

Site Characterization to Support Use of Monitored Natural Attenuation for Remediation of Inorganic Contaminants in Ground Water

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Background

The term “monitored natural attenuation,” as used in the following discussion and in the Office of Solid Waste and Emergency Response (OSWER) Directive 9200.4-17P (hereafter referred to as the 1999 OSWER Directive; USEPA, 1999), refers to “the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods.” When properly employed, monitored natural attenuation (MNA) may provide an effective remedy for ground water where a thorough engineering analysis informs the understanding, monitoring, predicting, and documenting of the natural processes. In principle, MNA provides a reasonable remedy for attaining ground-water cleanup objectives for some sites with inorganic contaminants (typically metals and radionuclides). Due to potential limitations in attenuation capacity within an aquifer, MNA is likely to be more applicable as a polishing step and/or under more dilute plume concentrations as compared to situations encountered in source zones or in more concentrated regions of a ground-water plume.

The objective of site characterization for assessing the viability of MNA as a component of ground-water cleanup is determination of the performance characteristics of the subsurface system with respect to achieving cleanup goals. As stated within the 1999 OSWER Directive, one of the primary processes that may result in natural attenuation of an inorganic contaminant in ground water is the transfer of the mobile contaminant into an immobile form within the aquifer solids; this process is generally referred to as “sorption”, inclusive of adsorption, co-precipitation, and precipitation reactions (See page 8 of USEPA, 1999; illustrative reactions shown in Table 1). The presumption for sites where “sorption” (hereafter referred to as immobilization) appears to result in

contaminant attenuation is that a specific mechanism (or mechanisms) controls contaminant partitioning to aquifer solids. Thus, in order to reliably evaluate the capacity for and stability of contaminant immobilization within the aquifer, the mechanistic characteristics of the partitioning process and the identification of the subsurface components that influence the extent of the immobilization reaction need to be understood. This requires information on the abundance and chemical speciation of solid phase reactants and products that participate in the immobilization reaction. The purpose of this Issue Paper is to highlight at what stage of the process solid phase characterization techniques need to be implemented in the site characterization process and to describe two case studies where the results of such techniques were critical to evaluation of MNA as a potential component of ground-water cleanup.

Introduction

The technical framework for evaluating the potential viability of MNA as a component of a ground-water remedy is presented in the document entitled “Monitored Natural Attenuation of Inorganic Contaminants in Ground Water: Volume 1 – Technical Basis for Assessment” (USEPA, 2007a). This document provides a detailed description of the objectives of the site characterization effort relative to the tiered analysis approach recommended in USEPA (2007a; Section IC). Specific data requirements and monitoring approaches to establish the existence of natural attenuation mechanism(s) for a range of non-radioactive, inorganic contaminants is provided in USEPA (2007b). As described in these documents, site characterization is conducted to develop and validate the conceptual site model and to evaluate performance characteristics of the natural attenuation process(es) that may be active within the aquifer. The data collection and analysis process is intended to support:

- development of a detailed knowledge of the system hydrogeology to establish transport pathway(s),
- determination of the **mechanism(s) and rate(s)** of contaminant attenuation,
- determination of the **capacity** of the aquifer to sustain attenuation of the mass of contaminant within the ground-water plume needed to achieve cleanup goals, and
- evaluation of the long-term **stability** of immobilized contaminants.

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Hydrogeologic characterization is used to determine the spatial and temporal variabilities in ground-water transport that ultimately dictate the types and amounts of aqueous- and solid-phase reactants which the contaminant will contact. Determination of attenuation mechanism(s) can be realized through evaluation of the ground-water chemical setting (e.g., pH, oxidation-reduction potential, and alkalinity), assessment of the chemical speciation of the contaminant and key reactants in ground water, and identification of the solid components within the aquifer with which the contaminant reacts (e.g., iron oxyhydroxides, represented by [=FeOH]) or are products of the overall reaction (e.g., Pb carbonate, Ni coprecipitated with FeS, or Cu adsorbed onto iron oxyhydroxide). In general, this aspect of the characterization effort is directed toward elucidation of the geochemical reaction(s) controlling contaminant removal from ground water, where the reaction products include the specific form of the attenuated contaminant (Table 1).

To support this evaluation effort, samples of both ground water and aquifer solids will need to be collected employing methods that maintain the in situ integrity of the samples. Field and laboratory measurements must then be employed to determine concentrations of reactants, the chemical speciation of the contaminant and/or reactant(s) in solution that participate in the reaction, and the chemical speciation of solid phase components that participate in and are produced from the reaction. This determination of the critical reaction parameters underpins the subsequent design of approaches to assess the capacity of the aquifer to sustain the attenuation reaction, as well as approaches to assess the stability of an immobilized contaminant relative to anticipated changes in ground-water chemistry. Determinations

of capacity and stability will likely include the application of laboratory-based tests employing site ground water and aquifer solids, as well as the application of models that adequately capture the details of ground-water transport and governing biogeochemical reactions. Ultimately, defining site-specific aspects of reaction mechanism(s), rates, capacity, and stability will rely on the development of multiple lines of evidence based on direct and indirect observations of the ground-water system.

Mechanisms for immobilization of inorganic contaminants can be grouped into three general categories: precipitation, coprecipitation, and adsorption (including ion exchange under limited circumstances). The tendency for precipitation of a contaminant to occur will depend on the concentrations of dissolved reactants in ground water relative to the solubility of potential precipitation products. For example, the precipitation of lead carbonate (cerussite or hydrocerussite) from ground water will depend on the concentrations of dissolved lead and inorganic carbon as well as the pH. Precipitation may occur under conditions in which the ground water is chemically oversaturated relative to the solubility of this solid phase. However, reliance on attenuation of lead via precipitation of a carbonate mineral will only be viable for conditions where this solid phase can maintain ground-water concentration below actionable levels and can be reasonably expected to resist dissolution that may be induced by future changes in ground-water pH and/or alkalinity. Coprecipitation reactions are distinguished from precipitation reactions, in that the inorganic contaminant is removed from ground water as a minor component of some other precipitating (or host) solid phase. For example, the host solid phase may be an iron oxyhydroxide that precipi-

Table 1. Examples of immobilization reactions that may be active within a contaminant plume for non-radioactive inorganic contaminants or radionuclides with long radioactive decay half-life (See also USEPA, 2007b and Rittmann et al., 2007.). Each attenuation process is organized according to the convention for depicting chemical reactions, i.e., Contaminant + Reactant(s) = Product(s), with notations to specify the sampled medium for each [(GW) = ground-water component, (S) = component in aquifer solids; [=FeOH]_(S) represents site of adsorption onto iron oxyhydroxide mineral]. The species containing the immobilized contaminant are highlighted with blue text.

