API Groundwater Arsenic Manual

Attenuation of Naturally-Occurring Arsenic at Petroleum Impacted Sites

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EXECUTIVE SUMMARY

In January, 2006 the United States Environmental Protection Agency (USEPA) lowered the maximum contaminant level (MCL) for dissolved arsenic in groundwater from 0.050 mg/L to 0.010 mg/L due to long term chronic health effects of low concentrations of arsenic in drinking water. This five-fold lowering of the MCL has heightened public and regulatory awareness of dissolved arsenic in groundwater. The World Health Organization (WHO) is considering a similar lowering of groundwater standards for arsenic.

Naturally-occurring arsenic may be mobilized into shallow groundwater by inputs of biodegradable organic carbon, including petroleum hydrocarbons. This manual was developed to explain the mobilization, transport and attenuation mechanisms of naturally-occurring arsenic in groundwater at petroleum impacted sites.

This manual:

1) Identifies and categorizes the potential sources of arsenic at petroleum impacted sites, including arsenic contained in native rock and soils and arsenic resulting from anthropogenic sources;

2) Provides information on the arsenic content of petroleum and refined products. Arsenic is not a common or significant trace element in petroleum, and petroleum is not known to be a significant source of mobile arsenic in groundwater.

3) Presents the fundamentals of arsenic biogeochemistry at petroleum impacted sites where the presence of hydrocarbons may result in dissolution of native arsenic due primarily to biodegradation and the resulting electrochemically-reduced conditions; and

4) Provides validated tools for the assessment of arsenic at petroleum impacted sites and its management through natural attenuation.

This manual is not a treatise on arsenic geochemistry but is focused on a very specific issue, the mobilization and attenuation of naturally-occurring arsenic at petroleum impacted sites. "Naturally-occurring arsenic" refers to arsenic that is present in the solid phase prior to any impacts by degradable organic carbon including petroleum hydrocarbons. Many of the issues and conditions relating to arsenic occurrence and mobility apply for other metals in the subsurface; although this manual only addresses arsenic specifically, further discussion of other metals can be found in the literature (USEPA, 2007a; USEPA 2007b).

Arsenic may be present as a natural trace metal in native rocks and soils or as a result of agricultural, industrial or mining activity. Arsenic may be present as specific minerals, as an amorphous phase, or adsorbed onto iron oxyhydroxides

and other soil constituents. Anthropogenic sources of arsenic include pesticide application, wood treating, or mine tailings. Arsenic is not a common or significant trace constituent in petroleum.

An important part of understanding the mobility of naturally-occurring arsenic at petroleum impacted sites is having a good characterization of the ambient arsenic geochemistry and of the hydrogeology of the site. An important part of this characterization is to determine the ambient, background level of dissolved arsenic. The dissolved arsenic level at petroleum impacted sites, even after attenuation, cannot be lower than background. If the background level of arsenic naturally exceeds the new MCL, then the MCL is unachievable as an attenuation or remediation goal. Ambient dissolved arsenic concentrations exceeding the new (or old) MCL can occur at sites with a high or low natural pH, or at sites that lack iron oxyhydroxides in the soil. Naturally-occurring dissolved arsenic concentrations above the new (and old) MCL are, in fact, common in many parts of the World.

The natural solubility of arsenic is controlled by redox conditions (Eh), pH and by the presence of metal oxyhydroxides that can adsorb and bind arsenic. Since the focus of this manual is on arsenic mobilization and attenuation at petroleum impacted sites, the aquifers most commonly encountered will, for the most part, be shallow and in contact with the atmosphere. Therefore, the most common background redox condition will be an aerobic environment in which arsenic will be present as the oxidized, less mobile, As^{+5}. The ambient groundwater concentration of the arsenic will be controlled by pH and the soil mineral content (i.e. iron oxyhydroxides). As^{+5}, present as the arsenate anion (AsO_4^{-3}), is more soluble at low pH (< 4) and high pH (>8). This is in contrast to natural groundwater pH values typically ranging between 4 and 8. Arsenate is also strongly adsorbed to iron oxyhydroxides, which are fairly ubiquitous.

When a petroleum release occurs at concentrations sufficient to reach the water table, the hydrocarbons come into contact with the groundwater. The more soluble hydrocarbon fractions dissolve into groundwater, stimulating biological activity. Bacteria degrade the dissolved hydrocarbons and sequentially consume the available terminal electron acceptors (TEAs), progressing from oxygen through nitrate, manganese, iron, sulfate and finally reach methanogenesis, creating progressively more reduced groundwater environments. The redox level attained is a function of the TEA availability and the amount of hydrocarbon released. Once the redox conditions are at or below the Eh for iron reduction, ferric oxides in the soils are reduced to the more soluble ferrous form. Because most soil arsenic is associated with ferric oxides, arsenic will also be released and mobilized into groundwater. Dissolution of ferric oxides not only releases arsenic to the groundwater, but also decreases the future adsorption sites for arsenic. Arsenic is also reduced from As^{+5} to the more soluble As^{+3}, which is present as the arsenite anion (AsO_3^{-3}), and further increases mobility.

Migration of the dissolved hydrocarbons and the resulting microbial activity can create overlapping hydrocarbon and arsenic plumes. The arsenic plume commonly extends slightly beyond the hydrocarbon plume, with arsenic remaining above background concentrations until aquifer redox conditions return to aerobic. This down-gradient portion of the plume is a transition zone where dissolved arsenic concentrations decrease as the aquifer becomes more oxidizing and the arsenic is immobilized.

The combined plume goes through three stages over time – an initial phase of plume expansion, a period of plume stability where the footprint is static, and a final stage in which the plume retreats toward the petroleum source area. Plume expansion occurs until the dissolution of hydrocarbons is balanced by their degradation and removal. When there are no longer sufficient hydrocarbons present to maintain the plume, the plume begins to retreat. As the plume retreats, redox conditions gradually revert to ambient conditions and the arsenic returns to its background level. Once the hydrocarbons are attenuated, the aquifer becomes aerobic, and the arsenic reverts back to the existing ambient (background) conditions.

When the petroleum hydrocarbons are attenuated, natural attenuation of arsenic will occur as the aquifer is restored to aerobic conditions. Arsenite is reoxidized to the less soluble arsenate. Reduced iron is reoxidized and re-precipitates on the soil particles as an oxyhydroxide. These iron oxyhydroxides adsorb and bind arsenate. Over time, the adsorbed arsenate can mineralize and become even more stable.

Proper management of a petroleum impacted site at which arsenic has become mobilized requires development of a site specific conceptual model (SSCM). The SSCM consists of four main elements:

1. The general site geology and hydrogeology of the groundwater bearing units (GWBU) that has been or can be impacted by a petroleum release;

2. The ambient arsenic geochemistry within the impacted GWBU;

3. The petroleum distribution and microbial conditions (redox zones); and

4. A survey of potential receptors and exposure pathways for arsenic that is mobilized.

A well constructed SSCM has a number of uses including:

- Determining the appropriate locations for long term monitoring;

- Determining the key parameters needed to monitor the effectiveness and status of natural attenuation at the site;

- Supporting the inclusion of a natural attenuation based approach in the remediation strategy;

- Illustrating the processes of mobilization and attenuation of arsenic at a petroleum impacted site for discussing with regulators and stakeholders; and

- Assessing whether efforts beyond natural attenuation are necessary.

In some circumstances the time line for arsenic attenuation is too slow and additional remediation effort is needed. This may include situations such as preventing third party impacts, protecting receptors, or property redevelopment. Under such circumstances, a proactive approach to remediate the hydrocarbon plume should be evaluated; once the hydrocarbons are depleted, the arsenic will attenuate. Many of the technologies that are effective in remediating hydrocarbons can also address arsenic particularly those that create aerobic or oxidizing environments.

If a receptor needs to be protected and natural attenuation or institutional controls are not adequate, adsorptive or reactive barriers can sometimes be emplaced near the receptor. Such barriers could include the use of iron oxyhydroxides such as goethite, basic oxygen furnace slag, conditioned red mud or zero valent iron. These barriers reduce arsenic concentrations as the groundwater moves through the emplaced material.

Four case studies from the petroleum industry are included in this manual to illustrate the basic principles of arsenic mobilization and attenuation. These case studies include:

1. An Operating Oklahoma Refinery – Arsenic mobilization associated with the presence of hydrocarbon LNAPL is present in an alluvial terrace sand aquifer. Correlations between iron and arsenic in both soil and groundwater indicate arsenic mobilization occurs with the loss of iron oxyhydroxide sorption sites due to changes in redox conditions. Concentrations of arsenic in groundwater downgradient of hydrocarbon impacts indicate that arsenic is not mobile under the ambient aerobic conditions at this site. Once the hydrocarbons are attenuated, aerobic conditions are re-established and the arsenic is re-oxidized and re-adsorbed onto the soil matrix.

2. A Former West Texas Refinery – The water bearing unit in a bluff underlying a former tank farm is impacted with hydrocarbon LNAPL and arsenic. The presence of iron oxyhydroxides is visually evident as orange and red staining of quartz grains in cored sediment from outside the hydrocarbon plume, while within the plume reducing conditions are evident by grey to black sandstone. Arsenic mobilization appears to be a result of changing redox conditions, leading to elevated arsenic in seepage water from the bluff.

3. A Former Exploration Reserve Pit – A former drill site reserve pit and gravel pad in northern Alaska received drilling waste, followed by

closure and corrective action activities. Samples of surface water surrounding the pit before corrective action revealed evidence of potential hydrocarbon impacts and elevated dissolved arsenic concentrations. Later samples showed decreases in dissolved arsenic concentrations as the geochemical parameters pH and dissolved iron returned to background aerobic conditions.

4. A Former Fuel Terminal – A former fuel terminal contains elevated hydrocarbon in soil and groundwater at various locations throughout the site. Ambient geochemical conditions are naturally reducing due to native organic carbon. Dissolved arsenic has been measured throughout and upgradient of the site where groundwater conditions are reducing. Removal of hydrocarbon impacts does not decrease arsenic concentrations due to the ambient reduced conditions that exist at the site.

This manual can be summarized by five basic principles that govern the fate and transport of arsenic in shallow aquifers impacted by petroleum hydrocarbons. These are:

1. If arsenic is not present in the site mineralogy, or if arsenic has not been emplaced due to human activity (agriculture, wood treating, mining, etc.), petroleum impacts will not cause arsenic impacts to groundwater.

2. For sites that have naturally-occurring arsenic-bearing minerals, sorbed arsenic phases, or aged anthropogenic arsenic sources, there is a stable arsenic geochemistry present that determines the ambient (background) level of dissolved arsenic in groundwater. The ambient dissolved arsenic level is controlled by complex geochemical interactions among Eh, pH and minerals able to adsorb, complex, or precipitate arsenic.

3. The introduction of petroleum hydrocarbons (or other degradable organics) may cause a perturbation to the existing geochemistry, resulting in the mobilization of arsenic at concentrations above the ambient level. Petroleum and other degradable organics lower the redox state to more reduced conditions. The primary mechanism for lowering the Eh is anaerobic biological activity.

4. The perturbation of the ambient arsenic geochemistry (and related arsenic mobilization) will persist until the soluble hydrocarbons are attenuated.

5. Once the hydrocarbons are attenuated, the arsenic will revert to its pre-existing stable geochemistry, which may be above or below the drinking water MCL for arsenic of 0.010 mg/L depending on the background geochemistry.

GLOSSARY

Absorption – The diffusion of an aqueous or adsorbed chemical species into a solid phase.

Acids – Materials which release a hydrogen ion (H^+) which results in a lowering of the pH. For example, hydrochloric acid: $HCl \rightarrow H^+ + Cl^-$. Acids can be monoprotic, HCl; diprotic, H_2SO_4; or, triprotic, H_3PO_4.

Adsorption – The accumulation of matter at the interface between the aqueous phase and a solid adsorbent without the development of a three-dimensional molecular arrangement. Adsorption of both As^{+3} and As^{+5} onto mineral surfaces exhibits a strong pH dependence.

Aerobic – Aerobic, or oxic, waters are those where dissolved oxygen is present. Often this term is used to indicate that the concentration of dissolved oxygen is sufficient for microbial respiration of organic matter to occur. The degree of aerobicity can vary; highly aerobic environments generally contain dissolved oxygen concentrations greater than 5 mg/L, mildly aerobic can contain approximately 1.5 to 2 mg/L (see also Redox Conditions).

Anaerobic – Anaerobic, or anoxic, waters are those where dissolved oxygen is not the dominant electron acceptor for microbial processes, and dissolved oxygen concentration is low or not present. Anaerobic conditions occur when microbial metabolism of organic carbon or hydrocarbon consumes all available dissolved oxygen. Further metabolism of carbon can occur with the use of alternate terminal electron acceptors. Anaerobic conditions extend from nitrate reduction to methanogenesis (see also Redox Conditions).

