

NATURAL ATTENUATION OF HAZARDOUS INORGANIC COMPONENTS: GEOCHEMISTRY PROSPECTIVE

유해 무기물의 자연정화: 지화학적 고찰¹

Suk Young (S.Y.) Lee, ChaeYoung Lee, and Jun Ki Yun
Research Institute of Technology Samsung Corporation

Summary

While most of regulatory communities in abroad recognize “natural attenuation” to include degradation, dispersion, dilution, sorption (including precipitation and transformation), and volatilization as governing processes, regulators prefer “degradation” because this mechanism destroys the contaminant of concern. Unfortunately, true degradation only applies to organic contaminants and short-lived radionuclides, and leaves most metals and long-lived radionuclides. The natural attenuation processes may reduce the potential risk posed by site contaminants in three ways: (i) contaminants could be converted to a less toxic form through destructive processes such as biodegradation or abiotic transformations; (ii) potential exposure levels may be reduced by lowering concentrations (dilution and dispersion); and (iii) contaminant mobility and bioavailability may be reduced by sorption to geomedia. In this review, authors will focus on “sorption” among the natural attenuation processes of hazardous inorganic contaminants including radionuclides. Note though that sorption and transformation processes of inorganic contaminants in the natural setting could be influenced by biotic

activities but our discussion would limit only to geochemical reactions involved in the natural attenuation. All of the geochemical reactions have been studied in-depth by numerous researchers for many years to understand “retardation” process of contaminants in the geomeia.

The most common approach for estimating retardation is the determination of distribution coefficients (K_d) of contaminants using parametric or mechanistic models. As typically used in fate and contaminant transport calculations such as predictive models of the natural attenuation, the K_d is defined as the ratio of the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. Unfortunately, generic or default K_d values can result in significant error when used to predict contaminant migration rate and to select a site remediation alternative.

Thus, to input the best K_d value in the contaminant transport model, it is essential that important geochemical processes affecting the transport should be identified and understood. Precipitation/dissolution and adsorption/desorption are considered the most important geochemical processes affecting the interaction of inorganic and radionuclide contaminants with geomeia at the near and far field, respectively. Most of contaminants to be discussed in this presentation are relatively immobile, i.e., have very high K_d values under natural geochemical environments. Unfortunately, the obvious containment in a source area may not be good enough to qualify as monitored natural attenuation site unless owner demonstrate the efficacy if institutional controls that were put in place to protect potential receptors. In this view, natural attenuation as a remedial alternative for some of sites contaminated by hazardous-inorganic components is regulatory and public acceptance issues rather than scientific issue.

¹ 본 원고는 발간되지 않은 타 저자의 초고 (draft) 들에서 인용된 부분이 많고 workshop 용으로 준비되었으므로 연구 논문에서의 인용을 삼가 해 주십시오.

Introduction

The objective of this review is to discuss major geochemical parameters involving mobility of hazardous inorganic components and their implication on alternative development and decision process for NA viability. Most of environmental engineers agree that cleanup of contaminated sites is hardly achievable at reasonable cost. Therefore, natural attenuation (NA) is widely discussed as an alternative approach to active remediation in the United States and European countries. In principal, the NA concept should be applicable for most hazardous contaminants including organic, inorganic and radioactive components in soils and groundwaters. However, organic contaminants in groundwaters have received most attention during recent years because most organic contaminants are biodegradable at a wide range of rates in geomedial. Within the natural attenuation processes, biodegradation is an important mechanism that results in the actual reduction of the mass of contaminants. Radioactive decay of alpha emitting radionuclides does a small reduction of mass but it is not significant for overall mass. Uptake by biomass could reduce concentration of inorganic contaminants but not enough to count as a major sink for attenuation. Therefore, NA of inorganic components violates the first approximation of the narrow concept "NA can be a valid concept for compounds which are sufficiently biodegradable" given by Wiedemeier *et al.* (1999). For the metals and radionuclides, retardation by varying natural geochemical mechanisms is the dominant attenuation process that could confine in source area and reduce the flux to accessible environment. Figure 1 shows processes and parameters need to be characterized prior to, during, and after site remediation (Brady *et al.*, 1998). The conceptual model shows that the retardation (geochemical characteristics) and permeability (hydrologic and geomedial characteristics) are indeed two major players in natural attenuation processes. Therefore, authors will present an in-depth review of retardation (distribution coefficients, K_d) mechanisms related to attenuation process for developing evaluation protocol and regulatory framework.

