The Science Advisory Board
For
Contaminated Sites in BC

Hydrogeological Assessment Tools

Overview by

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Hydrogeological Assessment Tools

SABCS was funded by BC MOE in 2005 to develop scientific tools for the identification, assessment and management of contaminated sites in BC.

Objective was to develop sophisticated hydrogeological assessment tools (HAT) for screening level and detailed risk assessments.

The HAT tools are intended for use by specialists in hydrogeology.

Hydrogeological Assessment Tools

The HAT tools were developed to address five key topics :

i. Vertical contaminant transport in groundwater;
ii. Contaminant transport in the unsaturated zone;
iii. Light non-aqueous phase liquid mobility;
iv. Biodegradation rate of organic contaminants in groundwater; and
v. Transport of metals in groundwater.

Hydrogeological Assessment Tools

The HAT documents:

- Promote current science but do not endorse policy;
- Have not been formally approved by BC MOE;

BC MOE may ultimately recommend only select tools for use at contaminated sites. Many of these tools have data requirements that are likely too onerous for typical site investigations.

Hydrogeological Assessment Tools

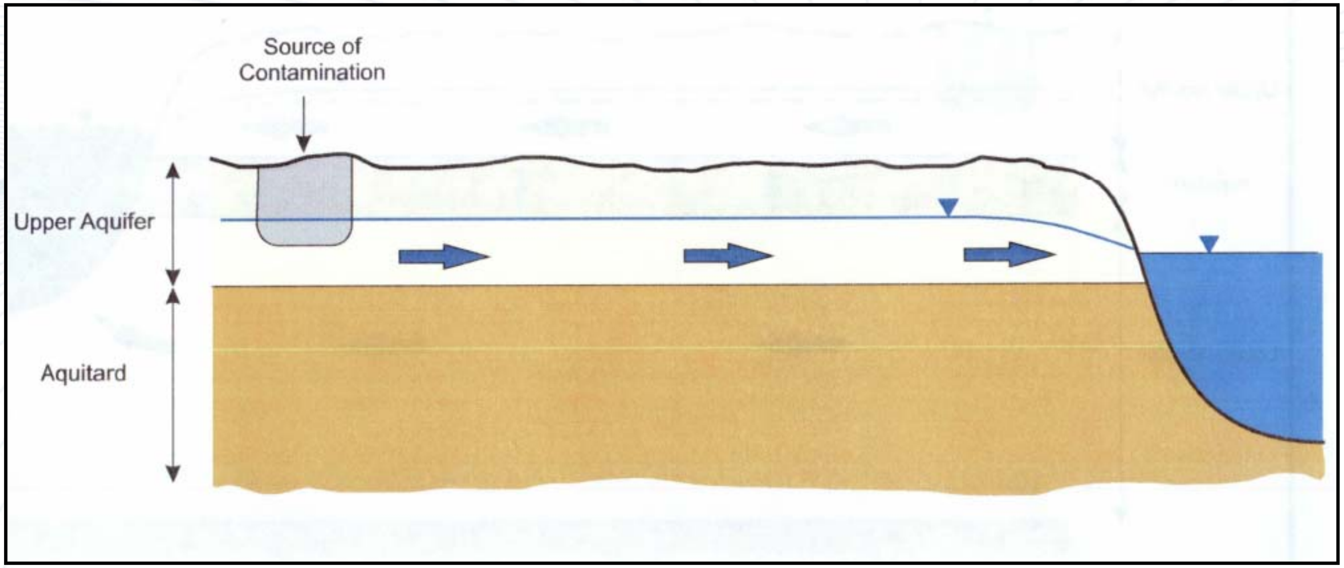
Regardless of their end use at contaminated sites, the HAT documents provide:

- An excellent summary of the current science and a detailed overview of theory and concepts for each topic;
- An array of approaches of varying complexity, including the advantages and disadvantages for each method and recommendations for their application;
- Numerous excellent reference documents in the Appendices.

The HAT documents are *not* manuals on how to use these hydrogeology tools.

Vertical Transport Assessment Tools

Current assessment tools for dissolved contaminant transport are conservative in BC, consider only horizontal migration:



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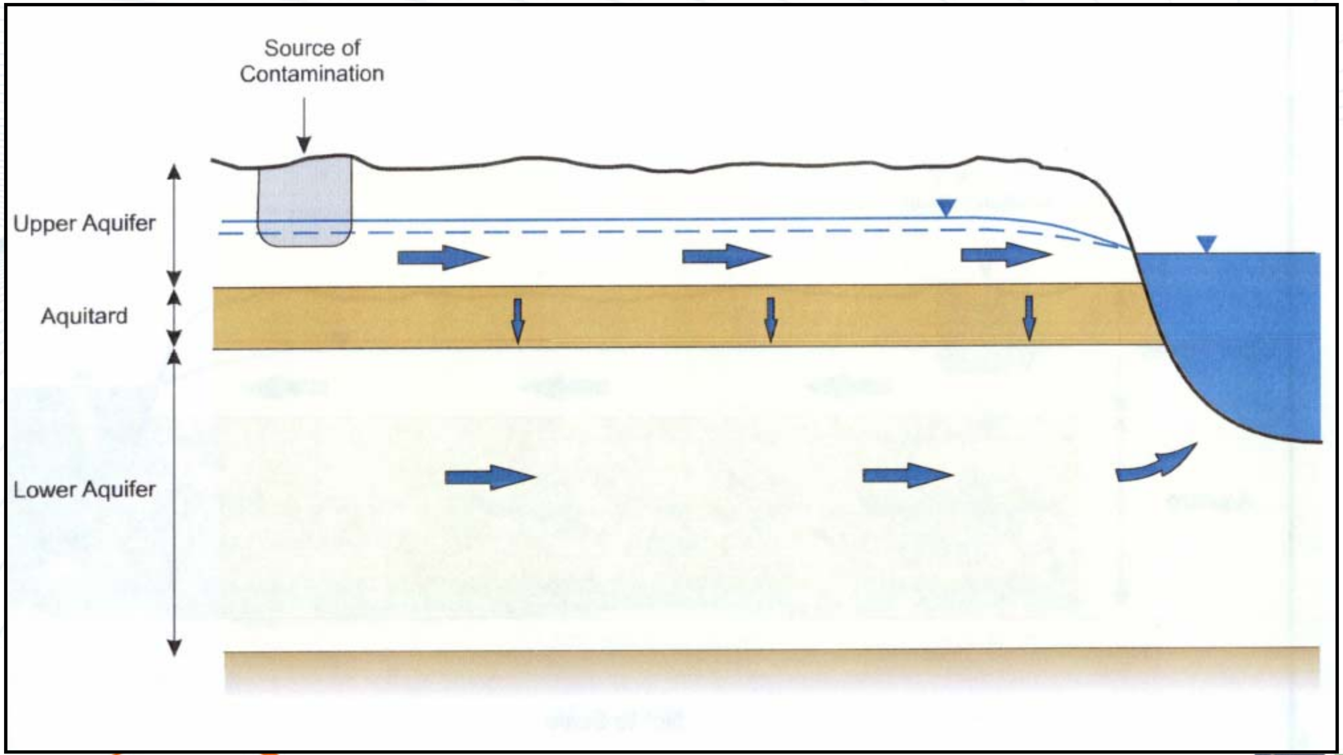
Vertical Transport Assessment Tools

Vertical transport tools consider either upwards or downwards flow:



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Vertical Transport Assessment Tools

Approach is based on a set of sequential questions:

Q1: How thick is the shallow aquifer and does the dissolved phase plume extend to its base

Q2: Is the deep aquifer present?

Q3: Is the vertical gradient down?