Anoxic – See Redox Conditions

Arsenate (AsO_4^{-3}; As^{+5}) – The arsenate anion is an oxyanion, composed of arsenic and oxygen in the formula AsO_4^{-3}. Arsenic in this anion is of the +5 valence, or oxidation, state, and is sometimes represented as As^{+5}. The arsenate anion is the oxidized arsenic species as compared to the arsenite anion, and is less mobile (soluble) in many natural waters.

Arsenite (AsO_3^{-3}; As^{+3}) – The arsenite anion is an oxyanion, composed of arsenic and oxygen in the formula AsO_3^{-3}. Arsenic in this anion is of the +3 valence, or oxidation, state, and is sometimes represented as As^{+3}. The arsenite anion is the reduced arsenic species as compared to the arsenate anion, and is more mobile (soluble) in many natural waters.

Bases – Materials which can accept a hydrogen ion (H^+) or release a hydroxide ion (HO^-). Bases cause the pH to increase. Examples of bases include

ammonia (accepts hydrogen ion): $NH_3 + H^+ \rightarrow NH_4^+$; or calcium
hydroxide (releases hydroxide): $Ca(OH)_2 \rightarrow Ca^{+2} + 2HO^-$.

Cationic metal surfaces – Minerals on which the surface is positively charged.
These minerals are usually oxides of iron, aluminum and calcium. The
cationic surfaces serve as adsorption sites for anions such as arsenate or
arsenite

Circumneutral - near neutral pH conditions. The term is applied to pHs in the
range of 5.5 to 7.4.

Colloid – An agglomeration of atoms or molecules suspended in a separate
aqueous phase. Particles with diameters less than 10 µm are generally
considered to be colloids.

COC – Abbreviation for Compound of Concern, Chemical of Concern, or
Contaminant of Concern. COCs are generally chemicals that are being
monitored in association with impacts at a given site.

Deprotonation - The removal of a hydrogen ion (H^+) from a molecule or a mineral
resulting in the conjugate base (anion). For example: sulfuric acid H_2SO_4
$\rightarrow HSO_4^- + H^+$, or a metal hydroxide, M-OH $\rightarrow$ M-O$^-$ + H$^+$.

Desorption – The release of a material sorbed to a surface. Desorption can occur
as a result of changes in solution geochemistry, such as pH or Eh.

Dissolution – The process by which a solid, liquid, or gas enters into the aqueous
phase.

Eh – The redox potential (Eh), or the potential for electron transfer (reduction-
oxidation) to occur, for a particular redox couple. The Eh can be related
to the ratio of this couple in solution by the Nernst Equation. For
standard states, the Eh can be expressed as E_0, which in turn can be
related to the Gibbs Free Energy (G_0). The Eh is specific to each redox
pair, or reaction, and therefore field measurements of oxidation-
reduction potential (ORP) may not provide a specific Eh, and must be
corrected for the reference electrode potential.

Ferric oxyhydroxide – see iron oxyhydroxides

Fermentation – Fermentation occurs under anaerobic conditions, where the
hydrocarbon acts as both the electron donor and the electron acceptor.
Fermenting microorganisms catalyze the breakdown of hydrocarbons
through internal electron transfers into simpler molecules such as
alcohols, fatty acids, hydrogen and carbon dioxide. These fermentation

products can be used by other bacterial species converting them into carbon dioxide and methane.

Hydrous ferric oxide - see iron oxyhydroxides

Iron oxyhydroxides – A metal oxyhydroxide (MO_xOH_y) of ferric iron, including goethite (FeO(OH)) and other polymorphs. The surface properties of these minerals make them potent sorption sites for ions. Iron oxyhdroxides are sensitive to changes in pH and Eh, and, if thus dissolved, will release associated sorbed ions into solution. Sometimes referred to as hydrous ferric oxide (HFO) or ferric oxyhydroxide – FeO(OH).

Maximum Contaminant Level (MCL) – The maximum contaminant level (MCL), is "the maximum permissible level of a contaminant in water which is delivered to any user of a public water system" (US Code Title 42 Section 300f). MCLs are set by the USEPA to ensure that drinking water does not pose either a short-term or long-term health risk. Some states set MCLs which are more strict than USEPA's. The MCL for arsenic was recently lowered (in 2006) to 0.01 mg/L from 0.05 mg/L. Depending on the potential exposure pathways and receptors present at or near a particular site, other (higher) concentration limits could be applicable to groundwater and surface water arsenic concentrations.

Methanogenesis – The reduction of carbon dioxide or low-molecular weight carbon (fatty acids or petroleum hydrocarbons) to produce methane. Methanogenesis occurs under strongly reducing conditions.

Monitored natural attenuation (MNA) – the U.S. Environmental Protection Agency defines monitored natural attenuation as 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" (USEPA, 1999). Natural attenuation processes include a variety of physical, chemical, or biological processes "that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants" (USEPA, 1999). Other agencies provide their own definitions, but the overall concept is shared

Non-aqueous phase liquid (NAPL) – An organic liquid, such as a petroleum hydrocarbon, that is insoluble in water, and therefore remains as a distinct phase when released to the subsurface. NAPL that is less dense

than water and floats on the water surface is referred to as light non-aqueous phase liquid (LNAPL); whereas a substance more dense than water and sinks in a water column is referred to as dense non-aqueous phase liquid (DNAPL).

Oxidation – The transfer of an electron from an atom or ion, changing its oxidation (often referred to as valence) state. For example, the arsenic ion in arsenite (AsO_3^{-3}) is of the +3 valence state, and can be oxidized to arsenate (AsO_4^{-3}), of the +5 valence state. An oxidant is a material that supplies electrons for oxidation.

Oxidation-reduction potential (ORP) – Also referred to as redox potential, or redox, the ORP is an expression, in volts, of the relative electron activity (as described above for Eh). Field measurements of ORP often are subject to error, and therefore are best used as a qualitative value. In many cases natural or impacted waters contain multiple redox couples that are not in equilibrium, and an Eh value cannot be assigned from field measurements of ORP.

Precipitation – The formation of a solid phase from a solution. The solid phase is generated by the combining of cations and anions to form a charge-neutral compound that separates from the aqueous phases. The likelihood of precipitation is governed by the solubility product constant K_{sp} which is the product of the molar concentrations of the combining cations and anions. For example the precipitation of ferric arsenate: $Fe^{+3} + AsO_4^{-3} \rightarrow FeAsO_4$; $K_{sp} = [Fe^{+3}]*[AsO_4^{-3}] = 6.3 \times 10^{-21}$

Redox – term used to generally describe oxidation-reduction reactions. These reactions may be chemically or biologically mediated.

Redox conditions – Aquifers vary in their electrochemical characteristics. Generally there is a spectrum of conditions. However, conceptually redox conditions are thought of as bipolar. The following list the common coupling of redox terms and their definitions. These couplings can be used interchangeably.

1. *Oxidizing-reducing*
    1a. *Oxidizing* – a reaction which removes electrons from an atom or molecule, thereby increasing the valence state. A reaction which adds oxygen to an atom or molecule.

    1b. *Reducing* – a reaction which adds electrons to an atom or molecule thereby decreasing the valence state. A reaction which removes oxygen or adds hydrogen to an atom or molecule.

2. *Oxic-anoxic*

    2a. *Oxic* – an environment which contains oxygen.

    2b. *Anoxic* – an environment or condition that is depleted of oxygen.

3. *Aerobic-anaerobic*

    3a. *Aerobic* – A condition created by the presence of oxygen; Biological definition: microorganisms which require oxygen to function.

    3b. *Anaerobic* – An environment that is free of oxygen. Biological definition: capable of living and functioning in the absence of oxygen.

Redox labile – a redox labile material is one that readily changes oxidation state under naturally occurring chemical or biological conditions. For example iron is redox labile. Reduced iron (Fe^{+2}) is easily oxidized by oxygen: $4Fe^{+2} + 4H^+ + O_2 \rightarrow 4Fe^{+3} + 2H_2O$. Oxidized iron is easily reduced by iron reducing bacteria: $6Fe^{+3} + -CH_2- + 3H_2O \rightarrow HCO_3^- + 7H^+ + 6Fe^{+2}$.

Reduction – The transfer of an electron to an atom or ion, changing its oxidation state. For example, the arsenic ion in arsenate (AsO_4^{-3}), of the +5 valence state, can be reduced to arsenite (AsO_3^{-3}), of the +3 valence state. A reductant is a material that absorbs electrons.

Sorption – A process of compound transfer from the aqueous to the solid phase that includes the three primary mechanisms of adsorption, absorption, and precipitation.

Sorptive capacity – The ability of a material or mineral to adsorb ions. Often expressed as cmol (centimole)/kg. Similar in concept to cation exchange capacity used in soil science

Standard electrode potential (E^0) - the electrode potential of a metal or ion measured at the anode under standard conditions; a temperature or 298^0K (25^0C), 1 atmosphere pressure and at 1 mole of the activity of redox participants of the half-reaction. It is expressed relative to the potential of the standard hydrogen electrode which has an E^0 of 0.00 V.

Terminal electron acceptor (TEA) – A compound that receives an electron (is reduced) as the terminal step of microbial metabolism (respiration) of carbon. TEAs include oxygen, as well as alternate TEAs such as nitrate, ferric iron, manganese, sulfate, and carbon dioxide. Certain carbon compounds can also act as TEA. The reactions involving these

compounds are sometimes referred to as terminal electron acceptor processes (TEAP).

Total organic carbon (TOC) – The quantitative measure of the total organic carbon in a sample. In a water sample, the TOC is dissolved organic carbon (DOC) plus suspended organic carbon (SOC).

Volatile fatty acids – An organic acid with a carbon chain of less than six carbons. These compounds are byproducts of microbial metabolism that can be metabolized further.

Valence state – Valence state reflects the electron balance on an atom. A positive balance indicates that one or more electrons have been lost, a negative balance indicates that one or more electrons have been gained.

1.0   *INTRODUCTION*

In January, 2006 the United States Environmental Protection Agency (USEPA) lowered the maximum contaminant level (MCL) for arsenic from 0.050 mg/L to 0.010 mg/L due to concerns about the long-term, chronic health effects of low concentrations of arsenic in drinking water. This five-fold lowering of the MCL has subsequently heightened public and regulatory awareness and concern with arsenic. For some, there is a concern that natural arsenic concentrations can exceed the new MCL due to the existing geology in certain areas of the country. For others, including the regulatory community, their concern stems from the fact that naturally-occurring arsenic may be mobilized into shallow groundwater by inputs of biodegradable organic carbon. These inputs may include petroleum hydrocarbon impacts.

Given these heightened concerns, it is important to understand the mobilization, transport and attenuation mechanisms of naturally-occurring arsenic at hydrocarbon impacted sites. This document was developed to facilitate this understanding when the arsenic is present at or above concentrations of concern. It was developed by ERM, Inc. in collaboration with the American Petroleum Institute (API) and the Petroleum Environmental Research Forum (PERF).

While this document is not intended to cover arsenic geochemistry or arsenic impacts on non-petroleum sites, it is useful to review some basic facts about arsenic in the environment to provide a context for discussing arsenic at petroleum impacted sites. This document will discuss the occurrence of arsenic in the subsurface and review the major biogeochemical factors affecting arsenic mobility and attenuation in groundwater at petroleum impacted sites. Assessment and site characterization strategies and techniques for the development of site-specific conceptual models are also reviewed.

1.1   *PURPOSE OF MANUAL*

The purpose of this manual is to provide the reader with an understanding of the factors that govern the fate and transport of naturally-occurring arsenic at sites impacted with petroleum hydrocarbons over the lifetime of the hydrocarbon impact. The central themes of the manual are that arsenic can be mobilized by the biodegradation of petroleum hydrocarbons at concentrations exceeding the natural ambient conditions and that when the hydrocarbon impact is mitigated (spatially or temporally), arsenic concentrations will revert back to the ambient geochemical conditions. Arsenic mobilization and attenuation are governed by simple, fundamental, and understandable principles.

1.2   *SOURCES OF ARSENIC – OCCURRENCE AND DISTRIBUTION*

Arsenic, a naturally-occurring, toxic metalloid, is a ubiquitous element, with a crustal abundance of 2.10 mg/kg. The average concentration of arsenic in surface water, world wide, is 0.001 mg/L, and 0.0023 mg/L in seawater. (www.webelements.com, 2008).

1.2.1   *Natural Sources of Arsenic*

Arsenic can be present in groundwater at a site due to either natural site mineralogy or geochemistry, or due to anthropogenic activity. As shown in Figure 1-1 (Ryker, 2001), there are broad areas of the United States where arsenic in groundwater already exceeds the previous MCL (0.050 mg /L) due to the naturally-occurring mineralogy. The southwestern and the upper midwest US have natural dissolved arsenic concentrations greater than either the current or previous MCL (0.01 mg/L and 0.05 mg/L, respectively).

Arsenic can be naturally found in many soils. It may be present as specific minerals or it may be present as an adsorbed phase on metal (primarily iron) oxyhydroxides and other clay minerals.