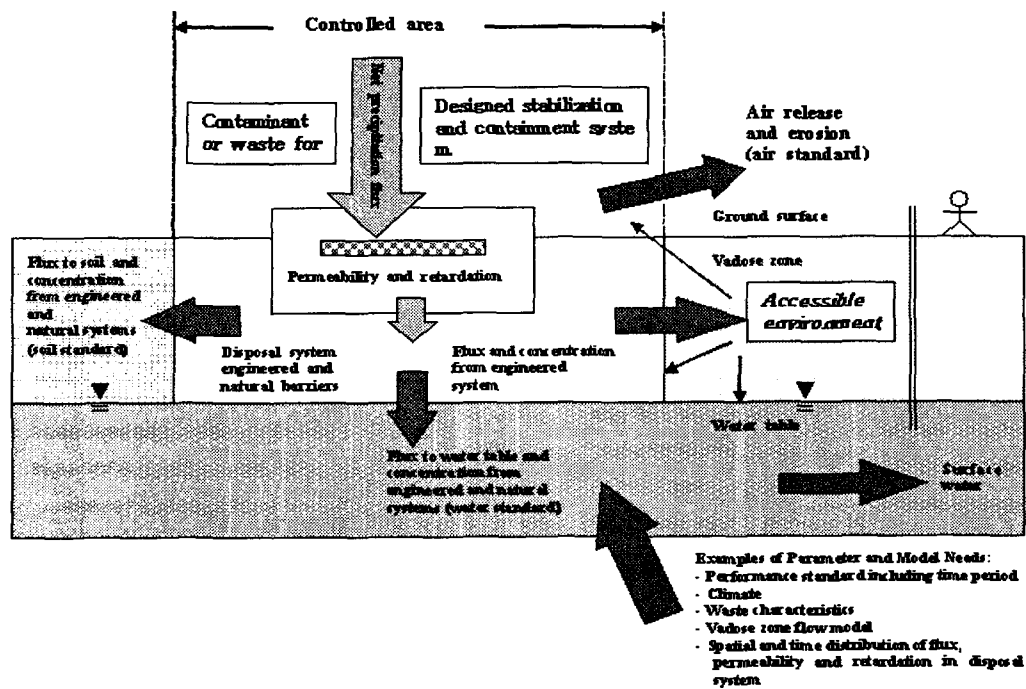


Figure 1. A conceptual model of site processes and characteristics required for describing contaminant transport (modified from Brady *et al.*, 1998).

In this presentation, authors will review briefly on: (i) source and geochemistry of selected hazardous metals and radionuclides, (ii) governing aqueous geochemical processes on natural attenuation, and (iii) K_d concept and model used in NA assessment.

Hazardous Inorganic Components Considered for Natural Attenuation

Although it depends on an exposed concentration, numerous inorganic chemicals could be hazardous to human health and environment. Author

selected most common inorganic chemicals regulated by government for discussion purpose. Each chemical has a different toxicity and behaves a different way in soils and groundwaters under a given environmental condition. The following inorganic chemicals are listed in drinking water, groundwater quality, and soil contamination standards. Although radionuclides are not common environmental problem in Korea, they were included in this review to introduce applicability of NA concept for environmental problems associated with an accidental release of the radionuclides from nuclear power plants. The following heavy metals and radionuclides are good candidates for the natural attenuation as a remedial tool because of their geochemical behaviors in soils and groundwater.

