



Report on:

**Hydrogeological Assessment Tools
for Modeling Transport of
Metals in Groundwater**

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Metals in Groundwater**

Submitted to
The Science Advisory Board for Contaminated Sites
in British Columbia

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EXECUTIVE SUMMARY

This report provides a scientific review of hydrogeological assessment tools that could be used to model the transport of metals and other inorganic compounds in groundwater. This report serves four main functions: describes the types of geochemical modelling tools that are available, some of their advantages and disadvantages, identifies several issues for discussion and recommends a proposed screening approach for evaluating the migration of metals along the groundwater to receptor pathway.

Geochemical models can be generally categorized by their level of complexity, or whether they are “empirical” or “process-based”. A fundamental step for any model is the creation of a conceptual model. Preparation of an appropriate conceptual model of the geochemical environment requires understanding of the components present in aqueous and solid phases, the significant reactions that are likely to occur, and the evaluation of the geochemical conditions of the groundwater system. A well-developed conceptual model will allow the modeler to formulate the appropriate questions and hypotheses to be evaluated.

There are three main categories of geochemical models: static, reaction path and coupled reactive transport. Within static models, there are models which determine speciation of dissolved constituents, solubility and dissolution-precipitation tendencies of solutes, and sorption of solute to aquifer materials. Sorption models can be further divided into models which are based on empirical isotherms, ion exchange reactions, and surface complexation reactions. Reaction path models solve equilibrium reactions for concentration changes along a flowpath. Coupled reactive transport models are at the state of the art and combine the solution of geochemical mass-action reactions and groundwater transport. Understanding the transport of metals in groundwater is a complex subject requiring considerable care to ensure that meaningful results are obtained. Serious constraints remain for all models due to lack of site-specific data and heterogeneity of subsurface conditions.

A fundamental concept of SLRA-2 is the objective of screening low-risk sites out of the regulatory process while ensuring that no moderate or high-risk sites are inadvertently screened out. If a site is screened out by the SLRA-2 process, then no further action is required. It is analogous to the “Groundwater Module” of the SLRA-2, but requires a geochemically oriented approach. A proposed overall screening process includes four steps: i) Site characterization of hydrogeology, aqueous, and solid phase geochemistry., ii) refinement of conceptual model, iii) reaction identification and verification, and iv) transport modeling study.

At the conclusion of the fourth step, a decision can be made as to when or whether the contaminant will arrive at the receptor, and whether it is likely that the concentration would exceed acceptable criteria. If the predicted concentration exceeds criteria, then further assessment or remediation is required. Otherwise, the predicted exposure is acceptable and there is no pathway to the receptor.

Several conclusions have been drawn from this work. The geochemistry of metals transport in groundwater can be complex and require a high degree of technical sophistication to accurately screen sites and quantify potential risk to receptors. The application of the K_d isotherm approach to metal transport in groundwater has several difficulties, and is not scientifically defensible at most contaminated sites. There are alternative approaches which are process-based and are more likely to provide accurate site-specific results. Contaminated sites containing metals in groundwater require some additional characterization that is specific to understanding the fate and transport of metals.

This involves site-specific characterization of aqueous and solid-phase geochemistry in addition to hydrogeology. A process for assessing risk at metal-contaminated sites should consider the following points: a good conceptual model is critical, the groundwater flow system must be understood, groundwater must be characterized for the dissolved metals of concern and geochemical parameters, composition and properties of the solid media must be characterized, water quality data must meet data quality objectives, accuracy of the thermodynamic database for geochemical models is important, modelling should include sensitivity and uncertainty analysis, and numerical analysis should be considered a tool to support or augment observations. Some complicated geochemical models have many parameters requiring considerable site-specific values which may be limited by the availability of, or ability to collect the necessary data, or the skill level of the user.

The following recommendations are made. The characterization requirements for contaminated sites which contain metals, in either soil or groundwater should be enhanced to include geochemical measurements of groundwater and characterization of all solid phases and aquifer mineralogy. Screening level and detailed risk assessments for the migration of metals in groundwater should be supported by geochemical calculations and modelling. The application of K_d -based transport models as an assessment tool should be discouraged. The minimum approach should include use of static models to identify potential reactions, characterization of mineral phases present and provide an opportunity to verify that reactions are actually occurring. The next level of assessment would involve a simple coupled reactive transport model. More sophisticated models could be applied depending on site characteristics, the results of the preliminary steps, and availability of supporting geochemical data. Due to the complexity of the issues associated with metals contaminated groundwater, and the need for geochemical interpretation, it is likely that many contaminated sites professionals would not have the background to adequately apply all of the tools described in this report. Training seminars for practitioners and regulators in the use of geochemical models should be considered.

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1 Introduction

King Groundwater Science, Inc. was retained by the Science Advisory Board for Contaminated Sites in British Columbia (SABCS) to prepare a critical review of the scientific literature to determine the current “state of the science” techniques that could be used to model the transport and behaviour of metals in groundwater. This report provides an overview of the findings and incorporates review comments received following a workshop in Burnaby, BC on 28 June 2005.

The techniques identified in this study are intended to be “Hydrogeological Assessment Tools” which might be applied in a pathway analysis of a contaminated site in British Columbia. These tools are intended for application at sites where generic numerical standards are exceeded; the objective of these tools is to identify (i.e., “screen”) sites where attenuative processes are sufficient to result in no adverse impact to receptors. Because of the complexity of metals behaviour in the subsurface, a higher degree of technical sophistication is needed to accurately quantify potential risk to receptors by groundwater transport. The hydrogeological assessment tools described in this report are intended to be used by qualified hydrogeologists and hydrogeochemists to describe the site-specific behaviour of contaminants depending on particular site needs. A key objective of this study is to identify scientifically defensible methods or tools that adequately describe metal transport in groundwater and that could be developed for use in British Columbia. It is not intended that each tool or method is appropriate for each site, and in some cases combinations of tools may be necessary to solve a particular problem.

The particular topic of metal transport in groundwater is a complex one. The current tools used in the BC and other regulatory environments have significant limitations (West, 2004) which may result in incorrect results, be non-conservative or too conservative¹. The current tools include a computer model which treats metal partitioning between sorbed and dissolved phases through a uniform, linear partitioning coefficient known as K_d . In British Columbia, K_d values for selected metals have been specified for use in the groundwater transport model. However, the selection of generic, site-independent K_d for metals is difficult to do in a scientifically defensible manner due to the geochemical complexity involved in the behaviour of metals in groundwater. A new procedure to address the leaching of metals from the vadose zone has been developed for the “Soil Module” which is part of the Screening Level Risk Assessment process.

The prediction of exposure and risk at a certain point in time and space necessarily requires the use of a model. The goal of simulating the arrival concentration of a contaminant at a downgradient receptor is the main focus of this report. However, the geochemical reactions that occur between ions dissolved in groundwater and minerals composing the host aquifer will affect the behaviour of the contaminant of concern. Geochemical modeling involves combining knowledge of the reactions between chemical components with the components that describe the hydrogeological conditions.