Process	Contaminant	Reactant(s)	Product(s)
Precipitation	$Pb^{2+}_{(GW)} +$	$HCO_3^{-}_{(GW)} =$	$PbCO_{3(S)} + H^{+}_{(GW)}$
Precipitation (redox)	$Cr^{(VI)}O_4^{2-}_{(GW)} +$	$3Fe^{2+}_{(GW)} + 4OH^{-}_{(GW)} + 4H_2O =$	$Cr^{(III)}(OH)_{3(S)} + 3Fe(OH)_{3(S)}$
Coprecipitation	$xNi^{2+}_{(GW)} +$	$(1-x)Fe^{2+}_{(GW)} + HS^{-}_{(GW)} =$	$Fe_{(1-x)}Ni_xS_{(S)} + H^{+}_{(GW)}$
Adsorption	$Cu^{2+}_{(GW)} +$	$2[=FeOH]_{(S)} =$	$2[=FeO]Cu_{(S)} + 2H^{+}_{(GW)}$

tates when ferrous iron, transported from an upgradient, reduced portion of a plume, encounters dissolved oxygen in more oxidizing, downgradient portions of the plume. An example of this type of attenuation reaction would be the coprecipitation of nickel during oxidation-precipitation of ferrous iron to produce the mineral, ferrihydrite. Likewise, one could envision an alternative scenario where nickel is coprecipitated with a ferrous sulfide mineral, such as mackinawite, in a zone where sulfate-reducing conditions have developed. Finally, adsorption reactions are defined as those where the inorganic contaminant partitions to the surface of a solid phase that is an existing component of the aquifer solids (i.e., the sorbent). Adsorption reactions will be governed by specific properties of the contaminant (i.e., the adsorbate), the abundance and properties of the sorbent(s) within the aquifer, and by the ground-water chemistry (e.g., pH, competing adsorbates, or dissolved complexing agents). Elucidation of the specific immobilization processes that are active within the aquifer provides the basis for evaluating the site-specific performance characteristics of the MNA remedy.

Site Characterization to Define Performance Characteristics

Developing a detailed site characterization strategy is facilitated by first considering general site characteristics that can influence the type of equipment and methods needed for sample collection, as well as the locations and frequency of sampling for the monitoring network. This type of information can often be derived from knowledge of the regional hydrogeologic setting in which the contaminant plume is located as well as historical records of the types and quantity of contaminant release(s). For example, knowledge of whether the plume is comprised of one or more inorganic contaminants or also contains organic contaminants needs to be factored into the selection of sampling and analysis protocols. This situation is illustrated in Figure 1, which shows how biodegradation of an organic co-contaminant within the plume may influence the type of immobilization reactions that might occur. The degradation of the organic can result in localized changes in redox conditions within the aquifer. It could also result in the production of ligands that affect speciation of the

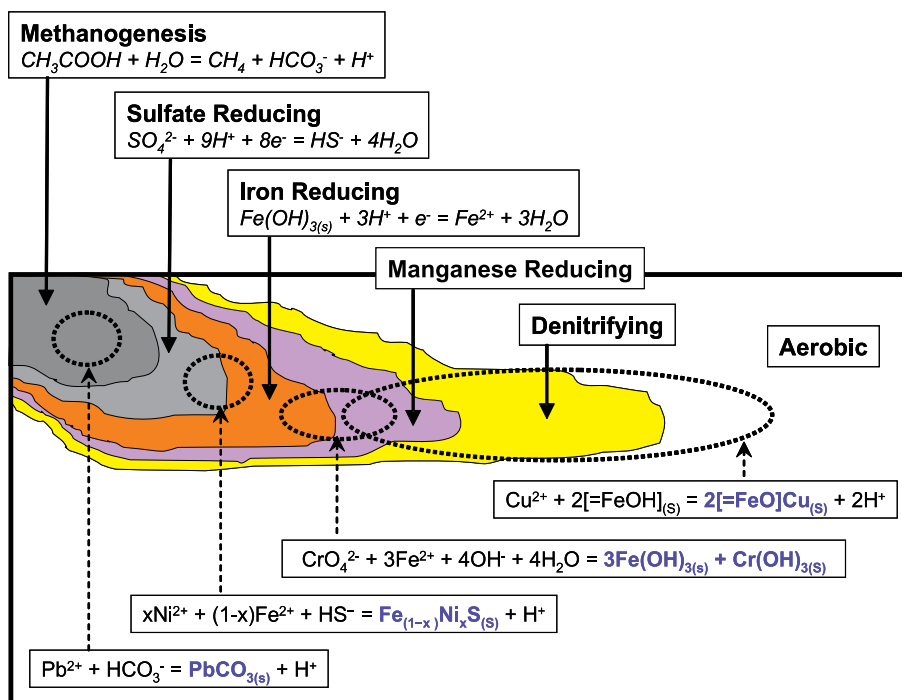


Figure 1. Illustration of ground-water geochemical conditions that may develop due to the presence of a biodegradable organic co-contaminant within the plume and potential immobilization reactions for a range of inorganic contaminants. Pertinent microbially-mediated reactions occurring under methanogenic, sulfate reducing, and iron reducing reactions are shown. Products of these reactions serve as reactants for a range of potential immobilization reactions listed at the bottom of the figure; immobilized contaminants are highlighted with blue text (=FeOH and =FeO represent sorption sites on iron oxyhydroxide mineral surfaces; “e-” refers to an electron transfer process involving other aquifer components). More detailed discussion of the impact of microbial processes on ground-water chemistry is provided in USEPA (1998, 1999b, 2002, and 2007a).

inorganic contaminant. The presence of multiple inorganic contaminants may necessitate use of analytical methodologies with different sensitivity and/or different approaches to sample collection and preservation. Relative to the subsurface setting, the spatial and temporal characteristics of ground-water flow and chemistry may also factor into the characterization strategy. Initial assessments of whether the aquifer is generally oxidizing or reducing, a shallow or deep system, and is or is not influenced by external hydrologic forces (e.g., ground water/surface water interactions, recharge from meteoric precipitation, or episodic regional withdrawals from the aquifer) need to be considered in designing the dimensions of the monitoring network and the frequency of data collection to characterize site chemistry and hydrology.