Lead (Pb): Lead is released to soil, surface water, and groundwater from metal smelting and processing, lead battery manufacturing and chemical manufacturing. Lead is considered as a divalent cation in soil solution and groundwater but forms aqueous complexes with hydroxyls. Lead hydroxy-carbonate solids at a higher pH (>7) are thought to limit the solubility of lead. Under reducing conditions, lead sulfide can form and limit aqueous lead concentrations. A significant fraction of lead could transport as colloidal particles or lead compounds incorporated in or on other components of particulate matter. Under the acidic and aerobic conditions, lead could be remobilized. However, lead associated with iron oxides could be remobilized through reduction and dissolution of the host phase under the reduced conditions. Lead could precipitate in soils if dissolved concentrations exceed about 4 mg/L at pH 4 and about 0.2 mg/L at pH 8. In the presence of phosphate and chloride, these solubility limits could be even much lower than above values (resulting a high K_d).

Chromium (Cr): Chromium is found in environment in three valence states (0, III, and VI). Most of them are produced by industrial processes, particularly coal and oil combustion, in metal plating and through use as an antimicrobial

agent. A plume containing high concentrations of chromium is more likely to be composed of Cr(VI) than Cr(III) because the former is less likely to adsorb or precipitate to the solid phase. Cr(III) sorbs strongly to soils, and forms a poorly soluble hydroxide that is limiting dissolved Cr concentrations to below drinking water concentrations. On the other hand, Cr(VI) hydrolyzes extensively forming only neutral or anionic species, including bichromate, chromate, and dichromate (Baes and Mesmer, 1976). Chromium (VI) is also appreciably more toxic than Cr(III). Concentrations of Cr(III) in soil solutions are typically controlled by dissolution/precipitation reaction therefore, adsorption reactions are not significant in soil Cr(III) chemistry. The redox state of the soil affects chromium adsorption. Ferrous iron associated with iron hydroxide minerals can reduce Cr(VI) that results in precipitation (higher K_d). Soils containing Mn oxides oxidize Cr(III) into Cr(VI) thus resulting in lower K_d values. The presence of competing anions reduces Cr(VI) adsorption and increasing pH decreases in K_d .

Zinc (Zn): Zinc is present as zinc bearing mineral in most rocks and carbonate sediments. Anthropogenic sources of zinc are mining activities and galvanizing processes. Sorption is the dominant divalent zinc immobilization reaction, and leads to the enrichment of zinc in sediments through sorption on iron and manganese oxides, clay minerals, and organic material. The stability of zinc complexes is pH-dependent, being greatest at high pH and the mobility is low under anaerobic conditions, possibly due to the formation of sulfide minerals.

Arsenic (As): Arsenic exists in most soils and groundwaters as arsenite (III) and/or arsenate (V) state under anaerobic and aerobic conditions, respectively. Both arsenite and arsenate form typically anionic species in the aqueous solutions and behaves chemically in the fashion similar to phosphate. Sorption of arsenate is greatest at low pH, but also depends on the availability of sorbing minerals. Sorption on organic material, iron, and/or calcium is also important processes that fix arsenic in poorly soluble forms.

Cadmium (Cd): Cadmium is often used in plating operations, and to make batteries as well as polyvinyl chloride pipe. Cadmium exists as divalent cation in contaminated soils and forms soluble aqueous complexes. The dominant cadmium aqueous species in groundwater at pH < 8.2 is the uncomplexed Cd²⁺ species but the dominant species at pH > 8.2 are aqueous cadmium carbonates. Cadmium sorbs strongly to most soils, particularly at high pH. Sorption by oxides and aluminosilicate-clay minerals, humic substances, precipitation as sulfide under reducing condition and as carbonate in alkaline soil, all can potentially limit transport of cadmium in soils and groundwaters. Transition metals and alkaline earth cations reduce cadmium adsorption by competition for available specific adsorption and cation exchange sites. Estimated range of K_d values for Cd was from minimum 1 to maximum 12,600 mL/g. The cadmium K_d values may be influenced by the presence of oxide minerals, CEC and clay contents in the soil, competing cations, and redox conditions.

Mercury (Hg): Mercury occurs naturally as a metallic mineral (quicksilver) and cinnebar (HgS). Major use for mercury at present is in mercury cell plants. Specific state and form in which the mercury is found in an environmental medium is dependent upon a number of factors, including the redox potential and pH of the medium. The solubility of mercury is very high under oxidized aquatic conditions due to its strong complexation with inorganic and organic ligands.