Models are simplified representations of complex natural systems which provide insight and understanding. Depending on the question(s) which are to be answered in a particular system, models can be applied with varying levels of complexity and sophistication. All models will suffer from uncertainty based on our understanding of the natural system, how we formulate the model and variability in input parameter values.

¹ A model which is too conservative may be acceptable as a screening tool

The migration of metals in groundwater will be affected by several factors (Zhu and Anderson, 2002):

- Chemical reactions which determine the partitioning of contaminants among different phases and species,
- Advective transport which moves dissolved species and causes mixing (dispersion),
- Biological processes which mediate reactions, transform compounds and often control the rate of kinetically controlled reactions
- Groundwater flow through an aquifer may be affected by precipitation or dissolution of the aquifer solid phase,
- Heat transport affects the rate of reaction.

This report serves four main functions: attempts to describe the types of geochemical modelling tools that are available, some of their advantages and disadvantages, identifies several issues for discussion and recommends a proposed approach for implementing tools for the migration of metals along the groundwater to receptor pathway.

2 Geochemical Modelling Tools

Geochemical models can be generally categorized by their level of complexity, or whether they are “empirical” or “process-based” (sometimes referred to as mechanistic). An empirical model, being a mix of theory and empirical parameters and tuning, may capture behaviour of a complex environment and can be calibrated for specific conditions, but may not be applicable at other sites as it has no theoretical basis. A process-based approach attempts to represent the fundamental processes that occur in a system due to thermodynamics or mass-action, leading to “reactive transport” models.

Complex models may have greater uncertainty than simpler models due to the number of parameters, reaction rate constants or nonlinear behaviour (Steeffel and Van Cappellen, 1998). Process-based models may also remove uncertainty provided that there is appropriate data to constrain the simulations. The simplest geochemical models involve no temporal or spatial information, and are called “static” models, and are based on equilibrium conditions. Reaction path models simulate sequential reactions in a series of steps and may include some spatial information. The most complex type of models are coupled reactive transport models which address the behaviour of a single or multiple components in both time and space by combining geochemical reactions with solute transport.

2.1 Conceptual Models

A fundamental step for any model is the creation of a conceptual model which describes the system and processes which are important to the model. Preparation of an appropriate conceptual model of the geochemical environment requires understanding of the components present in aqueous and solid phases, the significant reactions that are likely to occur, and the evaluation of the geochemical conditions of the groundwater system. A well-developed conceptual model will allow the modeler to formulate the appropriate questions and hypotheses to be evaluated.

At a contaminated site where metal transport is of concern, detailed mineralogical analyses are typically neglected. The lack of appreciation for the geochemical complexity of the solid-water interaction between the contaminants and the mineral surfaces results in oversimplification or

inability to determine the actual processes occurring and, therefore, behaviour of the metals in solution. Similarly, failure to characterize all phases present in a system, including organic phases, limits understanding of actual processes that may occur. This may lead to an insufficient conceptual model and ultimately causing poor site management decisions.

In order to be able to develop an appropriate conceptual model at metals-contaminated sites, specific data which may not normally be collected in a contaminated site characterization should be collected. This includes geochemical data about the groundwater, the aquifer mineralogy, and organic phases. With this geochemical information, the conceptual model becomes a useful assessment tool in identifying the likely reactions of concern, potential reaction products, and in assisting in selection of other assessment tools. There is additional discussion of site characterization in Section 3.

2.2 Static Models

Static models use computer codes to assess aqueous speciation, complexation and surface reactions, but reactive transport of the solution is not included in the simulation. A summary and comparison of models that include features useful for static geochemical modelling are shown in Table 1.

2.2.1 Speciation Models

The concentration of a metal in groundwater that is reported by a chemical laboratory represents the total concentration of that metal in solution: it is the sum of all species and complexes formed by the metal in the solution. Speciation models use the chemical analyses to determine the concentrations and activities of the ionic and complexed species in the solution, determine the saturation indices of mineral phases and the stable species that are likely to be present in a static solution (Zhu and Anderson, 2002). This requires a complete chemical analysis of a water including major ions, pH and knowledge of redox potential. All calculations are based on thermodynamic reaction constants and are assumed to be at equilibrium. The thermodynamic database used by the model should be as accurate as possible to ensure meaningful results. The basic questions that can be answered with this type of model involve the distribution of species and complexes in solution for given conditions and whether various mineral phases will have a tendency to dissolve or precipitate. Models in this category may also be useful for investigating knowledge gaps and areas requiring further research.

These models can be used to speciate a solution to assess the bioavailability of a species in groundwater as some elements such as Pb and As have different toxicities depending on their speciation (Davis et al., 1992).

Common examples of these models include MINTEQA2 (Allison et al., 1991), PHREEQC2 (Parkhurst and Appelo, 1999) and WATEQ4F (Ball and Nordstrom, 1991). These models are usually limited to dilute waters with ionic strengths less than seawater. The code PHRQPITZ (Plummer et al., 1988) is useful for calculations of geochemical reactions in brines and highly concentrated electrolyte solutions.

2.2.2 Solubility and Precipitation-Dissolution Modelling

The migration of dissolved metals in groundwater can be significantly influenced by the thermodynamic relationships between species in solution and aquifer solid phases. Attenuation of trace metals in groundwater can be caused by precipitation or co-precipitation of mineral phases. Determination of whether or not a metal species is soluble, or is likely to remain in solution at

concentrations of concern is a key consideration when contemplating the metals in groundwater pathway. The degree of saturation of a mineral is usually defined in most geochemical models by use of the Saturation Index (SI), through a thermodynamic analysis of Gibbs free energy for the reaction.

The standard Gibbs free energy of a reaction ($\Delta_r G^0$) can be stated as :

$$\Delta_r G^0 = -RT \ln K \quad (1)$$

where R is the ideal gas constant

T is temperature (°K)

K is the equilibrium constant for the reaction

The standard Gibbs free energy for the reaction can be determined from the difference in free energies of the individual reactants and products at standard temperature. In geochemical model databases, reaction data may be defined as either free energy of species or as log K for specified reactions. It is an important distinction for modelers to understand the form and accuracy of this data particularly when comparing data from various sources.

When the reaction involves a solid phase on one side of the reaction, the equilibrium constant (K) is known as the solubility product, K_{sp} . When the ion activity product (IAP) is equal to K_{sp} , the reaction is in equilibrium. If the IAP is less than K_{sp} , the reaction will be driven towards the reactants and the solid mineral phase will dissolve. Conversely, if IAP is greater than K_{sp} , the mineral will precipitate.

The Saturation Index (SI) can be defined as:

$$SI = \log \frac{IAP}{K_{sp}} \quad (2)$$

The relation between IAP, K_{sp} and SI is summarized below

IAP, K_{sp}	IAP/ K_{sp} Ratio	SI	Result
$IAP < K_{sp}$	< 1	Negative	Mineral Dissolves
$IAP > K_{sp}$	> 1	Positive	Mineral Precipitates
$IP = K_{sp}$	1	0	Equilibrium

(after Stumm and Morgan(1996))

These concepts can be useful in interpreting the significance of precipitation-dissolution reactions and solubility controls on metal mobility in groundwater, Speciation modeling complemented by solubility and precipitation-dissolution calculations should be considered to be fundamental to any geochemical assessment, and based on the results could assist conceptual model development and influence the choice of modeling approach or data collection.