There are over 500 naturally-occurring arsenic minerals. Naturally-occurring arsenic is frequently associated with volcanic deposits and sulfidic minerals (e.g., pyrite [FeS_2]). Forty percent of arsenic minerals contain iron and/or sulfur. Arsenopyrite (FeAsS), orpiment (As_2S_3), realgar (AsS) and enargite (Cu_3AsS_4) are the most abundant arsenic minerals. Sixty percent of arsenic minerals are predominantly arsenates (expressed as AsO_4^{-3} or As^{+5}). Some of the arsenates such as scorodite ($FeAsO_4 \cdot 2H_2O$), kankite ($FeAsO_4 \cdot 3.5H_2O$), or bukovskyite ($Fe_2AsO_4SO_4OH \cdot 7H_2O$) are products of the weathering of arsenopyrite. Less than 5% of the stable arsenic minerals contain arsenites (reduced arsenic, expressed as AsO_3^{-3} or As^{+3}) (www.webmineral.com, 2008). Since arsenites are generally more soluble than arsenates or sulfides and are easily oxidized, they typically do not form stable minerals. They may, however, be present as transitional minerals on sites with anthropogenic arsenic.

Over time, arsenic minerals may weather, redistributing arsenic in the soil matrix as a stable, adsorbed phase on ubiquitous metal (iron) oxyhydroxides. Geochemical processes such as oxidation and reduction, pH shifts, precipitation, and adsorption result in arsenic redistribution in soils and are the same processes that are important to the natural attenuation of arsenic mobilized by petroleum impacts.

Arsenic concentrations in at least 25% of samples exceed:

50 ug/L	Insufficient data
10	
5	
3	
1	
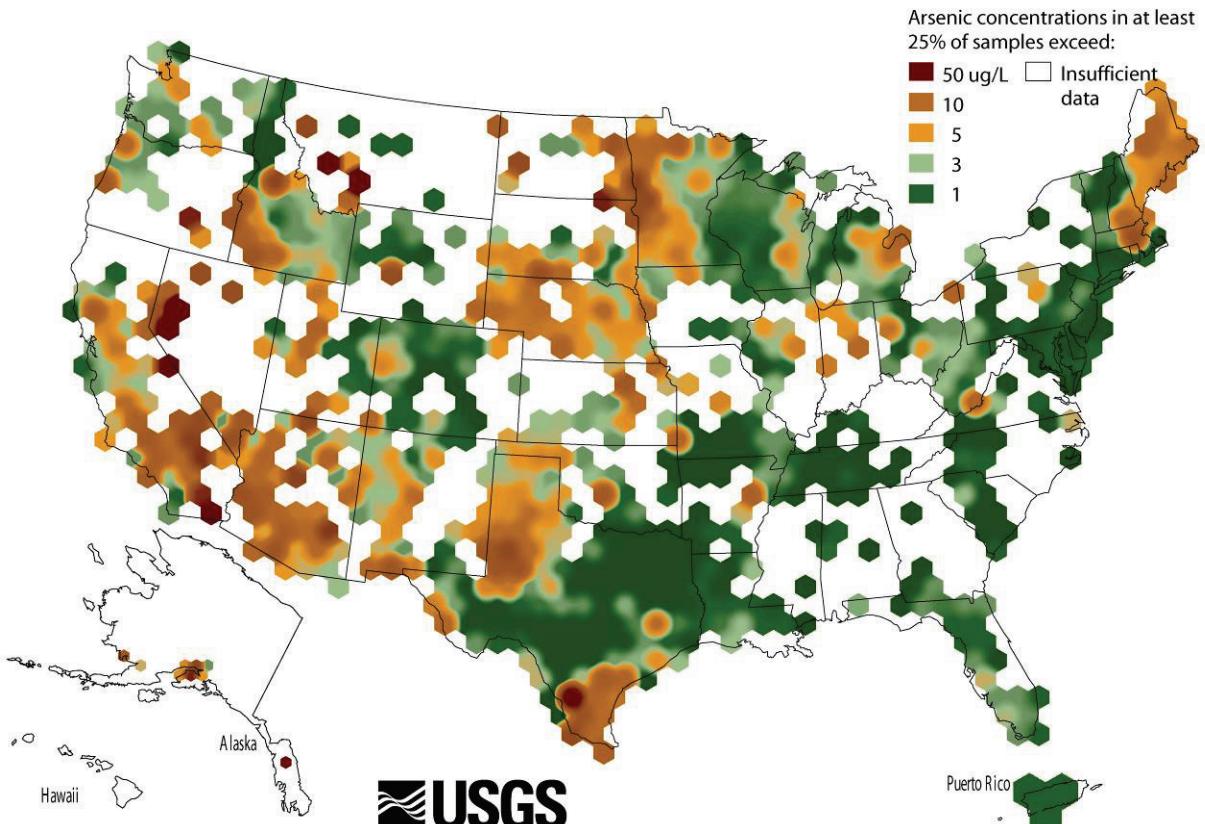
Figure 1-1: Arsenic Concentrations in Ground Water Across the U.S.

1.2.2   *Anthropogenic Sources Of Arsenic*

Arsenic also has many industrial uses (Table 1-1). It is used in agricultural applications for animals and crops, and in lawn care. Arsenic is also used for wood treating, as a flame retardant in plastics, in semiconductors, and as a rat poison. Arsenic can be found as an impurity in mine tailings from sulfidic mineral or phosphate deposits, as a component of waste material from the manufacture of sulfuric acid by burning pyrite, and even as a constituent of municipal landfills and leachate.

Industrial and agricultural uses of arsenic can result in both point source and non-point source impacts. Of greatest interest in this study are non-point sources of arsenic. Typically, these uses involve application of industrial chemicals (e.g. pesticides) over wide areas resulting in diffuse, low-concentration arsenic impacts. Obviously non-point source arsenic has the greatest potential to overlap with areas of petroleum impact. Historic sites with non-point source impacts, such as orchards, also have the potential to be redeveloped as housing or industrial sites, thereby increasing the future risks associated with petroleum releases.

Table 1-1: Industrial and Agricultural Uses of Arsenic (Historic and Current)

Use/Application	Form of Arsenic Used	Type of Ground Water Impact
Fruit Trees, Nut Trees	Arsenates (AsO$_4^{-3}$)	Non-Point Source
Golf Courses	Monosodium Methyl Arsenate (MSMA)	Non-Point Source
Animal Feed (Chickens)	Arsenates	Non-Point Source (manure spreading)
Rat Poison Manufacturing	Arsenates	Point Source
Flame Retarding Plastics Manufacturing	Arsenates	Point Source
Phosphate Fertilizer Manufacturing	Arsenates	Point Source (large plumes)
Wood Treating (Historic)	Arsenates	Point Source (large plumes)
Animal Dips (Sheep and cows for lice and hoof diseases)	Arsenates	Point Source
Pigments	Copper Arsenate, Arsenic Sulfides	Point Source
Semiconductors	Arsenic Metal	Point Source
Herbicide Application	Arsenate	Point Source and Non-Point Source
Defoliant	Arsenic trioxide	Non-Point Source

(Source: www.wikipedia.com, 2009)

1.3 FACTORS CONTROLLING ARSENIC FATE AND TRANSPORT

To understand the behavior of arsenic in aquifers impacted by petroleum hydrocarbons, it is important to understand the basic factors that control arsenic mobility in groundwater under any conditions. There are three primary factors that affect the fate and transport of arsenic in groundwater under both natural conditions and in response to inputs of organic chemicals: the redox environment, pH, and adsorption/precipitation of arsenic onto aquifer solids, particularly iron oxyhydroxides. These factors are governed by the geochemistry, hydrogeology and the mineralogy of the groundwater matrix, each of which may be affected by the presence of hydrocarbons.

Figure 1-2 (adapted from Boulding and Ginn, 2004) superimposes the redox conditions of groundwater on an Eh-pH diagram of arsenic. The diagram identifies the thermodynamically stable arsenic species for a given range of Eh and pH. Under oxidizing conditions (high Eh), arsenates are more stable. As shown in Figure 1-2, aquifers that are in contact with the atmosphere (unconfined conditions) will be mostly aerobic, and arsenic will be predominately in the pentavalent (As^{+5}; arsenate) valence state.

A transitional zone with depleted oxygen (anoxic conditions) and lower Eh values occurs below the aerobic zone in Figure 1-2. This zone has a mixed arsenic

speciation that is dependent on pH. At acidic pH values (pH <5), trivalent (As^{+3}; arsenite) species are dominant in the transition zone; at higher pH values (pH>5) pentavalent arsenic becomes present in increasing proportions as pH values increase above 5. Localized redox conditions in the transition zone can be lowered by the presence of soil organics which can cause reducing conditions, resulting in more arsenite (As^{+3}).

A reduced zone occurs below the transitional environment in Figure 1-2. The redox conditions in this zone will shift the arsenic speciation toward the arsenite ion. And, because trivalent arsenic species are more soluble than arsenates at most Eh-pH ranges, arsenic mobility and hence total arsenic concentrations in groundwater will increase.

Arsenic mobility in any of these redox zones will be mitigated by the presence of mineral precipitates on the soil grains, particularly iron oxyhydroxides. Both trivalent and pentavalent arsenic can be adsorbed by these materials, thus reducing their mobility.

Arsenic mobilization and attenuation will be discussed in this document in the context of hydrocarbon release, dissolution, and biodegradation. A general model of petroleum biodegradation in groundwater is presented in Figure 1-3 (adapted from API, 1996; USEPA, 1998a; USEPA, 1999). A wide spectrum of site-specific hydrogeological conditions may be observed at petroleum release sites, ranging from shallow, oxic, permeable units, with high hydraulic conductivity, to shallow or confined units with reducing (anaerobic) conditions, and with low permeability and hydraulic conductivity.

The following discussion assumes, as a base case, shallow, oxic conditions. However, the concepts that govern arsenic mobility apply to conditions across the hydrogeologic and redox continuum. Shallow, unconfined aquifers are typically aerobic with a pH of 4 – 8, and include low concentrations of natural organic material. Under such conditions arsenic will be in the pentavalent state and most likely sorbed to aquifer solids.
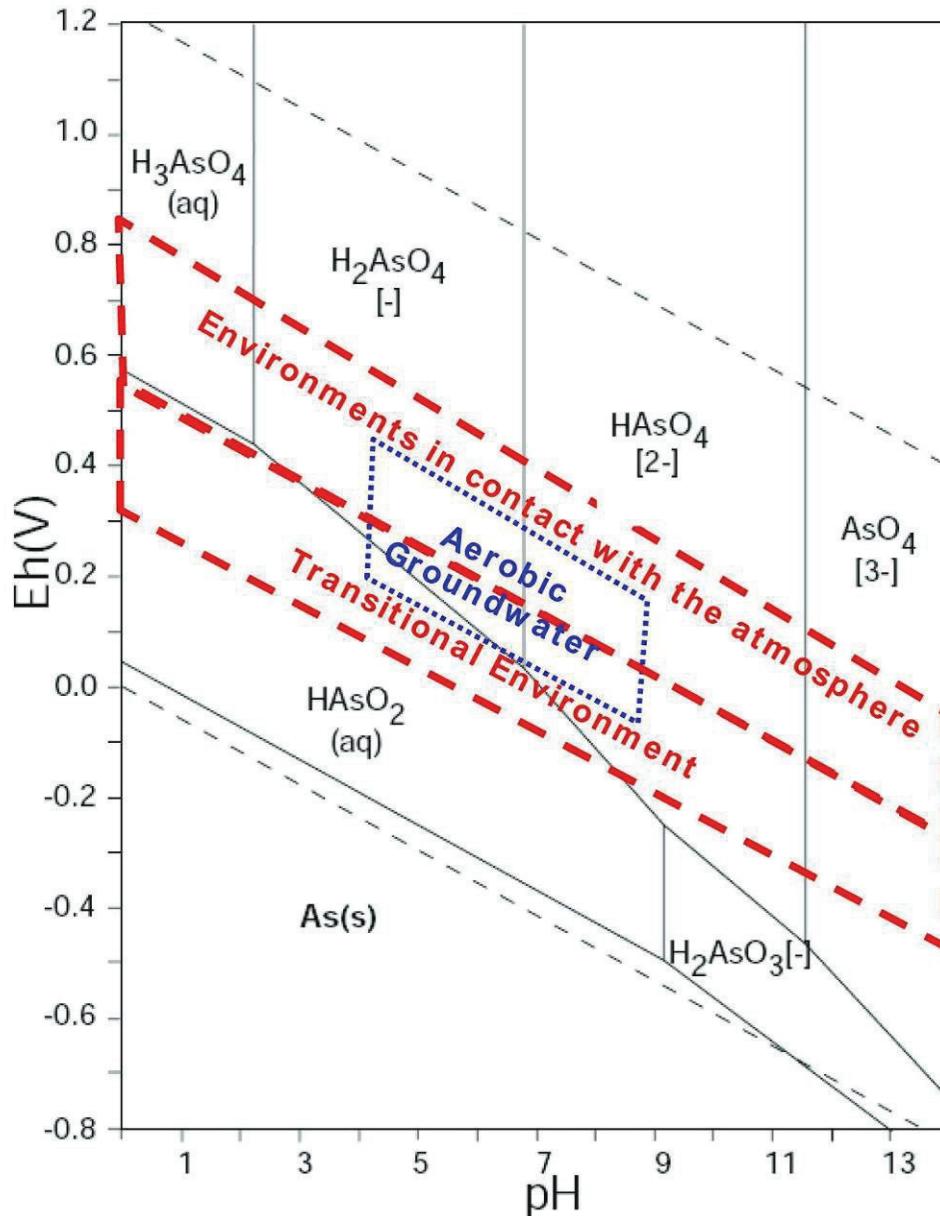
Figure 1-2: Arsenic Speciation in Ground Water Regimes

1.4   *IMPACT OF PETROLEUM HYDROCARBON RELEASES ON ARSENIC MOBILITY*

The primary impact of petroleum hydrocarbons on arsenic mobility is the change in the redox environment (lowering of) due to the consumption of oxygen by hydrocarbon biodegradation. The metabolism of petroleum hydrocarbons sequentially consumes oxygen and other terminal electron acceptors (TEA), successively lowering the redox. Many petroleum hydrocarbons are readily biodegradable under a number of different metabolic conditions. There are six common metabolic pathways under which petroleum hydrocarbons can degrade. These are, in decreasing order of redox potential, aerobic respiration, followed in

sequence by nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and finally, methanogenesis (Figure 1-3). It should be noted that some bacteria can also directly use arsenate as a TEA (Sheehan, 2005) in the presence of organic substrates. The reducing conditions attained depend on the amount of hydrocarbon present and the availability of the TEAs.

