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## **Natural Attenuation of Metals and Radionuclides: Report from a Workshop held by Sandia National Laboratories**

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***Natural Attenuation of Metals  
and Radionuclides:***

**Report from a Workshop held by Sandia National Laboratories  
at the Crowne Plaza Hotel  
in Albuquerque, New Mexico,  
June 18-20, 1997**

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**Abstract**

Natural attenuation is increasingly applied to remediate contaminated soils and ground waters. Roughly 25% of Superfund groundwater remedies in 1995 involved some type of monitored natural attenuation, compared to almost none 5 years ago. Remediation by natural attenuation (RNA) requires clear evidence that contaminant levels are decreasing sufficiently over time, a defensible explanation of the attenuation mechanism, long-term monitoring, and a contingency plan at the very least. Although the primary focus of implementation has to date been the biodegradation of organic contaminants, there is a wealth of scientific evidence that natural processes reduce the bioavailability of contaminant metals and radionuclides. Natural attenuation of metals and radionuclides is likely to revolve around sorption, solubility, biologic uptake and dilution controls over contaminant availability. Some of these processes can be applied to actively remediate sites. Others, such as phytoremediation, are likely to be ineffective. RNA of metals and radionuclides is likely to require specialized site characterization to construct contaminant and site-specific conceptual models of contaminant behavior. Ideally, conceptual models should be refined such that contaminant attenuation can be confidently predicted into the future. The technical approach to RNA of metals and radionuclides is explored here.



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## **PREFACE**

We greatly appreciate the participation of everyone who came to the workshop and especially thank Fran Kremer, for her leadoff overview of natural attenuation, and Prof. Janet Hering who contributed a large portion of chapter 5 and the conclusion of this document. We were likewise exceedingly grateful to the speakers for the efforts they put into all of this - Matt Eick, Paul Grossl, Joan McLean, Phil Jardine (and Scott Brooks), A. J. Francis, Jim Ryan, Brian Spalding, Andre Sobolewski, Don Metzler, and Dave Gallegos. Many thanks as well to Pradeep K. Aggarwal - IAEA, Ken Krupka - PNNL, Matt Kozak - QuantiSci, Ron Wilhelm - EPA, and Bill McKenty - EPA, Region 3, who were invited panelists who helped out immensely in the panel discussions. All that being said, this document was written with a few exceptions by a committee of the organizers, namely Pat Brady, Dave Borns, and Grace Bujewski. We've tried to reflect the input of the participants, and the general tone of the workshop. Any mistakes in the latter course are attributable to the organizers or authors of this report, and not to the speakers and invited panelists. This work was funded by an LDRD grant from Sandia National Laboratories and was supported by the United States Department of Energy under contract DE-AC04-94AL85000.

## 1.0 INTRODUCTION

Natural attenuation is defined as “naturally occurring processes in the environment that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media”. These in situ processes include “biodegradation, dispersion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants”. Natural attenuation has been extensively documented and is increasingly relied on for the cleanup of soils and groundwaters contaminated with fuel hydrocarbons, PAHs, and even chlorinated solvents. Often natural attenuation leads to a net decrease in remediation costs and provides substantial reductions in contaminant levels, risks to human health and the environment.

Sites contaminated with metals and radionuclides pose special problems for the application of the natural attenuation approach. Whereas natural attenuation of organic contaminants means breakdown by microorganisms; natural attenuation of metals often means sequestering or transformation by the soil matrix or dilution. Radionuclides, in turn, might be considered naturally attenuated if their interactions with soils result in transport times to possible receptors much greater than their radioactive half life.

Although laboratory and field evidence for the transformation and sequestration of inorganics is abundant, natural attenuation of metals and radionuclides has received less emphasis in the regulatory universe relative to the natural attenuation of organic contaminants. We expect this to change as the cleanup of the DOE complex picks up steam. The object of the workshop, held by Sandia National Laboratories, was to accumulate technical evidence for natural attenuation of inorganics and to examine how such technical evidence might best be applied to gain regulatory and stakeholder acceptance of natural attenuation as a remedial solution. Specific questions included:

- When does natural attenuation work; when does it not?
- What field/lab data are needed to support natural attenuation?

- What are the obstacles to regulatory/stakeholder acceptance?

The workshop was intended to specifically focus on metals and radionuclides present in contaminated soils and groundwaters. Surface water contamination was only considered if it was caused by seepage from contaminated groundwater. Although an important fraction of both the non-DOE and DOE waste is made up of organic contaminants, including fuel hydrocarbons and chlorinated solvents (TCE, PCE, etc.), organic molecules were only considered if they had the potential to affect the transport of metal and/or radionuclides. After an opening overview of natural attenuation by Fran Kremer of EPA, a series of presentations reviewed the geochemical and biological processes which control long-term transport of metals and radionuclides (Matt Eick - VPI; Paul Grossl and Joan McLean - Utah State; A. J. Francis - Brookhaven; Phil Jardine - Oak Ridge; Jim Ryan - USEPA). Subsequent presentations outlined the various technical approaches (e.g. constructed wetlands) which are presently used to control contamination (Brian Spalding - Oak Ridge and Andre Sobolewski - Microbial Technologies), followed by an overview of natural attenuation of uranium mill tailings sites (UMTRA; D. Metzler - DOE/GJPO), and an examination of the role of risk, uncertainty, and probability in remediation (Dave Gallegos - Sandia). Presentations were followed by a series of panel discussions (Immediately following the next paragraph are summaries of the material covered). The topics covered during the workshop are summarized in the following section.

Finally, the relationship between the regulatory and regulated communities is dynamic and is constantly evolving. Although natural attenuation has received considerable attention as a potentially viable remediation approach in recent years, the procedures for its implementation are far from agreed upon. The intent of this workshop was to specifically avoid the non-technical interaction between the regulated and regulatory communities and to instead explore the scientific basis for transport and bioavailability of metals and radionuclides. Nevertheless, an explicit consideration of regulatory constraints was prevalent (and planned) from the outset. The comments of state and federal regulators assured that the technical discussions remained 'down-to-Earth' and relevant to environmental remediation. Our intent was for the regulatory contribution to drive the technical discussions; not *vice versa*.

## **2.0 Summary of Presentations**

### **2.1 Overview (Fran Kremer - USEPA)**

The increasing recognition of natural attenuation by EPA does not constitute a change in cleanup goals; nor is it a walkaway, or default solution. The burden of proof remains on the proponent, not the regulator. EPA expects implementation to require extensive site characterization, long-term monitoring, risk assessment, and contingency measures. The net result is that implementation is site-specific.

Typically, natural attenuation has been applied in combination with more active remedial approaches, at sites where cleanup levels were not extensively exceeded in the first place, or after more proactive remediation efforts had been halted.

Generally, contingency plans requiring active remediation were in place.

Site characterization is typically demonstrated, in decreasing order of importance, through: 1. historical data showing declining contaminant levels in soils or groundwaters; 2. geological and/or geochemical data demonstrating natural attenuation processes or rates; and 3. field or soil microcosm studies. If the first criterion is satisfied, further effort is made to examine the other criteria. On the other hand, in the absence of historical evidence for reductions in contaminant levels, the argument for natural attenuation probably cannot be made solely on the latter two. In the end, the regulators make the decision whether natural attenuation is applicable.

The capacity of natural processes to attenuate contaminants must exceed the rate at which contaminants are introduced to the subsurface. Consequently, source control/removal is very important as it decreases contaminant fluxes and lowers the needed natural attenuation capacity. This capacity is probably contaminant and site-specific and depends on solubility, sorption, etc.

The future use of the site must be taken into account if remediation by natural attenuation is considered. RNA often takes longer to achieve cleanup goals than more active remediation measures. Land use concerns may consequently bias cleanup towards proactive, as opposed to passive remediation. Isolated sites with great distances from potential receptors are, therefore, more likely to be candidates for RNA compared to sites connected by short travel times to potential receptors.

The advantages and disadvantages of RNA are outlined in table 1.1:

Advantages	Disadvantages
minimizes transfer of contaminants to other media	may take longer
less intrusive	site characterization may be more involved
may be applied at all or part of site	long-term monitoring may be required
may be cheaper	by-products may be toxic
	if RNA fails active remediation may still be required

Table 1.1 Advantages and disadvantages of RNA

In summary, a number of milestones must be achieved to build support for RNA at a particular site. The source term must be controlled - either treated or removed, to limit subsequent contaminant fluxing. The plume and down-gradient areas must be monitored to establish plume dynamics. If contaminant levels are seen to decrease over time, a conceptual model to account for the decrease should be established, and if possible, refined to provide a basis for making defensible predictions of the long-term evolution of contaminant levels. These milestones are not necessarily easy or cheap to achieve, and in all cases the appropriate regulatory agency should be involved at the earliest stages.

In the subsequent question/discussion period, it was pointed out that EPA is in the process of preparing screening protocols for metals in soils. A suggestion was also made that less-than-predicted contaminant movement might count as crude evidence of natural attenuation. The importance of near receptors and institutional controls in the decision process was re-emphasized.

Existence of static, non-decreasing contaminant levels is probably a 'show-stopper' for RNA. By the same token, decreasing contaminant levels, in the absence of a defensible conceptual model for explanation and subsequent prediction, is probably an unacceptable basis for implementing RNA. The presentations outlined in the next section explore the individual geochemical and biological components of conceptual models for RNA of metals and radionuclides.

## **2.2 SCIENTIFIC BACKGROUND**

Metals and radionuclides can be removed from soil solutions and groundwaters by: 1. Sorption to mineral surfaces and/or soil organic matter (SOM); 2. Formation of insoluble solids; 3. Uptake by plants and organisms; and 4. occasionally through volatilization (e.g. methylation of mercury). Ignoring volatilization, and instead focusing on the formation of adsorbed species ('surface complexes'), insoluble solids and uptake by plants, we note that metal/radionuclide speciation depends primarily on the ambient biogeochemical conditions of the soil or groundwater: pH, redox state (electron availability), alkalinity, and the presence of chelating (e.g. EDTA, natural organic acids) or solid-forming (e.g. phosphate) ligands are critically important (ionic strength is probably a secondary factor). Because these processes often significantly reduce contaminant levels in solution, they collectively fall under the umbrella of natural attenuation as defined above. At the same time, the sequestering of metals/radionuclides out of the aqueous phase often makes their engineered extraction problematic. Corrosive soil leaches, vitrification techniques, and grout curtains are examples of the extremes which must be gone to in order to liberate or isolate metals in soils. In many cases the technical impracticability of metal/radionuclide extraction is a direct result of the natural attenuation processes. Nevertheless, contaminant immobilization cannot be assumed - some metals/radionuclides (e.g. chromate and pertechnetate) have very little interaction with the matrix, and can, consequently, move rapidly through soils and groundwaters. It is, therefore, necessary to explore sorption, plant uptake, and solubility in substantial detail. Ideally, this will, in the end, provide some basis for identifying the conditions (contaminant and soil type) where RNA might be plausible and, at the same time, where it clearly won't be.

### **2.2.1 Sorption (M. Eick)**

Sorption is particularly effective at limiting the concentrations of metals/radionuclides that are present in trace quantities. At high contaminant levels the actual amount of contaminant in solution is typically determined by the presence of contaminant-containing insoluble minerals. There are obvious exceptions. For example,  $\text{Cs}^+$  and  $\text{TcO}_4^-$  form no insoluble solids.

Obviously, the whole picture is relative as some contaminant-bearing minerals are more soluble than others.

To the extent that sorption reactions determine contaminant levels in solution, they also set the ultimate biotoxicity of the trace element. Sorption can be characterized as being 'reversible' or 'irreversible'. Contaminants sorbed reversibly to a surface can be desorbed instantaneously in response to a decrease in contaminant level in solution. In other words, the sorbed species remains in contact with the solution and responds rapidly to changes in solution composition. Irreversibly sorbed species typically do not reequilibrate rapidly with solutions once sorbed. Irreversible sorption may occur through a combination of occlusion (overcoating), diffusion into dead-end pores, or structural collapse of the mineral around the sorbed species.

Because equilibrium desorption cannot always be assumed it is important to split sorption into forward and backward reactions (respectively, adsorption and desorption) and treat them separately. Adsorption is very rapid and typically occurs over time spans less than a second, but sometimes longer. Adsorption from solution varies with pH, the type of mineral surface, the amount of surface coverage, the concentration of the trace element, and the composition of the soil solution. Ligands which form strong complexes with the contaminant may either decrease the total amount of sorption, or form ternary complexes with the surface. Mineral surfaces typically consist of hydroxylated broken bonds, which can be deprotonated, and negatively charged, or protonated, and positively charged. Electrostatic binding of cations to deprotonated sites and anions to protonated sites describes simplistically the interaction of many ions with metal oxides and hydroxides. At high pH negative surface charge is maximal; at low pH positive surface charge is greatest. As a result cation sorption increases with pH; anion sorption with decreasing pH. There is a continuum at high surface loadings though between sorption and the nucleation and precipitation of new metal-containing phases at the mineral surface.

Prolonged contact between sorbed species and mineral surfaces often leads to an incorporation of the former into the latter. This may occur through dehydration

of previously hydrated metals, recrystallization overcoating, or through diffusion of the sorbed species into the mineral structure. Formation of surface precipitates can also occur through the transfer of electrons to or from the mineral surface to the sorbed species with the resultant formation of a more stable surface species. While adsorption has received the most attention, in many cases desorption may be the more important control over metal/radionuclide release at contaminated sites. Routinely the most contaminated sections of a site are removed and/or stabilized leaving a plume of contamination behind wherein the contaminants are primarily sorbed to mineral surfaces. Almost all performance assessment calculations assume that desorption is reversible. Hence, when fresh recharge comes into contact with sorbed contaminants the latter are predicted to instantaneously equilibrate, in effect setting contaminant levels in solution. In reality desorption rates are often relatively slow, sometimes vanishingly so. The actual desorption rate will in many cases determine the net export of metal/radionuclide toxicity.

### 2.2.2 Plant uptake (P. Grossl and Joan McLean)

Plant uptake of metals and radionuclides (phytoremediation) has received considerable attention in recent years. Part of the motivation for this is that, whereas existing methods for extracting contaminants from complex soil matrices are rarely completely successful, many plants (hyperaccumulators) appear to be quite handy at taking up a wide variety of metals from soils (A secondary use for plants is to physically stabilize metal-contaminated soils against wind and water erosion.) Consequently, there is considerable interest in identifying plants which can be used to extract specific metals from contaminated sites. Extraction efficiencies vary widely from plant to plant by several orders of magnitude. Also, the extractability of a given metal from a soil depends on the speciation of the metal in the soil solution; i.e. whether it is sorbed loosely to a metal hydroxide, as an innerlayer species, or as a component of an insoluble solid.

There appear to be a number of factors which limit the effectiveness of phytoremediation. For one thing, although laboratory tests typically measure high accumulation levels, the actual efficiency in the field is often limited by the availability of the contaminant of concern. This is because a plant, which

accumulates high levels of a given metal from a metal-rich solution, will accumulate less when the solution is a less metal-rich, natural solution. Often solubility (and sorption) limit the availability of the metal of concern to solution, and the plant. More metal can be liberated if the biogeochemical behavior of the soil zone is modified. But this raises the question of whether metals which are non-bioavailable should even be cleaned up. For example, lower pH's, higher organic acid concentrations (root exudates), or the introduction of xenobiotic chelates (e.g. EDTA) might liberate otherwise sorbed or insoluble metals. Such manipulations would probably also increase the efficiency of a standard pump and treat approach.

### 2.2.3 Microbiologic Effects (I) (A. J. Francis)

Indigenous microbial populations often play a dominant role in the stabilization and/or transport of radionuclides and toxic metals. Aerobic and anaerobic microorganisms can mediate redox transformations. For example, redox-sensitive metals and radionuclides (e.g.  $\text{CrO}_4^{2-}$ ,  $\text{TcO}_4^-$ , and  $\text{UO}_2^{+2}$ ) can be reduced to insoluble solids or, alternatively, oxidized from the more stable reduced state to the mobile forms above. In addition microbes can change the soil Eh and pH; mobilize metals/radionuclides by producing chelating agents; sequester metals/radionuclides into biomass and biopolymers; transport metals/radionuclides as biocolloids; or limit their transport by breaking down soluble radionuclide-organic complexes.

Microbial action can be direct or indirect. Examples of direct action are the enzymatic reduction of metals pointed out above and the reductive dissolution of iron hydroxide, an important scavenger for metals in soils. An example of indirect action is the lowering of soil pH due to the production of organic acid metabolites.

### 2.2.4 Organic Effects (II) (P. Jardine)

Soil organic material is primarily made up of decomposing plant residues, organism byproducts, and soil humates, and represents the difference between primary productivity and decomposition. Dissolved organic carbon (DOC) (e.g. humic and fulvic acids), capable of complexing contaminant metals/radionuclides, is particularly mobile after storm events. DOC is polymeric and typically is resistant to further degradation (half-lives are on the time-scale of years). Because DOC is

appreciably hydrophobic, it tends to bond to solid-phase organic material in soils. In addition to non-specific, hydrophobic bonding, exchange of the ionizable functional groups can link natural organic matter (NOM) to ionized mineral surfaces as well. Because the latter is typically less important, NOM is found to be relatively mobile in hydrophilic soil matrices. Any metals/radionuclides complexed with ionizable NOM groups (e.g. carboxylate and hydroxyl groups) can therefore be potentially transported in the subsurface. Consistent with this, an inverse trend between DOC and  $K_d$ 's has been observed for a number of metals and actinides.

Synthetic organic contaminants co-mingled with metals/radionuclides often give rise to the same observation. NTA, EDTA, and DTPA are all synthetic organics, which show up at DOE sites. Citrate, and oxalate are two natural chelating agents of concern as well. Degradation rates of these chelates typically follows the trend:

citrate ~ oxalate >> NTA > EDTA > DTPA

Estimating transport of chelated metals and radionuclides requires that the coupled processes of metal chelation, sorption, and chelate breakdown be understood.

#### 2.2.5 Morning Summary/Discussion (D. Borns and others)

A number of points were made after the preceding talks by various panelists, workshop participants, and speakers.

1. Contingency plans are critical. If pollutants appear unexpectedly at a sentinel monitoring well a rapid remediation strategy must be in place.
2. Scaling up laboratory tests to predict behavior in the field is fraught with uncertainties. Field data are eminently preferable. Laboratory tests are probably best used only to constrain likely attenuation mechanisms.
3. There is very little institutional experience in conducting, or judging, natural attenuation-specific site characterization. Measuring total metal content in soils is typically done, but will probably overestimate biotoxicity if natural attenuation consisting of sorption and mineral growth has taken place. EPA has no standard method for analyzing soils.
4. The cost of monitoring while waiting for RNA to work may be much greater than up-front costs of remediation, particularly if RNA is not guaranteed to work.

5. Knowing the absolute capacity of a soil to attenuate contamination is important.
6. A critical question is how long the particular natural attenuation pathway can be assured. By 'natural attenuation pathway' we denote those biogeochemical processes which limit transport and bioavailability of a given contaminant.
7. Site characterization should be iterative so that the relevant data can be obtained that will allow the development and testing of a conceptual model. Typically though budgetary constraints and remediation schedules make site characterization a one-shot procedure.

#### 2.2.6 Solubility Controls (J. Ryan)

Whether contaminant concentrations in groundwater, or bioavailability is the issue, they both fall under the general topic of solubility. Lead is the primary pollutant at Superfund sites. It can either be physically removed, or made non-bioavailable. Application of sewage sludge is handy at achieving the latter. It appears that the chemical form of lead in the sludge is pyromorphite. By the same token, formation of autunite appears to be an effective means for sequestering uranium. Bioavailability assays are expensive (~50K\$) and often X-ray diffraction fails to identify bioavailability-controlling mineral phases due to their presence in typically minor amounts. Scanning electron microscopy may be a much better tool for this purpose.

#### 2.2.7 Panel Discussion

Additional points made in the subsequent panel discussion included the following.

1. Traditional site characterizations do not gather the relevant data to identify natural attenuation pathways, much less calibrate their effectiveness.
2. There probably is not one unique  $K_d$  value describing sorption.
3. Results from contaminant transport models may not satisfy regulators. Site specific determination of the natural attenuation pathways, and their longevity, is absolutely necessary. There is considerable uncertainty as to what the appropriate time frame for complete RNA should be.

4. Site characterization studies can rapidly add costs to site remediation with no clear upper limit. Yet an integrated remediation and characterization process coupled with a performance assessment program can avoid this.
5. Regulators to date have judged RNA by changes in groundwater, not soils. For a demonstration of RNA they want to see an equilibrium in the groundwater contaminant concentrations and a decrease in contaminant levels. Any models used for prediction must have some explicit treatment of uncertainty.

### 3.0 TECHNICAL APPROACHES

#### 3.0.1 Overview (P. Brady)

Table 3.1 outlines likely natural attenuation pathways for most of the radionuclides and metals of concern. Also shown are the potential caveats which must be kept in mind for each contaminant. Specifically, we have sought to identify what soil chemical parameters control the natural attenuation pathway, and, by extension, what changes in soil chemistry would work against the given natural attenuation pathways.

Chemical	Natural attenuation pathways	Caveats, Special Data Needs
Pb <sup>2+</sup>	Sorption to iron hydroxides, organic matter, carbonate minerals, formation of insoluble sulfides.	Low pH destabilizes carbonates, iron hydroxides. Commingled organic acids and chelates (e.g. EDTA) may decrease sorption. Low E <sub>H</sub> dissolves iron hydroxides, but favors sulfide formation.
CrO <sub>4</sub> <sup>2-</sup>	Reduction by organic matter, sorption to iron hydroxides, formation of BaCrO <sub>4</sub>	Low pH destabilizes carbonates, iron hydroxides. Low E <sub>H</sub> dissolves iron hydroxides. Are reductants available?
As(III or V)	sorption to iron hydroxides, formation of sulfides	Low pH destabilizes carbonates, iron hydroxides. Low E <sub>H</sub> dissolves iron hydroxides.
Zn <sup>2+</sup>	sorption to iron hydroxides, carbonate minerals, formation of sulfides	Low pH destabilizes carbonates, iron hydroxides. Commingled organic acids and chelates may decrease sorption. Low E <sub>H</sub> dissolves iron hydroxides.
Cd <sup>2+</sup>	sorption to iron hydroxides, carbonate minerals, formation of insoluble sulfides.	Low pH destabilizes carbonates, iron hydroxides. Commingled organic acids and chelates may decrease sorption. Low E <sub>H</sub> dissolves iron hydroxides, but favors formation of sulfides.
Ba <sup>2+</sup>	sorption to iron hydroxides, formation of insoluble sulfate minerals	Low pH destabilizes carbonates, iron hydroxides. Low E <sub>H</sub> dissolves iron hydroxides. What are sulfate levels?
Ni <sup>2+</sup>	sorption to iron hydroxides, carbonate minerals	Low pH destabilizes carbonates, iron hydroxides. Commingled organic acids and chelates may decrease sorption. Low E <sub>H</sub> dissolves iron hydroxides, but favors sulfide formation.
Hg <sup>2+</sup>	formation of insoluble sulfides	Is methylated by organisms
NO <sub>3</sub> <sup>-</sup>	reduction by biologic processes	

Radioactives		
$UO_2^{+2}$	sorption to iron hydroxides, precipitation of insoluble minerals, reduction to insoluble valence states	Low pH destabilizes carbonates, iron hydroxides. Comingled organic acids and chelates may decrease sorption. High pH and/or carbonate levels decrease sorption. Low $E_H$ dissolves iron hydroxides.
Pu(V and VI)	sorption to iron hydroxides, formation of insoluble hydroxides	May move as a colloid. Low $E_H$ dissolves iron hydroxides.
$Sr^{2+}$	sorption to carbonate minerals, formation of insoluble sulfates	Low pH destabilizes carbonates.
$Am^{3+}$	sorption to carbonate minerals	Low pH destabilizes carbonates. High pH increases solubility of Am-carbonate minerals.
$Cs^+$	sorption to clay innerlayers	High $NH_4^+$ levels may lessen sorption. How abundant are clays?
I <sup>-</sup>	sorption to sulfides, organic matter	Sorbs to very little else.
$TcO_4^-$	possible reductive sorption to reduced minerals (e.g. magnetite), forms insoluble reduced oxides and sulfides.	Sorbs to very little else.
$Th^{4+}$	sorption to most minerals, formation of insoluble hydroxide	may move as a colloid
$Co^{2+}$	sorption to iron hydroxides, carbonate minerals	low pH destabilizes carbonates. Low $E_H$ dissolves iron hydroxides

Table 3.1 Natural attenuation pathways for metals (and other inorganics)(from Brady et al., 1997).

Table 3.2 outlines the minimal geochemical data needed to determine if the particular natural attenuation pathway are operative. Data needs depend primarily on whether the likely fate of the compound is as a component of an insoluble solid, a sorbed contaminant, or, possibly, a species occluded on an iron hydroxide or carbonate mineral surface, or irreversibly sorbed to an innerlayer clay site.

Field data are probably going to be the coin of the realm. Models and lab data are best used to establish confidence that we know what we're doing.

Chemical	Data Needs
Pb <sup>2+</sup>	Iron hydroxide availability; pH, alkalinity, and Ca <sup>2+</sup> levels to answer if calcium carbonate is stable. E <sub>H</sub> , and if E <sub>H</sub> is low, sulfide levels. Organic carbon content.
CrO <sub>4</sub> <sup>2-</sup>	E <sub>H</sub> , electron donor levels, pH (reduction rates are faster at low pH).
As(III or V)	E <sub>H</sub> and, if E <sub>H</sub> is low, sulfide levels.
Zn <sup>2+</sup>	Iron hydroxide availability; pH, alkalinity, and Ca <sup>2+</sup> levels to answer if calcium carbonate is stable. E <sub>H</sub> , and if E <sub>H</sub> is low, sulfide levels.
Cd <sup>2+</sup>	Iron hydroxide availability; pH, alkalinity, and Ca <sup>2+</sup> levels to answer if calcium carbonate is stable. E <sub>H</sub> , and if E <sub>H</sub> is low, sulfide levels.
Ba <sup>2+</sup>	Sulfate levels.
Ni <sup>2+</sup>	Iron hydroxide availability; pH, alkalinity, and Ca <sup>2+</sup> levels to answer if calcium carbonate is stable. E <sub>H</sub> , and if E <sub>H</sub> is low, sulfide levels.
Hg <sup>2+</sup>	E <sub>H</sub> , and if E <sub>H</sub> is low, sulfide levels.
UO <sub>2</sub> <sup>+2</sup>	Iron hydroxide availability, pH, availability of reducing compound
Pu(V and VI)	Iron hydroxide availability, pH, availability of reducing compound
Sr <sup>2+</sup>	Iron hydroxide availability; pH, alkalinity, and Ca <sup>2+</sup> levels to answer if calcium carbonate is stable.
Am <sup>3+</sup>	Iron hydroxide availability; pH, alkalinity, and Ca <sup>2+</sup> levels to answer if calcium carbonate is stable.
Cs <sup>+</sup>	Clay content, cation exchange capacity.
I <sup>-</sup>	Metal sulfide mineral content
TcO <sub>4</sub> <sup>-</sup>	E <sub>H</sub> , and if E <sub>H</sub> is low, sulfide levels.
Co <sup>2+</sup>	Iron hydroxide availability; pH, alkalinity, and Ca <sup>2+</sup> levels to answer if calcium carbonate is stable.

Table 3.2 Data Needs for Natural Attenuation of Metals (from Brady et al., 1997)

### 3.1 *Manipulating Radionuclides in Groundwater (B. Spalding)*

Radionuclide contamination at Oak Ridge National Laboratory in Tennessee is one of the best studied cases of environmental transport of a suite of radionuclides. The primary radionuclides of concern are, in order of importance, <sup>90</sup>Sr, <sup>3</sup>H, <sup>137</sup>Cs and <sup>60</sup>Co, as well as a smaller inventory of transuranics. Contamination exists in burial sites, impoundments, tanks, and groundwater and sediments. Seven different approaches have been followed to maximize the immobilization of the contaminants:

1. Wait. Many of the isotopes have relatively short half-lives.
2. Control water flux,
3. Aerate/drain,
4. Heat
5. Add alkalinity. Sr, in particular, forms relatively insoluble carbonate minerals,
6. Add or adjust precipitating species,
7. Add adsorbing solids.

Treatments have consequently involved; (in the near surface) in situ grouting, vitrification, hydrologic barriers, chemical treatments and retrieval; (in the groundwater) the emplacement of hydrologic barriers, the application of chemical treatments, and through surface water control. Surface waters have been treated by dams, treatment plants, and diversions. The primary factors considered when selecting remediation technologies are, in order of importance; future land use, the nature of the contaminant, hydrologic setting, community input and lastly, soil geochemistry.

The field behavior of strontium is dominated by its interaction with calcium and its interactions with carbonate minerals, and to a lesser extent, exchangeable clays. After 30 years roughly 20% of the strontium is permanently fixed (irreversibly sorbed). The large majority of the remainder is on exchangeable clays. Isotope exchange techniques look to be one of the best ways to quantify the fraction which is irreversibly sorbed (see Appendix III).

### **3.2 Constructed Wetlands (A. Sobolewski)**

One of the most striking examples of metal attenuation in natural systems is observed when metal-rich solutions from abandoned mines encounter natural or constructed wetlands. Wetlands are effective natural filters for many metals/radionuclides and exist in a wide variety of climatic settings.

Metals/radionuclide sequestering occurs through sorption onto organic matter, sorption onto iron and manganese hydroxides, precipitation of metal hydroxides, and/or formation of reduced metal solids (e.g. metal sulfides). Copper, iron, manganese, vanadium, uranium, tantalum, and zinc, as well as several others (see

appendix III) have all been seen to be scavenged by wetlands. Occasionally, the metal enrichment in the wetland is sufficiently high that the wetland itself comes under consideration as a potential ore deposit.

Because of the observed extraction efficiency, constructed wetlands are increasingly considered as reasonably long-term, passive solutions to metal-rich drainage from mines. Numerous examples of high extraction efficiencies also highlight a number of the natural attenuation pathways alluded to earlier (e.g. sulfate reduction leading to metal sulfide formation - see section 3.0.1). Successful wetlands have a number of features in common; the most important one being that they remain wet. Drying out may lead to metal release as plants die and metal-rich sediments are exposed to the wind. Extraction efficiencies also tend to depend on what plants are found in the wetland - e.g. wetlands containing cattails tend to be better than those without.

### **3.3 *UMTRA Sites (D. Metzler)***

There are 24 abandoned Uranium Mine Tailing Remedial Action (UMTRA) sites left over from cold war activities. The RNA approach at UMTRA sites in Colorado and Wyoming demonstrates the technical, regulatory (EPA, NRC, and state), and stakeholder (county, city and tribe) issues that arise. RNA for the uranium mine tailings sites has gained preliminary regulatory and stakeholder acceptance for sites where (1) groundwater is of limited use; (2) complete restoration would cause more environmental harm than it would prevent; and (3) complete restoration is technically impracticable from an engineering perspective. Other similar criteria for successful application of RNA include sites where: (a) groundwater currently exceeds EPA standards; (b) groundwater is not currently nor projected to be a drinking water resource; and (c) advection, dispersion and attenuation can achieve cleanup goals within 100 years.

The approach utilized by Don Metzler in seeking regulator and stakeholder approval is similar to the general approach developed during the workshop and encompasses use of the following components:

1.13 years of baseline monitoring;

2. delineation of the significant processes and parameters (such as source term, hydraulic conductivities, flow gradient and direction, retardation factors and boundary conditions, and ecological considerations);
3. preliminary analytic modeling to build a conceptual understanding of contaminant transport at a given site and to identify data uncertainties and sensitivities
4. Identification of data needs; and
5. Revised numerical modeling to predict the time required for natural attenuation to meet the cleanup standard.

Modeling is used as a tool for identifying data uncertainties and sensitivities; for predicting the time required for natural attenuation to meet cleanup standard, and to build a conceptual understanding of contaminant transport at a given site.

### **3.4 Risk and Uncertainty (D. Gallegos)**

The purpose of this discussion was to present an approach by which risk evaluation and probabilistic analyses can effectively be used to guide decisions regarding the use of natural attenuation at contaminated sites, and evaluate the reliance of natural attenuation in a way that will establish confidence in the final decision. Within this context, "risk" is defined as the combination of what can happen (e.g., contaminants move through soil to ground water to a person), what is the likelihood or probability of occurrence of this event (e.g., what is the uncertainty in the natural attenuation process and its magnitude), and what are the resulting consequences (e.g., cancer occurs in an individual). This definition of risk provides a useful construct to analyze and make decision under uncertain circumstances. Decision analysis is integrated into the process to directly relate expenditures of resources (i.e., monetary costs and time) to understanding what can happen, changing what can happen, how likely it is to happen, and the consequences of it happening. As an example, we would like to evaluate which has more value: remediation of soil or proving the effectiveness of natural attenuation through additional data collection. In general, the decision that is being evaluated at these contaminated sites is: what action should be taken at this site to maximize the likelihood of long-term public health and safety (i.e., meet regulatory criteria).

The process proposes an integrated decision analysis and risk-based approach to define alternative options to reach this objective given certain constraints and desires, analyze these options in light of the current state of uncertainty, and decide on which is the most effective and efficient option to pursue. The process is iterative in that information/data collection is by definition one of a set of alternative options in the process that may have value, and if pursued is used to update the current state of knowledge. The process is not intended to be infinitely iterative, but rather define where reduction of uncertainty no longer has value (or when it has much value) and where particular decisions would not change regardless of the amount of information collected. In doing this, the approach ties data collection directly to the regulatory performance objectives, where data collection is directed toward reducing only the critical uncertainties, and thus provides an approach to defining meaningful DQOs.

The approach advocates the use of risk assessment and decision analysis early on, rather than after the fact (i.e., rather than after data collection / site characterization activities), to facilitate effective decision making regarding data and information collection and remediation. The approach proposes an approach to treatment of uncertainty whereby the analyst/site operator/regulator would identify sources of uncertainty such as uncertainty in models and parameter values, quantify and/or analyze those uncertainties, evaluate the impact of the uncertainty on the decision, and then reduce uncertainty only where it is necessary (i.e. where it would impact the decision being made). Formal decision analysis combined with a modified approach to sensitivity analysis has been proposed to facilitate this process.

### ***3.5 Panel Discussion - What would technical guidance for natural attenuation of metals and radionuclides look like?***

To begin with, there are some initial show-stoppers which would prevent any consideration of RNA. These may be technical or sociological. A tiered approach to considering natural attenuation would evaluate show stoppers first, followed by an increasingly complex examination of natural attenuation processes designed to develop a conceptual model. This would probably involve source term

characterization, searching for evidences of plume stabilization, identification of constituents of concern, etc.

At this stage a number of useful points were made that reflect on the previous proposition.

1. At each site, the mechanisms are likely to differ somewhat. Nevertheless, there is a reasonably finite number of natural attenuation pathways for metals and radionuclides.

2. The further the site is from the natural background, the less likely it is that RNA will be chosen as the remediation strategy.

3. Simple dilution as the primary natural attenuation mechanism will probably not be looked on favorably by EPA, though the actual standards remain to be set.

#### **4.0 TECHNICAL GUIDANCE FOR NATURAL ATTENUATION OF METALS AND RADIONUCLIDES**

There is no technical guidance for implementing natural attenuation of metals or radionuclides. Typically technical approaches to implementing natural attenuation of organic contaminants follow a format along the following lines. We have sought to follow the organic template while incorporating the various points made by participants in the workshop.

1. Review available site data. This should provide a useable hydrologic model, and roughly locate receptors, and pathways. This effort should also give some ideal of whether or not natural attenuation is a possibility. Specifically, it should be determined whether existing data suggests a decrease in contaminant bioavailability over time. At this point an explicit consideration of show-stoppers should be made.

2. Develop a preliminary conceptual model and assess the potential for natural attenuation. If contaminant levels in soil or groundwaters have decreased, or if the geochemical conditions appear to be favorable for natural attenuation (see e.g. table 3.1) a conceptual model outlining natural attenuation should be developed.

3. If needed, perform additional site characterization to support natural attenuation. Very rarely will the data required to test and calibrate a conceptual model be available at the outset. Instead additional data gathering (see table 3.2) will doubtless be required, particularly to support step 5 below.

4. Update conceptual model,

5. Simulate long-term site behavior. Obviously, this will require some estimate of the rate at which natural attenuation is occurring. Note that, whereas biodegradation of organic contaminants can relatively simply be fit to first order rate laws, there is less of a basis for predicting rates of the non-biodegradation natural attenuation pathways (e.g. irreversible sorption, solid formation, etc.).

6. Perform an exposure pathways analysis.

7. If natural attenuation is acceptable, prepare long-term monitoring plan (see below), as well as a contingency plan, and,

8. Present results to regulators.

Natural attenuation of organic contaminants is generally demonstrated using a wealth of evidence pointing to reductions in contaminant mass. The four most effective components used to convince a regulatory agency are: evidence of contaminant loss in the field, variations in electron donor/acceptor levels, appearance of degradation byproducts, and soil microcosm studies done in the lab. However, the same approach probably cannot be used for inorganics. The appearance of byproducts, or variation in acceptor/donor levels, probably cannot be used to monitor irreversible sorption or the growth of contaminant-bearing insoluble minerals. When a contaminant, such as lead, sorbs it will displace some other cation such as  $\text{Ca}^{2+}$ , which is likely to be far more abundant in solution. When  $\text{Cs}^+$  sorbs to a clay, chances are that it will be present in only trace amounts, and far less abundant in solution than the  $\text{Na}^+$  or  $\text{K}^+$  it displaces. As a result, while irreversible sorption of trace contaminants will dramatically affect solution levels of the latter, changes in other background metal concentrations will more than likely be minimal. The growth of contaminant-containing hydroxides, carbonates, and sulfides may

also cause undetectable variations in hydroxide, carbonate, and sulfide levels in solution because the latter are typically present in initially greater concentrations than the metals they combine with.

Standard geochemical codes (e.g. Bethke, 1984; Wolery, 1983) can be used to calculate whether contaminant levels are limited by the formation of an insoluble phase (e.g.  $Ba^{2+}$  by  $BaSO_4$  growth). Geochemical modeling to support uptake by sorption is not far enough along to be a stand-alone demonstration of metal sorption. Instead, uptake by sorption can be demonstrated by: 1. Demonstrating that the sorbing phase (e.g. Fe-hydroxides, calcium carbonate) is present in soils through a solubility calculation or direct observation; and 2. Showing that an appreciable fraction of the compound is associated with that phase. The latter is most directly done through sequential soil leaching procedures which dissolve specific minerals, along with any sorbed material. For example, citrate-Dithionate solutions remove iron hydroxides from soils. Hydroflouric acid removes silicates.  $H_2O_2$  removes organic matter. Acid acetate buffer solutions remove calcium carbonate. Appendix II outlines the soil digestion procedure. Obviously, supporting a conceptual model will be a site-specific exercise.

Metal desorption tests in the laboratory can be used to bracket mechanisms, though desorption rates measured over weeks to months in the lab don't say a whole lot about reactions occurring in soils over time spans of decades or more. The isotope dilution technique outlined by Brian Spalding (see Appendix III) appears to be a very effective way for quantifying irreversibly sorbed contaminants.

## **5.0 CAVEATS AND OBSTACLES (J. Hering and others)**

Natural attenuation, or any other remediation strategy, can only be assessed with regard to clearly-defined standards. It is important to consider what objectives can and cannot be attained by natural attenuation as well as the time scale over which various objectives may be attained. Environmental quality standards for the subsurface are defined for both the immobile phase (e.g., soil) and for groundwater.

Sorption processes, although they retard the migration of the contaminant toward potential receptors, necessarily involve association of the contaminant with

the immobile phase. Soil quality criteria are commonly defined in terms of the total metal concentration in the soil. Since metals are naturally-occurring substances, contamination can only be defined relative to some background level such as average crustal abundance (Table 5.1). If total metal concentration in the soil is taken as the operative standard, then natural attenuation can only be applied if some zone of contamination is excluded from this standard for an extended period or even in perpetuity. Over the very long term, flushing of contaminated subsurface material with uncontaminated groundwater may decrease the total metal concentration in the soil to background levels. It may, however, be reasonable to define alternative standards for soil quality that correspond to the *bioavailability* of soil metals. Although the determination of the bioavailable fraction is a complicated problem, it is appropriate to address this question in the context of the applicability of natural attenuation. Note that different standards may need to be applied if surficial contaminated soils are subject to erosion or scouring by wind.

Similarly, natural attenuation may only be applied for contaminated groundwater if the point of compliance is defined such that the contaminant concentration in the groundwater may be decreased to an acceptable level before the plume intersects the compliance point. Implicit in this definition is the allowance of groundwater quality standards to be exceeded within some zone bounded by the point of compliance.

There are a number of technical obstacles, which might potentially limit the effectiveness of natural processes in controlling contaminant movement and availability in the subsurface, and consequently, regulatory acceptance of its implementation. To begin with, unlike the biodegradation of some organic contaminants (e.g. fuel hydrocarbons), which results in the contaminant of concern 'going away', typically metals and long-lived radionuclides will remain in the subsurface (If radionuclides have sufficiently short half-lives they may 'go away' as well). In other words, many metals and radionuclides may still be present, though unavailable for biologic uptake. At the same time, dilution may lower contaminant levels to the point where they are acceptable in a regulatory sense, though there has been no net reduction in contaminant mass. Throughout the workshop, dilution

as a component of natural attenuation was viewed predominantly in two ways: 1. as an acceptable solution, and as 2. at best a politically, if not aesthetically, unappealing prospect.

One argument that dilution is acceptable is that there is almost always a measurable natural background of the of metals and some radionuclides (see table 5.1), as opposed to organic contaminants. This also points out a critical difference between natural attenuation of organic contaminants and metals/radionuclides. For example, dilution of TCE levels in a plume down to a regulatory target is unappealing to many because the natural state had zero levels of TCE. All the cleanup that money can buy won't return the water to pre-contaminated levels. On the other hand, dilution of metals and/or radionuclides, if extensive, can 'hide' any residual in the ambient background. Absolute (non-zero) cleanup levels are hard to choose because background levels vary from site to site.

<b>Table 5.1. Crustal abundance of selected trace elements</b>	
<b>element</b>	<b>crustal abundance (ppm)</b>
V	135
Cr	100
Ni	75
Zn	70
Ce	60
Cu	55
La	30
Nd	28
Co	25
Pb	13
Pr	8.2
Th	7.2
Sm	6.0
Cs	3
Sn	2
U	1.8
As	1.8
Eu	1.2
Cd	0.2
Hg	0.08
Se	0.05
Source: C. Klein and C.S. Hurlbut, Jr. (1993) Manual of Mineralogy, 21st ed., John Wiley & Sons, New York.	

The transport of contaminants that exist as components of insoluble solids or sorbed (reversibly or irreversibly) to mineral surfaces may, because of the ambient geochemistry, be severely limited. Contaminants which are strongly sorbed or in solid form in soils are likely to see much larger volumes of fresh recharge. Consequently, the potential for dilution is heightened. The immobility of sorbed and/or solid phase contaminants makes them plausible candidates for RNA. Critical to such an assessment is a clear understanding of the sequestering mechanism. Specifically, the speciation (e.g. Cs sorbed to an inner-layer clay, or immediately exchangeable on clay edge sites) of the contaminant needs to be known. Speciation needs to be known for three reasons: 1. to be able to predict the long-term stability of the sequestering in the face of possible changes in the ambient geochemistry; 2. to provide some clues as to how much time must elapse before the acceptable contaminant availability is achieved, and; 3. to allow an estimate to be made of the total attenuation capacity of a given soil/groundwater for the specific contaminant.

The preceding talks have outlined many, if not all, of the primary reaction pathways that limit the transport and bioavailability of metals and radionuclides. Also, many of the potential changes in the ambient geochemistry, which might remobilize metals and radionuclides have been covered (e.g. EDTA mobilization of cobalt). The potential for remobilization is a critical obstacle for acceptance of the remediation of metals and radionuclides. Obviously, time-spans are important. If remobilization of  $^{90}\text{Sr}$  or  $^{137}\text{Cs}$  (half-lives  $\sim 30$  years) occurs over time spans much greater than a hundred years, a very significant fraction of the radiotoxicity will have decayed away. For long-lived radionuclides and metals, dilution may be the only process decreasing potential releases which might occur with remobilization. It is not hard to imagine scenarios leading to the remobilization of most, if not all of the contaminants of concern. Drastic changes in hydrologic conditions and/or subsurface water chemistry may adversely affect natural attenuation processes. For example, a natural attenuation remedy that relies on limited infiltration may be invalidated by irrigation for agricultural development. Cs 'irreversibly' bound to interlayer

clay sites in a soil could be very rapidly released if ammonium-rich fertilizer were subsequently applied for agricultural purposes. By the same token, lead sorbed to iron hydroxides in an initially aerated soil might be released if the soil became flooded, then anoxic, followed by destabilization and dissolution of the iron hydroxide host. On the other hand, the composition ranges of soil and groundwaters is typically very limited, primarily because there are a host of biogeochemical processes which tend to control the pH, redox state, alkalinity, etc. of natural waters. Although drastic changes in the compositions of natural waters are more the exception than the rule, it will probably be impossible for site-owners to demonstrate that remobilization will never occur. This is a critical obstacle to the implementation of natural attenuation for metals and radionuclides. If monitoring is required in perpetuity to guard against remobilization, natural attenuation will probably never be the chosen remedy for metals, but may be for radionuclides with a sufficiently short half-life.

Additional points of contention are dealt with in the following question and answer format.

### **What is the role of site characterization and monitoring?**

The respective roles of site characterization and monitoring were two questions, which received a considerable amount of attention during the workshop. The argument was made that site characterization should specifically provide the means to develop a conceptual model of natural attenuation and, to the extent possible, calibrate that model so that contaminant availability can confidently be predicted in the future. Unless RNA is exceedingly fast (which is often not the case) it will be difficult to calibrate a kinetic model for RNA given the time allowed for a site characterization. Ultimately, long-term measurement might be required. Nevertheless, this should not be confused with long-term monitoring. Long-term monitoring should, quite simply, provide the means for assessing whether or not RNA is working. If the conceptual model for RNA is sufficiently effective at reproducing measured trends in contaminant levels, it should allow the frequency of monitoring to be significantly reduced.

## **Should natural attenuation be excluded from consideration at some sites?**

Natural attenuation is a strategy to mitigate potential risks to human health and the environment. If there is an existing or near-term potential impact on receptors, then natural attenuation is clearly insufficient to control all of the problem. Existing impacts may include inhalation exposure due to scouring of contaminated surface soils, contaminant loading to surface waters through erosion of contaminated surface soils, and contamination of a sole water supply. It may, however, be difficult to define existing impacts unambiguously. For example, groundwater contamination on private or public lands may be unacceptable even if no water supply system is affected because of the possible future liability (and consequent decrease in property values) associated with the contamination.

Observed groundwater contamination at levels significantly exceeding groundwater quality criteria would be an indication that sorption and dispersion processes are insufficient to achieve the necessary reduction in contaminant concentrations. Natural attenuation would be feasible in such cases only if interception of the contaminated groundwater plume by surface water afforded sufficient dilution at the point of compliance.

## **Is natural attenuation appropriate for a specific site?**

An important consideration in evaluating the applicability of natural attenuation for a given site is its intended land use. Natural attenuation may be considered as part of the remediation strategy for a contaminated site or as a component of the permitting of an existing facility. The latter case necessarily involves some on-going release of contaminants into the environment and the relevant question is whether natural attenuation would afford sufficient protection to human health and the environment. In the former case, source control is probably (but not necessarily) a prerequisite to application of natural attenuation.

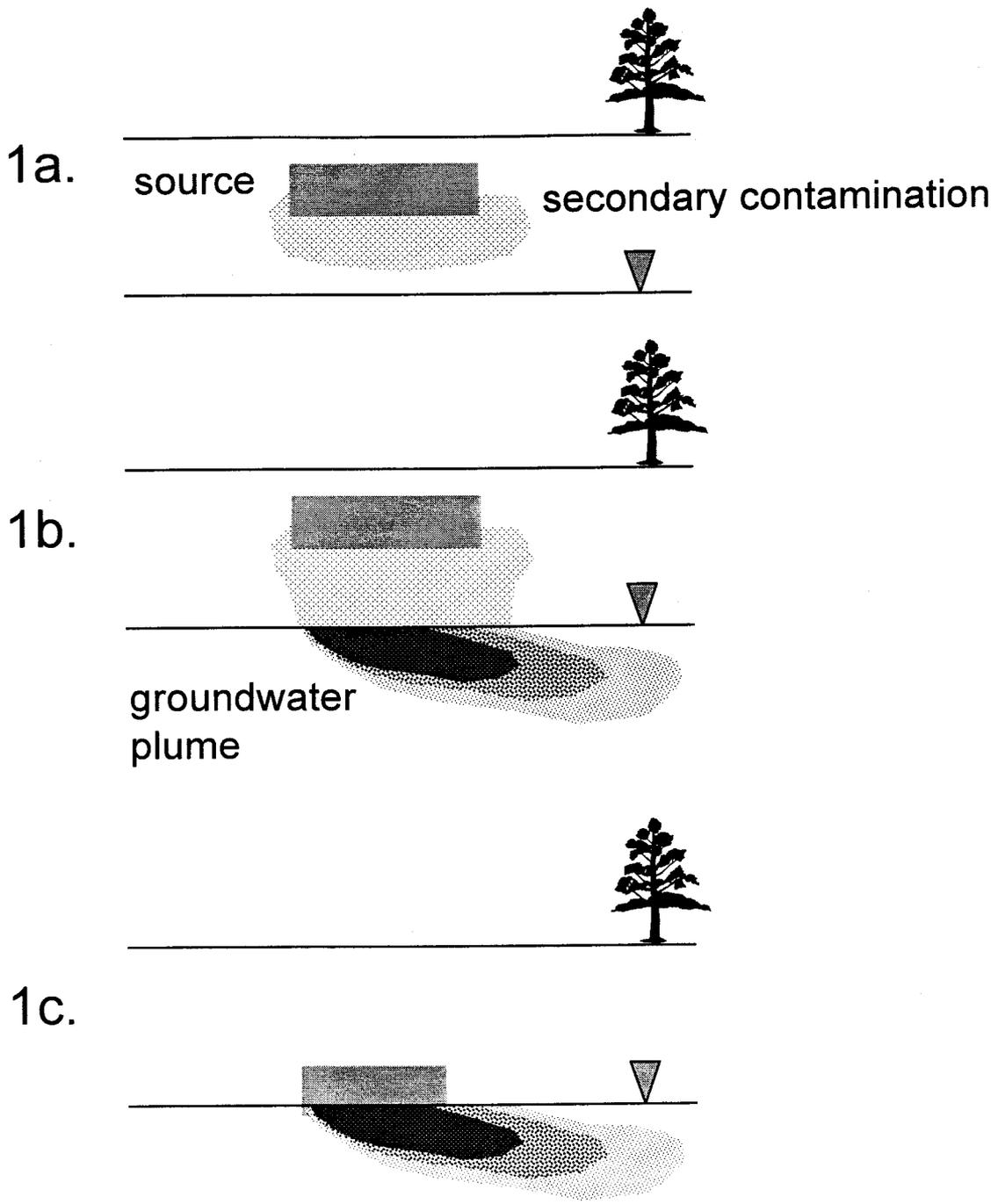
The efficacy of natural attenuation will depend on numerous factors including the type and extent of primary and secondary contamination (where primary

contamination is associated with the original source and secondary contamination with dispersal of contaminants from the source), the hydrologic regime and hydrogeology, subsurface geology, and potential receptors. For a given site, these factors must be evaluated with regard to their likely effects on the sorption and dilution processes by which natural attenuation of metals and radionuclides may be accomplished.

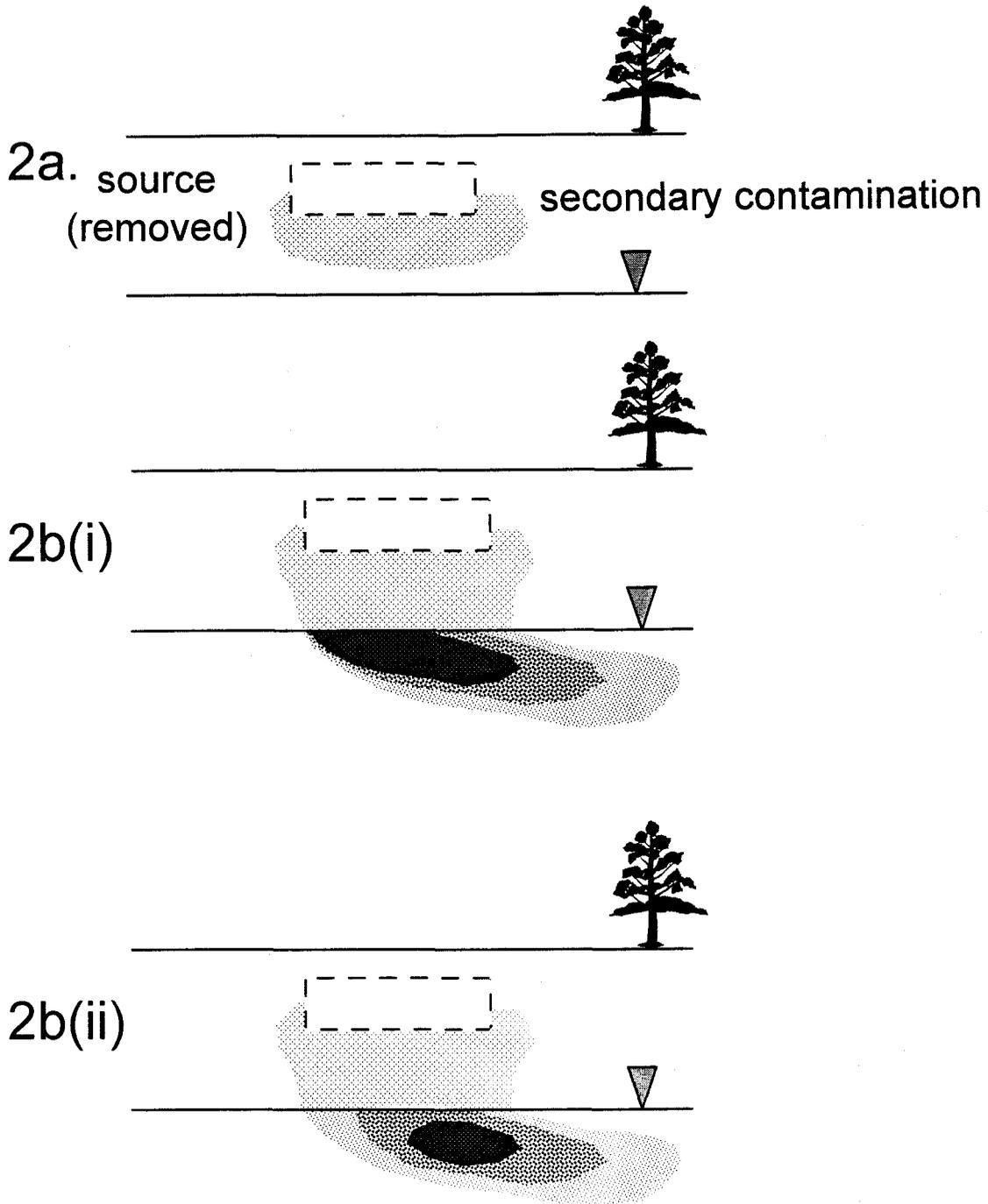
Because of the inherent site specificity of natural attenuation, it is unlikely that its feasibility can be evaluated in the general case. A better approach might be to examine classes of contaminated sites for their suitability for natural attenuation. Some classes of contaminated sites are shown in Figures 1 and 2; in Figure 1, the (primary) source of contamination remains in place while, in Figure 2, the source has been removed. Note that these figures are meant to be illustrative rather than exhaustive. In both Figures 1 and 2, three sub-classes are illustrated: (a) with secondary contamination only in the vadose zone, (b) with secondary contamination extending through the vadose zone to the groundwater table and a plume of contaminated groundwater present, and (c) with the (primary) source currently in Figure 1c or formerly in Figure 2c at or below the groundwater table and a plume of contaminated groundwater present.

In evaluating the potential application of natural attenuation at a specific site, the available data should be reviewed to determine (to the extent possible) whether natural attenuation processes are indeed operative at the site. For example, is the limited migration of contaminants in Figures 1a and 2a due to sorption and restricted migration or to limited infiltration at the site? Consideration of the type of contaminant(s) and the sorptive properties of the subsurface material(s) would provide some insight into this question. Direct evidence for the possible alternatives could be obtained by comparison of the behavior of the contaminant of concern with that of another constituent of the waste source that behaves conservatively (e.g., bromide or chloride). In cases where the source term has been removed, patterns of subsurface contamination may be indicative of migration or stabilization of the contaminants. For example, two possibilities are shown in Figures 2b and 2c: case (i) where a contaminated plume has been established but does not appear to

migrate after the source term is removed and case (ii) in which contaminant migration is indicated. In the cases illustrated in Figures 2b(ii) and 2c(ii), natural attenuation would only be applicable if there was a loss of contaminant mass from the groundwater (i.e., by sorption to subsurface materials) during migration or if interception of the contaminated groundwater by surface water would afford sufficient dilution of the contaminant before the point of compliance.

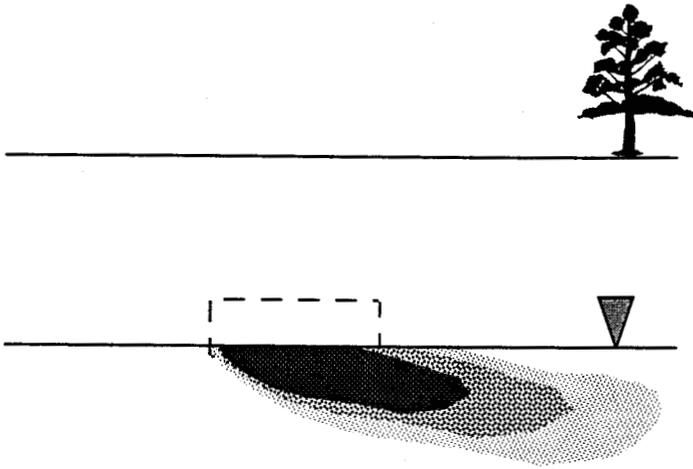


Figures 1 : Three sub-classes are illustrated with source still present: (a) with secondary contamination only in the vadose zone, (b) with secondary contamination extending through the vadose zone to the groundwater table and a plume of contaminated groundwater present, and (c) with the (primary) source currently at or below the groundwater table and a plume of contaminated groundwater present.

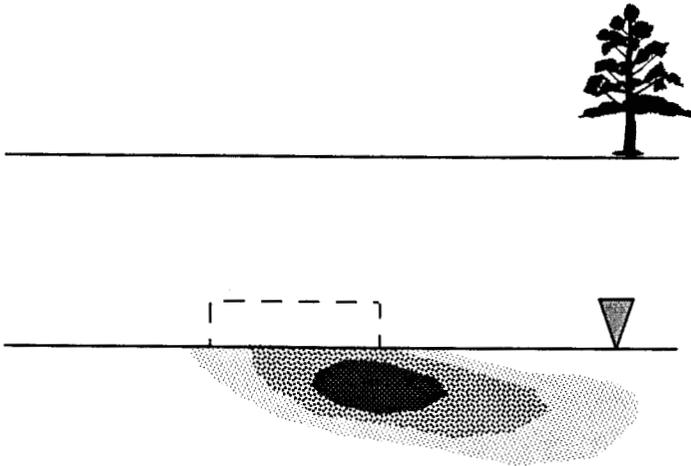


Figures 2 : Three sub-classes are illustrated with source removed with case (i) plume does not migrate after source is removed and case (ii) plume migrates after source is removed: (a) with secondary contamination only in the vadose zone, (b) with secondary contamination extending through the vadose zone to the groundwater table and a plume of contaminated groundwater present, and

2c(i)



2c(ii)



Figures 2 (continued) : ...and (c) with the (primary) source currently at or below the groundwater table and a plume of contaminated groundwater present.

## 6.0 CONCLUSION

Although natural attenuation encompasses several natural processes, it is important to recognize that only a few of these processes are operative for metals and radionuclides. For *both* metals and radionuclides, the operative processes are **dilution** and **sorption**. **Dilution** may occur by dispersion of dissolved contaminants in groundwater and/or by dilution of dissolved contaminants into surface water (e.g., upon interception of surface water by contaminated groundwater). **Sorption** may be defined generally to include the processes of adsorption, coprecipitation, precipitation, and diffusion into the matrix, processes by which solutes become associated with the immobile, solid phase. Sorption may either be **reversible** (i.e., definable by a constant for equilibrium partitioning between solid and dissolved phases or  $K_D$ ) or **slowly reversible**. Slowly reversible sorption processes may be considered as effectively “irreversible” if the time scale for re-release of the contaminant from the solid phase (i.e., by desorption and/or dissolution) is long relative to some time scale of interest or observation. Slowly-reversible sorption of contaminants from solid phases exposed to uncontaminated groundwater may also contribute to dilution of the contaminant. The extent of dilution will be determined by the rate of contaminant release into solution relative to the velocity of groundwater flow.