Q4: Is the horizontal flux in the deep aquifer high?
Is the vertical flux in the aquitard significant

Vertical Transport Assessment Tools

Presents quantitative methods to assess the potential for deep transport pathways. Tools range from simple to complex:

- Darcy’s Law and equation for mixing
- Composite analytical models (e.g. Bear)
- Numerical modelling (primarily 2-D)

Metals Transport Assessment Tools

Three main geochemical models are presented:

- Static models
- Reaction path models
- Coupled reactive transport models

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Metals Transport Assessment Tools

Static Models:

Assess aqueous speciation, complexation and surface reactions, but not reactive transport. Static models include:

- Speciation models
- Solubility and precipitation-dissolution models
- Sorption models:
  - Isotherm based models
  - Ion exchange models
  - Surface complexation models

Metals Transport Assessment Tools

Table 1 Static Geochemical computer codes (adapted from Crawford, 1999)

COMPUTER CODE	Forward Modelling	Inverse Modelling	Isotope Balancing	Reaction Path	Mixing Processes	Kinetics	Aqueous Complexation	Precipitation/Dissolution Mass Balancing	Gas Exchange Mass Balancing	Redox Reaction	Ion-Exchange	Simple Adsorption	Surface Complexation	Fix Species Activity (e.g. pH)	Davies Activity Model	Extended Debye-Huckel Activity Model	Pitzer Activity Model	Graphical Interface	Chemcial Retion Database Included	Transport Capability	Public Domain
AquaChem	X	X		X	X		X	X	X	X	X		X	X	X	X		X	X	1-A	
CHESS	X			O	X	X	X	X	X	X		X	X	X	X	X			X	FB	X
EQ3/6	X			X	X	X	X	X	X	X				X	X	X	X		X	FB	
Geochemist's Workbench	X			X		X	X	X	X	X			X	X	X	X	X	X	X		
MinEQL+ (v 4.0)	X			X			X	X	X	X	X		X	X	X			X	X		
MINTEQA2	X			O			X	X	X	X	X	X	X	X	X	X		T	X		X
NETPATH		X	X		X		X	X	X	X	X				X	X		T	X		X
PHREEQC2	X	X		X	X	X	X	X	X	X	X		X	X	X	X			X	1-AD	X
PHRQPITZ	X			X	X		X							X			X	T	X		X
SteadyQL	X			X		X	X	X	X	X										FB	
WATEQ4F	X						X			X				X	X	X		T	X		X
WHAM	X						X	O	?	?			X	?	?	?	?	?	X		

Notes:

Notes:	X	indicates capability
	O	indicates partial capability
	T	Text-based interface
	FB	Flow-through batch reactor simulator
	1-A	1D advective transport
	1-AB	1D advective dispersive transport
	?	unknown capability

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Metals Transport Assessment Tools

<u>Reaction Path Models:</u>

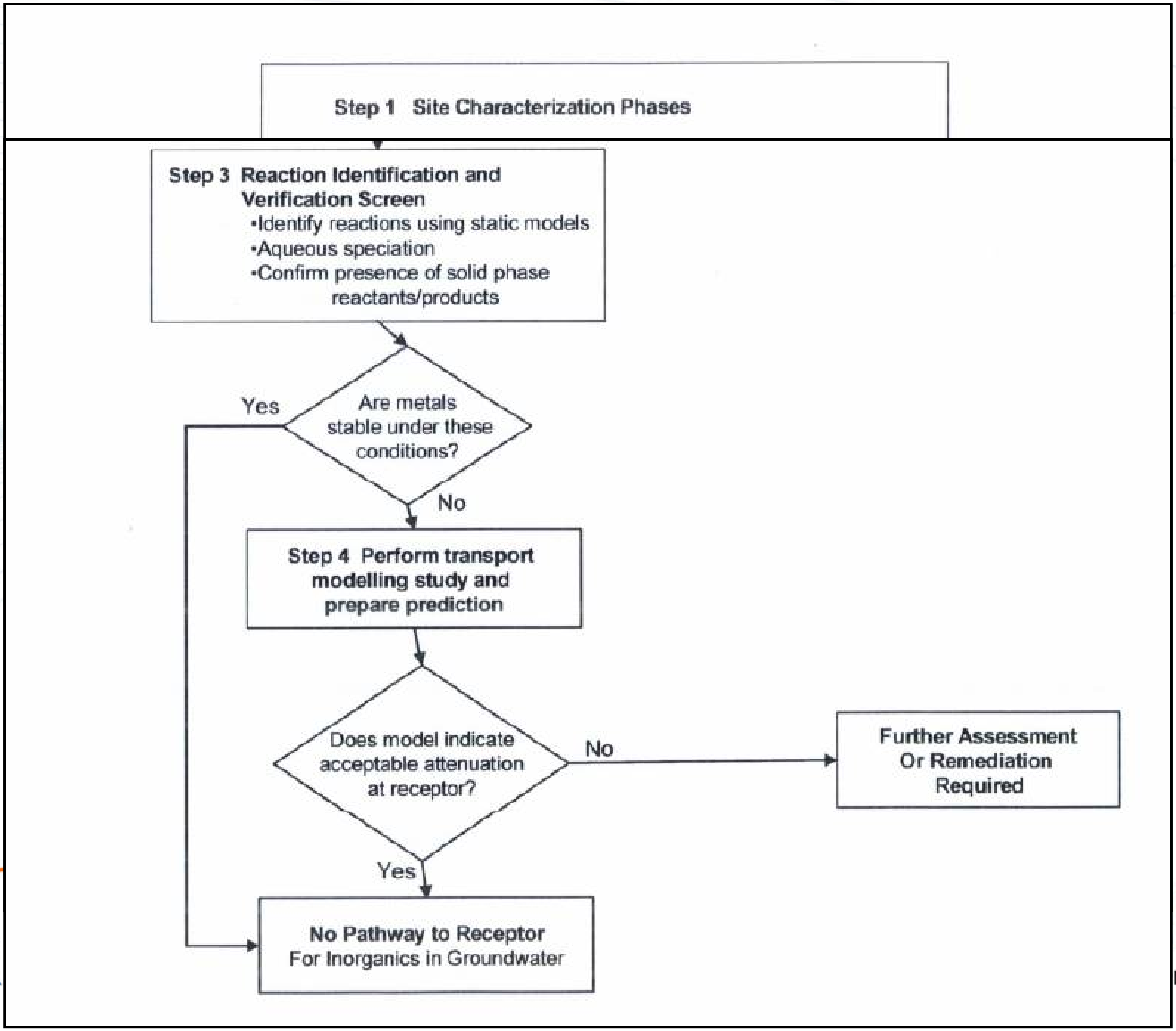
- Calculate and solve a series of equilibrium reactions in response to changes in concentration along a flowpath (e.g. NETPATH)
- Are capable of assessing dissolution, precipitation, ion exchange, oxidation/reduction, degradation, mixing, evaporation, dilution, isotope fractionation and gas exchange.
- Can not incorporate temporal or spatial changes
- Constrained by assumptions of aquifer composition along flowpath
- Typically used to identify reactions causing changes in chemistry between two points.

Metals Transport Assessment Tools

Coupled Reactive Transport Models:

- Link the process-based approaches to the geochemical mass-action reactions and the differential equations for ground water transport.
- Capable of assessing advective-dispersive transport of chemically reactive substances.
- Can simulate how a geochemical system evolves over time along a flowpath in 3D.

Metals Transport Assessment Tools



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Metals Transport Assessment Tools

Conclusions in HAT for Metals Transport:

- There are serious constraints for all models due to lack of site-specific data and heterogeneity of subsurface conditions.
- Application of the K_d isotherm approach to metal transport is not scientifically defensible at most contaminated sites.
- Due to the complexity of issues associated with metals transport and the need for geochemical interpretation, many contaminated sites professionals would not have the background to apply all the tools described in this document.