Figure 1-4 shows the results of two studies (USEPA, 1998a; Wiedemeier, 1999) that examined the attenuation of hydrocarbon plumes. While the relative proportions of the metabolic pathways vary, both studies suggest that sulfate reduction and methanogenesis are the two most prevalent natural attenuation pathways for hydrocarbons. These pathways occur at, and contribute to, reducing groundwater conditions, under which arsenic generally becomes more mobile. As will be discussed, arsenic reduction and mobilization occurs at Eh values equal to or below iron oxyhydroxide reduction (Fe^{+3} to Fe^{+2}). Reducing conditions shift the arsenic speciation from arsenate to the more soluble arsenite.

Biodegradation of hydrocarbons can also impact other geochemical factors controlling arsenic mobility such as pH and sorption. Changes in these factors can exacerbate or mitigate arsenic mobility.
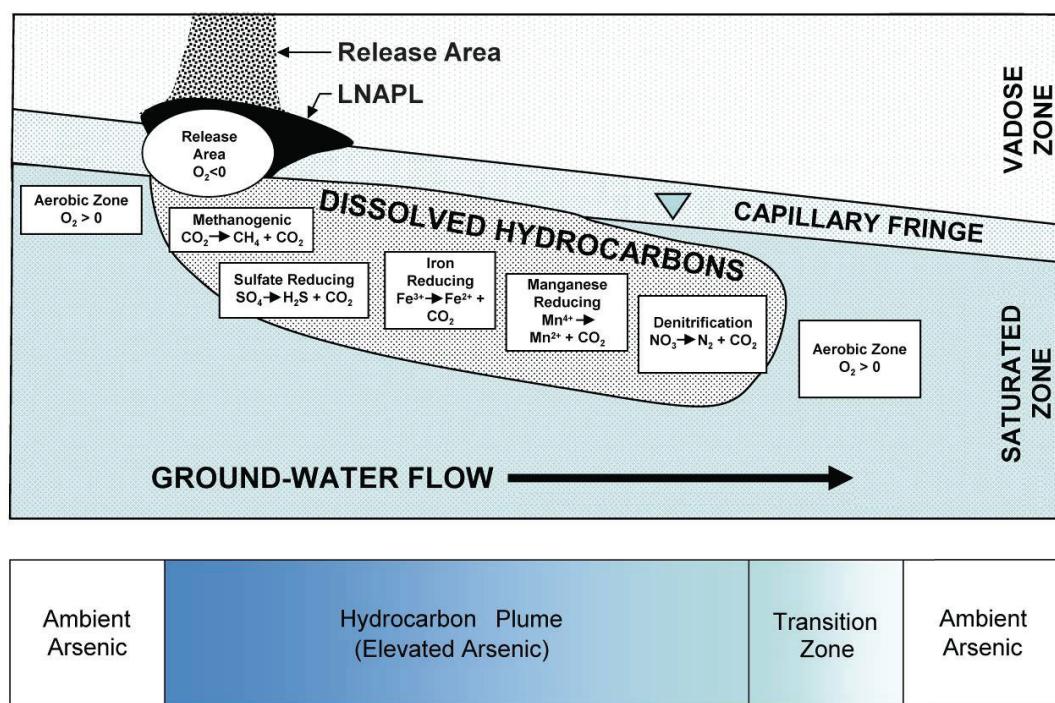
Figure 1-3: Conceptual Model of Biodegradation of a Petroleum Hydrocarbon Plume

a) Summary of Biodegradation Processes at 25 Sites
(USEPA, 1998)

Iron Reduction (8%)
Denitri-fication (14%)
Aerobic Respiration (10%)
Sulfate Reduction (29%)
Methanogenesis (39%)
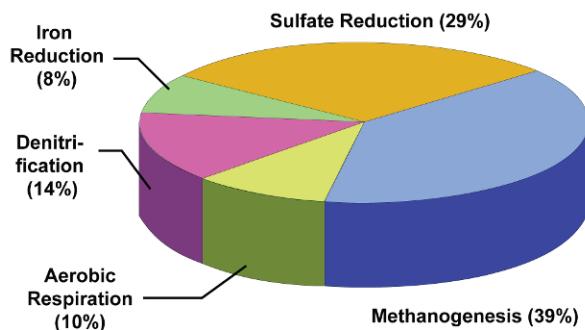
b) Summary of Biodegradation Processes at 42 Sites
(Weidemeier, 1999)

Methano-genesis (16%)
Aerobic Respiration (3%)
Denitrification (3%)
Iron Reduction (4%)
Sulfate Reduction (74%)
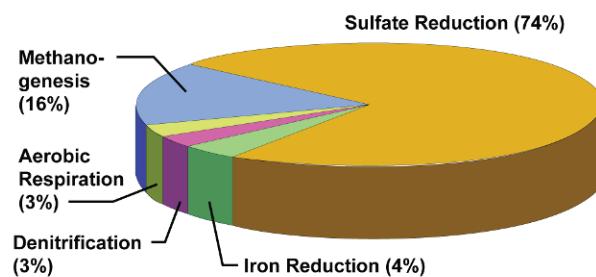
Sulfate reduction was the major "TEAP" (Terminal Electron Acceptor Process) at the majority of sites.

Figure 1-4: Attenuation of Dissolved Plumes at Petroleum Sites

1.5   *GOVERNING PRINCIPLES*

There are several principles that govern the fate and transport of arsenic in shallow aquifers impacted by petroleum hydrocarbons. These are:

1. Arsenic is not a common or significant trace constituent in petroleum (Table 1-2). If arsenic is not present in the site mineralogy, or if arsenic has not been emplaced due to human activity (agriculture, wood treating, mining, etc.), petroleum impacts will not cause arsenic impacts to groundwater.

2. For sites that have arsenic bearing minerals, sorbed arsenic phases, or aged anthropogenic arsenic sources, there is a stable arsenic geochemistry present that determines the ambient (background) level of dissolved arsenic in groundwater. The ambient dissolved arsenic level is controlled by complex geochemical interactions between Eh, pH and the presence of minerals which can adsorb, complex, or precipitate arsenic.

3. The introduction of petroleum hydrocarbons (or other degradable organics) causes a perturbation to the existing geochemistry, which may result in the mobilization of arsenic at concentrations above the ambient level (Figure 1-5). Generally, petroleum and other degradable organics

lower the redox potential to more reduced conditions. The primary mechanism for lowering the Eh is anaerobic biological activity.

4. The perturbation of the ambient arsenic geochemistry (and related arsenic mobilization) will persist until the hydrocarbons are attenuated either spatially (i.e., downgradient of the source) or temporally (i.e., plume-wide attenuation).

5. Once the hydrocarbon is attenuated, the arsenic will revert to its pre-existing stable geochemistry, which may be above or below the MCL, "the maximum permissible level of a contaminant in water which is delivered to any user of a public water system" (US Code Title 42 Section 300f), for arsenic (0.010 mg/L). Depending on the potential exposure pathways and receptors present at or near a particular site, other concentration limits could be applicable to groundwater and surface water arsenic concentrations.

Figure 1-5 presents a conceptual model of the changes in redox conditions and arsenic concentration in a shallow aquifer impacted by hydrocarbons. Ambient conditions exist upgradient of the hydrocarbon plume. As hydrocarbon concentrations increase in the groundwater, redox potentials decrease (become more reducing), and arsenic concentrations increase within the plume. Further downgradient, hydrocarbon concentrations decrease, redox conditions return to the ambient state (more oxidizing), and dissolved arsenic concentrations return to ambient, or background, concentrations (Figure 1-5). The fundamental concepts presented in this model are that the presence of hydrocarbon perturbs the ambient geochemistry, and that arsenic reverts to ambient conditions once hydrocarbons are attenuated. This conceptual model, and the changes observed in these trends with time, will be further discussed in Section 2.4.

The data needed to develop a site-specific conceptual model (SSCM) are discussed in Section 3. There are three basic elements needed to develop a SSCM – defining the ambient (background) arsenic geochemistry; defining the nature of the petroleum plume; and, identifying existing arsenic attenuation processes.

Table 1-2: Summary of Arsenic Concentration in 26 Crude Oils

Arsenic Concentrations in 26 Crude Oils	
(Data are in mg/kg oil, unless otherwise noted.)	
Mean	0.06
Minimum	Not Detected
Maximum	0.57
Detection freq	7
Method Detection Level	0.08
EPA reporting limit	0.5
Mean US Soil Conc (USGS)	5.2 mg/kg soil

Source: Magaw, et al., 2001.
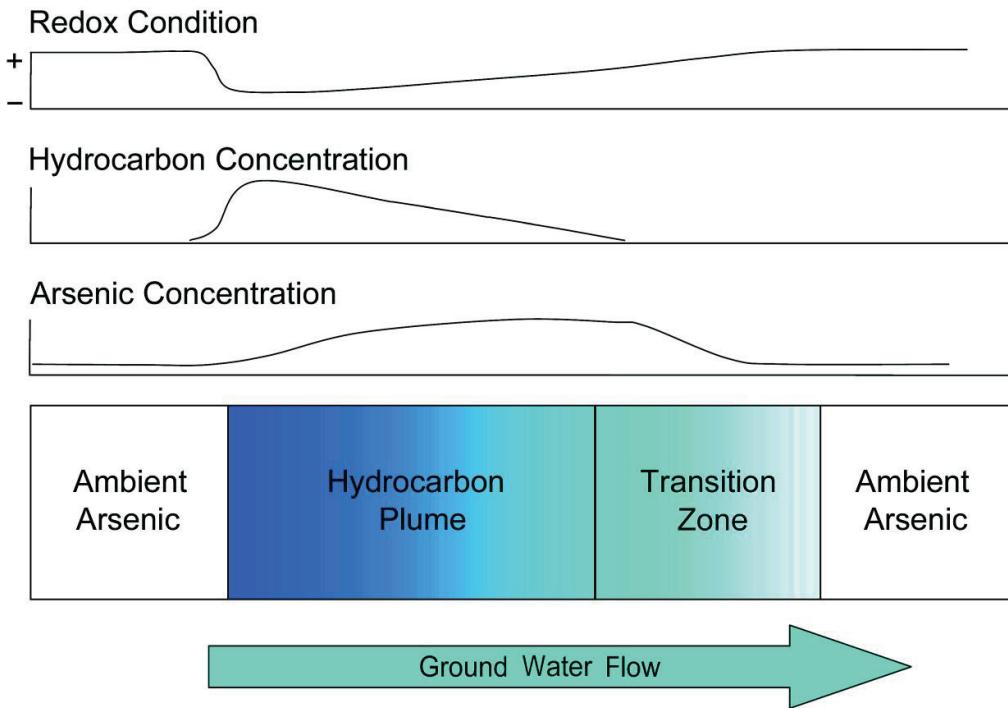
Figure 1-5: Conceptual Model of Arsenic Mobility and Attenuation at a Petroleum Hydrocarbon Plume

1.6   *ORGANIZATION OF MANUAL*

This manual on the Attenuation of Naturally-occurring Arsenic at Petroleum Impacted Sites is organized into four main sections:

Section 2: *Fundamentals of Arsenic Geochemistry and Natural Attenuation as Applied to Petroleum Impacted Sites* covers:

- The Fundamentals of Arsenic Geochemistry (Section 2.1), which discusses the key geochemical factors of Eh, pH, and sorption that govern arsenic mobility under all conditions;

- Mechanisms of Arsenic Mobilization/Solubilization at Petroleum Impacted Sites (Section 2.2), which discusses the basic principles of petroleum hydrocarbon biodegradation and its effect on arsenic mobility;

- Natural Attenuation Mechanisms for Arsenic (Section 2.3), which discusses how arsenic attenuates downgradient of the petroleum impact(s) and in conjunction with hydrocarbon attenuation; and

- Conceptual Models for Arsenic Natural Attenuation (Section 2.4), which discusses arsenic mobility at three different stages of the petroleum plume lifetime: an expanding, stable, and retreating hydrocarbon plume.