Strontium-90 (⁹⁰Sr): The primary source of ⁹⁰Sr in the environment has been fallout from nuclear testing and accidental releases from processing plants and disposal sites. Strontium-90 has a half-life of approximately 29 years. It decays to ⁹⁰Y with the emission of beta particle. The ⁹⁰Y decays to stable ⁹⁰Zr power with the emission of beta particle (half-life = 64 hours). Because ⁹⁰Sr is one of the radiologically most toxic contaminants and one of more mobile radionuclides in soil and groundwater, ⁹⁰Sr is likely to dominate environmental and human health risks at many sites and, thus, to exert the most constraint on

the selection of remedial actions (Bready *et al.*, 1998). Strontium belongs to the alkaline metal group and thus, behaves somewhat like calcium and barium. The parameters that could influence the K_d value of ^{90}Sr are included clay content, pH, CEC, surface area, solution calcium concentrations and solution strontium concentrations. In this review, ^{90}Sr is chosen to demonstrate the significance of radioactive decay on the NA processes as a remedial remedy. Retardation of ^{90}Sr in a given geochemical environment is playing critical role for NA assessment, radioactive decay is more important for overall risk assessment because ^{90}Sr has relatively short half-life.

Cesium-137 (^{137}Cs): The primary source of ^{137}Cs is fallout from nuclear testing and accidental releases from processing plants and nuclear waste disposal sites. Cesium-137 has a half-life of 30.2 years and decays to metastable $^{137\text{m}}\text{Ba}$, and then to stable ^{137}Ba with emission of gamma ray that is most concern from a health perspective. Cesium is likely to exist in aqueous solution as uncomplexed Cs^+ cation (Baes and Mesmer, 1979), which adsorbs rather strongly to most minerals, especially micaceous minerals. The micaceous minerals have a very high selectivity for Cs^+ over other cations. Many researchers showed that the exchange of trace cesium on those minerals was nearly irreversible, meaning that cesium adsorbs and fixed because of the size of the ionic cesium and the geometry of hexagonal hole in the interlayer surfaces of the micaceous minerals. Estimated range of K_d literature values (mL/g) for cesium varied from 30 to 66.700 depending on CEC and clay content. About nine of the 45 Superfund National Priorities List sites have been identified as radioactive cesium contaminated sites.

Uranium-234,235,238 ($^{234,235,238}\text{U}$): Uranium is a naturally occurring element consisting of three isotopes. Anthropogenic sources of uranium include mine and mill tailings, depleted uranium from the enrichment processes, and reprocessing of spent fuel from nuclear reactor. The uranium isotopes have a very long half-life (>250,000 years) and decay through a series of radionuclides

to stable lead isotopes, emitting alpha and beta particles and gamma rays. In all geologic environments, U(IV) and U(VI) are the most likely valence states in reducing and oxidizing conditions, respectively. There are several ancillary environmental parameters affecting uranium migration. The most important of these parameters influencing K_d values include redox status, pH, and ligands (carbonate, fluoride, sulfate, phosphate and dissolved carbon), concentration, aluminum- and iron-oxyhydroxide minerals concentrations, and uranium concentrations (Ellis and Lee, 2002). For examples, the uranium K_d values increases from approximately three orders of magnitude at pH values < 5, to approximately three to four orders of magnitude from pH 5 to 7, and four to five orders of magnitude at pH values from 7 to 9.

Aqueous Geochemical Processes Affecting on Natural Attenuation

Groundwater modelers are usually provided with the total concentration of a number of dissolved substances in and around a contamination plume. The total concentrations give little insight into the forms in which the metals and radionuclides are present in the plume or their mobility and bioavailability. Contaminants can occur in a plume as soluble-free, soluble-complexed, adsorbed, organically complexed, precipitated, or coprecipitated species (Sposito, 1989). Those species are the products of several significant reactions in a localized chemical environment of geomeia. The important geochemical processes are discussed briefly in this section:

Aqueous complexation: Most of metals (radionuclides) form metal-ligand complexes, which may be either inner-sphere or outer-sphere. Inner-sphere complexes are much more stable than outer-sphere complexes, because the outer-sphere complexes cannot easily involve ionic or covalent bonding. The stability is affected by the ionic strength of the aqueous phase and presence of

competing reactions. Complexation will lower the activity of free species of metal, which results in lowering potential for adsorption and increasing its solubility, both could enhance migration potential of the metals in groundwater.