Biodegradation Rate Assessment Tools

- Summarizes tools that can be used for quantitative risk assessment to determine biodegradation rate constants for the transport of organic compounds in shallow groundwater.

- Reviews methods to differentiate the effects of degradation from other attenuation processes.

- Methods to estimate biodegradation rate constants are divided into three categories:
  - Laboratory methods
  - Field techniques
  - Modelling

Biodegradation Rate Assessment Tools

A process is recommended for screening out low risk sites:

- Approach is conservative.
- Must provide evidence that biodegradation is occurring
- Applies only to contaminants where a high level of understanding exists for biodegradation processes
- Hydrogeology must be well characterized
- Biodegradation processes must be sustainable
- Degradation products must be of low concern

Biodegradation Rate Assessment Tools

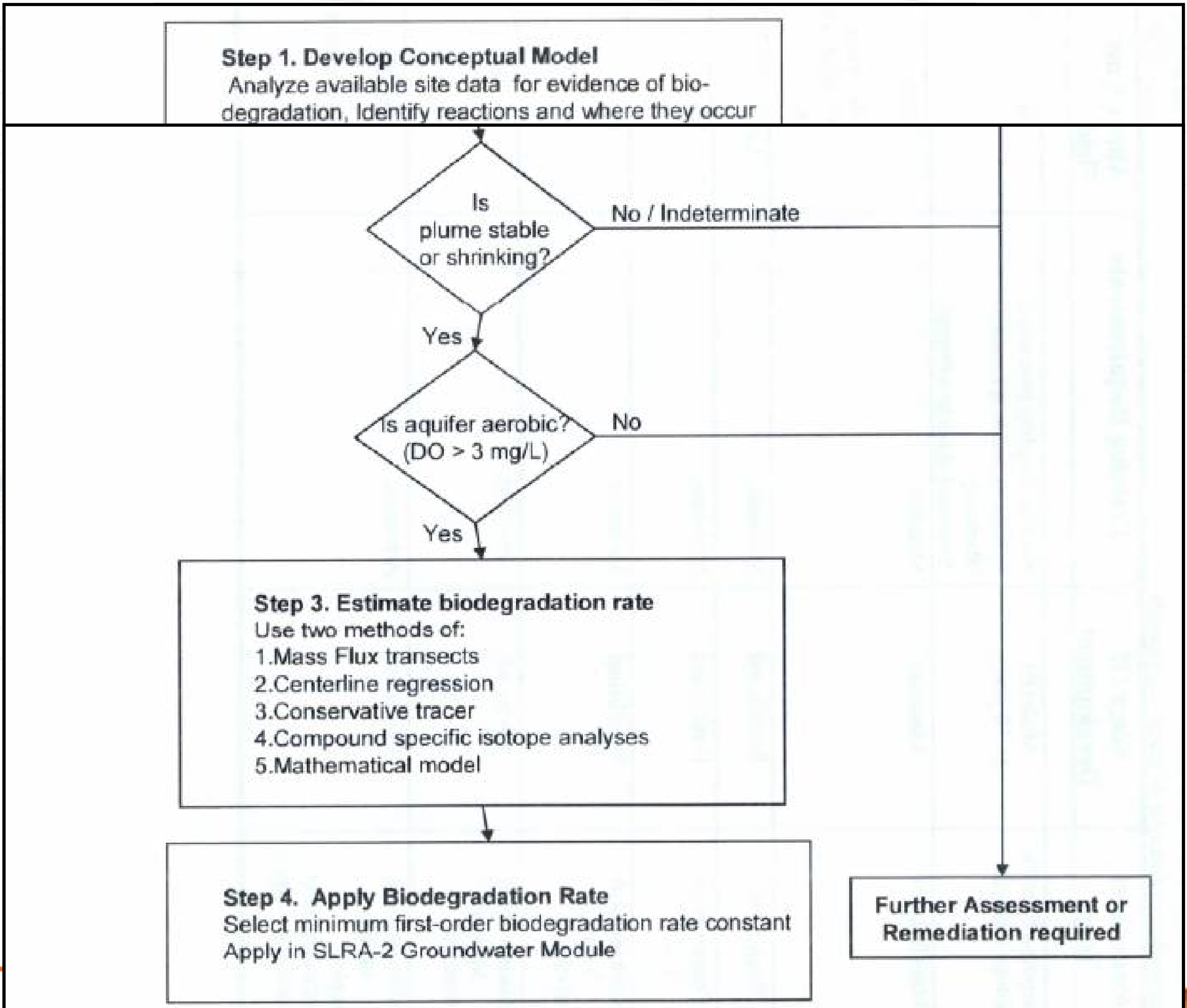

Figure 1 Screening process for biodegradation rate estimate in SLRA-2 Groundwater module

Biodegradation Rate Assessment Tools

- Provides an excellent overview of natural attenuation processes including Monod kinetics and the associated assumptions and limitations:
  - First order rate constants
  - Zero order rate constants
- Importance of site-specific factors
- Does not address groundwater-surface water interaction (hyporheic zone)

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Biodegradation Rate Assessment Tools

Laboratory techniques:

- Microcosm studies
- Column studies

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Biodegradation Rate Assessment Tools

Field Experiment Techniques:

- Push-pull tracer tests
- Well to well injection tests
- Biotracer tests
- Circulating well tests
- In situ tests

Biodegradation Rate Assessment Tools

Field Characterization Techniques:

Presents a wide variety of tools for evaluating field data and the assumptions and limitations of each method

- Plume stability tests:
  - Visual methods
  - Statistical methods
  - Prescriptive tests
  - Multi-method approaches

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Biodegradation Rate Assessment Tools

Field Characterization Techniques (cont'd):

- Mass Flux Estimates:
  - Transect Method
  - Pumping Wells
  - Passive Flux Meter

Biodegradation Rate Assessment Tools

Field Characterization Techniques (cont'd):

- Compound specific isotope analysis
- Mass Balances
- Regression
- Conservative tracers

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Biodegradation Rate Assessment Tools

Evaluation Using Complex Models:

- Discusses models that have the ability to include detailed processes that effect contaminant fate and transport
- Presents analytical models, numerical models and hybrid models of each
- Provides a qualitative comparison of the applicability of each model, including the advantages and disadvantages
- Lists public domain codes

Biodegradation Rate Assessment Tools

Table 2 Assessment tools for assessing biodegradation - Field

TYPE	ASSESSMENT TOOL	APPLICATION	ADVANTAGES	LIMITATIONS
Field Techniques	Push-Pull tracer test	• injection of water containing reactive and non-reactive tracers • best results if site groundwater used • provides indication of biodegradation and rate in aquifer	• derive a field scale rate • test a large volume of aquifer • use site groundwater to prepare solution • can assess the effects of dispersion	• aquifer heterogeneity may limit/confine spread of tracer • potential mass loss of tracer due to poor recovery • solution chemistry may be altered prior to injection • time and analytically intensive to monitor breakthrough
	Well to Well injection	• can use either natural-gradient or forced-gradient conditions • provides indication of biodegradation and rate derived from breakthrough curve analysis • provide indication of biodegradation in aquifer	• derive a field scale rate • test a large volume of aquifer • can control flow field and injection	• natural gradient test needs extensive monitor well control • aquifer heterogeneity must be well understood • potential alteration of aquifer conditions by injected solution • time and analytically intensive to monitor breakthrough
	Biotracer	• injection of appropriate reactive and non-reactive compounds provides indication of biodegradation and rate • applied in well to well type setup	• biotracers are structurally similar to compounds of interest • can be used to assess spatial variability of processes	• need to be low toxicity • need appropriate physicochemical properties • time and analytically intensive to monitor breakthrough • recently developed technique
	Circulating Well injection	• controlled vertical circulation of a solution around one well • injection of a reactive and non-reactive tracer provides indication of biodegradation and rate	• derive a field scale rate • test a large volume of aquifer • can control flow field and injection	• aquifer heterogeneity affects vertical circulation effectiveness • possible loss of tracer due to incomplete capture • potential alteration of aquifer condition by injected solution • time and analytically intensive to monitor breakthrough
Field Techniques	Mass Flux Estimates a) Transect	• Concentration data from wells along a transverse plane to estimate mass discharge • Reduction in mass flux between	• can provide rates over longer time periods • can produce a first-order rate	• must distinguish biodegradation from dispersion • better result with increased horizontal and vertical discretization which may be

