investigator should proceed to more sophisticated techniques to provide evidence in support of IR (assimilative capacity, microcosm studies or modelling). In general, shrinking or stable plumes suggest that IR is a suitable remedial option for hydrocarbon-contaminated sites. An expanding plume should be evaluated further to determine if natural attenuation will be sufficient to eventually reduce concentrations to acceptable levels before pathways to receptors are completed. An expanding plume may also indicate the need for another remedial method to be used, either alone or in conjunction with IR.

3. LABORATORY MICROCOSM TESTING

Microcosm techniques can be used as part of the IR assessment procedure. Such tests involve an evaluation of biodegradation under controlled conditions in the laboratory. Laboratory microcosm tests can provide the IR proponent with the following information:

- Information on the availability of micro-organisms (aerobic, anaerobic).
- Evidence that micro-organisms have the potential to biodegrade site contaminants.
- Possible information on degradation rates and electron acceptor requirements.

Salanitro (1993) emphasizes caution when using microbial counting techniques alone as they are often a poor indicator of biodegradation. Salanitro showed that in the presence of sufficient oxygen, BTEX biodegradation was independent of microbe numbers. Microcosm studies are often not necessary for hydrocarbon-contaminated sites because the biodegradation of petroleum-hydrocarbons (particularly BTEX) is well documented (ASTM, 1996 *Draft*). Bacteria are typically present in sufficient numbers once acclimated to a particular hydrocarbon source and limitations are more likely to arise from oxygen and/or nutrient deficiencies or elevated hydrocarbon (e.g. >25,000 mg/kg) or metal levels in soil which are toxic to micro-organisms.

4. EVALUATION OF EXPOSURE PATHWAYS AND RECEPTOR CHARACTERISTICS

An evaluation of pathways and receptors (risk assessment) forms an integral part of the IR process in order to evaluate whether the continued presence of hydrocarbon contaminants will result in unacceptable risk to human health and/or the environment.

Exposure Pathways
As a minimum, the following exposure pathways should be considered:

- Inhalation of vapours (vapours from separate phase and/or dissolved-phase groundwater plume, ambient vapours or soil vapours during excavation)
- Soil ingestion
- Dermal contact
- Water ingestion (impacted groundwater and/or surface water)

The above-noted pathways should be considered both for human receptors and in the context of potential environmental receptors (plants and animals (both aquatic and terrestrial)) and their habitats. Based on site-specific conditions, other pathways may have to be considered.

Potential Receptors
Receptors should include humans potentially impacted by one or more of the pathways noted above and behaviour characteristics (e.g. drinking water consumption, residence time, activity patterns). The need for, and extent of, an ecological risk assessment must be evaluated on a site-specific basis (see Gaudet, 1994). Both on-site and off-site receptors should be considered. Each site must be evaluated on a case-by-case basis. The IR assessment process is dependent on the identification of potential receptors and the potential for exposure pathways to be completed. If potential receptors are not present and are unlikely to exist in the future, then IR is a viable remedial option. Institutional controls may be required to ensure that exposure pathways do not develop in the future.

5. EVALUATION OF INTRINSIC REMEDIATION

Each of the processes identified in Section 1 and discussed in further detail in **TAB # 21**, has the potential for promoting and affecting natural attenuation of BTEX and other hydrocarbon parameters. **Table 1** outlines the potential site-specific mechanisms affecting contaminant fate and transport at IR sites.

As indicated in this table, some processes are more active in reducing mass loss of contaminants along the groundwater flow path than others. A semi-quantitative estimate of the mass of hydrocarbons (BTEX compounds in this example) per litre of groundwater that can be converted to carbon dioxide by aerobic and anaerobic biodegradation under the existing groundwater conditions can be determined. This factor is referred to as the assimilative capacity and represents a theoretical mass that can be biodegraded. However, the assimilative capacity does not give any indication of degradation rates.

The following subsection provides a detailed discussion of the interpretation and evaluation of intrinsic remediation to determine the assimilative capacity at a hypothetical hydrocarbon-contaminated site.

Table 1: Potential Natural Attenuation Mechanisms

Mechanism	**Description**	**Potential for BTEX Attenuation**	**Typical IR Trends**
Physical/Chemical			
Advection	Contaminants are moved by average linear velocity of flowing groundwater.	No net loss of mass.	No mass loss
Dispersion	Mechanical and molecular mixing processes reduce concentrations.	Decreases concentrations, but does not result in a net loss of mass.	No mass loss
Sorption	Contaminants partition between the aqueous phase and the soil matrix. Sorption is controlled primarily by the organic carbon content of the soil.	Sorption retards plume migration, but does not permanently remove BTEX from groundwater as desorption may occur.	Decreases in dissolved masses; proportional to organic carbon content of material.
Volatilization	Contaminants are removed from groundwater by volatilization to the vapour phase in the unsaturated zone.	Normally minor contribution relative to biodegradation. More significant for shallow or highly fluctuating water table.	Minor mass loss, proportional to permeability of material and concentration of contaminant.
Abiotic Chemical Reactions	Contaminants may be transformed into other compounds through direct chemical reactions	Chemical degradation is minor compared to biological degradation.	Minor mass loss from chemical reactions compared to biologically-mediated reactions.
Biological			
Aerobic	Microbes utilize oxygen as an electron acceptor to convert contaminant to CO_2, water, and biomass.	Most significant attenuation mechanism if sufficient D.O. is present. (D.O.• 1-2 mg/L).	Significant mass loss
Anaerobic Denitrification Fe Reducing Sulphate Reducing Methanogenic	Alternative electron acceptors NO_3^-, SO_4^{2-}, Fe^{3+}, CO_2 are utilized by microbes to degrade contaminants.	Rates are typically much slower than for aerobic biodegradation.	Moderate mass loss