Oxidation-reduction chemistry: An oxidation/reduction (redox) reaction is a very important chemical reaction in which electrons are transferred from one species to another. The redox reaction does control most of dissolution/precipitation of many redox sensitive contaminants. The range of pE ($-\log e^-$) in the natural environment varies between 7 and 1.7 in the vadose zone (Sposito, 1989). If anoxic conditions exist, than pE may get as low as -3. The most important chemical elements affected by redox reactions in ambient groundwater are oxygen, nitrogen, manganese, iron, sulfur, and carbon. In the contaminated groundwater, redox reactions of above chemical species would affect directly redox reactions of contaminants including arsenic, chromium, mercury, and uranium among the metals and radionuclides described for this presentation. There are many other redox-sensitive hazardous components including many organic compounds. Redox-mediated reactions are incorporated into most geochemical codes and can be modeled conceptually. The results of model calculation could be used to predict potential solubility controls and adsorption potential. Many redox reactions have been found to be kinetically slow in natural groundwater some of them may never reach redox equilibrium between their oxidation states.

Adsorption/desorption: Adsorption/desorption is the net accumulation of aqueous species at the interface between a solid phase and an aqueous-solution phase. Adsorption differs from precipitation because it does not include the development of a 3-dimensional molecular structure. On the charged particle (clay mineral) surface, adsorption could take place via several mechanisms: inner-sphere surface complex, outer- sphere surface complex and diffuse-ion swarm, and anion adsorption as inner-sphere surface complexation and diffuse-ion swarm association. One of the most common adsorption reactions is ion-

exchange, i.e., replacement of one ionic species on a solid phase by another ionic species taken from an aqueous solution in contact with the solid. There are numerous ion-exchange models described by many researches. But, despite well-documented evidence of irreversible adsorption of metal and radionuclides by geomedial, existing transport codes do not reflect the irreversibility of adsorption/ desorption processes. Because this sink often removes a major fraction of some metals and radionuclides from contaminated groundwaters, it is particularly critical that this sink be included in natural attenuation evaluation as remedial options.

Precipitation: The precipitation reaction of dissolved species is a special case of the complexation reaction in which the complex formed by two or more aqueous species. Precipitation or co-precipitation is more likely to occur in the near-field as a result of high concentrations in the aqueous contaminant source or leachate with a large pH or pe gradients in the environment. Precipitation of radionuclide may not be a dominant reaction in far field or non-point source plumes because the contaminant concentrations may not be high enough to push the equilibrium towards precipitation direction. Solubility-controlled models assume that a known solid is present or rapidly forms and controls the concentration in the aqueous phase of the constituents being released. All of solubility models are thermodynamic equilibrium models and typically do not consider the time required to dissolve or completely precipitate.

Other transport processes: Other processes such as diffusion and subsurface colloidal transport are not considered as geochemical process but should be evaluated for site-specific validity of natural attenuation. The transport of contaminants in the absence of bulk flow is referred to as diffusion. The flux of contaminants due to diffusion is proportional to the concentration gradient and is a molecular process. The effective diffusion coefficients used in the transport models are influenced by chemical retardation of reactive constituents as well as the physical hindrance to the contaminant mobility caused by the small pore

sizes and tortuosity of the geomeia. Another process could impact on contaminant transport and NA evaluation is formation of mobile colloids. Presence of the mobile colloids associated with contaminants could enhance not only the amount of contaminant that is transported, but also the rate of contaminant transport. The colloidal particle can be attached on or detached from the aquifer media as a result of changes in the groundwater chemistry, such as ionic strength and/or ionic composition.