Biodegradation Rate Assessment Tools

Table 4 Comparative Summary of Assessment Tools

Assessment Tool	Stage Of Development	Training Requirements	Applicability To Field Conditions	Practicality	Relative Cost
Microcosm	Established	Specialized Usually subcontracted to specialized laboratory	Low	Low	Moderate
Column Studies	Established	Specialized Usually subcontracted to specialized laboratory	Low	Low	Moderate
Push-Pull tracer test	Established	Advanced hydrogeologic skills Knowledge of tracers	High	Moderate	Moderate
Well to Well injection	Established	Advanced hydrogeologic skills Knowledge of tracers	High	Low - Moderate	High
Biotracer	Early (Research level)	Advanced hydrogeologic skills Knowledge of tracers	High	High potential	Moderate
Circulating Well injection	Early	Advanced hydrogeologic skills Knowledge of tracers	High	Moderate	Moderate
Mass Flux Estimates Transect	Moderate	Moderate	High	High	Low – High Affected by number of monitoring locations needed
Mass Flux Estimates Pumping Wells	Early	Advanced hydrogeologic skills	High	Low	Moderate Affected by treatment requirements for pumped groundwater
Mass Flux Estimates Passive Flux meter	Early (Research level)	Moderate Easily installed with standard procedures	High	High	Unknown
In Situ Microcosm Testers	Established	Advanced skills required to design and conduct experiments	Moderate	Low Requires long time periods	Moderate

Unsaturated Zone Contaminant Transport

- Summarizes approaches and methods to evaluate the fate and transport of chemicals in the unsaturated zone
- Focus is on the leaching of chemicals from contamination sources within unsaturated soil and the migration of dissolved chemicals to the saturated zone
- Presents fundamental aspects related to the soil-water characteristics curve and unsaturated zone hydraulic conductivity
- Does not address the migration of vapours or NAPL

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Unsaturated Zone Contaminant Transport

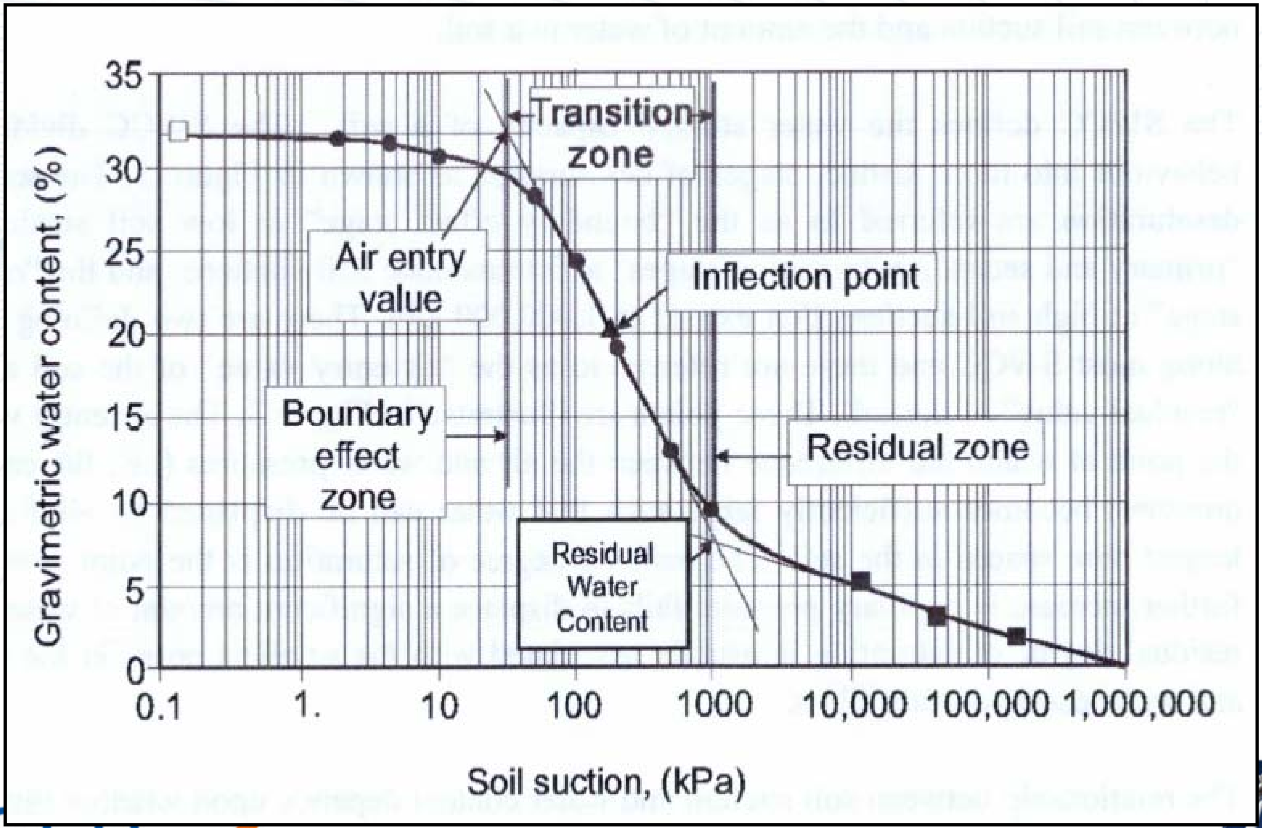
Provides an excellent overview of unsaturated zone transport fundamentals including:

- An overview of vadose zone processes
- Common water retention or soil-water characteristics curve models
- Methods to estimate unsaturated hydraulic conductivity

Presents a range of concepts and approaches to evaluate solute transport through the unsaturated zone from simple closed-form analytical solutions to complex numerical models

Unsaturated Zone Contaminant Transport

Common mathematical functions to describe SWCC and various methods for laboratory and field measurement are presented



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Unsaturated Zone Contaminant Transport