For example, if it can be determined that mineral dissolution or precipitation is significant to metal attenuation, then sorption-based models (see below) would likely be inadequate and reactive transport models might be more appropriate. Or determination that a particular metal is not soluble at concentrations of concern for certain conditions at a particular site could lead to the conclusion that the risk of exposure is low. On the other hand, if mineral dissolution-precipitation are not significant and conditions are expected to remain constant along a groundwater pathway, sorption processes may be the focus for assessment.

Common examples of models which can assess solubility, and precipitation-dissolution reactions include MINTEQA2 (Allison et al., 1991), PHREEQC2 (Parkhurst and Appelo, 1999) and WATEQ4F (Ball and Nordstrom, 1991). These models are usually limited to dilute waters with ionic strengths less than seawater. The code PHRQPITZ (Plummer et al., 1988) is useful for calculations of geochemical reactions in brines and highly concentrated electrolyte solutions. These models also assume that aqueous-solid reactions occur under equilibrium conditions, although this may not be achieved for some reactions within the timescale associated with migration rates of groundwater. Modeling of kinetic effects may be important at some sites, but is another level of complexity.

Inherent in any type of modeling involving transport of metals in groundwater is the constraint that there are fundamental assumptions and chemical principles which requires specific knowledge for the practitioner. A complete discussion of aquatic chemistry and thermodynamics is beyond the scope of this document, however, extensive discussion of these topics can be found in reference books, such as (Langmuir, 1997) or (Stumm and Morgan, 1996).

2.2.3 Sorption Models

Sorption models are used to describe the interaction between dissolved ions and mineral surfaces. This can remove ions from solution and slow the migration of metals in groundwater.

2.2.3.1 Isotherm Based Models

The interaction between dissolved ions in solution with solid mineral phases can be described through the use of isotherms. An isotherm is a plot of the mass sorbed on the solid surface versus the concentration of the constituent in solution, at a fixed temperature. As the concentration of the sorbate is increased, the mass sorbed also increases in a linear or non-linear manner. Isotherms are empirically derived from laboratory batch or column experiments.

The slope of a linear isotherm is known as K_d or the distribution coefficient. The distribution coefficient approach uses one parameter to describe partitioning between solution and solid matrix that may be due to several geochemical processes, and it is usually assumed to be constant in an aquifer. Equilibrium and reversibility of reactions is assumed. Site mineralogy is an important factor, but is neglected (Zhu and Burden, 2001). This simple method of describing ion sorption can be easily incorporated into a mathematical solution of the advection-dispersion equation, that can be solved analytically or by numerical methods. As a result most groundwater solute transport model codes use an isotherm approach to describe surface-solute interaction and retardation. However, the assumptions and difficulties associated with K_d 's make the applicability of these models to environmental problems concerning metals questionable.

Although deficiencies in the K_d approach have been known for some time (Bethke and Brady, 2000; Brady and Bethke, 2000; Cherry et al., 1984; Reardon, 1981), models using K_d are still applied to metals in groundwater problems (Sandia National Laboratories, 1999; U. S. EPA, 1996a; U.S. EPA,

1999; U.S. EPA, 2001). Attempts have been made to make the K_d approach more appropriate through the use of generic K_d vs. pH relationships and selectivity coefficients derived from a geochemical model (U. S. EPA, 1996b) or including non-linearity and probabilistic approaches (U. S. EPA, 1996a).

Some factors which most affect dissolved metal concentrations are the total concentrations of metal in the soil, soil solution pH, organic matter content, and the presence of iron and manganese oxides (Sauve et al., 2000b). Redox conditions are also important. Distribution coefficients of a metal can vary over several orders of magnitude for given pH, total metals in soil or organic matter content. Given the multivariate influences that affect metal concentration in solution, it is unlikely that empirical approaches alone will be successful in predicting metal transport at a particular contaminated site (Sauve et al., 2000a).

There are however, some advantages of the K_d based model approach which include:

- Simple and easy to include in transport models
- Many models are available with this formulation
- Retardation concept is easily understood
- Works best for weakly sorbing, low concentration, contaminants which participate in few reactions and where chemical conditions and pH do not vary.

Some disadvantages of the K_d based model approach include:

- simplistic and compromises the role of geochemistry
- can only simulate one solute at a time (Zhu and Anderson, 2002)
- assumes an unlimited number of sorption sites and does not include competition
- a site specific K_d does not ensure correct assessment of fate under transient system conditions
- changes in aqueous speciation are not accommodated (Langmuir, 1997)
- typically overestimate plume advance and underestimate “tailing” (Brady and Bethke, 2000)

2.2.3.2 Ion Exchange Models

Adsorption of a dissolved ion onto a mineral surface necessarily involves the exchange of another ion in order to maintain the electrical neutrality of the solution. When an ionic species desorbs, it leaves a vacant site which another ion may then occupy. Most soil surfaces are primarily negatively charged, thereby attracting cations. Cation exchange capacity is a common laboratory test indicator which can be used to characterize the capacity of a soil surface to exchange ions in solution.

A simple exchange reaction between two ions can be written as:



where X represents the exchange site. An equilibrium reaction constant and selectivity coefficient can be derived for this reaction.

Exchange reactions assume the sorbate mineral has a constant surface charge, sorption is controlled by valence and size of the ions, and sorption is electrostatic. Simple ion exchange can accurately model binary exchange of many cationic species at trace and major concentration levels (Langmuir, 1997). But, when several competing species are present, the exchange reactions can become quite complicated.

Vulava et al. (2002) compared various cation exchange models to the breakthrough of Ca^{2+} and Na^+ in column studies and found good agreement. The most reliable predictions were obtained with

multisite cation exchange models with a distribution of various types of exchange sites (single- or multi-valence). Ion exchange reactions may need to be included with other geochemical reaction models in order to adequately describe observed processes. For example, van Breukelen et al. (1998) found that ion exchange, kinetically limited oxygen consumption and denitrification, and equilibrium calcite reactions were needed to describe reactions when river water was recharged to an aquifer. A model with cation exchange and specific sorption reactions can successfully predict the transport of Cd, Zn and Ni in soil columns (Voegelin et al., 2001). In general, the most successful ion exchange simulations were done in laboratory experiments with detailed and well-constrained data sets.

Ion exchange modelling does not explicitly assist with temporal or spatial transport issues and needs to be coupled with a transport code to evaluate mobility of heavy metals.

Some advantages of Ion Exchange Models include:

- Already incorporated into many existing solute transport models
- Parameters are easily measurable (e.g. CEC, selectivity coefficients)
- Numerical approach is robust and relatively easy to use
- Can easily be incorporated with other geochemical reactions in a consistent numerical framework

Some disadvantages include:

- Not suitable for changing pH conditions
- Ion exchange parameters are not transferable from site to site, and requires site specific characterization
- Can't model behaviour of metals beyond the range of laboratory characterization or to other metals
- Surface properties are fixed. i.e. changes in solution characteristics are not reflected in changes in surface properties

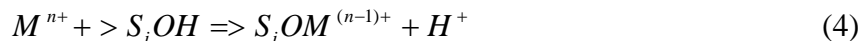
2.2.3.3 Surface Complexation Models

Describing the sorption of a dissolved ion to a mineral surface to form a "surface complex" is called a surface complex model (SCM). Common hydrous oxides of iron, aluminum, manganese and silicon are the dominant sorbents in nature because they are finely dispersed and coat other particles (Dzombak and Morel, 1990) and are electrostatically active. Sorption of inorganic ions onto these oxide coatings or other surfaces is dependent on pH, ionic strength and competition from other ions in solution.