For radionuclides *only*, radioactive decay is an additional process contributing to natural attenuation. In some cases, however, the ingrowth of daughter nuclides may result in an increasing hazard over time that counterbalances or even outweighs the benefit due to loss of the parent nuclide.

We see the building of conceptual models for RNA as one of the primary challenges to its successful implementation. The most important sinks for metals and radionuclides in soils and groundwaters are fairly well understood (microbiological effects less so). Nevertheless, field-based techniques for demonstrating that contaminants are being taken up into otherwise inaccessible and/or non-bioavailable fractions of the soil matrix are few and far between, and

therefore a critical need. SEM, isotope exchange techniques, and soil digestions may provide a means for addressing this need.

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# APPENDIX I: Workshop Agenda

Day 1  
Wednesday - June 18, 1997

## *Scientific Background for Natural Attenuation of Metals and Radionuclides*

- 8:00 Check in - Continental Breakfast
- 8:30 AM Introduction and logistics. Patrick Brady - Sandia.
- 8:40 AM An Overview of Natural Attenuation. Fran Kremer - EPA/ORD.
- 9:10 Adsorption/desorption of trace metals from soil constituent surfaces: I. Effect of residence time. Matt Eick - VPI.
- 9:40 Adsorption/desorption of trace metals from soil constituent surfaces: II. Phytoremediation: Potential and deficiencies for trace metal clean-up. Paul Grossl and Joan McLean - Utah State.
- 10:10 Microbial Mobilization and Immobilization (Stabilization) of Toxic Metals and Radionuclides. A.J. Francis - Brookhaven.
- 10:40 BREAK
- 11:10 Influence of synthetic and natural organics on the fate and transport of toxic metals in subsurface environments. Phil Jardine - Oak Ridge.
- 11:40 Discussion
- 12:00 LUNCH in Atrium
- 1:00 Summary of morning work. David Borns - Sandia.
- 1:15 Phosphate-metal interactions. Jim Ryan - EPA/ORD.
- 1:45 Discussion - What are the gaps in science (and/or technology)?
- 2:30 BREAK
- 3:00 Discussion - What are agency and industry-specific science/technology needs?
- 4:30 ADJOURN
- 4:45 Cocktail reception in Atrium

Day 2  
Thursday - June 19, 1997

*Technical Approaches to Remediation of Metals and Radionuclides*

- 8:00 Continental Breakfast
- 8:30 Introduction and Overview. Patrick Brady - Sandia.
- 9:00 Manipulating Radionuclides in Groundwater: The Changes, They Are a Timing. Brian Spalding - Oak Ridge - Grand Junction.
- 9:30 Metal attenuation from mineralized seeps and mine drainage by natural wetlands. André Sobolewski - Microbial Technologies.
- 10:00 BREAK
- 10:30 Implementation of natural attenuation at UMTRA sites. Don Metzler - DOE - Grand Junction.
- 11:30 LUNCH in Atrium
- 1:00 Summary. David Borns - Sandia.
- 1:15 General Approach for Treating Uncertainty Associated with Natural Attenuation using Probabilistic and Risk-Based Approaches. David Gallegos - Sandia.
- 1:45 Discussion - What are the obstacles to implementation of natural attenuation?
- 3:00 Subgroup meetings
- 4:30 ADJOURN

Day 3  
Friday - June 20, 1997

*Conclusion*

- 8:30 AM Continental Breakfast
- 9:00 Meeting of available panelists, working group members, and interested parties to outline final workshop report
- 11:00 ADJOURN

## APPENDIX II: Soil Digestion Procedures

The sequential extraction of mineral and organic soil components is described in detail by Jackson (1969), in Dragun (1988), and in Yong et al. (1993). The latter approach relies on a combination of equilibrium speciation calculations and sequential leaching procedures. As noted earlier, chemical speciation is critical to the prediction of metal transport and toxicity. Sequential extraction analysis is particularly useful because it provides a rough measure of the capacity for a given soil (or backfill) to attenuate heavy metal toxicity (Yong et al., 1993).

In the approach of Yong et al. (1993) metals are assumed to populate one of 5 distinct pools; exchange sites, in/on carbonate minerals, in/on metal (hydr)oxides, in/on organic matter, and everything else. Metals associated with 'everything else' are considered to be those heavy metals which have managed to work themselves tightly into silicate mineral matrices. Heavy metals on exchange sites are loosely held by electrostatic attraction to clay minerals, organic matter, and amorphous materials (Yong et al., 1993). Washing of contaminated soils in high levels (1M) of dissolved salts such as  $MgCl_2$ ,  $NaNO_3$ , and  $CaCl_2$  removes most exchangeable heavy metals from the solid phase and into solution. Analysis of the supernatant for the metal(s) of interest then quantifies the fraction on exchange sites. At the same time, such leaches do not otherwise appreciably disturb heavy metals in the other pools. This is important because the idea is to interrogate the soil with progressively more corrosive leaches.

Heavy metals associated with carbonate minerals are removed from soils by exposing the latter to acid solutions which destroy the carbonate host. A 1M HOAc-NaOAc solution (Ac = acetate) is recommended to remove calcite and dolomite, two of the most common carbonate phases, while leaving behind metal (hydr)oxides and organic matter. Extraction of the metal (hydr)oxide fellow travelers must not, in turn, cause the release of heavy metals from organic matter or the tightly-held silicate fraction. Yong et al. (1993) recommend a combination of 1M hydroxylamine hydrochloride cut with one part in four by volume of acetic acid.

Ascribing heavy metals to soil organic matter is difficult because metals associated with organic matter is the sum of both exchangeable and organic-specific

sites. The first will be lumped in with the first sequential extraction. The latter are generally removed by oxidation of the organic matter itself. The 'everything else'-silicate fraction is not considered by Yong et al. (1993) to be large. In any case, digestion in HF, and subsequent analysis, can put a number on the latter.

### **APPENDIX III: Hardcopy of Speakers Slides**

### **APPENDIX IV: Workshop Participants**

Dr. Fran Kremer - US EPA

## 1. NATURAL ATTENUATION

Naturally occurring processes in the environment that act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in those media. These in situ processes include biodegradation, dispersion, dilution, sorption, volatilization, and/or chemical biological stabilization or destruction of contaminants.

2.

- Use of NA does not signify change in OSWER's remediation goals
- NA is not a "no action", "default", or "presumptive remedy"
- Remedy using NA should include contingency measures

## 3. PROGRAMS THAT MAY LOOK AT NATURAL ATTENUATION IN CLEANUP

- UST
- CERCLA
- RCRA
- State Voluntary Cleanup Programs
- Brownfields Sites

## 4. HOW HAS NATURAL ATTENUATION BEEN USED

- Variety of sites, including MLF's, industrial LF's, refineries, recyclers, etc.
- At all but six sites, natural attenuation used in combination with active remedy components
- Often have low exceedences of cleanup levels
- Contingencies for active measures

## 5. Remediation at LUST has shifted to Using Natural Attenuation

- In 1993, landfilling was the predominant remediation for soils, and pump-and-treat the most common groundwater treatment.
- As of 1995, NA of soils (28%) only second to landfilling (34%), while NA of groundwater (47%).

[Information obtained from EPA's Office of Underground Storage Tanks (OUST)]

## 6. NATURAL ATTENUATION

- Determination is site specific
- Requires extensive site characterization
- Requires a risk assessment

## 7. APPLICATIONS OF NATURAL ATTENUATION

- Concurrent with active measures such as source control and treatment
- Subsequent to active treatment

## 8. AFTER PROACTIVE REMEDIATION

Is the spread of contamination contained by natural attenuation?

- Yes? Go into long-term monitoring
- No? Implement another approach

## 9. NATURAL ATTENUATION

1. Demonstrating Efficacy through Site Characterization
2. Historical groundwater and/or soil data demonstrates trend in declining concentrations
3. Geological and/or geochemical data demonstrates NA processes and rates
4. Field or microcosm studies

Unless #1 is of sufficient quality and duration, #2 and possibly #3 will be required. This is a regulatory decision.

## 10. EQUILIBRIUM

- Eventually, natural attenuation exceeds rate of source output, and concentration of contaminants(s) stabilizes or decreases.
- Importance of source control as the primary remedial alternative

## 11. WHEN/WHERE IS EQUILIBRIUM REACHED?

- Site factors - Soil type, precipitation influx...
- Contaminant factors - Solubility, concentration, carrier...

## 12. Considerations in the Use of NA

- Current and future use of impacted resource
- Timing for the demand of the impacted resource
- Time frame to achieve remediation objectives
- Regional resource issues affecting remedy selection

### 13. WHAT IS A REASONABLE TIME FRAME?

- Depends on amount of contaminant, toxicity, and mobility
- Proximity of receptors-humans, environmental
  - Especially sensitive human, threatened/endangered species
  - Public-private water supplies
- Potential use of aquifer
- Reliability/enforceability of institutional controls

### 14. NATURAL ATTENUATION ADVANTAGES

- Minimize transfer of contaminants to other media
- Less intrusive
- May be applied at all or part of a site
- Overall remedial costs may be lower than for "active" remedy

### 15. DISADVANTAGES OF NATURAL ATTENUATION

- Longer time frame may be needed to achieve goals
- Site characterization may be more complex and costly
- Responsibility for long term monitoring and costs
- Toxicity of by-products
- Potential for continuous contaminant migration/transport
- If NA fails, other alternatives may be required

### PROMOTING GREATER ACCEPTANCE OF NATURAL ATTENUATION

- Communicate that natural attenuation is a responsible, managed remediation approach (not a walk-away)
- Present site-specific data and analyses that demonstrate occurrence
- Develop defensible conceptual model supporting natural attenuation
- Build defensible predictive models, where appropriate

- Control/treat/remove sources
- Thoroughly monitor plume and downgradient areas
- Include contingencies for other measures if natural attenuation fails to meet desired goals
- Involve regulatory agencies early in process

#### NATURAL ATTENUATION

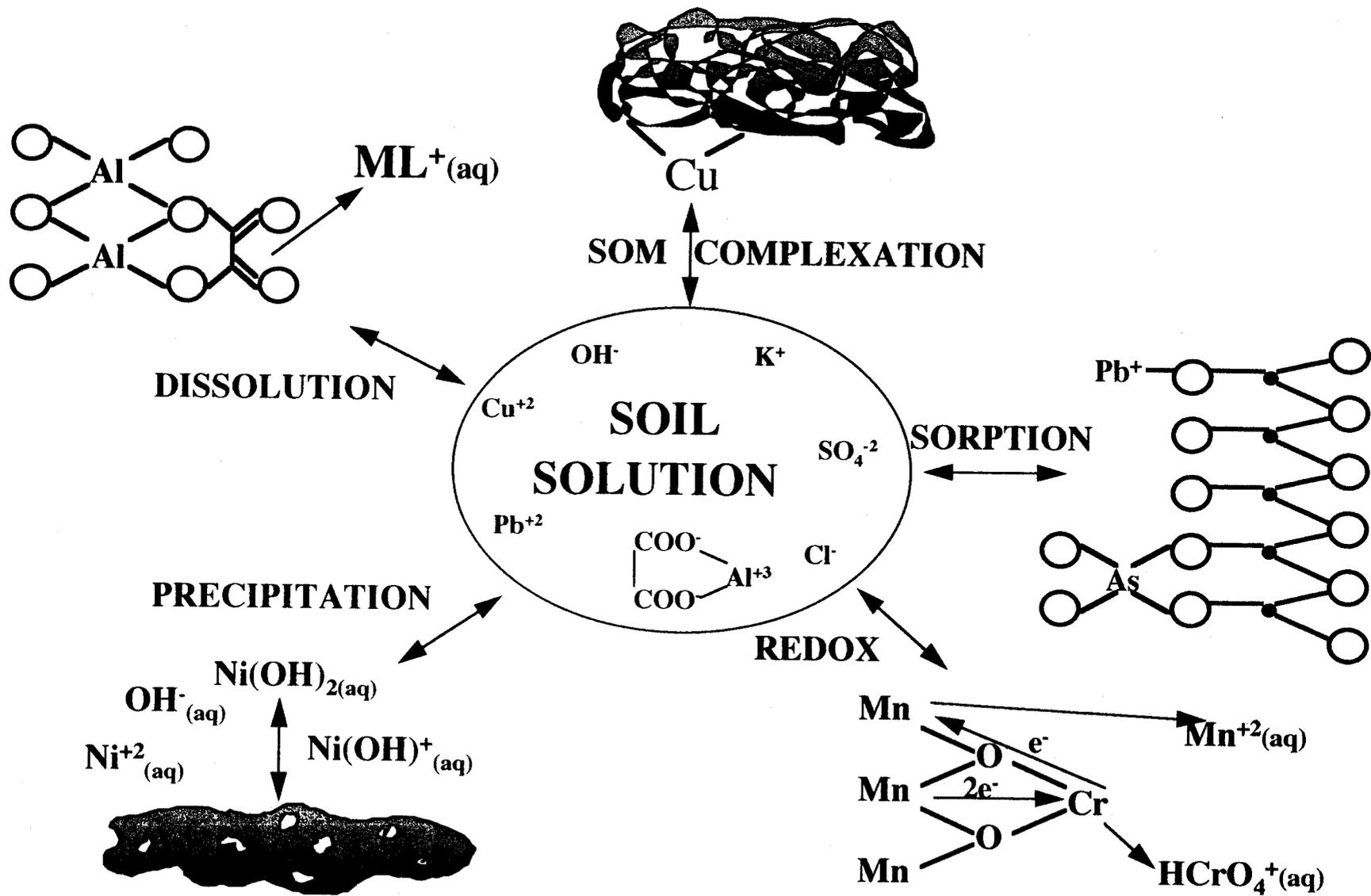
- Burden of proof is on the proponent, not the regulator
- Not a default technology or presumptive remedy
- Not complete until goals of the regulatory agency have been reached to their satisfaction

**ADSORPTION/DESORPTION  
OF TRACE METALS FROM  
SOIL CONSTITUENT  
SURFACES: I. EFFECT OF  
RESIDENCE TIME**

**M.J. Eick**

**Virginia Polytechnic Institute and  
State University**

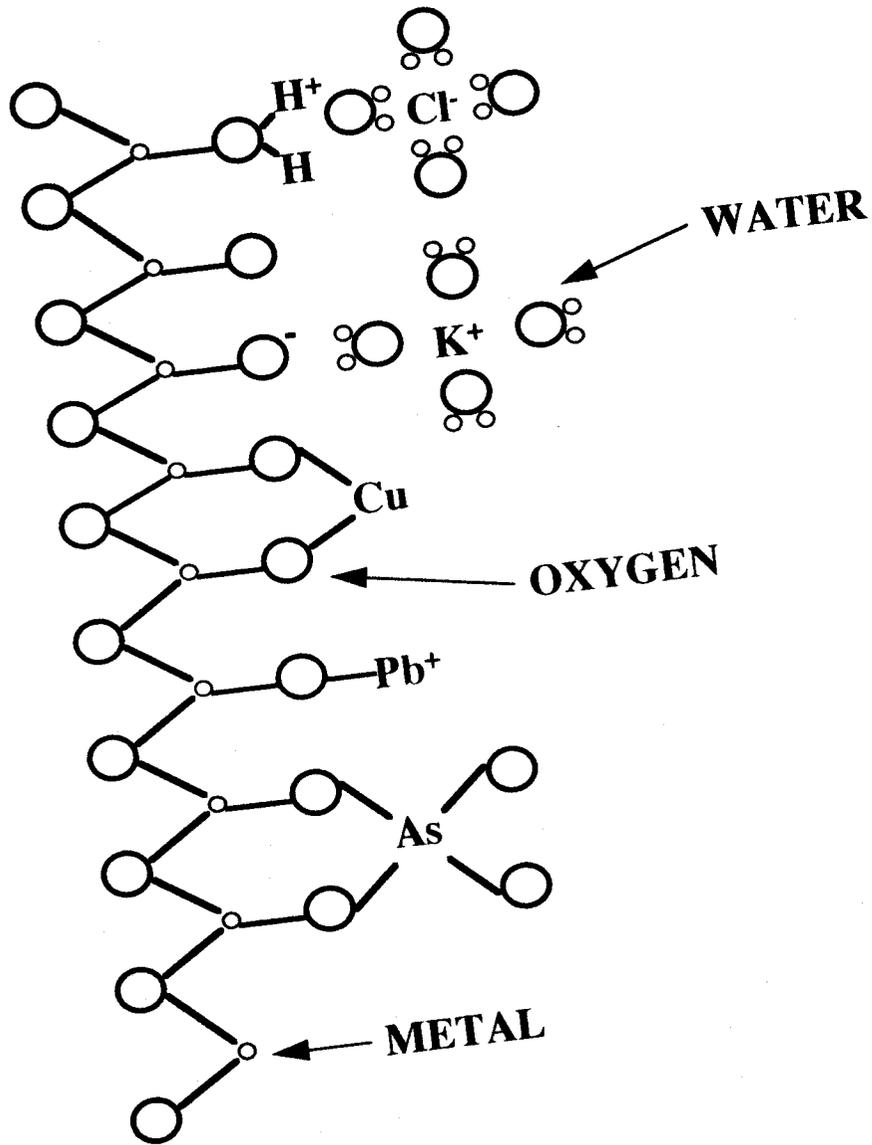
MJE-2



# Why Study Adsorption/ Desorption Processes in Soils?

- These processes are extremely important in controlling solution concentrations of trace elements
- Soil solution concentrations will ultimately control trace element bioavailability and potential toxicity

MJE-4



**OUTER-SPHERE  
COMPLEXES  
OR  
NONSPECIFIC  
ADSORPTION**

**INNER-SPHERE  
COMPLEXES  
OR  
SPECIFIC  
ADSORPTION**

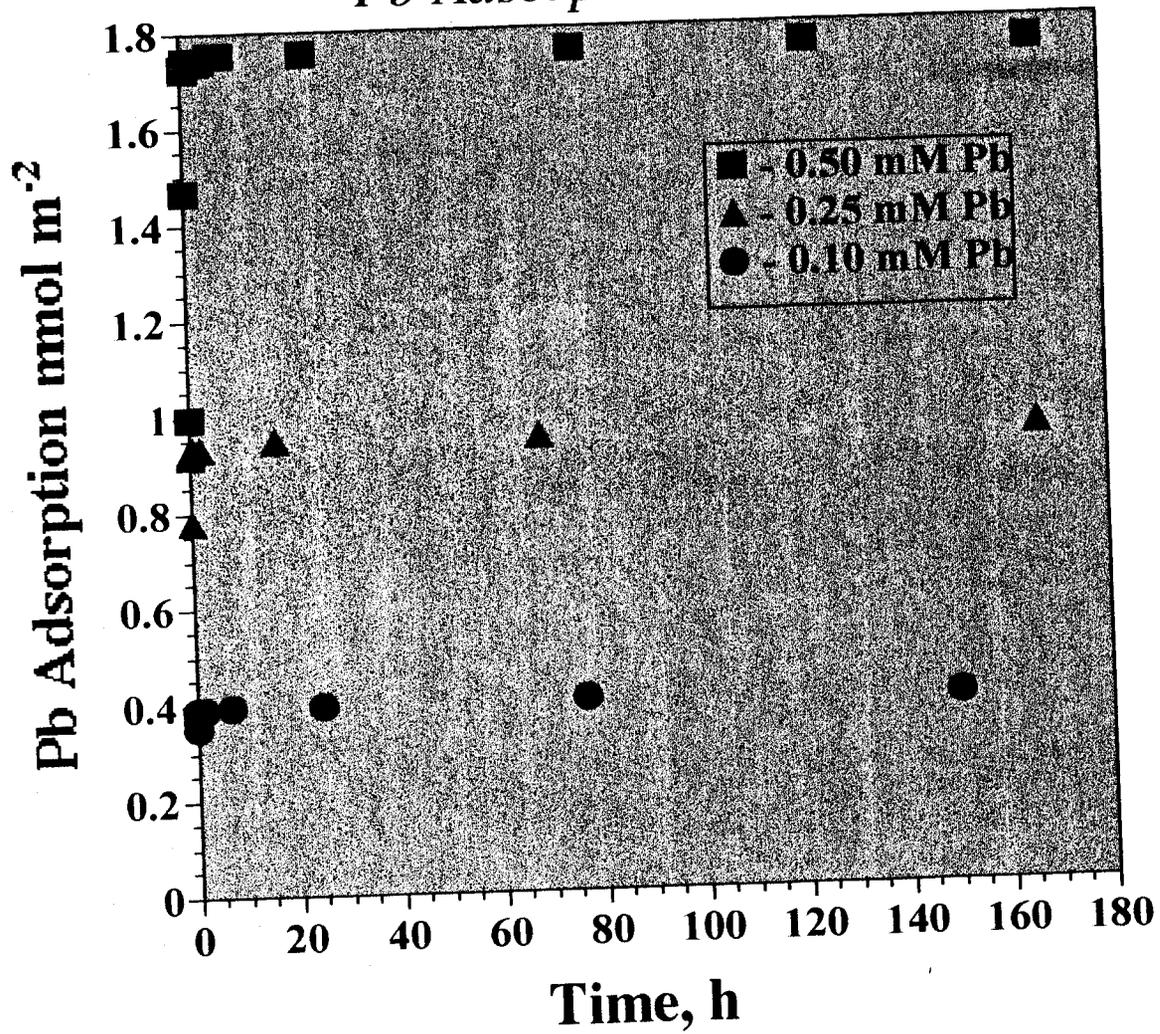
From Sparks, 1995

# Methods to Study Adsorption/ Desorption Phenomena

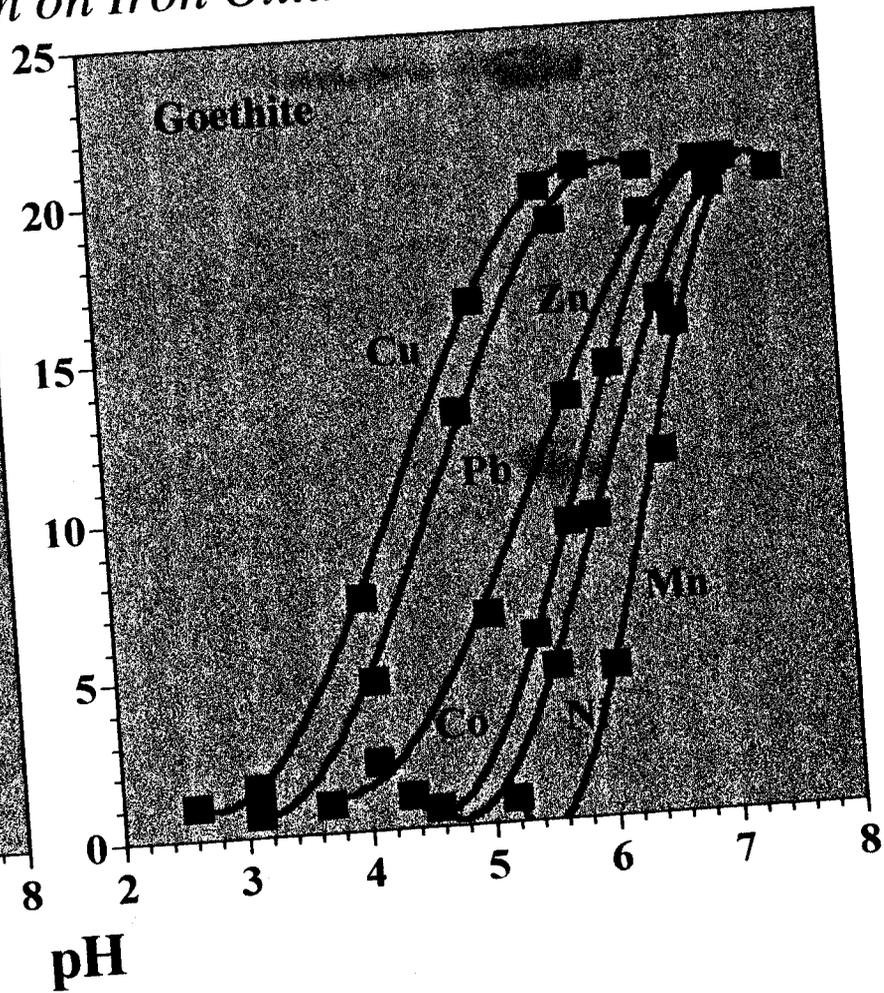
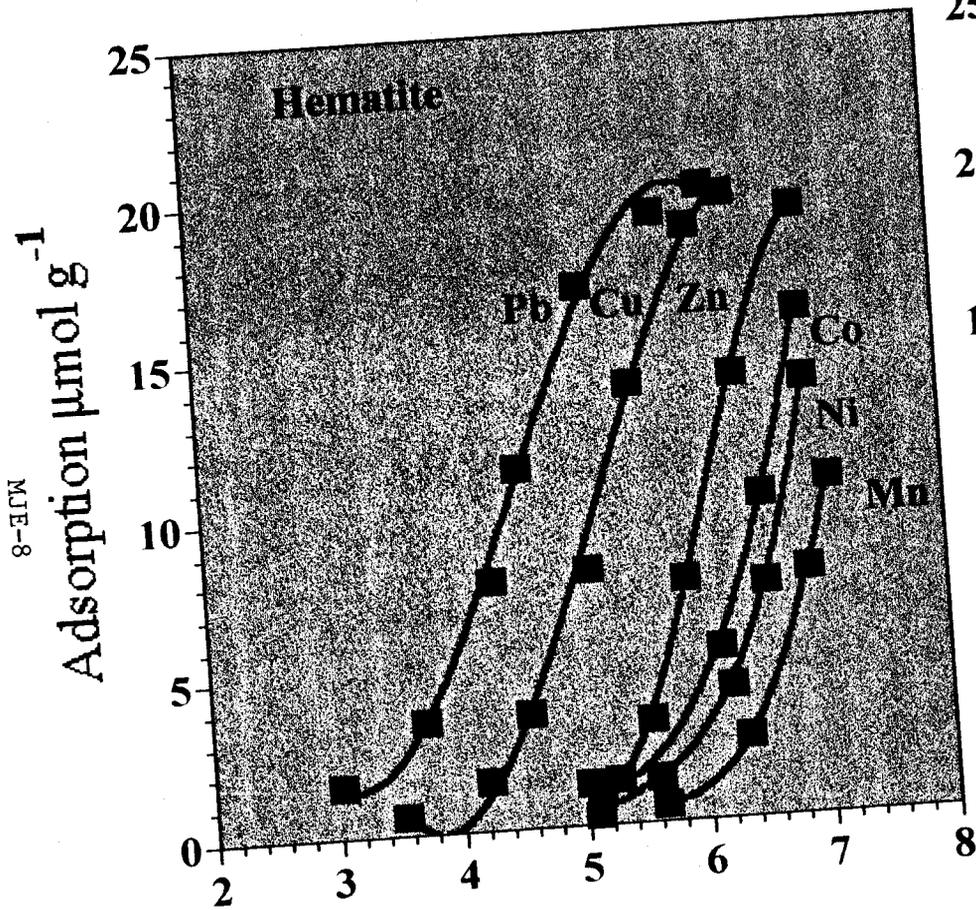
- Macroscopic measurements
  - Equilibrium Studies
  - Kinetic Studies
- Microscopic/Spectroscopic techniques
  - AFM, TEM, SEM
  - XAFS, FTIR, EPR, Raman
- Research has focused primarily on adsorption phenomena

# Adsorption

- Rapid
- Varies with:
  - pH
  - Type of Mineral Surface
  - Surface Coverage
  - Trace Element Concentration
  - Composition of Soil Solution (e.g. Ligands)

*Pb Adsorption on Goethite*

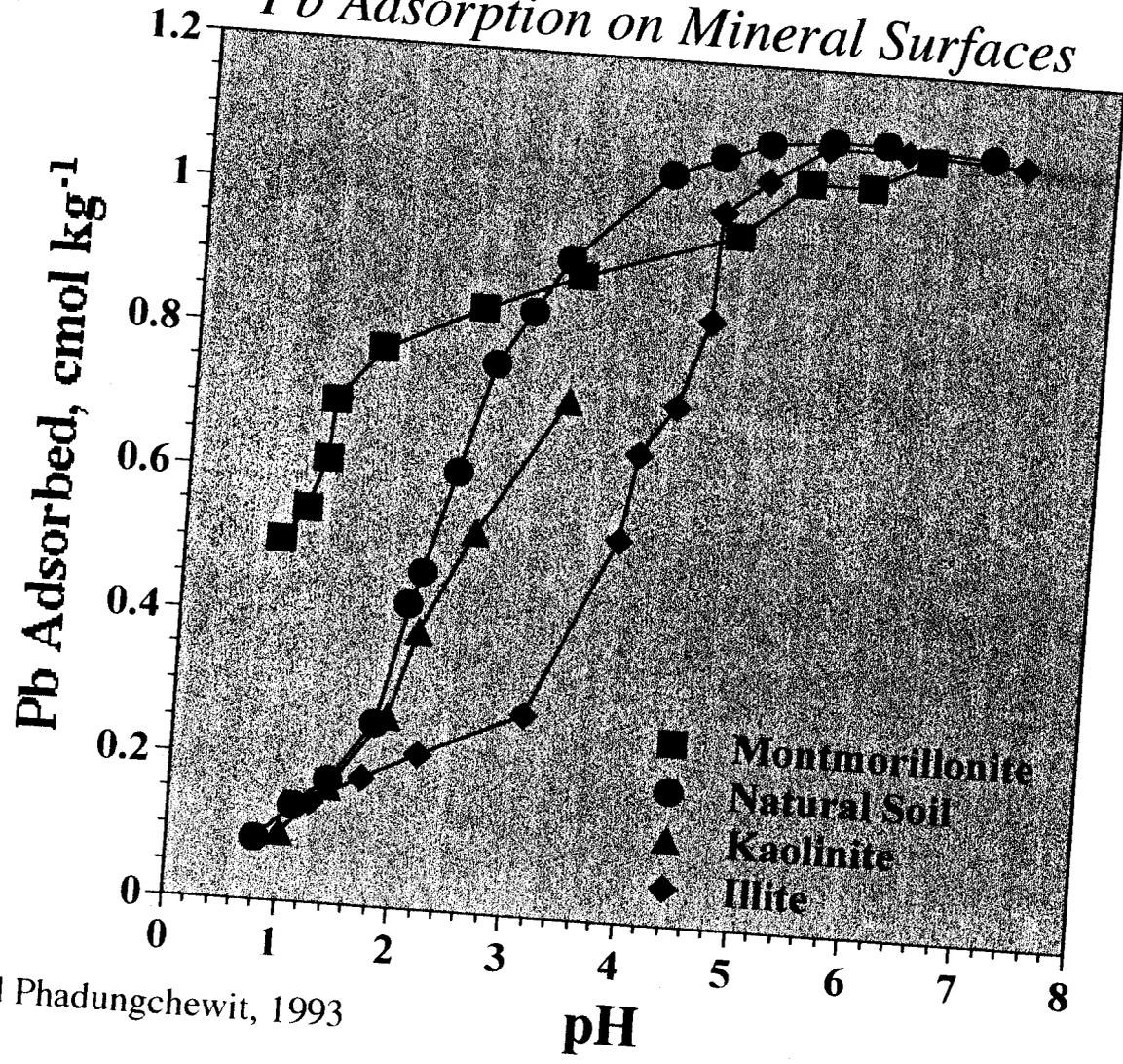
# Cation Adsorption on Iron Oxides



From McKenzie, 1980

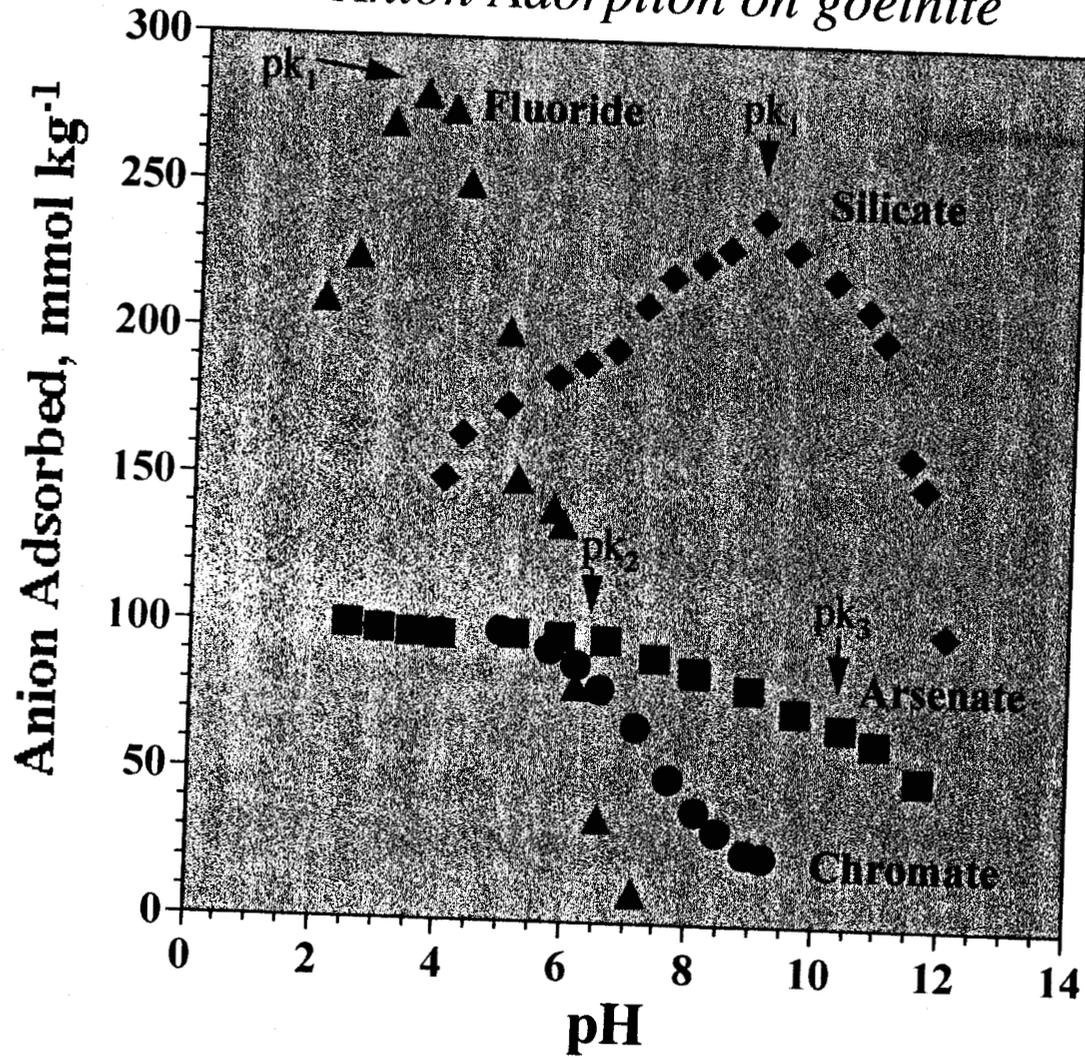
MJE-8

# Pb Adsorption on Mineral Surfaces



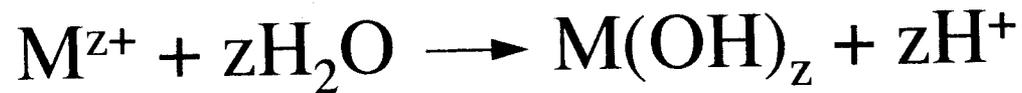
From Yong and Phadungchewit, 1993

### Anion Adsorption on goethite



# Cation Adsorption

- Increases as pH is raised (hydrolysis characteristics):



- Fine line between adsorption/nucleation/precipitation (sorption)

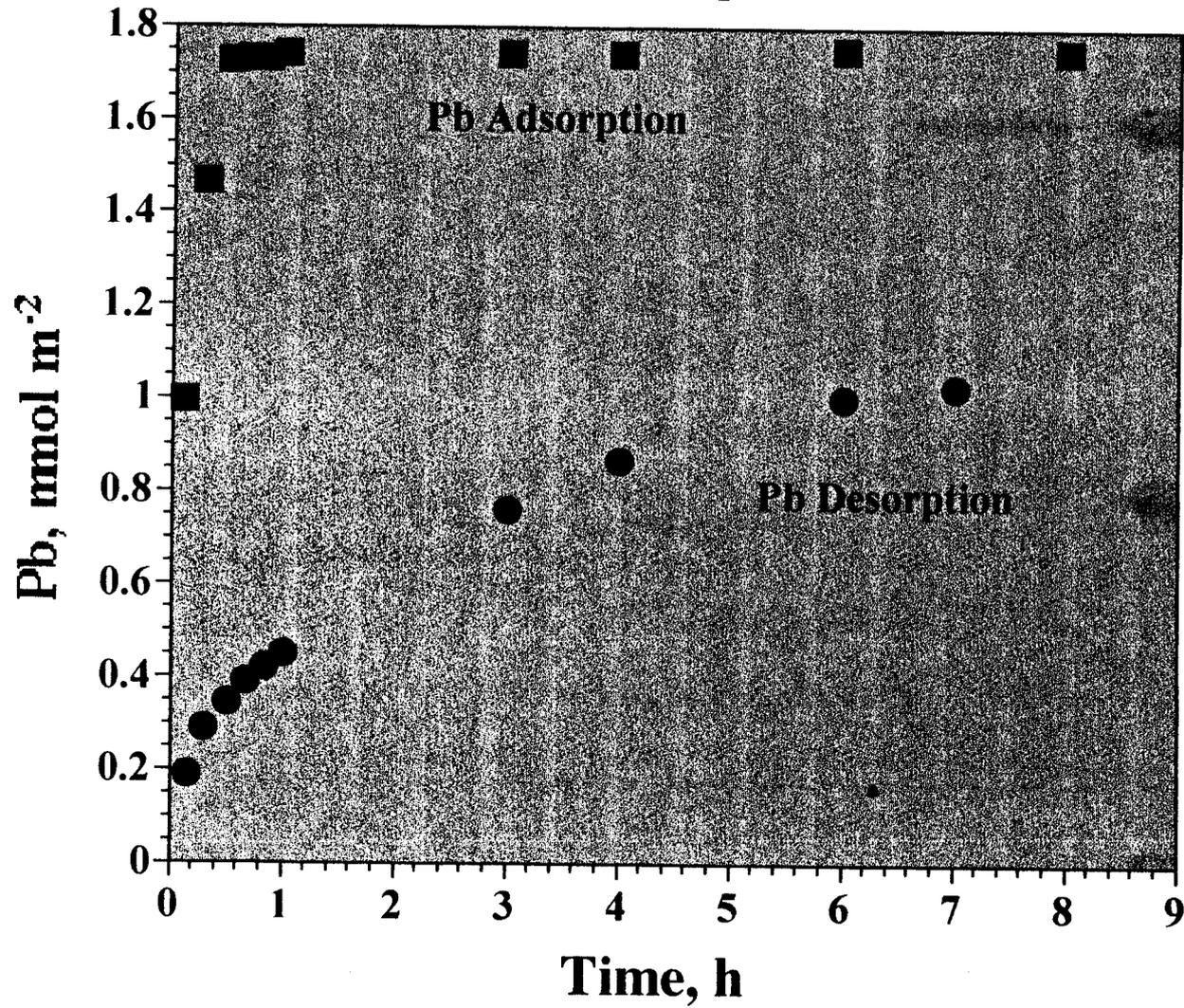
# Anion Adsorption

- Oxyanions of weak acids (moderate to high pH)
- Oxyanions of strong acids (low pH)
- Maximum adsorption near  $pK_a$  for monoprotic acids
- Slope breaks near  $pK_a$  for polyprotic acids

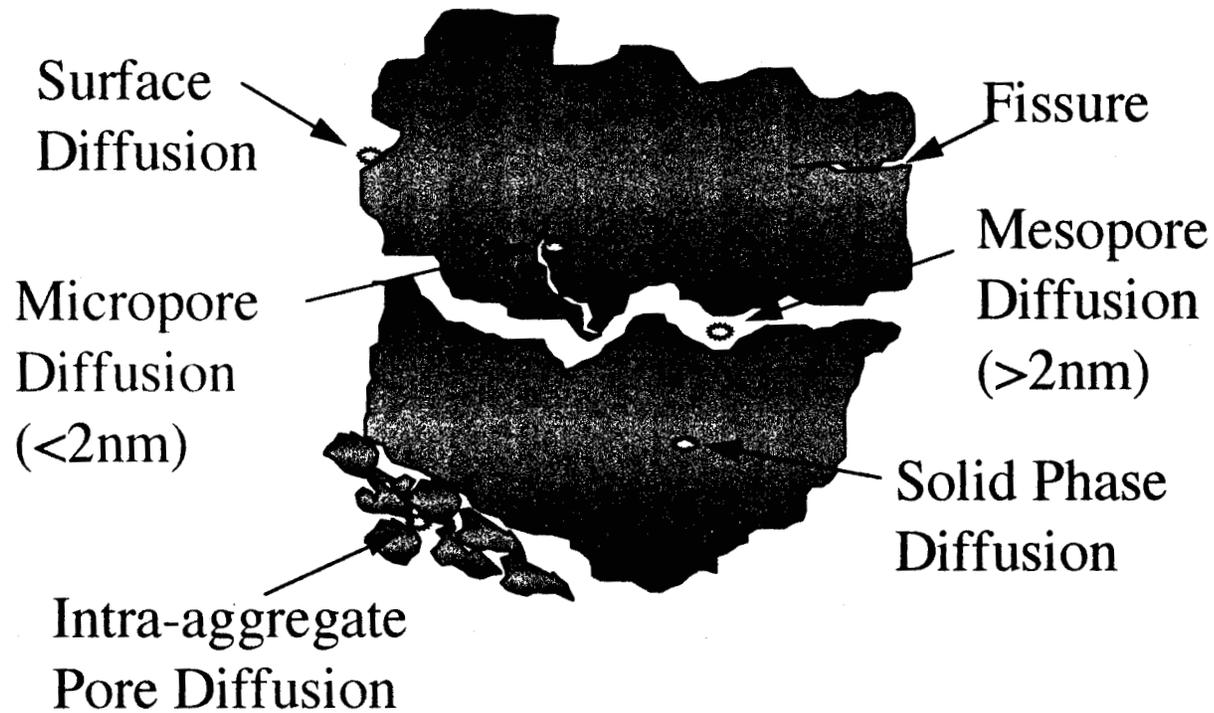
# Desorption

- Often Orders of Magnitude Slower
- Hysteresis or nonsingularity
- Varies with:
  - pH
  - Type of Mineral Surface
  - Surface Coverage
  - Trace Element Concentration
  - Composition of Soil Solution (e.g. Ligands)
  - Residence Time?

# *Pb Adsorption/Desorption on Goethite*



# Aging Effect Caused by Diffusion

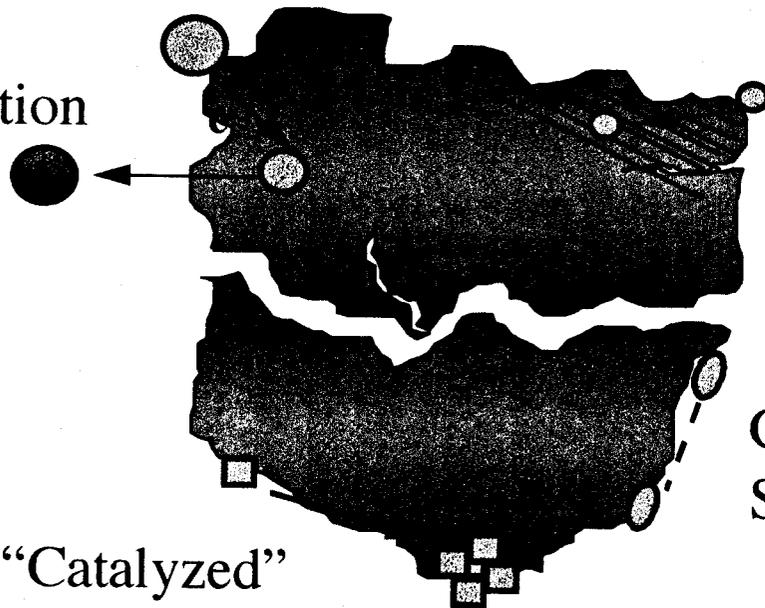


MJE-15

From Strawn, 1997

# Aging Effect Caused by Sorption

Surface Promoted  
Oxidation and  
Solid Incorporation



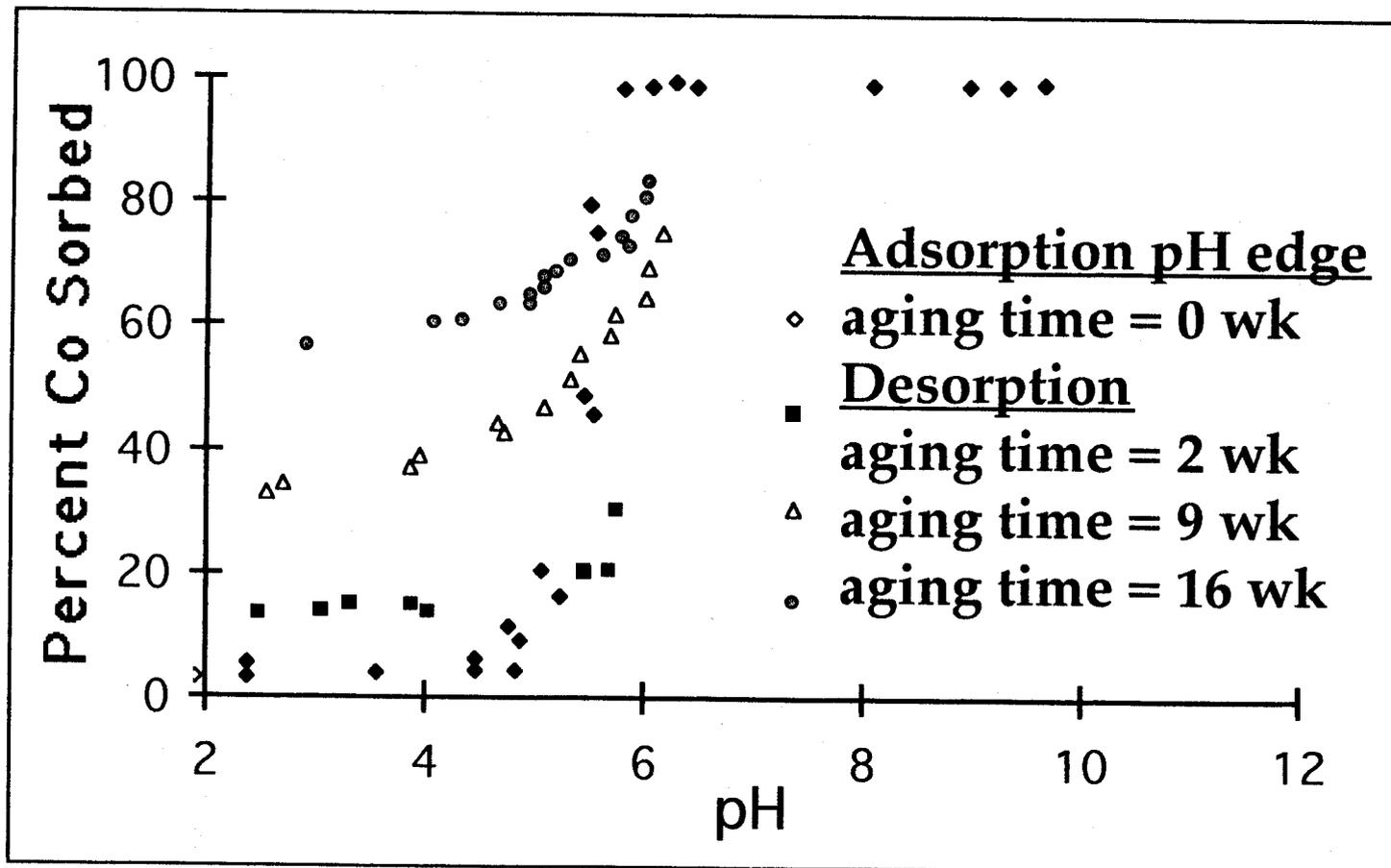
Incorporation into the  
Oxide Structure  
via recrystallization

Change in Surface  
Site Geometry

Surface "Catalyzed"  
Precipitation

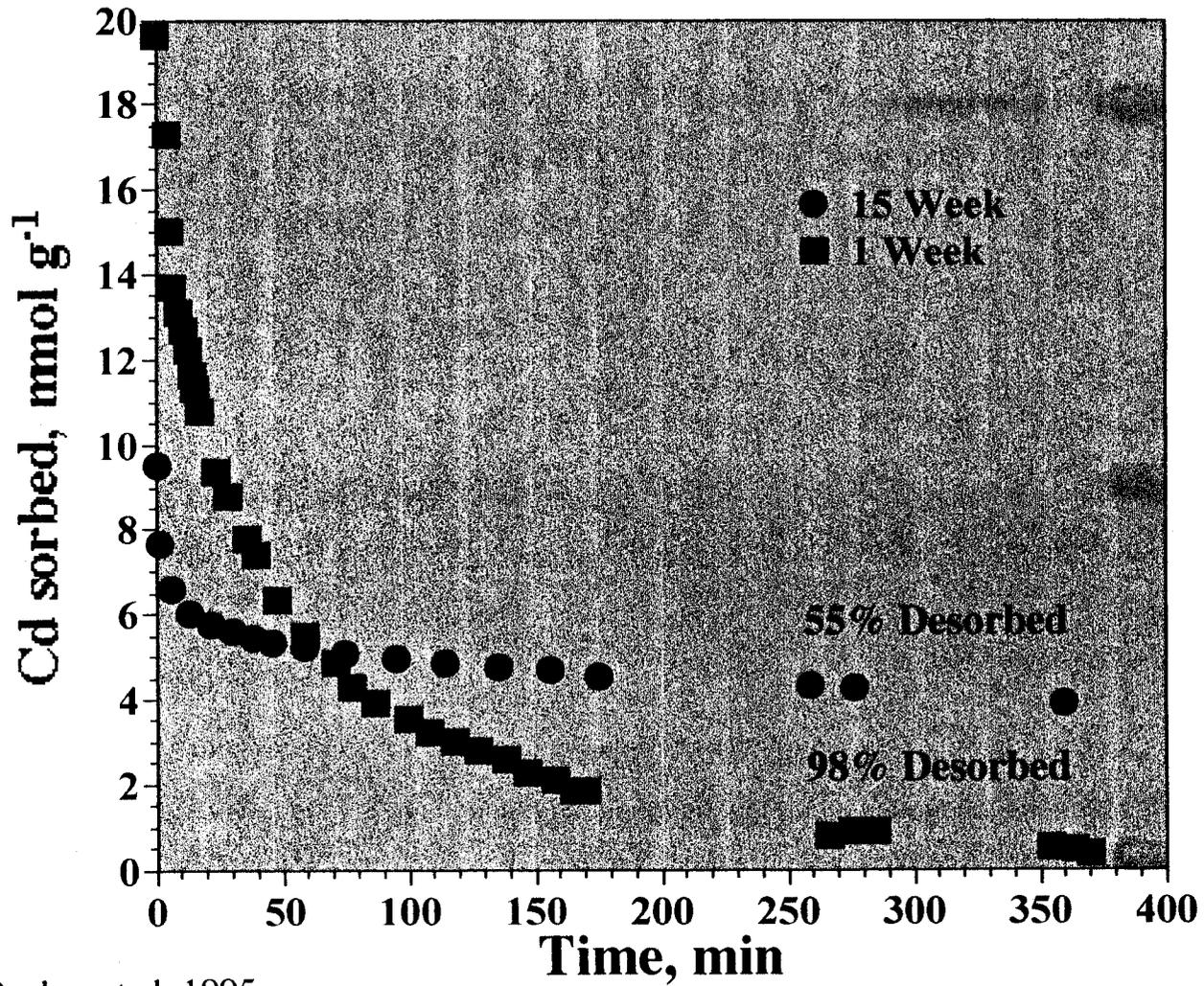
# Adsorption/Desorption of Cobalt on Hydrous Fe-Oxide