Section 3: *Assessment and Site Characterization to Evaluate Arsenic Natural Attenuation* covers:

- Development of a SSCM (Section 3.1), which covers data needs including defining the ambient arsenic geochemistry and general site conditions, defining the hydrocarbon plume conditions, identifying the operable attenuation mechanisms, and assessing the potential exposures and risks due to arsenic mobilization; and

- Uses of the SSCM (Section 3.2), which discusses how the SSCM can be effectively used to manage the effects/impacts of the petroleum plume on arsenic mobilization.

Section 4: *Remediation Technologies for Arsenic in Groundwater Impacted by Petroleum Hydrocarbons* covers:

- Current Hydrocarbon Remediation Technologies (Section 4.1), which discusses the importance of hydrocarbon remediation as the primary means of arsenic mitigation, and which hydrocarbon remediation techniques may enhance arsenic attenuation; and

- Arsenic Treatment Technologies (Section 4.2), which discusses *in-situ* treatments (mainly adsorption) that can be used to protect receptors which may be or are impacted by dissolved arsenic.

Section 5: *Case Studies for Arsenic Mobilization and Attenuation at Petroleum Impacted Sites,* which provides four case studies from the petroleum industry that illustrate aspects of arsenic mobilization and attenuation discussed in this manual.

2.0   *FUNDAMENTALS OF ARSENIC GEOCHEMISTRY AND NATURAL
ATTENUATION AS APPLIED TO PETROLEUM IMPACTED SITES*

Fundamental to understanding the natural attenuation of arsenic at petroleum
impacted sites is the fact that such sites have a pre-existing or ambient arsenic
geochemistry that becomes perturbed by the introduction of the hydrocarbons.
Given this concept, it is important to understand the basic geochemical factors
that control the ambient (background) concentrations of arsenic in groundwater.
Furthermore, it is necessary to understand how those concentrations respond to
changes in geochemistry that result from petroleum hydrocarbon impacts; and
finally, how the increased concentrations of arsenic that result are affected by the
mitigation or attenuation of the hydrocarbon impacts.

The following discussion reviews the fundamentals of arsenic geochemistry as
they pertain to petroleum hydrocarbon sites. Further details on the geochemical
mechanisms mentioned here are available in the literature (Smedley &
Kinniburgh, 2002; Bostick, et al., 2005; Wilkin, et al., 2003; Dzombak and Morel,
1990). Arsenic speciation and mobility as a function of Eh, pH, and the potential
for sorption are described below. The influence of hydrocarbon impacts on these
three factors is described as it relates to mobilization of arsenic. Likewise, the
geochemical changes that occur as petroleum hydrocarbons are attenuated, and
the mechanisms of arsenic attenuation that result, are addressed. The basic
model of a hydrocarbon plume, the biodegradation processes, the resulting
geochemical changes, and the change in arsenic mobility are summarized in the
conceptual models discussed below.

2.1   *FUNDAMENTALS OF ARSENIC GEOCHEMISTRY*

The groundwater chemistry of arsenic is dominated by the fact that arsenic is
redox-labile, readily changing its oxidation state or chemical form through
chemical or biological reactions that are common in the environment. Therefore,
rather than solubility equilibria controlling the aqueous behavior of arsenic, it is
controlled primarily by redox conditions and pH. These two factors control,
mineral formation/dissolution and adsorption/desorption reactions.

2.1.1   *Redox Chemistry of Arsenic*

The common valence states of arsenic are As^0, As^{-3}, As^{+3}, and As^{+5}. The latter two
are the most commonly encountered valence states in natural, shallow aquifers as
the oxyanions AsO_3^{-3} (arsenite) and AsO_4^{-3} (arsenate). Arsenite is generally more
soluble that arsenate. These two species can vary in relative concentration in
groundwater depending on the redox state of the groundwater (see Figure 1-2).
In aerobic aquifers, As^{+5} dominates; in anoxic or reduced aquifers, As^{+3} is
dominant. The standard electrode potentials for arsenic are shown in Figure 2-1.
Specific redox values are a function of pH, and the standard electrode potentials
are reported at a pH of 7.0 (www.webelements.com).

	+5		**+3**		**0**		**-3**
acidic solution	H_3AsO_4	—0.560—	$HAsO_2$	—0.240—	As	—-0.225—	AsH_3
basic solution	AsO_4^{3-}	—0.560—	AsO_2^-	—0.240—	As	—-0.225—	AsH_3
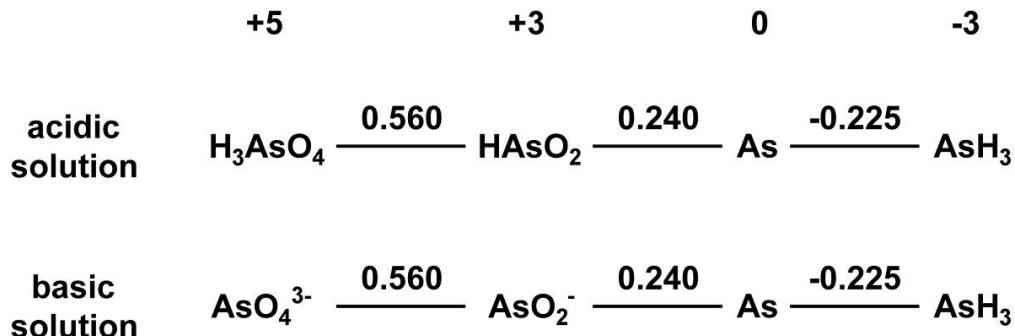
Figure 2-1: Standard Electrode Potential for Arsenic

The mineralogy of arsenic suggests that there are two redox environments that form stable arsenic minerals. Arsenates (As^{+5}) exist in oxidized or aerobic environments, which are typical conditions for shallow aquifers. On the other hand, sulfidic minerals, such as arsenopyrite (FeAsS), or realgar (As_4S_4 or AsS), are formed in strongly reducing, anoxic environments where sulfate reduction occurs. The speciation of arsenic in these environments under different redox and pH conditions, and in the presence of iron, are shown in Figure 2-2.

Typically, groundwater redox values are determined by the Eh from the relative concentrations of a specific redox couple such as the iron III – iron II couple. Thus arsenic speciation will be controlled by the dominant redox couple and the Eh of that couple in the aqueous phase.   In most hydrocarbon impacted aquifers, the iron couple would be the dominant couple. However, in anoxic or reduced aquifers, arsenite can also be formed by the abiotic reduction of arsenate by organic matter:

$$2H_3AsO_4 + C \rightarrow 2HAsO_2 + HCO_3^- + H_2O + H^+ \qquad \textit{(Eq. 2-1)}$$
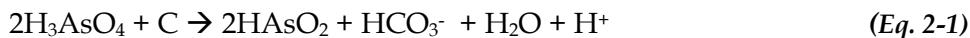
This abiotic reaction is slow because soil organic matter can be relatively nonreactive. However, more labile organic matter can be the electron donor substrate in biological reactions, driving reduction reactions such as the one shown in Eq. 2-1. The ratio of arsenite to arsenate in anoxic and reduced aquifers is a function of the Eh, which is a function of the balance between: the dissolution of atmospheric oxygen; the electron transfer activity resulting from a host of electrochemical reactions resulting from the biological degradation of hydrocarbons; and the rates of abiotic or biotic reduction.
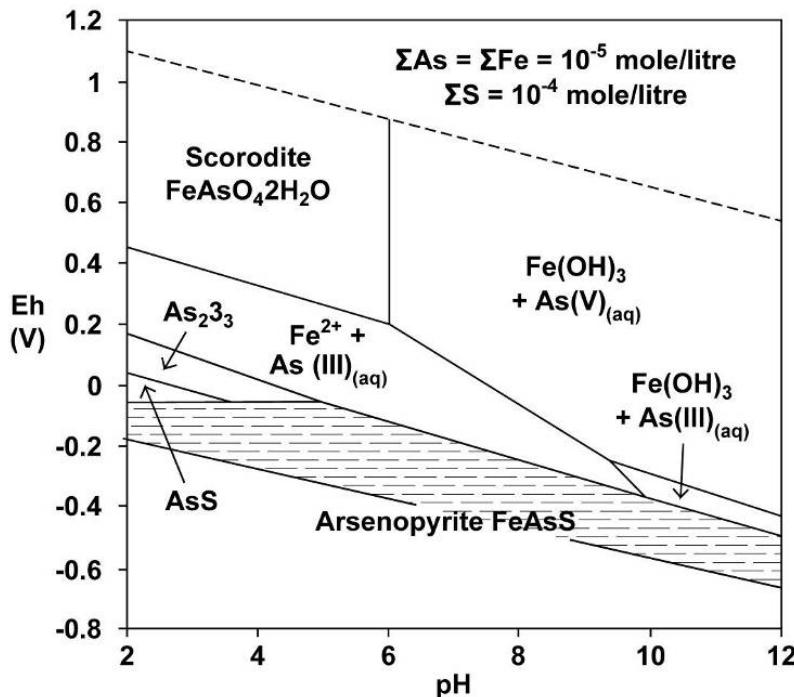
Figure 2-2: Eh-pH Diagram for As-Fe-S

Other arsenic species can be found in groundwater under special conditions. Under highly reduced conditions arsenic may be found in the -3 valence state (As^{-3}) as arsene (AsH_3). In organic rich environments arsenic may be found as methyl arsenates or methyl arsenites, which are produced biologically. These two conditions are typically not found at petroleum impacted sites. Under very strongly reducing conditions, in the presence of sulfate, arsenic-sulfur species can be formed, which include arsenic sulfide and thioarsenates. In the presence of iron, thioarsenates can precipitate and can form minerals such as arsenopyrite.

2.1.2   *pH*

The pH of the groundwater is the second most important factor controlling the ambient solubility of arsenic. The pH has two primary effects. First, it affects the ionic form of the arsenic. At high pH, arsenite and arsenate species are deprotonated, shifting chemical equilibria and increasing the solubility of arsenic species. Second, as further discussed in Section 2.1.3, pH affects the sorption of arsenic oxyanions. At very low (acidic) pH, the metal sorption site is attacked, often dissolving the metal and releasing any sorbed arsenic. At high pH, the sorption of the oxyanions will also decrease as they are displaced by hydroxide ions (Sutherson and Horst, 2008). The optimal pH range for sorption is 4 to 8, which is also the typical pH range for shallow aerobic aquifers.

Oxyanions of arsenic readily sorb to solid phase metal oxyhydroxides such as goethite, which are often abundant in an aquifer matrix (Figure 2-3). The primary forms of inorganic arsenic in both oxidizing and reducing groundwater are oxyanions or thioanions (Ferguson and Gavis, 1972; Wilkin et al., 2003; Bostick et al., 2005). Adsorption of these arsenic species at mineral surfaces occurs as a result

of a set of chemical reactions between aqueous species and surface sites (Dzombak and Morel 1990; Davis and Kent, 1990).

The most important reactive surface phases for arsenic attenuation in many soil and subsurface systems are cationic metal surfaces, including iron, aluminum, and calcium mineral phases. Arsenic sorption has been demonstrated for a wide range of minerals common to soils and sediments with iron oxides and sulfides playing a dominant role in oxidizing and reducing environments (Goldberg and Glaubig, 1988; de Vitre et al., 1991; Morse, 1994; McNeill and Edwards, 1997; Manning et al., 1998; Chiu and Hering, 2000; Wolthers et al., 2005).