The SCM approach involves using mass action equations to describe the adsorption of a dissolved metal ion onto surface sites of a mineral phase. There are four fundamental tenets (Davis and Curtis, 2003):

1. mineral surfaces have chemical functional groups that react with dissolved species to form a surface-complex species
2. the adsorption reaction can be described by an equilibrium mass action equation
3. The binding constants for the mass action equations are empirical parameters related to thermodynamic constants
4. Electrical charge at the surface is determined by the chemical reaction of the mineral functional groups and the formation of ion pairs and complexes.

An example of a surface complexation reaction is:



where $>S_iOH$ represents one of a series of adsorption sites with different affinity for metal ion M^{n+} . Equilibrium constants can be obtained by fitting experimental data obtained from site-specific materials.

There are several types of surface complexation models that have been proposed. The generalized two-layer model describes sorption at oxide surfaces as a reaction with specific surface sites. Other variations include the constant-capacitance model, and triple-layer model (Dzombak and Morel, 1990).

The majority of publications on surface complexation modelling have involved well-controlled column experiments. However, there are applications of SCM to field cases where trace metals in groundwater are of concern. Kent et al. (1995) conducted a field experiment and injected a solution containing Br, Cr(VI), Se and other tracers in an aerobic sand and gravel aquifer. Steep rising limbs and long tails in breakthrough curves were consistent with the equilibrium adsorption assumed in the SCM approach. It was noted that chemical conditions such as pH, competition from adsorbing solutes, and redox conditions strongly influence the transport of weakly adsorbing redox-sensitive solutes.

Davis et al.(1998) studied the migration of Zn^{2+} in the Cape Cod aquifer. Using a “generalized component” modelling approach to surface complexation with three adjustable parameters, it was found that Zn^{2+} adsorption could be simulated over a range of chemical conditions that would cause several orders of magnitude variation in a K_d value for Zn^{2+} in this aquifer. In the same aquifer, Stollenwerk (1998) used diffuse-layer surface complexation models coupled to a transport code to simulate adsorption and two-dimensional migration of molybdate (MoO_4^{2-}), sulfate and phosphate. The important processes that were found to be of concern in this case, were non-linear adsorption on hydrous iron and aluminum oxide coatings, competitive sorption, and decreasing sorption of the anion with increasing pH. A combination of field measurements and laboratory experiments aided the simulations. Kent et al. (2000) were able to account for the influence of variable pH on adsorption and transport of Zn in an aquifer contaminated by sewage effluent using a semi empirical SCM approach.

Wen et al. (1998) examined the adsorption of heavy metals Cd and Cu to natural river sediments using three versions of surface complexation models. Sorption was strongly pH dependent and good agreement to the data was obtained for all three models. Relative errors were estimated to be within 15%.

Surface complexation models have been applied to multicomponent, complex mine sites where acid mine drainage impacted groundwater quality. Identification of the controlling processes and comparisons with field data indicated these geochemical modelling approaches were reasonable (Davis and Curtis, 2003; Zhu and Burden, 2001).

Alternate applications of the SCM approach include coupling stochastic advective-reactive transport modelling with SCM in a system with variable flow and multicomponent reactions. Injection of oxygen to an aquifer to create an adsorptive hydrous iron oxide coating and increase Cr and As sorption is a novel remediation technique (Martin and Kempton, 2000). The accuracy of predicting

the incremental effects in column studies suggested that their models could be applied to other metal contaminants that also have an affinity for hydrous ferric oxide.

The data required for surface complexation models are often based on laboratory experiments of adsorption on pure mineral phases. Natural soils are more complicated, commonly containing mixtures of minerals and amorphous mineral coatings. Unless a user can defend the assumption that the adsorption of a specific contaminant is dominated in a specific soil-water system, for example, by a particular reactive mineral surface such as goethite, the user is still left with the challenge of extrapolating these modelling results for pure mineral substrates to complex heterogeneous soil-water systems (U.S. EPA, 1999).

Some advantages of surface complex modelling include:

- superior to the K_d method because the linkage between surface and aqueous species is retained (Davis et al., 1998)
- there are few reactions, so a low number of fitting parameters are needed
- changes in solution characteristics are reflected in surface properties
- large compilations of reaction constants are available for some surface phases (Dzombak and Morel, 1990)

Some disadvantages of SCM include:

- high level of surface characterization required. i.e. difficult to determine the type and density of adsorption sites
- predictive capabilities limited by availability of key geochemical parameters (Bain et al., 2001)
- model may assume reactions occur onto a specific set of solids which may not be the principal adsorbers, or the solids are actually likely to be mixtures or heterogeneous at the field site
- application of SCM to heterogeneous aquifer materials is not well documented

2.3 Reaction Path Models

Reaction path models are designed to calculate and solve a series of equilibrium reactions in response to incremental changes in concentration along a flowpath. Their main application has been in identifying reactions causing changes in chemistry between two points. The model can simulate many reactions and can be constrained by the available geochemical or isotopic data. These models are not capable of incorporating effects of spatial compositional changes.

An example is NETPATH which is a public domain code developed by the US Geological Survey to interpret net geochemical mass-balance reactions between initial and final waters along a hydrologic flow path. The program uses chemical and isotopic data for waters from a hydrochemical system. The processes of dissolution, precipitation, ion exchange, oxidation/reduction, degradation of organic compounds, incongruent reaction, gas exchange, mixing, evaporation, dilution, isotope fractionation, and isotope exchange can be considered.

Some advantages of reaction path models:

- Interprets mass balance reactions
- Constraining reactions can be included

Some disadvantages include:

- Not possible to distinguish equally likely reaction paths
- Do not incorporate temporal or spatial changes
- Constrained by assumptions of aquifer composition along flowpath

2.4 Coupled Reactive Transport Models

This type of model is formulated to describe advective-dispersive transport of chemically reactive substances. “Coupled transport and reaction models can be used to simulate how a geochemical system evolves over time along a fluid flowpath in one, two, or even three dimensions” (Crawford, 1999). Two main modules consisting of the process-based approaches to solving the geochemical mass-action reactions, and a module to solve the differential equations for groundwater transport are linked together. A summary and comparison of coupled reactive transport computer codes that are available in the public domain are shown in Table 2.

Some coupled transport and reaction models have developed as extensions of existing flow and transport models developed to study groundwater flow. Others have developed out of geochemical models into which transport capabilities were subsequently added. In either case, the resulting mathematical formulations for multicomponent, coupled reactive transport models are complex (Lichtner, 1996; Steefel and MacQuarrie, 1996) and computational demands can be large (Walter et al., 1994). Recent advances in computing power and solution schemes have made use of high resolution, multidimensional, multicomponent reactive transport models more efficient and able to take on complex hydrogeochemical problems (Yabusaki et al., 1998).