Distribution Coefficient (K_d) Values

As it was discussed in the introduction, the applicability of NA concept for the metals and radionuclides depends on the degree of retardation in geological media (i.e., soils, sediments, and rocks). The retardation factor is the empirical parameter commonly used in transport models to describe the chemical interaction between the contaminants and geomeia. The contaminant retardation factor includes processes such as surface adsorption, absorption into the soil structure, precipitation, and physical filtration of colloids. The simplest and most common method for estimating contaminant retardation is based on the distribution coefficients (K_d). As typically used in fate and contaminant transport calculations, the K_d is defined as the ratio of the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. The K_d value is obtained from laboratory experiments including laboratory batch method, in-situ batch method, laboratory flow-through or column method, and field modeling method. Unfortunately, generic or default K_d values can result in significant error when used to predict contaminant migration rate and to select a site remediation alternative. Therefore, a direct measurement of K_d values at site-specific conditions is absolutely essential for site-specific calculations.

The Distribution Coefficient (K_d) Models

Constant K_d Model: The constant distribution coefficient is a measure of sorption expressed as a mass action. Describing the K_d in terms of simple mass action assumes that unoccupied adsorption sites are in great excess with respect to the total dissolved adsorbates remaining in solution at equilibrium, and that the activity of adsorbate on the solid is equal to one. The K_d term is valid only for a particular adsorbent and applies only those aqueous chemical conditions in which it was measured. Also inherent in the K_d term is the assumption that the system is reversible and is independent of the tracer concentration used for radionuclides in the aqueous phase. Essentially all of the assumptions associated with the thermodynamically defined K_d value are violated in the common used to measure K_d values for use in contamination transport codes. When the K_d term is incorporated in to retardation factor, the retardation term is also devoid of sorption mechanisms as discussed.

Parametric K_d model: The parametric K_d model is another conceptual adsorption model. In this model, the K_d value varies as a function of empirically derived relationships with aqueous and solid phase independent parameters. Thus, it has the distinct advantage of being more robust and removes the burden of determining new K_d values for each environmental condition. Because the values of K_d term are a function of large number of variables, it is common to systematically vary several parameters simultaneously in an experimental study. Factorial design is commonly used to determine the systematic change resulting from varying the independent variables on the dependant variables typically K_d . This approach has been used to develop an empirical relationship describing a K_d value in terms of other variables. The empirical equations take the form of a nonlinear polynomial expression. When the parametric model is used in the transport equation, the code must keep track of the current value of the independent variables at the point in space and time to continue update the concentration of the independent variable affecting the K_d value. The

complexity in solving the transport equation with parametric K_d sorption model and its empirical nature may be the reasons this approach has been used sparingly.

Mechanistic adsorption models: Mechanistic models accommodate for the dependency of K_d values on contaminant concentration, competing ion concentration, variable surface charge on the absorbent, and solute species solution distribution. Incorporating mechanistic or semi-mechanistic adsorption concepts in to transport models is attempted because the model become more robust and, more importantly from the standpoint of regulators and the public, scientifically defensible. However, the complexity of installing these mechanistic adsorption models into transport codes is difficult to accomplish. The mechanistic model also requires a more intense and costly data collection effort than will likely be available to the majority modelers and site remediation managers. Interactions at the mineral-electrolyte interface can be represented mathematically through two different ways: empirical models and mechanistic models. The empirical models refer to models defined as a mathematical description of the experimental data without particular theoretical basis, for example, the K_d model, Freundlich and Langmuir isotherms are considered by this definition. The mechanistic models refer to models based on thermodynamic concept such as reactions described by mass action laws and material balance equations, for example, the Helmholtz, Gouy-Chapman, Stern, and Triple Layer models are in this class. The empirical models are mathematically simpler than mechanistic models and suitable for characterizing sets of experimental data with a few adjustable parameters or interpolating between data points (Westall, 1986). The adjustable parameters are required for both mechanistic and empirical models, except K_d model. On the other hand, mechanistic models contribute to an understanding of the chemistry at the interface and are often useful for describing data from complex multi-component systems. However, truly mechanistic models rarely applied to complex natural soils because the surfaces of the natural mineral are very

irregular and difficult to characterize. These surfaces consist of different microcrystalline structures and/or coatings of amorphous phases that exhibit quite different and complex chemical properties when exposed to solutions.