For sites where immobilization is the dominant attenuation process, understanding the types of solid phase components that participate in the evolution of the contaminant plume is critical to reducing the level of uncertainty in the selection of MNA as a component of the ground-water remedy. These solid phase components can be grouped into three different categories: 1) components that contribute to the source of contaminant mass within the plume, 2) components (biotic and abiotic) that participate directly or indirectly during the attenuation process, and 3) the solid form of the immobilized contaminant. Relative to the first category, the solid phase speciation of the contaminant in source areas does not necessarily affect the specific

mechanism(s) of attenuation in the downgradient plume. However, the total mass and rate of contaminant release from concentrated source areas can exert direct impact on the adequacy of the inherent capacity for the aquifer to attenuate contaminant transport. As illustrated in one of the case studies presented later, consideration of the residual mass of contaminant within source areas following removal efforts is important to evaluation of attenuation capacity within the aquifer. The latter two solid phase component categories bear directly on evaluation of the mechanism, capacity, and stability of the immobilization process. Solid components that participate indirectly include aquifer minerals that buffer ground-water geochemistry (e.g., alkalinity buffering by carbonate minerals or ion exchange with clay minerals) and/or subsurface microbial communities whose activity can directly affect ground-water chemistry (e.g., iron- or sulfate-reduction) and precipitation/dissolution of new reactive minerals (e.g., iron sulfides). Finally, evaluation of the chemical form of the attenuated contaminant provides confirmation of the active mechanism and provides the basis for assessing the long-term stability of the immobilized contaminant relative to future changes in ground-water chemistry that might be reasonably anticipated. For convenience, a summary of several important data objectives to consider relative to the three identified solid phase component categories is provided in Table 2.

Table 2. Data objectives to consider relative to solid phase characterization activities supporting evaluation of the mechanism, capacity, and stability of contaminant immobilization. More detailed discussions of data requirements and methodologies for data acquisition are provided in USEPA (2007a).

Solid Phase Category		Data Objectives Relevant to Site Characterization
Contaminant Source		<ul style="list-style-type: none"> • Mass of contaminant and rate of release • Interaction dynamics of contaminant source with system hydrology and chemistry • Chemical form of contaminant transported from source area
Reactants	Abiotic	<ul style="list-style-type: none"> • Identity and accessible/available mass of aquifer solids that control concentrations of soluble reactants • Identity and accessible/available mass of aquifer solids that react directly with contaminant during immobilization • Spatial distribution of solid components that participate directly or indirectly in contaminant immobilization along critical ground-water flow paths
	Biotic	<ul style="list-style-type: none"> • Microbial community activities that affect ground-water chemistry and indirectly impact contaminant immobilization • Direct interactions of microbial community with contaminant during immobilization • Type and mass of substrates and bioavailable terminal electron acceptors used by microbial community
Immobilized Contaminant		<ul style="list-style-type: none"> • Chemical speciation of immobilized contaminant • Stability of immobilized contaminant relative to current and potential future ground-water chemical conditions

In order to illustrate the issues one may need to consider during development of the site characterization strategy, a hypothetical situation will be considered in which nickel in ground water is attenuated as a result of iron sulfide mineral precipitation within a plume. The process is presented in Table 1 as an example of a coprecipitation reaction. In the following analysis, questions will be posed relative to three of the general information needs identified in the Background section (i.e., “mechanism and rate”, “capacity”, and “stability”). Potential measurements that one may undertake to address these questions will then be identified. Measurements that require the collection and characterization of solid materials from the aquifer are highlighted to illustrate the importance of solid phase characterization.

As previously stated, identification of the mechanism controlling contaminant attenuation depends on determination of the key components that participate in the reaction. As indicated by the entries in Table 1 for this hypothetical scenario, iron, sulfur, and ground-water pH may exert direct control on nickel attenuation. This leads to some specific questions that need to be addressed in order to confirm that the proposed process is actually occurring within the aquifer:

Question	Potential Measurements
<ul style="list-style-type: none"> • Is dissolved sulfide in ground water? If not, is sulfate in ground water? 	<ul style="list-style-type: none"> • Ground-water chemistry (field colorimetry for sulfide, field or laboratory measurement for sulfate)
<ul style="list-style-type: none"> • Is ferrous iron in ground water? 	<ul style="list-style-type: none"> • Ground-water chemistry (field colorimetry)
<ul style="list-style-type: none"> • Does decrease in ground-water nickel concentration coincide with decreases in dissolved sulfide/sulfate and/or ferrous iron? 	<ul style="list-style-type: none"> • Ground-water chemistry (laboratory measurement for nickel; see above for sulfide, sulfate, and ferrous iron)
<ul style="list-style-type: none"> • Is iron sulfide present in aquifer solids? 	<ul style="list-style-type: none"> • Laboratory measurement for iron sulfide content (acid volatile sulfide extraction of preserved solids)
<ul style="list-style-type: none"> • Is nickel associated with iron sulfides in aquifer sediments? 	<ul style="list-style-type: none"> • Laboratory measurement (acid volatile sulfide extraction with measurement of co-extracted nickel) • Electron microscopy with element mapping to demonstrate Fe-Ni-S association • Spectroscopic methods to directly identify nickel solid phase speciation
<ul style="list-style-type: none"> • What is the rate of nickel attenuation in locations where iron sulfide precipitation is occurring? 	<ul style="list-style-type: none"> • Examination of spatial or time trends in nickel and iron/sulfide loss from ground water • Controlled laboratory tests using site-derived ground water or synthetic water solutions that simulate ground-water chemistry

The results from these measurements will provide both direct and indirect lines of evidence to determine whether the hypothesized attenuation mechanism is active within the plume. Since the geochemical setting in this situation is likely reducing with little or no oxygen, using proper procedures to acquire and preserve samples of ground water and aquifer solids is critical to insuring data accuracy (e.g., USEPA, 2006a). For ground-water samples, one approach to minimize potential alterations to the chemical speciation of ferrous iron and dissolved sulfide is to conduct the measurement in the field with a sampling procedure that minimizes air contact (USEPA, 2002). Available methods and equipment for these field measurements are sufficiently sensitive to evaluate concentration trends of relevance to a contaminant plume.

Subsequent to identifying the mechanism of contaminant attenuation, it will then be necessary to determine if sufficient capacity exists within the aquifer to attenuate the mass of nickel that will be transported through the aquifer. In simple terms, the goal of this effort is to account for the mass of aquifer components available to react with the contaminant to result in a sufficient level of immobilization to achieve cleanup goals (e.g., drinking water standards, ambient water quality criteria, or risk-based criteria). In addition, the spatial distribution of the relevant aquifer components relative to the spatial distribution of contaminant flux needs to be considered during this accounting exercise. Thus, in addition to the use of appropriate sampling, preservation, and analytical methodologies, the monitoring network from which environmental samples are retrieved needs to adequately capture the dimensions and physical heterogeneity of the plume. Relative to the hypothetical immobilization mechanism currently being considered, the following questions need to be addressed in order to assess capacity:

Question	Potential Measurements
<ul style="list-style-type: none"> • What is the source of ferrous iron and dissolved sulfide? • If source is from microbial reduction, is there sufficient electron donor and acceptor supply? • Is the mass flux of ferrous iron and dissolved sulfide sufficient to capture nickel given knowledge of process efficiency? 	<ul style="list-style-type: none"> • Site information on source area waste constituents (liquid and/or solid) as potential source • Ground-water chemistry data to map out spatial distribution of ferrous iron and/or dissolved sulfide • Ground-water chemistry data to infer microbial processes (USEPA, 2007a; Section IIIC) • Direct identification of microbial community characteristics (USEPA, 2007a; Section IIIC.4) • Ground-water or aquifer solids chemistry data to estimate available mass of electron donor (e.g., dissolved and/or solid organic carbon) • Ground-water or aquifer solids chemistry data to estimate available mass of electron acceptor (e.g., dissolved sulfate and/or iron oxyhydroxide minerals) • Ground-water concentration and flow data for reactants • Laboratory tests to assess efficiency of nickel coprecipitation with iron sulfides under chemical conditions expected to be encountered along transport pathway(s)