There are also varying degrees of complexity and sophistication of coupled reactive transport model codes. The simplest may involve one-dimensional groundwater transport coupled with an ion exchange geochemical model for a single component. A more complex code could involve flow in a heterogeneous aquifer where several spatially variable components react in a three dimensional domain. Many coupled reactive transport models are also capable of including biological processes which can have significant importance to metal transport (Brun and Engesgaard, 2002; Hunter et al., 1998; Mayer et al., 2002; Tebes-Stevens et al., 1998).

As with any groundwater solute transport model, these models require appropriate conceptual model development, assumptions, boundary conditions and numerical solutions in order to represent groundwater flow. They also require the appropriate development of a conceptual model, identification of reactions and selection of appropriate geochemical parameter values to solve the geochemical reactions.

Recent applications have included modelling the geochemical evolution of groundwater contaminated with Cr(VI) and trichloroethylene as it flowed through a permeable reactive barrier (Mayer et al., 2001), the migration of metals and geochemical interactions due to acid mine drainage (Bain et al., 2001; Mayer and Blowes, 2002; Zhu and Burden, 2001), biogeochemical processes and redox zonation in a landfill plume (van Breukelen et al., 2004), and the transport of highly concentrated aqueous solutions leaking from underground tanks (Zhang et al., 2005).

Within the context of the groundwater transport pathway for metals and risk assessment, the advantages for using a coupled reactive transport model include:

- The transport process is included explicitly
- Mechanistic approach to description of mass-action reactions based on thermodynamic principles leads to more accurate result
- Kinetic and equilibrium reactions can be included

- Multiple components are considered in geochemical reactions
- Model results can be easier to compare to available observations (such as plume distribution)

The main disadvantages for using a coupled reactive transport model include:

- Higher complexity requires higher level of input data
- Computational requirements may be large for complicated, multi-dimensional models
- Uncertainty or missing thermodynamic data for some reactions (as for all geochemical models)
- Many adjustable parameters
- Detailed mineralogical data often not available
- Greater skill required to create models and interpret the results

3 Discussion

Understanding the transport of metals in groundwater is a complex subject requiring considerable care to ensure that meaningful results are obtained. It is apparent that the state of the art regarding modelling of the transport of metals in groundwater is in the application of coupled reactive transport models. Advances in algorithms and computing power in recent years has enabled highly complicated combinations of geochemical and hydrologic processes to be combined in one computer code. A wide range of hydrogeochemical problems can be investigated with these models. However, serious constraints remain for all models due to lack of site-specific data and heterogeneity of subsurface conditions.

Efforts have been made to incorporate “semi-mechanistic” processes into the simpler, easier-to-use, empirically-based K_d models to make them more robust and defensible (U.S. EPA, 1999). This approach may prove to be useful at some sites, but there are still fundamental deficiencies of the isotherm based models. This is an ongoing area of research which seeks to determine the circumstances for when an empirical or process-based model would be appropriate to evaluate a contaminated site. The level of analysis of a model solution will reflect the complexity of the problem, the level of certainty needed and the site-specific conditions. For risk assessment purposes at high risk sites, it is difficult to envision a situation where an isotherm based transport code would meet the level of analysis required, without considerable supporting evidence.

For the requirements of the Screening Level Risk Assessment 2 (SLRA2) process for metals in groundwater, it is recognized that there will be a variety of site-specific requirements and assessment tools that could be used to provide the necessary screening. A proposed overall screening process within which these tools could be applied is shown in Figure 1, and described in Section 4. A discussion of general requirements for the “metals in groundwater module” of SLRA-2 is provided below.

3.1 Selection of Assessment Tools or Models

Field studies and model applications have shown that the mechanisms and characteristics which control the transport of inorganic contaminants at field sites are highly site specific. Therefore, specification of a generic model, with generic parameters, for prediction of the fate and transport of inorganic contaminants would be inappropriate. The mechanisms controlling metal transport vary from site to site, as do concentration ranges of dissolved constituents and the characteristics of the aquifer materials.

For any geochemical modelling exercise, the choice of model and approach will depend on the question which is to be answered. It may require only one, or a combination of geochemical model calculations to provide the understanding necessary to predict the appropriate outcome. Therefore, specification of performance standards is more desirable than specifying that a particular model must be used in a screening or detailed risk assessment. Rather than specify that a particular code be used, the selection of a code should be left to the proponent of a risk assessment to meet site-specific needs, and performance requirements should be specified by the regulator. If a geochemical computer code is used, it should be non-proprietary, peer-reviewed and transparent.

To set up a geochemical model, specific information is needed to describe the geological system, conceptualize the chemical reactions that occur, and the thermodynamic, kinetic and surface

properties within the specific hydrogeologic system of interest. Therefore, in addition to characterization of the hydrogeologic conditions that affect groundwater transport, basic geochemical data must be collected at contaminated sites where metals are likely to be present, for both the dissolved and solid phases. Requirements for minimum data collection during the characterization phase are discussed below.

3.2 Site Characterization

3.2.1 Hydrogeology

It is expected that in order to adequately address the metals in groundwater issue, that a sufficient degree of site characterization has been carried out to allow understanding of hydrogeologic conditions, the extent and distribution of any contaminant plumes and sources. Generally, the requirements for a Detailed Site Investigation would have to be obtained to address this pathway. The collection of data needed to construct the conceptual model will be an iterative, evolutionary process.

3.2.2 Aqueous Chemistry

Characterization of geochemical conditions within an aquifer requires careful collection of data which has typically not been considered part of most contaminated site investigations. This is because the information required to assess geochemistry or necessary for input into geochemical models (e.g. major ions) are not thought of as “contaminants”, and their value is underestimated for many sites. However, in order to understand the behaviour of metals in groundwater, characterization of the aqueous chemistry is critical. The sensitivity of many metals to redox conditions also require that precautions must be taken during sampling and analysis to ensure results are obtained which are representative of groundwater chemistry.

The following parameters are considered “Core Parameters for Groundwater” (U.S. EPA, 2002) which are appropriate for all metals-contaminated sites:

- Temperature
- Eh, pH, alkalinity
- Turbidity²
- Total and Ferrous iron
- Dissolved oxygen
- Specific conductance
- Dissolved organic carbon
- Major ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, S²⁻, SO₄²⁻, NO₃⁻, Ammonium, Phosphate)
- Aluminum, Silica, Manganese

² Turbidity has importance as a sampling equilibration parameter during low-flow sampling, and evaluating the influence of particulates on metals concentration or data anomalies

In addition to the core parameters, “Site-Specific Parameters for Groundwater” may also be measured as appropriate, and they include:

- Dissolved inorganic carbon
- Total dissolved solids
- Fluoride
- Hydrogen
- Methane
- Sulfide

Specification of the appropriate methodology for the collection and analysis of the above listed parameters is beyond the scope of this document, however, descriptions of techniques and methods can be found in U.S. EPA(2002) and the U.S. Geological Survey online field manual (U.S. Geological Survey, Variously dated). It is important to note that certain parameters must be measured in the field due to stability issues and others are recommended to be field measurements.