Adsorption of both As^{+3} and As^{+5} onto mineral surfaces exhibits a strong pH dependence, with a pH range of 4 to 8 being optimal, because:

1. Most adsorption reactions between As^{+3} and As^{+5} and mineral surface sites have H^+ as a reactant;

2. Arsenic speciation varies with pH; and

3. The electrostatic contribution to the free energy of adsorption of arsenic species onto most minerals varies with pH.

The extent to which As^{+3} or As^{+5} anions adsorb at mineral surfaces will also be influenced by the concentrations of other anions, which can compete for surface sites, and cations, which can influence the electrostatic contribution to anion adsorption.
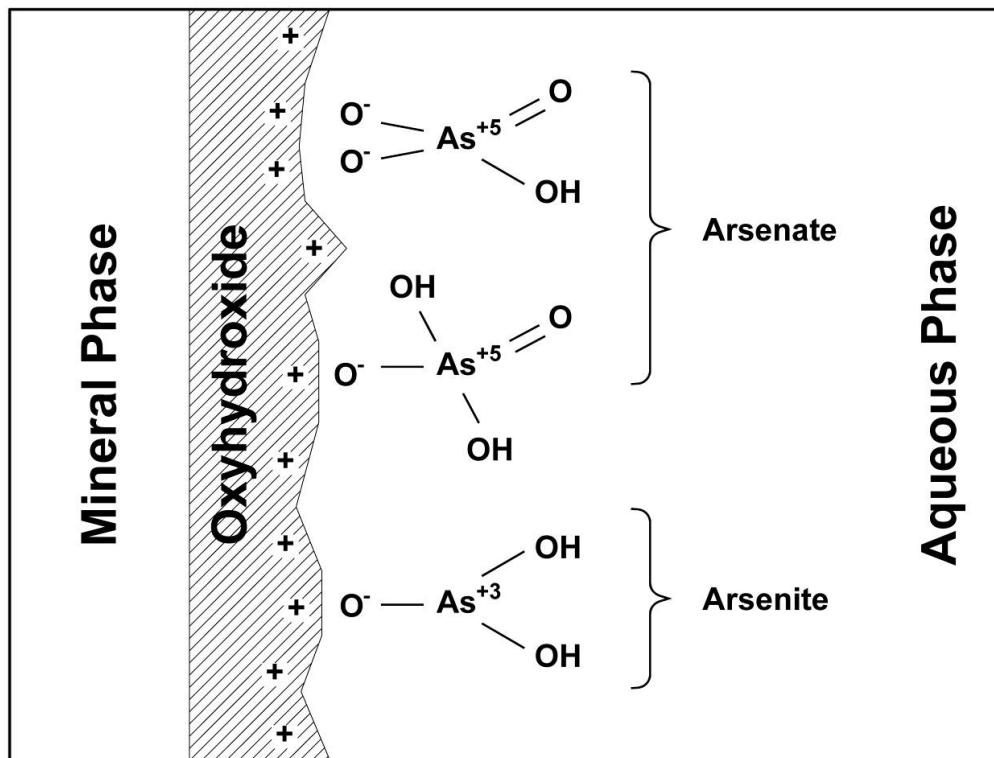
Figure 2-3: Adsorption of Arsenic Oxyanions to Oxyhydroxide Coating on Mineral Grain in an Aquifer

2.2   *MECHANISMS OF ARSENIC MOBILIZATION/SOLUBILIZATION AT PETROLEUM IMPACTED SITES*

A fundamental concept of arsenic mobility at petroleum hydrocarbon sites is that a petroleum hydrocarbon release changes the ambient arsenic geochemistry in groundwater by creating more reducing conditions, driven by the bacterial metabolism of the hydrocarbon compounds (Section 1.4). The primary mechanisms of arsenic reduction and mobilization are, therefore, induced by microbiological processes. To understand the impact of these processes, the ambient arsenic geochemistry must first be understood in order to evaluate the degree of arsenic mobility and attenuation at petroleum impacted sites.

2.2.1   *Microbiology of Petroleum Hydrocarbon Spills*

When petroleum hydrocarbons are released to groundwater, there is a progression from aerobic to anaerobic conditions with an associated reduction in the redox conditions of the ground-water system. Typically, the most reducing conditions are in the source area and the least reducing conditions (i.e., aerobic conditions) are at the plume boundary. The relative reaction rates and concentrations of microbial activity under each of these different metabolic environments are controlled by the availability of the TEAs, the types and concentrations of organic substrate(s) that can be utilized by the bacteria, and specific type and population of the microbial community (Salanitro, 1993). This redox progression results in a loss of organic carbon and depletion of various electron acceptors from the aquifer system as well as a progression in the types and metabolic activity of the indigenous bacteria. Figure 2-4 shows that the relative areas of metabolic activity vary both in the direction of groundwater flow as well as in the transverse direction. The most reduced conditions are found in the source area. The aquifer conditions become less reducing in the direction of groundwater flow and as one progresses outward, perpendicular to the plume axis. Aerobic conditions generally bound the plume in both directions.
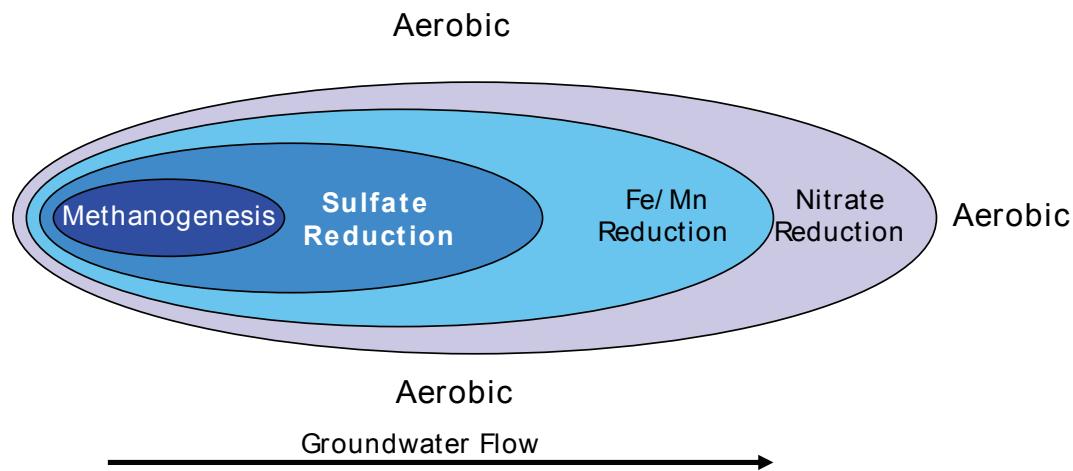
Figure 2-4: Plan View of Metabolic Zones in Hydrocarbon Plume

If microbial activity is high and there is sufficient dissolved hydrocarbon, the aquifer environment will progress rapidly through these different metabolic

conditions. The following describes the series of terminal electron accepting processes (TEAPs), encountered on hydrocarbon impacted sites. The availability of each TEA varies site to site.

- Dissolved oxygen (DO) – the primary source of oxygen is atmospheric. The maximum DO level in groundwater is about 8 - 10 mg/L under atmospheric conditions. In the presence of petroleum hydrocarbons, dissolved oxygen diffuses slowly into groundwater relative to the microbial metabolism of hydrocarbons and dissolved oxygen concentrations become very low. Once available oxygen is consumed, active aerobic populations begin to shift next to nitrate respiration. It takes approximately 3 to 3.5 mg DO to degrade 1 mg of hydrocarbon.

- Nitrate (NO_3^-)– the primary sources of nitrate are agricultural (nitrate fertilizers, livestock feed lots, etc.) and atmospheric. Secondary sources are industrial (use of nitric acid). Nitrate reduction can produce nitrogen gas or ammonia. It takes about 2.4 to 2.7 mg of nitrate, if reduced to nitrogen, to degrade 1 mg of hydrocarbon. It takes 3 to 3.3 mg of nitrate, if further reduced to ammonia, to degrade 1 mg of hydrocarbon. Nitrate is not commonly found in aquifers at high concentrations, except in areas of intense agricultural activity. Nitrate reduction will continue until available nitrate is depleted, or usable carbon sources become limiting. As nitrate is depleted, populations which reduce manganese may dominate.

- Manganese (Mn^{+4}) – the primary source of manganese is mineralogical. The most commonly available mineral form in shallow aquifers is pyrolucite (MnO_2). Manganese is commonly associated with iron in soils, but is not as prevalent. It takes 16.7 to 18.9 mg of manganese (MnO_2) to degrade 1 mg of hydrocarbon. Manganese is not generally soluble, except under reducing conditions. The dissolved hydrocarbon must come into contact with the manganese bearing minerals in order for degradation to occur. Bacterial metabolism of petroleum hydrocarbons by manganese-reducing populations will continue until the concentration of manganese oxide becomes limiting. At this point, iron reduction becomes the predominant reaction mechanism.

- Iron (Fe^{+2}, Fe^{+3}) – the primary source of iron is mineralogical. Iron is ubiquitous and is often responsible for the color of aquifer solids (browns, reds, orange are oxidized iron; grays, greens, black are reduced; white or tan are usually iron deficient). Iron in the solid phase can exist as ferric (Fe^{+3}), ferrous (Fe^{+2}) or mixed ferric-ferrous (e.g., magnetite). Most iron minerals encountered in shallow aquifers will be oxides, silicates, or carbonates. It takes 21 to 24 mg of iron (as Fe) to degrade 1 mg of hydrocarbon. Oxidized iron is not very soluble at normal pH, but reduced iron is soluble. The dissolved hydrocarbon must come into contact with the iron bearing minerals in order for degradation to occur. Iron reduction continues until iron mineral limitations allow sulfate-reducing bacteria to become active.

- Sulfate (SO_4^{-2}) – the primary sources of sulfate are mineralogical/geochemical, industrial and agricultural. Atmospheric sulfate (acid rain) is a secondary source. Mineralogically, sulfate can be sourced as sulfate or sulfide, which oxidizes to sulfate in the presence of dissolved oxygen. It takes 4.6 to 5.2 mg of sulfate to degrade 1 mg of hydrocarbon. Sulfate is reduced to sulfide, which generally reacts with metals (such as iron) that are present.   Sulfate is generally present in dissolved form but may be in equilibrium with minerals. If there are sulfate minerals such as gypsum present, the aqueous sulfate would be replenished over time. If sulfate limitations occur, methanogenic bacteria are able to dominate.

- Carbonate (CO_3^{-2}) (Methanogensis) – the primary sources of carbonate are mineralogical and atmospheric (CO_2). Carbonate is present both in dissolved form and in mineral form. It takes 4.8 to 5.4 mg of carbonate (as $CaCO_3$) to degrade 1 mg of hydrocarbon.

- Fermentation – occurs under anaerobic conditions. The hydrocarbon acts as both the electron donor and the electron acceptor. Fermenting microorganisms catalyze the breakdown of hydrocarbons through internal electron transfers into simpler molecules such as alcohols, fatty acids, hydrogen and carbon dioxide. These fermentation products can be used by other bacterial species converting them into carbon dioxide and methane.

2.2.2 *Effect of Petroleum Biodegradation on Arsenic Mobility*

Hounslow (1980) and Smedley and Kinniburgh (2002) identified three geochemical triggers that lead to arsenic mobilization in subsurface systems. These include:

1. Desorption/dissolution resulting from a change to a reducing environment;

2. Desorption as a result of changes in pH; and

3. Mineral dissolution.

As will be discussed, petroleum biodegradation will have an impact on all three of these geochemical triggers.

Shallow groundwater systems are, for the most part, open to the atmosphere and are typically aerobic (oxidizing conditions) environments (Figure 1-2). This suggests that, prior to the impact of petroleum hydrocarbons, the arsenic mineralogy in a shallow aerobic aquifer would be primarily metal arsenates. Input of hydrocarbons to aerobic aquifers generally results in more reducing conditions and arsenic mobilization.

There are also some shallow aquifers that may be anoxic or mildly reducing. Under anoxic conditions, arsenic would exist as mixed speciation (As^{+3}, As^{+5}). If the aquifer is fully reduced, as may be the case in and under some wetlands for instance, the speciation would be dominated by the arsenite anion. The net change in groundwater arsenic concentration as a result of hydrocarbon impact is

a function of the initial, or ambient, conditions. In aquifers that exhibit reducing conditions, mobile arsenic may already be present near or above MCL in groundwater, and a petroleum hydrocarbon would only increase the mobile arsenic slightly, if at all.

The mobilization of arsenic due to the biodegradation of organic chemicals is not unique to petroleum releases. The mobilization of naturally-occurring arsenic in a ground-water aquifer was documented (Hounslow, 1980) during transport of carbon-substrate enriched landfill leachate, where arsenic was not significant in the source leachate. Thus, the introduction of labile organic compounds to an aerobic shallow aquifer has the potential to stimulate microbial activity that can result in release of arsenic from aquifer solids and result in mobilization and transport of arsenic oxyanions in groundwater. Many of the concepts that are discussed in this document within the context of petroleum hydrocarbon releases can be applied to sites with a different source of labile organic carbon.

The following sections discuss how the biodegradation of hydrocarbons impacts the geochemical factors that control arsenic mobility.

2.2.2.1   *Redox*

When petroleum releases occur in shallow aquifers, the redox environment is substantially changed. The redox is driven to more strongly reducing conditions (more negative Eh values) primarily because of the increased biodegradation of the petroleum. The shift to more reducing conditions can have a substantial effect on arsenic mobility.

Table 2-1 shows the difference in solubilities for arsenite and arsenate after addition of some common cations to precipitate arsenic. The initial arsenic concentrations were the same for the arsenite and arsenate solutions. When metals like ferric iron, aluminum, and calcium are present in an aquifer, arsenate will readily precipitate to form solids resulting in a greater than 90% reduction in arsenate. Arsenite is less likely to precipitate and remains more in solution. The arsenite concentrations are only reduced 20 to 50% by the addition of the metals and the precipitation of metal arsenites. This table demonstrates that the reduction of arsenate to arsenite will increase the mobility of arsenic.