MJE-17



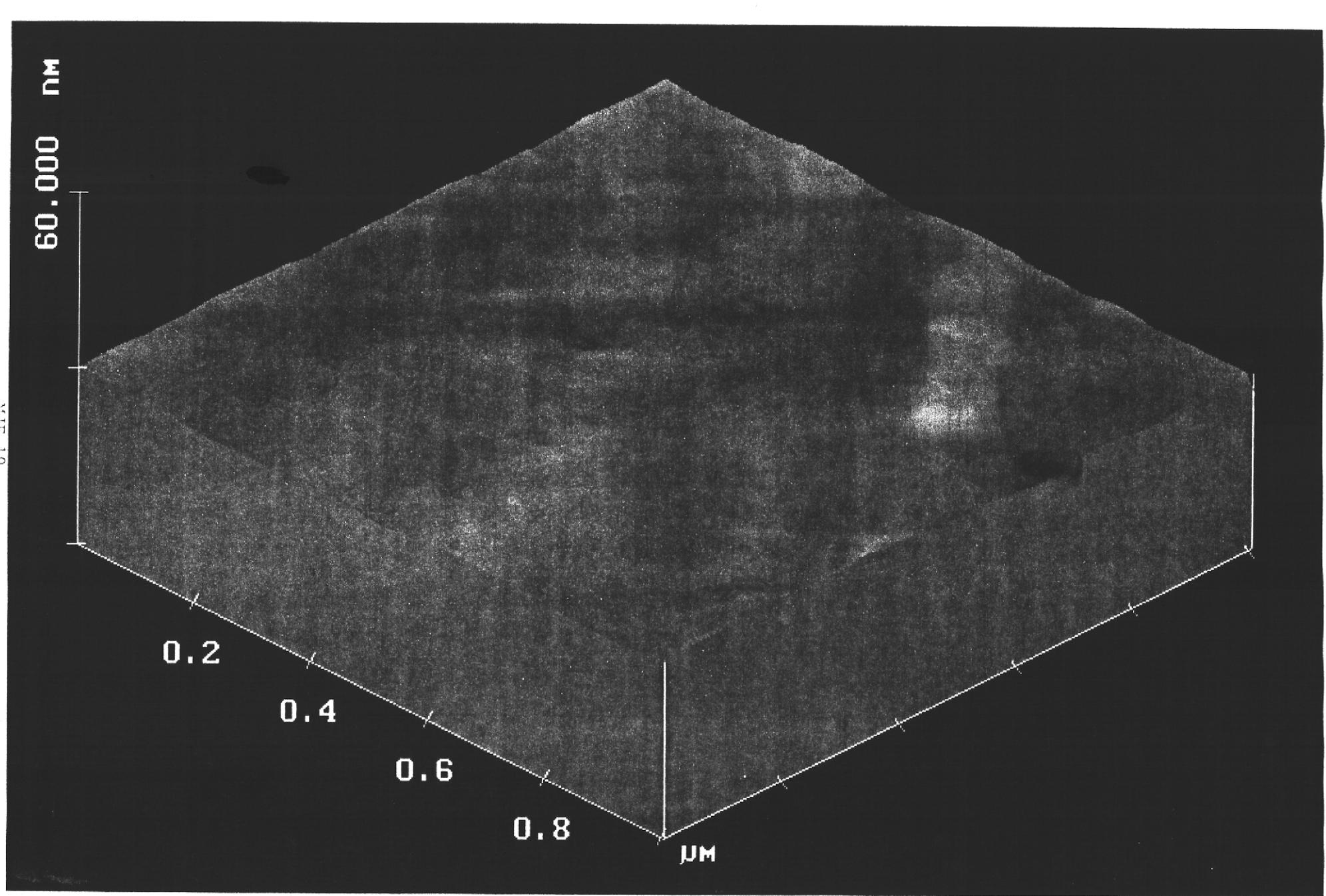
From Ainsworth et al., 1995

# Cadmium Desorption Kinetics from Goethite



MJE-18

From, Backes et al, 1995



MTE-20

60.000 nm

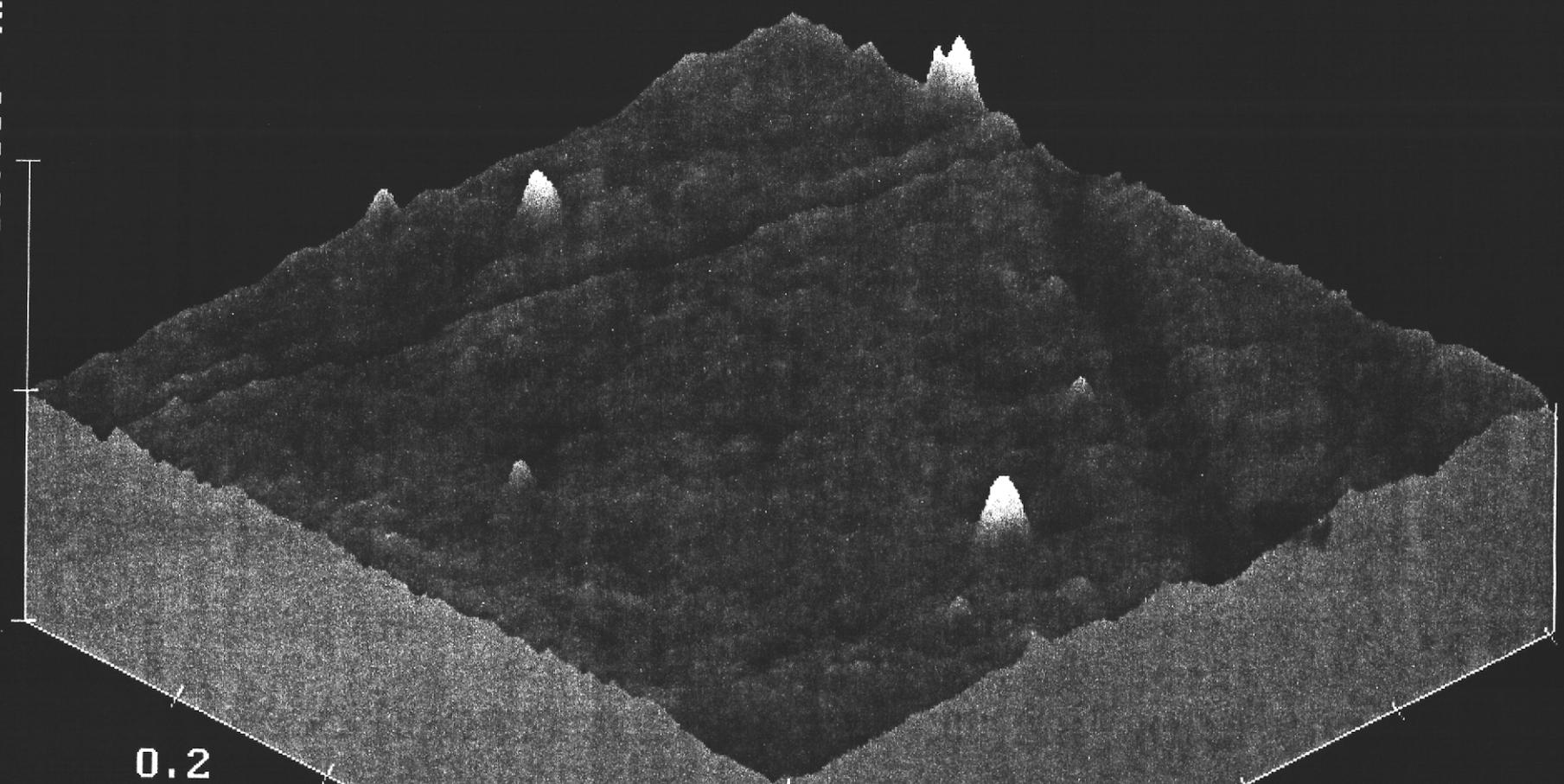
0.2

0.4

0.6

0.8

μm



10 11A

60.000 nm

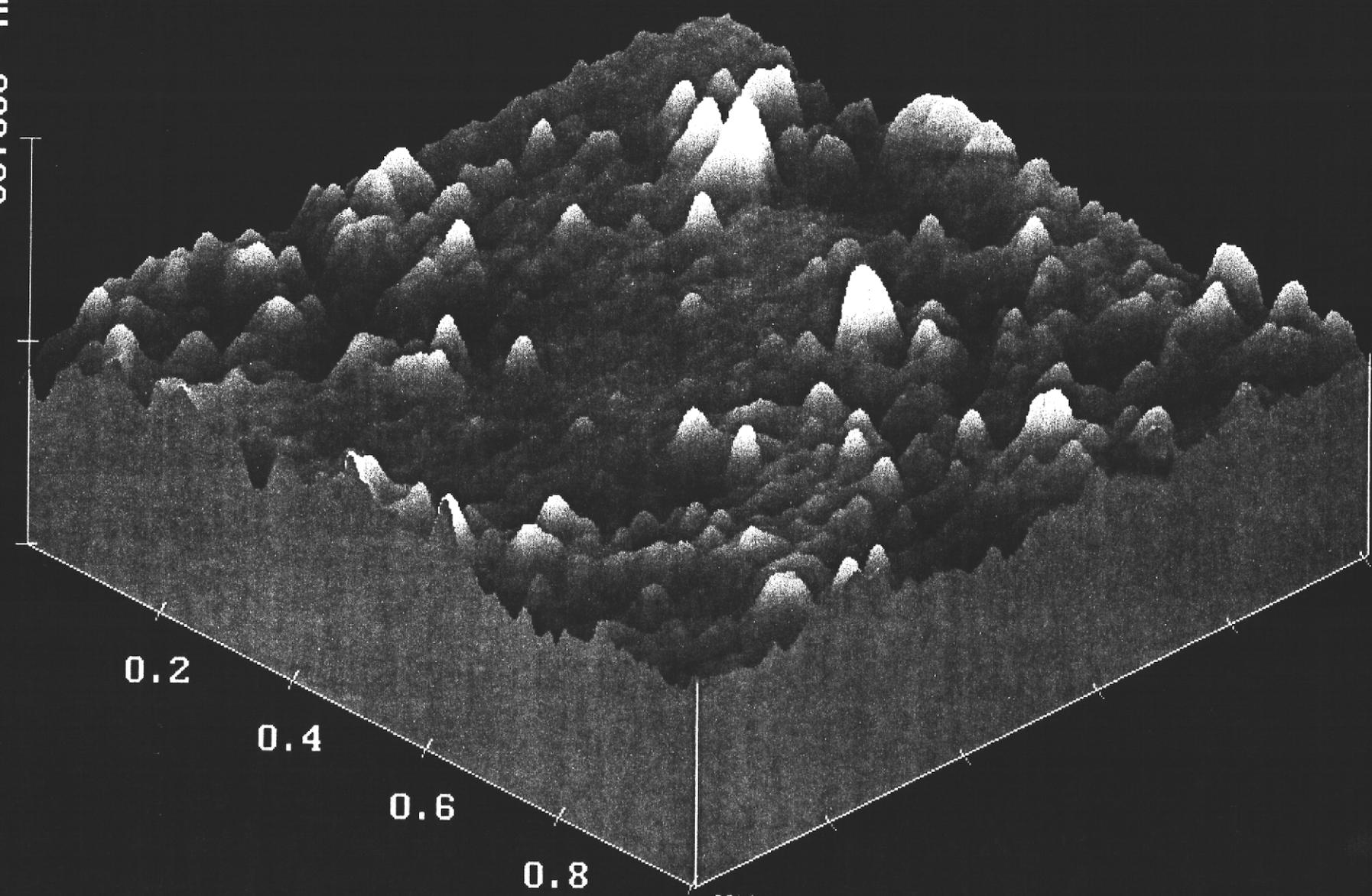
0.2

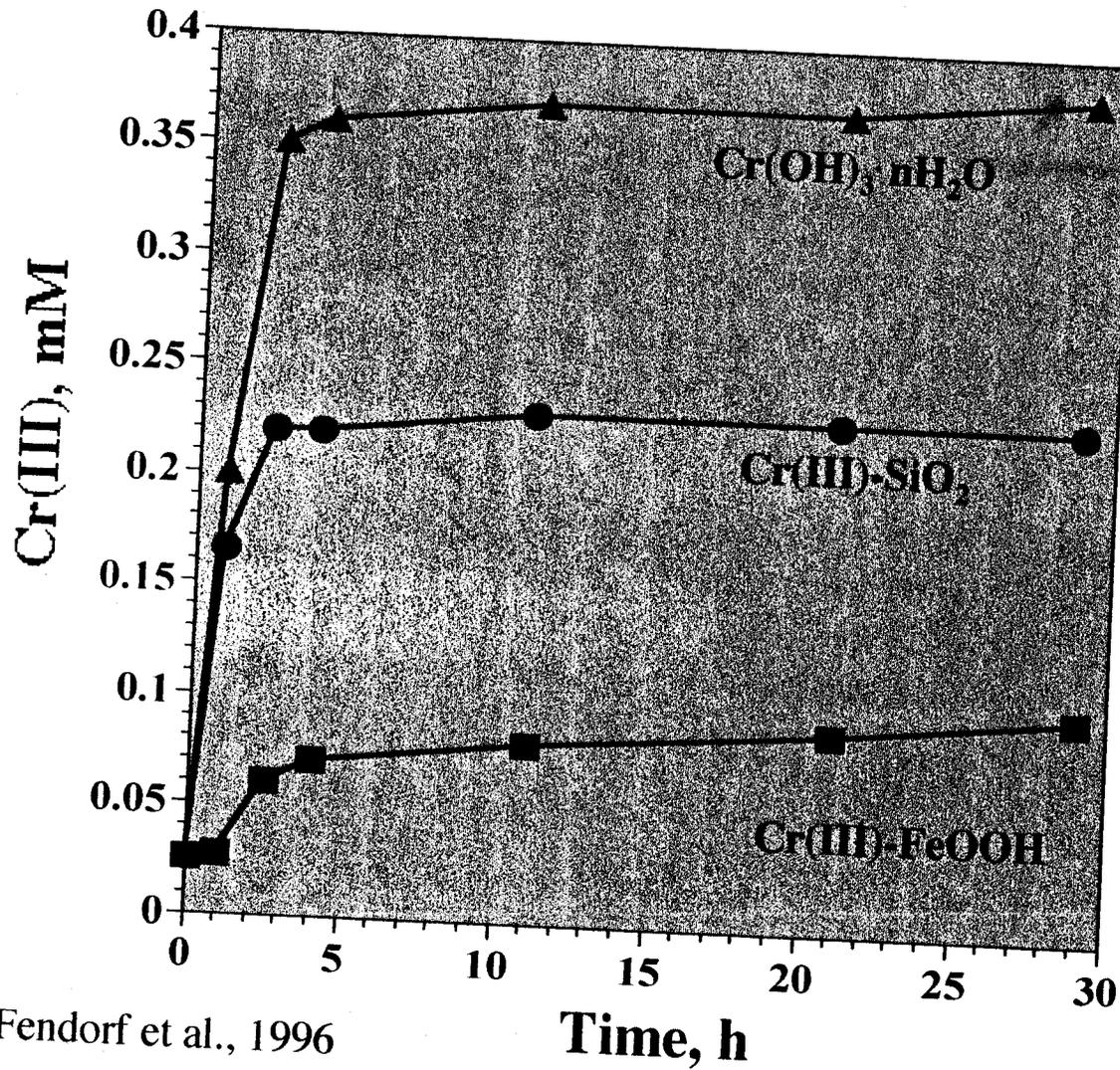
0.4

0.6

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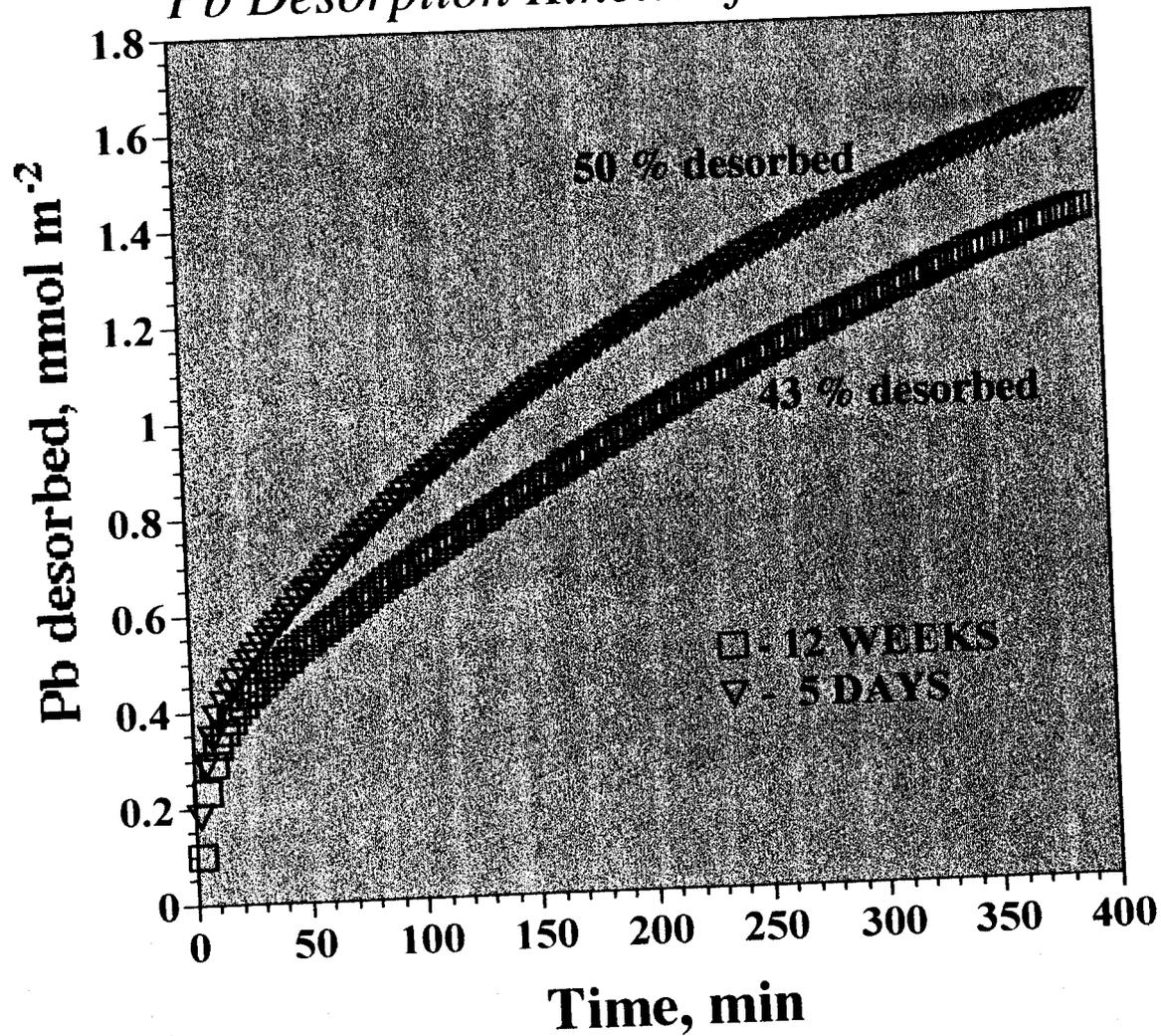
μm





From Fendorf et al., 1996

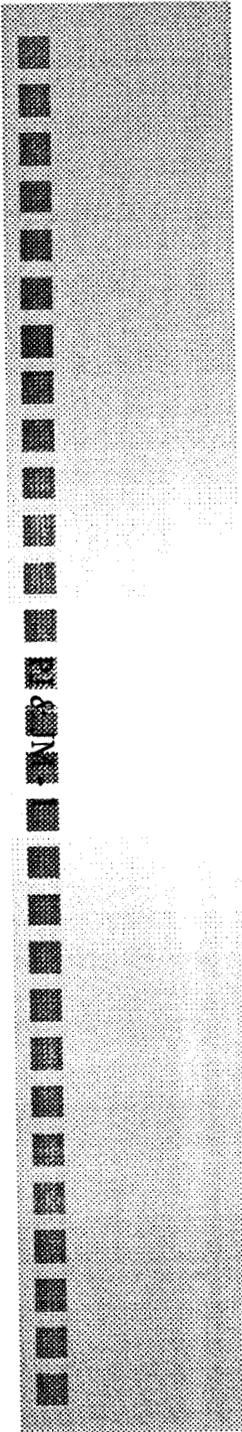
# *Pb Desorption Kinetics from Goethite*



# Summary

- Adsorption/Desorption reactions are dependent on many chemical and physical factors
- Research has primarily focused on the adsorption reaction
- Desorption reactions will control solution concentrations of trace elements

- Recent evidence has demonstrated residence time effects in pure systems
- Residence time effects should be more pronounced in natural systems
- Better predictions of the fate/mobility of contaminants in the subsurface
- Development of sound and cost-effective remediation strategies

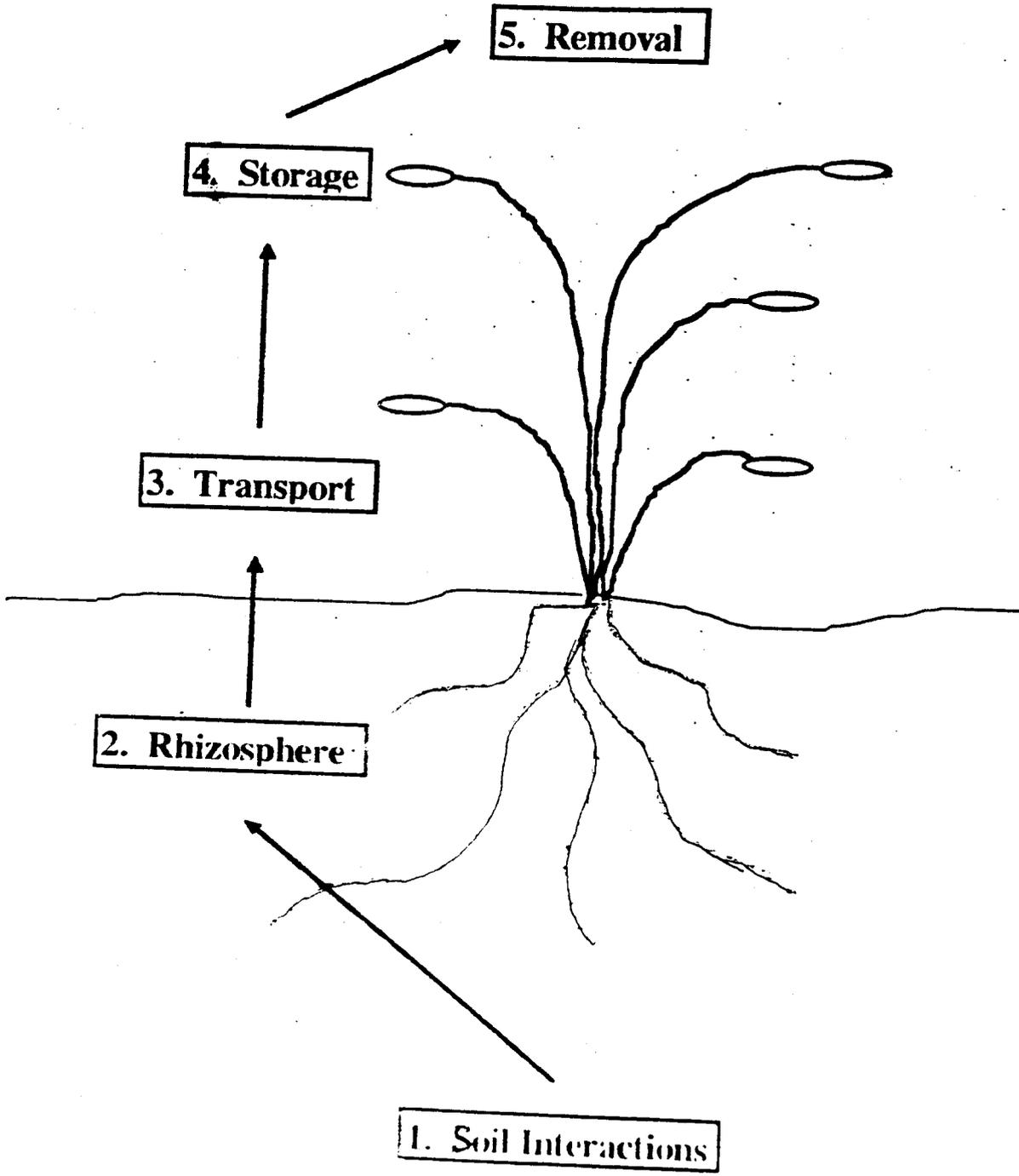


PHYTOREMEDIATION:  
POTENTIAL AND DEFICIENCIES  
FOR THE CLEAN-UP OF METAL  
CONTAMINATED SOILS.

Paul R. Grossl and Joan E. McLean  
UTAH STATE UNIVERSITY

# PHYTOREMEDIATION

- Use of plants to remove (extract) metals from soils.
  - ◆ Metal hyperaccumulating plants
- Use of plants to stabilize metal contaminated soils.
  - ◆ Reduce metal mobilization by preventing wind and water erosion



Phyto-extraction

PJ&JM-3

Element	Low	Normal	High	Hyperaccumulators	
Fe	10.00	60.0	600	2,500*	
Mn	5.00	20.0	400	2,000	10,000 - 50,000
Zn	5.00	20.0	400	2,000	10,000 - 50,000
Cd	0.03	0.1	3	20	100 - 3,000
Pb	0.01	0.1	5	100	1,000 - 8,000
Ni	0.20	1.0	10	100	1,000 - 40,000
Co	0.05	0.2	5	50	1,000 - 10,000
Cr	0.05	0.2	5	50	1,000 - 2,500
Cu	1.00	5.0	25	100	1,000 - 12,500
Se	0.01	0.1	1	10	100 - 6,000

\* Iron levels in a few species can be up to 35,000 mg/kg.

Table 1. Normal and abnormal concentrations of elements in plant leaves (mg/kg).

Metal uptake by hyperaccumulators.

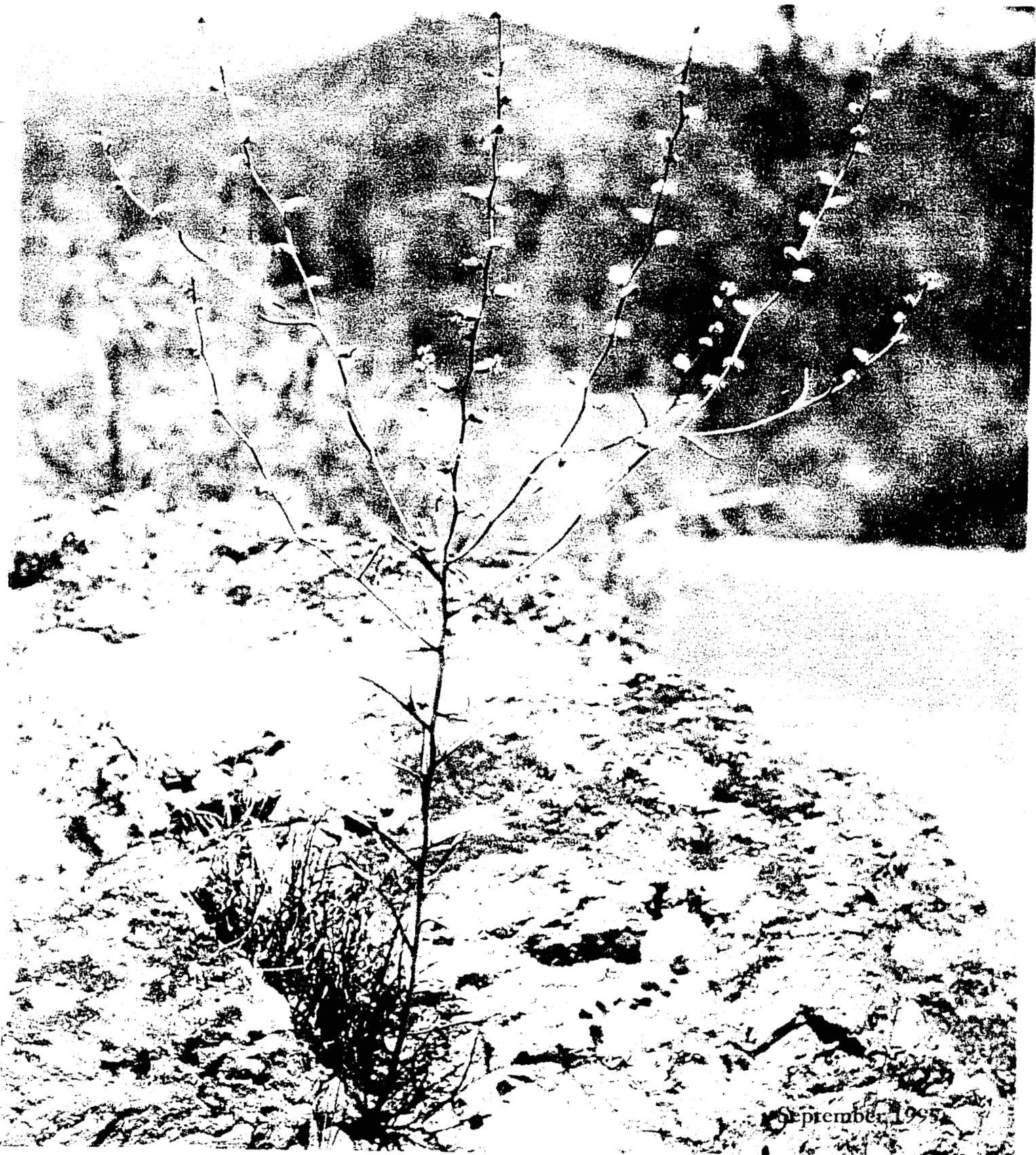
Reeves, R. D., A. J. M. Baker, and R. R. Brooks  
 1995. Abnormal accumulation of trace metals by plants.  
 Mining Environmental Management 3:4-8/



Clockwise from top left:

*Thlaspi caerulescens* found in Western Europe is a zinc accumulator; it can also hyperaccumulate nickel (A.J.M. Baker). *Alyssum bertolonii*, the first plant recognised as a hyperaccumulator of nickel, at Monte Ferrato, near Florence, Italy (R.D. Reeves). *Justicia lanstyakii* is distributed sporadically through much of South America. Specimens collected from ultramafic soils near Niquelândia, Goiás State, Brazil, contain nickel at concentrations of 1,700-2,700 mg/kg (R.D. Reeves). *Euphorbia heli-næ*, a newly-discovered nickel hyperaccumulator from Cuba (A.J.M. Baker).

Hyperaccumulators, from Reeves, Baker, and Brooks, 1995.  
Mining Environmental Management 3:4-8.



*Streptanthus Polygaloides*

Cover of Mining Environmental Management 1995, vol. 3

PJ&JM-6

# *STREPTANTHUS POLYGALOIDES*

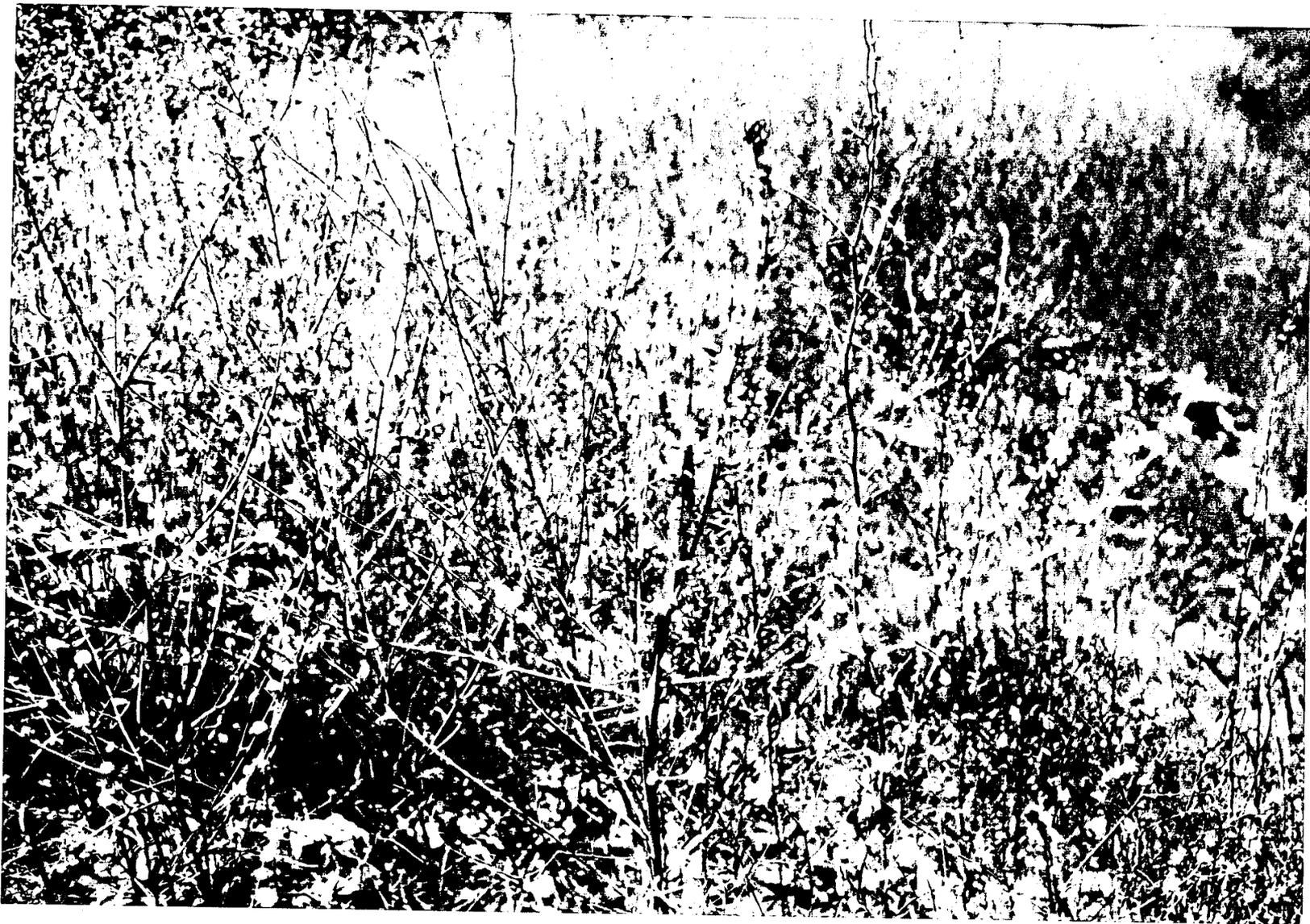
- US BUREAU OF MINES STUDY
  - ◆ Larry Nicks and Mike Chambers
- RED HILLS, CALIFORNIA



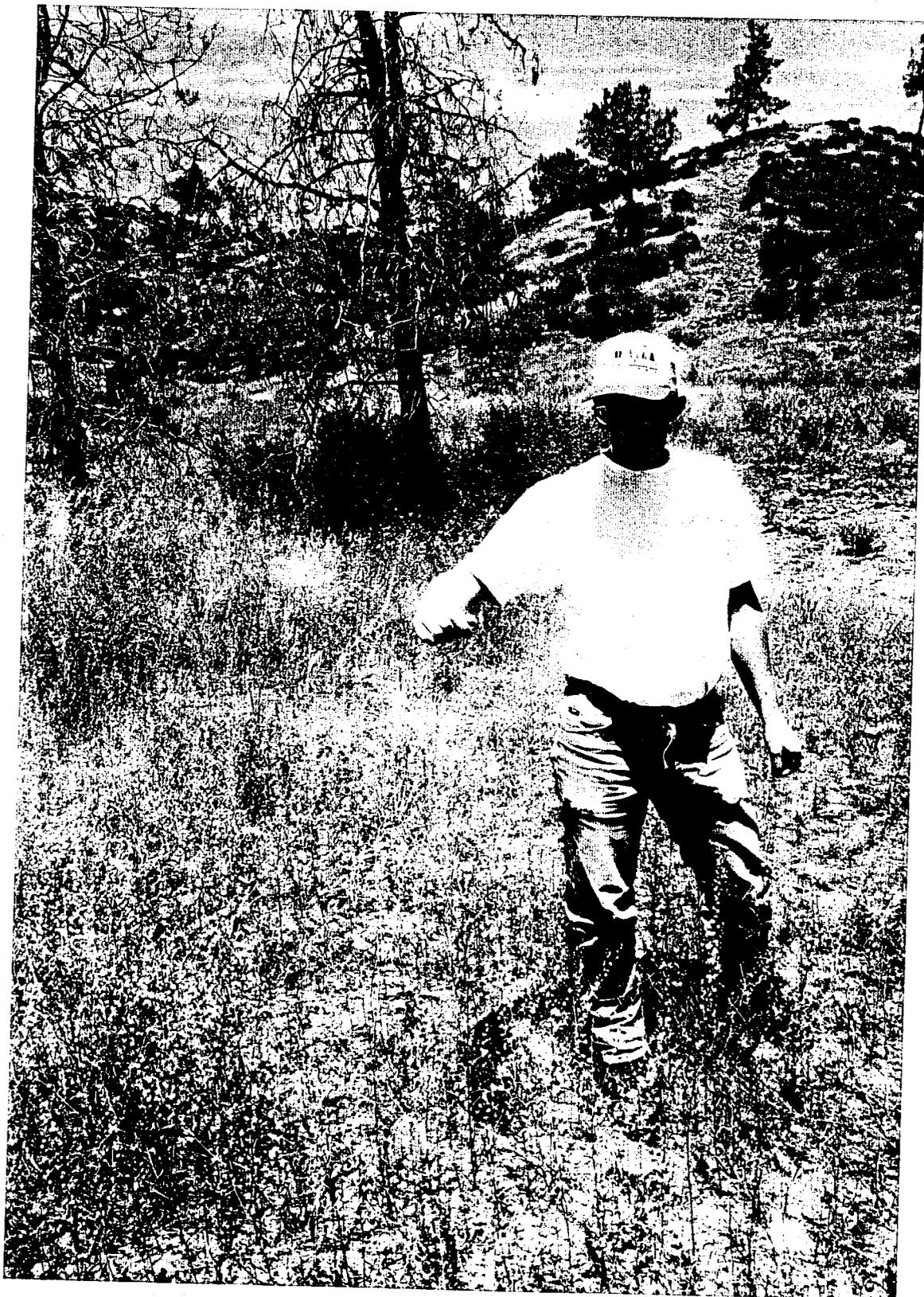
Figure 1. Ultramafic outcrops in California and Oregon.

Field Site: Streptanthus Study  
L. J. Nicks and M. F. Chambers, 1995.  
Farming for metals. Mining Environmental Management 3:15-18.

PJ&JM-9



Streptanthus at field site



Streptanthus - height - 2-4'

PJ&JM-10

# SERPENTINE SOILS

- pH ~ 7.0
- TOTAL METALS (ACID EXTRACT)
  - ◆ 6.2 % Fe, 8100 ppm Cr, 3000 ppm Ni, 150 ppm Co, 110 ppm Zn
- PLANT AVAILABLE METALS (DTPA EXTRACT)
  - ◆ 9 ppm Fe, Cr (non-detectable), 35 ppm Ni, 1.5 ppm Zn

# RED HILLS SITE FIELD DATA

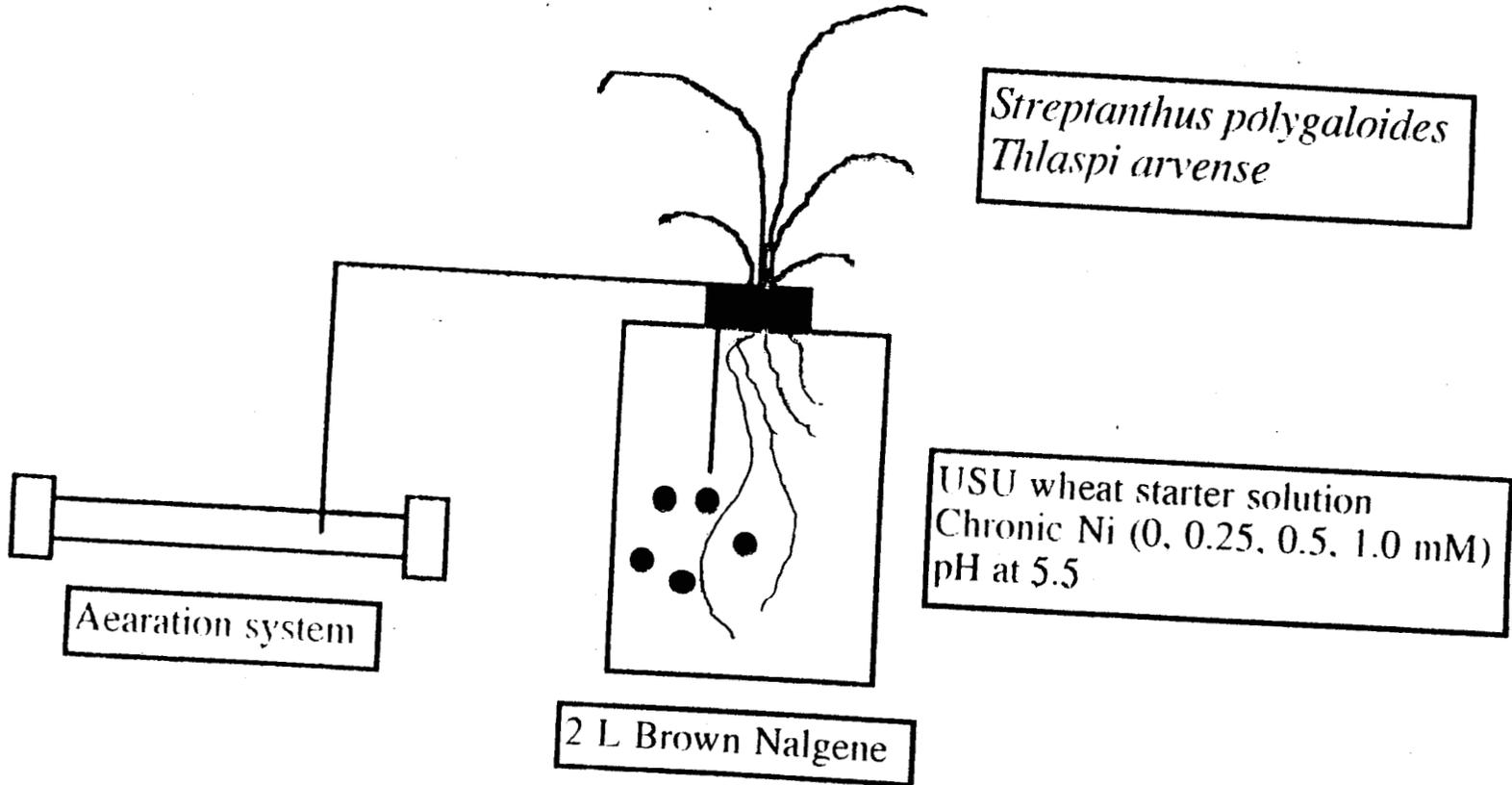
## ■ *STREPTANTHUS*

- ◆ Yield ~ 500 g/m<sup>2</sup>
  - ◆ Ni uptake ~ 2200 - 5300 ppm
- Removal (bio-mining) of 50-100 lbs  
Ni/acre/year

# HYDROPONIC METAL TOLERANCE STUDY

- Determine maximum metal levels that *Streptanthus* can tolerate.
  - ◆ Metal treatments (Ni, Co, Cr, Pb, Cd, Zn, Cu)
  - ◆ Treatment levels (100 TO 20,000 micromolar)

# HYDROPONIC SYSTEM



PJ&JM-14

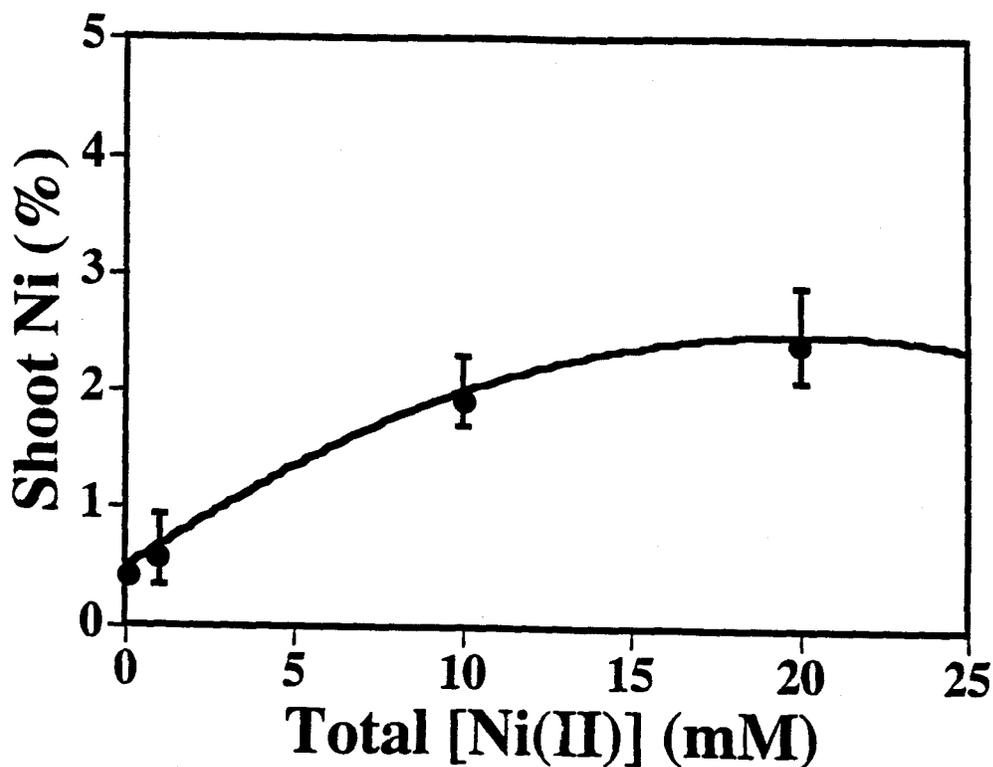
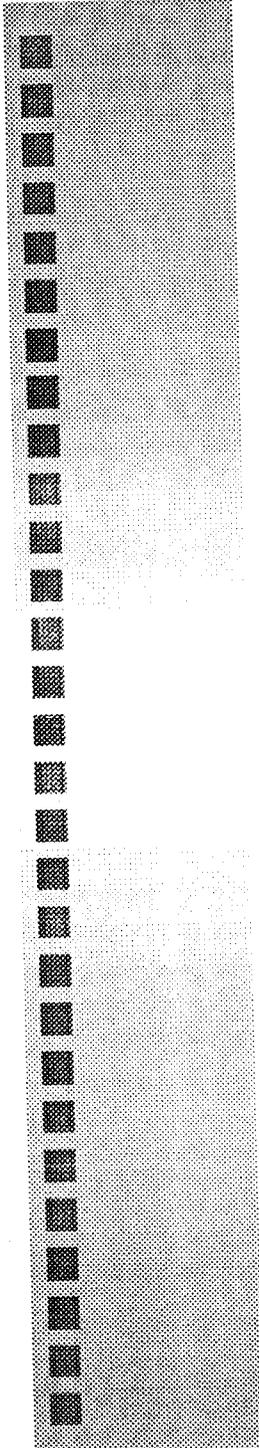


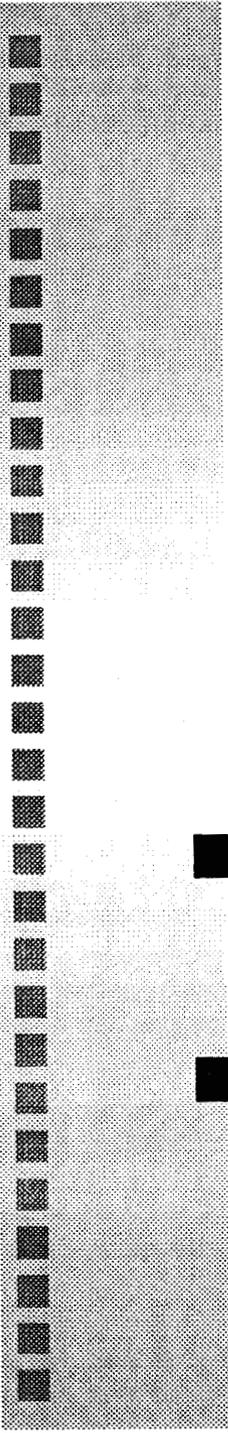
Fig.1. Plot of Ni accumulated in dry shoot tissue (%) as a function of initial Ni concentrations added to hydroponic nutrient solutions.

Table 1. Tolerance and accumulation levels of metals in *Streptanthus polygaloides*.

<u>Metals</u>	<u>Tolerance levels (mM)</u>	<u>Maximum Accum.(ppm)</u>
Ni	10	25,000
Co	1	3,000
Zn	1	4,000
Cr	<1	4,000 ?
Pb	<1	<100
Cu	<0.5	1,000 ?
Cd	<0.5	<100



Plants can only obtain maximum metal accumulation levels if adequate metal levels are present in the soil solution.

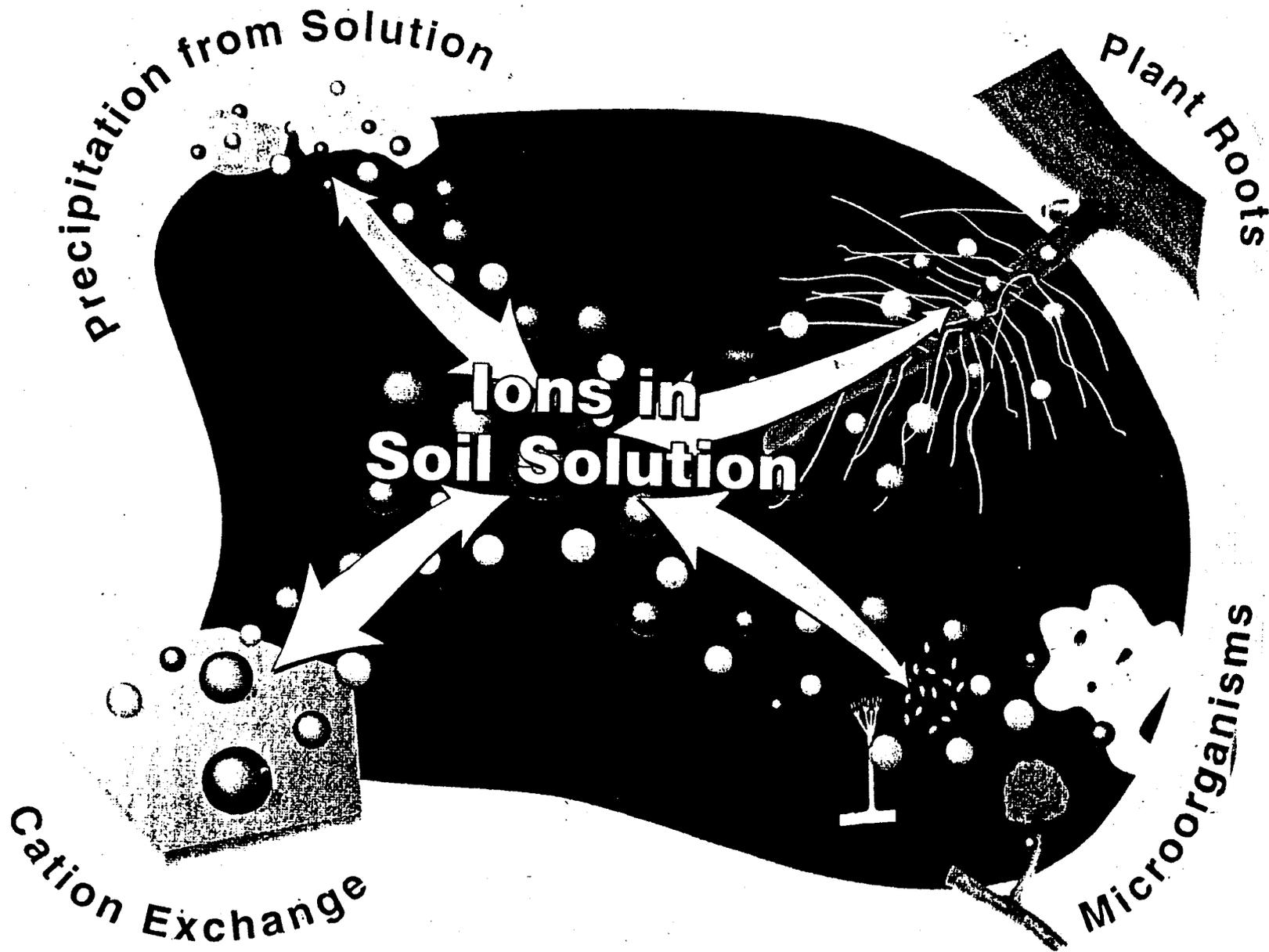


What Ni activity must be present in the soil solution for *Streptanthus* to reach a Ni accumulation level of 2 to 2.5%.

- Assume 400 to 500 kg of water are transpired to produce 1 kg of dry biomass.
- The Ni activity of the soil solution must be about 1mM to accumulate ~ 2 % Ni.

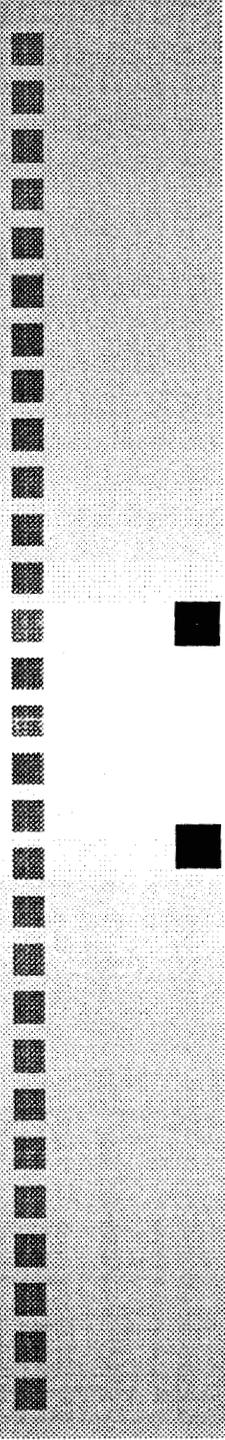
Most soils control Ni at solution levels of 0.1 mM and less. Rhizosphere will need to be manipulated to increase Ni solubility.

- Reducing pH
- Stimulating root exudate production
- Adding chelates (???)



From: Pollution Science 1996  
Ed. I. Pepper, C. P. Gerba, M. L. Brusseau  
Academic Press, NY Fig. 6-3. p. 69

If metals are not bioavailable,  
is it necessary to clean-up  
soil?



# Hydroponic study: Continuous Ni Exposure

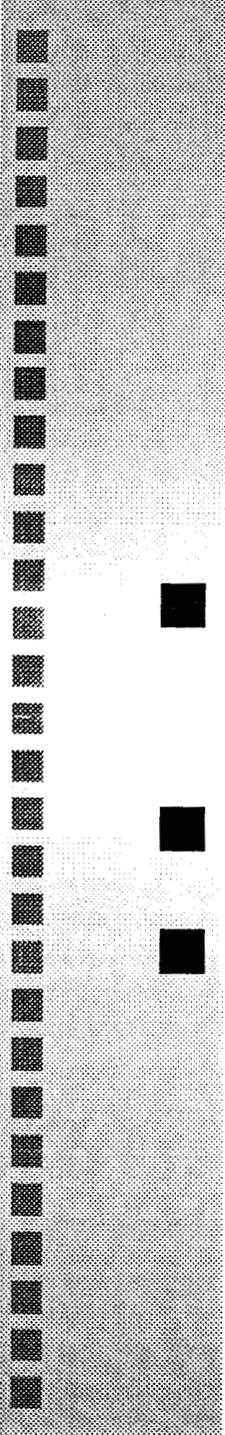
- *Streptanthus* was able to accumulate 0.84% Ni at a solution concentration of 0.25mM.
- Above 0.25 mM *Streptanthus* accumulated > 1 % Ni, however, plants showed signs of Ni toxicity.



Streptanthus in hydroponic solutions with Ni

PJ&JM-23





# Soil study: Ni removal by *Streptanthus*

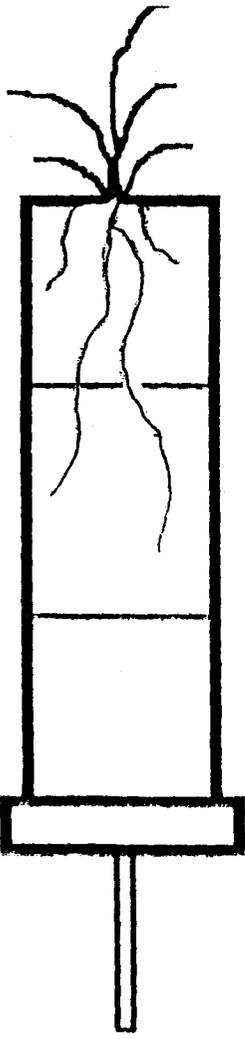
- Ni contaminated calcareous soil (3000 ppm)
- Serpentine soil
- Optimum management

# GREENHOUSE SYSTEM

Top 7" layer:  
Calcareous w/ Ni or Serpentine

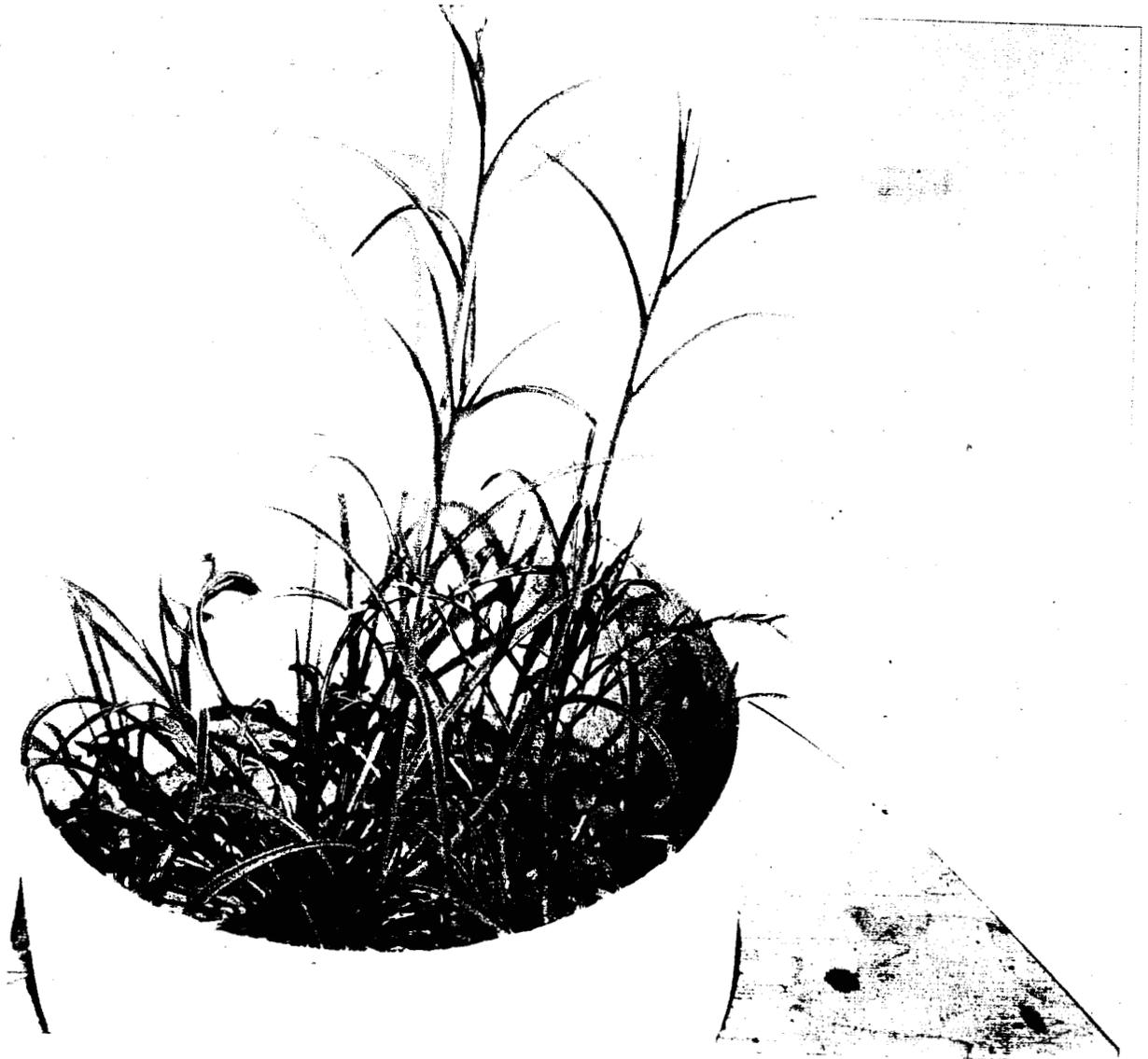
Middle 7" layer:  
Calcareous

Bottom 7" layer:  
Calcareous



*Streptanthus polygaloides*  
Alfalfa

Drainage

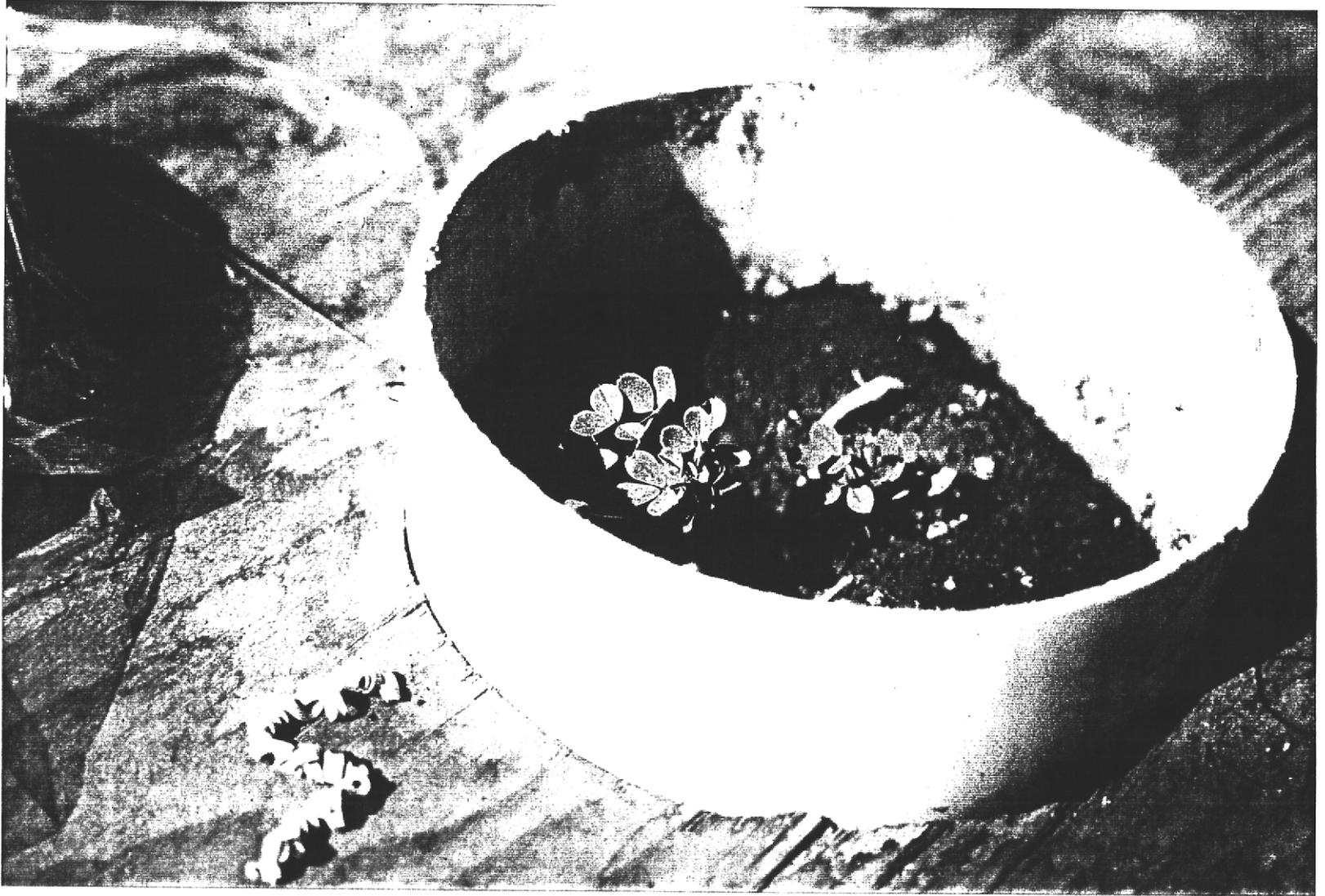


Streptanthus growing in Ni-contaminated Serpentine soil

PJ&JM-27



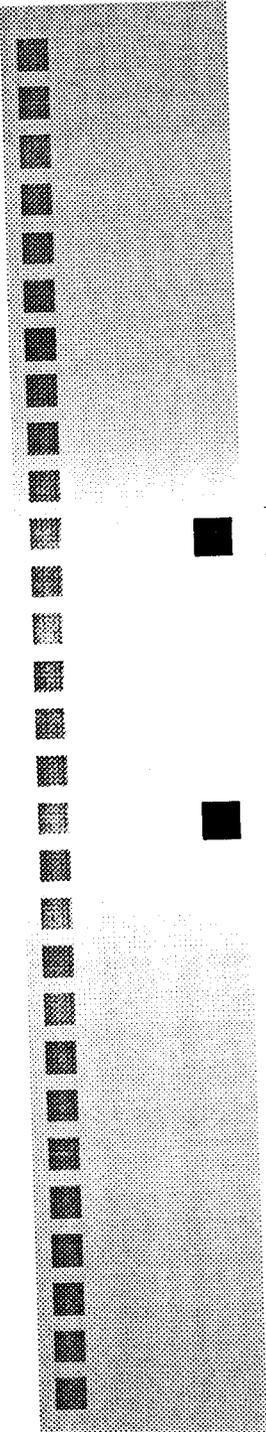
Alfalfa in uncontaminated soil



Alfalfa in serpentine soil severely stunted

# Soil Study: Results

- *Streptanthus* can remove 75 kg/ha Ni (34 ppm) per growing season from a contaminated calcareous soil.
- *Streptanthus* can remove 28 kg/ha Ni (12 ppm) per growing season from a serpentine soil.



Nickel in contaminated calcareous soil is more bioavailable than Ni in serpentine soil.

- Bioavailable Ni in serpentine soils is weakly bound Ni desorbed from organic matter and Fe-oxide surfaces.
- Bioavailable Ni in calcareous soils is exchangeable Ni and possibly controlled by the solubility of Ni hydroxide solids.

Use of *Streptanthus* in removal of metals is limited.

- ◆ Time ?
- ◆ Management ?
- Stabilization and bio-mining are more feasible options.