Some parameters *must* be measured in the field: temperature, pH, Eh, dissolved oxygen, turbidity. Use of flow through cells is recommended. Specific conductance and alkalinity are recommended for field analysis. Redox indicators such as Fe(II), S²⁻ and H₂ should also be measured in the field rather than the laboratory.

3.2.3 Solid Phase Geochemistry

Solid phase characterization should be included for sites where metals or other inorganic contaminants in groundwater are being evaluated for SLRA-2, a detailed risk assessment, or for remediation feasibility planning. The solid phase should be tested to confirm the form of the metal associated with the mineralogy of the solid phase, and to determine its stability or mobilization potential (U.S. EPA, 2002). If immobilization is necessary to pass a risk assessment, then it should be required to know the conditions under which the metal may be mobilized.

Examples of useful solid phase characterization techniques include: optical analysis of the mineralogy by a geologist/geochemist, x-ray diffraction (XRD) or microprobe analysis to determine the presence of elements and minerals, cation exchange capacity, neutralization or acid-generation capacity, and extraction of amorphous iron or aluminum coatings to assess mass of sorptive material on mineral surfaces. Depending on site-specific needs, a useful approach would be to use mineralogical identification tools to *confirm* mineralogy, followed by chemical extraction to *quantify* mass of the mineral. Organic coatings or other organic matter on the solid phase can exert significant geochemical influence on groundwater and should be characterized.

There are a number of site-specific parameters which can be used to characterize solid-phase materials as needed:

- Oxidizing capacity
- Reducing capacity
- Neutralization capacity
- Adsorption capacity
- Cation exchange capacity

- Acid generation capacity
- Iron/aluminum extraction
- Mineralogy (XRD)
- Total organic carbon
- Sulfur extraction

Collection of solid phase samples in the field for later mineralogical analysis also requires careful attention and handling in order to preserve conditions as they are in the aquifer. Minerals that are stable under a reducing environment (such as in an aquifer) will be subject to alteration when exposed to oxygen. Removal of pore water from the sample may also cause some transformations. Significant changes in reactivity may result from changes in mineral structure and surface area due to drying at even slightly elevated temperatures. Therefore, careful handling will be necessary for proper preservation of solid samples for subsequent characterization.

Specification of precise procedures for sampling and handling of solid-phase samples is beyond the scope of this report. But, it is necessary that solid-phase characterization be included as part of site investigations where groundwater is contaminated with metals, and that additional planning and expense will be involved compared to typical current site characterization practices. For example, recommended procedures for sample cores obtained in the field for mineralogical or other solid-phase characterization is that they should be immediately capped and frozen, placed in a cooler or freezer, and later thawed under an oxygen-free or inert atmosphere (U.S. EPA, 2002). Procedures will vary depending on site-specific concerns and the analyses being performed. It is reasonable to expect that characterization will be necessary at locations within contaminated and uncontaminated areas of an aquifer with the number of samples related to the degree of heterogeneity.

3.3 Verification of Reactions

A useful approach to confirm that a set of geochemical reactions or processes are actually occurring at a site is to include verification as part of the site assessment. This is particularly appropriate for metals in groundwater where dissolution-precipitation or adsorption reactions are dominant. After inferring that a set of reactions are occurring based on the aqueous geochemistry, actual observation of the solid phase mineralogy can confirm the presence of a species, and that the reactions are valid. For example, if it is inferred that the presence of a particular mineral phase is necessary to control the solubility of a metal (and hence its concentration), then it is important to confirm that the mineral actually exists in the aquifer. This independent approach provides confidence that both the geochemical and conceptual models are correct.

3.4 Interpretations and Results

In making regulatory decisions, there may be compromises made between scientific rigour and the benefit of simplifying, conservative assumptions. Practicality would suggest this, but due to the difficulties in fully characterizing the site-specific behaviour of metals at some high-risk sites, this would have to be done with great care. Conservative assumptions or bounding calculations, could lead to simpler geochemical questions and solutions as long as the result remains protective.

There are basic considerations and data needs that must be collected, but it would be appropriate to begin a site analysis with simple easy-to-apply models and advance to more complex codes as conditions require. It should be recognized that there are cost-benefit limits in the choice of some

models due to the data collection requirements that might be needed, but these will have to be evaluated on a site-by-site basis.

The model practitioner, and reviewing regulator, must be suitably trained to fully understand how the model is formulated and the implications of the choices that must be made. It is anticipated that in order to adequately understand the geochemical processes involved, the user would need academic training in aqueous geochemistry and instruction in the application of models. Although there should not be relief for users from understanding geochemical models, the models should be accessible at a level that is useable and not overly complicated.

The utility of a geochemical model is limited by errors introduced during development of the model and the ability to model certain processes (U.S. EPA, 2002). The model which is developed is dependent on accurate physical and chemical data from the site, and data collection is the first opportunity to introduce error into the interpretation. Therefore, the accurate collection of data from the field using appropriate and accepted procedures should be emphasized in all site characterizations.

4 Application to Screening Process

A qualitative screening level risk assessment protocol for contaminants in soil and groundwater has been proposed for British Columbia (SABCS, 2004). The SLRA-2 is designed to evaluate the soil-to-groundwater transport pathways for the purposes of screening out sites which pose an acceptable risk to the receptor. Acceptable risk is defined to mean that either i) contaminants in soil are not expected to result in groundwater concentrations in excess of applicable standards, or ii) concentrations of contaminants in groundwater at the receiving environment are not expected to exceed applicable standards. The screening process described in this chapter is intended to provide a method to evaluate the transport of metals in groundwater at contaminated sites. It is analogous to the “Groundwater Module” of the SLRA-2, but requires a geochemically oriented approach.

A fundamental concept of SLRA-2 is the objective of screening low-risk sites out of the regulatory process while ensuring that no moderate-risk sites are inadvertently screened out. Conservatism in the process is necessary and intentional, as one potential outcome is that contaminants which exceed numerical standards will be left in the subsurface in perpetuity without remediation. If a site is not appropriate for SLRA-2, then a detailed risk assessment (DRA) may be undertaken which does not have the restrictive assumptions of SLRA-2.

If a site is screened out by the SLRA-2 process, then no further action is required. If a site is not screened out by SLRA-2, then further assessment or remediation would be required.

4.1 Proposed SLRA-2 Metals in Groundwater Screen

This screening process is appropriate for identifying sites which are likely to be protective of receptors, those sites which should be addressed in the SLRA Soil Module, and those sites which require further assessment or remediation.

A process flow chart indicating four main steps involved in the screening is shown in Figure 1. Each step is described below.

Step 1 Site Characterization Phases. As described in Section 3.2, there are three aspects relevant to metals transport that must be characterized during the site investigation. These are characterization of the hydrogeology, the aqueous geochemistry and the solid-phase chemistry. Important differences exist between the information needed for geochemical characterization compared to typical site investigations. These include sampling and analysis of groundwater for major ion chemistry, redox parameters, mineralogical testing, and specific sampling and handling requirements as appropriate for site-specific needs.