6. ASSIMILATIVE CAPACITY CALCULATIONS

A key piece of supporting evidence to show that intrinsic remediation is a suitable remedial method at hydrocarbon-contaminated sites, is the determination of the assimilative capacity of a groundwater system. The evaluation of assimilative (destruction) capacity involves the determination of the theoretical ability of the groundwater system to biodegrade the dissolved hydrocarbon compounds which are present in the subsurface under both aerobic and anaerobic conditions. These calculations are based on the stoichiometric relationships outlined in **TAB # 21**. The chemical data for electron acceptor and metabolic by-product concentrations in groundwater are used to determine the assimilative capacity. An example of such a data set is presented in **Table 2**. **Table 3** presents sample calculations using the data in **Table 2** to estimate the capacity of groundwater to mineralize or assimilate dissolved BTEX chemicals.

From the calculations completed in **Table 3**, the hypothetical groundwater on site has a capacity to assimilate approximately 7.8 mg/L (7,800 µg/L) of total BTEX chemicals. In practice, if the maximum concentration of dissolved BTEX measured at a site is significantly below the assimilative capacity, IR is likely an acceptable remedial method. It suggests that there is significant capacity to reduce the concentrations of BTEX at the source and downgradient from the source. Similar calculations can be performed for hydrocarbons other than BTEX based on similar stoichiometric relationships.

7. CONCEPTUAL INTRINSIC REMEDIATION MODEL

Based on the site contaminant characterization and geochemical characteristics, a conceptual model of intrinsic remediation at a particular site should be developed. Typically, a 3-dimensional model of the subsurface groundwater flow system, contaminant source, contaminated soil zone, groundwater contaminant plume and the intrinsic remediation processes occurring in and around the contaminated zone is developed.

Two treatment zones (aerobic and anaerobic) with an intermediate transition zone can be identified. The anaerobic biodegradation treatment zone usually occurs around the main source area. It is characterized by depressed dissolved oxygen, nitrate and sulphate and elevated iron (Fe II) concentrations. The aerobic biodegradation zone typically occurs at the limits of the contaminant plume and extends in a downgradient direction. This aerobic treatment zone is characterized by elevated dissolved oxygen concentrations (D.O. >2 mg/L). A transitional zone in which the interface between the anaerobic and aerobic treatment zones fluctuates may also be present. The fluctuations are related to recharge of oxygenated waters, seasonal variations in groundwater flow and contaminant dissolution when a separate phase is present.

Once the site has been assessed and the subsequent IR evaluation is complete, it should be compared with other remedial options. Additional work such as modelling (Section 9) may be required at this time. IR may be selected based upon its effectiveness, cost or other factors. If selected, the IR process can continue until the development of a monitoring program as noted in the flow chart in the Appendix of **TAB #19**.

8. SIMULATION OF INTRINSIC REMEDIATION

Site-specific data, obtained during the assessment stages, can be incorporated into mathematical models, which in turn can be used to assess the fate and transport of the contaminants under the physical, chemical and biological processes occurring in the subsurface.

The accuracy of a simulation depends on the amount and quality of data available for calibration. Where very little or no data exist, analytical solutions may provide sufficiently accurate results. When more data are available, more processes can be included and they can be more accurately simulated, using more advanced numerical models. However, to accurately simulate Intrinsic Remediation, each of the attenuation processes outlined in **Table 1** must be represented in the model. In general, and especially for petroleum hydrocarbon sites, the most important and common process is aerobic biodegradation.

Table 2 : Example of Electron Acceptor and Metabolic By-product Concentrations for Assimilative Capacity Calculations

Electron Acceptor or Metabolic By-product	**Background Concentration (mg/L)**	**Concentration in Core of Plume (Well with Highest BTEX Concentration) (mg/L)**
Dissolved Oxygen	10.0	1.0
Nitrate	5.0	0
Iron (II)	0.01	2.0
Sulphate	20	2.0