# Abandoned Mine Site Survey

- 10,000 - 20,000 abandoned mines in Utah
- Pacific Gulch Mine
  - ◆ Vegetation
  - ◆ Water
  - ◆ Soils and Sediments

PJ&JM-33



Pacific Gulch Mine

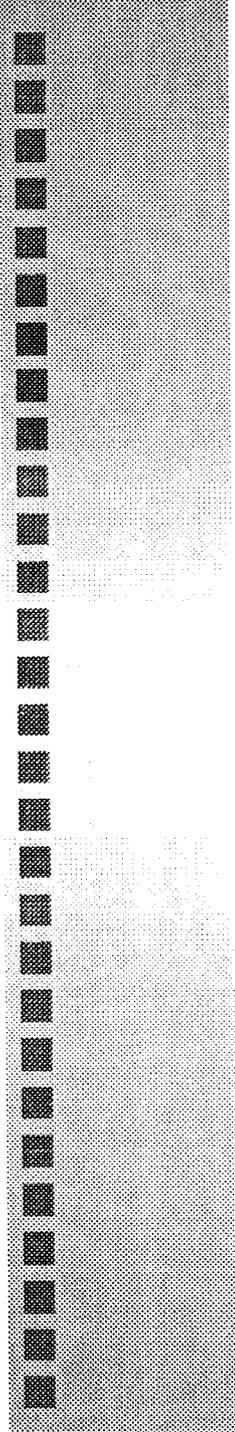
PJ&JM-34



Pacific Gulch Mine - looking toward American Fork River and prime trout habitat

# Tailings Metal Data (Total)

- Cd - 28 ppm
- Cu - 154 ppm
- Pb - 7300 ppm
- Zn - 3700 ppm



# Water birch (*Betula occidentalis*)

- metal tolerant

- ◆ accumulated 900 ppm Pb

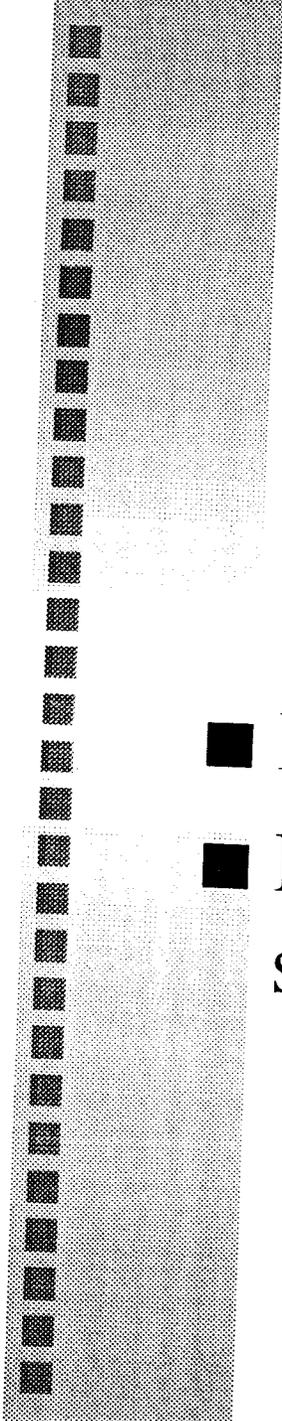
- ◆ potential for soil stabilization

- ◆ hydraulic control

PJ&JM-37



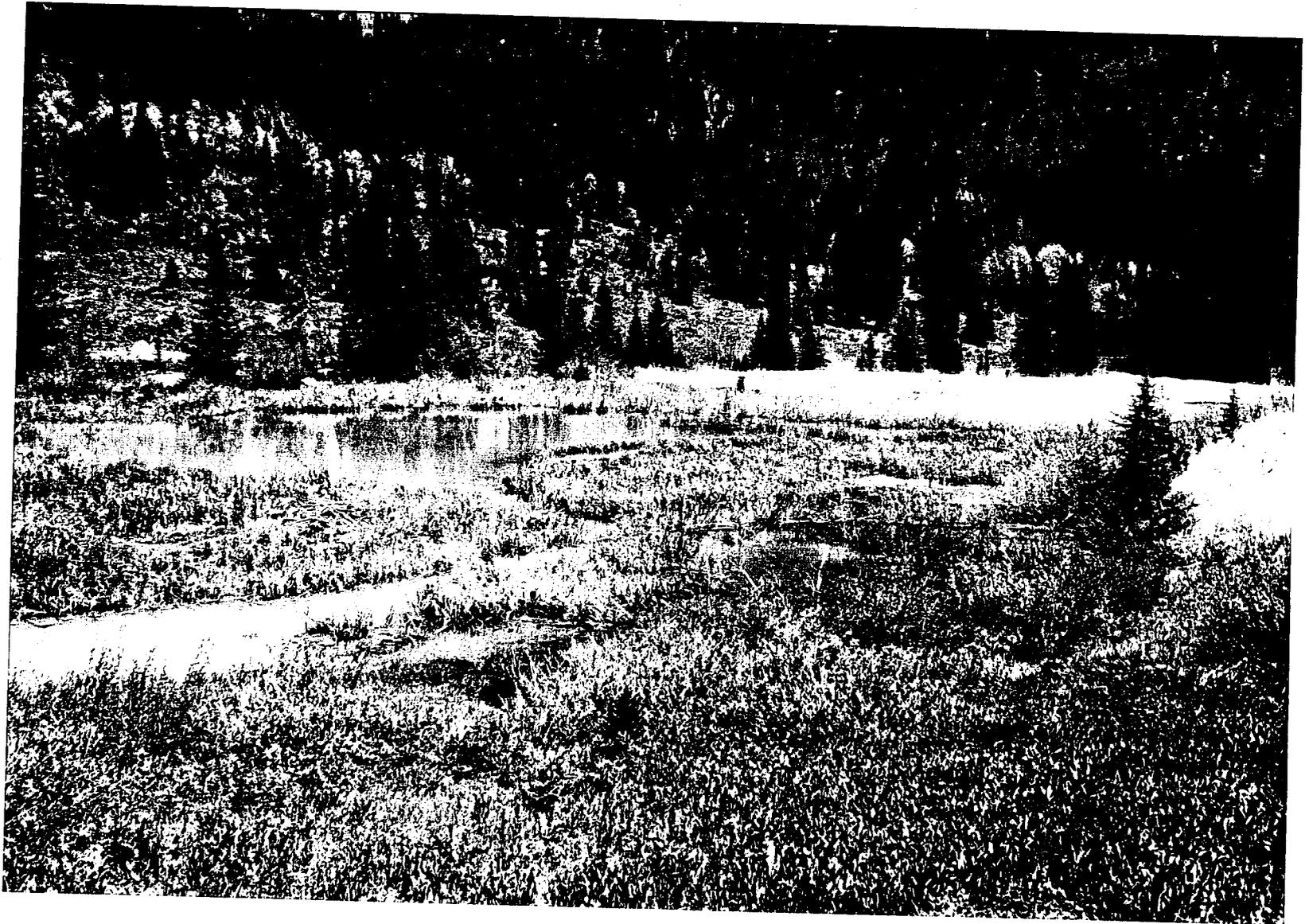
Water birch growing at site



Microbial populations are 10 to 100 X greater in the rhizosphere than in the bulk soil.

- Roots provide food for microbes.
- Roots exude organic acids, sugars and other soluble plant components.

PJ&JM-39

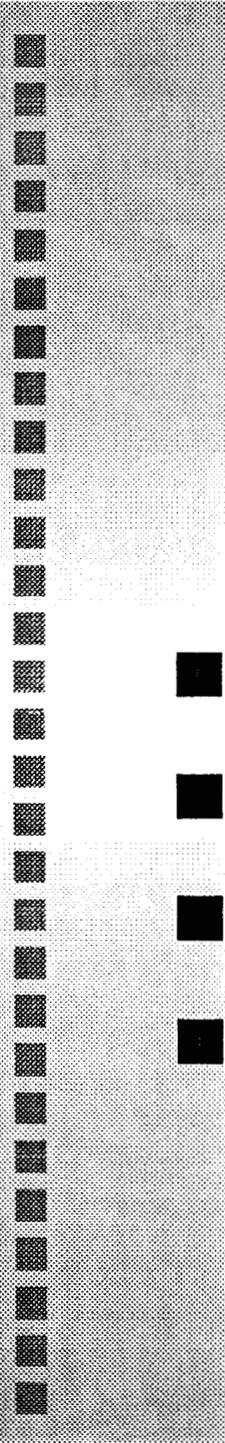


Beaver Pond - Natural Wetland

# Beaver Pond Metal Data

<i>Metal</i>	<i>Water (ppb)</i>	<i>Solids (ppm)</i>
<i>Cd</i>	10.5	25
<i>Cu</i>	7.2	1600
<i>Pb</i>	<160	2600
<i>Zn</i>	1110	19,000

---



Sediments in pond act as a sink for metals. Need a better understanding of the following :

- phases controlling metal bioavailability
- saturation level
- pH effects
- redox effects

# CONCLUSIONS

- Use of hyperaccumulating plants to remove metals is limited.
  - restricted by time, management, and metal bioavailability
- Use of metal tolerant plant species to stabilize soils has potential.
  - ◆ prevent erosion losses
  - ◆ hydraulic control ?
  - ◆ enhanced metal immobilization in rhizosphere?
- Wetland systems provide a sink for metals.
  - ◆ need to understand metal interactions at the water/sediment interface to assess potential of natural attenuation

# MICROBIAL MOBILIZATION AND STABILIZATION OF RADIONUCLIDES AND TOXIC METALS

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Department of Applied Science  
Brookhaven National Laboratory, Upton, New York 11973

Contamination of soils, water, and sediments by radionuclides and toxic metals from the disposal of radioactive wastes is a major concern. Unlike organic contaminants, the metals cannot be destroyed, but must either be converted to a stable form or removed. The radionuclides and toxic metals in wastes are present in various forms, such as elemental, oxide, coprecipitates, inorganic, and organic complexes, and naturally occurring minerals. Microorganisms play a major role in the transformation of radionuclides and toxic metals in the subsurface environments. These include (i) oxidation-reduction reactions; (ii) changes in pH and Eh; (iii) chelation or production of specific sequestering agents; (iv) biosorption by biomass and biopolymers; and (v) biodegradation of radionuclide-organic complexes. Dissolution or immobilization of radionuclides is brought about by the direct and indirect actions of aerobic and anaerobic microorganisms. An understanding of the mechanisms of biotransformation of radionuclides and toxic metals under various microbial process conditions will be useful in developing appropriate remediation and waste management strategies as well as predicting the microbial impacts on the long-term performance of the waste repositories.

Fundamental research on the mechanisms of microbial transformations of radionuclides and toxic metals in the subsurface environments and in wastes has resulted in the development of two treatment processes (i) stabilization of radionuclides and toxic metals and (ii) removal and recovery of radionuclides and toxic metals from contaminated materials, soils, sediments, and wastes.

I. Stabilization of Radionuclides and Volume Reduction of Wastes: Anaerobic microbial treatment of uranium wastes resulted in the removal of a large fraction of soluble non-toxic metals such as Ca, K, Mg, Mn, Na, and Fe; enrichment and stabilization of Cd, Cr, Cu, Ni, Pb, U and Zn; and overall volume and mass reduction. In this novel approach to treatment of wastes, the unique metabolic capabilities of the dual action anaerobic bacteria were exploited to solubilize and/or precipitate radionuclides and toxic metals by direct enzymatic action and indirect action due to production of organic acid metabolites. The non-hazardous materials in the solid phase were solubilized and removed from the waste resulting in volume reduction. The remobilized radionuclides and toxic metals are stabilized by precipitation reactions and redistributed with stable mineralogical fractions of the waste. The radionuclides and toxic metals being in a more stable form are available for recovery, recycling or disposal.

II. Removal and Recovery of Uranium and Toxic Metals from Contaminated Soils and Wastes: Citric acid, a naturally occurring compound, was used to extract metals such as Cd, Co, Cr, Ni, Sr, and Zn and radionuclides Th, and U from depleted uranium wastes by formation of soluble metal-citrate complexes. Citric acid forms mononuclear bidentate, tridentate, or polynuclear complexes with various metal ions. The citric acid extract containing radionuclide/metal was subjected to biodegradation followed by photochemical degradation under aerobic conditions. Several metal citrate complexes were biodegraded, and the metals were recovered in a concentrated form with the bacterial biomass. Uranium, however, forms a binuclear complex with citric acid and was not biodegraded. With exposure to light, the uranyl citrate was photodegraded to a stable oxide ( $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ). This treatment process, unlike others which use caustic reagents, does not generate secondary waste streams, causes little damage to soil, and removes environmentally and economically important metals in a concentrated form for recovery and recycling.

# **Microbial Transformations of Radionuclides and Toxic metals**

- **General Problems, Definitions**
- **Review of Key Microbial Processes**
- **Mechanisms of Transformations by Aerobic and Anaerobic microbes**
- **Application of basic research in Bioremediation of Contaminated Soils and Wastes**
  - I. Stabilization and Volume Reduction**
  - II. Removal and Recovery**

# **Dissolution and Immobilization of Radionuclides**

## ***Direct and Indirect Actions of Aerobic and Anaerobic Microorganisms***

- Oxidation-reduction reactions**
- Changes in pH and Eh**
- Chelation or production of sequestering agents**
- Biosorption by biomass and biopolymers**
- Transport by bacteria as biocolloids**
- Biodegradation of radionuclide-organic complexes**

# MECHANISMS OF ACTION

## *DIRECT ACTION*

- Enzymatic reduction of metals from higher oxidation state to lower oxidation state (*dissolution of Fe or precipitation of U*)

## *INDIRECT ACTION*

- Dissolution due to organic acid metabolites or lowering of pH of medium

# Waste Characterization

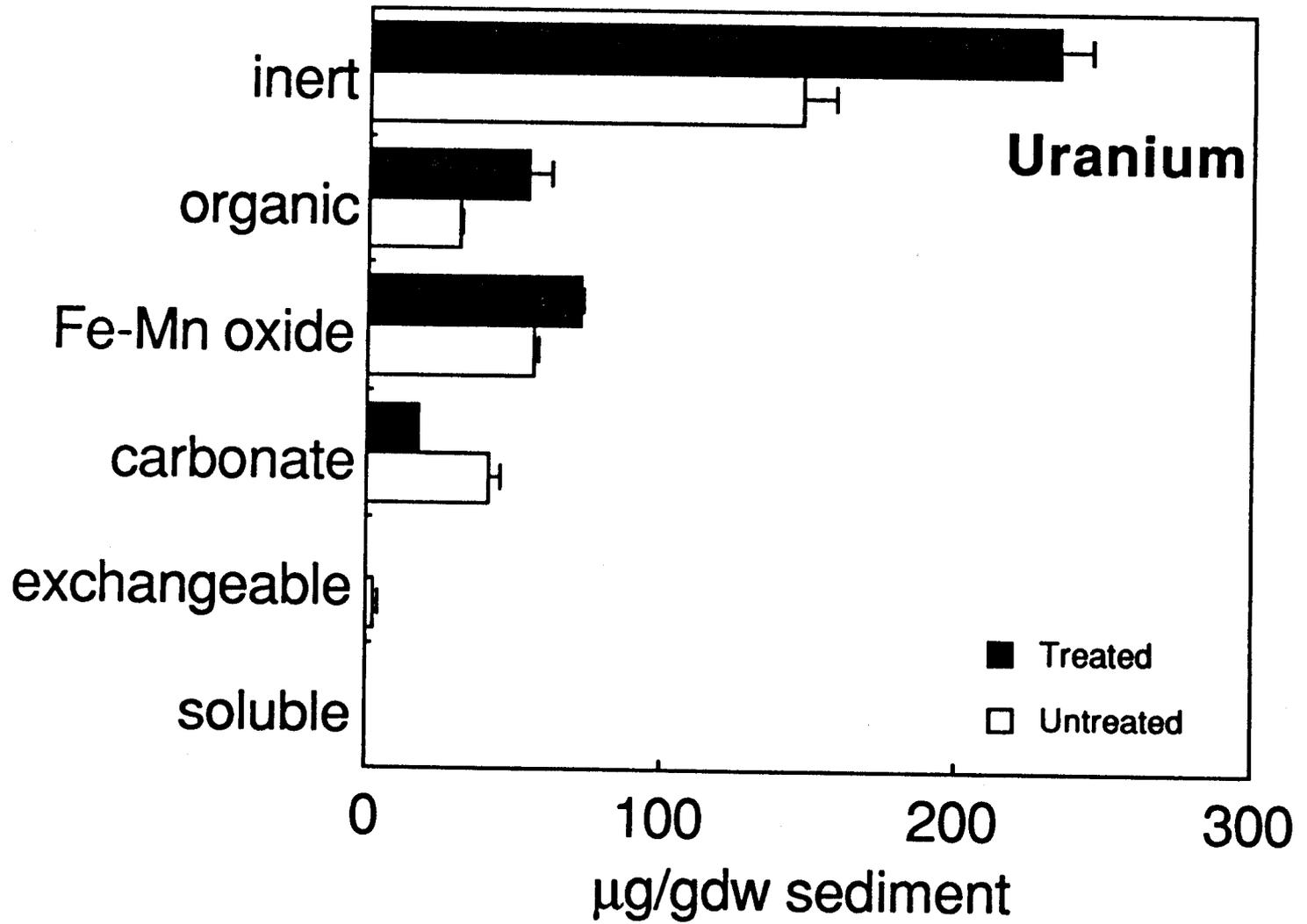
- *Physical*
- *Chemical*
- *Microbiological*

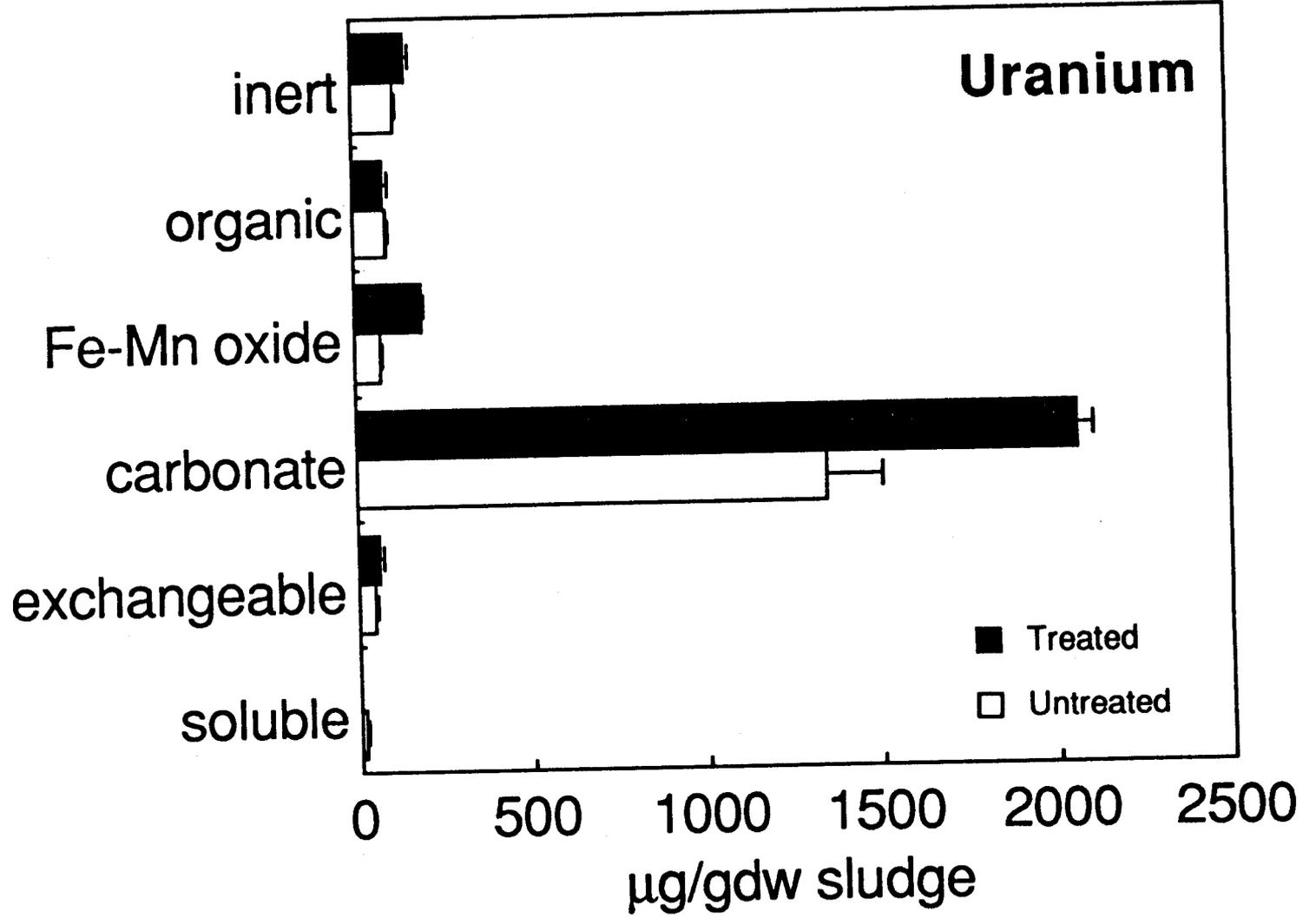
# CHARACTERIZATION OF SLUDGE

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<b>Constituents</b>	<b>Sludge</b>
<b>PHYSICAL, %</b>	
Moisture	63
Ash	59
<b>CHEMICAL, %</b>	
Carbon	1.22
Nitrogen	0.11
Sulfate	2.32
<b>MAJOR METALS, %</b>	
Aluminum	5.26
Calcium	36.4
Iron	0.47
Magnesium	0.99
Potassium	0.05
Sodium	1.87
<b>TRACE METALS, ug/g dry wt</b>	
Arsenic	1.2
Cadmium	80.6
Chromium	450
Cobalt	38.7
Copper	392
Lead	360
Manganese	209
Mercury	9.6
Nickel	1200
Selenium	<1
Uranium	3080
Zinc	703

---





# **Bioremediation of Radionuclides and Toxic Metals in Soils and Wastes**

## **I. Stabilization of Uranium and Toxic Metals in Waste**

*- Anaerobic Microbial Process (patented)*

## **II. Removal and Recovery of Uranium and Toxic Metals from Contaminated Soils and Waste**

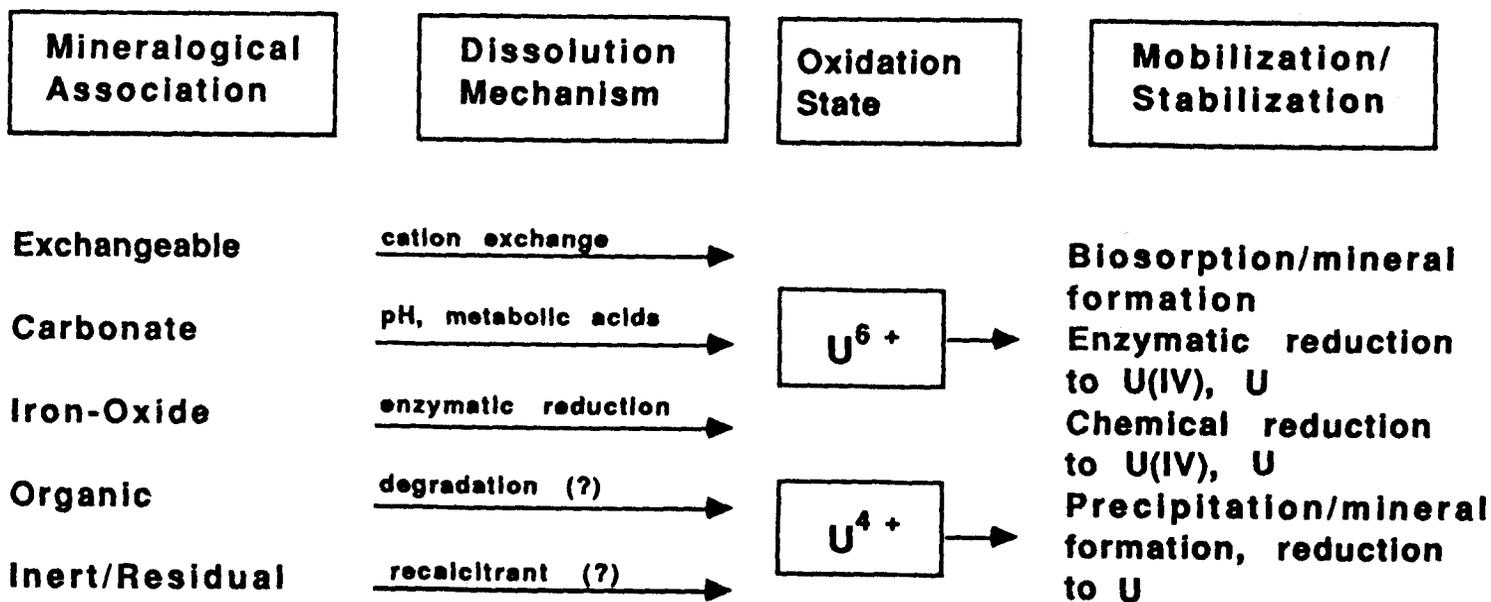
*- Aerobic Microbial/Photochemical Process (patented)*

# **I. STABILIZATION AND MASS REDUCTION OF WASTES CONTAINING URANIUM AND TOXIC METALS**

- *Depleted Uranium Waste from DOE Y-12 plant, Oak Ridge, TN*
- *Anaerobic Microbial Process*
- *Clostridium sp. isolated from Uranium waste*

## ANAEROBIC MICROBIAL TRANSFORMATIONS OF URANIUM IN MIXED WASTES : MECHANISMS OF ACTION

A3F-11



# Anaerobic Microbial Stabilization/ Volume Reduction

**Uranium Waste**

**Anaerobic Bacterial Treatment**  
*(Clostridium sp. plus Carbon and Nitrogen)*

**Solids**

- Stabilization of Al, Cd, Cr, Cu, Ni, Pb, U, Zn
- Enrichment of Metals
- Volume Reduction

**Supernatant**

- Dissolution and Removal of Ca, Fe, K, Mg, Mn, Na

# **ANAEROBIC MICROBIAL STABILIZATION OF URANIUM WASTE**

## ***SUMMARY***

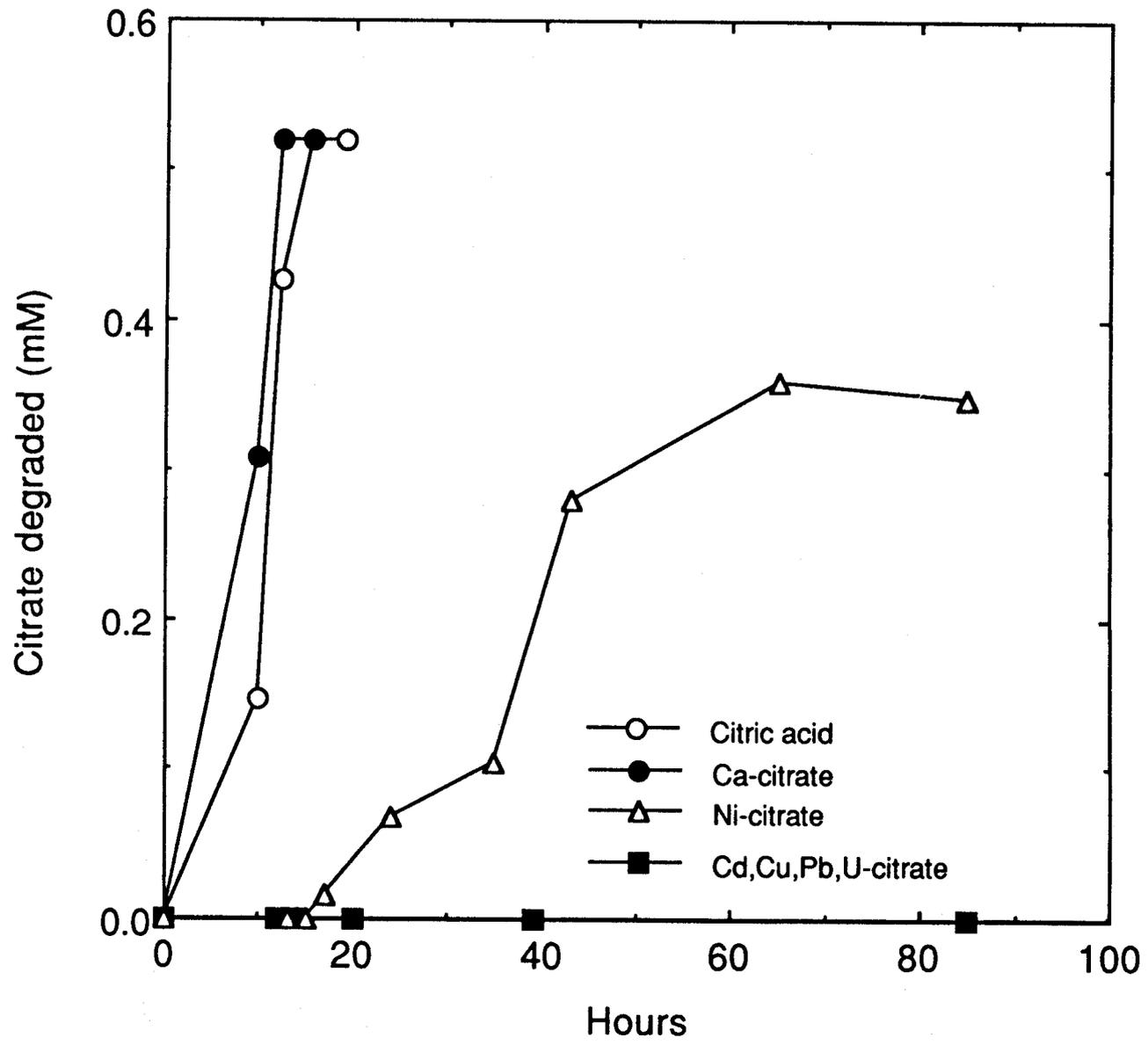
- **Anaerobic microbial treatment resulted in immobilization and enrichment of U, Al, Cd, Cr, Cu, Ni, Pb, and Zn in the waste due to**
  - (i) precipitation,**
  - (ii) biosorption, and**
  - (iii) redistribution with stable mineral phases**
  
- **Dissolution of Ca, Fe, Mg, and Mn resulted in significant volume and mass reduction**

## **II. WASTE SITE RECLAMATION WITH RECOVERY OF RADIONUCLIDES AND METALS**

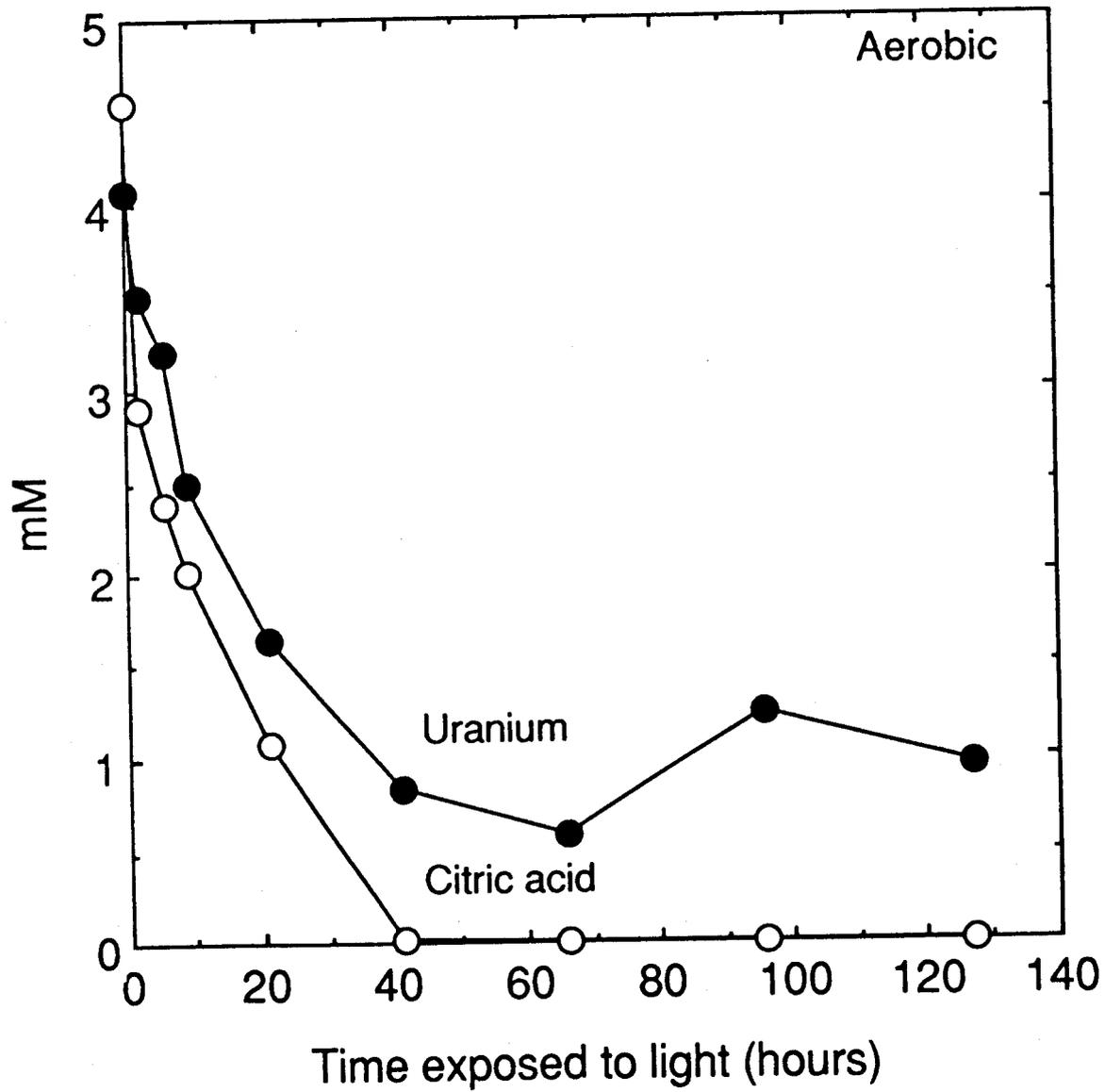
- *Depleted Uranium Waste from DOE Y-12 plant, Oak Ridge, TN***
- *Extraction of Uranium and Metals by Citric acid***
- *Biodegradation of Metal citrate Complexes by *Pseudomonas fluorescens* isolated from waste***
- *Photochemical Degradation of Uranium citrate***

# Degradation of 1:1 Metal Citrate Complexes

AJF-15



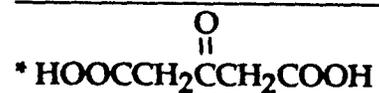
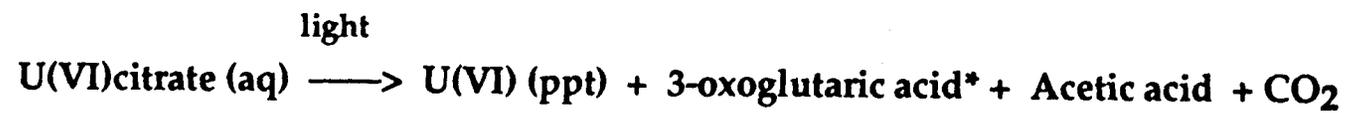
# Photodegradation of 1:1 Uranium Citrate Complex



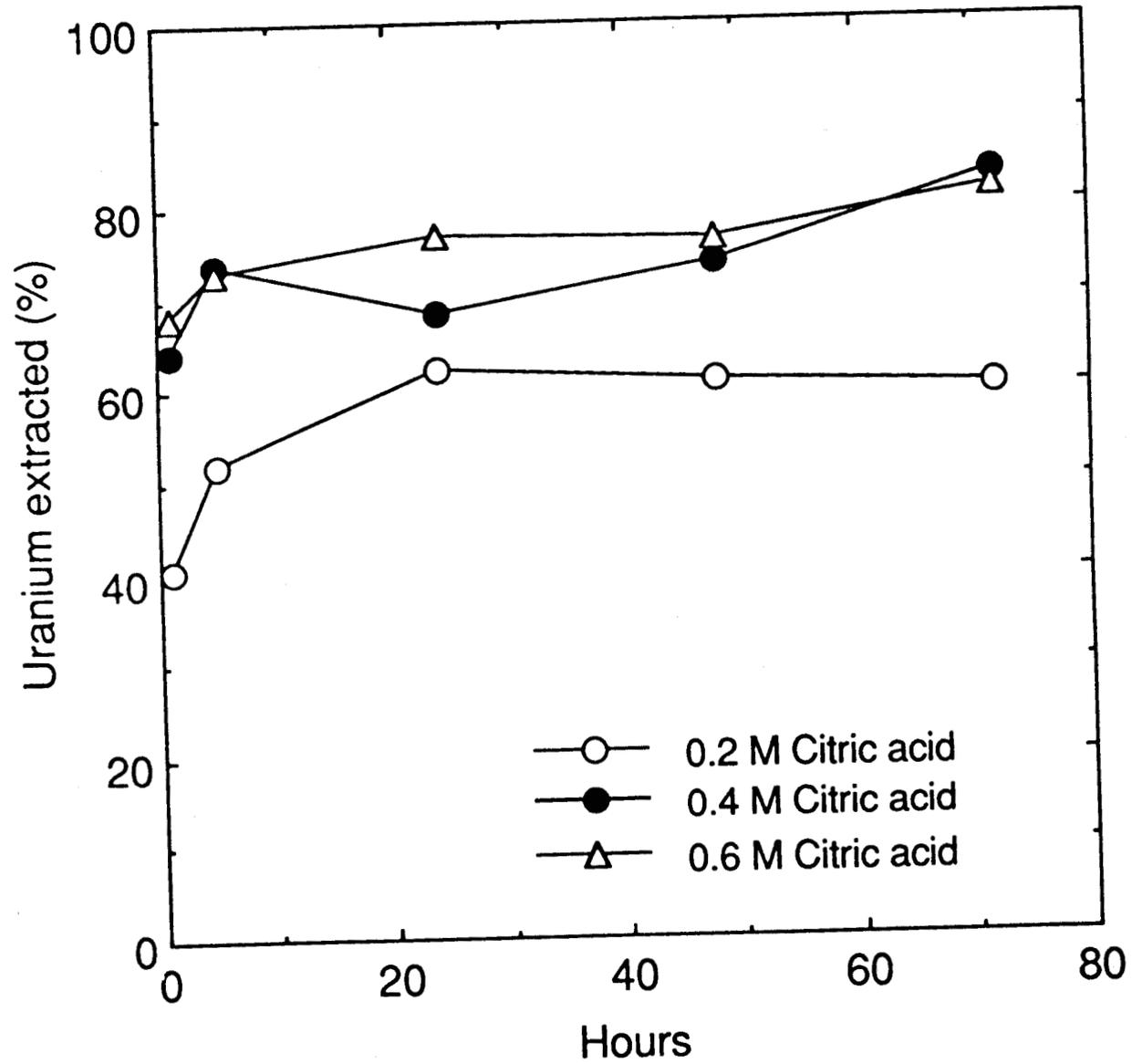
AJF-16

# PHOTOCHEMICAL DEGRADATION OF URANIUM CITRATE COMPLEX

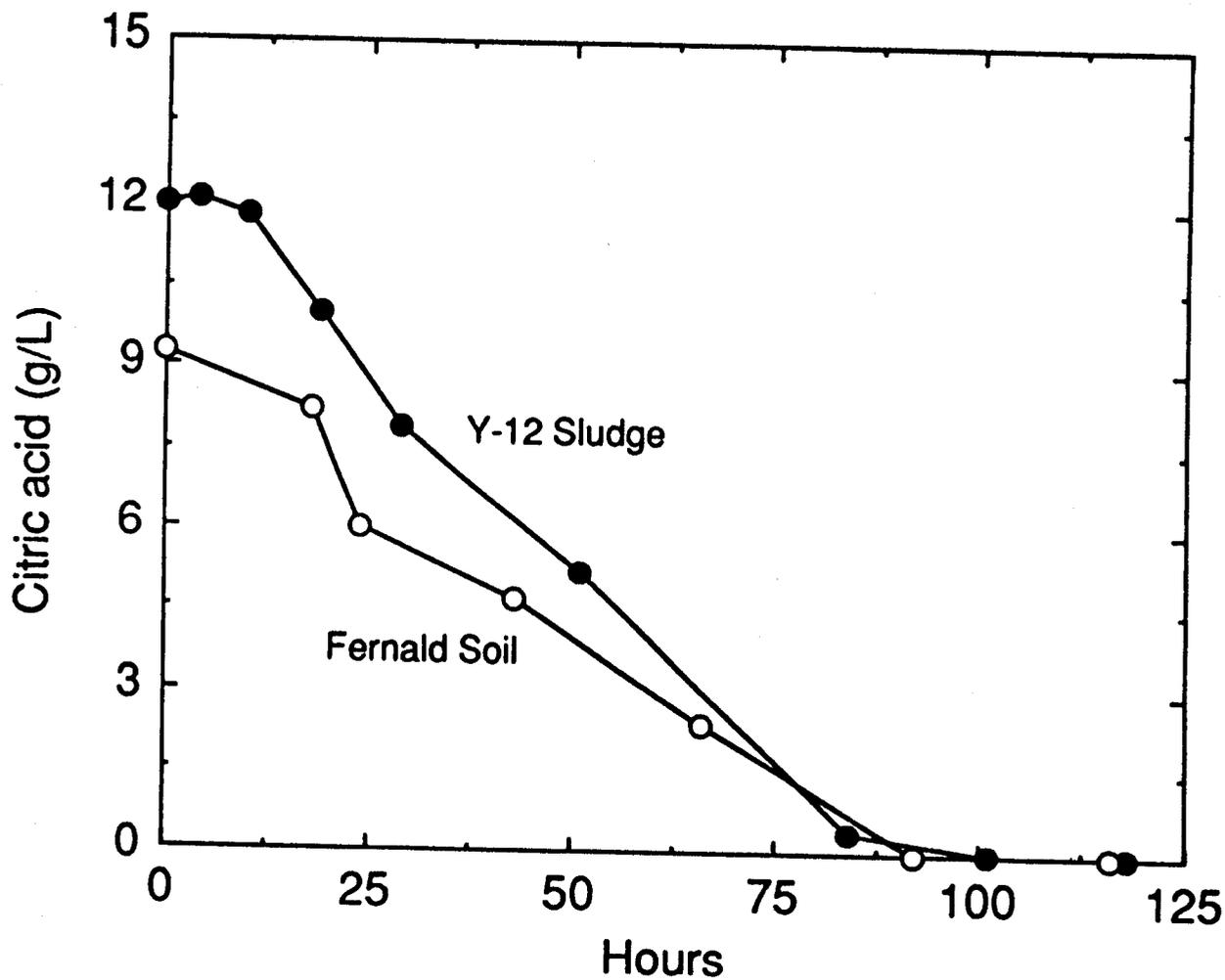
## AEROBIC



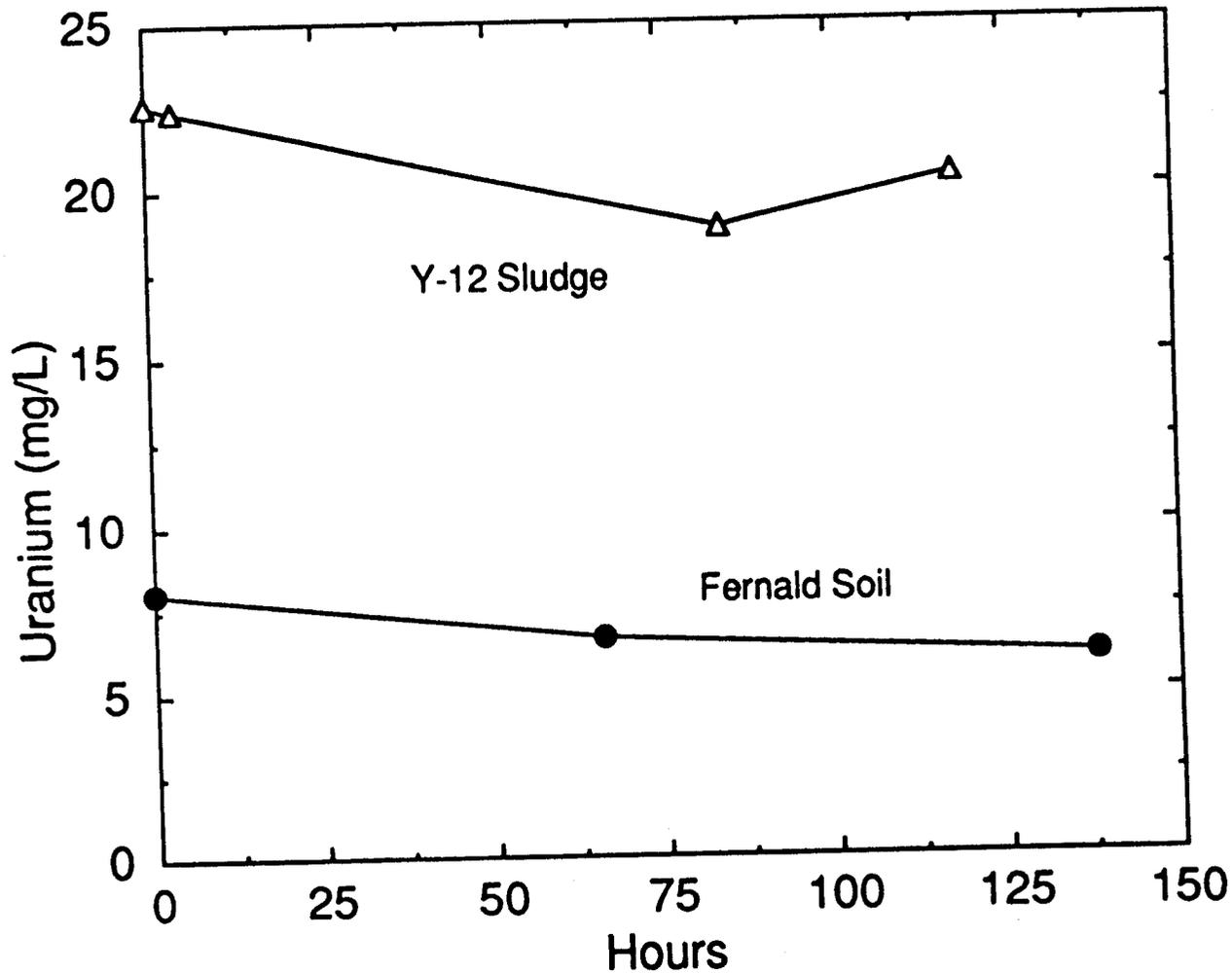
# Extraction of Uranium From Sludge With Citric Acid



# Comparison of Biodegradation of Citric Acid Extracts

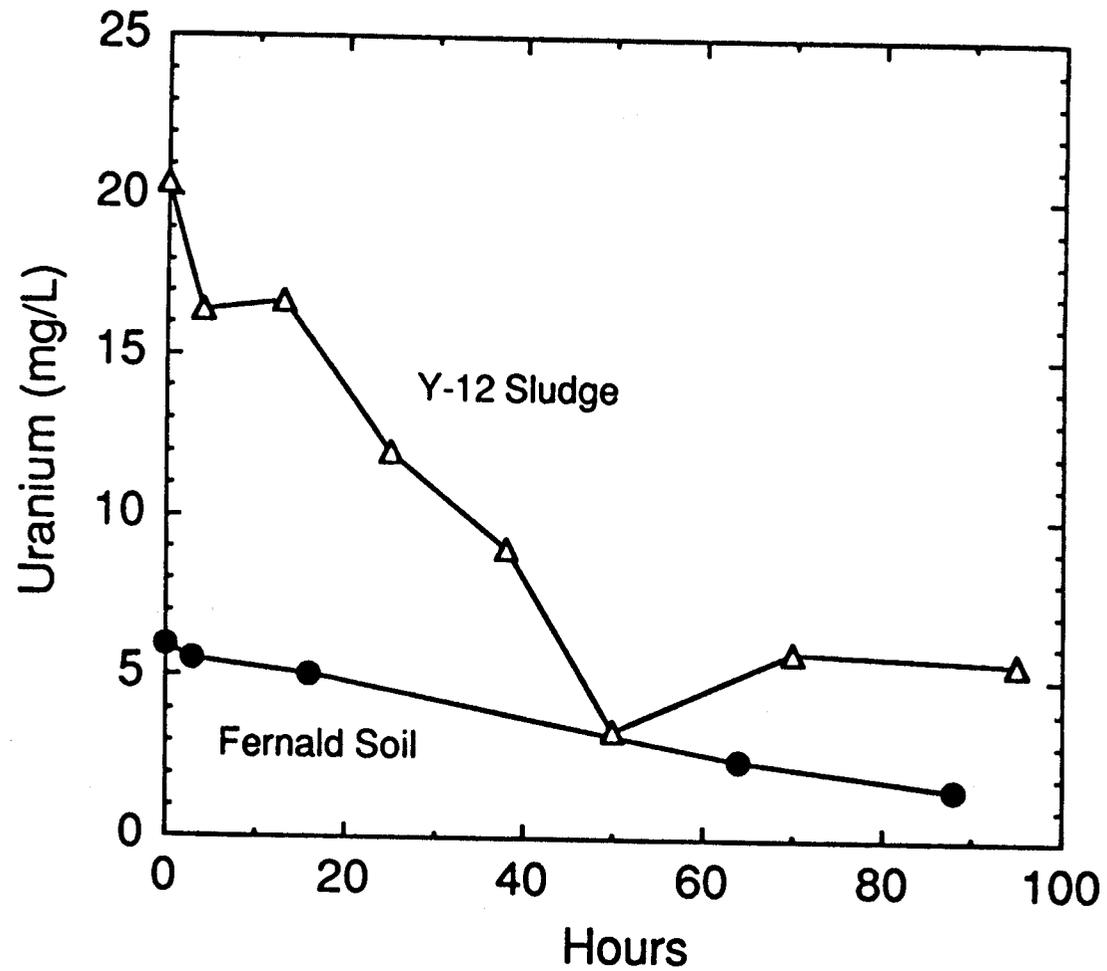


# Uranium Removal During Biodegradation of Citric Acid Extract



[Uranium removal from solution during biodegradation (%):  
Y-12 sludge, 10; Fernald soil, 25].

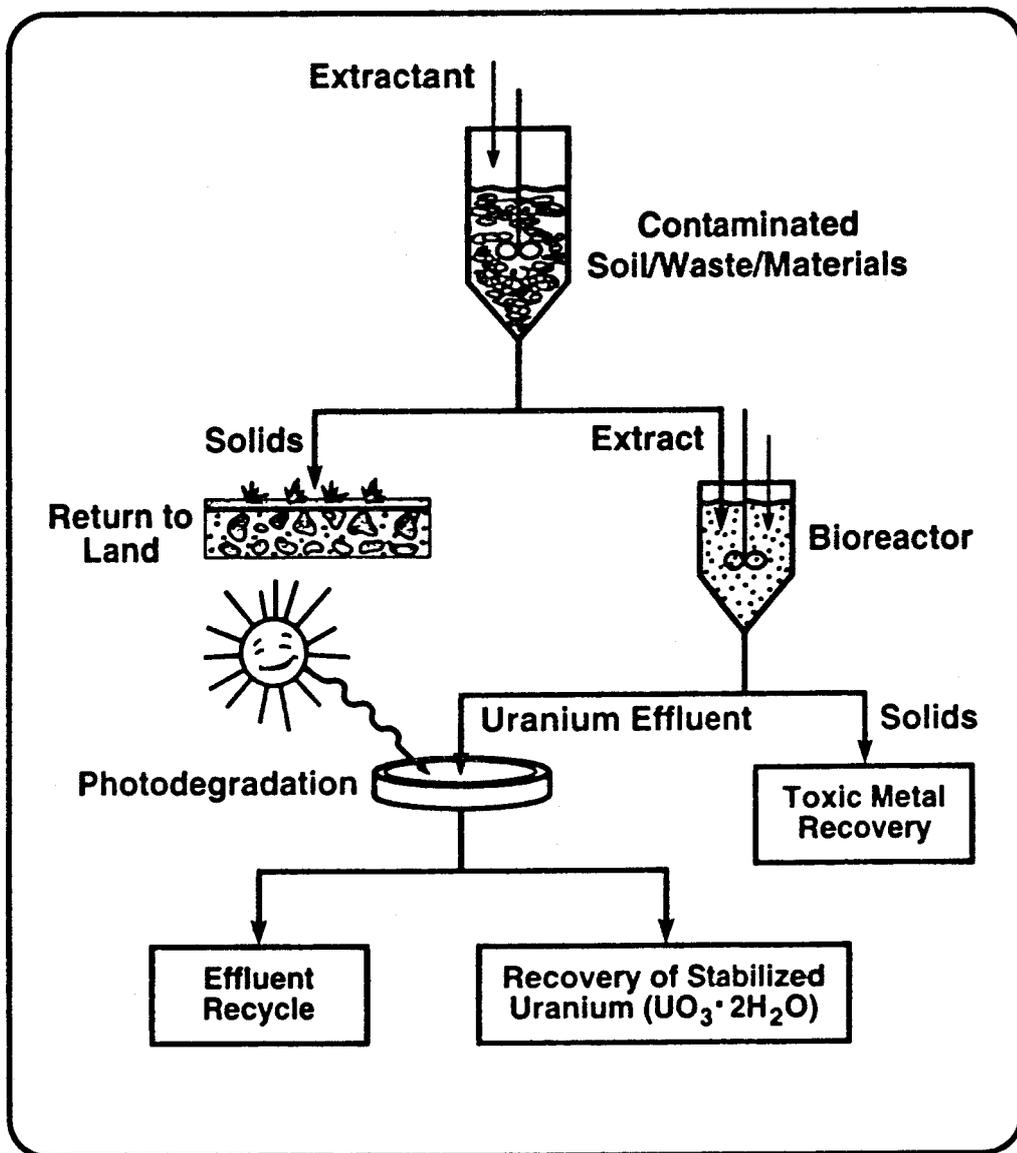
## Photochemical Removal of Uranium After Biodegradation



[Total removal efficiency of uranium (%): Y-12 sludge, 87; Fernald soil, 80].

# Removal and Recovery of Radionuclides and Toxic Metals

## BNL Citric Acid Process



# **WASTE SITE RECLAMATION WITH RECOVERY OF RADIONUCLIDES AND METALS**

## ***SUMMARY***

- Al, Ba, Co, Cr, Mg, Mn, Ni, Sr, Th, Ti, U, Zn, and Zr were extracted from sludge by citric acid**
- Microbial treatment of citric acid extract resulted in the removal of Al, Ba, Co, Mn, Ni, Sr, Th, Ti, Zn, and Zr**
- Photochemical treatment of citric acid extract after biodegradation resulted in the removal of Cr and U**

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Francis, A. J. Bioremediation of radionuclide and toxic metal contaminated soils and wastes. "Bioremediation of Contaminated Soils", Soil Science Society of America (in press).

Francis, A. J. Microbial Treatment of Radioactive Wastes. In Chemical Pretreatment of Nuclear Wastes for Disposal, W. W. Schulz and E. P. Horwitz, Editors, pp. 115-131, Plenum Publ. Co., New York, 1995.

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### DISSOLUTION AND STABILIZATION OF METALS

Francis, A. J. and C. J. Dodge. Anaerobic microbial remobilization of toxic metals coprecipitated with iron oxide. *Environ. Sci. Technol.* 24:373-378 (1990).

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Clayton, C. R., Halada, G. P., Kearns, J. R., Gillow, J. B., and Francis, A. J. Spectroscopic study of sulfate reducing bacteria-metal ion interactions related to microbiologically influenced corrosion (MIC). In Microbiologically Influenced Corrosion Testing, ASTM STP 1232, J. R. Kearns and B. J. Little, Editors., pp. 141-52, American Society for Testing and Materials, Philadelphia, 1994.

Dodge, C. J., Francis, A. J., and Clayton, C. R. X-ray spectroscopic studies of microbial transformations of uranium. In Applications of Synchrotron Radiation in Industrial, Chemical, and Materials Science, L. J. Terminello, K. L. D'Amico, and D. K. Shuh, Editors, Plenum Publishing, pp 159-168, NY. 1996.

### BIOTRANSFORMATION OF METAL CITRATE COMPLEXES

Francis, A. J., C. J. Dodge, and J. B. Gillow. Biodegradation of metal citrate complexes and implications for toxic-metal mobility. *Nature* 356:140-142 (1992).

Francis, A. J., Joshi-Tope, G. A., Dodge, C. J. Biodegradation of nickel-citrate and modulation of nickel toxicity by iron. *Environ. Sci. Technol.* 30:562-568 (1996).

Dodge, C. J. and A. J. Francis. Photodegradation of uranium citrate complex with uranium recovery. *Environ. Sci. Technol.* 28:1300-1306 (1994).

**Influence of Natural and Synthetic Organics on the Fate and Transport  
of Toxic Metals and Radionuclides in Subsurface Environments**

**Philip M. Jardine  
Oak Ridge National Laboratory  
June 1997**

## **Mechanisms of Metal Attenuation**

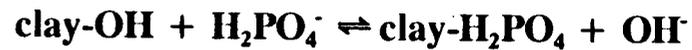
- **Chemical Processes**
- **Microbial Processes**
- **Physical Processes**

## Chemical Attenuation Processes

- **Coulombic Exchange**



- **Chemisorption**

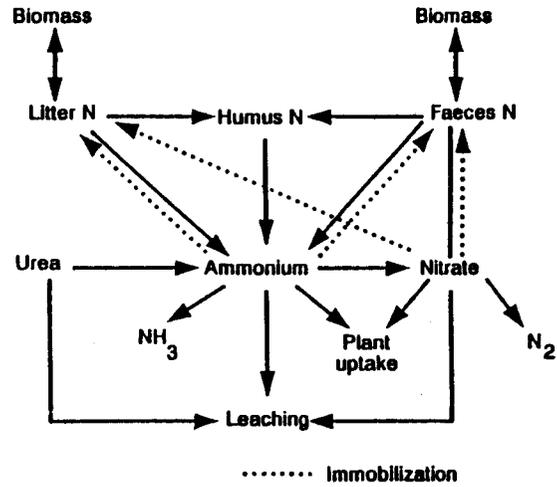


- **Oxidation/Reduction**



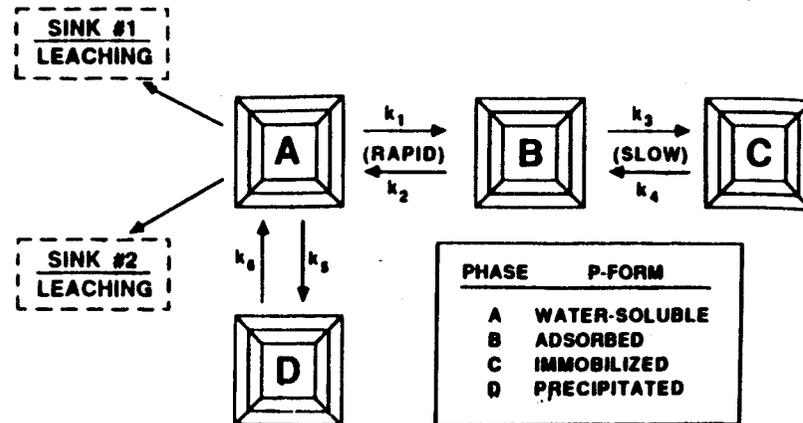
# Chemical Attenuation Processes (cont.)

- Transformation



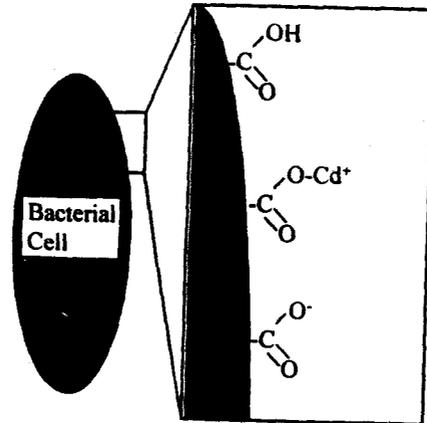
PMJ-4

- Precipitation/Dissolution



## Microbial Attenuation Processes

- **Biosorption**



- **Electron Transfer Reactions**

**Example:**

**Dissimilatory U reduction by metal-reducing bacteria**



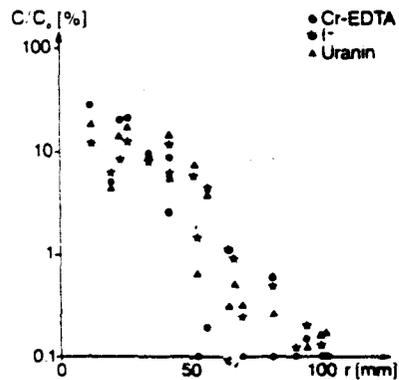
**soluble/mobile      virtually insoluble**

## Physical Attenuation Mechanisms

- Dispersion

Mixing of solute with the resident solution during displacement + molecular diffusion.

- Matrix Diffusion



Typical structured or fractured media:

$$\theta_m = 0.01 - 0.10$$

$$\theta_{im} = 0.90 - 0.99$$

Large majority of pore water held within the small pores of the matrix.