Finally, the stability of the immobilized contaminant needs to be assessed relative to potential fluctuations or anticipated long-term changes in ground-water chemistry. Potential fluctuations in ground-water chemistry may result from natural hydrologic events such as recharge from surface infiltration or water level fluctuations in surface water bodies that are hydraulically connected to the aquifer. Alternatively, fluctuations in ground-water chemistry may result from changes induced by active remediation (Sutherson and Horst, 2008), which may precede implementation of MNA as a follow-on component of the overall ground-water remedy. Long-term changes may result from dissipation of the contaminant plume accompanied by the influx of upgradient ground water into the portion of the aquifer previously occupied by the plume. Assessing the long-term stability is critical because contaminant immobilization may occur under ground-water chemical conditions that are far removed from future conditions following plume diminution. For example, precipitation or co-precipitation reactions often occur where plume characteristics induce dramatic changes in ground-water chemistry parameters such as oxidation-reduction potential, pH, or alkalinity. In

these situations, the immobilization process may result in accumulation of a new solid component that, while stable under existing plume conditions, is unstable with respect to natural conditions in the aquifer outside of the plume. Contaminant immobilization may also be temporary in situations where adsorption to existing aquifer solids controls contaminant retardation, since these reactions are often sensitive to changes in ground-water pH or major ion chemistry. Ultimately, analysis of contaminant stability must be guided by knowledge of the chemical conditions driving immobilization relative to natural or anticipated future ground-water conditions. Relative to the hypothetical immobilization mechanism currently being considered, the following questions need to be addressed:

Question	Potential Measurements
<ul style="list-style-type: none"> • Are natural ground-water pH and/or major ion chemistry significantly different as compared to existing plume conditions? • Is natural ground water oxidizing? • Is nickel released from iron sulfide upon exposure to upgradient ground-water chemistry? • Does chemical form of immobilized nickel change upon exposure to upgradient ground-water chemistry? 	<ul style="list-style-type: none"> • pH and/or major ion chemistry of upgradient ground water or other sources of recharge along relevant transport pathways • Dissolved oxygen concentration and/or oxidation-reduction potential of upgradient ground water or other sources of recharge along relevant transport pathways • Laboratory tests using contaminated aquifer solids with samples of upgradient ground water or other sources of recharge • Chemical extraction methodologies to examine nickel solid phase association and/or speciation in laboratory test samples and/or sampled aquifer solids • Spectroscopic and/or electron microscopy to examine nickel solid phase association and/or speciation in laboratory test samples and/or sampled aquifer solids

It should be noted that the last recommended measurements imply additional collection and analysis of the solid phase speciation of the immobilized contaminant during performance monitoring of the MNA remedy. A change in contaminant solid phase speciation indicates a change in immobilization mechanism. Knowledge of this change is important both to the conceptual understanding of factors controlling the long-term stability of the immobilized contaminant and to the development of chemical speciation and/or reactive transport models that may be employed to estimate attenuation capacity and project permanence of the MNA remedy.

Case Studies Illustrating Importance of Solid Phase Characterization

The preceding descriptions of solid phase characterization measurements and their application as part of the tiered analysis approach for site characterization illustrate the rigorous effort that is needed to reduce the uncertainty in selecting MNA as a component of the ground-water remedy (USEPA, 2007a; Section IC). This level of effort is justified since the performance characteristics of the natural attenuation process are not known in the absence of site-specific data. It should also be noted that many of the measurements undertaken to characterize conditions within the plume are similar to those that would be implemented during selection, optimization, and performance monitoring of an engineered remedy that is designed to manipulate subsurface chemistry. Thus, the high level of effort required for conducting these characterization tests will likely prove beneficial regardless of the final remedy selected. To illustrate the importance of solid phase characterization measurements, summary descriptions of two case studies are provided for sites where MNA was under consideration as a component of a remedy to address inorganic contaminants in ground water. These case studies provide clear examples of the importance of the characterization of solids from the subsurface and the potential impacts of hydrologic dynamics on the effectiveness of natural attenuation reactions for controlling contaminant mobility.

Industri-Plex Site Arsenic Plume

The Industri-Plex Superfund Site is a former chemical and glue manufacturing facility in Massachusetts. Chemicals such as lead-arsenic insecticides, acetic acid, and sulfuric acid were produced for local textile, leather, and paper manufacturing industries from 1853 to 1931 (Durant et al., 1990). Chemicals manufactured by other facilities at the site include phenol, benzene, and toluene. Industri-Plex was also used to manufacture glue from raw animal hide and chrome-tanned hide wastes from 1934 to 1969. The by-products and residues from these industries contaminated the soils at the site with elevated levels of metals, such as arsenic, lead and chromium. During the 1970s, the site was redeveloped for industrial use. Excavations uncovered and mixed industrial by-products and wastes accumulated over 130 years. During this period, residues from animal hide wastes used in the manufacture of glue were relocated on-site from buried pits to piles near swampy areas on the property. Many of the hide piles and lagoons were leaching toxic metals into the underlying shallow aquifer. Estimates suggest that 270 metric tons of arsenic may still exist within the site boundaries (Aurilio et al., 1995). In response to public health concerns, a Record of Decision (ROD) for the Industri-Plex Superfund Site was signed in 1986, addressing the stabilization of on-site soil, sediment, and hot spot ground-water contamination under Operable Unit 01 (USEPA, 1986). It is hypothesized that leached organic degradation products from site disposal areas have contributed to the transport of arsenic via ground water to a wetland that flows to the Aberjona River (Davis et al., 1994). The aquifer underlying North Woburn, MA, including

the Industri-Plex Superfund Site, has been designated as a non-drinking water source area by the state of Massachusetts. Under the 1986 ROD, the USEPA was required to conduct a Multiple Source Groundwater Response Plan (MSGRP) which served as a second operable unit (OU-2) for the Industri-Plex site. The MSGRP was required to investigate other potential contamination impacts on the regional aquifer, and determine if additional remedies were necessary to clean up the aquifer within the Industri-Plex Study Area.