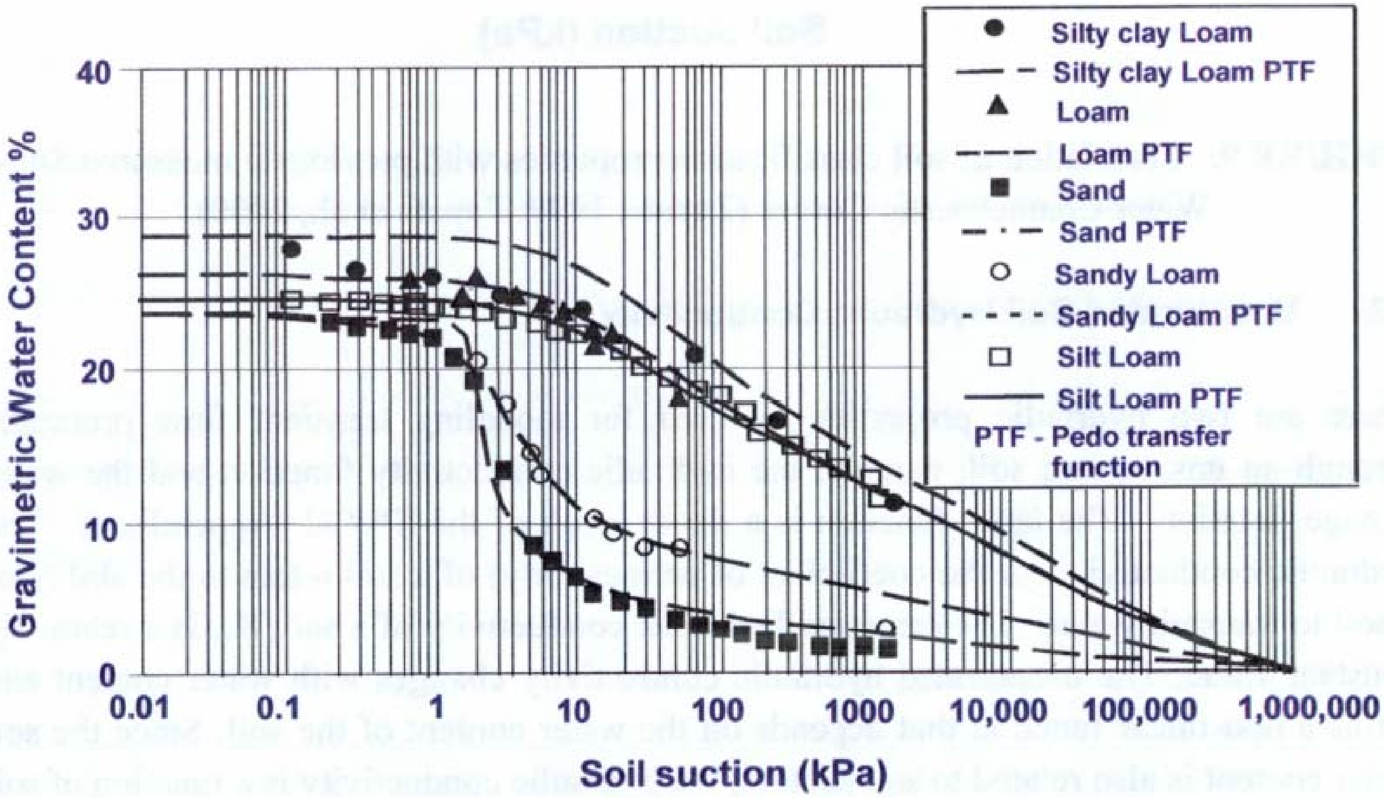


FIGURE 8. Soil-Water Characteristic Curves computed from grain-size distribution data for a variety of soil types.

Unsaturated Zone Contaminant Transport

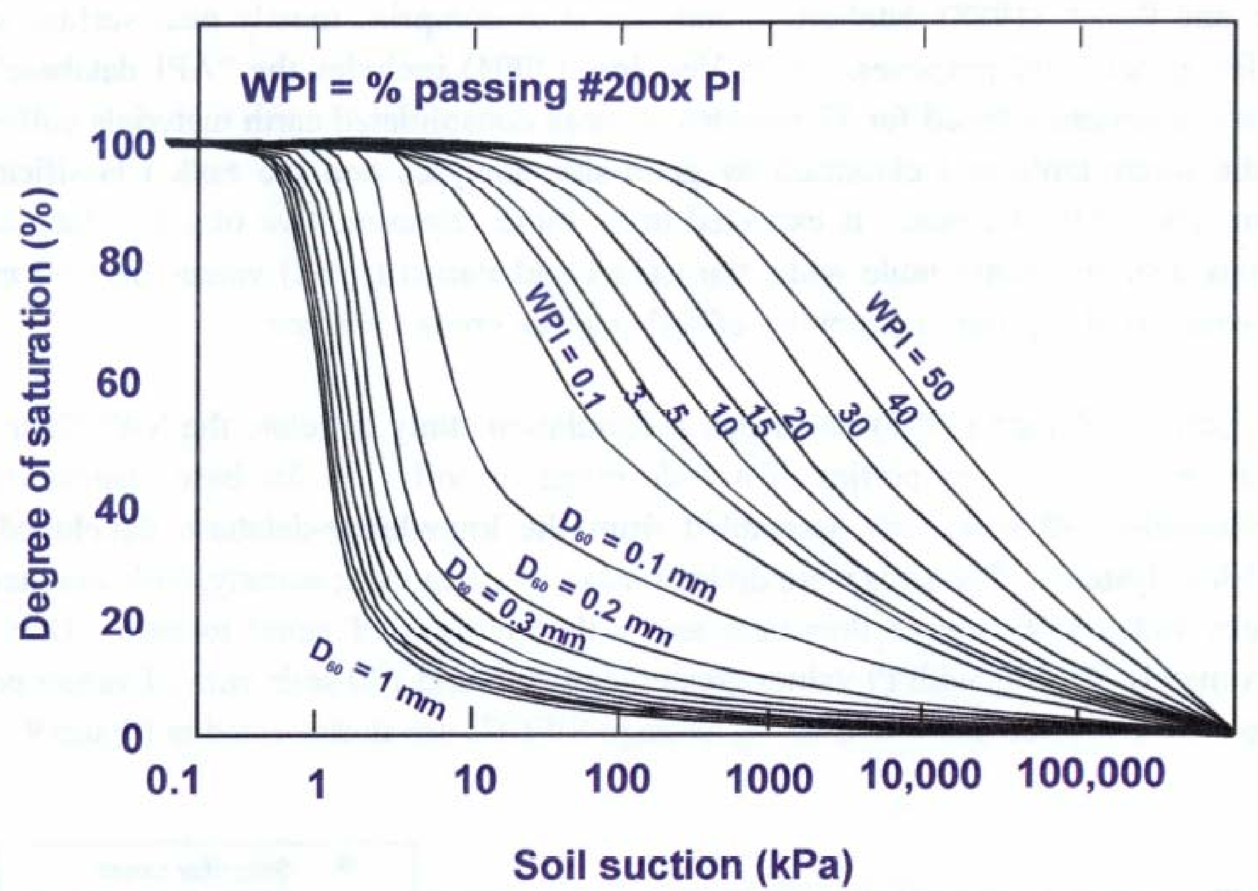


FIGURE 9: Correlation of soil classification properties with previously measured Soil-Water Characteristic Curves (Zapata, 1999; Zapata et al., 2000).