This step is intended to link directly to current site characterization requirements for contaminated sites in British Columbia. When this screening process is initiated, a site owner would already have performed at least a preliminary site investigation, expected metals to be potential contaminants of concern and developed a preliminary site conceptual model. Hydrogeologic and subsurface characterization is a required component, and could require iterative phases of investigation to determine the extent and nature of contamination by metals. It can be anticipated that solid phase characterization would not be necessary unless the results of aqueous analyses indicated a concern with metals in groundwater.

Step 2 Refine Conceptual Model The conceptual model is fundamental to any site characterization and evaluation, and is included here for emphasis of its critical nature. A proponent should show a good understanding of site subsurface conditions, the presence and spatial distribution of contaminants of concern, and gained an understanding of geochemical conditions in the aquifer.

It is assumed that a site conceptual model had already been prepared during preliminary site assessment and the site characterization phases. Following Step 1, the conceptual model should be refined with respect to geochemistry and the fate and transport of metals at the site.

Once an understanding of site conditions has been obtained, a proponent should be able to answer the questions “Are metals above criteria only in soil?”. If metal contamination is only in soil and not in groundwater, then the SLRA Soil Module process should be implemented. The Soil Module addresses the leachability of metals in soil and provides a method to determine likely future impact on groundwater. If metals are either in groundwater or, groundwater and soil, above standards then further screening should be performed in Step 3.

Step 3 Reaction Identification and Verification Screen This step is the critical one with regard to identifying the reactions which affect the metals of concern, the speciation and form of dissolved metals, and their interaction with the minerals on the aquifer solid phase. Utilizing the information from Step 1, a proponent should be able to identify the contaminated zones, concentration levels in the aquifer, migration rates, redox conditions or zonation, the minerals which are present, and the expected reactants or products from reactions involving the dissolved metal(s) and solid phase.

This step involves the use of a static model (Section 2.2) to determine equilibrium dissolved species and complexes present in the groundwater, and to identify those minerals with the tendency to dissolve or precipitate. Once a set of geochemical reactions are inferred that control the behaviour of metals, they should be confirmed through observation of the solid phase.

This step also allows the question to be posed “Are metals stable under these conditions?”. Stability refers to whether the metals of concern will remain in solution at the observed concentration levels, or whether they would tend to increase or decrease in concentration through dissolution, precipitation or other geochemical reactions. It does not refer to plume stability. For example, sulfide minerals, which produce acidic drainage when exposed to oxygen, would be considered to be stable if present in the aquifer since oxidation would be inhibited, but unstable if located in the vadose zone. In order to demonstrate stability, a geochemical explanation must be provided which could include:

- identification of reactions affecting the metal,
- supporting geochemical model results,
- evidence that any reactants required to maintain a reaction will be available for the foreseeable future (in British Columbia this is considered to be 100 years),
- verification and observational data.

If the metals can be shown to be stable, then there would be no pathway to the receptor for metals within the regulatory time of interest, and further assessment would not be required. If not, proceed to Step 4.

Step 4 Perform Transport Modelling Study This step combines geochemistry and groundwater transport so that a prediction can be made as to when (or if) a metal would arrive at a receptor location and the exposure concentration. The effort required for this step will be highly dependent on the complexity of the geochemical reactions and the hydrogeologic setting. However, as a minimum, the model selected should be a coupled reactive transport code which solves both geochemical and transport equations along a one-dimensional domain. Most situations can be addressed sufficiently in one-dimension, due to inherent uncertainties. An example code is PHREEQC2 (Parkhurst and Appelo, 1999) which is easily available, becoming widely used and accepted, with many geochemical capabilities and one-dimensional solute transport.

A transport modelling study should include the following aspects:

- summary of geochemical and hydrogeologic conceptual models
- geochemical reactions which are being modeled
- description of model(s) used
- assumptions used in the model
- limitations of the model
- sources of thermodynamic and kinetic data
- model input data
- comparison of modeling results with field and laboratory data
- model predictions
- sensitivity analysis (It may not be appropriate to include the SLRA-2 S_I and S_{II} Cross-plot technique for metals in groundwater. However, a sensitivity analysis for basic transport parameters should be provided with the model result)
- Identification of areas of uncertainty.

At the conclusion of Step 4, a decision can be made as to when or whether the contaminant will arrive at the receptor, and whether it is likely that the concentration would exceed acceptable criteria. If the predicted concentration exceeds criteria, then further assessment or remediation is required. Otherwise, the predicted exposure is acceptable and there is no pathway to the receptor.

5 Conclusions and Recommendations

The following conclusions have been drawn concerning tools that can be used to assess the migration of metals in groundwater.

1. The geochemistry of metals transport in groundwater can be complex and require a high degree of technical sophistication to accurately screen sites and quantify potential risk to receptors.
2. The application of the K_d isotherm approach to metal transport in groundwater has several difficulties, and is not scientifically defensible at most contaminated sites. There are alternative approaches which are process-based and are more likely to provide accurate site-specific results. The limitations of process-based models should not be used as justification for retaining simple, K_d based modeling approaches.
3. Coupled reactive transport models are now available which combine geochemical reactions with the transport of metals in groundwater.
4. Contaminated sites containing metals in groundwater require some additional characterization that is specific to understanding the fate and transport of metals. This involves site-specific characterization of aqueous and solid-phase geochemistry in addition to hydrogeology.
5. A process for assessing risk at metal-contaminated sites should consider the following points:
 - a good conceptual model is critical
 - the groundwater flow system must be understood
 - groundwater must be characterized for the dissolved metals of concern and geochemical parameters
 - composition and properties of the solid media must be characterized
 - water quality data must meet data quality objectives
 - the accuracy of the thermodynamic database for geochemical models is important
 - modelling should include sensitivity and uncertainty analysis
 - numerical analysis should be considered a tool to support or augment observations
6. Some complicated geochemical models have many parameters requiring considerable site-specific values which may be limited by the availability of, or ability to collect the necessary data, or the skill level of the user.

The following recommendations are made.

1. The characterization requirements for contaminated sites which contain metals, in either soil or groundwater should be enhanced to include geochemical measurements of groundwater and characterization of all solid phases and aquifer mineralogy.
2. Screening level and detailed risk assessments for the migration of metals in groundwater should be supported by geochemical calculations and modelling.
3. The application of K_d -based transport models as the only assessment tool should be discouraged.
4. The minimum approach for screening metals-contaminated sites should include use of static models (e.g. MINTEQA2, PHREEQC2) to identify potential reactions, characterization of mineral phases present and provide an opportunity to verify that reactions are actually occurring. Simple coupled reactive transport models or more sophisticated models could be applied depending on site characteristics, the results of the preliminary steps, and availability of supporting geochemical data.
5. Due to the complexity of the issues associated with metals contaminated groundwater, and the need for geochemical interpretation, it is likely that many contaminated site professionals would not have the background to adequately apply all of the tools described in this report. Training seminars for practitioners and regulators in the use of geochemical models should be considered for metals-contaminated sites.

6 Closure

This report is intended for the use of the Science Advisory Board for Contaminated Sites in British Columbia, and has taken a technical approach to the issue. It is recognized that portions of this document may be used to develop guidance, as appropriate, by the Ministry of Environment for use at contaminated sites in British Columbia.