Table 2-1: Relative Solubilities of Arsenite and Arsenate

Cation Added	Initial As Conc.	Final Concentration	
		Arsenate	Arsenite
Ferric Iron	350 µg/L	6 µg/L	140 µg/L
Ferric Iron	300 µg/L	6 µg/L	138 µg/L
Aluminum (Alum)	350 µg/L	74 µg/L	263 µg/L
Aluminum (Alum)	300 µg/L	30 µg/L	249 µg/L
Aluminum (Alumina)	100 µg/L	4 µg/L	~100 µg/L
Calcium	2 mg/L	20 µg/L	160 µg/L

Figure 2-5 superimposes the arsenic reduction reaction on the list of previously discussed TEAPs that can occur when an aquifer is impacted with petroleum hydrocarbons. The primary reductive processes for arsenic, based on the Eh-pH diagram in Figure 2-5, is reduction of arsenate to arsenite (Eh⁰ +50 mv) which occurs at or below the Eh of iron reduction.

If the aquifer becomes strongly reducing (i.e., sulfate reduction), then the mobilization of arsenic may be reversed. Under sulfate reducing conditions, arsenite can react with sulfide to form thioarsenites, thioarsenates and arsenic sulfide minerals. Depicted on Figure 2-5 is the formation of arsenic +3 sulfides, thioarsenite and realgar, through the exchange of oxygen with sulfide. Thioarsenates and thioarsenites are generally less soluble than are arsenites (Stauder 2005). They are, however, not stable under aerobic conditions and are easily oxidized if the aquifer conditions revert back to aerobic conditions.

Redox Potential (E_h°) in millivolts @ pH = 7 and 25 degrees Celsius

Aerobic

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \, (E_h^{\circ} = +820)$

$2NO_2^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$ $(E_h^{\circ} = +740)$

Anaerobic

$MnO_2(s) + HCO_3^- + 3H^+ + 2e^- \rightarrow MnCO_3(s) + 2H_2O$ $(E_h^{\circ} = +520)$

$4H^+ + HAsO_4^{-2} + 2e^- \rightarrow H_3AsO_3 + H_2O \, (E_h^0 = \sim +50)$

$FeOOH(s) + HCO_3^- + 2H^+ + e^- \rightarrow FeCO_3 + 2H_2O$ $(E_h^{\circ} = -50)$

$3H_3AsO_3 + 9H^+ + 5S^{-2} \rightarrow AsS_2^- + As_2S_3 + 3H_2O$

$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O \, (E_h^{\circ} = -220)$

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \, (E_h^{\circ} = -240)$

Decreasing Amount of Energy Released During Election Transfer

Oxidation-Reduction Potentials for Various Electron-Accepting Processes (modified from Bouwer, 1994)

Figure 2-5: Arsenic Reduction in Relation to Biological Processes

2.2.2.2   *pH*

The main arsenic species at high pH values for both As⁺³ and As⁺⁵ are oxyanions. As the pH increases these oxyanions are increasingly deprotonated and more soluble. As a result, arsenic solubility generally increases with increasing pH.

The pH of groundwater in a hydrocarbon impacted aquifer can be affected by the microbial consumption of the hydrocarbons. The nature of the pH effect will depend on the microbial metabolic pathway(s) that is active (Table 2-2). If the aquifer is anaerobic, the pH will generally increase as a result of biological

activity. Increases in pH generally increase the solubility of arsenic. The pH shift that results due to biodegradation is, however, small, less than 1-2 pH units, and the effect on arsenic solubility would also be small.

Table 2-2: Effect of Microbial Metabolic Pathways on pH

Pathway	Effect on pH
Oxygen Reduction	Decrease pH
Nitrate Reduction	Increase pH
Manganese Reduction	Increase pH
Iron Reduction	Increase pH
Sulfate Reduction	Increase pH
Methanogenesis	Decrease pH

2.2.2.3   *Sorption*

Under natural conditions arsenic solubility is controlled to a great extent by its adsorption on calcium, iron and aluminum bearing minerals. Adsorption is a function of pH and of the redox state of arsenic. Figure 2-6 shows that arsenite (reduced) is less strongly adsorbed to metal oxyhydroxides, such as HFO, than is arsenate (oxidized). The adsorption of arsenic and, therefore, its solubility is a function of pH. At high pH (pH>8-9), both arsenate and arsenite become more soluble because they are displaced on the mineral surface by hydroxide. At low pH (pH< 4), the solubility of arsenic species also increases due to dissolution of the underlying adsorptive mineral.

As previously discussed, the biodegradation of hydrocarbons affects the solubility of arsenic by changing the valence state of the arsenic and by changing the pH of the groundwater. The biodegradation of petroleum in groundwater and the resulting reducing conditions can also affect arsenic mobility by removing the sorption sites that are binding arsenic. These sorption sites are generally present as ferric oxyhydroxide mineral coatings on aquifer solids. The ferric iron in the oxyhydroxides is reduced to ferrous iron by biological activity. Ferrous iron is soluble. This reduction of ferric iron eliminates the sorption sites and releases the adsorbed arsenic to groundwater. The reductive dissolution of hydrous ferric oxide **(**HFO) is a key process in arsenic mobilization.

2.3   *NATURAL ATTENUATION MECHANISMS FOR ARSENIC*

Before discussing the natural attenuation of arsenic at petroleum impacted sites, there are three key concepts to reiterate.

- First, natural attenuation can only restore arsenic concentrations to the ambient conditions in the aquifer. If there is arsenic in the groundwater due to ambient geochemical conditions, natural attenuation or active remediation cannot practicably be expected to result in lower arsenic concentrations.
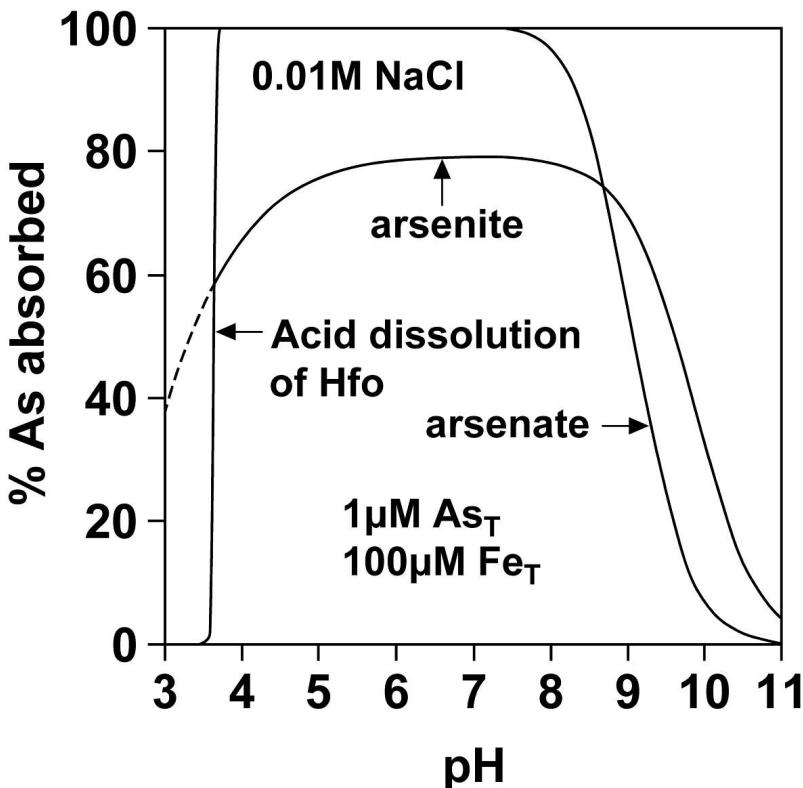
Figure 2-6: Adsorption of Arsenate and Arsenite on Hydrous Ferric Oxide (HFO) as a Function of pH (from Smedley and Kinniburgh, 2002)

- Second, once the petroleum impacts are mitigated, the arsenic concentrations will similarly attenuate to background concentrations. As the hydrocarbon plume is contained and shrinks, arsenic concentrations will decline in perimeter monitoring wells. Once the petroleum impacts are attenuated, the arsenic will revert to its background concentrations determined by the ambient geochemistry in the aquifer.

- Third, arsenic attenuation may be viewed as reversing the geochemical changes that were caused by the presence of the petroleum. Thus, attenuation may be seen as the "mirror image" of mobilization.

The ultimate fate of arsenic due to attenuation processes is sorption in stable form to aquifer solids. To evaluate the potential for the attenuation of mobilized arsenic, potential arsenic sorption sites (e.g. iron oxyhydroxides) and the chemical conditions (i.e. Eh, pH) that result in its uptake onto aquifer solids should be identified. The mobilization of arsenic on petroleum impacted sites is primarily driven by reducing conditions resulting from the biodegradation of the petroleum. The attenuation of the mobilized arsenic is driven by oxidizing conditions, which may be chemically or biologically mediated.

Arsenic is most stable in the solid phase under aerobic conditions. Sufficient dissolved oxygen is present in groundwater under aerobic conditions for iron and manganese oxyhydroxides to remain as solids in the aquifer because their

oxidized forms are more stable. These oxyhydroxides provide sorption sites for arsenic. The aerobic redox conditions favor arsenates, which are more readily adsorbed.

With time, geochemical conditions downgradient of the petroleum hydrocarbon source release area will begin to return to ambient conditions that were present in the aquifer prior to the release. As the carbon substrate from the release area is consumed by the microbial community in the groundwater, the reduced redox state will begin to reverse and eventually pass from anaerobic to aerobic conditions. The aerobic conditions will result in oxidation of the reduced arsenic, iron and manganese dissolved in the groundwater. Low solubility iron and manganese oxyhydroxides will precipitate from solution carrying the arsenic into the solid phase or creating new surfaces in the aquifer matrix to sorb the arsenic. Further downgradient, in areas not impacted by hydrocarbon release, unaffected areas containing solid phase iron and manganese oxyhydroxides can act as additional sorption sites for arsenic that migrates past the plume extent.

The following sections describe the changes in arsenic mobility resulting from changes in redox brought on by the depletion of hydrocarbons.

2.3.1   *Arsenic Oxidation*

When the dissolved hydrocarbons are depleted, there is no longer a sink for dissolved oxygen. As the dissolved oxygen concentrations in groundwater rebound, reduced As^{+3} will be oxidized.

In aerobic aquifers, the reduced species As^{+3} can be oxidized by dissolved oxygen because arsenite is thermodynamically unstable under aerobic conditions. Because the E^0 for both reactions (acidic and basic) is positive (Eq. 2-2 and 2-3), the Gibbs free energy is negative and both reactions proceed spontaneously (ΔG = -nFE). The reaction with oxygen is, however, slow, with a half life of 1-3 years. (Eary and Schramke, 1990).

$$2HAsO_2 + 2H_2O + O_2 \rightarrow 2H_3AsO_4 \quad pH \leq 7, E^0_{\,Cell} = 0.67 \text{ V} \qquad \textit{(Eq. 2-2)}$$

$$2AsO_2^- + 4OH^- + O_2 \rightarrow 2AsO_4^{-3} + 2H_2O \quad pH>7, E^0_{\,Cell} = 1.08 \text{ V} \qquad \textit{(Eq. 2-3)}$$
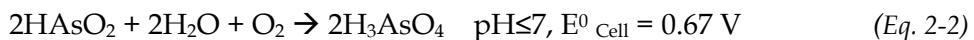
The oxidation of arsenite can be catalyzed by ferric iron or Mn^{+4}. With both metals, arsenite is likely oxidized by the metal oxyhydroxide and the reduced metal (Fe^{2+} or Mn^{2+}) is, in turn, reoxidized by dissolved oxygen:

$$HAsO_2 + 2H_2O + 2Fe^{+3} \rightarrow 2H_3AsO_4 + 2Fe^{+2} + 2H^+ \qquad \textit{(Eq. 2-4)}$$

$$4Fe^{+2} + 4H^+ + O_2 \rightarrow 4Fe^{+3} + 2H_2O \qquad \textit{(Eq. 2-5)}$$

$$MnO_2 + 2H^+ + HAsO_2 \rightarrow H_3AsO_4 + Mn^{+2} \qquad \textit{(Eq. 2-6)}$$

$$2Mn^{+2} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^+ \qquad \textit{(Eq. 2-7)}$$
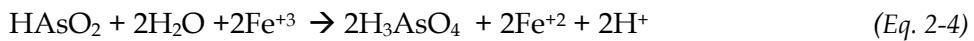
In the presence of iron or manganese oxyhydroxides, the reaction is much more rapid than with oxygen alone. Thus, in shallow, aerobic groundwater systems, which typically will contain iron and/or manganese oxide phases, the arsenic would preferentially be in the +5 valence state. These processes will occur at a petroleum hydrocarbon release site as hydrocarbon is attenuated (biodegraded), and the groundwater redox returns to ambient, aerobic conditions.