Natural Attenuation Assessment Based on Distribution Coefficients

The K_d values have been utilized in transport and risk assessment models during the evaluation of natural attenuation because of their simplicity in understanding, measuring, and providing analytical solution to the models. However, there are inherent difficulties associated with utilizing K_d as the sole parameter to define the geochemical properties of the solute as it migrates through a subsurface environment (Whelan *et al.*, 1996). Although K_d values can be thermodynamically or experimentally defined, their meaning becomes less clear in the real world.

When calibrating a groundwater model to monitored information at a monitoring well, the model must predict the correct concentration and arrival time at the correct location. Therefore, time, location, and concentration are three crucial elements associated with the calibration of model, and K_d impacts two of three elements (i.e., travel time and concentration). In the process of NA assessment, monitoring wells and receptor locations, i.e., distance, are predetermined. Once the distances have been defined, the calibration requires modifications to parameters that govern travel times and concentration levels. As the model complexity increases, the number of parameters increases, and the calibration process becomes more complicated. Figure 2 illustrates the relative relationships between input data quality, output uncertainty, and type of problems addressed by each level of assessment (Krupka *et al.*, 1999).

The computational requirements tend to be less at the earlier stages of an assessment when available data are less, and the uncertainty with the output results tend to be greater. As the assessment progresses, improved site-

characterization data and conceptualization of the problem increase, thereby reducing the overall uncertainty in risk estimates. The figure also illustrates some of the characteristics and relationships between screening-level (ranking), analytical (prioritization and preliminary assessments), and numerical (detailed) models. The screening models are used to identify environmental concerns such as the Hazard Ranking System (EPA, 1994). Numerical models such as MODFLOE are used for detailed analyses of solute transport as a part of NA assessment (McDonald and Harbaugh, 1988). The analytical-assessment models are codes with physics-based algorithms whose components can be utilized in a detailed or an initial screening (Krupka *et al.*, 1999).