# **Influence of Natural Organic Complexants on Metal Attenuation**

**Source/Abundance/Stability of Natural Organic Carbon**

**Solid Phase Reactivity and Transport of Dissolved Organic Carbon**

**Metal Complexation by Dissolved Organic Carbon**

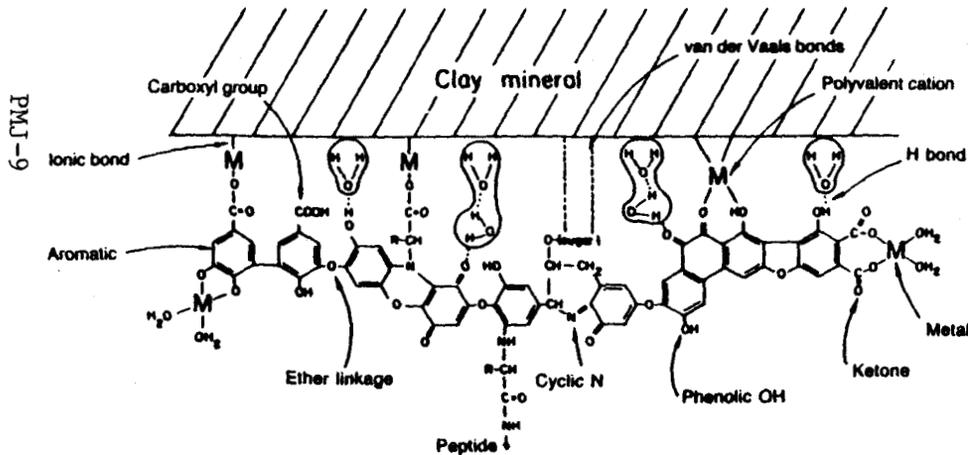
**Enhanced Transport of Metals and Radionuclides by Natural Organics**

## **Source/Abundance/Stability of Natural Organic Carbon**

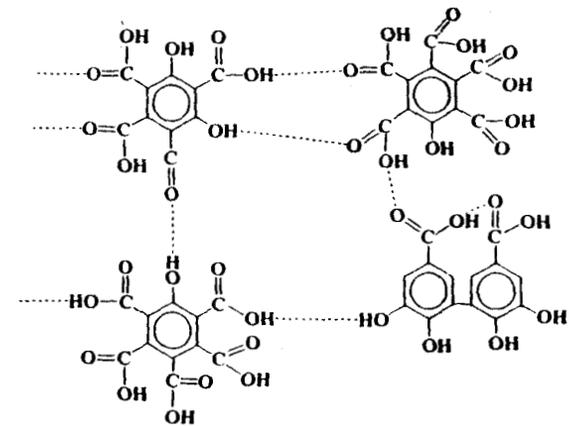
- **Soil organic matter (SOM) is composed of decomposing residues, primarily plants, by-products formed by organisms and the organisms themselves, and more resistant soil humates.**
- **The quantity of SOM is dependent on the balance between primary productivity and the rate of decomposition, which is temperature and moisture dependent.**
- **Water soluble fulvic and humic acid, or dissolved organic carbon (DOC), is generated during storm events.**

## Source/Abundance/Stability of Natural Organic Carbon (cont.)

- DOC has a polymeric structure that contains a variety of different type of functional groups and varies in its hydrophobicity. The average molecular weight ranges from a few hundred to several hundred thousand grams per mole.
- Resistant to microbial degradation with half-lives on the time scale of years.



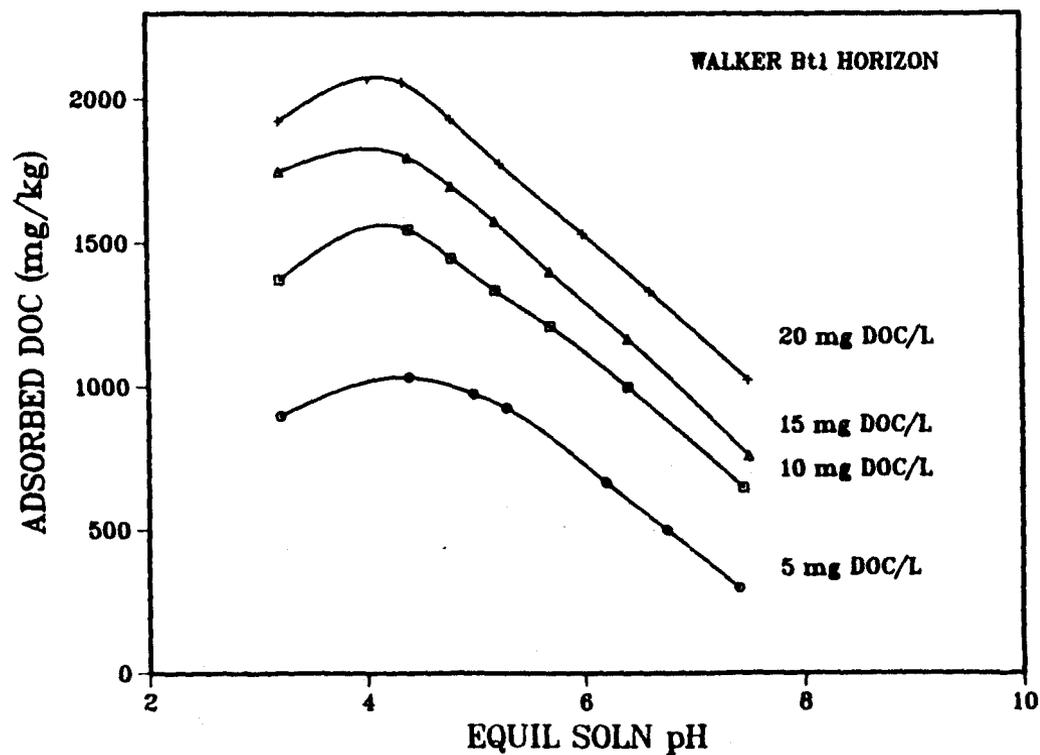
**Humic Acid**



**Fulvic Acid**

## Solid Phase Reactivity and Transport of Dissolved Organic Carbon

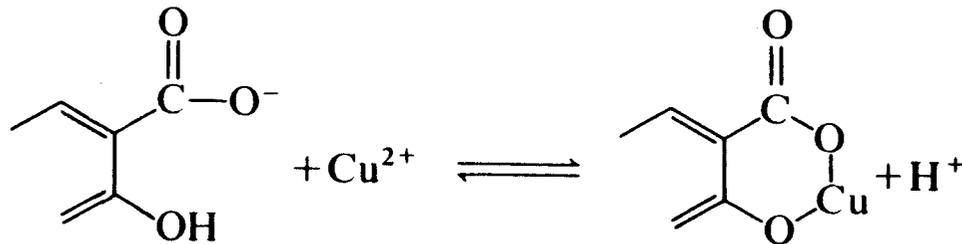
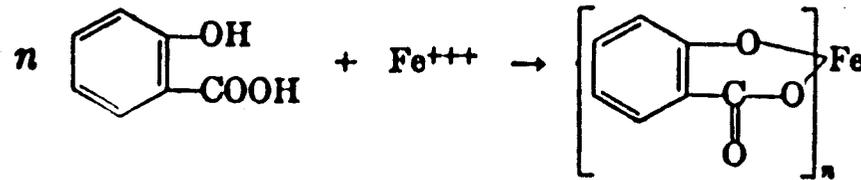
- Significant attenuation of DOC by subsurface media is possible.
- Sorption mechanism is primarily hydrophobic binding with lesser contributions from ligand exchange, anion exchange, Van der Waal forces, and cation bridging.



## Metal Complexation by Dissolved Organic Carbon

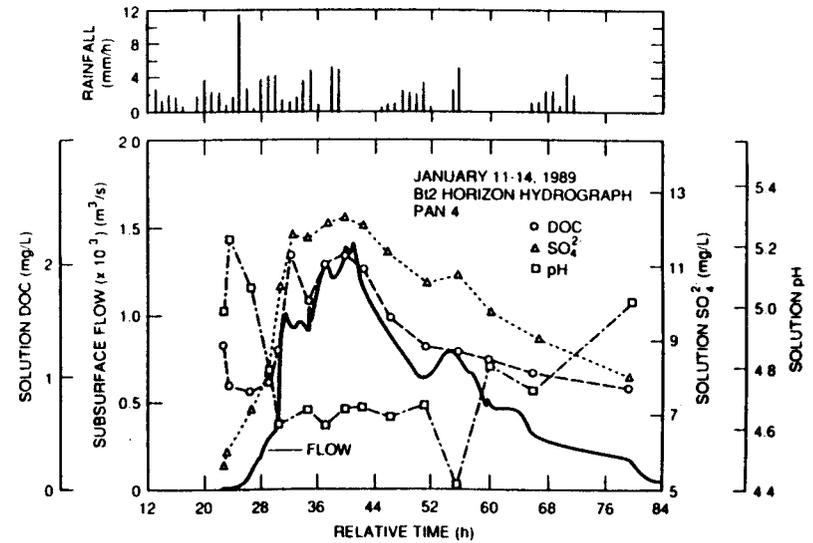
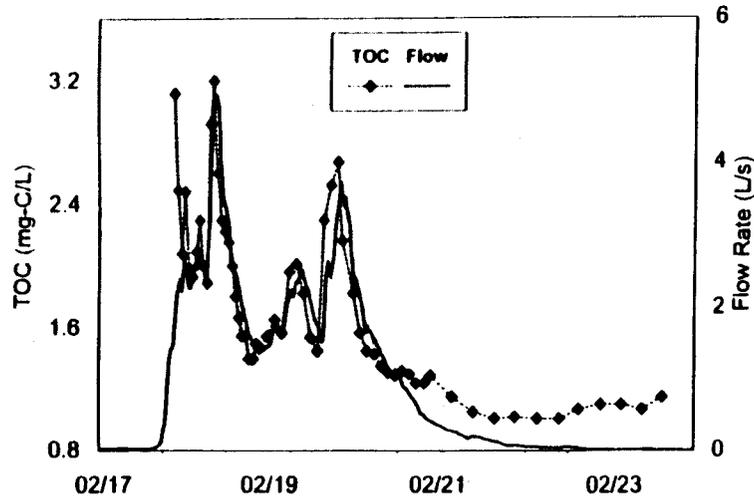
Formation of strong covalent bonds

Common scenario during soil forming processes (i.e. podzolization).



Even though DOC is attenuated by solid phase material, it is still highly mobile in many subsurface environments, particularly hydrophilic sources. The hydrophilic component of DOC is more likely to bind metals and radionuclides since it contains a high concentration of carboxyl and hydroxyl functional groups.

PMJ-12



## Enhanced Transport of Metals and Radionuclides by Natural Organics

### Examples in the Literature:

Seppard et al., 1980 Environ. Sci. Technol.  
Sr, Cs, U, Np, Am

Champ et al., 1984 Water Poll. Res. J. Canada  
Co, Ce, Cs, Eu, Sb, Zr, Ni, Pu

Nelson et al., 1985 Environ. Sci. Technol.  
Pu

Hargitai, 1989 Sci. Total Environ.  
Pb, Ni, Cd

Penrose et al., 1990 Environ. Sci. Technol.  
Pu, Am

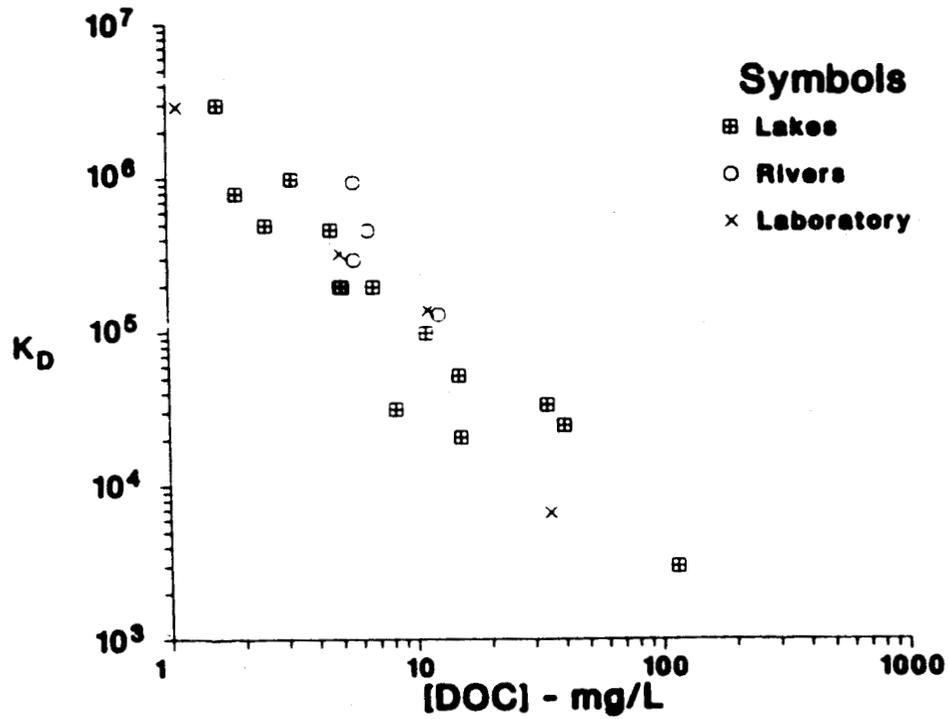
Dunnivant et al., 1992 Environ. Sci. Technol.  
Cd, PAH

McCarthy et al., 1997 J. Contam. Hydrol.  
Actinides

Nelson et al., 1985

Distribution coefficient for Pu(III/IV) on sediments as a function of dissolved organic carbon content.

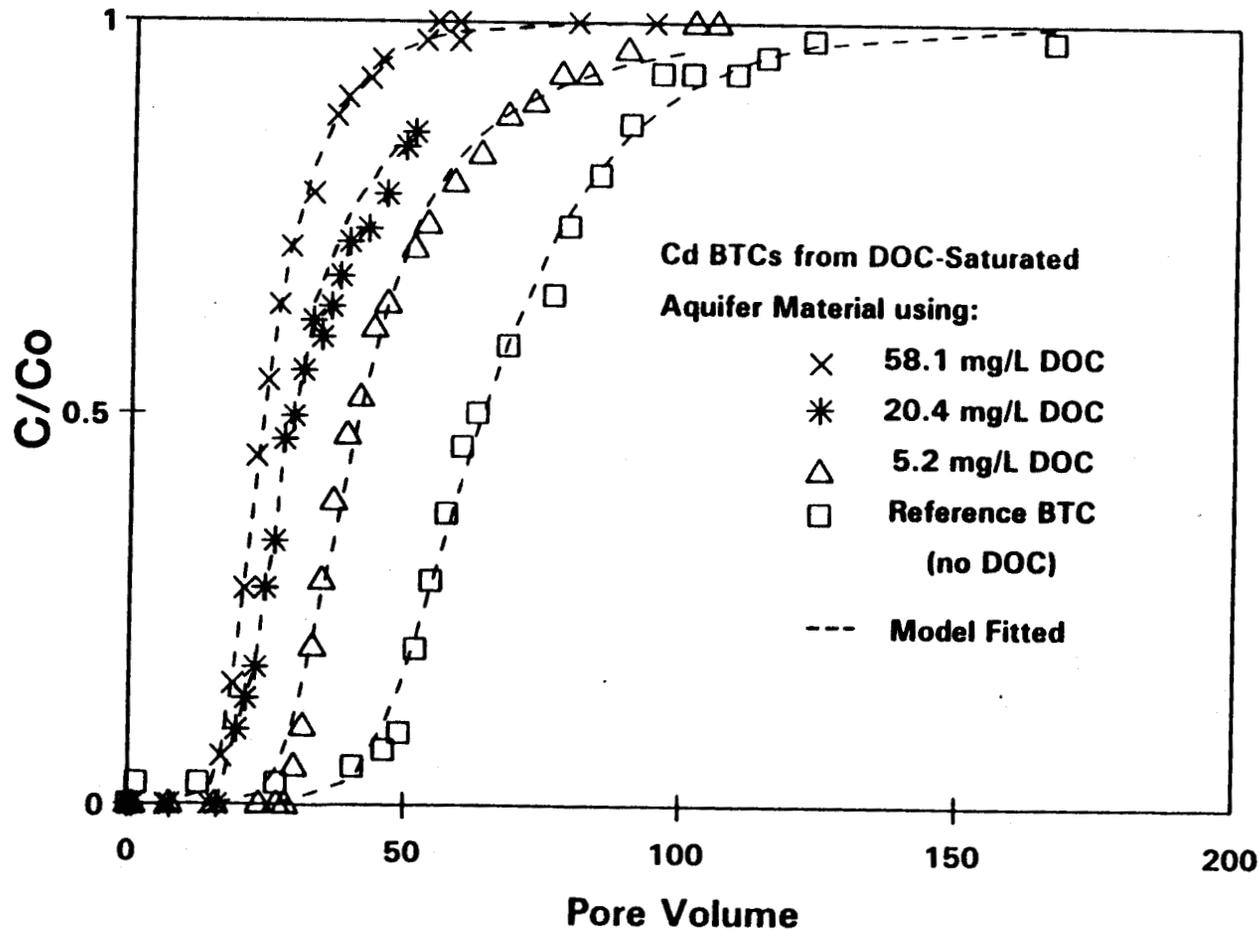
A decrease in  $K_D$  with increasing DOC suggests that Pu is more likely to remain in the mobile solution phase with high DOC concentrations.



Dunnivant et al., 1992

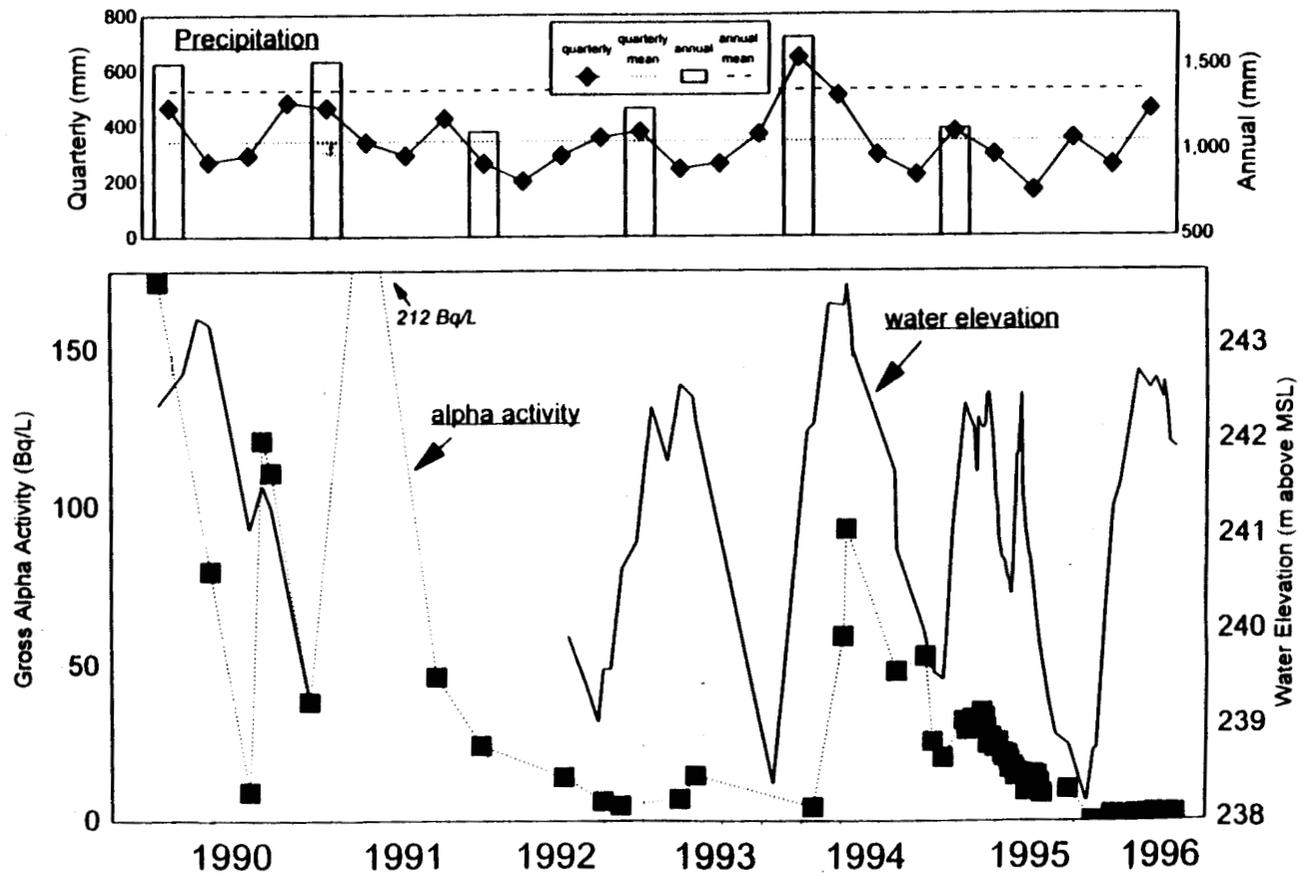
Displacement of Cd through aquifer sediments in the presence of four different DOC concentrations.

A shift in the breakthrough curves to the left with increasing DOC suggests enhanced transport of Cd by the DOC.



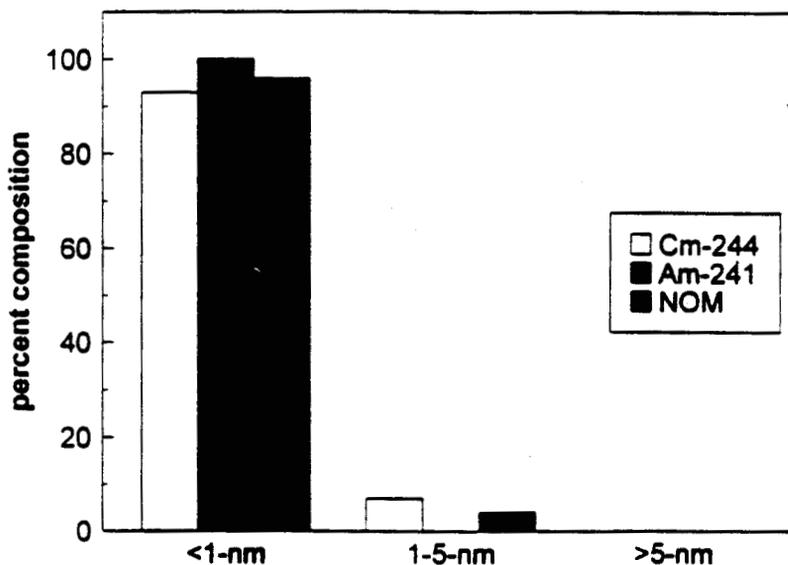
McCarthy et al., 1997

(a) Gross alpha activity (Bq/L) and water elevation (m above msl) as a function of time at a contaminated field site on the Oak Ridge Reservation. Large releases of gross alpha radioactivity occur during wetter-than-average years when disposal trenches are inundated with groundwater.

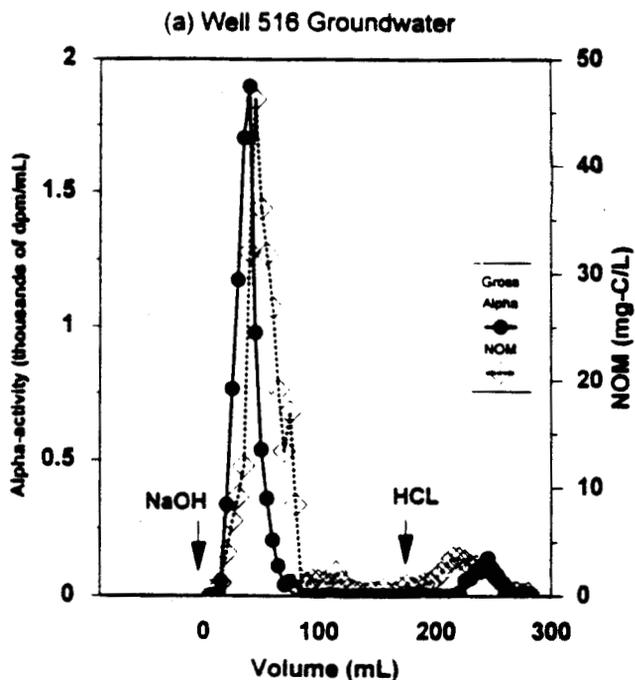


McCarthy et al., 1997 (continued)

- (b) The fraction of  $^{244}\text{Cm}$ ,  $^{241}\text{Am}$ , and DOC passing through 1 nm and 5 nm amicon tangential flow filters during on-line filtration of groundwater. Results suggest that gross-alpha activity is not associated with inorganic colloids.



- (c) DEAE-cellulose chromatography of groundwater. Gross-alpha activity and DOC bind to DEAE-cellulose anion exchanger and co-elute from the column. Results suggest the enhanced transport of actinides by DOC.



# **Influence of Synthetic Organic Complexants on Metal Attenuation**

**Source / Abundance / Stability of Synthetic Chelates**

**Metal Complexation Mechanisms**

**Solid Phase Reactivity and Transport of Organic Ligands**

**Enhanced Transport of Metals and Radionuclides by Synthetic Organics**

## Source / Abundance / Stability of Synthetic Chelates

- **Low-level radioactive waste generated within DOE facilities is typically composed of inorganic fission byproducts mixed with various chelating agents and organic acids.**
- **Chelating agents and organic acids were used in decontamination efforts since they form stable, water soluble complexes with a wide variety of metals and radionuclides.**
- **Common chelating agents - aminopolycarboxylates NTA, EDTA, DTPA**
- **Common organic acids - citrate, oxalate**
- **DOE has 3000 inactive waste disposal areas. Riley et al. (1992) report that wastes are typically ill-defined mixtures of metals, radionuclides, and organics. Binary and ternary contaminant mixtures were reported at 64 and 49% of the waste sites, respectively, with the most common contaminant mixtures being metals and radionuclides, many of which are associated with chelating organic ligands.**

## Source / Abundance / Stability of Synthetic Chelates (continued)

- Metal-chelate complexes are typically quite stable, with the magnitude of the stability constant dependent on the metal and chelate type.

Example:  $^{90}\text{SrEDTA}$        $\log K = 10$

$^{60}\text{Co(II)EDTA}$        $\log K = 16$

$^{60}\text{Co(III)EDTA}$        $\log K = 40$

- Microbial degradation of organic acids and chelates is often dependent on the type of associated metal. Nevertheless, degradation follows:

$\text{citrate} \approx \text{oxalate} \gg \text{NTA} > \text{EDTA} > \text{DTPA}$

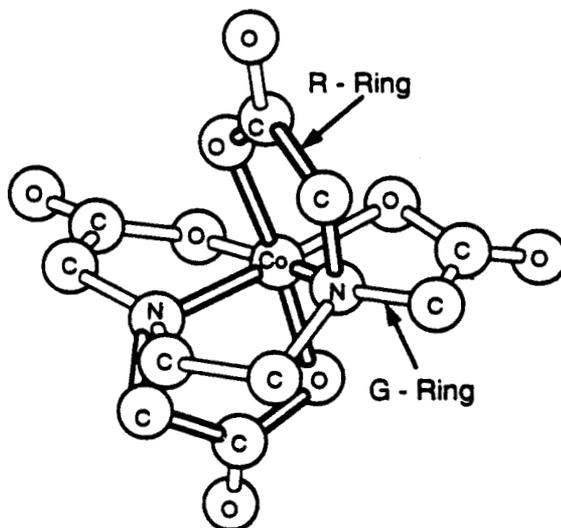
with time scales ranging from hours to years.

## Metal Complexation Mechanisms

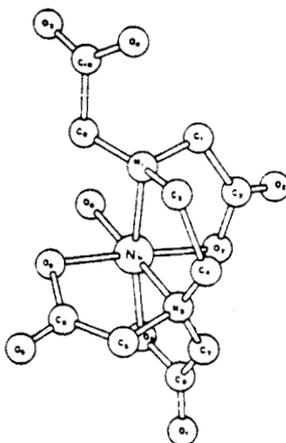
Strong covalent bond between organic ligand and metal ion. Chelates generally form cage-like structure around metal or radionuclide. Stability dependent on metal electronegativity, valence, and size.

Example:

Co(III)EDTA - Co(III) coordinated with 4 carboxylate O and two ethylenediamine N.

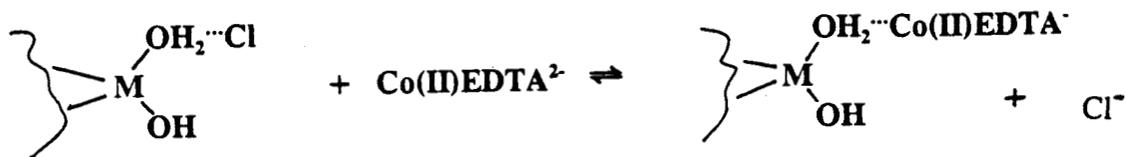


Ni(II)EDTA - Ni coordinated with 3 carboxylate groups and one carboxylate group is free.



# Solid Phase Reactivity and Transport of Organic Ligands

- Sorption

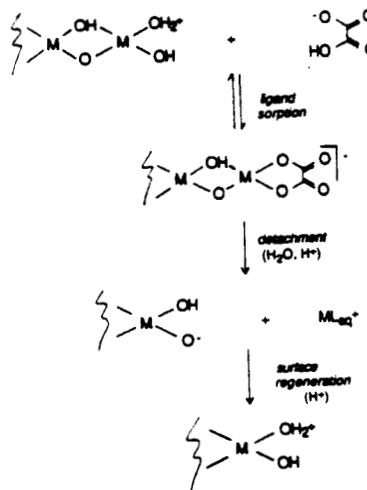


- Solid-Phase Dissociation of Complex

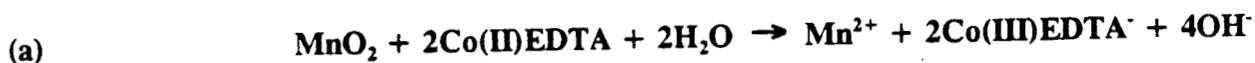


$$\log K = 16$$

$$\log K = 25$$



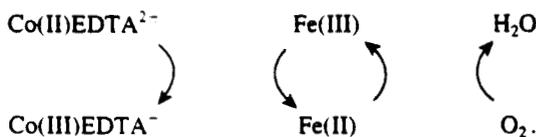
- Oxidation



$$\log K = 16$$

$$\log K = 40$$

(b)



## Enhanced Transport of Metals and Radionuclides by Synthetic Organics

Examples in the literature:

Means et al., 1978 Science  
<sup>60</sup>Co-EDTA

Swanson, 1981, 1982, 1983 PNL-reports  
Ni, Co, Eu, EDTA, DTPA, NTA

Elliott and Denny, 1982 J. Environ. Qual.  
Cd, EDTA, NTA, oxalate, acetate

Champ et al., 1984 Water Poll. Res. J. Canada  
Co, Ce, Cs, Eu, Sb, Zr, Ni, Pu

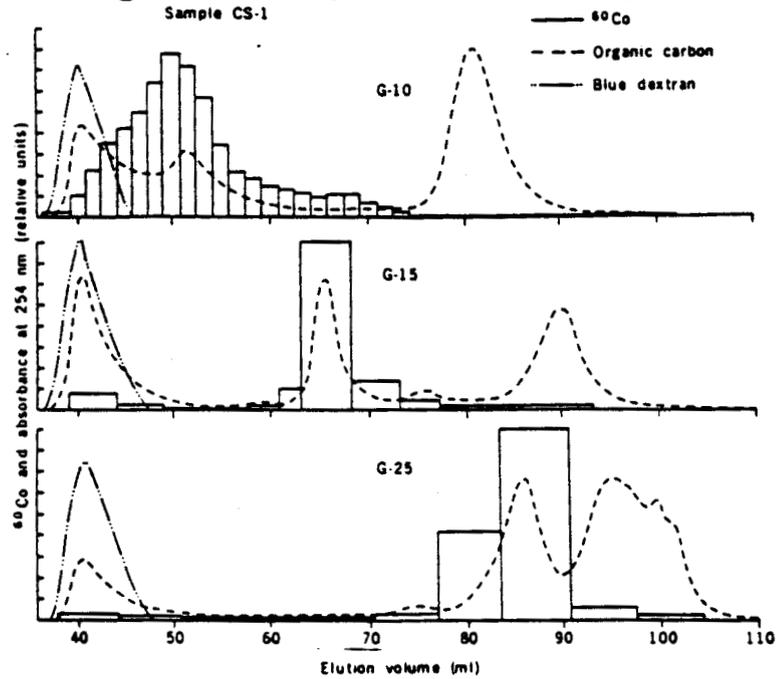
Olsen et al., 1986 Geochim. Cosmochim. Acta  
variety of radionuclides/organic ligands

Huang et al., 1988 Water Res.  
Zn-EDTA

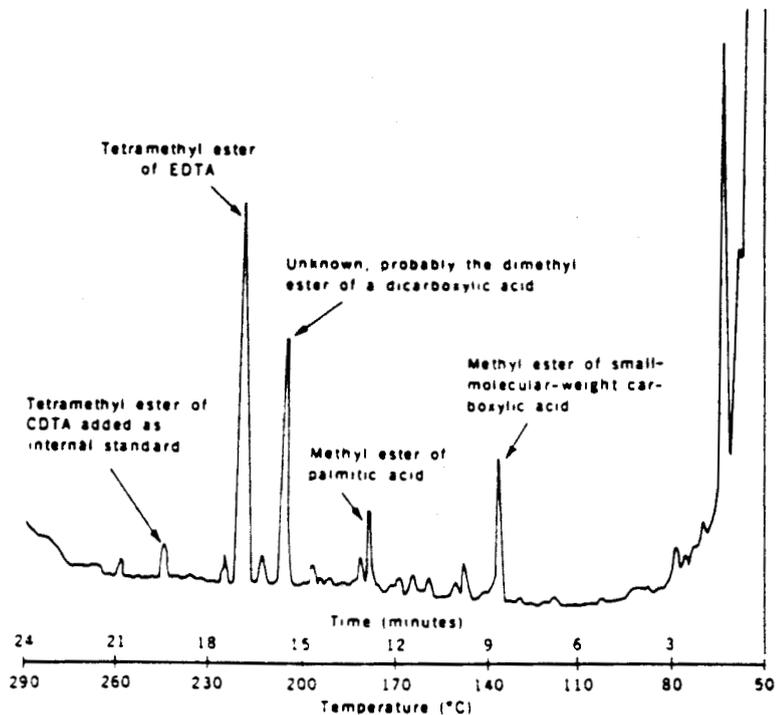
Jardine et al., 1993 Soil Sci. Soc. Am. J.  
Co, Sr, EDTA

**Means et al., 1978**

**Gel filtration chromatography elution profiles for groundwater obtained from waste sites on the Oak Ridge Reservation. Between 90-95% of  $^{60}\text{Co}$  was correlated with organics having a molecular weight less than 700.**



**GC-MS analysis of the groundwater sample indicated that a substantial concentration of EDTA. Results suggested that  $^{60}\text{Co}$  was chelated by EDTA and this resulted in enhanced transport of the radionuclide in subsurface environments.**

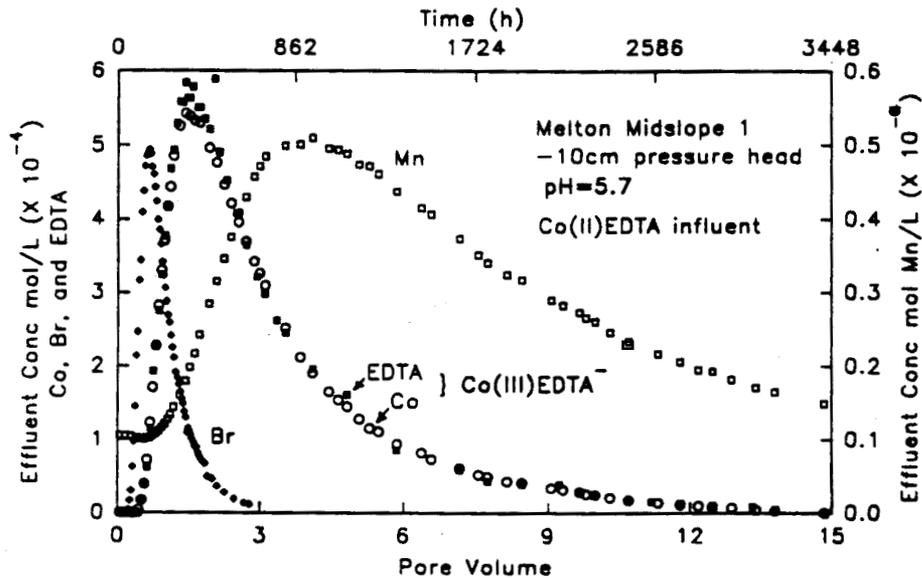


Jardine et al., 1993

Observed solute effluent concentrations for  $\text{Co(II)EDTA}^{2-}$  displacement through weathered, fractured shale at -10 cm pressure-head.

Subsurface  $\text{MnO}_2$  oxidized  $\text{Co(II)EDTA}$  ( $\log K = 16$ ) to  $\text{Co(III)EDTA}$  ( $\log K = 40$ ) during transport.  $\text{Co(III)EDTA}^-$  was reactive with the solid phase, and its retardation was most likely a function of the redox reaction.

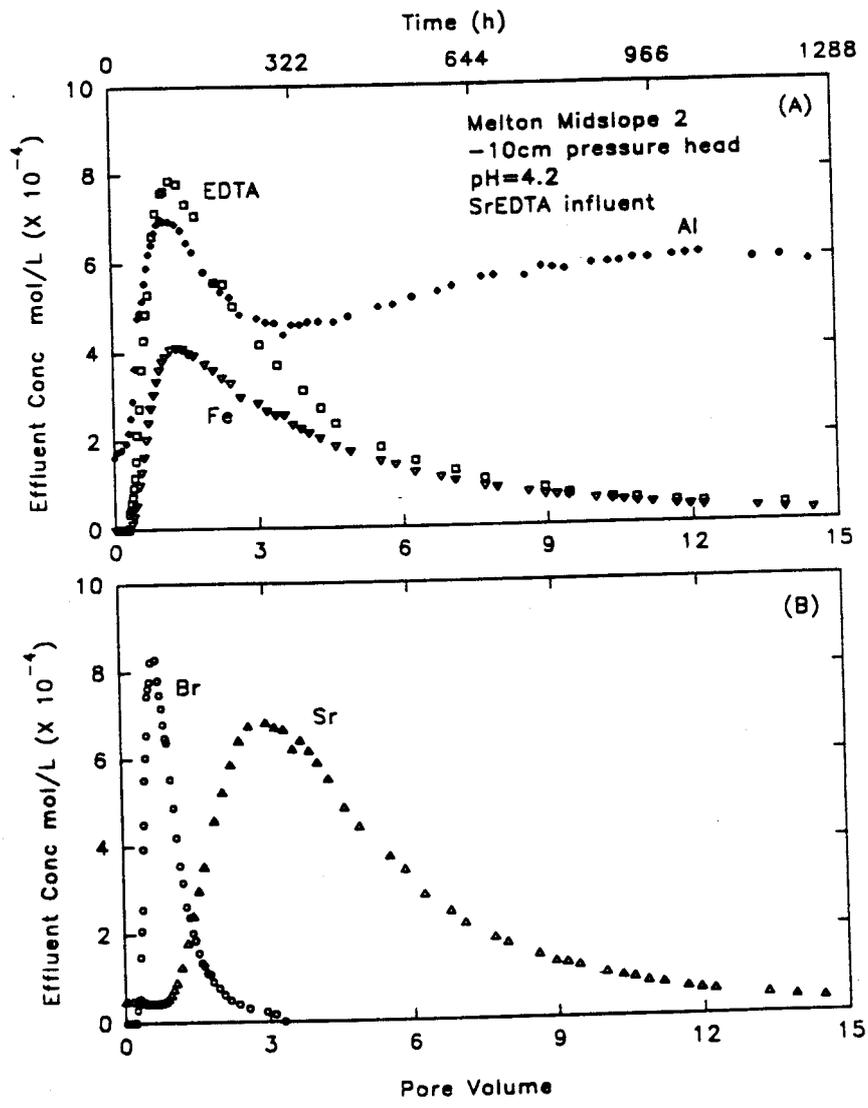
The redox process results in a significantly more stable Co complex which will enhance its persistence and transport in subsurface environments.



**Jardine et al., 1993**

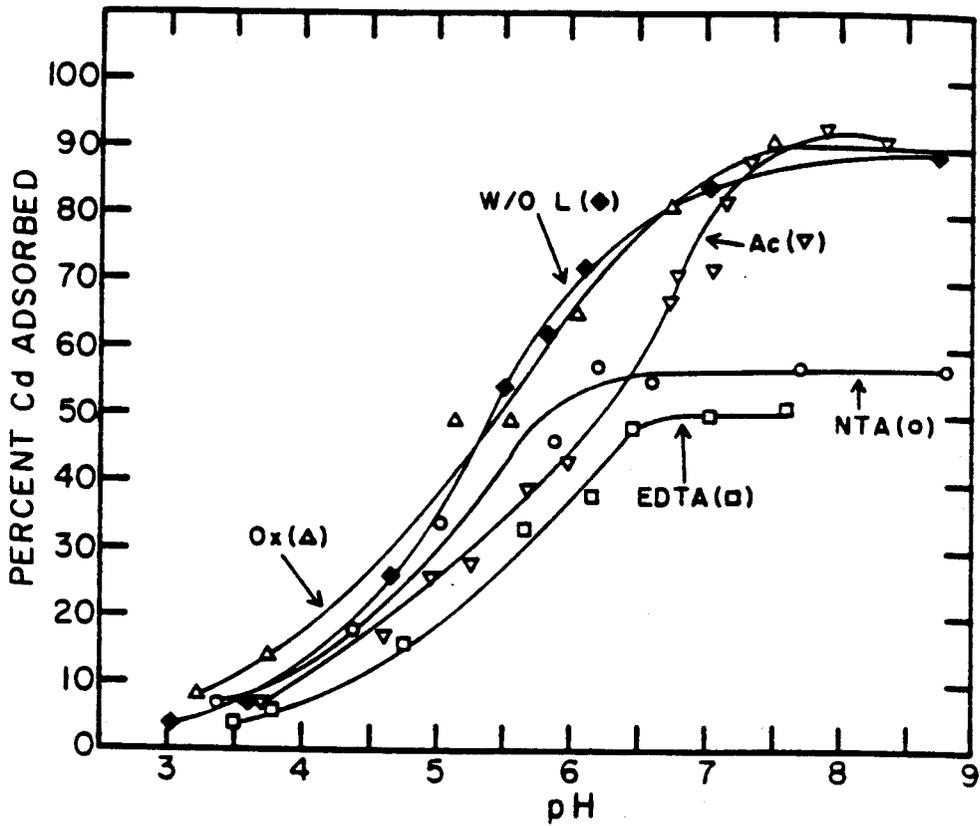
**Observed solute effluent concentrations for SrEDTA<sup>2-</sup> displacement through weathered, fractured shale at -10 cm pressure-head.**

**Subsurface Fe and Al sources effectively dissociated the Sr-EDTA complex and Sr was transported as a reactive divalent cation. The EDTA was complexed by surface bound Al and Fe-oxides and resulted in the time-dependent formation of Fe(III)EDTA<sup>-</sup> (log K = 25) and Al(III)EDTA<sup>-</sup> (log K = 18).**



**Elliott and Denny, 1982**

The pH dependent adsorption of Cd on soil in the presence of various organic ligands. EDTA and NTA inhibited Cd sorption much more than the organic ligands acetate and oxalate.



## **Implications of Organo-Metal Complexes in Subsurface Environments**

- **Natural and synthetic organics can significantly alter metal and radionuclide attenuation processes by altering their bioavailability and geochemical behavior in subsurface environments.**
- **Understanding the mechanisms that control the fate and transport of organo-metal complexes is critical to our ability to (1) accurately assess risk and health concerns and (2) design and implement remedial strategies at contaminated sites.**

## INSITU SOIL LEAD REMEDIATION

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(513) 569-7653

### INTRODUCTION

Lead, a naturally occurring metal, has always been present in soils, surface waters and ground waters. Lead content of agricultural soils ranges from  $> 1$  mg/kg to 135 mg/kg with a median value of 11 mg/kg (1). Inner-city neighborhoods in most of our major cities have mean or median soil Pb concentrations in excess of 1000 mg/kg (2-6) with values as high as 50,000 mg/kg being reported (7). Most of these elevated lead concentrations observed in the urban soils are assumed to come from various anthropogenic sources: industrial emissions, vehicular emissions and exterior lead paint (8). Additionally, lead has been added to soil as the insecticide lead arsenate, impurity in fertilizers as well as from mining and smelting activities (9). Further, lead is a contaminant of concern in about one third of the National Priority List (NPL) sites and over 400 Superfund sites have excessive soil Pb concentrations (10). Thus, its use by society; paints, chemical additives, tools and weapons, as well as other consumer and industrial products, coupled with inadequate disposal or recycling by society have caused environmental systems (soils) to become repositories for the metal. It is also apparent that not only are soils the repository for environmentally released Pb, but it is retained in the zone of addition (9).

According to the Center for Disease Control (CDC) lead poisoning is the most common and most devastating environmental disease affecting young children. Over the past decade the blood Pb level associated with impairment has decreased from 25  $\mu\text{g/dL}$  to 10  $\mu\text{g/dL}$ , as we have learned that levels above 10-15  $\mu\text{g/dL}$  can significantly reduce IQ and learning ability in children (11). Because of the reduction of Pb in automotive emissions, and reduction of Pb in food due to changes in canning technology, both food and automotive emission Pb levels have decreased nearly 10 fold in the past 15 years (12). During the same time frame median blood Pb levels in suburban children have fallen from about 20-25  $\mu\text{g/dL}$  in 1970 to 3-4  $\mu\text{g/dL}$  in 1990. With the normal variance (and varied amounts from Pb in plumbing systems) some suburban children exceed 15  $\mu\text{g/dL}$ . But over 50% of children in the center city exceed 15  $\mu\text{g/dL}$  limit (13). Thus, lead risk to young children is now recognized as the most sensitive limit for Pb in the environment (11). CDC estimates that Pb poisoning in children costs billions of dollars in medical and special education expenses and decreased future earnings. Lead paint, Pb in drinking water and Pb in soil are

the major sources of exposure. Children exposed to high levels of soil and dust Pb have been found to have high blood Pb in numerous cases (7). Lead in soils contaminated by smelter emissions, automotive emissions, or paint residue have been found to cause increased blood Pb in children when soil Pb exceeds 500-1000 mg/kg (14-17). In other cases, social factors and/or soil chemical factors alter exposure and/or bioavailability of the soil Pb and little or no increases in blood Pb are observed even with soils containing 5000 mg Pb/kg (18). Further, Pb in mining soils appears to have lower bioavailability than Pb in urban dusts (19-21). Cotter-Howells and Thornton (18) reported low blood Pb levels in children living in an area with soils (about 5000 mg/kg) derived from PbS mining wastes. Studies have found the relationship (slope of blood Pb/soil Pb) for children in smelter and urban areas to range from 1.1 to 7.6  $\mu\text{g/dL}/1000$  mg/kg, while for children in mining areas the relationship ranges from 0 to 4.8  $\mu\text{g/dL}/1000$  mg/kg (22). Suggesting that Pb in soils contaminated from mining activities is less bioavailable than Pb in soil derived from urban and smelting sources. Three possible explanations have been offered for the observations: the size of the Pb containing particle, the species of Pb in soil, and the geochemical matrix incorporating the Pb species. These results are interpreted as indicating that because of specific adsorption, soil Pb bioavailability increases with increasing soil Pb concentration and that the form of soil Pb alters its bioavailability.

Programs to reduce exposure from Pb paint and Pb in drinking water are moving forward. No program exists on contaminated soil Pb because, according to CDC and EPA, there is insufficient information available on which to base such a program. They state that far less is known about the hazards of soil Pb-- and how to address those hazards-- than about paint or water. Thus, information is needed to better characterize the problem, determine pathways of exposure, and determine effective remediation methods.

Remediation treatments for soils attempt to capitalize on the differences in physical and chemical properties between a contaminant and soil constituents. For example, remediation efforts for metal contaminated sites use properties such as solubility, density, particle size distribution, surface chemistry, boiling point or magnetic susceptibility to allow separation and recovery. Metals found as relatively soluble species or weakly sorbed to soil clays might be solubilized by the application of mild organic acids. If the metals are present as separate mineral particulates, then their typically higher density might permit the physical separation of these species from the less dense aluminosilicate and organic constituents of soils. Otherwise, these forms could be bound in a solid cement or vitreous glass matrix. If the metal species are volatile, then a soil heating method might allow recovery. Separation methods relying on the magnetic susceptibility of ferromagnetic or

strongly paramagnetic metal species have also been attempted. More detailed discussions of remediation technologies can be found in the literature (23-28).

Many biological, chemical and physical process have been proposed for soil remediation. Some of the processes can be either applied to excavated soil or used in situ. However, reduction in exposure to soil Pb has typically been accomplished by soil removal for off site disposal, covering, or diluting by mixing with uncontaminated soil. Cost, logistical concerns, and regulatory requirements associated with excavation, ex situ treatment and disposal can make in situ treatment an attractive option. Our current understanding of Pb exposure and factors which effect its bioavailability as well as its environmental chemistry may allow development of less costly and environmentally less disruptive methods of remediation.

## METHODOLOGY

In response to the need for cost effective technology to immobilize Pb, we collaborated with Ohio State University to examine the feasibility of Pb immobilization by phosphate rocks. This approach is based on the hypothesis that Pb phosphates are one of the most insoluble Pb minerals, these materials are resistant to acid weathering, and these materials are less bioavailable than other Pb forms. As a result of this effort, an RTDF project "IINERT" was initiated to address three major hypothesis: 1) Surrogate relationships can be identified/confirmed among Pb availability to humans, pigs, rats, and glassware extractions (single and sequential); 2) Good correlations exist between soil components (e.g. Pb species non Pb containing components) and the soil Pb hazard; and 3) Engineering addition of materials to Pb contaminated soils will induce the formation of less hazardous Pb forms, providing a practical approach to in-place inactivation. The experimental approaches utilized have been laboratory scale solution studies, resin studies, dialysis studies, soil studies, feeding studies and field studies.

## RESULTS

We have shown that Pb is rapidly and effectively precipitated from solution by orthophosphate (aqueous P, hydroxyapatite, or phosphate rock) to form a series of Pb phosphates (29-31). We have used hydroxyapatite and phosphate rock as the primary P source and have shown that they are effective in attenuating Pb in aqueous solution, exchangeable form and contaminated soil material, to below the U.S. EPA action level of 15  $\mu\text{g/L}$  dissolved Pb. Phosphate rocks from Florida, North Carolina and Idaho are also shown to be effective in removing Pb from aqueous solution (29). The final product of Pb immobilization is primarily hydroxypyromorphite ( $\text{Pb}_{10}(\text{PO}_4)_6(\text{X})_2$  where X=OH, F or Cl), which is stable even at pH as low as 3. Results of chemical and x-ray diffraction (XRD) analysis,

scanning electronic microscopy (SEM), and scanning transmission electronic microscopy (STEM) strongly support the mechanism of dissolution of hydroxyapatite and precipitation of pyromorphite.

Aqueous P concentration is a key factor in determining the effectiveness of Pb immobilization and the formation of pyromorphite. Thus pH is important since it determines solubility of hydroxyapatite or phosphate rock. Hydroxyapatite or phosphate rock not only supplies P to immobilize Pb, but may provide Ca to replace Pb from exchange sites.

We have also shown that hydroxyapatite can effectively immobilize aqueous Pb in the presence of common soil solution anions:  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$  as well as cations: Zn, Cd, Ni, Cu,  $\text{Fe}^{2+}$ , and Al. Further, hydroxyapatite is effective at attenuating these metals (30, 31). Hydroxyapatite also removed  $\text{Pb}^{2+}$  from Pb-EDTA solution in the presence of excess EDTA. Indicating that basic Ca-phosphates can sequester Pb even in the presence of strongly complexing organic ligands. We have illustrated that goethite adsorbed Pb is readily converted to pyromorphite in the presence of apatite(33) Further, we have confirmed formation of pyromorphite formation from Pb-contaminated soil( 4,000-50,000 mgPb/kg), Paint chips (30% Pb, w/w), cerrusite, anglesite, galena, and Pb-humic complexes.

In animal feeding experiments we have illustrated that Pb bioavailability followed the order: Pb-acetate >> contaminated soil > pyromorphite = control and that the addition of apatite or rock phosphate to the contaminated soil reduced the bioavailability of the contaminated soil Pb. Thus, illustrating that the formation of pyromorphite in soils not only reduce the solubility of the soil Pb, but reduce its bioavailability. In fact even without allowing time for reaction, the addition of the phosphate (apatite or rock) to the contaminated soil was effective at reducing soil Pb bioavailability. We have illustrated that the addition of apatite to Pb contaminated soil reduces the plant uptake of Pb. SEM and XRD analysis indicate that apatite reacted with the Pb to form pyromorphite and formation of pyromorphite on root surfaces was also noted (33).

## CONCLUSIONS

Our results strongly demonstrate that both hydroxyapatite and phosphate rocks were effective in reducing Pb solubility and bioavailability through dissolution of hydroxyapatite or phosphate rocks and precipitation of pyromorphite. The effective and rapid  $\text{Pb}^{2+}$  immobilization from solution and contaminated soils by hydroxyapatite or phosphate rock, the limited effects from other minerals, anions, and cations, the apparent environmental stability of the reaction products, along with the ready availability and low-cost of hydroxyapatite or phosphate rock suggest that this approach might have great merit for cost-effective in situ immobilization of Pb contaminated water, soils, and wastes. The RTDF effort is evaluating the effectiveness of this and other in-situ techniques for reducing

soil Pb bioavailability in a field experiment.

In companion studies we have illustrated the formation of autunite when uranium is reacted with apatite.

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# Natural Attenuation of Metals and Radionuclides: An Overview\*

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James L. Krumhansl - Sandia National Labs

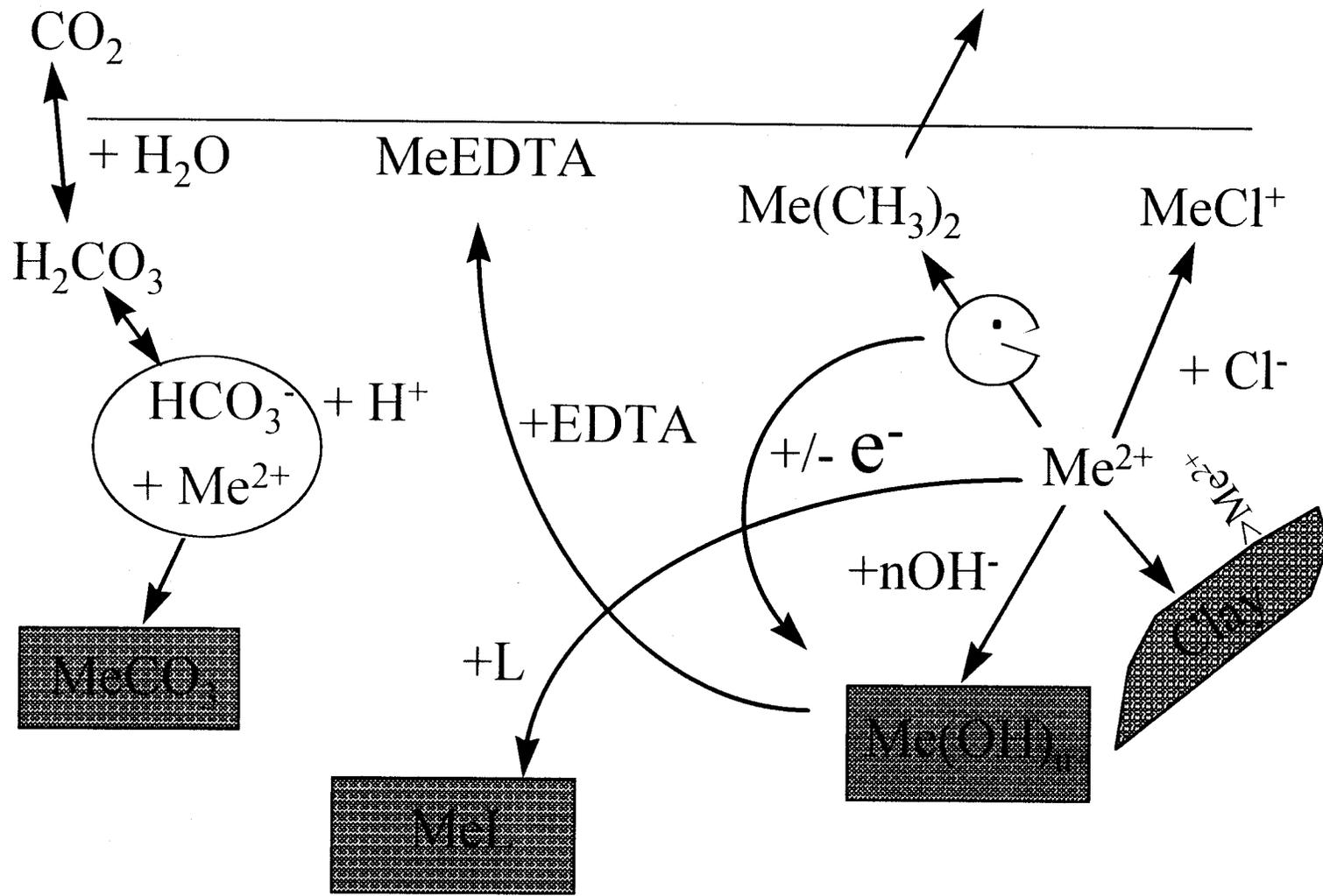
Malcolm D. Siegel - Sandia National Labs

Hans W. Papenguth - Sandia National Labs

\*Thanks for funding from the US-NRC and Sandia National Labs

## **SOIL BACKGROUND LEVELS**

<b>Silver</b>	<b>30 ppb - 8 ppm</b>
<b>Arsenic</b>	<b>2-10 ppm</b>
<b>Barium</b>	<b>80-800 ppm</b>
<b>Beryllium</b>	<b>1-2 ppm</b>
<b>Cadmium</b>	<b>100 ppb-1 ppm</b>
<b>Cobalt</b>	<b>2-20 ppm</b>
<b>Chromium</b>	<b>7-220 ppm</b>
<b>Copper</b>	<b>6-60 ppm</b>
<b>Lead</b>	<b>10-80 ppm</b>
<b>Mercury</b>	<b>20-400 ppb</b>
<b>Uranium</b>	<b>2-5 ppm</b>
<b>Zinc</b>	<b>20-120 ppm</b>



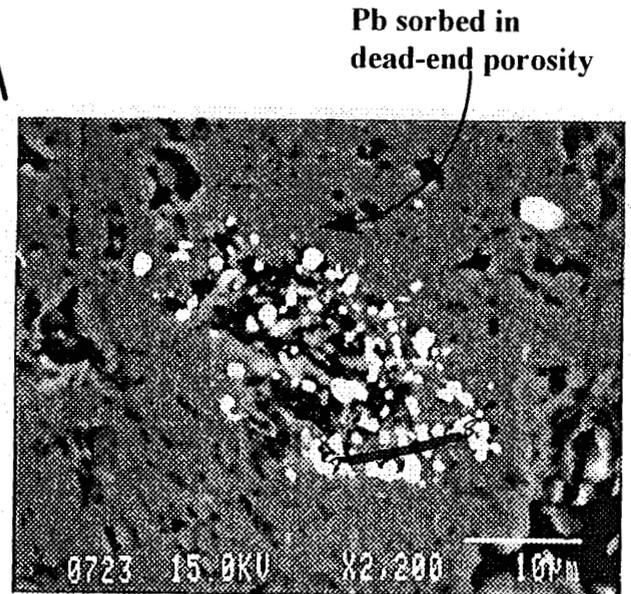
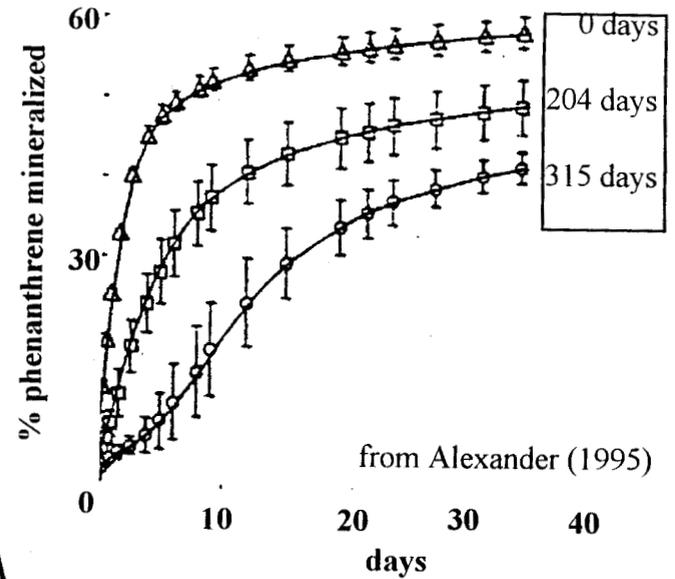
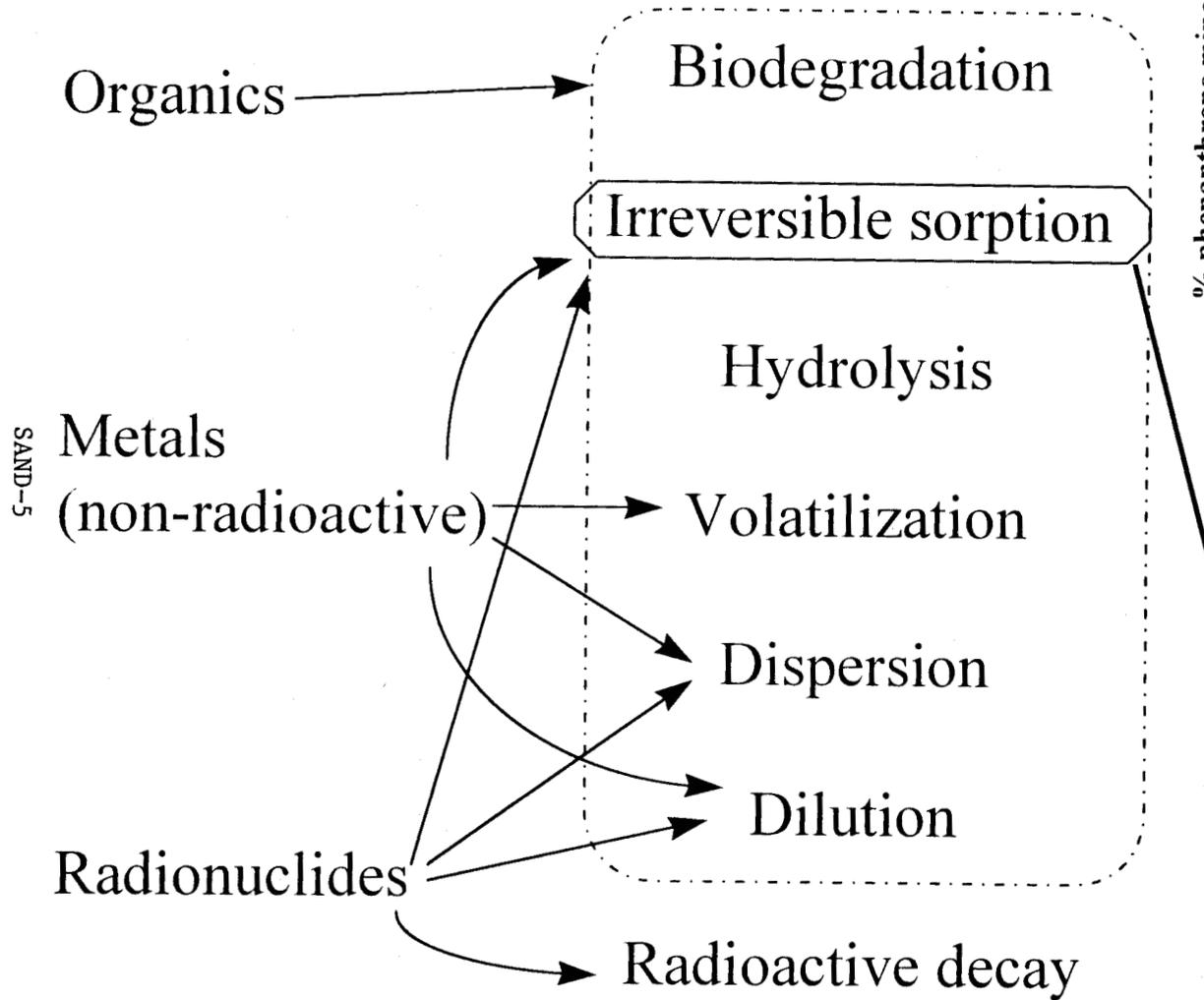
Natural Attenuation is “the biodegradation, dispersion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the ecosystem” USEPA (1995).