Characterization of the ground-water plume that migrates beyond the southern boundary of the Industri-Plex site was documented as part of the MSGRP Remedial Investigation (USEPA, 2005a). Information from site monitoring revealed that the plume primarily discharges into a pond known as the Halls Brook Holding Area (HBHA) Pond. This surface water feature was constructed during the early 1970s to serve as a hydraulic retention basin to mitigate flooding during periods of peak surface water discharge. Sources of surface water to the HBHA Pond include Halls Brook, a perennial stream located on the western edge of the pond, and an intermittent stream (Atlantic Avenue Drainway) that conveys water from an upgradient wetland and stormwater runoff from Atlantic Avenue and nearby parking facilities. Historical surface water data from the outlet of the HBHA Pond indicated significant reduction in arsenic concentration from that expected for the discharging ground-water plume, presumably due to oxidation-precipitation of ferrous iron and sequestration of arsenic by iron oxyhydroxides that are subsequently deposited onto sediments in the HBHA Pond (e.g., Aurilio et al., 1994; Davis et al., 1996). These observations suggested that natural attenuation processes occurring within the HBHA Pond could contribute to the overall ground-water remedy. During the period 1999-2001, a field investigation was conducted to characterize the chemical and hydrologic processes impacting the fate and mobility of arsenic entering the HBHA Pond following plume discharge. The results of this site characterization effort are documented in a series of publications (Wilkin and Ford, 2002; USEPA, 2005b; USEPA, 2005c; Ford et al., 2006; USEPA, 2006a; Wilkin et al., 2006).

In summary, the results of this field investigation revealed that natural attenuation of arsenic was not occurring within the aquifer and that the HBHA Pond attenuated only a fraction of the arsenic derived from plume discharge. Consistent with historical observations, ground-water geochemical conditions along flow paths from the Industri-Plex source areas to the HBHA Pond were sufficiently reducing to maintain arsenic (and iron) in a mobile form. Upon discharge to the HBHA Pond, ferrous iron did undergo oxidation-precipitation in the presence of dissolved oxygen, efficiently sequestering arsenic from the plume (Figure 2A). However, upon settling to the sediment layer in anoxic zones within the bottom of the HBHA Pond, much of the arsenic-laden iron oxyhydroxides re-dissolved to release arsenic and ferrous iron to the water column. These dissolved constituents could diffuse back up towards the water surface, where oxidation-precipitation of ferrous iron would again sequester dissolved arsenic via coprecipitation with

newly formed iron oxyhydroxides. The internal recycling of iron and arsenic within the HBHA Pond following plume discharge is illustrated in Figure 2B. Characterization of arsenic speciation in sediments indicated that a fraction of the arsenic load to the sediment layer was transferred to iron sulfides due to sulfate reducing conditions. The generally low stability of the co-precipitated arsenic within the HBHA Pond resulted in high concentrations of dissolved arsenic within the deep surface water (Figure 2A). During base flow conditions, arsenic was primarily retained within the pond due to stratification that limited vertical transport of arsenic to shallow surface water. However, during large surface water flows, portions of the pond were mixed leading to increased flux of arsenic at the pond outlet (USEPA, 2005a; USEPA, 2005b). These observations supported the conclusion that MNA was not a viable option for treatment of the arsenic plume. However, characterization of the physicochemical controls on arsenic fate within the HBHA Pond enabled use of the surface water body as a component of the selected remedy, in which engineered enhancements to control system hydraulics and oxidation processes will be incorporated (USEPA, 2006b).

Differences in supporting information available before (“Original”) and after the 1999-2001 investigation (“Revised”) are listed in Table 2. Significant limitations of the initial

site characterization effort included the lack of information supporting analysis of system capacity for attenuation and analysis of the stability of arsenic partitioned to solids across the transition zone from ground water to surface water, as well as improper collection/preservation methods for solid samples that contained oxygen-sensitive components. Improper collection/preservation techniques led to an incomplete analysis of arsenic attenuation processes and overestimation of attenuation capacity. While there were active processes sequestering arsenic derived from plume discharge, the instability of arsenic solid phase associations in concert with the periodic occurrence of hydrologic events that disturbed system functionality precluded use of MNA as a remedy at this site. This example illustrates how cost savings may be realized during site characterization, since reiteration of the characterization effort to address limitations in the original conceptual site model (CSM) entailed significant added cost. Specifically, many of the shortcomings of the original site data compilation could be attributed to improper collection, preservation, and processing methods for site-derived samples. Knowledge of general site characteristics, in this case a biologically productive wetland setting, should alert those designing the characterization effort to consider sources of potential analytical bias from use of inappropriate sampling or analysis protocols.

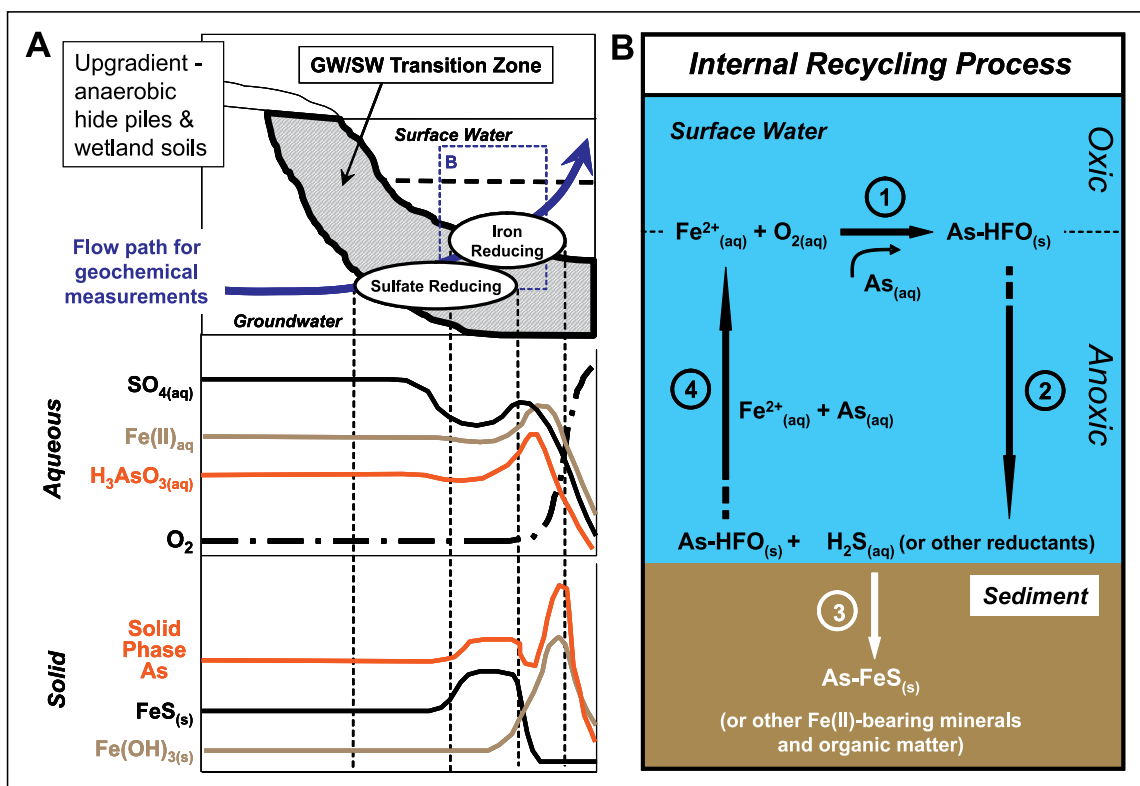


Figure 2. Conceptual depiction of (A) the spatial distribution of aqueous and solid components along a flow path (solid blue arrow) across the ground water/surface water (GW/SW) transition zone at the Industri-Plex Superfund Site (blue dotted rectangle highlights area of detail shown in Panel B) and (B) solid-solution partitioning dynamics of arsenic within the Halls Brook Holding Area (HBHA) Pond.