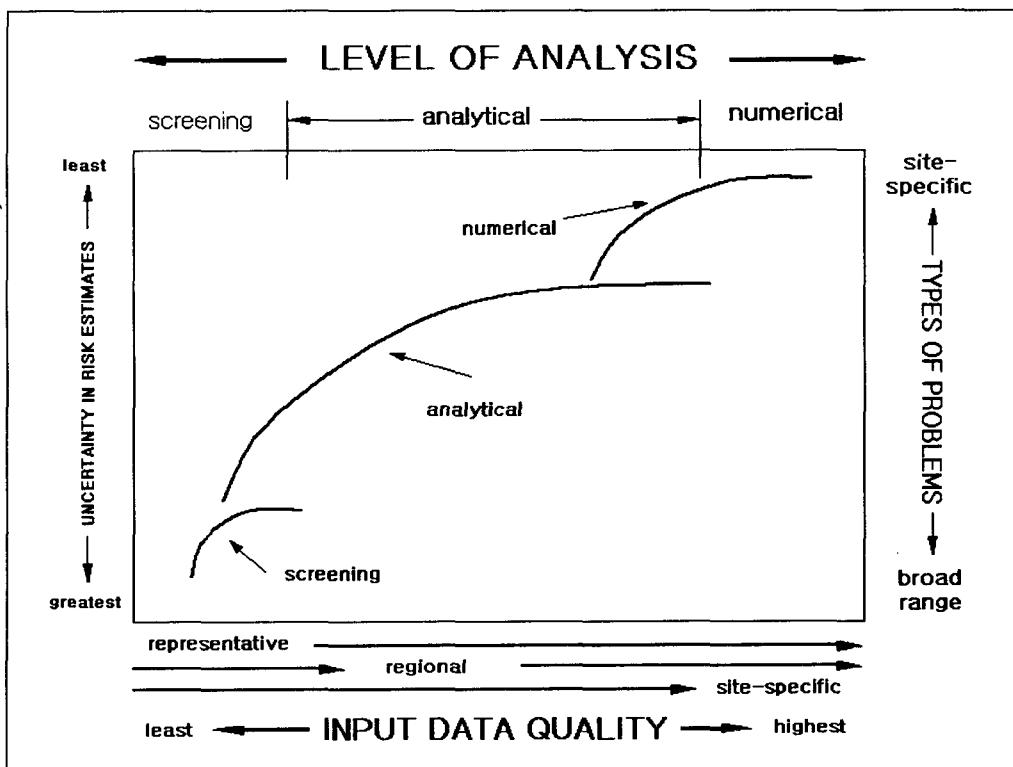


Figure 2. Relative relationships between input-data quality, output uncertainty, and types of problems addressed by each level of assessment (after Krupka *et al.*, 1999).

When calibrating of models for NA assessment, parameters can only be varied within ranges that physically make sense for the site and its conditions. If unrealistic output is a result of the analysis, then the (i) conceptual site model has to be reevaluated, (ii) input data must be re-examined, or (iii) model must re-evaluated to ensure that the assessment does not violate the assumptions, limitations, and constrains associated with the mathematical constructs of the code. The intent of calibration process is to get a contaminant from a source to monitored location at the proper time with the appropriate concentration. As note earlier, the K_d would directly impact the travel time and concentration of contaminant during calibration for NA assessment.

Implementation of NA for Metals and Radionuclides

In the above sections, authors reviewed geochemistry of candidate inorganic and radionuclide component for NA consideration, overview of geochemical processes of the hazardous components, and relation of distribution coefficients of the components with natural attenuation assessment. In practical aspects, implementation of NA for metals and radionuclides is far more difficult than organic compounds. Brady *et al.* (1998) stated that conceptual model must be demonstrated the following conditions for implementation of natural attenuation:

1. *Attenuation elements (geochemical and environmental factors) are present along the flow path and in sufficient quantities to decrease contaminants to acceptable values by the time a receptor is reached.* The exposure of contaminants to attenuating media and the full extend to which attenuation will occur will depend on hydrological paths and travel times. For attenuation of most metals, reactive minerals that sorb or sequester contaminants must be present along the travel path. For example, chromate can be reduced to concentrations below the maximum contamination level (MCL) by reduction

to Cr(III), followed by its precipitation and/or sorption, if sufficient suitable electron donors are available along the path. For long-lived radionuclides, the combined effects of sorption and dilution must be able to reduce dissolved concentrations below allowable, dose-based limits. The travel time of relatively short-lived radionuclides must be sufficiently long that ten half-lives have elapsed before the nearest receptor is reached.

2. *Attenuation will occur rapidly enough to decrease contaminant concentrations to regulatory targets.* This will depend on at least a semiquantitative assessment of attenuation rates. For metals, the rate of irreversible uptake may be most critical. For radionuclides, irreversible uptake and hydrologic travel time must be taken into account. For chromate and uranium, rate of reduction must be considered. Longer travel times require less rapid attenuation and vice versa.
3. *Changes in geochemical conditions will not occur that mitigate against the first two factors.* For metals, an sequential extraction procedures of the contaminated soil/aquifer material provides the first condition above. The second condition above requires a clear assessment of chemical transformation rates that are not always well understood for metals and radionuclides. The largest fraction of irreversible sorption of metals appears to occur quite rapidly on environmental time scale of years. Quantification of the attenuation capacity of a flow path is relatively straightforward. For example, if irreversible sequestration of metals by iron hydroxides is identified as a primary sink, the available mass of the iron hydroxides likely to be encountered by the contaminant in transit from the source to the nearest receptor must be estimated and then compared to total mass of containment.

In conclusion, it is clear that the ability to forward model natural attenuation to estimate horizons for achievement of regulatory targets posed the greatest challenge to the implementation of natural attenuation. Authors will discuss

further on this aspect at presentation. Authors wish to have your participation on this important subject for developing a protocol for natural attenuation assessment of metals and radionuclides.

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