Unsaturated Zone Contaminant Transport

TABLE I-1: Some empirical hydraulic conductivity equations

Reference	Equation	Description
Wind (1955)	$K_w = \alpha\psi^{-n}$	α , and n are fitting parameters
Gardner (1958)	$K_w = \dfrac{K_s}{(\alpha\psi^n + 1)}$	α and n are fitting parameters
Brooks and Corey (1964)	$K_w = K_s$ for $\psi \leq \psi_{aev}$ $K_r = (\dfrac{\psi}{\psi_{aev}})^{-n}$ for $\psi > \psi_{aev}$	
Rijtema (1965)	$K_w = K_s$ for $\psi \geq \psi_{aev}$ $K_r = \exp[-\alpha(\psi - \psi_{aev})]$ for $\psi_1 \leq \psi < \psi_{aev}$ $K_w = K_1(\psi/\psi_1)^{-n}$ for $\psi < \psi_1$	ψ_1 = residual soil suction K_1 = hydraulic conductivity at ψ_1

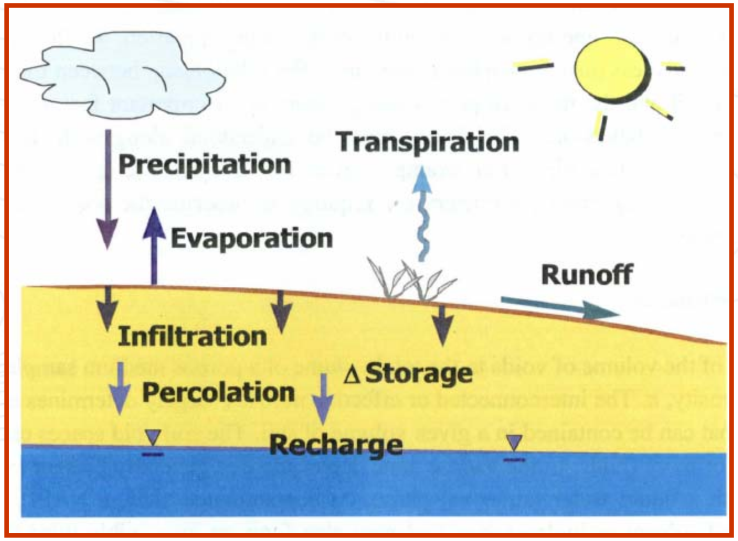
A number of empirical models are presented for the estimation of the hydraulic conductivity function for an unsaturated soil

Unsaturated Zone Contaminant Transport

- Groundwater seepage in the unsaturated zone is addressed primarily through modelling tools
- Solute transport options presented include analytical models such as the BC Environment CSST model and more complex numerical codes
- Numerous tools are discussed to derive water balance estimates required as inputs to many of these models

Unsaturated Zone Contaminant Transport

- Water balance methods:
  - Water balance equations
  - Water balance modelling (HELP, SESOIL)



- Empirical methods
  - Measurement of rainfall infiltration
  - Natural and experimental tracers
  - Specialized field equipment
  - Geophysics

Unsaturated Zone Contaminant Transport

Different approaches are evaluated for the application of recharge estimates:

- Derivation of a site-specific leachate-groundwater dilution factor
- Calculation of an average seepage velocity

Unsaturated Zone Contaminant Transport

TABLE 2: Average Seepage Velocities, cm/yr
(from Charbeneau and Daniels, 1993)

Soil Type	Average annual infiltration, cm			
	5	10	25	50
Clay	16	31	75	148
Clay loam	19	34	86	164
Loam	26	49	113	211
Loamy sand	53	99	225	416
Silt	21	39	88	164
Silt loam	22	41	93	174
Silty clay	16	30	74	145
Silty clay loam	16	30	72	137
Sand	68	127	286	527
Sandy clay	18	35	82	158
Sandy clay loam	25	48	112	212
Sandy loam	39	73	167	308

Note: The above values represent average seepage velocities for four categories of infiltration rates.

Unsaturated Zone Contaminant Transport

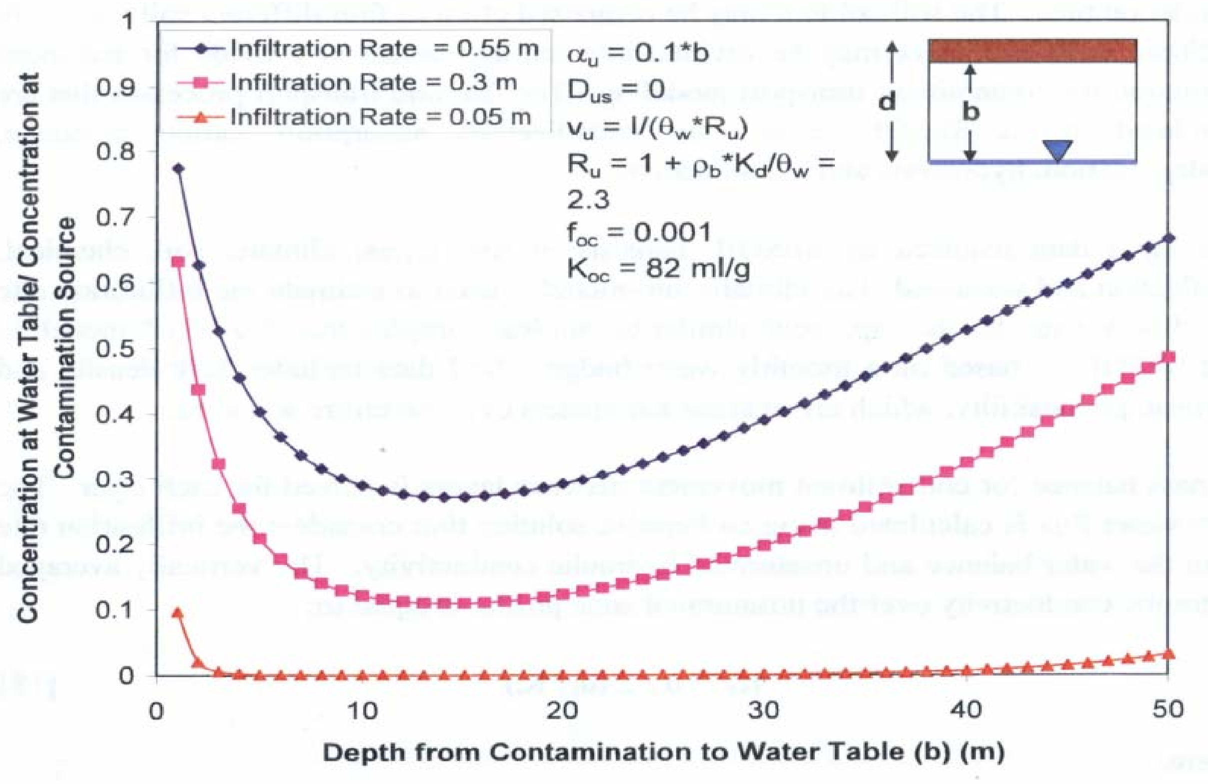


FIGURE 10: Predicted Benzene Concentrations at Water Table Based on 1-D Unsaturated Zone Steady State Model for Advection, Dispersion, Sorption and Decay.

- Provides a detailed review and comparison of various solute transport models (e.g. SESOIL, VLEACH, HYDRUS-2D, VS2DT, SVFlux)
- Qualitative tools (Drastic, API)

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LNAPL Mobility Assessment Tools

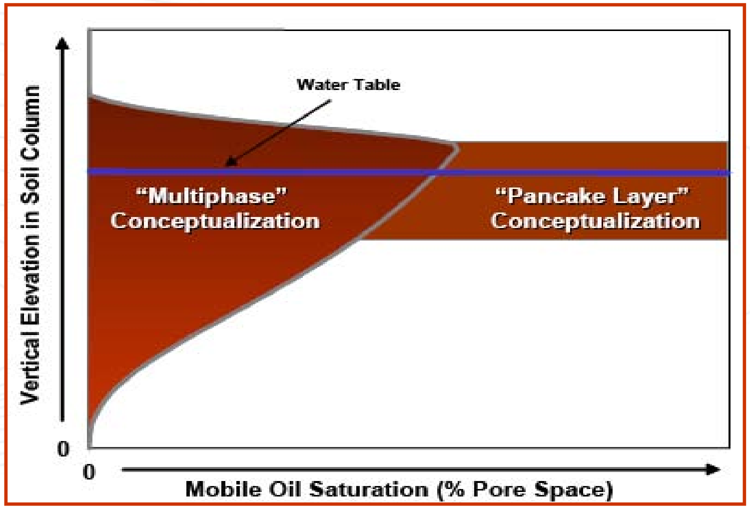
- Provides a set of useful approaches and quantitative tools for the evaluation of LNAPL mobility
- Provides an excellent overview of NAPL fundamentals
- Provides an appreciation for the complexity in defining realistic endpoints for LNAPL recovery
- A number of complementary methods are recommended in a “toolbox approach”
- Not intended to address DNAPL sites