Table 2. Comparison of site characterization efforts during original and revised consideration of MNA as a component of the ground-water remedy for the Industri-Plex Superfund Site (OU-2). Solid phase characterization measurements are highlighted in bold.

Data Category	Site Characterization to Support MNA Evaluation	
	Original	Revised
Hydrology	<ul style="list-style-type: none"> • Particle track modeling using measured water levels to characterize plume discharge and capture within HBHA Pond • Direct measurement of ground-water flux into HBHA Pond • Measurement of surface water flow inputs and outputs to calculate ground-water flow contribution 	<ul style="list-style-type: none"> • Measurement of ground-water chemistry in temporary and permanent nested well clusters to map out plume dimensions adjacent to and underneath HBHA Pond
Reaction Process	<ul style="list-style-type: none"> • Characterization of elemental arsenic and iron association in pond sediments using chemical digestion • Scanning electron microscopy with energy dispersive spectroscopy for a subset of sediment samples to evaluate microscale As-Fe association and infer controlling mineralogy • Determination of the presence of sulfide minerals using acid volatile sulfide (AVS) extraction on unpreserved sediment samples (USEPA, 2006a) 	<ul style="list-style-type: none"> • Measurement of redox chemistry in water within the plume, sediment pore space, and HBHA Pond water column using in-situ techniques or sampling procedures that avoided air-exposure • Direct measurement of arsenic speciation in water by HPLC-ICP-MS and in solids samples using X-ray absorption spectroscopy in combination with chemical extraction methodologies • Field measurement of ferrous iron using colorimetric techniques in combination with total iron by atomic emission spectroscopy • Identification of iron-bearing minerals in suspended solids and sediments, along with element correlations in solids via bulk extraction and SEM-EDS measurements
Attenuation Capacity	<ul style="list-style-type: none"> • Laboratory measurements of arsenic sequestration capacity using unpreserved sediment samples 	<ul style="list-style-type: none"> • Depth-discrete measurements of dissolved and particulate arsenic and iron throughout entire water column and sediment layer within the HBHA Pond at locations within and outside of the influence of plume discharge
Stability of Attenuation	<ul style="list-style-type: none"> • Historical measurements of arsenic concentrations in plume discharge and depth-integrated pond water samples to infer negligible release of sorbed arsenic 	<ul style="list-style-type: none"> • Field measurement of arsenic release during deposition of arsenic-iron oxyhydroxide coprecipitates on the pond bottom via time-series sampling across the ground water-surface water transition zone following a large surface water flow event • Mineralogical identification of components controlling arsenic attenuation in suspended solids and shallow sediments in combination with geochemical models to assess theoretical stability under measured field geochemical conditions

Hanford 300 Area Uranium Plume

The U.S. Department of Energy's Hanford Site is a 586-square-mile federal facility located in southeastern Washington along the Columbia River (Duncan, 2007). The Hanford Site was established during World War II, as part of the Manhattan Project, to produce plutonium for nuclear weapons. One of the primary waste components from this production effort was uranium. The 300 Area, which encompasses approximately 1.35 square kilometer (0.52 square mile), is adjacent to the Columbia River and approximately 1.6 kilometer (1 mile) north of the city limits of Richland, WA. The 300 Area terrain is generally level, with a steep embankment dropping to the river. The 300 Area was established as a fuels fabrication complex in 1943. Liquid process wastes generated during these operations were disposed in unlined surface ponds and trenches that are included in the 300-FF-1 Operable Unit under CERCLA. A portion of these liquid wastes containing elevated levels of uranium infiltrated into the vadose zone and underlying unconfined aquifer adjacent to the Columbia River. Subsequently, a plume of uranium has developed in the unconfined aquifer, which migrates towards and discharges into the river (Figure 3A). Selection of the remedy for cleanup of surface and subsurface contamination within the 300 Area was documented in the 1996 Record of Decision (ROD; USEPA, 1996). Removal of contaminated soil and debris was selected as a component of the remedy for Operable Unit 300-FF-1. Ground-water contamination (Operable Unit 300-FF-5) was addressed through selection of an interim remedial action that included institutional controls to restrict use of ground water and continued monitoring of ground water to verify decreasing trends in contaminant concentrations (uranium, trichloroethene, and 1,2-Dichloroethene) with future review to determine the need for active remedial measures.¹ Selection of the interim remedy for ground water was supported by contaminant transport model projections that indicated uranium concentrations would decrease to <20 µg/L due to natural processes over a period of 3-10 years following removal of contaminated surface soils (DOE, 1994; DOE, 1995).

The development and implementation of a contaminant transport model for uranium in the unconfined aquifer played a key role in the selection of the interim remedial action for Operable Unit 300-FF-5. It is instructive to evaluate what assumptions were made in constructing the model descriptions of water transport and uranium partitioning to aquifer solids. Waichler and Yabusaki (2005) provide a useful description of the assumptions inherent to the original transport model and the associated limitations for describing uranium transport in the unconfined aquifer. In general, the following assumptions appear to have been critical relative to disparities between model projections and the subsequent observed behavior of the plume: 1) removal

of contaminated surface soils eliminated the source of uranium from which the plume developed; 2) ground-water flow was unidirectional towards the Columbia River, which was treated as a constant head boundary; and 3) partitioning of uranium to aquifer solids could be described using a constant equilibrium sorption isotherm (K_d) independent of water chemistry and aquifer mineralogy. Subsequent investigations to determine the cause of sustained elevated uranium concentrations in the plume have demonstrated that a lack of information on the spatial distribution of uranium within subsurface solids and the chemical speciation of solid phase uranium were important limitations to the reliability of the contaminant transport model. First, failure to consider that a fraction of the uranium transported through the vadose zone was retained in the subsurface in a range of solid forms (Wang et al., 2005; Catalano et al., 2006; Arai et al., 2007; McKinley et al., 2007) led to overly conservative projections of the long-term flux of uranium that could be transported through the saturated aquifer. Characterization of subsurface solids collected from under former waste process areas indicated elevated uranium concentrations bound to the solids in both precipitated (co-precipitated in CaCO_3 , uranium-phosphate precipitates) and adsorbed (e.g., muscovite in aquifer solids) forms. As demonstrated by subsequent hydrologic investigations, water level fluctuations induced by periods of recharge from the Columbia River, causes a portion of residual uranium solids within the lower vadose zone (i.e., the smear zone in Figure 3A) to be cyclically leached into the underlying plume (Qafoku et al., 2005; Zachara et al., 2005; Bond et al., 2007; Peterson et al., 2008; Yabusaki et al., 2008). Finally, aquifer recharge by river water with low dissolved carbonate concentrations results in cyclical increases in uranium adsorption to aquifer solids within the plume, which has resulted in slower dissipation of the plume due to flushing from the aquifer. Tests with contaminated subsurface solids have demonstrated that dissolved carbonate is the most important parameter in site ground-water chemistry with respect to impacting uranium mobility; uranium adsorption to aquifer solids decreases with increasing alkalinity (e.g., Serne et al., 2002; Bond et al., 2007). The revised conceptual site model including identification of the important subsurface zones is provided in Figure 3A (Peterson et al., 2005; Nimmons, 2007), and the solid phase distribution and chemical speciation of uranium as a function of depth below source areas are shown in Figure 3B.