SAND-4

## Soil and Groundwater Contamination

	Fuel Hydrocarbons	Chlorinated Solvents	Metals/Radionuclides
site owners	private, state, DOE, DOD	private, state, DOD, DOE	DOE + private
Natural Attenuation Protocols?	Yes, ASTM, EPA, USAF, Ca., other states	Yes, USAF, some states	NO

# Mechanisms of Natural Attenuation in Soils/Groundwaters



# Natural Attenuation of Metal Contaminants

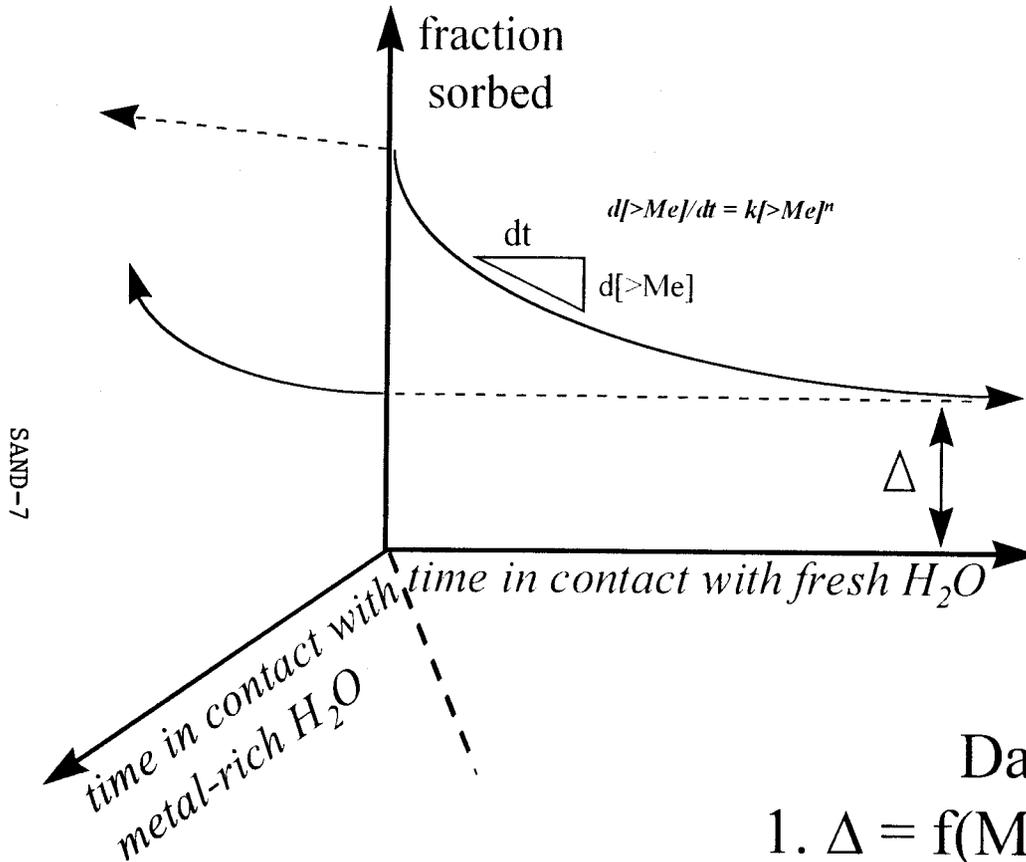
Unlike what happens to many organic contaminants over time, metals in soils and groundwaters don't typically 'go away'. Nevertheless, a number of soil processes cause significant reductions in the bioavailability of a large number of metal contaminants. The most important processes are the formation of insoluble solids and irreversible sorption. The first tends to reduce the fraction of metal contamination available for transport. The latter results in a net decrease in both the transport fraction and the amount of the metal that is bioavailable. For many of the radionuclides radioactive decay leads to significant reductions in metal toxicity over environmentally relevant time-scales. Specifically, if solubility and sorption limit the mobility of a radionuclide for time-scales much longer than the decay half-life the likelihood of natural attenuation becomes quite large.

Irreversible sorption occurs by three mechanisms:

- 1. Occlusion and overcoating,**
- 2. Interlayer collapse of clays, and**
- 3. Sequestering in dead-end pores**

# Irreversible Sorption of Metals

Observation:  
Many metals once sorbed  
can't be desorbed.



Implications:

1. Bioavailability is severely limited
2. Soil leaching will be extremely difficult and/or destructive, and because of 1, probably unnecessary

Data Needs

1.  $\Delta = f(\text{Me, mineral, time})$
2.  $k, n = f(\text{Me, mineral})$

Mechanistic understanding

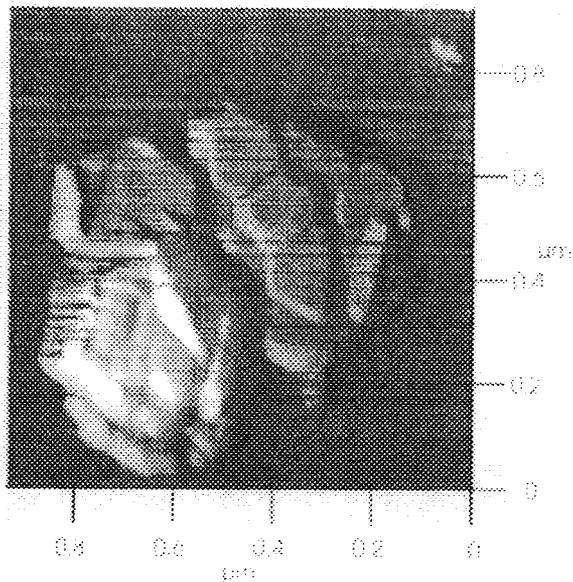
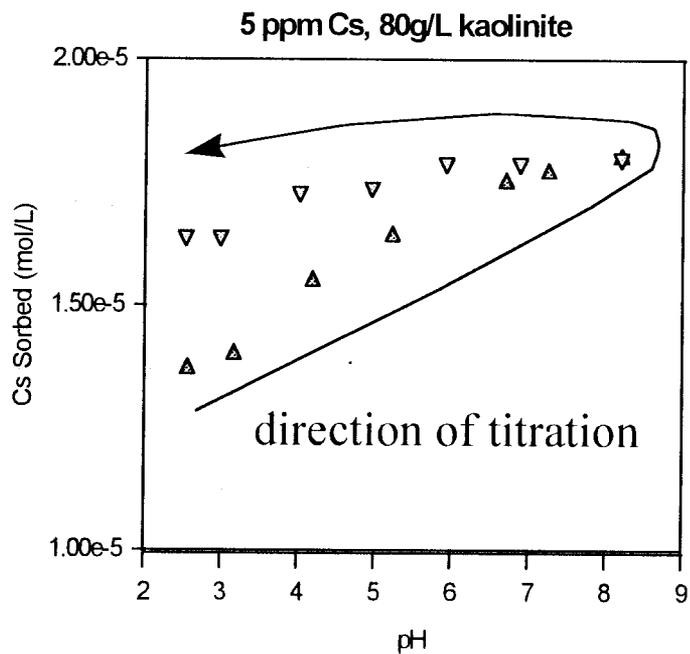
+

Field Calibration

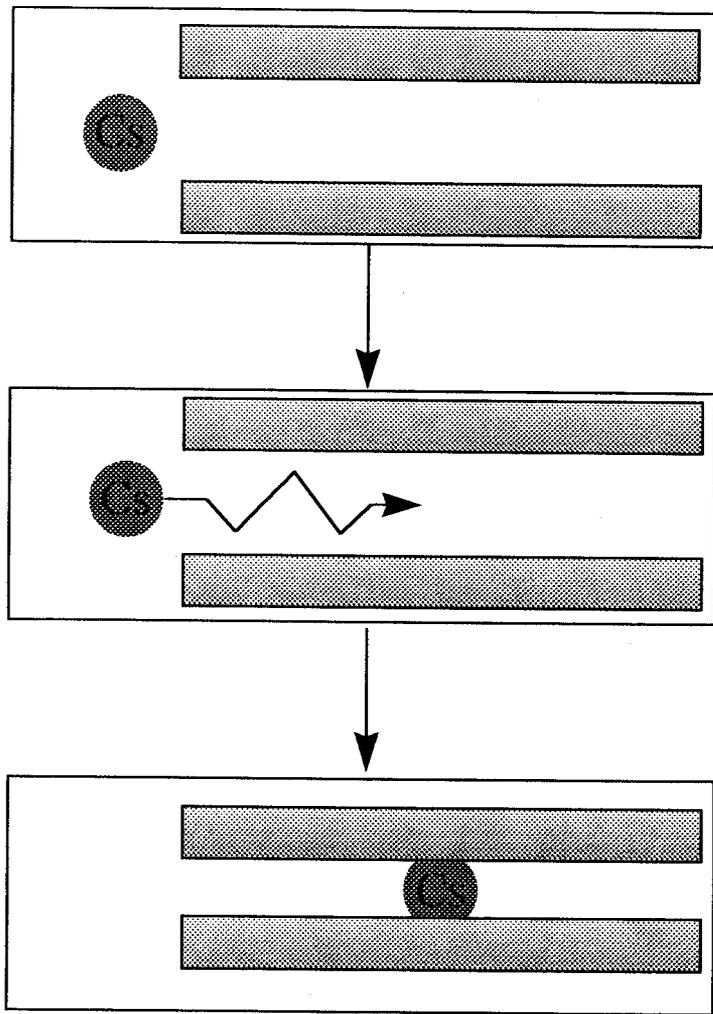
Metal Ion	Mineral(s)	Process
$\text{Cs}^+$	Clays	Migration to charge-deficient innerlayer sites.
$\text{Sr}^{2+}$	Calcite, Clays	Calcite - dehydration and incorporation; Clays - attachment to kink sites, frayed edges (?)
$\text{UO}_2^{+2}$	Fe-(hydr)oxides	Dehydration and occlusion
$\text{Pb}^{2+}$	Fe-(hydr)oxides	Dehydration and occlusion

SAND-8

SAND-9



# Cs Sorption to Clays

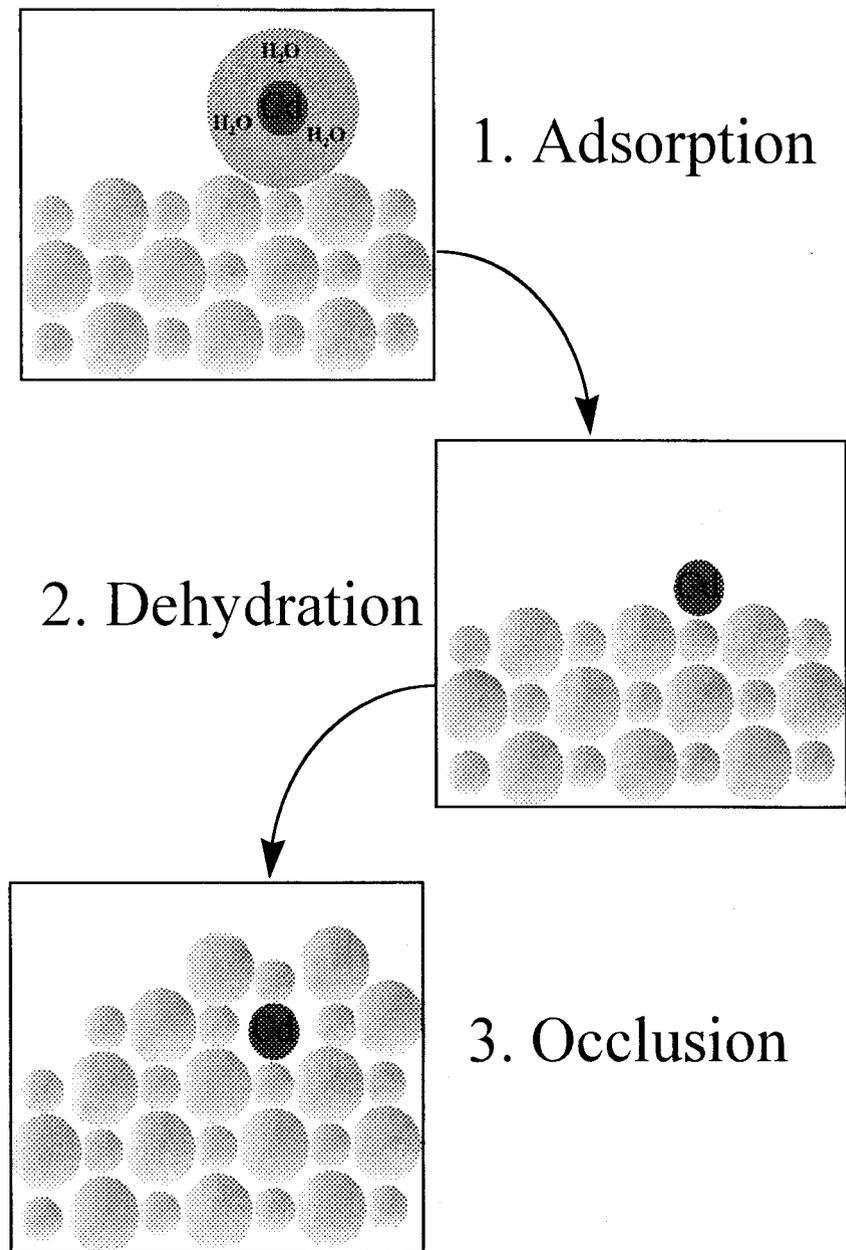
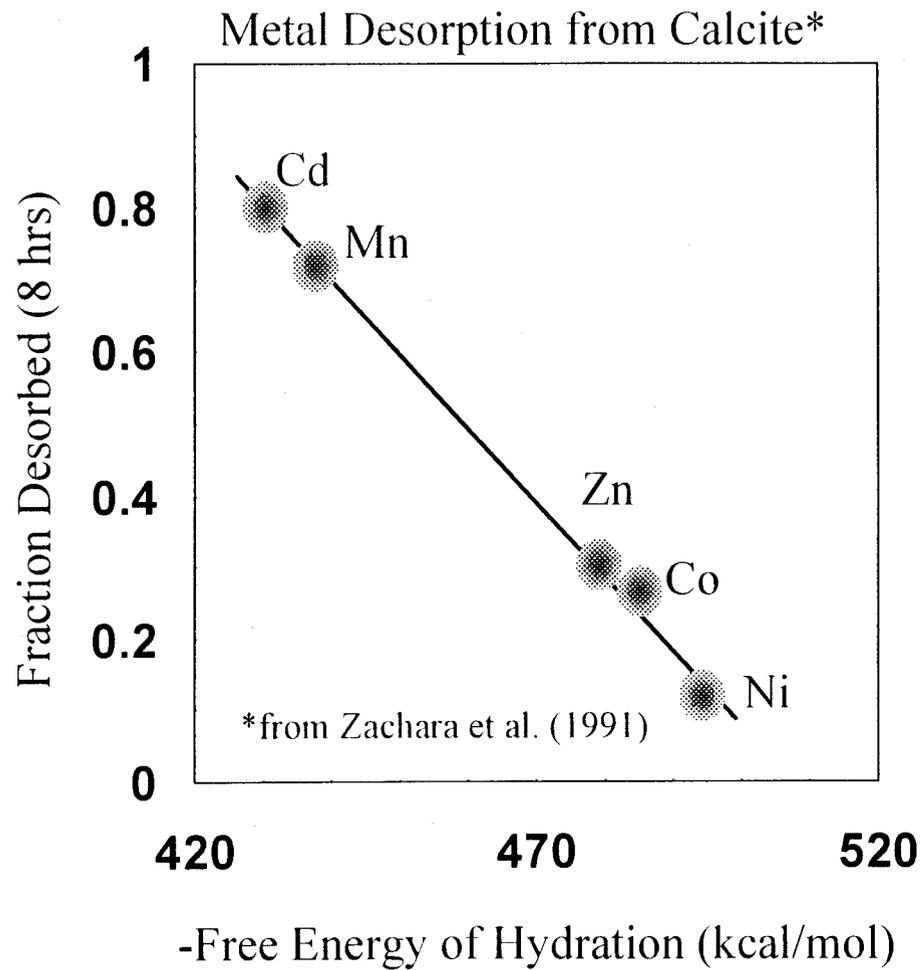


**1. Adsorption**

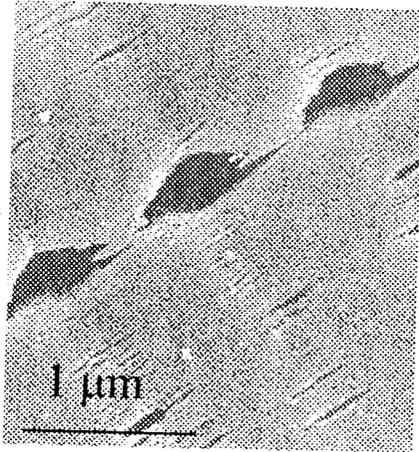
**2. Migration**

**3. Collapse**

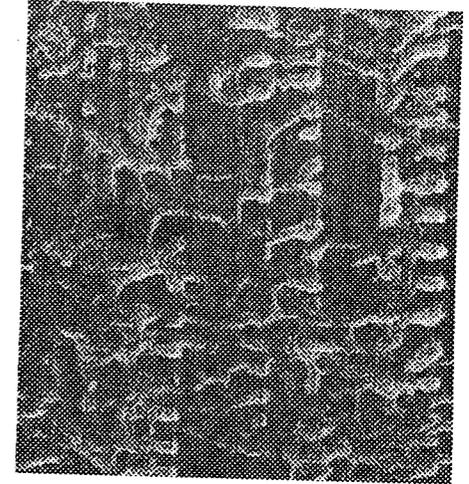
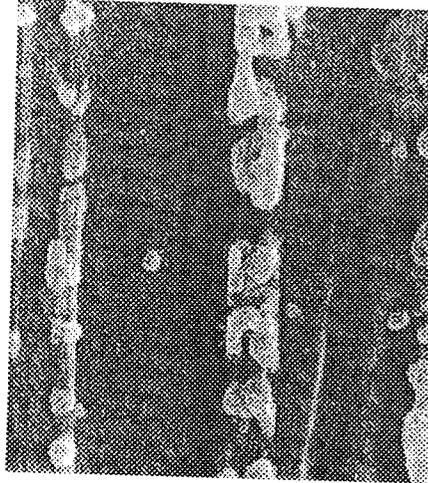
(Courtesy of K. L. Nagy)



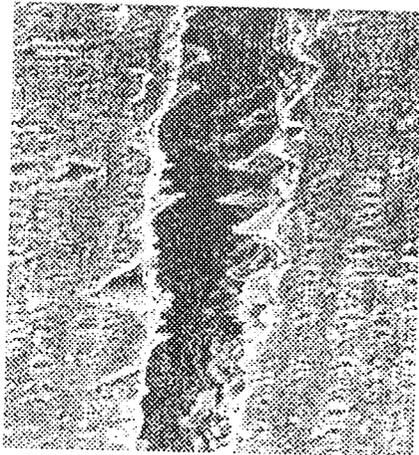
Augite



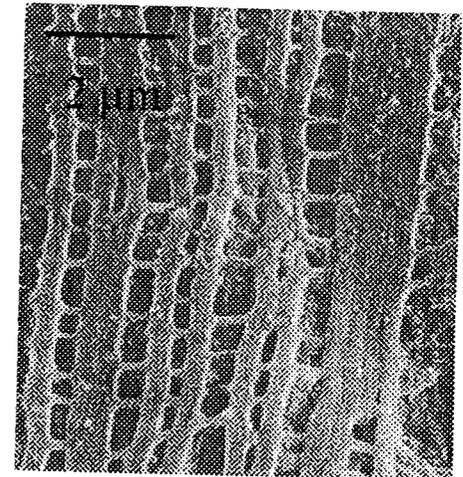
Feldspar



from Berner and Schott (1982)



from Inskeep et al. (1991)

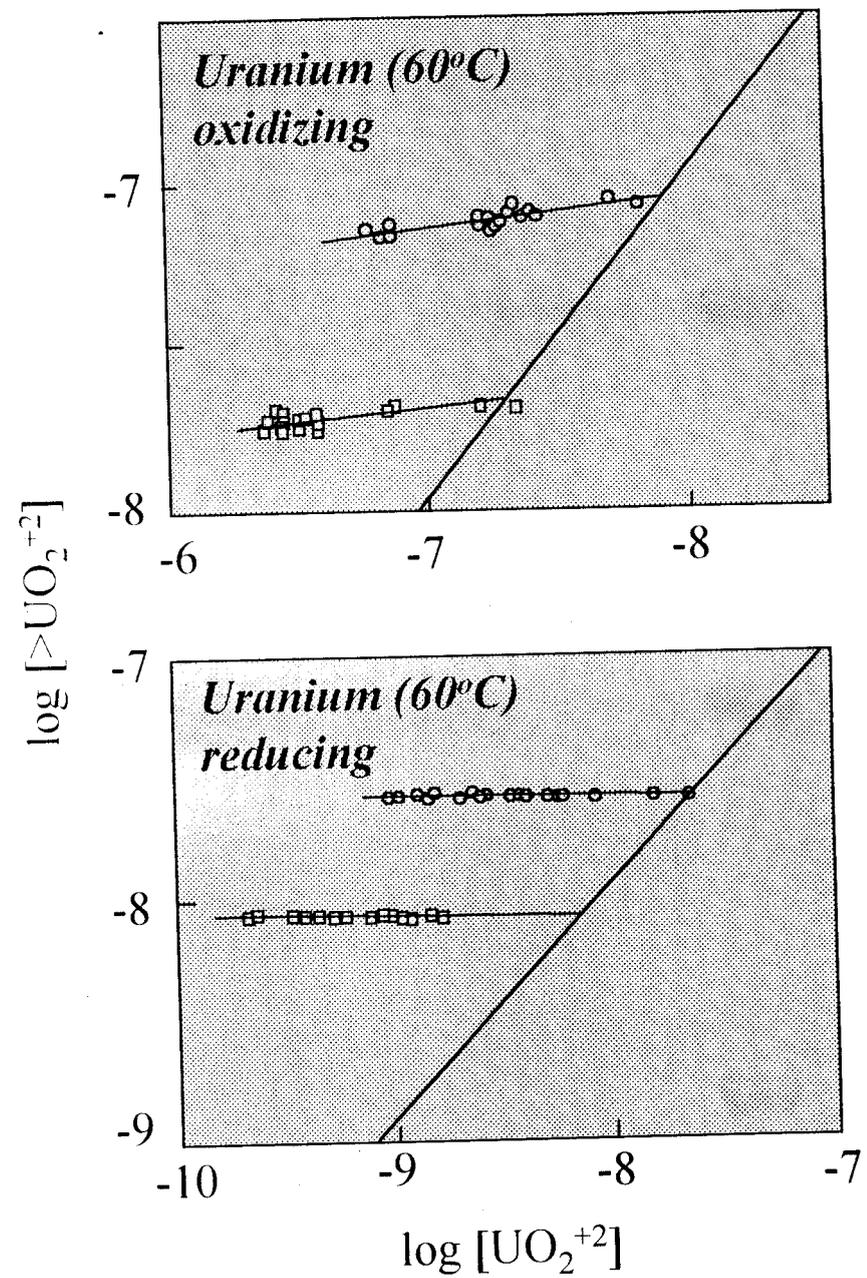


SAND-11

Uranyl sorption on Interbed  
Materials from the Columbia  
River Basalt Formation\*

- Quartz.
- Feldspars.
- Smectite Clay.
- Glass.
- Biotite.
- Hornblende.
- Nontronite.
- Pyroxenes

SAND-12



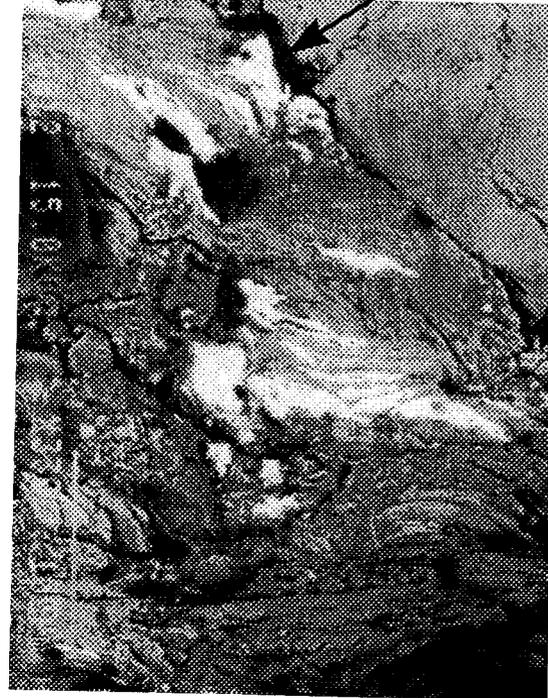
from Barney (1984)

# Feldspar-hosted Contaminants

Cadmium + Iron



Mercury



Vanadium

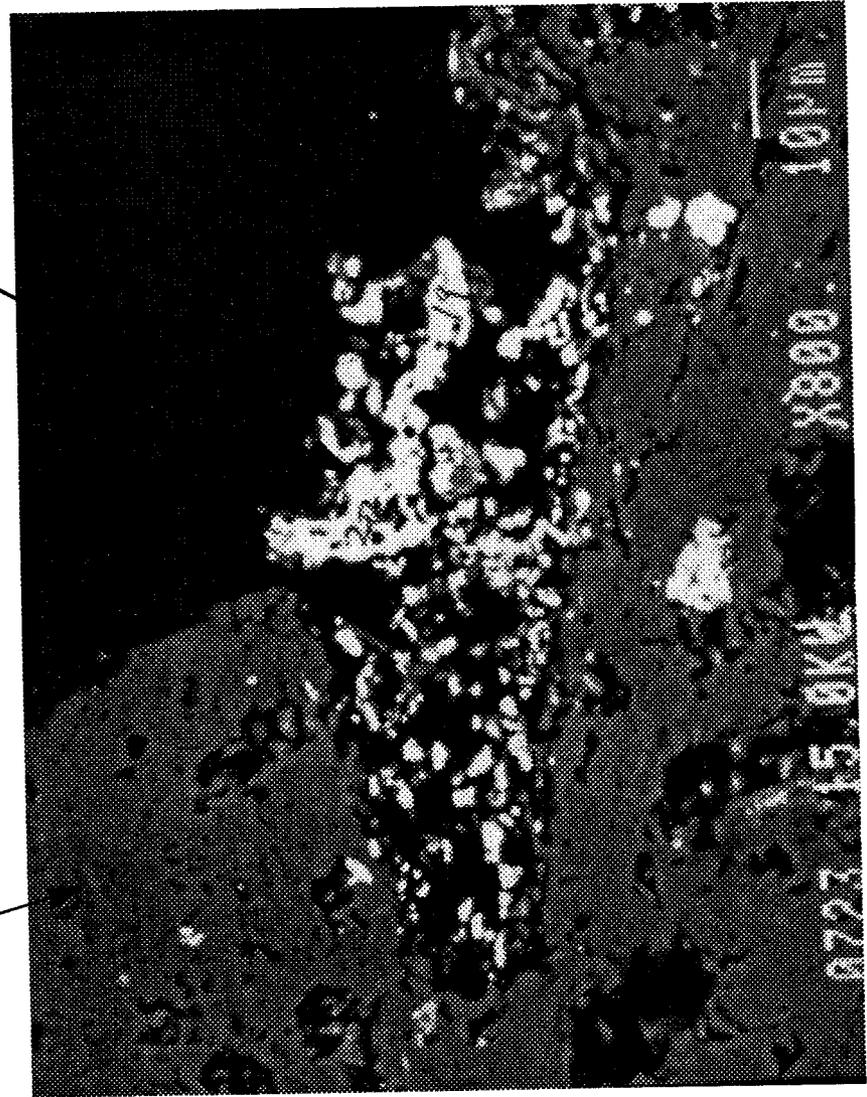


SAND-13

(Courtesy of  
Ron Dorn-ASU)

Pb + FeOOH

Feldspars + Olivine



SAND-14

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Manipulating Radionuclides in Groundwater:  
The Changes, They Are a Timing

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Albuquerque, New Mexico  
June 19, 1997

# Radionuclides of Concern in Oak Ridge:

$^{90}\text{Sr} \gg ^3\text{H} > ^{137}\text{Cs} = ^{60}\text{Co} > \text{TRU} > \text{U}$

Major Off-Site Pathway: Surface Water

(Fishing, Drinking, and Recreation)

Sources: Burial Sites, Impoundments, Tanks, Reactors,  
Groundwater, Sediments.

Control Points and Techniques:

## Source

in situ grouting

in situ vitrification

hydrologic barriers

chemical treatments

retrieval

## Groundwater

hydrologic barriers

chemical treatments

surface water control

## Surface Water

dams

treatment plants

diversions/routing

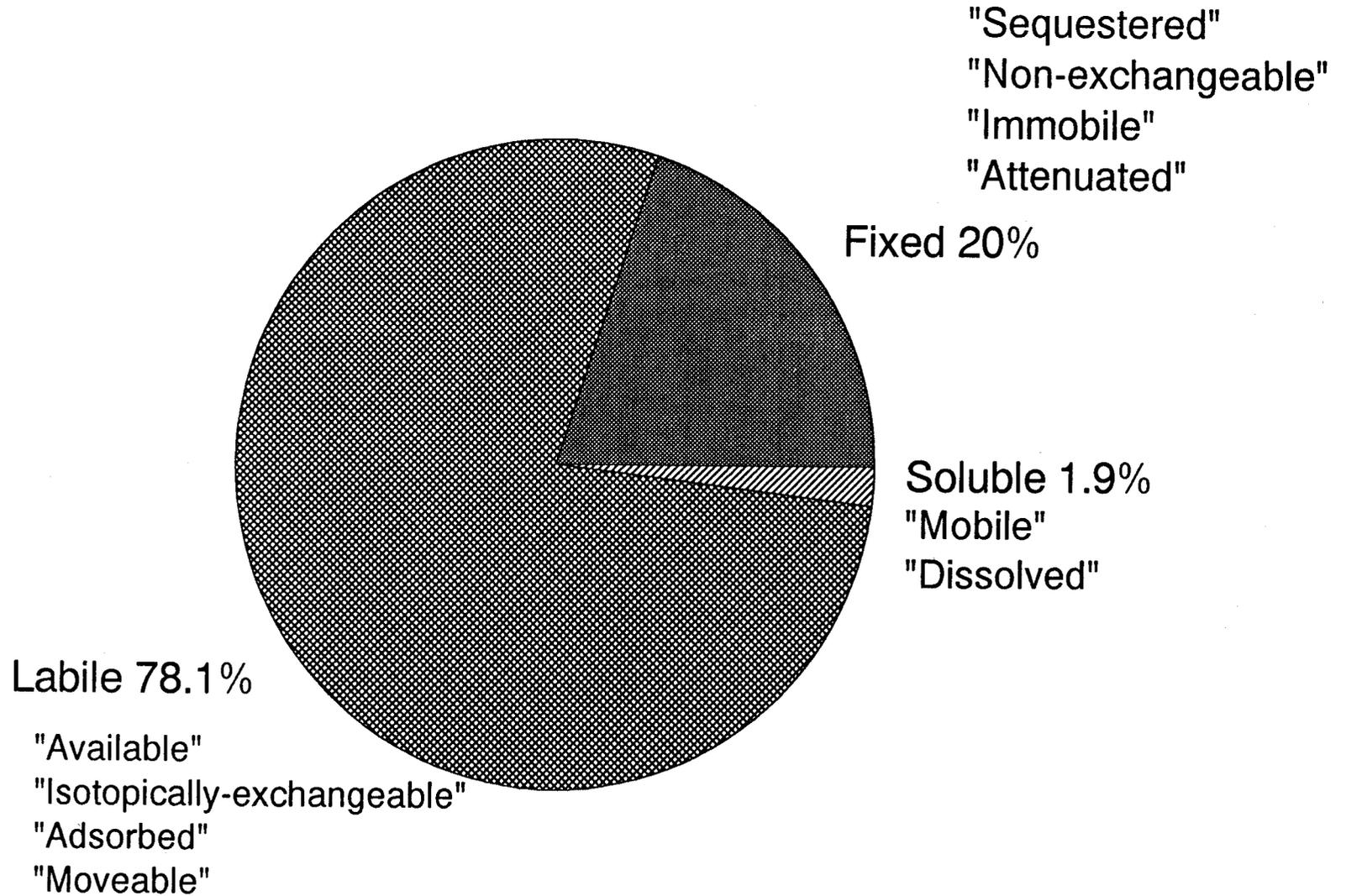
# Approaches to Maximizing Fixed Contaminant Fractions

1. Wait
2. Control Water Flux
3. Aerate/Drain
4. Heat
5. Add Alkalinity
6. Add or Adjust Precipitating Species
7. Add Adsorbing Solids

# Factors Impacting Selection of Remediation Technology (Ranked by Magnitude)

1. Future Land Use
2. Nature of Contaminant(s)
3. Hydrologic Setting or Computer Graphics Glitz
4. Community Advisory Input
5. Soil/Rock/Aquifer Chemistry
6. DOE Funding to Regulatory Agencies
7. Source Term Treatment Technology Effectiveness
8. Anecdotal Information, Legends, and Records

# Typical Distribution of $^{90}\text{Sr}$ in Soil



# Attributes of Radionuclide Contaminants

- Have no effect on concentrations of elements
- Often function as tracer for their stable element
  - $^{90}\text{Sr}$  for stable Sr
- Can function as tracer for similar stable element
  - $^{137}\text{Cs}$  for K       $^{60}\text{Co}$  for Mn
- Are not in equilibrium with total element content
  - $^{137}\text{Cs}$  for Cs in feldspar     $^{90}\text{Sr}$  for Sr in plagioclase
- Are not in equilibrium with total similar element content

# Approaches to Measuring Fixed Contaminant Fractions

1. Exhaustive Leaching vs. Total Contaminant
2. Selective Extractants vs. Total Contaminant
3. Isotopic Dilution of Spike

BPS-7

Examples of Isotopic Exchange:

$^{85}\text{Sr}$  distribution in  $^{90}\text{Sr}$  - contaminated soil

Change in specific activity of a soluble spike of  $\text{Zn}/^{65}\text{Zn}$

## Example of Radioisotopic Dilution to Measure Non-Labile Zinc

A soil is known to contain 1000 ppm total Zn.

A 10:1 (solution:soil) equilibrated groundwater has 1 ppm Zn.

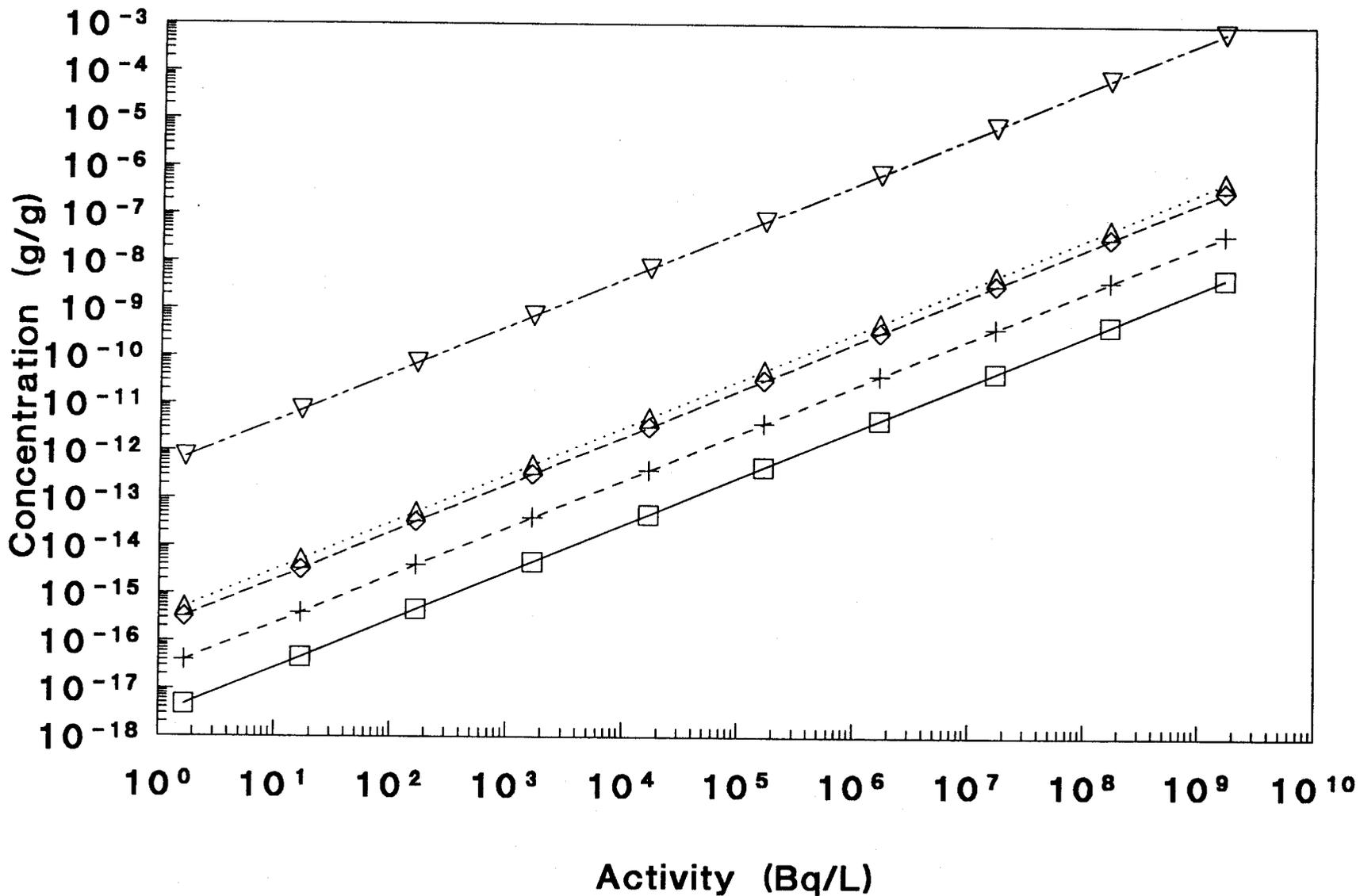
Thus, 99% of the Zn is insoluble.

The system, when spiked with  $^{65}\text{Zn}$ , shows 90% of this isotope is adsorbed at the same equilibrium.

Because the soluble Zn is undisturbed by the  $^{65}\text{Zn}$  spike, the soluble Zn is only in equilibrium with 100 ppm of Zn.

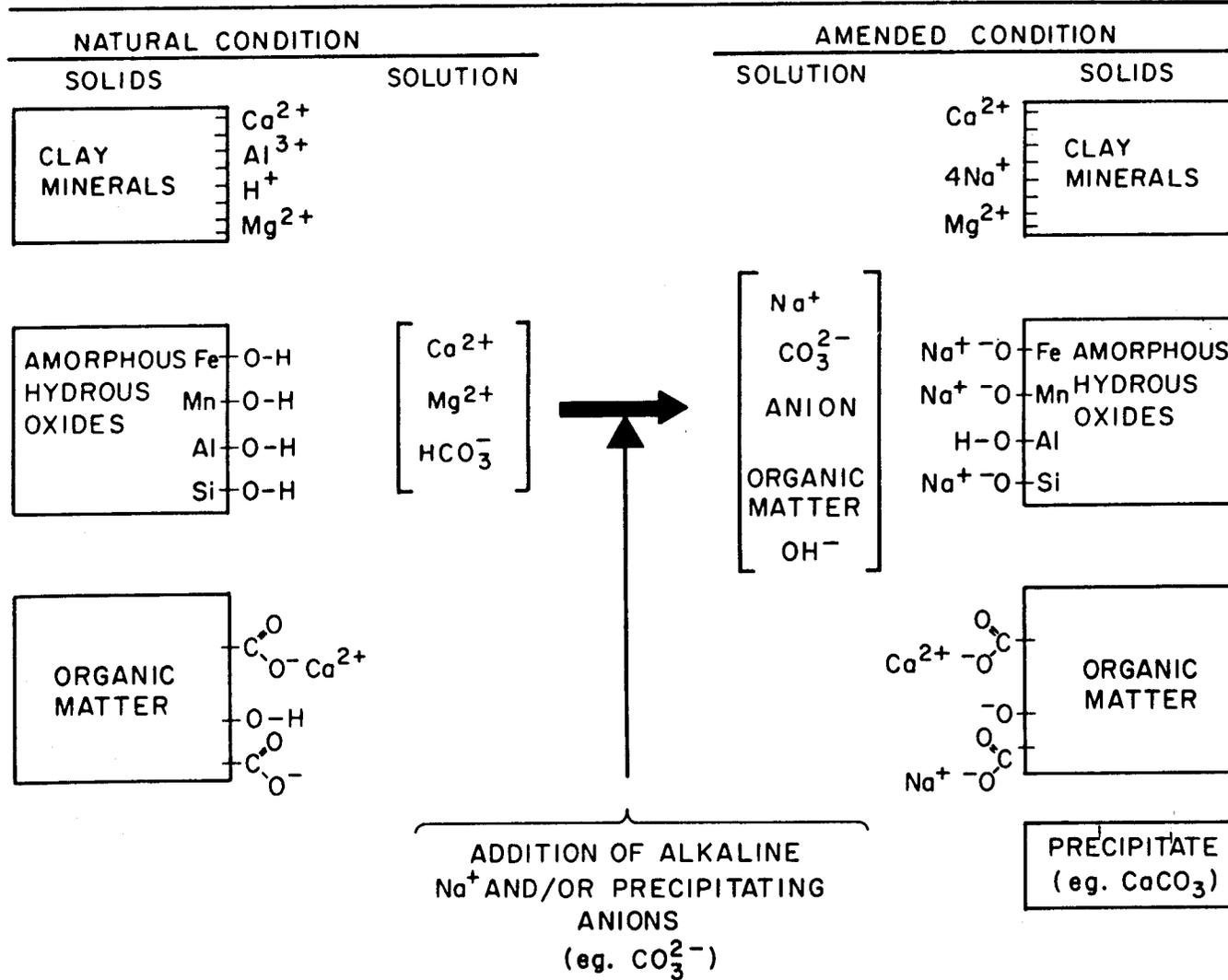
Thus,  $990 - 90 = 900$  ppm (or 90%) of the total soil Zn is not accessible.

# Activity-Concentration Relationships for Selected Radioisotopes



—□—  $^3\text{H}$     - - + - -  $^{60}\text{Co}$     - -◇- -  $^{90}\text{Sr}$     ···△···  $^{137}\text{Cs}$     - -▽- -  $^{239}\text{Pu}$

SOIL COMPONENTS



BPS-10

**EFFECTS OF CHEMICAL AMENDMENT OF BURIAL  
GROUND 6 TRENCH BOTTOM SOIL ON THE  
ADSORPTION COEFFICIENT ( $K_d$ ) FOR  $^{85}\text{Sr}$**

AMENDMENT <sup>1</sup>	$K_d$ <sup>2</sup> 0.002M $\text{CaCl}_2$
NONE	27
LiOH	30000
NaOH	55000
KOH	30000
$\text{Na}_2\text{CO}_3$	470
$\text{Na}_2\text{C}_2\text{O}_4$	122
$\text{K}_2\text{C}_2\text{O}_4$	92
NaF	2440
KF	11000
$\text{Na}_3\text{PO}_4$	3600
$\text{Na}_2\text{SiO}_3$	1300
$\text{Ca}(\text{OH})_2$	123
$\text{NaAlO}_2$	40000

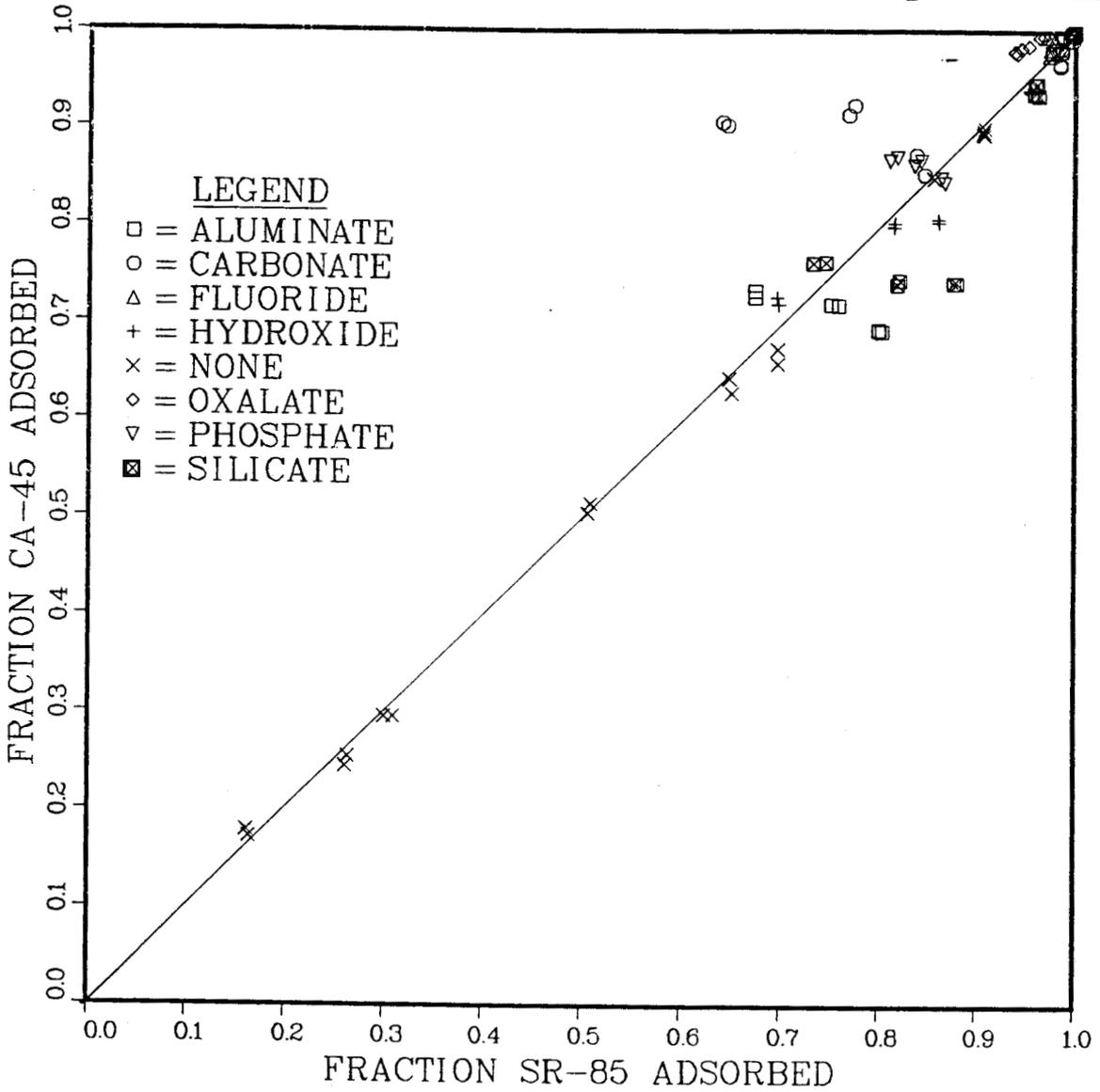
<sup>1</sup>ALL TREATMENTS WERE 0.2 MILLIEQUIVALENTS  
OF CATION PER GRAM OF SOIL.

<sup>2</sup> $K_d = \text{dpm/g SOIL} \div \text{dpm/ml WATER}$

ISOTOPIC DISEQUILIBRIUM DUE TO NON-EXCHANGEABILITY OF  
SR-85 IN PRECIPITATED PHASES IN SOIL

CHEMICAL	Observed	Calculated*	Difference
	(percent of activity in solid phase)		
Na-fluoride	97	85	12
Na-oxalate	97	85	12
Na-phosphate	87	77	10
Na-carbonate	74	56	18

\*Calculations based on equilibrium among precipitable exchangeable, and soluble phases.



# THE CAPACITY OF NATURAL WETLANDS TO AMELIORATE WATER QUALITY: A REVIEW OF CASE STUDIES

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## Abstract

Published and unpublished reports document the extraordinary capacity of natural wetlands to remove metals from mineralized water or mine drainage. Wetlands reviewed herein are located in tropical, temperate, sub-alpine, and arctic climates. They range in size from a few square metres to more than 2,000 hectares, with flow rates ranging from mere trickles (< 0.1L/min) to nearly 7,000 L/min. A wide variety of metals/metalloids, including aluminum, arsenic, cadmium, copper, iron, lead, manganese, nickel, selenium, silver, uranium, and zinc, can be retained by natural wetlands. Wetland sediments can accumulate very high metals concentrations: cupriferous bogs in the Sackville area (New Brunswick, Canada) have up to 10% copper, while some uraniferous wetlands in Sweden reportedly contain as much as 3.1% uranium. A wide variety of plant species are represented in these wetlands, including cattails (*Typha latifolia*, *T. orientalis*), sedges (*Carex aquatilis*, *C. rostrata*, *Eriophorum angustifolium*, *Cyperus* species), rushes (*Scirpus* and *Eleocharis* species.), mosses (*Sphagnum* moss, *Pohlia nutans*), and others. Processes reported to effect metal removal include sorption onto organic matter, association with iron and manganese oxides, metal hydrolysis, reduction to non-mobile forms, and sulphate reduction. The perceived limitations of this technology should be reconsidered in light of the widespread distribution of wetlands capable of ameliorating water quality in mining environments.

**Keywords:** *Natural wetlands, mine drainage, passive treatment, metal removal, mine closure*

## Introduction

Mining operations usually introduce or redirect the flow of water in their immediate vicinity. These discharges may flow into existing wetlands, or stagnate in flat reaches or depressions, wherever wetlands will form naturally. In a surprising number of instances, these wetlands have been observed to improve the quality of the mine water. This has given rise to the concept of using wetlands for treatment of mine drainage.

Despite some attractive features, the mining community has been ambivalent towards wetland (or passive) treatment systems. Their chief advantage is their perceived lower cost, particularly when treatment is required following mine abandonment. However, their use is considered to be restricted to a few circumstances, such as treatment of seeps with low flows and/or low metal loadings, or coal-generated acid mine drainage in the Eastern United States, where they have been shown to be effective. Although there is a vague sense that they might be effective in other regions (or climates), their lack of demonstrated success elsewhere has supported this "niche" categorization.

The Canadian experience with wetlands fits very well the above characterization. Interest was sparked by the apparent success of wetland treatment systems in the Eastern United States.

Studies to examine the viability of this option were commissioned in the 1990's by MEND (Mine Environment Neutral Drainage, Canada's clearinghouse on the problem of mine drainage). Of the four studies MEND sponsored, one indicated that wetlands provide no treatment for low pH, metal contaminated seepages (MEND 1990); two concluded that they only provide treatment for mine drainage with low flows or low metal concentrations (Kalin, 1993, Gormely *et al.*, 1994), and one indicated some removal of iron from partially submerged tailings (Davé 1993). This has hardly been encouraging to environmental managers with serious problems.

However, similar failures, false starts, and partial successes characterize the experience of the United States. For instance, initial reports that *Sphagnum*-type bogs ameliorate coal-generated acid mine drainage (Huntsman *et al.*, 1978; Wieder and Lang, 1982) led to the development of many *Sphagnum*-based wetlands. All these wetlands proved to be short-lived in treating mine drainage, due to the limited capacity of peat to extract metals from mine water (Wieder, 1993). The use of a limestone base or mushroom compost (usually lime-fortified) often obscured the ineffectiveness of early wetlands treating net acidic water. Until anoxic limestone drains (ALD's) were introduced, such systems typically failed within 1 - 2 years of being built (e.g., Ramey *et al.*, 1992). In spite of these setbacks, progress has been made, and new-generation systems can now treat high flows of acidic water (D. Kepler, Clarion, Pennsylvania, United States. Personal communication). Moreover, properly designed cattail-based wetlands have been effectively treating mine water for 10 years or more (e.g., the Simco constructed wetlands, Stark *et al.*, 1994; L. Stark, University of Nevada, personal communication).

These encouraging results have not fully addressed the abovementioned skepticism. What about flows which exceed, say, 1,000 L/min (264 gpm)? What about colder climates, where winter lasts more than 5 months, and where cattails do not grow? What about drainage from metal mines, which may contain arsenic, cadmium, copper, lead, nickel, zinc? What about less common contaminants, like selenium or uranium?

This paper presents several examples which counter such pessimism and makes a case for more widespread usage of wetlands. Few examples of constructed wetlands treating metal mine drainage are available. However, the ability of natural wetlands to ameliorate water quality has often been noted, though these reports are not widely known. In reviewing this literature, the present paper demonstrates that wetlands are capable of retaining a wide variety of metals, perform this function in cold as well as tropical climates, need not be cattail-based, and have frequently satisfactorily treated parts or all of a mine discharge. The paper concludes that limitations in using constructed wetlands do not lie with the wetlands themselves, but in our knowledge of them.

## **Minerotrophic wetlands**

Minerotrophic wetlands (typically fens) receive substantial inputs of groundwater rich in dissolved minerals (Mausbach and Richardson, 1994). If the groundwater dissolves metals by coming in contact with zones of mineralization, these wetlands will receive a steady input of metals at low concentrations. Brooks (1972) reports that the occurrence of "mineral bogs" (wetlands which retain metals and metalloids in high concentrations) has been repeatedly documented since the 1920's, with some reports dating as far back as 1824 (Townshend, 1824, quoted in Brooks, 1972). Levinson (1980) indicates that wetlands frequently accumulate copper,

iron, manganese, uranium, and zinc. Other elements have also been reported to accumulate in wetland sediments (e.g., molybdenum and vanadium, Szalay and Szilágyi, 1968). These reports have largely been unnoticed by environmental managers concerned with acid mine drainage.

The above metals can be retained in wetland sediments at very high concentrations. Uranium reportedly accumulates to concentrations 0.3 - 0.6% in some wetlands of the Western United States (Owen and Otton, 1995). Szalay (1964) reports that some “uraniferous bogs” in Sweden contain as much as 3.1% uranium, on a dry weight basis! Geologists exploring in Northern Canada regularly encounter “pyritic bogs”, in which iron, as pyrite, constitutes 1 - 5% by weight (L. Greene, North Vancouver, British Columbia, Canada; R. Boyle, Ottawa, Ontario, Canada. Personal communications). The conditions in these wetlands apparently resemble those of coastal marshes, where abundant sulphate and organic matter sustain highly active populations of sulphate-reducing bacteria and high rates of pyrite formation (Skyring, 1987; Giblin, 1988).

The organic matter in two “cupriferous bogs” (fens) in Sackville, New Brunswick, Canada, average 2 to 6% copper (Boyle, 1977). At copper concentrations above 0.1%, the wetlands are vegetated exclusively by the “copper moss” *Pohlia nutans*, which can accumulate up to 12% copper (dry weight; dw) in its tissues!<sup>1</sup> While these deposits could not be mined economically, the peat-born copper lodes in the Parys Mountain (Isle of Anglesey, U.K.) were mined since the Bronze age, and at one point in the late 1700’s were the single largest copper producers in Europe (Boyle, 1977). Similarly, copper (metallic, and as sulphide and carbonate minerals) was recovered economically from peat at the Turf Copper Mine in North Wales (Boyle, 1977). The “mineral bogs” at Otanmäki, in Finland, had very high iron (as pyrite), titanium, and vanadium concentrations, and helped to locate an ore body eventually developed as a mine (Salmi, 1955, Brooks *et al.*, 1995). It is possible that the high metal concentrations reported to accumulate in the above wetlands represent upper limits for wetlands treating mine drainage.

Unlike wetlands treating mine drainage, water flowing in minerotrophic wetlands usually contains metal concentrations below 1 mg/L (ppm). Nonetheless, similar biogeochemical processes must be acting in these systems, including interaction with organic matter through adsorption, cation-exchange and chelation (Szalay, 1964), formation of insoluble sulphides (from the biogenic production of hydrogen sulphide), and transformation to elemental or relatively immobile forms, as for copper, selenium (Zhang and Moore, 1996) or uranium (Johnson *et al.*, 1987; Zielinski and Meier, 1988). Therefore, it is possible that wetlands could be designed to attenuate the same elements from mine drainage as minerotrophic wetlands do from seeps.

## Case studies of natural wetlands treating mine drainage

Many natural wetlands have been shown to improve the quality of mine drainage. Those wetlands listed in Table 1 represent only a fraction of them – namely the ones whose performance could be verified for this review<sup>2</sup>. Data regarding wetlands treating mine drainage

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<sup>1</sup> Unfortunately, this moss grows slowly and produces a low biomass, limiting its utility in removing metals.

<sup>2</sup> It should be noted that dilution by groundwater as a possible attenuation mechanism was rarely investigated. In most cases, its contribution to overall water quality improvement cannot be assessed.

elsewhere, such as the wetlands reportedly removing uranium from the McLean Lake or Cigar Lake operations in Saskatchewan, Canada, or the wetland at the Hilton Mine (Queensland, Australia), which reportedly removes Fe, Mn, Tl, and Zn (Jones and Chapman, 1995), could not be fully verified for this report. Furthermore, natural wetlands removing nitrate from mine water were omitted from review, though they are known to exist.

What is striking is that natural wetlands receiving part or all of the discharge from 11 mines listed in Table 1 have treated them to a satisfactory degree. While none of these discharges are acidic, the wetlands can clearly remove an impressive array of potential contaminants.

Information on some of the wetlands listed in Table 1 will be presented as case studies in this section. Each provides a useful lesson. In aggregate, these case studies give a sense of the extraordinary capacity of wetlands to ameliorate the quality of mine drainage.