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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	Chemical Reaction 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: 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

Table 2 Coupled Reactive Transport and Geochemical Reaction Transport computer codes (adapted from Crawford, 1999)

COMPUTER CODE	Advection	Diffusion / Dispersion	Dimensionality	Saturated Transport	Unsaturated Transport	Gas Transport	Colloid Transport	Heat Transport	Simple Degradation / Decay Kinetics	Monod Kinetics	General Homogeneous Reaction Kinetics	Heterogeneous Reaction Kinetics	Mobile Mineralization Fronts	Unsteady State Calculations	Quasi-Steady State Calculations	Internal Flow Field Calculations	Dynamic Boundary Conditions	Spatially Variable Material Properties	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	Multiprocessor Enabled Code	Chemical Reaction Database Included	Public Domain		
2DFATMIC	X	X	12	X	X				X	X				X		X	X	X				O		X									X		
3DFATMIC	X	X	123	X	X				X	X				X		X	X	X					O		X									X	
BIOMOC	X	X	12	X					X	X				X		X		X					O		X									X	
BIOPLUME III	X	X	12	X					X	X				X		X	X	X					O	X	X						X			X	
BIOSCREEN	X	X	12	X					X					X									O		X									X	
CHEMFLO	X	X	1	X	X				X					X		X								X										X	
FEHM	X	X	123	X	X	X			X	X				X		X	X	X	X		X		O		X									X	
FLOTTRAN	X	X	123	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X		?	?				X		
HST3D	X	X	123	X					X	X				X		X	X							X										X	
HYDROBIOGEOCHEM	X	X	123	X	X				X	X	X	X	X	X			X	X	X	X	O		X	X	X	X		X				X		X	
MOC	X	X	12	X					X					X		X		X						X	X									X	
MOC3D	X	X	123	X					X					X		X		X						X	X						X			X	
MOFAT	X	X	12	X	X	X			X					X		X	X	X						X	X						X			X	
MPATH	X		1	X									X	X		X			X	X	X	X	X	?	?	?		?	?				?	X	
MIN3P	X	X	123	X	X	X			X	X	X	X	X	*	X	X	X	X	X	X	X	X	X	X	X	X		X	X				X		
MT3D	X	X	123	X					X					X		X	X						O		X									X	
PHAST	X		123	X					X	X	X	X	X	X		X	?	X	X	X	X	X	X	X		X	X	X	X				X	X	
PHREEQC 2	X	X	1	X					X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X				X	X	
RITZ	X		1	X	X				X					X		X	?	?						X											X
RT3D	X	X	123	X					X	X	X	X		X		X	X						O		X										X
SUTRA	X	X	12	X	X				X	X				X	X	X	X	X						X											X
UNSATCHEM	X	X	1	X	X	X			X				X	X		X		X	X	X	X		X				X	X	X	X				X	
VLEACH	X		1	X	X	X								X		X	?				X			X										X	
VS2DT	X	X	12	X	X				X					X		X		X						X											X

Notes: X indicates capability
 O indicates partial capability
 T Text-based interface
 ? unknown capability
 * uses GIM (global implicit solution method), can be used in this mode as any other code that uses the GIM

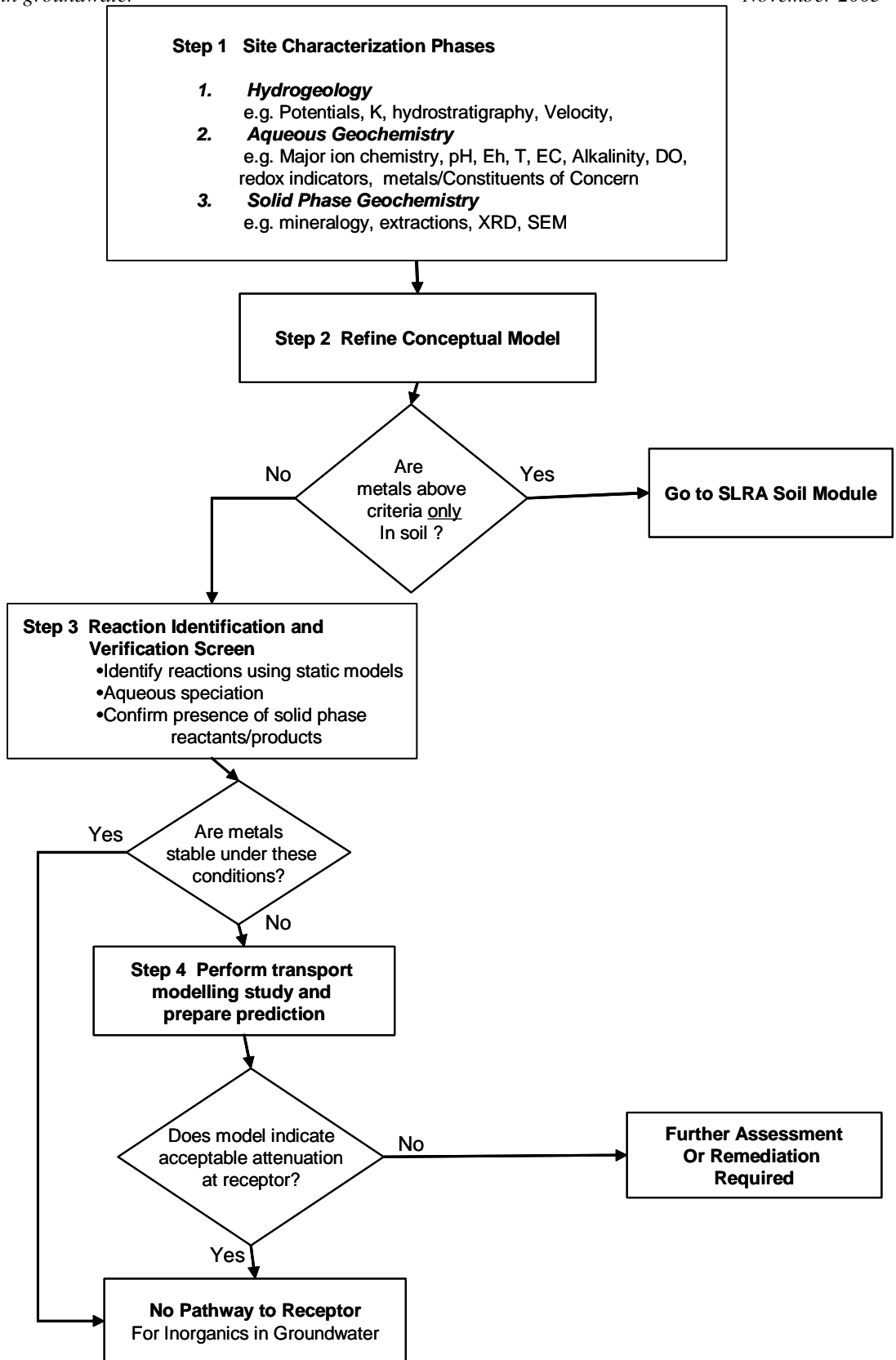


Figure 1 Screening process for metal contaminated sites