A summary of site characterization efforts supporting interim remedy selection under the 1996 ROD and subsequent solid phase characterization studies for the ground-water system is provided in Table 3. Comparison of the information collected under the "Original" and "Revised" column listings illustrates the disparity between what was known at the time of the 1996 ROD and the present. The site-specific knowledge of hydrologic dynamics and uranium geochemistry within the vadose zone and ground-water plume gained from the various tests and characterization methods employed using field samples has significantly reduced the level of uncertainty relative to the processes controlling plume dynamics. Based on

¹ The 1996 ROD was prepared prior to publication of the 1999 OSWER Directive in which expectations for assessment and use of MNA as a remedial action alternative were documented. Documentation of more recent site investigations is available at <http://www.hanford.gov/cp/gpp/library/programdocs-300.cfm> or <http://ifchanford.pnl.gov/publications/>.

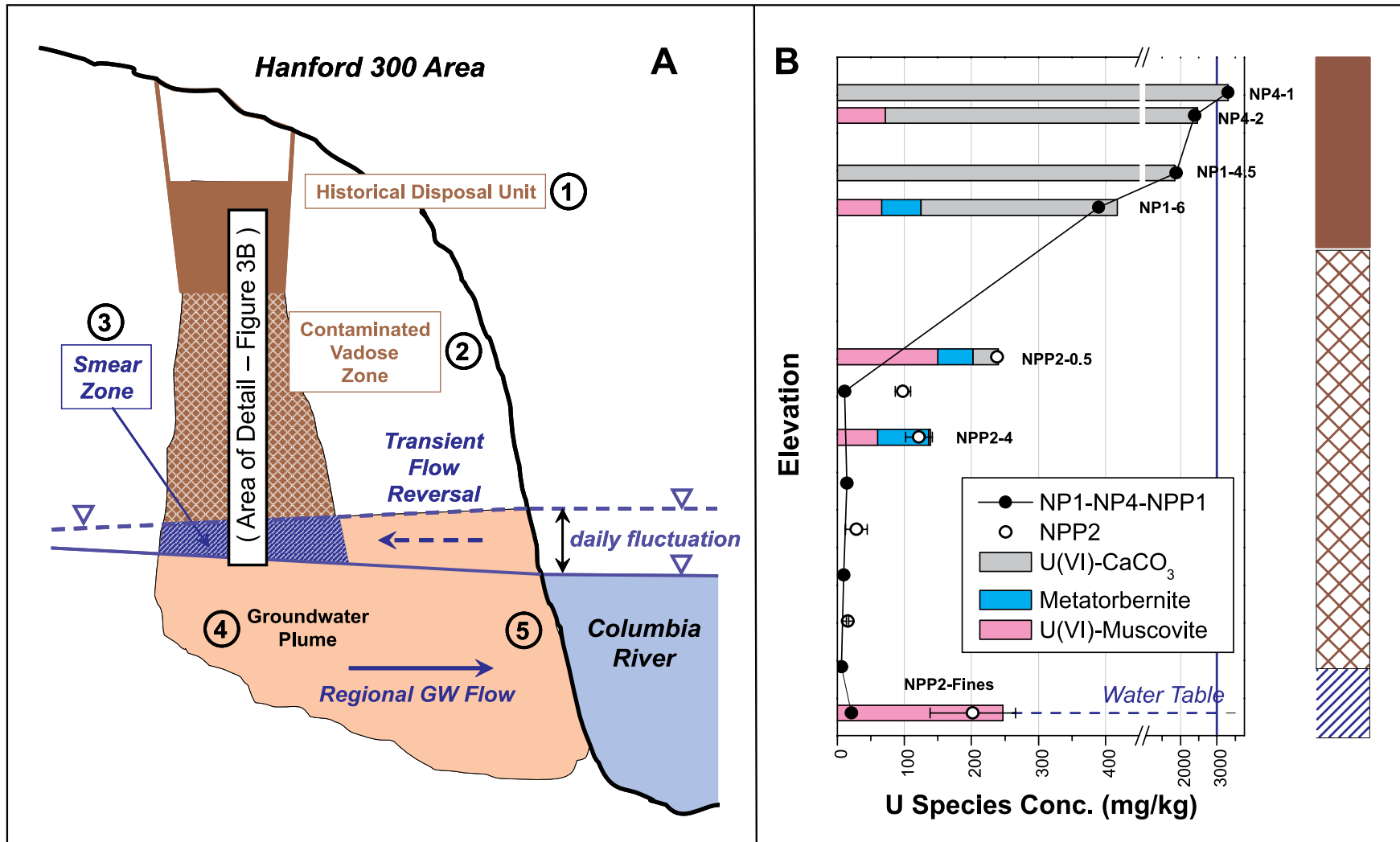


Figure 3. Subsurface uranium contamination within the Hanford 300 Process Waste Sites area. A) Primary hydrogeologic features impacting plume migration to the Columbia Region (vertical dimension is exaggerated; CSM zones identified with circled numbers after Nimmons, 2007). B) Concentrations and speciation of solid phase uranium in vadose zone above (North Process Ponds solids and contaminated aquifer solids) and within the influence of ground-water level fluctuations (smear zone). Note break in x-axis scale; "Water Table" is approximate location of ground-water surface at the time of subsurface excavations; closed and open symbols represent two sampling locations; graph generated using information from Wang et al. (2005), Catalano et al. (2006), Arai et al. (2007), McKinley et al. (2007).

the current site knowledge, a decision has been made to use active remedial technologies to control the flux of uranium entering into ground water from the vadose zone and the zone of fluctuating water table (i.e., “smear zone” in Figure 3A). It is anticipated that by minimizing the flux of uranium contributing to concentrations in the ground-water plume, natural attenuation processes may be successful

in achieving cleanup objectives in more dilute portions of the plume. In general, the revised information on the mass and speciation of uranium in aquifer solids relative to relevant transport pathways has contributed to more realistic expectations of the role that MNA may play as a component of the ground-water remedy.