**Table 1. Natural wetlands shown to ameliorate mine drainage.**

WETLANDS WHICH ONLY PARTLY IMPROVE MINE WATER QUALITY				
Mine	Location	Dominant plant Species	Acidic Drainage	Water quality parameter
Carbonate Mine	Montana	<i>Carex rostrata</i>	Yes	Al, Fe, Pb
Coal mines	Eastern United States	<i>Typha, Scirpus</i> spp.	Yes	pH, Al, Fe, Mn
Coal mine	Mpumalanga mining district, South Africa	<i>Typha</i> , spp.	Yes	pH, Al, Fe, Mn
Dunka Mine	Minnesota, United States	Peat bogs	Yes	Cu, Ni
Equity Silver	British Columbia, Canada	Sedges	Yes	Cu
Mt. Washington Mine	British Columbia, Canada	<i>Eriophorum angustifolium</i>	Yes	Cu, Al
Ranger Mine	Jabiru, Australia	<i>Eleocharis sphacelata</i> <i>Typha</i> species	No	U
WETLANDS WHICH IMPROVE MINE WATER QUALITY TO FULL ENVIRONMENTAL COMPLIANCE				
Birchtree Mine	Manitoba, Canada	<i>Agrostis, Carex</i> spp. <i>Typha latifolia</i>	No	Ni
Cluff Lake, Rabbit Lake	Saskatchewan, Canada	<i>Carex</i> species <i>Sphagnum</i> moss	No	U
Con Mine	Northwest Territories, Canada	<i>Carex</i> species <i>Sphagnum</i> moss	No	CN', As
Hilton Mine	Mt. Isa, Queensland, Australia	Reeds, algae	No	Fe, Mn, Tl, Zn
Quirke Mine	Ontario, Canada	<i>Typha latifolia</i>	Some	Fe, Ra-226
Silver Queen	British Columbia, Canada	Sedges	No	Zn
Star Lake, Jolu	Saskatchewan, Canada	<i>Carex</i> species <i>Sphagnum</i> moss	No	CN', Cu
Tom's Gully Gold Mine	Darwin, Australia	<i>Melaleuca, Typha domingensis</i>	No	As, Co, Cu, Fe, Pb, Mn, Ni, Zn
United Keno Hill Mines	Yukon Territories, Canada	<i>Carex</i> species <i>Sphagnum</i> moss	No	Fe, Mn, Pb, Ag, Zn
Woodcutter's Mine	Darwin, Australia	<i>Typha</i> species	No	Cd, Mn, Pb, Zn

## **Wetlands in the Keno Hill area, Yukon Territory, Canada**

In 1965, Robert Boyle, an exploration geologist with the Canadian Geological Survey, made the following comments about wetlands in the Keno Hill area (Boyle, 1965):

"Streams and springs that dissipate their water into bogs have their zinc (as well as other metals) largely removed. Initially this zinc is loosely bound (but) with aging, the zinc partakes of the organic colloidal complexes and is then (...) unavailable to most extractants. Numerous bogs that extract the zinc from surface waters were observed in the Keno Hill area. One of these into which the mine water from the Hector-Calumet mine flows, effectively removes all of the zinc (40 ppm) in less than 2,000 feet."

This is apparently the first report of a wetland treating contaminated mine drainage. It also documents the highest level of zinc effectively removed from mine drainage (notwithstanding the limitations of analytical techniques at the time).

Interestingly, the area below the former Hector-Calumet mine is presently sparsely vegetated (A. Sobolewski, unpublished observation). Since water stopped flowing through the wetland when mining ceased, it is probable that its vegetation died for lack of water. The present "kill zone" may have been caused by the release of zinc previously accumulated, or because the bog vegetation was more zinc-tolerant. A similar situation was observed for wetlands which had received copper-containing water at another mine. Following mine closure, one wetland which continued to receive a constant flow of water retained its copper, whereas another wetland which did not released its copper to rain water (apparently because the dessicated vegetation "flakes off", physically releasing the metal in particulates).

Two other wetlands removed zinc from water draining the mine complex in the Keno Hill area (A. Sobolewski, unpublished observation). One was a small (11.5 x 3.5 x 0.2 m) wetland, densely vegetated by *Carex aquatilis*, a sedge common in the area. The near-neutral water (pH 6.5) at the inlet had zinc concentrations of 3.2 ppm (mg/L), whereas the wetland discharge had 0.3 ppm zinc. The hydraulic retention time was estimated at approximately 10 to 15 days. Iron, manganese, lead and silver also accumulated in these wetlands.

The second wetland, by the Silver King mine, received a highly acidic (pH 1.1), slow flowing discharge from a waste rock pile (See photograph, opposite; A. Sobolewski, unpublished observation). The water pH was neutralized to 6.6 within a distance of seven to eight feet, as it flowed through the vegetated area of the wetland! Unfortunately, the water chemistry and the wetland were not further characterized. Nonetheless, this



example vividly demonstrates that successful treatment is determined not by water chemistry *per se*, but rather by the relationship between contaminant loading (in this case acidity loading) vs treatment capacity (in this case alkalinity production).

## Natural wetlands removing aluminum, iron, and manganese, Eastern United States

Several natural wetlands have been reported to increase water pH and reduce aluminum, iron, and manganese from acid mine drainage. For instance, a *Typha*-dominated wetland in the Wills Creek watershed (Coshocton County, Ohio) removed at least 89% of input iron and 77% of input manganese from two acidic seeps (pH 4.1 and 5.8, Fe: 449 and 56 ppm, and Mn: 3.85 and 0.08 ppm, respectively) (Fennessy and Mitsch, 1989). Unfortunately, water flows were not reported in this study, precluding the full determination of metal loading rates and removal efficiency.

Thirty-five natural wetlands in Pennsylvania were surveyed to determine their capacity to ameliorate water quality (Stark, 1990). They ranged in size from 30 to 1570 m<sup>2</sup> (median area = 225 m<sup>2</sup>), typically had a shallow surface flow (median depth = 3.0 cm), were mostly *Typha*-dominated, and received acid mine drainage with characteristics shown in Table 2.

**Table 2. Water quality parameters for 35 natural wetlands treating mine drainage**

Parameter	Inlet		Outlet	
	Range	Mean	Range	Mean
Flow rate	1.8 - 193 L/min	50.4 L/min	Same	
pH	3.03 - 6.95	5.01	3.00 - 7.50	4.69
Acidity	-127 - 675 ppm	126 ppm	-150.7 - 393.2 ppm	93.5 ppm
Alkalinity	0 - 254 ppm	53.7 ppm	0 - 191 ppm	32 ppm
Al	1.0 - 106 ppm	11.7 ppm	1.1 - 44.1 ppm	9.85 ppm
Fe	0.5 - 164 ppm	52.5 ppm	0.2 - 113 ppm	20.9 ppm
Mn	0.7 - 97.7 ppm	27.1 ppm	0.2 - 87.1 ppm	23.5 ppm

These natural wetlands were most effective in reducing iron (average 60% reduction) and acidity (average 26% reduction). Metal removal varied considerably among wetlands, but a few were able to achieve >95% removal for iron and for manganese. However, iron and acidity had to be low (< 2.5 and 15 mg/L, respectively) to obtain high (> 50%) removal of manganese. Aluminium removal never exceeded 60%, perhaps because it was usually present at relatively low concentrations.

Similar findings of limited metal removal have also been reported for other, sedge-based wetlands. Swamp Gulch wetland covers 73 hectares (ha), but only a *Carex rostrata*-dominated 4 ha area is mine-impacted. This wetland reportedly reduced input iron by up to 70% from drainage of the abandoned Carbonate Mine (Montana) for the past 55 years (Dollhopf *et al.*, 1988). In 1987-88, the acidic (pH 3.0) discharge flowed at approximately 30 L/min and contained mainly iron (21 ppm), aluminium (6.5 ppm), and manganese (3.9 ppm). Aluminium was also removed in the wetland, but performance data are unavailable. Another wetland at St. Kevin Gulch (Colorado) reportedly removed 50% to 75% of the iron load, but little zinc, from an acidic (pH 3.5) mine discharge (Walton-Day, 1994). In both cases, metal balances and wetland performance could not be fully evaluated because they had multiple discharge points and unquantified groundwater input.

### **Star Lake/Jasper and Jolu, Saskatchewan, Canada**

Several natural wetlands, typical *Sphagnum* and sedge-dominated boreal fens (commonly referred to as bogs or muskeg), were used at Cameco's former Jolu and Star Lake/Jasper operations (Saskatchewan) to polish tailings pond overflow by removing residual cyanide and copper (Gormely *et al.*, 1990). They provided seasonal treatment, mine water being sprinkled over the wetlands during the ice-free season. The Star Lake/Jasper wetlands consistently removed input cyanide by 94% and copper by 98%, on loadings of approximately 1 kg/ha-d (for both contaminants). Processes thought to effect their removal include volatilisation, sorption onto organic matter, biodegradation<sup>3</sup>, and possibly formation of insoluble copper sulphides<sup>4</sup>. The Jolu wetland only removed the above contaminants by 73% and 91%, respectively, but this seemed to be a minimum, as the system had only been in operation for a few weeks when investigated.

### **Cluff Lake, Saskatchewan, Canada**

Cluff Lake is a uranium mining operation in Saskatchewan which benefits (serendipitously, not by design) from the treatment capacity of a wetland. This boreal fen (referred to as bog or muskeg), several hectares in extent, is located along the flow path of portions of the mine discharges. For over 15 years, it has reduced uranium concentrations in the mine drainage (slightly alkaline) by 90% (TAEM, 1995), essentially down to background levels. Since sulphate concentrations are also reduced by a factor of 10 in this fen, it is likely that the wetland sediments are highly anaerobic and reduce the ionic uranium oxide ( $UO_2^{2+}$ ) to the less mobile U(IV) species. Alternatively, the oxide may be complexed with organic matter, in which case only anions capable of forming stable soluble complexes (e.g.,  $H_2SO_4$ ,  $> 0.01 M HCO_3^-/CO_3^{2-}$ , or pyrophosphate) may remobilize it (Zielinski and Meier, 1988). Other metals, notably molybdenum and nickel, are also attenuated by this fen.

### **Silver Queen, British Columbia, Canada**

An adit discharging at 10 to 100 L/min at the former Silver Queen mine, near Houston, British Columbia, has its zinc attenuated as it flows through vegetated areas of the property. The adit discharge has enabled wetland vegetation to become established in and below the tailings pond. The tailings pond stores water in the first half of the year, particularly the highly contaminated discharge produced during the spring freshet. The area below the tailings pond covers 1 - 2 hectares, and has sections of open water (caused by beaver dams) as well as shallower areas vegetated with cattails (*Typha latifolia*) and sedges.

The 2 - 60 ppm dissolved zinc in the (slightly alkaline) adit discharge decreases to 0.5 - 5 ppm in the tailings pond overflow. Zinc is further removed as this water flows below the impoundment through the wetland, to less than 0.1 ppm at a discharge point where compliance is monitored. There is not enough information to determine whether zinc removal results from the extended retention time afforded by the system, or whether the wetland vegetation plays an active role. Even

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<sup>3</sup> Cyanide-degrading microorganisms were detected in the wetlands.

<sup>4</sup> A strong odour of hydrogen sulphide emanated from one of the wetlands at the site.

if it was strictly a question of retention time, the attenuation observed below the tailings ponds would likely not occur if the tailings pond discharged into a creek, instead of the complex wetland system which naturally developed. This is a good example of the (beneficial) development of wetlands which can occur when mining operations redirect water to areas where it was previously absent, as described in the Introduction.

### ***Birchtree Mine, Manitoba, Canada***

For almost 30 years now, nickel has been removed from mine water and atmospheric deposition by a 95 ha fen at the Birchtree Mine, in Thompson, Manitoba (A. Hambley, INCO Ltd, Thompson, Manitoba. Unpublished observations). The mine water flows at an average 320 L/min (only during the ice-free season), is alkaline (pH 8.4) and contains an average 5.1 ppm Ni. In addition, nickel is deposited as dust from a nearby smelter at an average rate of 0.17 kg/ha/m, from dust created by haulage trucks on the adjacent road (by an undetermined amount), and from rainfall. Accounting for all sources, the wetland retains a minimum of 96% of input nickel, mostly within an area measuring 1.8 ha.

### ***Con Mine, Northwest Territories, Canada***

The tailings pond at the Con Mine decants into a series of lakes and wetlands (boreal fens, or muskegs, typical of the area), before its final discharge into Great Slave Lake. The wetlands reportedly attenuate arsenic, cyanide, and copper by better than 90%, from initial concentrations of between 0.4 and 2.0 ppm (Ball, 1993). Although the geochemistry underlying metal removal has not been fully elucidated, the combination of biodegradation (for cyanide), sorption onto organic matter (for copper) and formation of insoluble sulphides (for arsenic and copper) have all been implicated.

### ***Tom's Gully Gold Mine, Northern Territory, Australia***

From 1987 until 1991, when mining ceased, excess water from the Tom's Gully Gold Mine was discharged into a natural wetland (a 20 x 100 m ox-bow billabong<sup>5</sup>) at a rate of approximately 70 L/min (P. Wood, ERA - Ranger Mine, Jabiru, Australia. Personal communication). Most (typically >95%) of the arsenic and metals (Cu, Co, Fe, Mn, Ni, Pb, U, and Zn) in this water (pH 6.8 - 7.0) were retained in the wetland, before it overflowed or seeped into adjacent Mount Bunday Creek (Noller *et al.*, 1994). A follow-up study determined that metals were retained in the wetland surface sediments, mostly associated with iron, and showed no sign of dispersion from the wetland (Eapaea *et al.*, 1995).

### ***Woodcutters Mine, Northern Territory, Australia***

Since mining began in 1984, excess water from the Woodcutter's lead-zinc mine has been discharged into a small, intermittent creek, into and along which large stands of *Typha orientalis* developed (Woods and Noller, 1995). Mine dewatering now produces 10 ML/day (<7000 L/min) or less, which is discharged into the 150 x 2,000 m channel/natural wetland. This saline,

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<sup>5</sup> The wetland is formed when water overflows the banks of Mount Bunday Creek during the wet season, and is subsequently retained.

carbonate-rich water has buffered against acidification from the oxidation of sulphides in the ore and the waste rock, but it contains elevated concentrations of cadmium, manganese, lead and zinc. All these metals are reduced on average by 95% or better, to below acceptable environmental standards (Noller *et al.*, 1994). Ammonia and nitrate are also reduced as water flows through the wetland.

## Conclusions

The treatment of mine drainage “in perpetuity” is an unresolved environmental problem facing the mining industry today. Progress has been made in preventing the generation of acidic discharges, but many mines at closure will still have waste rock piles and adits discharging water of unacceptable quality. Many of them are so remotely located that the economics of operating a treatment plant are prohibitive. For these mines, a passive treatment system would be a sensible option.

Unfortunately, aside from abandoned coal mines, there are few examples of mines using engineered passive treatment systems. Thus, for many people this concept remains untested. The case studies reviewed here provide counter-examples to this view.

The list of elements which can be attenuated in wetlands is extensive. Both commonly encountered elements (As, Cu, Cd, Fe, Pb, Mn, Ni, and Zn) and less common ones (Co, Mo, Ra, Se, Ag, Tl, Ti, U, and V) have been shown to be retained in the natural wetlands mentioned in this review.

Equally surprising is the high concentrations to which they can accumulate in wetland sediments. The available data suggest that metals such as copper, iron, uranium, and perhaps nickel concentrations can reach up to 3 - 6% (dw) in wetland sediments. Quite possibly, these represent the upper limits on the capacity of wetland-based passive treatment systems.

The majority of case studies reviewed here are of mines located in Northern Canada. This reflects the fact that a quarter of the land mass in northern latitudes is covered by wetlands, as well as a bias in the research for this review<sup>6</sup>. It demonstrates that:

1. Wetlands need not be cattail-based to be effective, and
2. Passive treatment of mine drainage in northern latitude is feasible.

The example of the Silver Queen mine is particularly instructive. The onset of mining activity introduced water to the relatively flat area below the tailings impoundment, resulting in the establishment of wetland vegetation. With a suitable habitat and ample food, beavers followed soon thereafter, modifying the landscape to provide greater water retention and further metal removal. The tailings impoundment is so designed as to retain water during the winter and spring seasons – affording better metal removal for the most heavily metal-contaminated water – while water is continuously supplied to the wetland during summer and fall, when it might otherwise dry out.

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<sup>6</sup> I live in Canada, and have more contacts in this country.

Although it was a natural development, we could hardly have designed it better. We would do well to learn from this example.

Undoubtedly, the wetlands reviewed were not optimal from the standpoint of performance. Interpretations of their effectiveness is often confounded by movement of water into or out from the subsurface. No wetland treating acidic water produced environmentally acceptable discharges. It is now known that effective removal of aluminum, iron, and manganese from acidic mine drainage requires a substantial addition of alkalinity, through ALD's or SAPS (Successive Alkalinity Producing Systems), as well as a surface area matched to the contaminant load (Hedin *et al.*, 1994; Kepler and McCleary, 1994; Skousen *et al.*, 1994). It should not be surprising, then, that natural wetlands are not nearly as effective as well-designed and properly constructed treatment wetlands.

One major difference between the wetlands reviewed in this paper and constructed wetlands is their obviously maturity. A well developed detrital layer is often absent in immature constructed wetlands, resulting in less effective metal removal. For example, the Simco wetlands mentioned earlier reached full maturity after approximately 6 years, and this maturation process coincided with increased removal efficiency (Stark *et al.*, 1994).

Diagenetic processes are also more fully evolved in mature wetlands, yielding clues about the possible long-term fate of metals retained in constructed wetlands. The frequent occurrence of organically-bound metals (copper, uranium) or sulphides (arsenic, copper, iron) clearly indicates the importance of organic matter and sulphate reduction in the long-term retention of these metals in wetlands. The high metal concentrations measured in some wetlands suggest that it may even be possible to recover economically metals retained in old treatment wetlands.

The wetland at the Hector-Calumet mine provides another useful lesson: metals will be retained by wetlands as long as they remain wet. Once mining ceases, wetlands may release the metals they accumulated if water is no longer supplied to them and their vegetation dies out. Thus, a necessary component in the design of a passive treatment system for use at closure is the assurance of a constant water supply.

Even in cases where chemical treatment is the preferred method for removing metals, it may still make economic sense to use wetlands as a polishing step. A combination active/passive treatment system may be designed, whereby a treatment plant removes the bulk of metals while a wetland system removes residual metals. Savings would be accrued from reduced reagent costs and from lower sludge disposal costs (reflecting both the smaller volumes produced and possibly the absence of leachable metals). The above review indicates that most elements requiring treatment could be removed in a wetland.

In conclusion, the case studies reviewed in this paper strongly suggest that constructed wetlands are a viable option for passive treatment of mine drainage. These examples demonstrate that with ingenuity, the capability of wetlands to ameliorate water quality can be exploited and significantly enhanced.

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Metal attenuation from mineralized  
seeps and mine drainage by  
natural wetlands

André Sobolewski

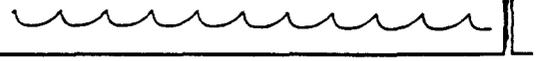
Microbial Technologies

# Key points of presentation

- Wetlands are natural sink for metals
- Many metals can be retained
- Provide long-term treatment
- Worldwide distribution
- Can be designed for efficient metal removal

# Order of presentation

- Uraniferous wetlands in USA
- Flodelle Creek, Washington State
- Cluff Lake, Canada
- Woodcutters Mine, Australia
- Birchtree Mine, Canada
- United Keno Hill Mine, Canada
- St Hilary Mining District, UK



**CLUFF LAKE OPERATION**

**STATUS OF THE  
ENVIRONMENT REPORT**

Prepared for:

**Cogema Resources Inc.  
Saskatoon, Saskatchewan**

Prepared by:

**Terrestrial & Aquatic Environmental Managers Ltd.  
and  
SENES Consultants Ltd.**

**March 1995**

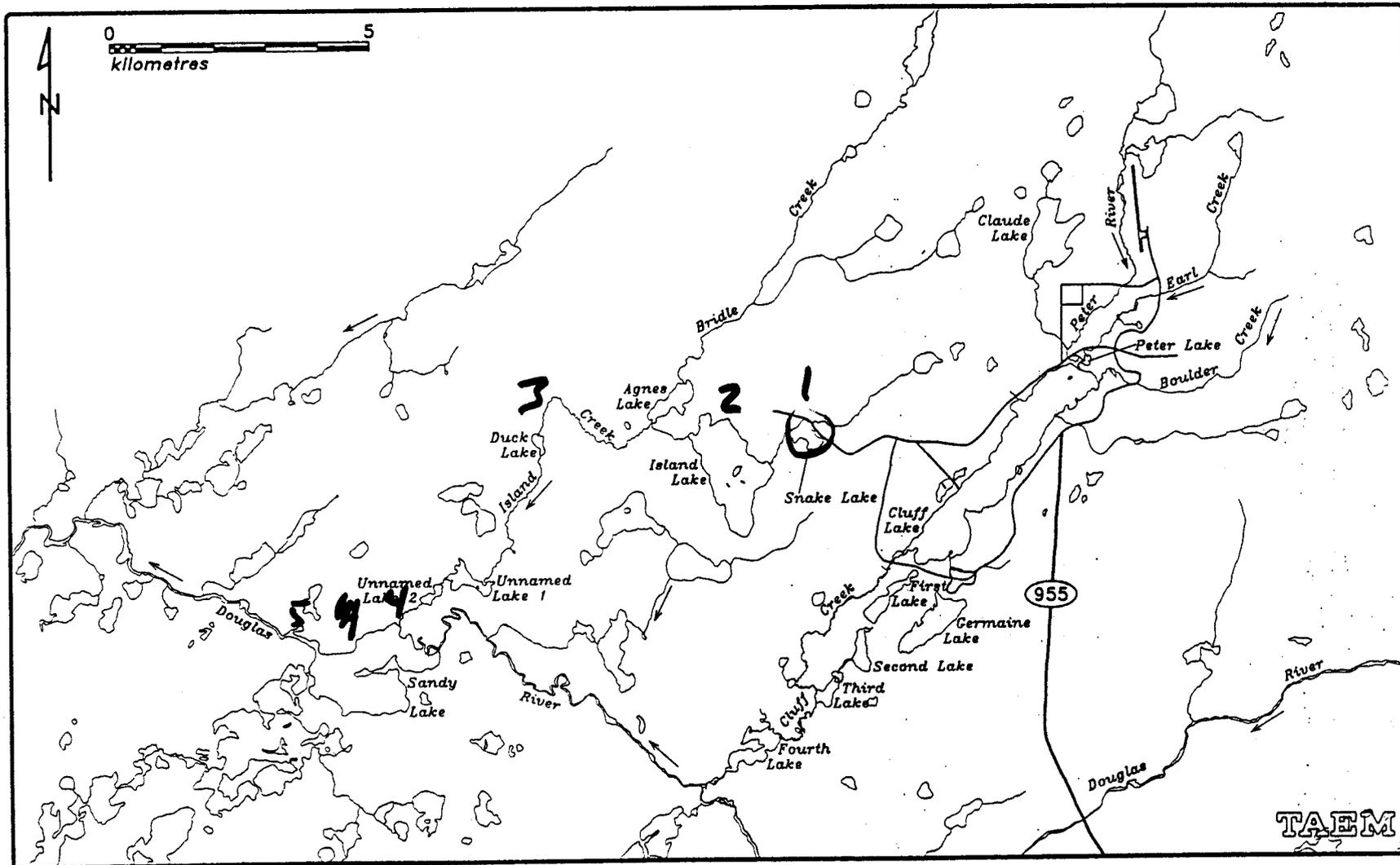


FIGURE 1.1-2 Study area.

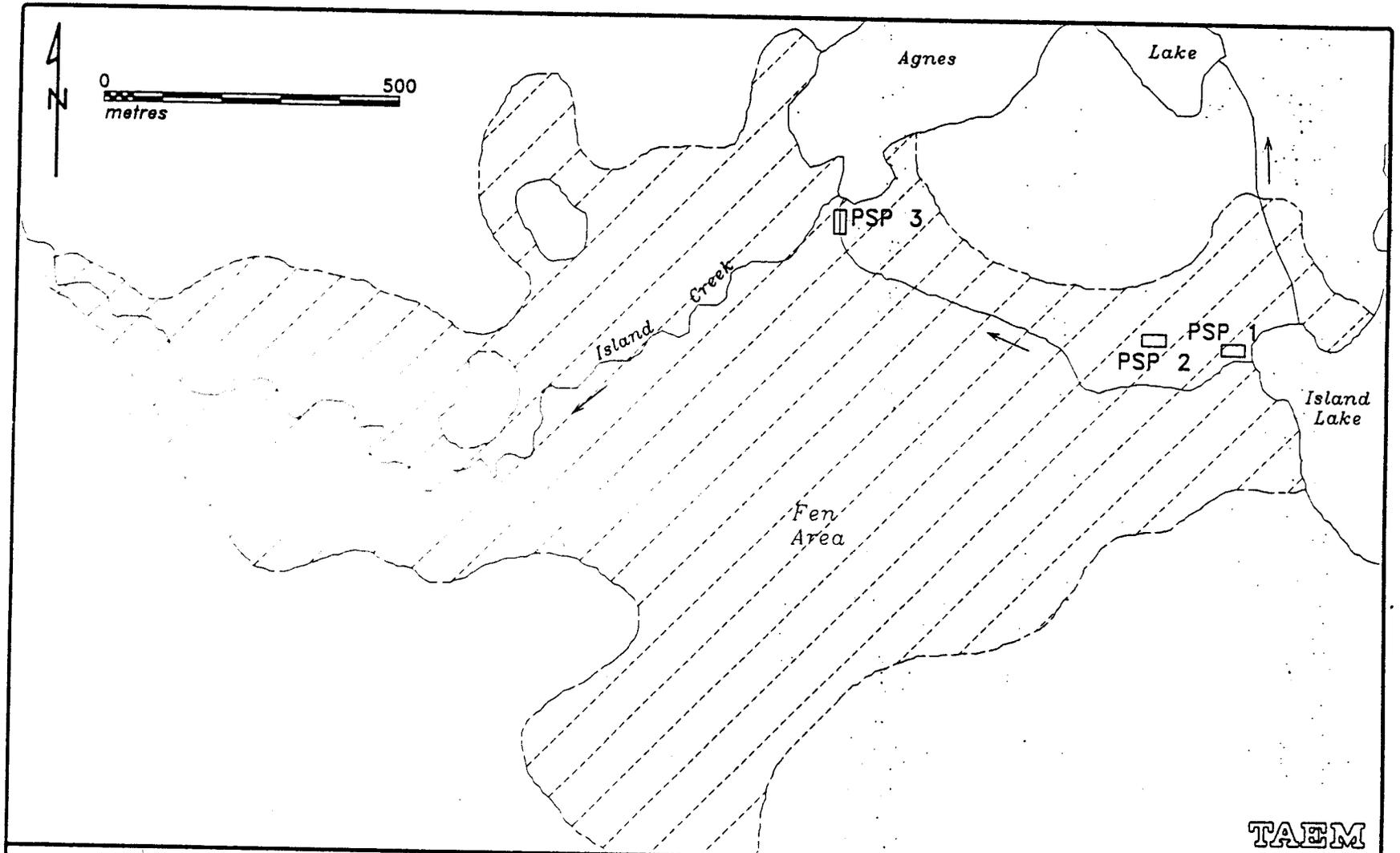
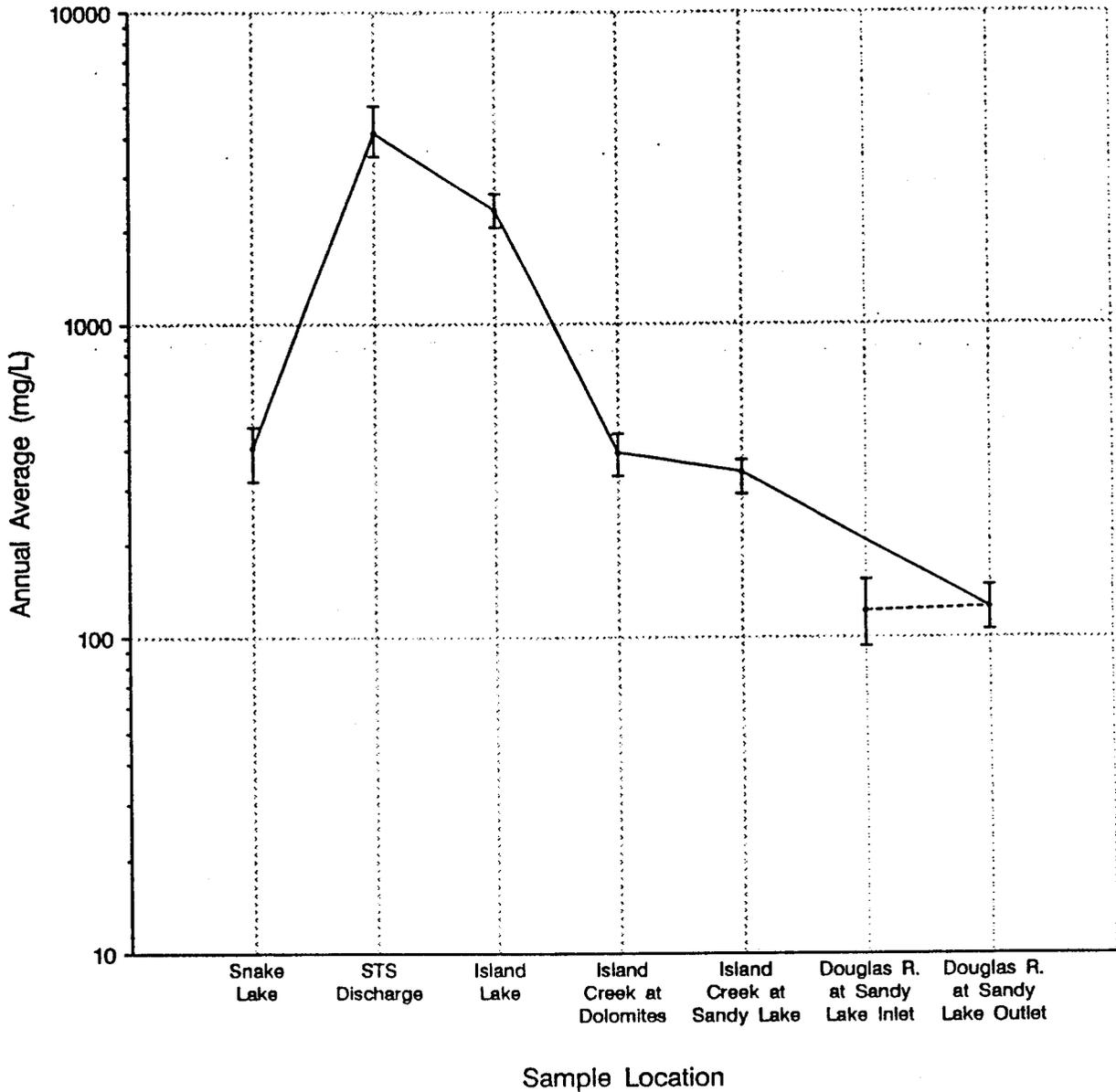


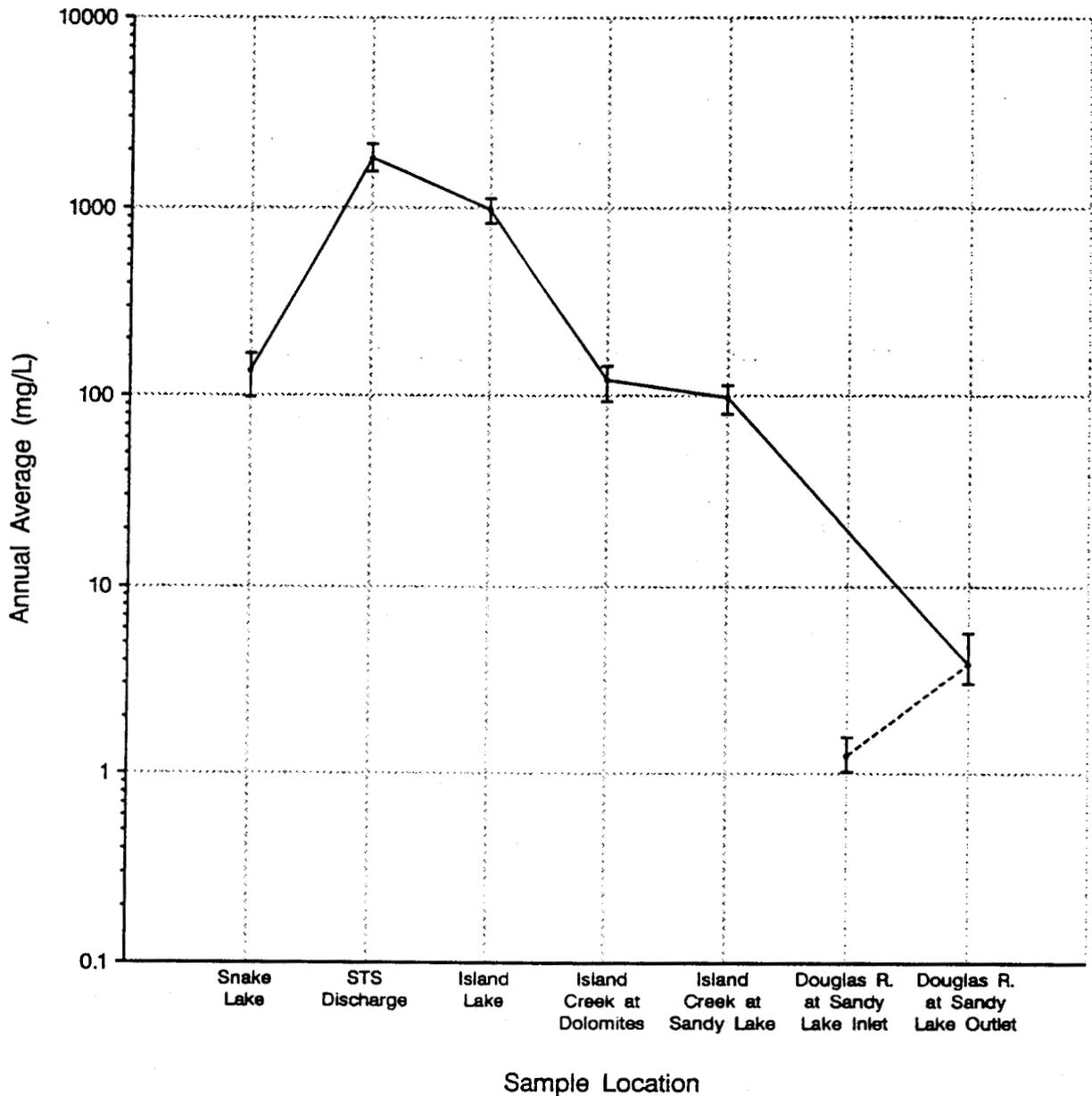
FIGURE 3.5.2-2 Location of Permanent Sample Plots (PSP's) in the Cluff Lake Project area.

Change of Water Quality along Drainage System  
 - Total Dissolved Solids



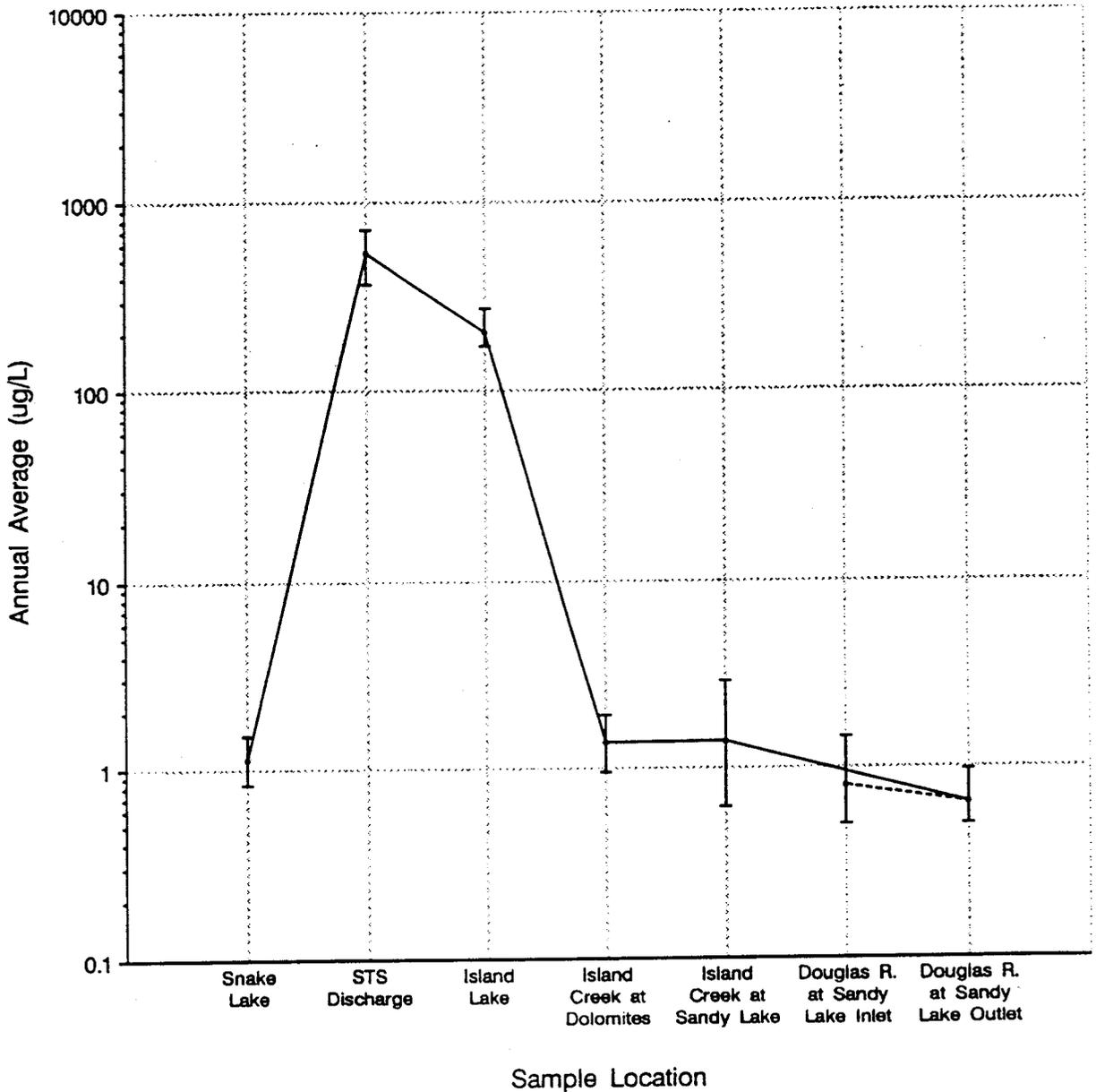
Vertical bars show the range of annual averages in 1989-1994 period.  
 Solid line represents system starting from Snake Lake and dotted line indicates water quality of Douglas River at Sandy Lake inlet and outlet

Change of Water Quality along Drainage System  
 - Sulphate



Vertical bars show the range of annual averages in 1989-1994 period.  
 Solid line represents system starting from Snake Lake and dotted line indicates water quality of Douglas River at Sandy Lake inlet and outlet

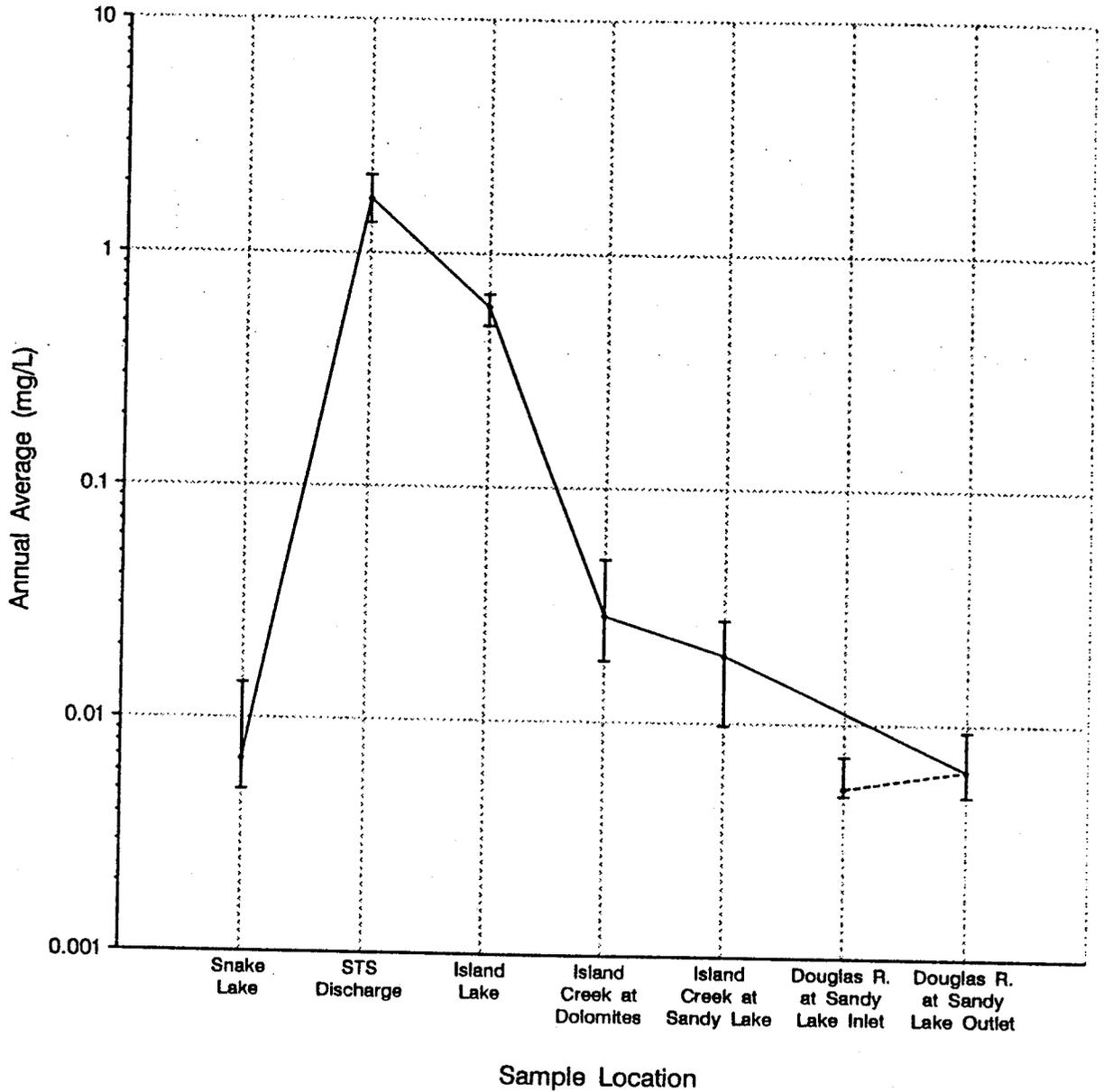
Change of Water Quality along Drainage System  
 - Uranium



Vertical bars show the range of annual averages in 1989-1994 period.

Solid line represents system starting from Snake Lake and dotted line indicates water quality of Douglas River at Sandy Lake inlet and outlet

Change of Water Quality along Drainage System  
 - Molybdenum

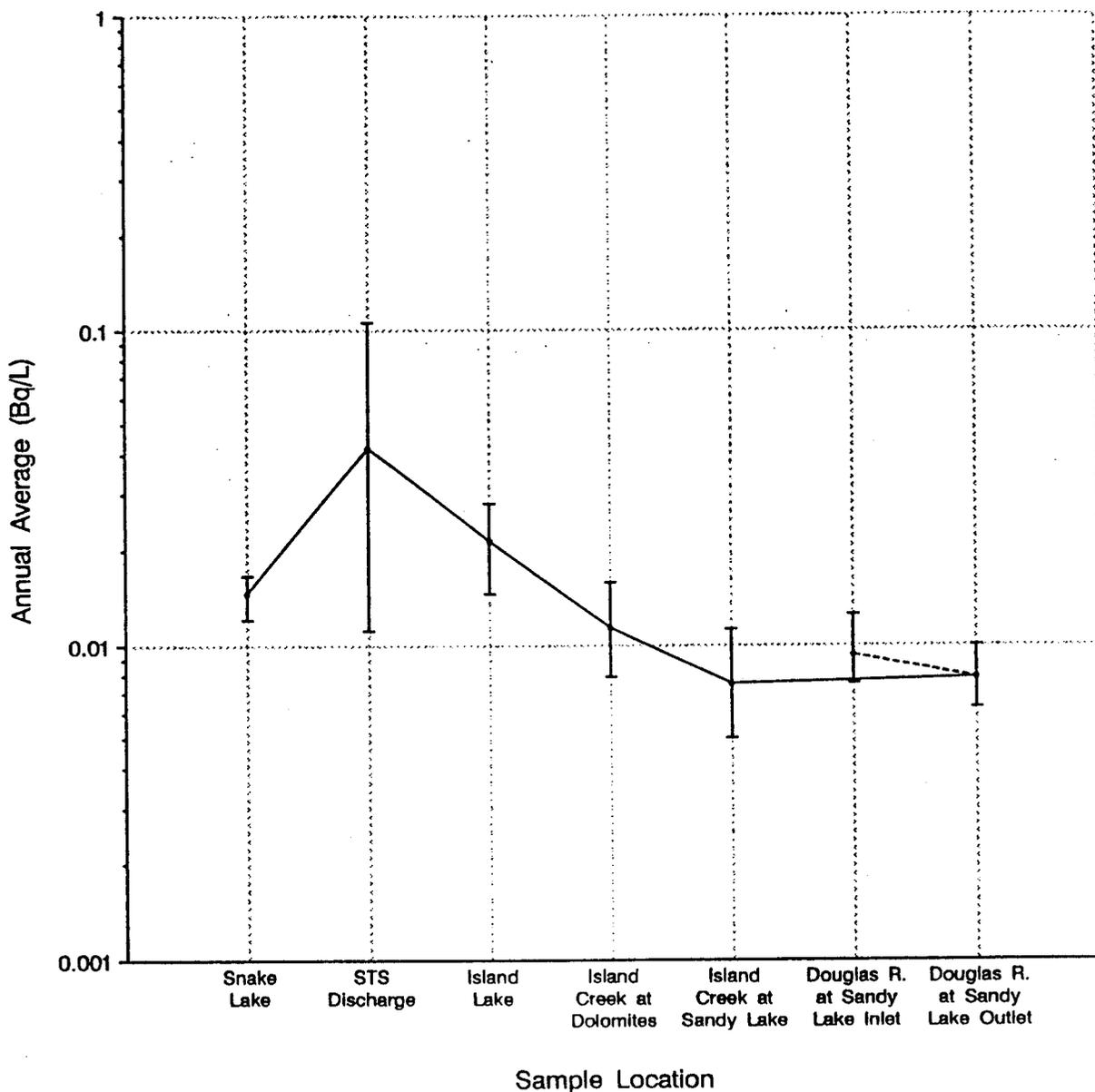


Vertical bars show the range of annual averages in 1989-1994 period.  
 Solid line represents system starting from Snake Lake and dotted line indicates water quality of Douglas River at Sandy Lake inlet and outlet

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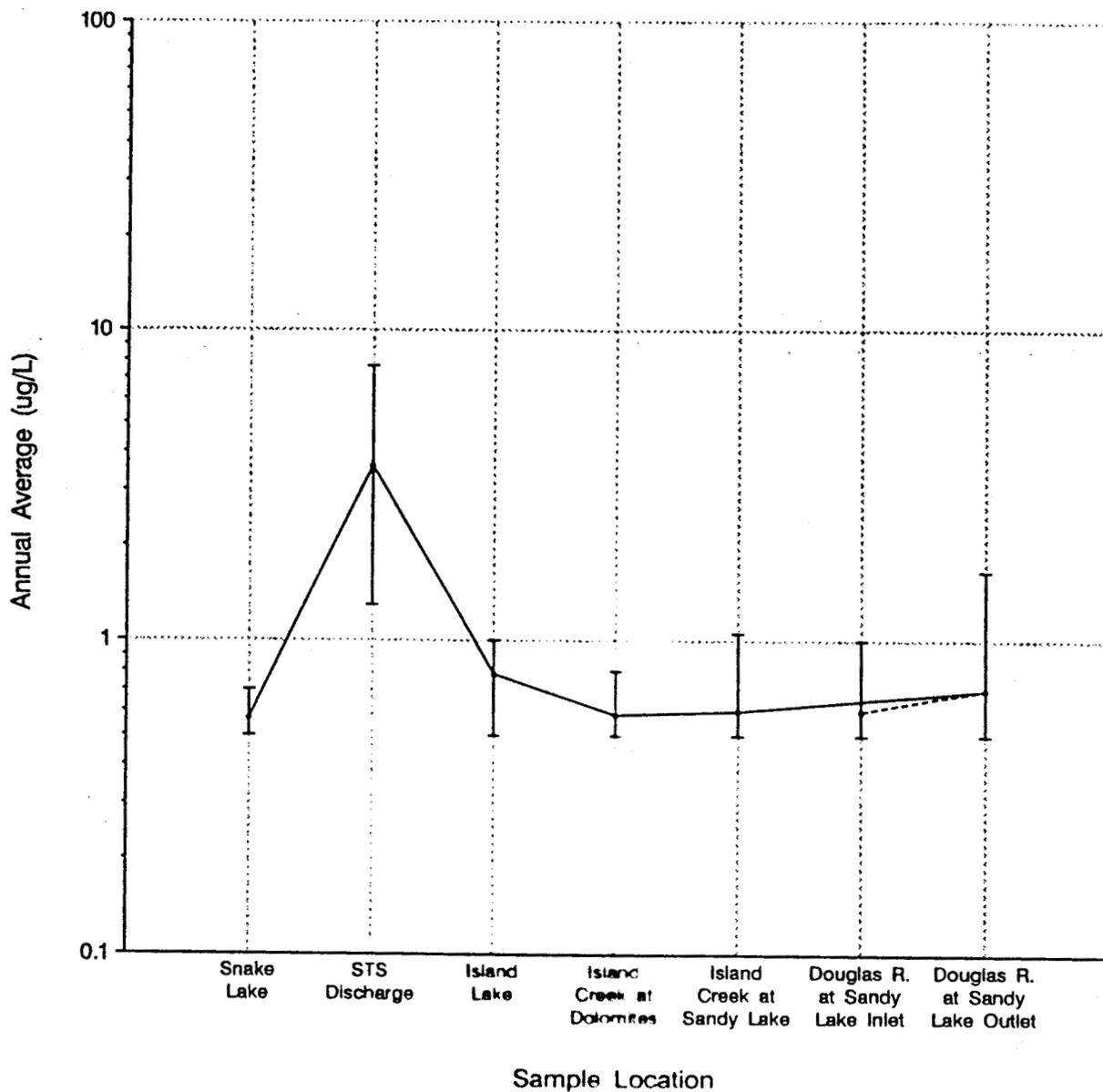
Change of Water Quality along Drainage System

- Ra - 226



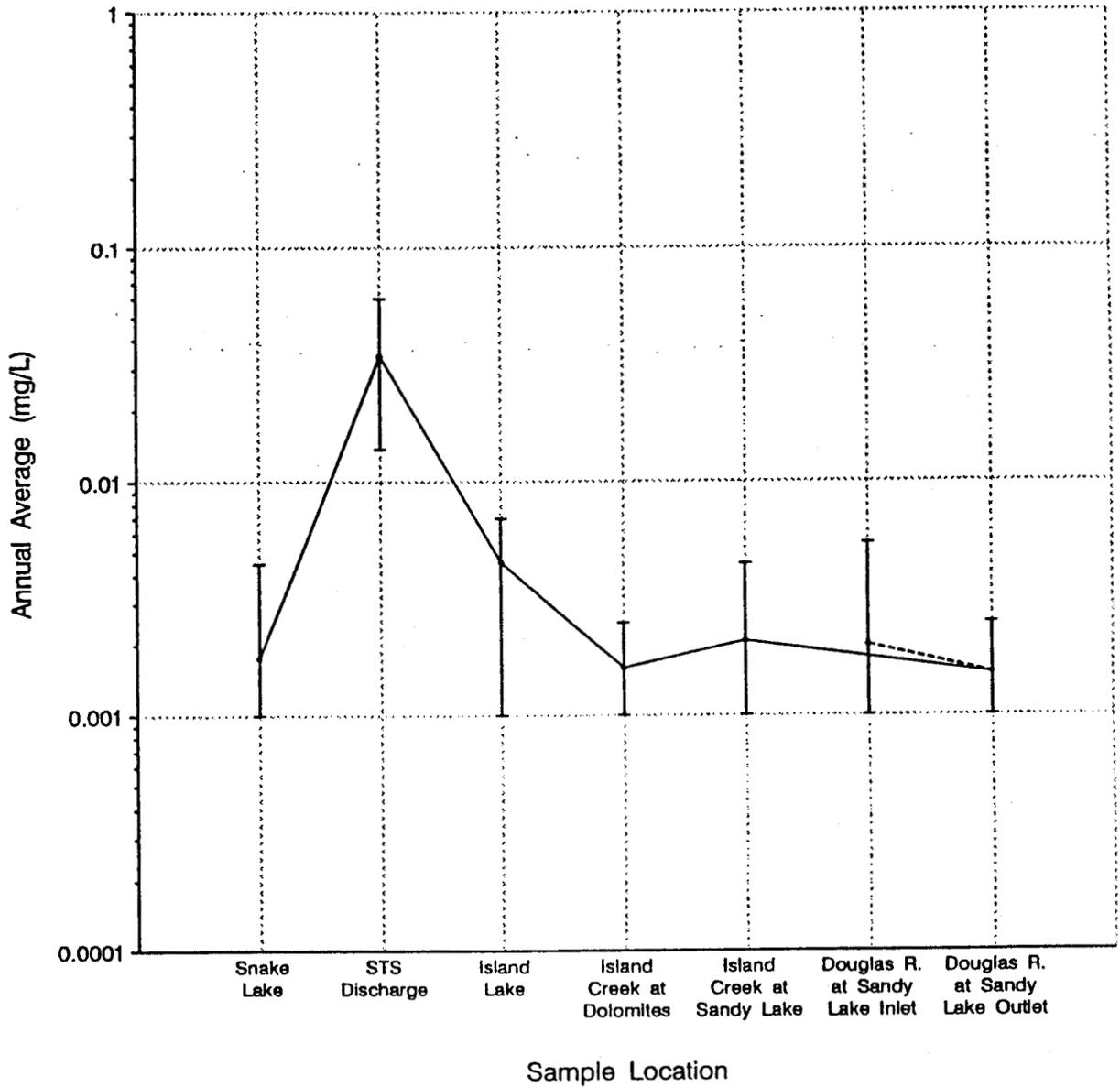
Vertical bars show the range of annual averages in 1989-1994 period.  
 Solid line represents system starting from Snake Lake and dotted line indicates water quality of Douglas River at Sandy Lake inlet and outlet

Change of Water Quality along Drainage System  
 - Arsenic



Vertical bars show the range of annual averages in 1989-1994 period.  
 Solid line represents system starting from Snake Lake and dotted line indicates water quality of Douglas River at Sandy Lake inlet and outlet

Change of Water Quality along Drainage System  
 - Nickel



Vertical bars show the range of annual averages in 1989-1994 period.  
 Solid line represents system starting from Snake Lake and dotted line indicates water quality of Douglas River at Sandy Lake inlet and outlet

## Woodcutters Mine, Northern Territory, Australia

Water from the Woodcutters lead-zinc mine has been discharged since 1984 into a small, intermittent creek, into and along which have developed large stands of cattails (*Typha orientalis*) and sedges (*Eleocharis* spp.) (opposite photo. J. Milne, Northern Territory Dept. Mines & Energy, Australia).

Mine dewatering now produces 10 ML/day (<7000 L/min) or less, which is discharged into the 150 x 2,000 m channel/natural wetland. The water contains elevated concentrations of cadmium, manganese, lead and zinc. The metal concentrations are reduced on average by 95% or better, and meet acceptable environmental standards, as indicated in Table 1 (Noller *et al.*, 1994; Woods and Noller, 1995). Ammonia and nitrate are also reduced as water flows through the wetland.



**Table 1. Metal concentrations (ppb) in discharge from Woodcutters Mine.**

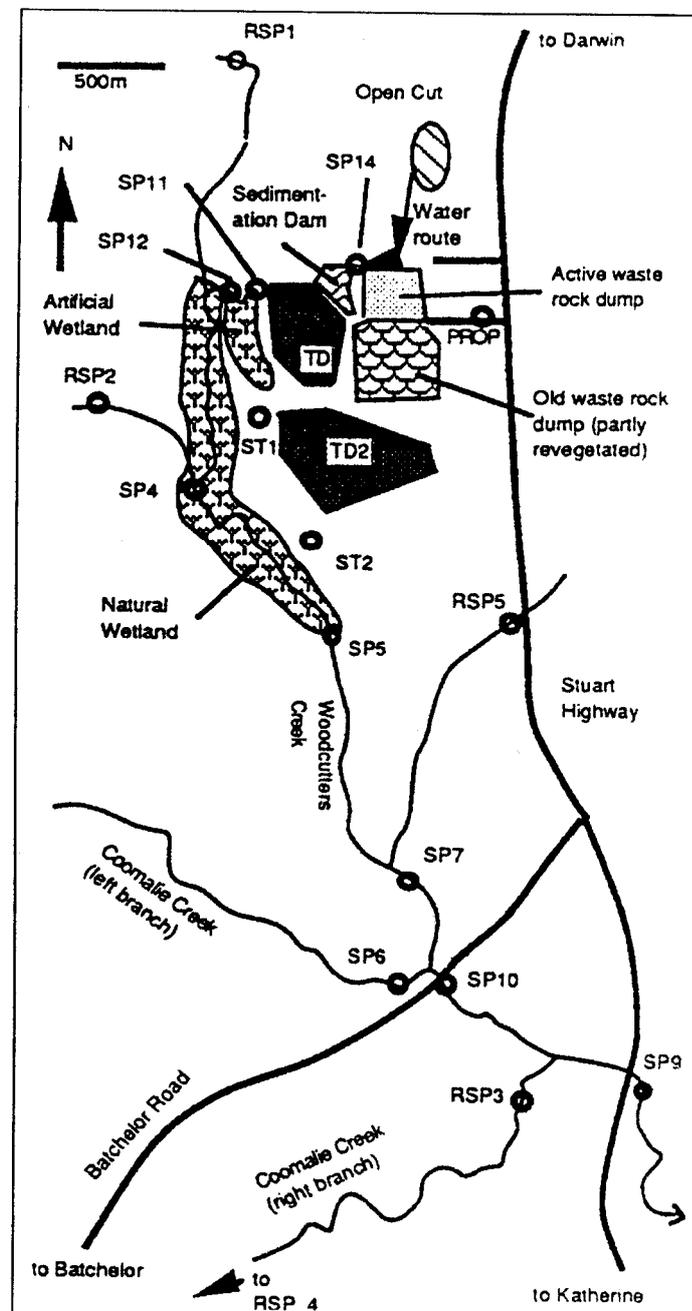
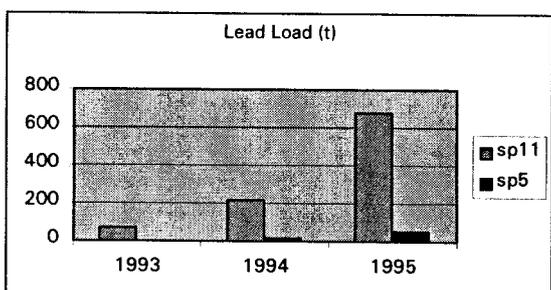
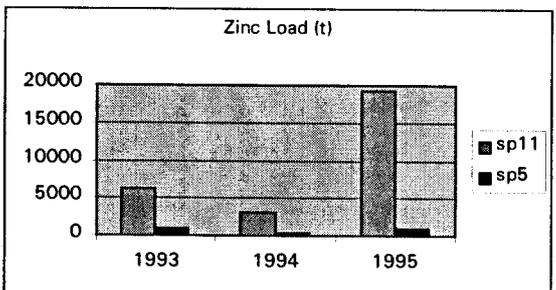
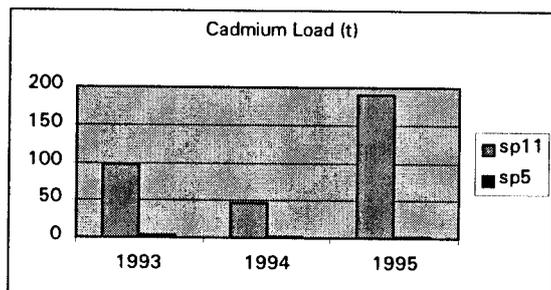
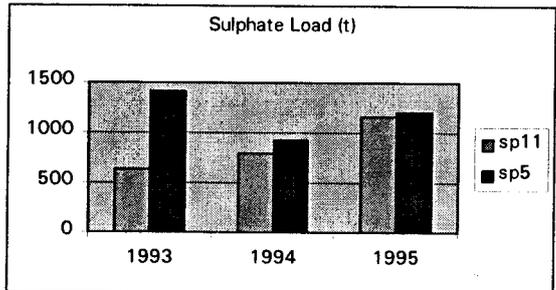
Sampling point	As	Cd	Cu	Mn	Pb	Zn
Wetland inflow (0.0 km)	5	63	1.4	600	12	6,900
Mid-point (0.8 km)	3	63	1.7	580	7.3	5,600
Wetland discharge (2.0 km)	1	7.8	0.6	17	<0.2	1,700

### References:

Noller, B.N., P.H. Woods, and B.J. Ross. 1994. Case studies of wetland filtration of mine waste water in constructed and naturally occurring systems in Northern Australia. *Water Sci. Tech.* 29: 257-266.