LNAPL Mobility Assessment Tools

LNAPL Conceptual Model:

- Early conceptual models based on a “pancake” conceptualization for LNAPL distribution and migration
- LNAPL was considered to spread horizontally as a continuous single-phase fluid
- LNAPL was assumed to ‘float’ as a separate layer on the water table
- Ignored the critical influence of capillarity, resulting in over predictions of LNAPL volume and recoverability

LNAPL Mobility Assessment Tools



Updated Conceptual Model:

- Updated paradigm is based on a "multiphase model", where LNAPL, water and air coexist
- LNAPL movement is constrained by the capillary pressures needed to displace water from the soil pores
- LNAPL is conceptualized as an iceberg at sea, largely submerged
- LNAPL saturations do not reach 100%

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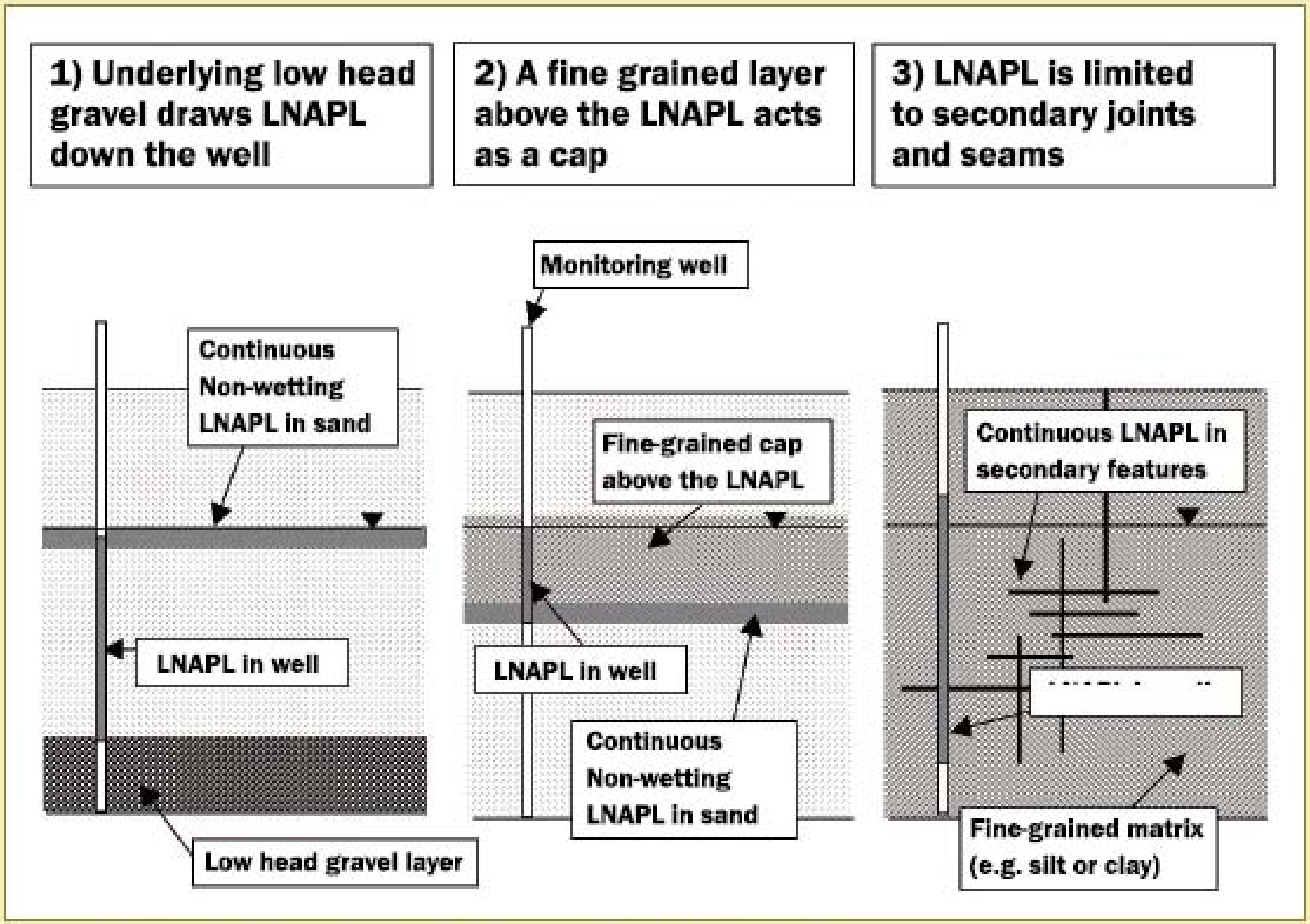
LNAPL Mobility Assessment Tools

Based on the multiphase LNAPL paradigm, the document provides an overview of:

- LNAPL volume and mobility relationships to soil types
- Effect of water table fluctuations
- Conditions effecting the thickness of LNAPL in wells
- Various assumptions and limitations of the multiphase model

LNAPL Mobility Assessment Tools



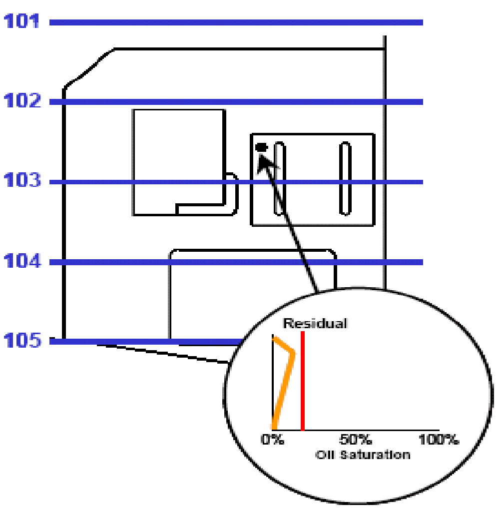
Conditions effecting the thickness of LNAPL in wells

LNAPL Mobility Assessment Tools

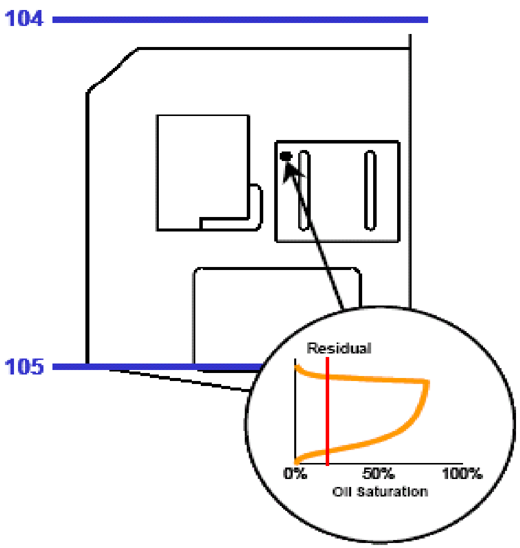
Presentation of LNAPL mobility and stability concepts