Table 3. Comparison of site characterization efforts during original and revised consideration of MNA as a component of the ground-water remedy for the Hanford 300 Area (OU 300-FF-5). Solid phase characterization measurements highlighted in bold.

Data Category	Site Characterization to Support MNA Evaluation	
	Original	Revised
Hydrology	<ul style="list-style-type: none"> • Water level measurements in aquifer and stage measurements in Columbia River • Modeled ground-water transport assuming average river stage as downgradient boundary condition 	<ul style="list-style-type: none"> • Higher time frequency measurements of river stage and ground-water level • Modeled ground-water transport to account for time-variant changes in water flux and direction
Reaction Process	<ul style="list-style-type: none"> • Modeled sorption of uranium to aquifer solids assuming fixed Kd independent of ground-water chemistry and aquifer solids mineralogy 	<ul style="list-style-type: none"> • Laboratory tests with aquifer solids from various depths to assess influence of ground-water chemistry on the extent and rate of uranium sorption-desorption • Direct measurement of uranium speciation in vadose zone pore water using fluorescence spectroscopy to identify mobile aqueous species • Direct measurement of uranium speciation in aquifer solids as a function of depth using bulk and microfocused X-ray spectroscopy/diffraction and electron microscopy in combination with chemical extraction methodologies • Determination of uranium distribution as a function of particle size in aquifer solids • Identification of reactive clay minerals in aquifer solids • Modeled contaminant transport to account for rate-limited sorption-desorption processes and influence of ground-water chemistry on uranium sorption to aquifer solids
Attenuation Capacity	<ul style="list-style-type: none"> • Estimated sorption contribution based on Kd and mass of aquifer solids along ground-water flow path • Assumed no additional inputs of uranium from overlying vadose zone into plume 	<ul style="list-style-type: none"> • Laboratory measurements with aquifer solids to estimate mass flux of uranium derived from smear zone
Stability of Attenuation	<ul style="list-style-type: none"> • No measurement of stability of uranium partitioned to aquifer solids 	<ul style="list-style-type: none"> • Laboratory tests to evaluate reversibility of uranium sorption as a function of contact time and/or uranium solid phase speciation • Geochemical modeling to assess theoretical stability of identified solid phase uranium species under relevant field geochemical conditions

Future Technical Development Issues

The case studies reviewed above illustrate several types of measurements that provide information on the characteristics and behavior of solid phase components involved in contaminant transport and attenuation. For both studies, identification of the solid components participating in contaminant attenuation was clearly important. In addition, knowledge of the chemical speciation of the contaminant (beyond its mineral association) was important for identifying the specific reaction mechanism(s) controlling attenuation, as well as understanding factors that may influence the efficiency and stability of the immobilization process. It should also be evident that selection of 1) sampling locations and frequencies, 2) sampling procedures and 3) the specific measurement techniques needs to be conducted with knowledge of the ground-water hydrology and biogeochemical characteristics of the plume. While not discussed in detail within this document, information derived from characterization of the flow system (pathways and dynamics in velocity and/or direction), as well as the general chemical conditions within the plume bear directly on design of the sampling and analysis program applied to solid phase characterization for a site (USEPA, 2007a; Sections IIIA and IIIB, respectively). As an example, subsurface redox conditions will dictate to a large extent what sampling, preservation, and processing procedures are most suitable to ensure that the in situ characteristics of the solid samples are preserved prior to analysis (USEPA, 2002; USEPA, 2006a).

The analytical techniques employed for characterization of solid samples at the two sites varied in their commercial availability and technical complexity. Procedures used to determine element compositions in solid samples (e.g., total digestion or acid-extractable with element-specific detection, X-ray fluorescence spectroscopy; Amonette, 2002) are generally routine and readily available through commercial laboratories. There are a range of laboratory-based instruments that can be used to measure bulk mineralogical characteristics of solid samples (Hawthorne, 1988; Amonette, 2002; Ulery and Drees, 2008). Frequently, the detection capability of these instruments can be improved through physical manipulation of the solid sample to concentrate the targeted component of interest. While the general availability of these types of instruments varies across the commercial laboratory network, the accessibility to these methods and the availability of technical personnel capable of collecting and interpreting the resultant solid phase characterization data are not anticipated to constrain more routine application for site characterization. In contrast, the use of X-ray absorption spectroscopy or related advanced spectroscopic techniques is generally not routine and requires a high level of technical knowledge and experience in data interpretation. However, these limitations should not eliminate these techniques from consideration. Rather, it may be necessary to consider use of these techniques for a more limited number of high-value samples with correlation of information to more conventional techniques that can be applied to a greater number of samples to fully characterize site conditions. The value of advanced

spectroscopic techniques is that they provide improved capability for directly assessing chemical characteristics of the contaminant even at very low concentrations; this is critical because a contaminant is often present only as a minor component for even highly contaminated samples.

The scarcity of studies evaluating correlation of data from a range of direct and indirect measurements for the purpose of defining contaminant speciation in solid samples represents a current limitation for more routine application of solid phase characterization to support selection of MNA as a component of ground-water remedies. A specific example is the complementary use of chemical extraction methodologies and spectroscopic techniques to characterize solid phase components within an aquifer. Chemical extraction methodologies are generally sensitive and can be applied in a cost-effective manner to a large number of samples. However, there are analytical limitations to the accuracy of the information derived from these tests (USEPA, 2007a, Section IIIB.2.4; USEPA, 2007b, individual contaminant chapters). While specific chemical extraction methodologies that might be used to characterize contaminant speciation in solid samples have been proposed, there has been limited effort to confirm the applicability of these tests with direct evaluations of in situ speciation using spectroscopic techniques. Additional work is needed to validate the appropriate use of chemical extraction methodologies in order to support the more routine application of solid phase characterization analysis in the evaluation of MNA as a potential remedy. As reflected in the two case studies reviewed above, research organizations across the federal sector are actively pursuing work to address this limitation. The goal of these efforts is to provide regulatory agencies and site remediation managers with the necessary tools for conducting rigorous assessment of MNA as a component for ground-water restoration. The underlying basis of this assessment is a good conceptual site model derived from a site characterization plan that considers potential reactions of the contaminant with the solid phase, as well as changes to the solid phase that may impact contaminant mobility. As described earlier in this report, acquisition of this site-specific information is critical for developing technical and public acceptance of MNA as a viable remedy.

Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described for the Industri-Plex Superfund Site. This report and referenced USEPA publications were subjected to the Agency's peer and administrative review and approved for publication as an EPA document.

Quality Assurance Statement

All research projects making conclusions or recommendations based on environmentally-related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance (QA) program. Preparation of this report did not involve the collection or use of environmental data and, as such, did not require a Quality Assurance Project Plan.

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