Table 3 Example Assimilative Capacity Calculations

Dissolved Oxygen	$BTEX_{Bio.DO} = 0.32(O_B-O_M)$ Where: $BTEX_{Bio.DO}$ = reduction in BTEX concentration by aerobic respiration 0.32 = mg/L BTEX degraded per mg/L dissolved oxygen consumed O_B = background dissolved oxygen concentration (mg/L) = 10.0 mg/L O_M = lowest measured dissolved oxygen concentration (mg/L) = 1.0 mg/L $BTEX_{Bio.DO}$ = 2.9 mg/L
Nitrate	$BTEX_{Bio.N} = 0.21(N_B-N_M)$ Where: $BTEX_{Bio.N}$ = reduction in BTEX concentration via denitrification 0.21 = mg/L (average) BTEX degraded per mg/L nitrate consumed N_B = background nitrate concentration (mg/L) = 5.0 mg/L N_M = measured nitrate concentration (mg/L) = 0 mg/L $BTEX_{Bio.N}$ = 1.0 mg/L
Iron	$BTEX_{Bio.FE} = 0.05(FE_M-FE_B)$ Where: $BTEX_{Bio.FE}$ = reduction in BTEX concentration via iron reduction produced 0.05 = mg/L (average) BTEX degraded per mg/L iron (II) FE_B = background iron (II) concentration (mg/L) = 0.01 mg/L FE_M = measured iron (II) concentration (mg/L) = 2.0 mg/L $BTEX_{Bio.FE}$ = 0.1 mg/L
Sulphate	$BTEX_{Bio.S} = 0.21(S_B-S_M)$ Where: $BTEX_{Bio.S}$ = reduction in BTEX concentration via sulphate reduction 0.21 = mg/L (average) BTEX degraded per mg/L sulphate consumed S_B = background sulphate concentration (mg/L) = 20 mg/L S_M = measured sulphate concentration (mg/L) = 2.0 mg/L $BTEX_{Bio.S}$ = 3.8 mg/L
TOTAL ASSIMILATIVE CAPACITY = 7.8 mg/L of BTEX can be Biodegraded	

Several public-domain software packages are available that can be used to model Intrinsic

Remediation to various degrees of accuracy. For example, BIOPLUME II is a program for the two-dimensional, two-species numerical simulation of the biodegradation of benzene in groundwater (Rifai *et al*., 1988). First-order decay of a single species can be simulated in three dimensions, such as the popular MODFLOW/MT3D combination. Numerical models for the three-dimensional, multi-component intrinsic remediation of chlorinated solvents are currently being developed, such as the RT3D code (based on MT3D) being developed by the Pacific Northwest National Laboratory, in Richland, Washington (USA). Unfortunately, the public-domain versions of most of these computer codes do not have user-friendly, graphical interfaces. Several pre- and post-processors have been developed to improve user friendliness for models such as MODFLOW and MT3D and are readily available (e.g. Visual MODFLOW). More specific information on models and computer software can be found in Wiedemeier *et al*., 1995.

9. MONITORING REQUIREMENTS

In general, all remedial options require some form of monitoring before, during and after remediation to ensure that the process has been effective in removing contaminants to the desired level. A monitoring program for intrinsic remediation is used to determine if initial IR predictions were correct. Each monitoring program must be developed on a site-specific basis with sufficient monitoring points and frequency of measurement to ensure that remedial objectives are met and that the plume status is understood at all times.

Long-term monitoring (LTM) is especially important when IR is used, because the natural system cannot be manipulated to adjust remediation. A long-term monitoring program is designed to collect the data required to confirm that natural attenuation is occurring at the predicted rates to ensure protection of human health and the environment. A comprehensive data set for monitoring at a particular site should be maintained. Regular review of the data will allow evaluation of trends in order to track plume status and the progress of remediation. If, based on the results of an LTM program, IR is not functioning, then active remediation may be necessary, after which IR may again be applied.

As noted above, the presence of receptors drives the need for remediation. If no receptors are present or if exposure pathways to receptors cannot be completed, then monitoring may not be essential. Institutional controls such as restrictions on future land use, physical barriers (e.g. fencing) and zoning restrictions can be used to ensure future exposure pathways and receptors do not develop.

Once it has been shown through monitoring that a plume is shrinking or that there is sufficient evidence in combination with monitoring results, that exposure pathways will not be completed, the LTM program can cease or be reduced in scale.

SOURCES

ASTM (1996). *ASTM Guide for Remediation by Natural Attenuation at Petroleum Release Sites, Draft.*

Gaudet, C. (1994). *A Framework for Ecological Risk Assessment at Contaminated Sites in Canada: Review and Recommendations*. Environment Canada, Ecosystem Conservation Directorate, Evaluation and Interpretation Branch, Ottawa, Ontario. Scientific Series No. 199, 108 p.

Rifai, H.S., Bedient, P.B., Wilson, J.T., Miller, K.M. and J.M. Armstrong. (1988). *Biodegradation modelling at an aviation fuel spill site.* J. of Environmental Engineering, Vol. 114, No. 5, pp. 1007-1029.

Salanitro, J.P. (1993). *The Role of Bio-attenuation in the Management of Aromatic Hydrocarbon Plumes in Aquifers.* Ground Water Monitoring and Remediation, pp. 150-161.

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.

For further information please contact:

Environment Canada
Ontario Region - Environmental Protection Branch
Environmental Contaminants &
Nuclear Programs Division
4905 Dufferin Street
Downsview, ON M3H 5T4
Telephone: (416) 739-4826
Fax: (416) 739-4405

Our TABs can be found on the Internet at:
http://www.on.ec.gc.ca/pollution/ecnpd/