Woods, P.H. and B.N. Noller. 1995. Medium-term performance of wetlands improving water quality of near-neutral mine drainage in the Northern Territory. In: National conference on Wetlands for water quality control. James Cook University, Townsville, Australia. 25-29 September.

# Woodcutters Mine, ctd

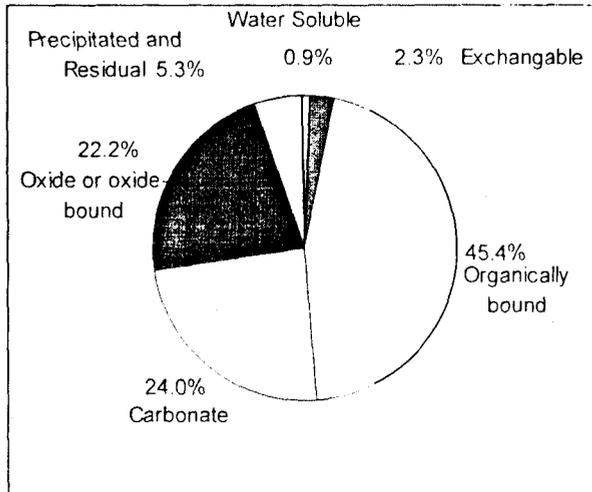




# Birchtree Mine, Thompson, Manitoba, Canada

Water from the Birchtree nickel mine has been discharged for the past 30 years into an extensive 95 ha sedge-dominated fen (opposite photo. A. Hambley, INCO Ltd, Thompson, Manitoba). Its flow averages 320 L/min. during the ice-free season. The water is net alkaline (pH 8.4) and contains an average of 5.1 mg/L Ni. In addition, nickel is deposited as dust from a nearby smelter at an average rate of 0.17 kg/ha/m, from dust created by haulage trucks on the adjacent road (by an undetermined amount), and from rainfall.

Accounting for all sources, the wetland retains a minimum of 96% of input nickel, mostly within an area measuring 1.8 ha. Nickel concentrations at its outlet averaged 0.08 mg/L. Nickel is entirely retained in sediments, in the forms indicated below.



## References:

Hambley, A.G. 1996. Removal of nickel from mine water by a natural wetland in Northern Manitoba. M. N.R.M. University of Manitoba, Winnipeg, Manitoba, Canada.

## United Keno Hill Mines, Yukon Territory, Canada

While on assignment with United Keno Hill Mines, I found several wetlands which remove zinc and other contaminants from mine drainage. As early as 1965, Robert Boyle noted that:

“Numerous bogs that extract the zinc from surface waters were observed in the Keno Hill area. One of these into which the mine water from the Hector-Calumet mine flows, effectively removes all of the zinc (40 ppm) in less than 2,000 feet.”

One wetland, densely vegetated by the sedge *Carex aquatilis* reduced zinc concentration by 90%, from 3 mg/L to 0.3 mg/L. This removal rate was achieved when the net alkaline water (pH 6.4) was retained in the wetland for 10 to 15 days.

This and other wetlands (e.g., opposite photo) removed several metals from mine drainage, which they retained in their sediments, included cadmium, copper, iron, lead, manganese, nickel, and zinc. None of these metals were taken up by the plants, indicating that they would not be transmitted through the food chain (Sobolewski, 1996).

In one of these wetlands, half or more of the metals were retained as sulphides, indicating that sulphate-reducing bacteria played an important role in metal removal. This was subsequently confirmed in a pilot-scale wetland treating mine drainage (Sobolewski, 1997). Other significant removal processes include sorption onto organic matter and iron and manganese oxides.



### References:

Boyle, R.W. 1965. Geology, geochemistry, and origin of the lead-zinc-silver deposits of the Keno Hill-Galena Hill area, Yukon Territory. Geol. Surv. Can. Bull. 111. 302 p.

Sobolewski, A. 1996. Development of a Wetland Treatment System at United Keno Hill Mines, Elsa, Yukon Territory. Twentieth Annual Mine Reclamation Symposium. Kamloops, B.C. June 17-20. pp. 64-73.

Sobolewski, A. 1997. Sobolewski, A. 1997. Wetlands for Treatment of Mine Drainage. WWW document located at URL: <http://www.enviromine.com/wetlands/Welcome.htm>

## United Keno Hill Mines, ctd

This small wetland measured approximately 11.5 x 3.5 x 0.2 m. The water entering this wetland had zinc concentrations measuring **3.2 ppm (mg/L)**. The water exiting the wetland measured **0.3 ppm** zinc. The pH along the water flow path ranged from 6.4 to 6.6.



Several other metals were retained by this small wetland. Their concentrations in sediments and in plants (aboveground) are presented in the table below. Note that despite the higher metal levels in sediments of the wetland receiving mine drainage, plant tissues in both wetlands have essentially the same metal concentrations. Clearly, metal uptake did not occur. This could be because the metals were *biologically unavailable*, or because the plants were actively regulating their uptake.

Metal	Impacted		Unimpacted	
	Plants	Sediments	Plants	Sediments
Cadmium	0.50	66	<0.50	23
Copper	2.81	110	4.27	46
Lead	<2.5	98	4.7	<50
Zinc	102	10,345	132	1,114

**Metal concentrations (ppm) in plant tissues and sediments of wetland unimpacted and impacted by mine drainage.**

# St Hilary Mining District, West Cornwall, United Kingdom

A relatively well-defined 2.7 hectares wetland dominated by the rush *Juncus effusus* and the reed *Phragmites australis* received drainage from abandoned mines in the St Hilary Mining District. Ores of tin, copper, arsenic and zinc were produced from this area, with nearly all the mines producing both Sn and Cu.

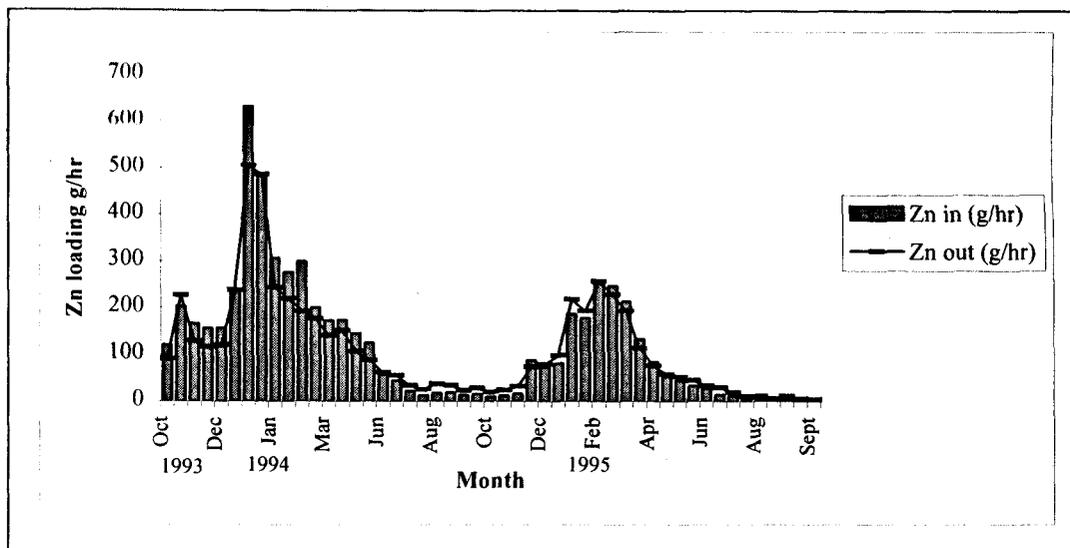
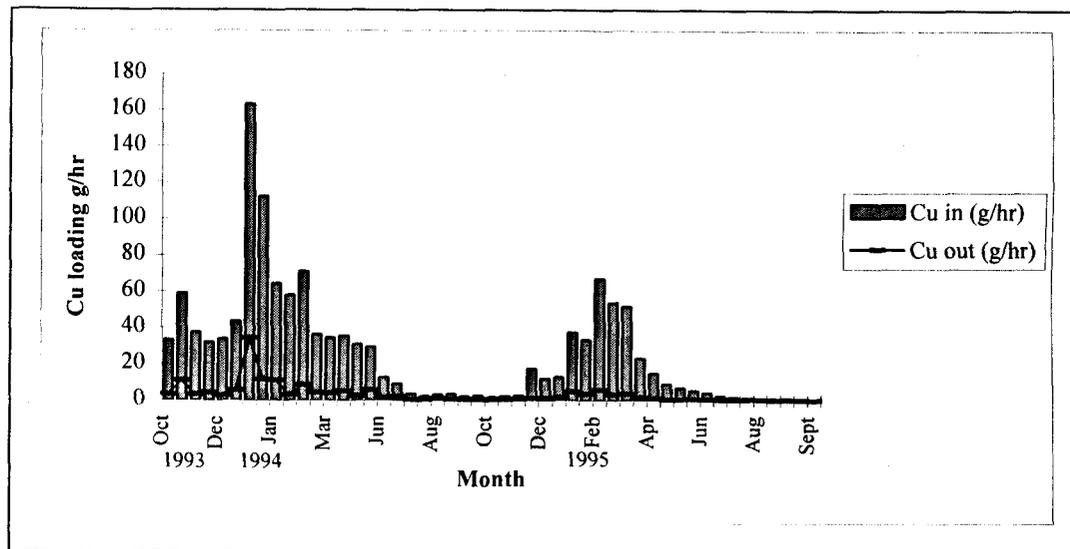
Flow rates into the wetland were seasonal, but they averaged 1.13 ML/d for 1993-1995. Concentrations of the major contaminants, Cu and Zn, are both decreased by passage of water through the wetland. However, copper is retained efficiently, whereas zinc is not, as shown in Table 1.

**Table 1. Mass balance for Cu and Zn**

		<b>Cu (kg)</b>	<b>Zn (kg)</b>
<b>Year 1</b> (1993-4)	Input	273.80	1352.82
	Output	38.28	1180.10
	<b>Retained</b>	<b>235.52</b>	<b>172.72</b>
<b>Year 2</b> (1994-5)	Input	122.65	601.24
	Output	11.55	634.83
	<b>Retained</b>	<b>111.10</b>	<b>-33.59</b>

**Reference:**

Melanie M. Brown. Camborne School of Mines. Unpublished thesis.



## Coal and Base Metal Mines, United States of America

Several natural wetlands in the Eastern and Western United States are reported to partially improve the quality of acid mine drainage (See References in paper). These wetlands range in size from a few square meters to several hectares. Cattails (*Typha*) most commonly dominate in these wetlands.

Most of the natural wetlands investigated receive low pH/high acidity water. Typically, iron concentrations are reportedly reduced by 25-75%, whereas aluminium and net acidity are reduced somewhat less, by 10-50%. Manganese can also be removed, but usually by a more modest 10-20%. Better metal removal rates are achieved when the mine water is net alkaline. However, it is impossible to properly determine metal balances (hence wetland performance) in most cases because the contribution of groundwater to water quality improvement is not fully assessed.

A typical example of a *Typha*-dominated wetland is shown below. The photograph, taken just before dormancy breaks, shows an iron-stained seep on the left, feeding the wetland from a deep coal mine. The mine water flows at approximately 100 L/min. This net alkaline water (pH 6.1) had much of its iron removed in the wetland, with inflow concentrations of 80 mg/L reduced at the outlet to 10 mg/L. Although the wetland surface area is more than sufficient to completely remove the iron, its effectiveness is curtailed by substantial water channeling.

These points highlight some of the reasons why constructed wetlands generally perform better than natural wetlands. Thus, effective performance is achieved by designing tight wetland bottoms, by controlling the water flow to avoid short-circuiting, and by pre-treating net acidic water with alkaline-generating material.



You can find out more about wetlands treating mine drainage on the Internet. Go to the web site titled:

**“Wetlands for Treatment of Mine Drainage”**

located at URL

**<http://www.enviromine.com/wetlands/Welcome.htm>**

# Update on Groundwater Corrective Action

(Experience to Date)

by

Don Metzler

U.S. Department of Energy

# Background / History

- How did we get to where we are today?
  - Ongoing since the early 1980's involving EPA, NRC, DOE, the courts, and public.



# Background / History

- Congress directed EPA to set standards
  - 1983, EPA publishes standards (40 CFR Part 192)
  - 1985, U.S. Court of Appeals remanded to the EPA the groundwater provisions of the standards
    - Treat toxic chemicals that pose GW risk same as Title II regulations
    - More RCRA like (numerical / prescriptive)

# Background / History

- Congress directed EPA to set standards
  - 1987, EPA publishes proposed standards for Title I (40 CFR Part 192)
  - 1991, EPA publishes final groundwater standards (60 FR 2854-2871)
    - Only minor changes from proposed standards
      - No mention of ALARA
      - Limited use definition replaces Class III aquifer

# DOE Title I Approach to Groundwater Compliance

## ■ Philosophy

- Protect human health and the environment
- Make informed objective decisions
- Select cost - effective strategies
- Involve stakeholders
- Verify conceptual model using reasonable monitoring practices

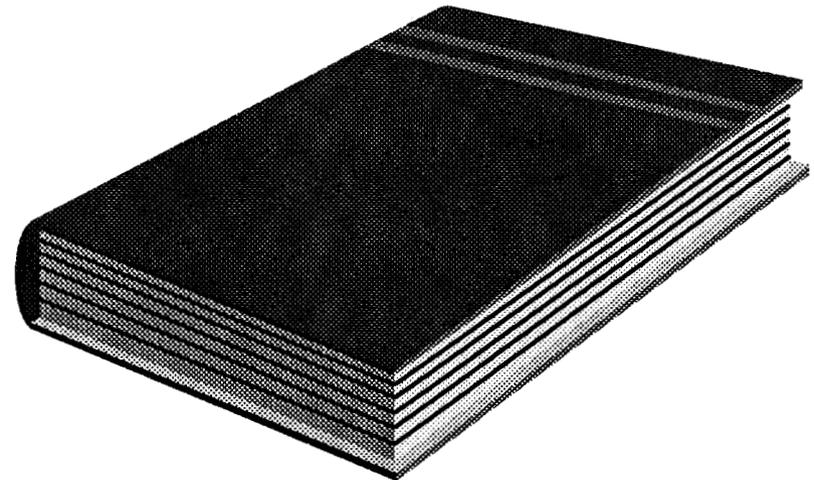
# Title I GW Logic Framework for Decision Making

## ■ Goals:

- Sound technical basis
- Consistent from state to state and from tribe to tribe
- Considers risk and cost
- Couples risk based approach with prescriptive standards

# Logic Framework

- Identified in the Final Groundwater PEIS October 1996
- Included in handout



# 40 CFR Part 192

- Provides for unique regulatory provisions in Subpart A, B, and C
  - Supplemental standards
  - Natural Flushing with Institutional Control
  - Alternate Concentration Limits

DOE has targeted many of the Title I sites for groundwater compliance based on these provisions.

# Supplemental Standards Overview

- Purpose
- Criterion
- Implementing Supplemental Standards

# Purpose

- Supplemental Standards may be applied as compliance actions under certain site conditions in lieu of prescriptive standards.
- Conditions must be protective of human health and the environment.

# Criterion

- The criterion for applying supplemental standards addressing the residual contaminated groundwater are identified in 40 CFR Part 192.21 Subpart C.

# Implementing Supplemental Standards

- May be granted if:
  - groundwater at a site is of limited use [192.11(e)] in the absence of contamination from residual materials; or
  - complete restoration would cause more environmental harm than it would prevent; or
  - complete restoration is technically impracticable from an engineering perspective.

# Limited Use Groundwater

- Means groundwater that is not a current or potential source of drinking water
  - Because:
    - TDS > 10,000 mg/L; or
    - Widespread, ambient contamination not due to activities involving RRM, that cannot be cleaned up using treatment methods reasonably employed in public water systems; or
    - Sustained yield < 150 gpd

# Natural Flushing

- Applicability
- Title I Targeted Sites
- Target Basis
- Data Needs
- Modeling
- Future Approach

# Applicability

- Sites where groundwater currently exceeds EPA standards
- Sites where groundwater is not currently nor projected to be a drinking water resource
- Sites where advection, dispersion, and attenuation can achieve cleanup goals
- Meet EPA standards (MCLs or background) within 100 years

# Target Title I Sites

- Durango, CO
- Grand Junction, CO \*
- Gunnison, CO
- Naturita, CO
- Rifle, CO (2 sites) \*
- Riverton, WY
- Slick Rock, CO (2 sites)

# Basis for Targeted Strategy

- 13 years baseline monitoring period
- Constituents of concern, hydrologic and geochemical properties identified
- Preliminary analytical modeling
- Identification of data needs
- Revised modeling (numerical)

# Identification of Data Needs

- Reduce uncertainties in conceptual model
  - Source term properties
  - Hydraulic conductivities
  - Flow gradient and direction
  - Retardation factors
  - Boundary conditions
  - Ecological considerations

# Modeling

- Tool for assisting in identifying data uncertainties and sensitivities
- Predicting natural flushing duration to meet cleanup goals
- Build understanding of site flow and transport

# Future Approach

- Site Observational Work Plans
- Remedial Action Plan modifications, or
- Groundwater Compliance Action Plans
- NRC Technical Evaluation Report
- NRC concurrence
- 100 year clock begins
- Transfer to LTSM program
- Verification monitoring

# Institutional Controls

- An institutional control is defined by the EPA in 40 CFR Part 192, III. “Changes and Clarifications in Response to Comments”

# Goals

- Least restrictive to property owners and general public
- Protective of public health and safety
- Enforceable, but flexible

# Definition

- “Having a high degree of permanence and which will effectively protect public health and the environment and satisfy beneficial uses of the groundwater... and which is enforceable by the administrative or judicial branches of government entities.”

# Authority Under Local Government Jurisdiction

- County or city level
- Can restrict new water development
- Ordinance to require proof of potable water with a zone of contamination
- Case history - Rifle, CO

# Authority Under State Government Jurisdiction

- Most states have control over their water sources
- Western states generally follow appropriation system of water law
- Most states have regulatory powers to restrict access to contaminated groundwater
- Case histories - Vitro (SLC) and Green River, UT

# Authority Under Tribal Government Jurisdiction

- Many tribes have comprehensive water codes
  - govern the use of surface and groundwater
- Case history - Arapahoe-Shoshone Tribes, Riverton, WY

# Authority Under Federal Jurisdiction

- The U.S. Department of Energy (DOE) could exercise its broad regulatory authority under Section 109 of the Uranium Mill Tailings Radiation Control Act (UMTRCA) to control access to the contaminated groundwater.

# Alternate Concentration Limits

- Established under NRC's regulatory program
- Must provide same level of protect as EPA's RCRA procedures

# Definitions

- Alternate Concentration Limits (ACL)
  - A concentration determined for a given constituent that will not pose a substantial present or potential hazard to human health and the environment as long as the ACL is not exceeded

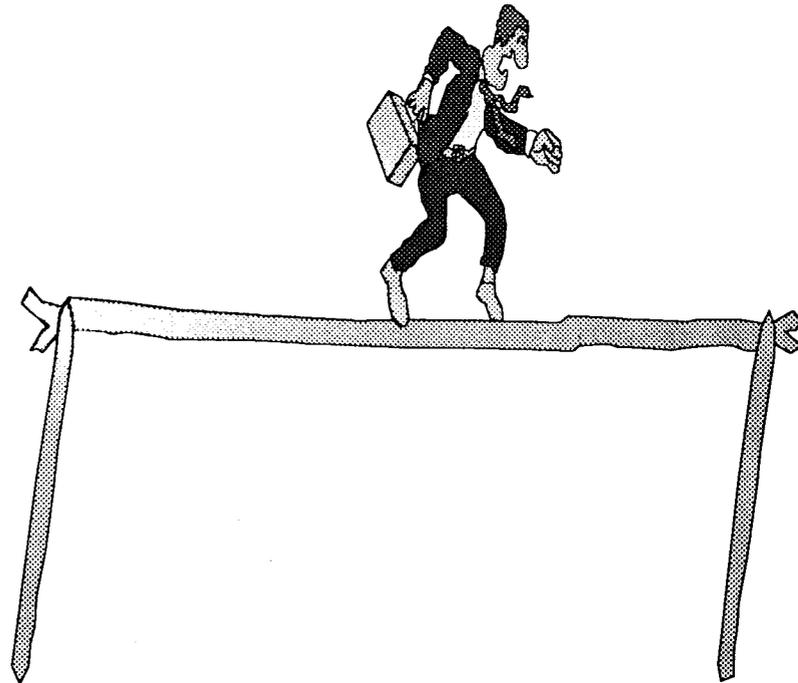
# Implementing an ACL

- Many factors must be considered
  - Potential adverse effects on groundwater quality
  - Potential adverse effects on hydraulically-connected surface water quality
  - Point of compliance
  - Point of exposure

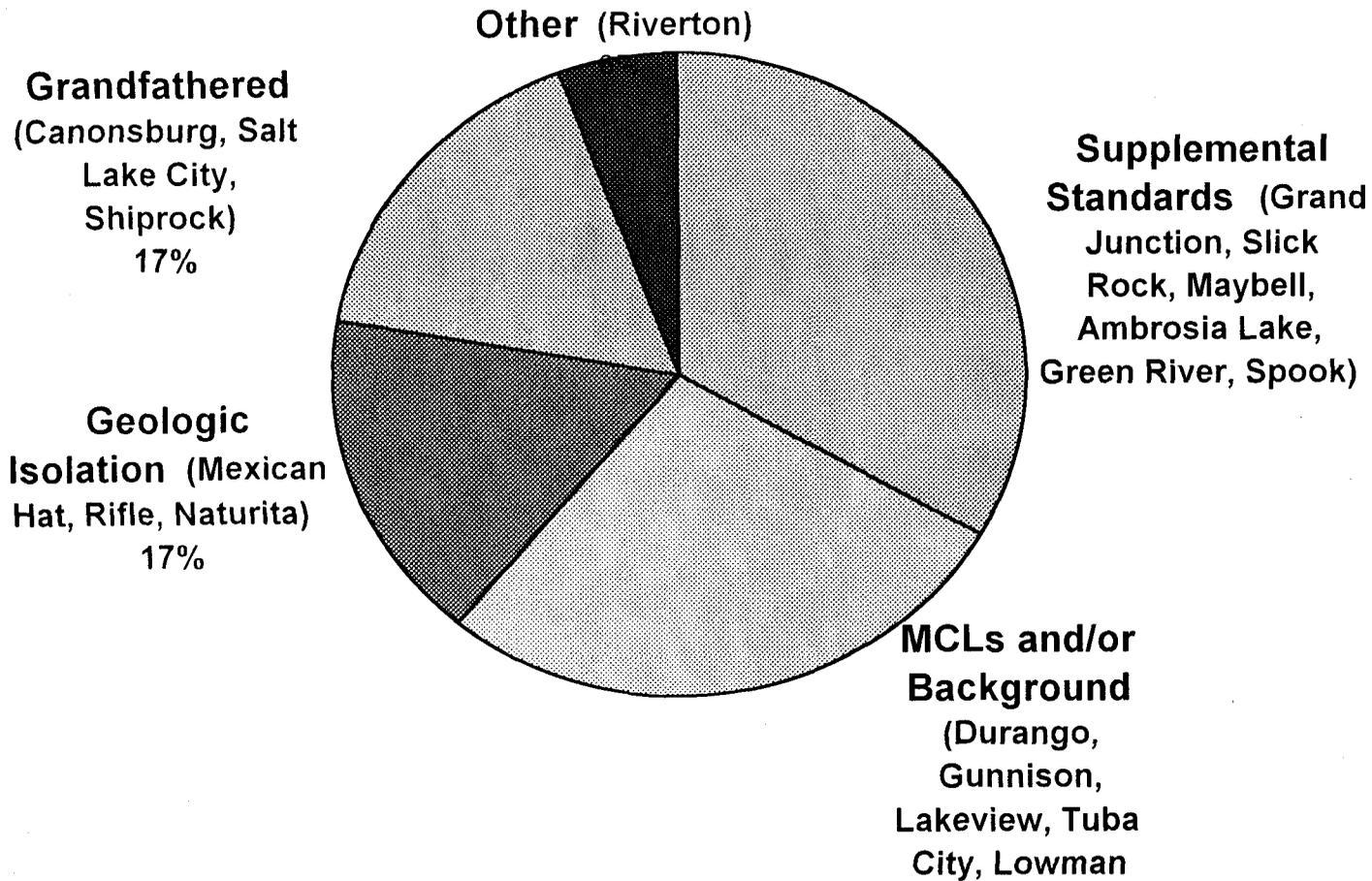
# ACL Determination Guidance Documents

- EPA Interim Final ACL Guidance (EPA/SW - 87 - 017)
- NRC Draft Technical Position Paper on ACLs for Title II Sites (59 FR 13345)

- An Approach to Balancing Dollars, Risk, and Perceptions



# Types of Title I GW Protection Compliance Strategies



# **Maximizing the Value of Natural Attenuation using Probabilistic Risk- Based Assessment and Decision Analysis**

**Workshop on Natural Attenuation of Metals and Radionuclides:  
Moving from the Lab to the Field  
June 19, 1997  
Albuquerque, NM**

**David P. Gallegos, Stephen H. Conrad, Thomas A. Feeney  
Sandia National Laboratories**

# Risk

## Risk-Based Approach Addresses:

- What can happen (e.g., contaminants move through soil to ground water to a person)
- What is the likelihood/probability of occurrence (e.g., what is the uncertainty in the natural attenuation process and its magnitude)
- What are the resulting consequences (e.g., cancer)

 this definition of risk can be used to assess any of the defined performance objectives (e.g., concentration limits, dose limits, risk goals)

 this definition of risk explicitly accounts for natural attenuation (i.e., consequences) and uncertainty in the effects of natural attenuation (i.e., likelihood/probability)

# Regulatory Performance Objectives

## ■ Concentration

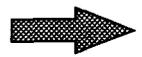
- limits based on pre-defined generic exposure scenario and pathway

## ■ Dose

- allows site specific information to be used in exposure scenario and pathway definition

## ■ Risk

- allows site specific information to be used in exposure scenario and pathway definition
- for decision making, CERCLA definition is not much different than dose (does not really consider uncertainty)



typically, these are defined as deterministic quantities (thresholds)

# The Decision at a Contaminated Site

## ■ The Decision

- What action do I take at this site to maximize the likelihood of long-term public health and safety (i.e., meet regulatory criteria)

## ■ Constraints and desires

- minimize cost (desire and perhaps a constraint)
- meet regulatory performance objectives (constraint)

## ■ Uncertainties

- physical behavior of the system
- human activities at the site in the future
- cost of alternative actions
- effectiveness of alternative action

# Decision Analysis

## Definition:

**A Decision is a commitment of resources that is revocable only at some cost (Hagen, Decision Analysis Mechanics, 1996)**

## Decision Analysis:

**Directly relates expenditures of resources to understanding what can happen, changing what can happen, how likely it is to happen, and the consequences of it happening**

## Example

**Which has more value:**

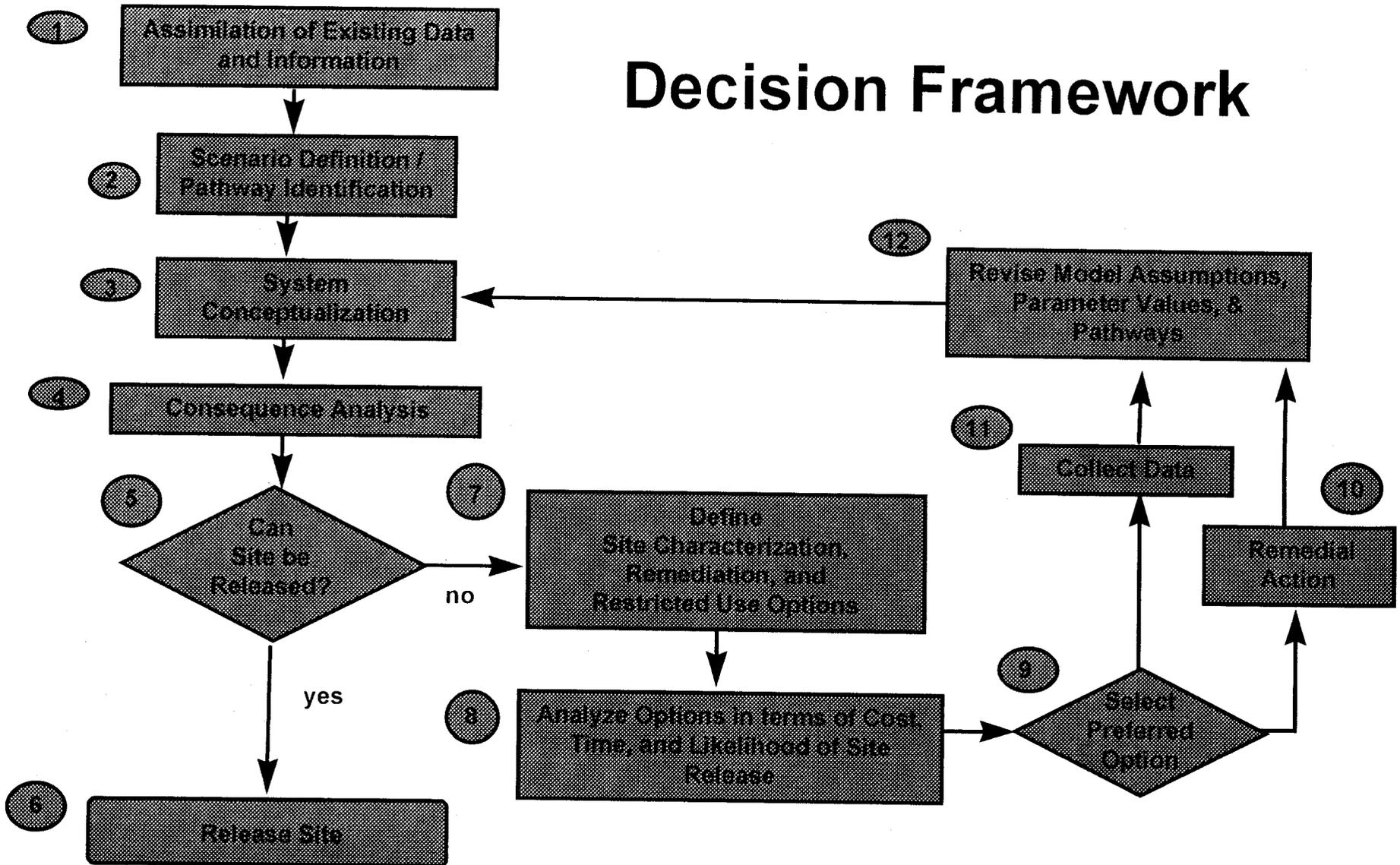
- **remediation of soil**
- **proving the effectiveness of natural attenuation**

# **Risk Assessment and Decision Making**

**Risk assessment should be used as a tool to facilitate decision making.**

- provides an approach to define and defend natural attenuation**
- should not be used for an after-the fact evaluation**
- uncertainty should be explicitly treated to ensure good decisions**

# Decision Framework



SAND2-7

# Proceeding Through the Framework

## ■ First Iteration

- evaluate site with the least conservative models and parameters that can be defended for decision-making purposes and using existing information

## ■ If dose/risk/concentration is less than performance objective

- done

## ■ If dose/risk/concentration is greater than performance objective

- define and evaluate alternative actions
- do not stop at this point and define clean-up levels based on the initial assessment

## Proceeding Through the Framework (cont.)

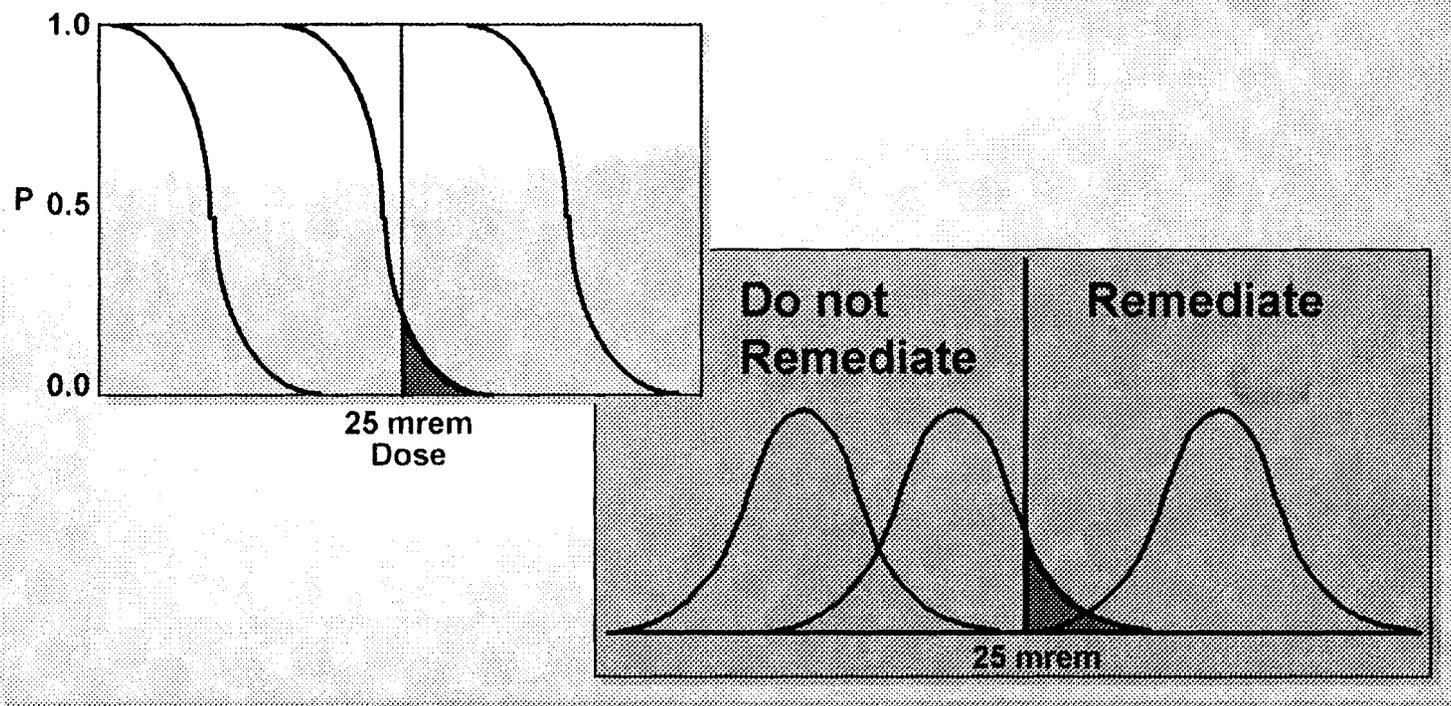
- Define alternative actions including data collection, site use restrictions, remediation, and combinations of these
- Evaluate alternatives against decision objectives (cost, likelihood of success, etc.)
- Select best alternative and proceed with action
- If necessary, update information based on knowledge gained and re-evaluate consequence
- Decision
  - If meet performance objectives - done (good decision, good outcome)
  - If fail to meet performance objectives - re-evaluate alternative actions (good decision, bad outcome)



# Performance Decision Point

Evaluate the results of Consequence Analysis and compare with predefined performance objectives

- Do I have an unambiguous answer? (Red or Yellow Curves)
- Do I need more information to make a decision? (Purple Curve)



# Defining Alternative Actions (Building Decision Branches)

- **Actions that reduce uncertainty (and thus rely on natural attenuation)**
- **Actions that reduce contamination (i.e., remediation) or exposure (i.e., land-use restrictions)**
- **Other considerations (decisions, constraints, uncertainties)**
  - **cost of action**
  - **expression of the uncertainty in the effectiveness of the alternative action (i.e., probability of success)**
  - **uncertainty in cost and time**
  - **constraints (cost, time, feasibility)**
  - **impact on downstream actions (e.g., data collection that reduces remediation costs)**
  - **acceptability of action**



# **SENSITIVITY ANALYSIS**

## **(Identifying Data Collection Options)**

**For input parameters to be considered important, they must meet three criteria:**

- the uncertainty in the input parameter has an impact on the uncertainty in the output parameter (traditional definition)**
- the input parameter is indeed uncertain (and not simply variable) and data collection activities could reduce the uncertainty**
- a reduction in the uncertainty would change the decision**

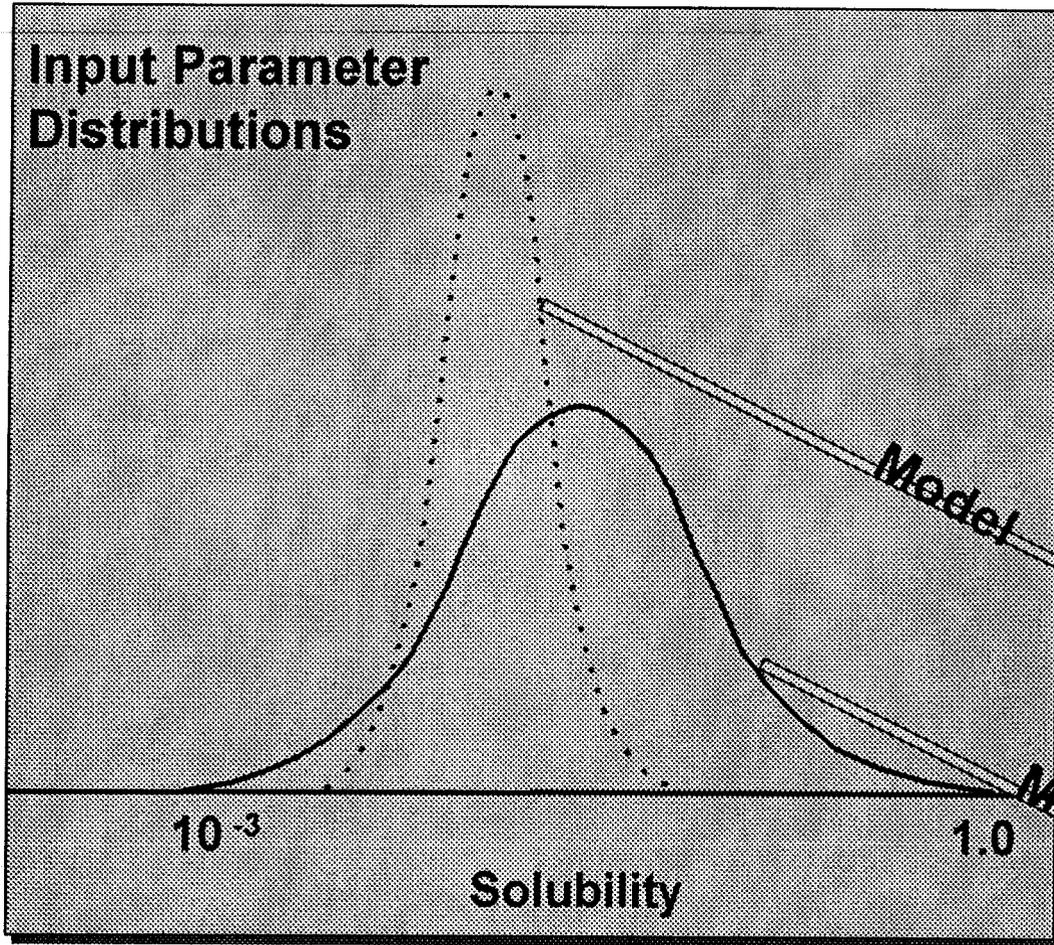


**mechanism for culling out certain data collection / research activities**

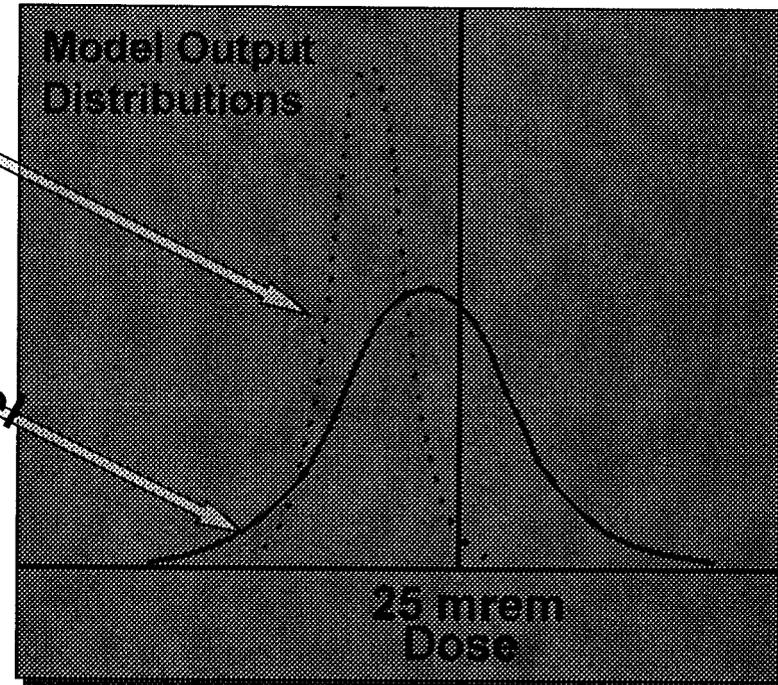


**provides the framework for defining probabilities of success of specific activities**

# Sensitivity Analysis

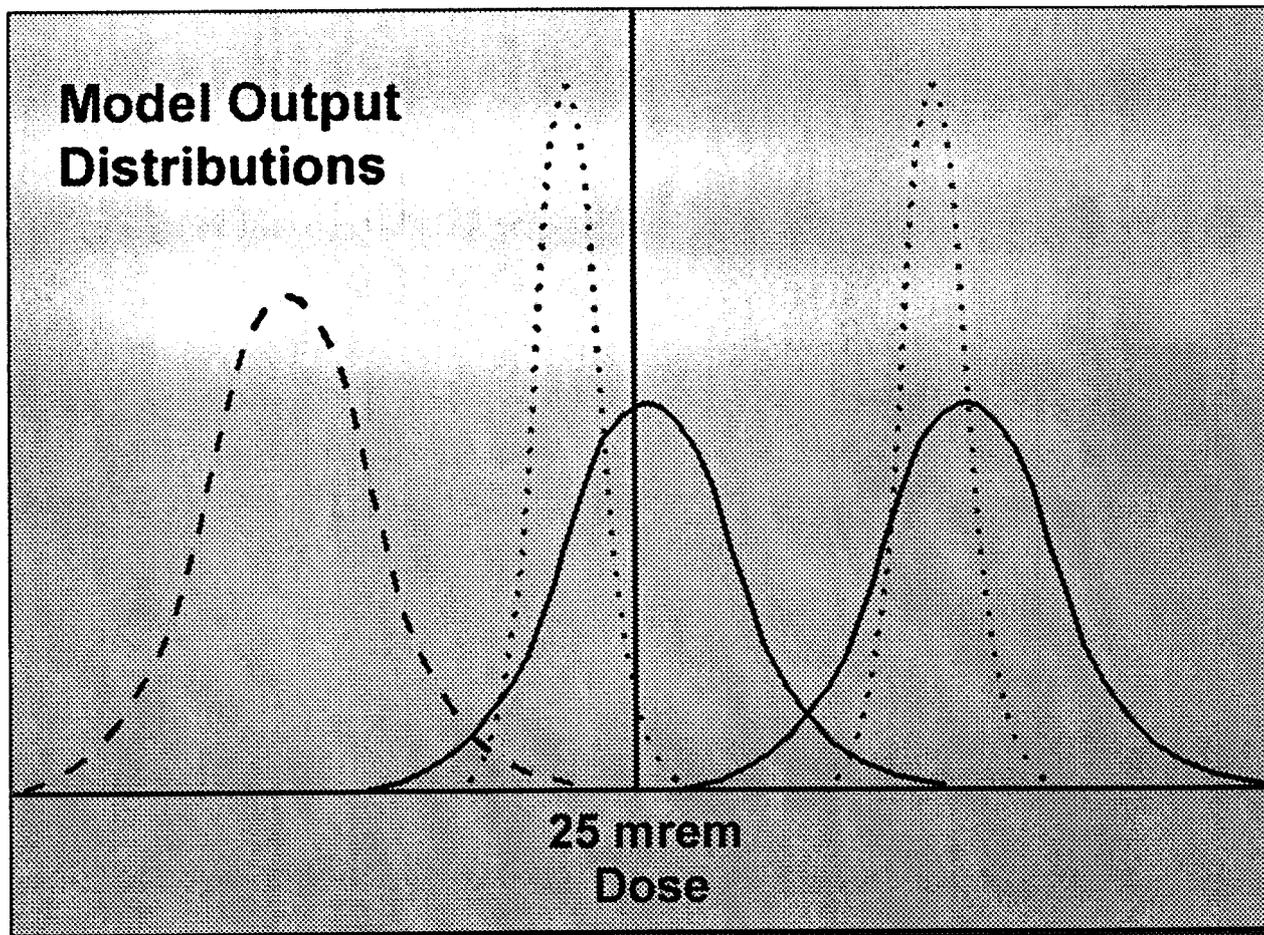


- Original (prior) distribution
- ..... necessary posterior distribution



# When Does Collecting More Data Make Sense?

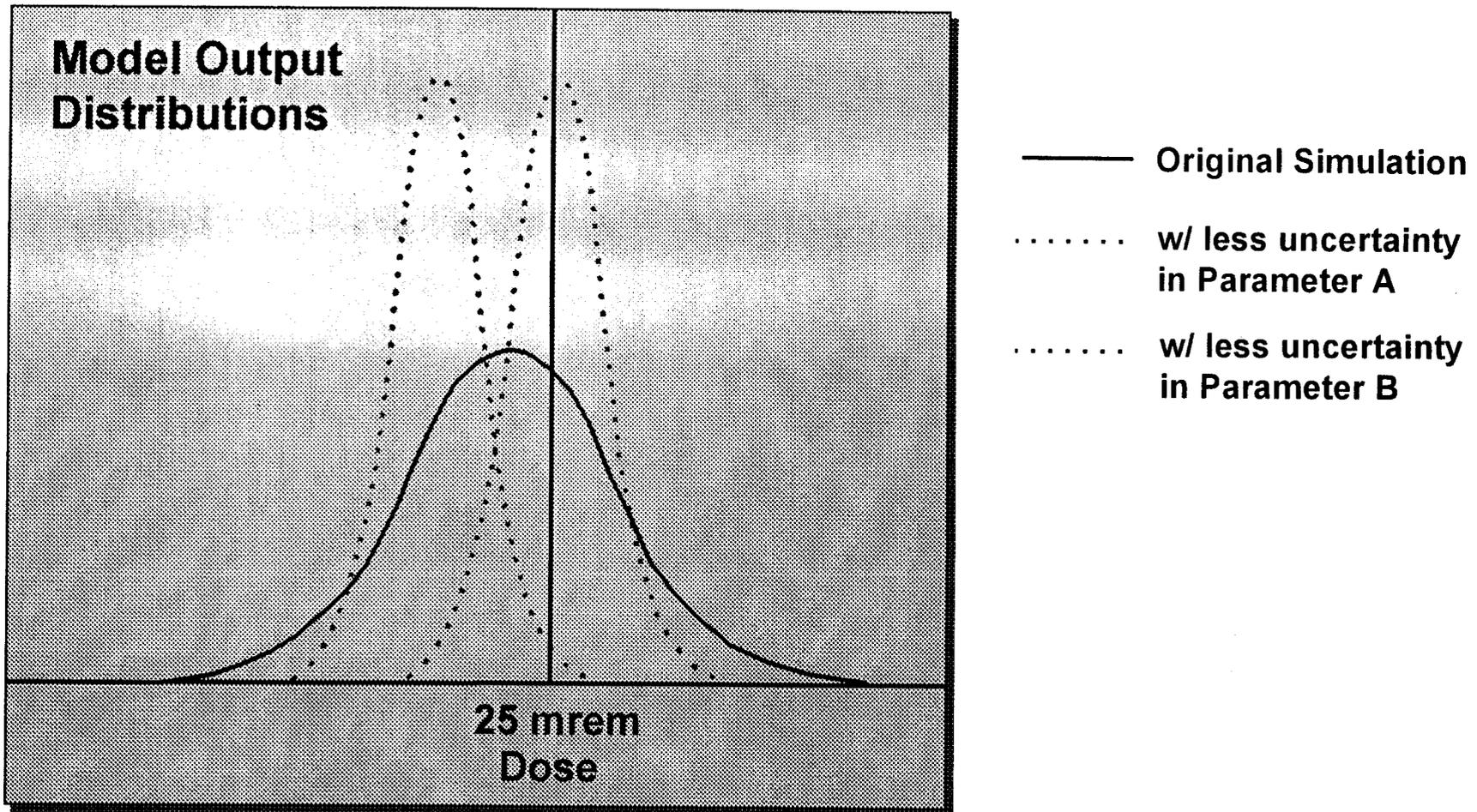
- It adds more value than it costs



- Original Simulation
- ..... w/ less parameter uncertainty
- - - w/ less model uncertainty

# When Does Collecting More Data Make Sense?

- It adds more value than collecting other data



# Evaluating and Comparing Alternatives

- Probability weighted outcome (i.e., expected value)

$$E(\text{cost}) = P(\text{success}) * C1 + P(\text{failure}) * (C1 + C2)$$

**C1 = cost of characterization activity**

**C2 = cost to remediate problem**

**P(failure) = 1.0 - P(success)**

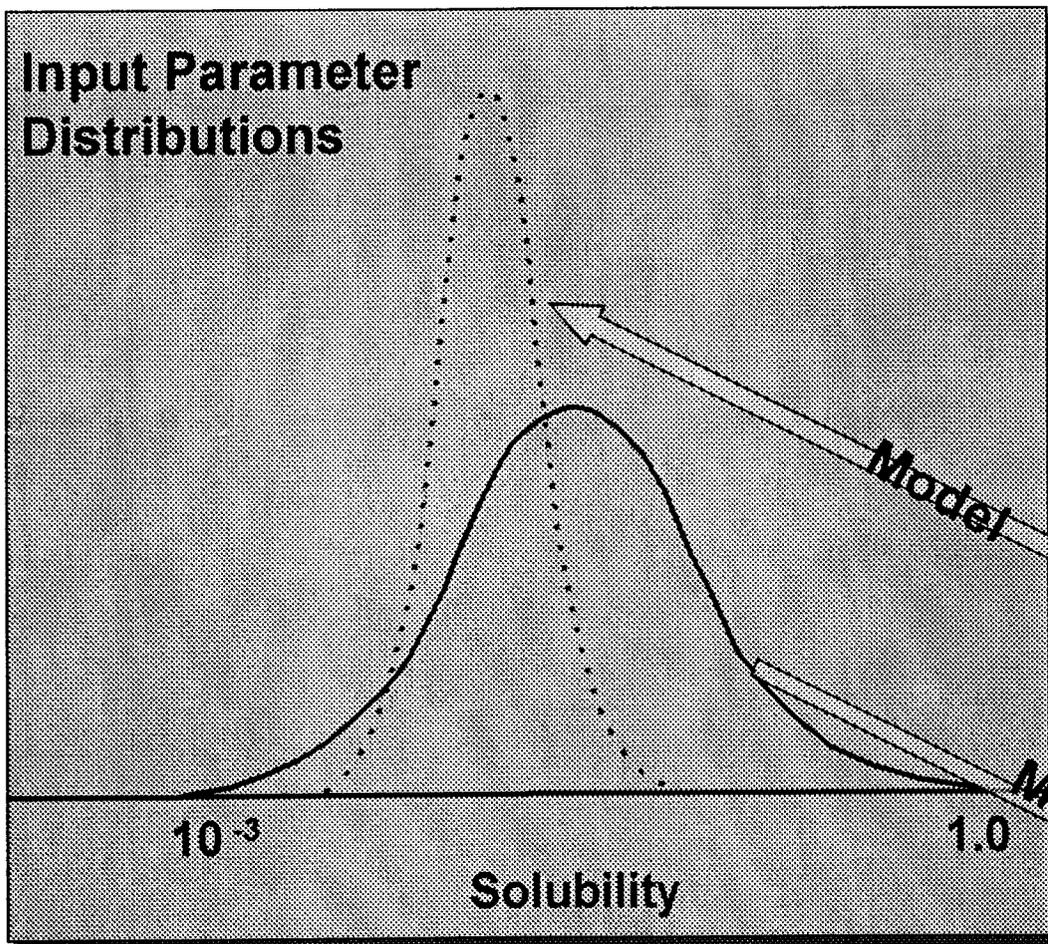
# Probability of Success

## Definitions

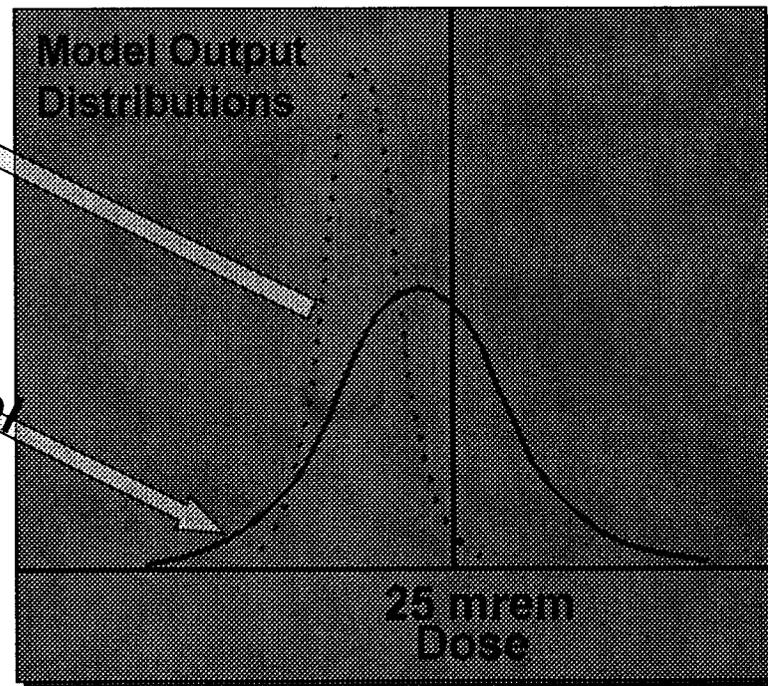
### ■ P (success)

- (1) Characterization - the likelihood that you will be successful in collecting the data that you need to reduce the uncertainty in the output to change the decision (within specified constraints - time, cost) → Natural Attenuation
- (2) Remediation - the likelihood that you will reduce the contamination to a level that will result in acceptable performance (within specified constraints - time, cost)
- (3) Site use restrictions - the likelihood that a specified restriction will be effective for a required time period (within a specified cost)

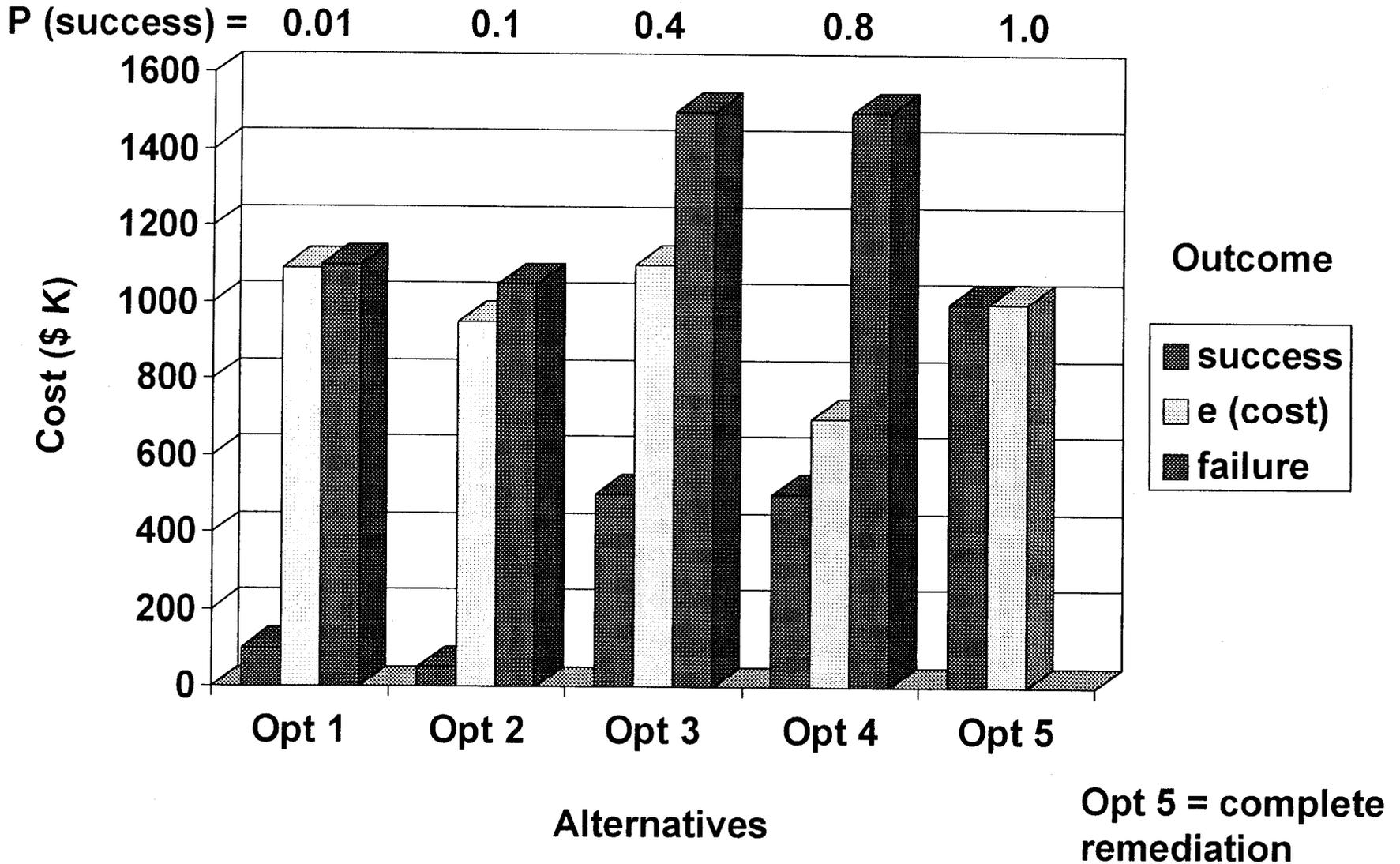
# Updating Parameter Distributions and Determining Likelihood of Success



- Original (prior) distribution
- ..... necessary posterior distribution



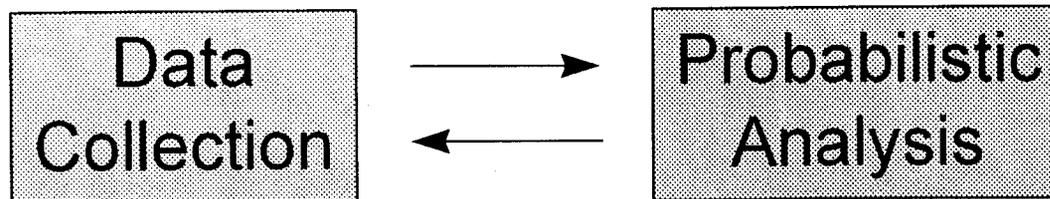
# Comparison of Alternatives



# ATTRIBUTES OF METHODOLOGY

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- Probabilistic -** Explicitly treat uncertainty to provide for meaningful sensitivity analysis and decision making
- Quantitative -** provides direct comparison to performance objectives and means for coming to closure on decision-making.
- Iterative -** Ties data collection directly to regulatory performance objectives. Only data collection to reduce important uncertainties.
- Model-Based -** The analysis and decisions are constrained by the physical models of the system. Implicitly incorporates natural attenuation.



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- **Sandia Environmental Decision Support System (SEDSS) Project supported by**
  - NRC Office of Research
  - EPA Office of Radiation and Indoor Air
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  - NRC Office of NMSS

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