- Small scale mobility
- Plume scale mobility

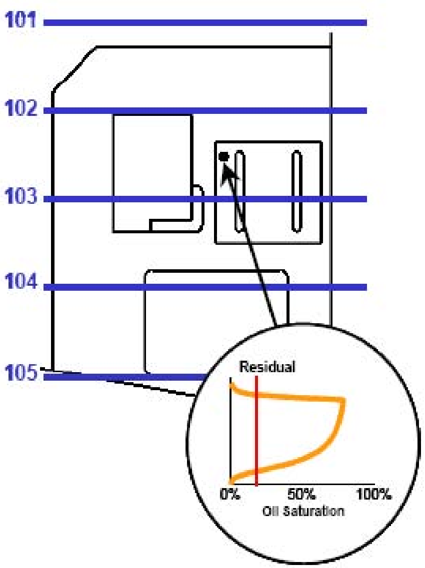
A) •**LNAPL Not Mobile**
(low oil volume)
•**Plume Stable**



B) •**LNAPL Mobile**
•**Plume Stable**
(insufficient gradient)



C) •**LNAPL Mobile**
•**Plume Unstable (Migrating)**



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LNAPL Mobility Assessment Tools

Several approaches are discussed for evaluating LNAPL mobility:

1. Observational approach
2. LNAPL recovery analysis
3. Theoretical methods to estimate LNAPL plume mobility
4. Evaluation of pore-scale movement at plume front
5. Laboratory tests

LNAPL Mobility Assessment Tools

- Recommendation is to use a combination of these tools to evaluate LNAPL mobility based on multiple lines of evidence
- Emphasis is on observational data at wells and field tests to assess LNAPL presence and mobility
- Primary field-based tools include analysis of soil cores, laser induced fluorescence, product bail-down tests and short term pilot tests of LNAPL recovery

LNAPL Mobility Assessment Tools

Theoretical estimates of LNAPL mobility:

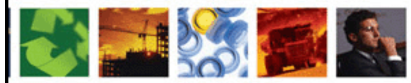
- Intrinsic permeability
- Relative permeability
    - Theoretical estimates from LNAPL thickness in wells
    - Field LNAPL bail-down tests
- LNAPL gradient
- Automated tools (e.g. API Interactive LNAPL Guide)
- Implications of mobility estimates and *de minimus* values

LNAPL Mobility Assessment Tools

TABLE 2: Recommended Methods and Data Sources for Theoretical Estimates of Potential LNAPL Mobility

Parameter	Method or Data Source
Relative Permeability	Theoretical analysis based on LNAPL thickness in well and capillary properties is currently recommended. Bail-down tests are not currently recommended, but may in the future become a viable approach as experience is gained with this test.
Water Retention Model	There is no clear preference over whether to use Van Genuchten (VG) or Brooks-Corey water retention model, although recent guidance gives precedence to use of the Van Genuchten model.
Capillary Parameters (Van Genuchten model)	Fitting of VG soil characteristic parameters to water retention test (*e.g.*, RETC model), conducted on undisturbed soil core or re-compacted sample (preferred) or API Interactive LNAPL Guide Database values
Capillary Parameters (Brooks and Corey model)	Fitting of BC soil characteristic parameters to water retention test on undisturbed soil core or re-compacted sample (preferred) or default values from Charbeneau (2003)
LNAPL Physical Properties (density, viscosity, interfacial tensions)	Laboratory tests on LNAPL from site (preferred) or API Interactive LNAPL Guide Database

Note: method for residual saturation to be determined.

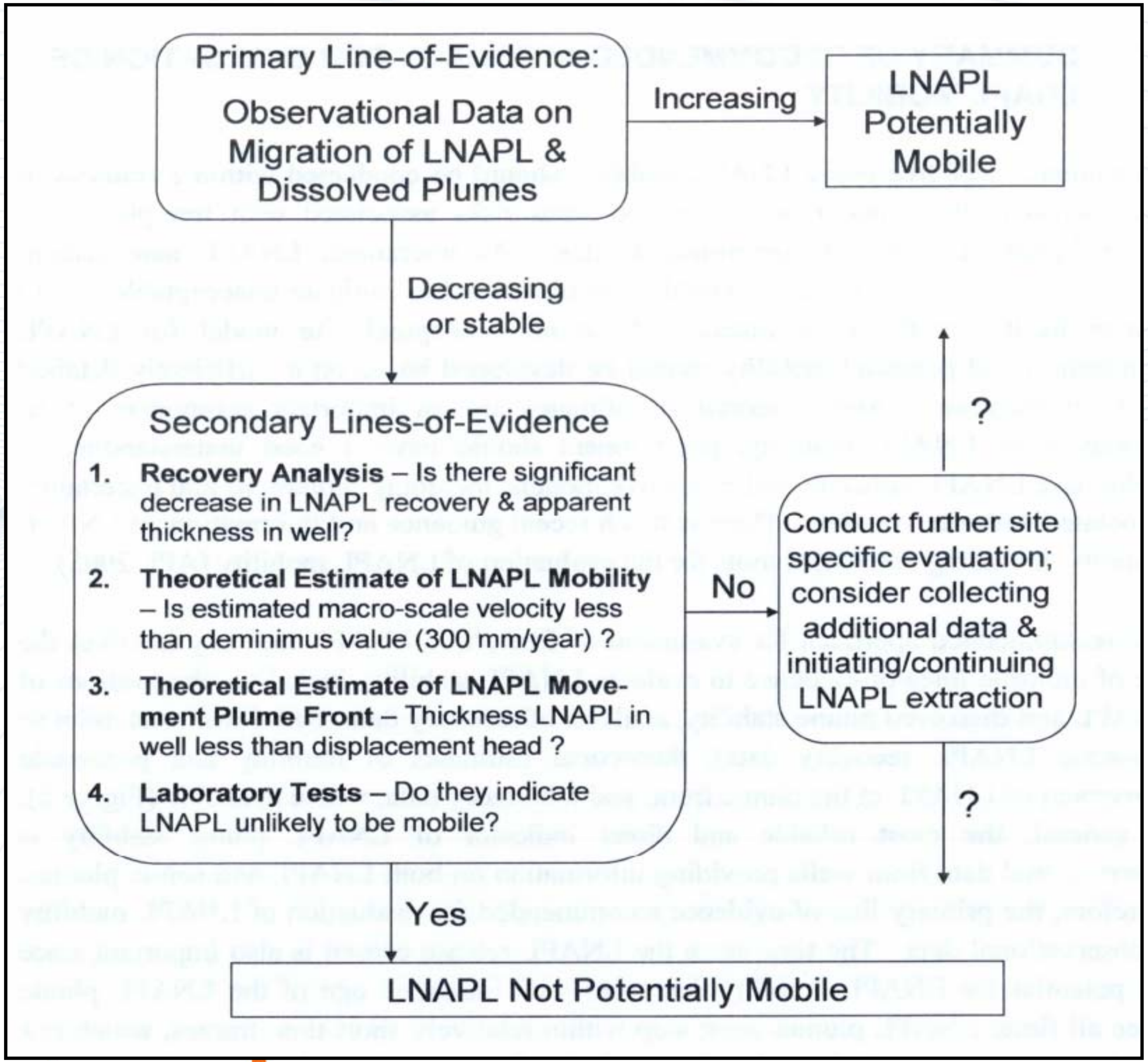


LNAPL Mobility Assessment Tools

Theoretical methods in summary:

- Emphasis on determination of capillary parameters for the water retention (soil characteristic) curve
- Theoretical models not considered appropriate as stand-alone tools to determine LNAPL mobility:
  - Methods are complex and in relatively early stages of development
  - Difficulty in measuring parameters
  - Significant spatial variation in parameters

LNAPL Mobility Assessment Tools



Conceptual approach for LNAPL mobility evaluation

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Summary

Three common threads in SABCS HAT documents:

- Importance of developing a sound conceptual site model
- Tool box approach
- Recommendations favour approaches that are conservative, well known and less complex

Hydrogeological Assessment Tools

The HAT documents can be found online at the SABCS website:

http://www.sabcs.chem.uvic.ca/

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