2.3.2   *Arsenic Immobilization Through Sorption*

The next factor that affects the attenuation of arsenic in shallow (aerobic) aquifers is the interaction between arsenite and arsenate with soil minerals. Both arsenate and arsenite can form insoluble compounds with a wide variety of metals. Table 2-3 lists a number of low solubility metal arsenates.

The significance of this table is that metals that form insoluble arsenates will also have a tendency to adsorb arsenic. Of the metals listed, aluminum, iron, manganese, calcium, and magnesium are the most common in soil minerals. Of these five, iron and calcium are fairly ubiquitous. The following discusses these five metals in terms of their sorption of arsenic, their geochemistry, and how their sorption of arsenic would be impacted by petroleum hydrocarbons.

- *Aluminum.* Aluminum is found in soil minerals both as a cation (Al^{+3}), as an aluminate anion (e.g., AlO_2^-, AlO_3^{-3}) or as an aluminosilicate anion (e.g., $Al_2Si_2O_8^{-2}$); the aluminates and aluminosilicates are more prevalent than are the cationic aluminum minerals. Cationic aluminum minerals are generally oxyhydroxides, sulfates or phosphates. In general, only the cationic forms of aluminum will adsorb arsenic. In the environment, aluminum is monovalent; only a +3 valence is found. As a result, changes in the redox will only affect the adsorption of arsenic on aluminum through the reduction of arsenates to the less strongly adsorbed arsenites. Adsorption of arsenites and arsenates on aluminum will also be affected by pH. They will desorb under strongly acid or basic conditions (i.e., 4>pH>8).

- *Iron.* Iron is found in soil minerals only as a cation in the form of oxyhydroxides. It does, however, have two valences – ferrous (Fe^{+2}) and ferric (Fe^{+3}). Changes in redox affect both iron and arsenic. Petroleum hydrocarbon degradation would promote desorption/dissolution of iron arsenates by reducing both the iron and the arsenic. When a petroleum-impacted aquifer reverts back to aerobic conditions after the hydrocarbons are attenuated, the iron and arsenic will both re-oxidize and the arsenic will re-adsorb. Reduced iron is easily oxidized by dissolved oxygen and will, in turn, promote the oxidation of arsenites. Iron-arsenic species will also dissolve/desorb under strongly acidic or basic conditions (i.e., 4>pH>8).

- *Manganese.* Manganese is found in soil minerals as a cation. There are three common valences Mn^{+4}, Mn^{+3}, and Mn^{+2}. The most common manganese mineral is pyrolucite (MnO_2). Manganese is quite redox labile. Mn^{+4} is readily reduced biologically to soluble Mn^{+2}. Manganese

reduction is a common metabolic pathway and occurs under less reducing conditions than does iron reduction. Under aerobic conditions, manganese appears to catalyze the re-oxidation of arsenic in groundwater. Manganese arsenate compounds are only moderately insoluble. Given the moderate solubility of manganese-arsenic compounds, manganese is not a strongly adsorbing mineral for arsenic.

- *Calcium.* Calcium occurs only as a cation. It has a single valence state, existing as Ca^{+2}. Calcium may be present as carbonates, oxyhydroxides, sulfates or phosphates. Calcium will adsorb both As^{+3} and As^{+5}. The adsorption of arsenic by calcium is not significantly affected by the reducing conditions caused by petroleum impacts, since it is not reduced and it adsorbs both forms of arsenic. Calcium adsorption is pH dependent, being favored at pH values of 6-8. However at pH values above 9, such as in high carbonate waters, the arsenic will not adsorb. Calcium forms the arsenic equivalent of apatite (Bothe and Brown, 1999).

- *Magnesium.* Magnesium behaves similarly to calcium. Magnesium has a single valence – Mg^{+2}. It is present as oxyhydroxides, carbonate and phosphate minerals. It will adsorb both arsenites and arsenates. Its adsorption is enhanced under basic conditions.

The re-establishment of aerobic conditions in the affected aquifer will reduce arsenic concentrations. The formation of iron oxyhydroxides, in particular, results in re-adsorption of arsenic that removes it from the aqueous phase. Thus, the restoration of sorptive capacity for arsenic is an important condition to be considered in the affected aquifer upon the attenuation of the petroleum hydrocarbons. Table 2-3 lists the solubility (as Log K_{sp}) of metal arsenates, which provide a rough indicator of sorption. In general, the lower the K_{sp} the more strongly adsorbed arsenic will be to that metal. The iron-arsenic mineral has the lowest K_{sp} of the four common cations (Al, Ca, Mg, and Fe), and therefore, iron minerals would adsorb arsenic most strongly.

Table 2-3: Solubility of Metal Arsenates

Metal Cation	Compound	Log K_{SP}
Al	$AlAsO_4$	-15.8
Mg	$Mg_3(AsO_4)_2$	-19.7
Ca	$Ca_3(AsO_4)_2$	-18.2
Ba	$Ba_3(AsO_4)_2$	-13
Cr	$CrAsO_4$	-20.1
Fe	$FeAsO_4$	-20.2
Ni	$Ni_3(AsO_4)_2$	-25.5
Cu	$Cu_3(AsO_4)_2$	-35.12
Zn	$Zn_3(AsO_4)_2$	-27
Pb	$Pb_3(AsO_4)_2$	-35.39
Mn	$Mn_3(AsO_4)_2$	-10.7

2.3.3   *Mineral Phase Formation*

Arsenic adsorbed onto mineral surfaces can further stabilize with time. Adsorbed chemicals can become incorporated into minerals that are present or that form as a result of recrystallization or mineral transformation processes in soils and sediments. Examples include incorporation of As^{+5} anions into hydrous ferric oxide and transformation to ferric arsenates such as scorodite ($FeAsO_4 \bullet 2H_2O$), kankite ($FeAsO_4 \bullet 3.5H_2O$), or bukovskyite ($Fe_2AsO_4SO_4OH \bullet 7H_2O$) (e.g., Ford, 2002). These minerals are more stable and less soluble than are simple adsorbed arsenic.

2.3.4 *Precipitation*

In cases where very high concentrations of dissolved iron and arsenic are present, the re-establishment of aerobic conditions can lead to the actual precipitation of metal arsenates. In general, mineral precipitation is not a dominant process in arsenic immobilization. When it occurs, it is best understood in the context of two processes:

- Precipitation from solution: Precipitation of arsenic may occur in the formation of sparingly soluble arsenates and arsenites, and, in anoxic systems, thioarsenates. Many precipitation reactions have a strong dependence on pH.

- Coprecipitation: Coprecipitation is incorporation of an element as a trace or minor constituent within a precipitating phase. In this case, arsenic substitutes for a more concentrated component in the crystal lattice (isomorphous substitution); for example, the coprecipitation of As^{+5} in iron hydroxides, sulfates or carbonates, where the anionic arsenic species displaces other anions.

These precipitation reactions are concentration dependent and can also be both pH and redox dependant.

As discussed in Section 2.3.2, precipitation and adsorption are related processes. After precipitation occurs, any residual dissolved arsenic may be further attenuated through adsorption.

2.3.5 *Stability and Reversibility*

There are two factors that will control the long-term stability of the arsenic.

1. The continued presence of degradable organics. This includes both petroleum hydrocarbons and their metabolites such as volatile fatty acids. The presence of degradable carbon can be determined by measuring biological oxygen demand (BOD) and/or total organic carbon (TOC).

2. The ambient aquifer geochemistry. The long-term arsenic concentrations will be determined by the Eh, pH and mineralogy (i.e. presence of iron) of the surrounding aquifer. In particular, the more oxidized the aquifer the more stable the arsenic will be.

The ambient conditions over time will re-establish themselves in the former hydrocarbon plume area. If the ambient conditions are more oxidizing than are

the conditions in the attenuated plume, then arsenic will remain in the solid phase. The stability of arsenic will depend upon the long-term ground-water chemistry relative to the conditions that were prevalent at the time of immobilization.

If there are significant changes in the ground-water chemistry following arsenic immobilization/attenuation, then the potential exists for re-mobilization of arsenic; especially if the groundwater redox conditions become more reducing.

If arsenic was immobilized through partitioning to mineral sulfides within aquifer sediments under sulfate-reducing conditions brought on by a petroleum hydrocarbon release, there is a potential that the mineral sulfides could reoxidize under aerobic conditions. Arsenic associated with sulfide minerals could potentially re-mobilize by sulfide oxidation if the aquifer were to return to more oxidizing conditions upon attenuation of the hydrocarbon plume. However, with time, the remobilized arsenic will attenuate when the aquifer conditions become fully aerobic. The arsenic will oxidize to arsenate and iron will oxidize to form ferric oxyhydroxides. The arsenic will then resorb to the newly formed ferric oxyhydroxides. Any remobilization of arsenic associated with sulfidic minerals will be transitory.

2.4   *CONCEPTUAL MODELS FOR ARSENIC NATURAL ATTENUATION*

The conceptual model for the natural attenuation of arsenic at petroleum impacted sites is best understood as an overlay of two spatial/temporal processes. One is the dissolution, migration and attenuation of hydrocarbons; the other is the concomitant changes in arsenic geochemistry. The fundamental concepts that determine the fate and transport of arsenic at petroleum impacted sites are:

1. The presence of hydrocarbons perturbs the existing, ambient arsenic geochemistry, resulting in a mobilization of the arsenic, and

2. When the hydrocarbons are sufficiently attenuated, the geochemistry reverts to pre-release conditions and arsenic reverts to the ambient concentrations.

The conceptual model has three temporal stages based on the attenuation of the petroleum. The first stage is the release of the petroleum and subsequent hydrocarbon plume expansion. The second stage is hydrocarbon plume stabilization and formation of steady state conditions. The final stage is plume shrinkage as the hydrocarbon is depleted.

Within each of these temporal stages, there is a spatial "footprint" based on the amount of petroleum present, the site hydrology, the biogeochemical reactions of the petroleum, and the resulting aqueous geochemistry of the arsenic. Within this footprint are two reaction zones – the hydrocarbon plume and a transition zone. The hydrocarbon plume has sub-zones defined by the different metabolic pathways, which are controlled by the availability of TEAs. The transition zone is devoid of hydrocarbons and transitions between a reduced

groundwater chemistry and the surrounding, ambient groundwater chemistry. These two reactive zones are bounded by the ambient aquifer conditions. The length and width of each reactive zone will vary site to site and with each temporal stage. This general conceptual model was presented in Figures 1-3 and 1-5 in Section 1. The three major temporal stages and their related reaction zones are discussed in more detail below.

2.4.1 Release and Plume Expansion

The first temporal stage is release and plume expansion. When petroleum hydrocarbons are released to soil and groundwater, the free phase hydrocarbons migrate through the soil. Depending on the type of hydrocarbon, a portion of the release may volatilize into the vadose zone where it can be aerobically biodegraded. Dissolution of the more soluble compounds in the petroleum hydrocarbon adsorbed to soil or present in the pore spaces establishes a plume of dissolved hydrocarbon compounds in the aquifer, downgradient from the source area. As the plume develops, microbial activity also develops that soon changes oxidizing conditions to more reducing anaerobic conditions. TEAs are consumed sequentially going from oxygen to carbonate (methanogenesis) establishing different redox (metabolic) zones. The most reducing zone is closest to the source area, which is the most depleted of TEAs having been exposed for the longest time to hydrocarbon. The metabolic zones that are established after some time, in downgradient order from the original spill area, would be methanogenesis, sulfate reduction (assuming significant SO_4 as a TEA), and iron reduction, manganese reduction, nitrate reduction, and finally the surrounding aerobic conditions (pictured in Figure 1-3). The presence and extent of the zones depend on the availability of the individual TEAs in the aquifer matrix, the seepage velocity of groundwater, the level of microbial activity, and the amount of solutes in the affected groundwater. The hydrocarbon plume continues to expand in the downgradient direction until the hydrocarbons in the plume front are completely removed by biological activity and/or volatilization.

Many of the redox conditions engendered by the petroleum release are capable of affecting iron mobilization from the solid phase and releasing arsenic from its solid phase state to the aqueous phase, predominantly in the form of the arsenite oxyanion.

Figure 2-7 depicts the conceptual model for an expanding plume and includes redox conditions, hydrocarbon concentrations, and arsenic concentrations along the plume axis. In addition, Table 2-4 summarizes the key factors affecting arsenic mobilization during the plume expansion stage.

In Figure 2-7, the redox is most negative closest to the source area where biological activity has expended most TEAs and methanogenic conditions are attained. The redox values increase in the downgradient direction as the dissolved hydrocarbon content is degraded, and metabolic conditions shift to less reducing conditions. The dissolved hydrocarbon content is at a maximum near the source area and decreases downgradient. Dissolved arsenic reaches a maximum downgradient of the source area in the zone of iron reduction and then gradually decreases through adsorption and re-oxidation. Elevated arsenic

concentrations persist past the boundary of the hydrocarbon plume until the aquifer is fully aerobic; this is the transition zone.
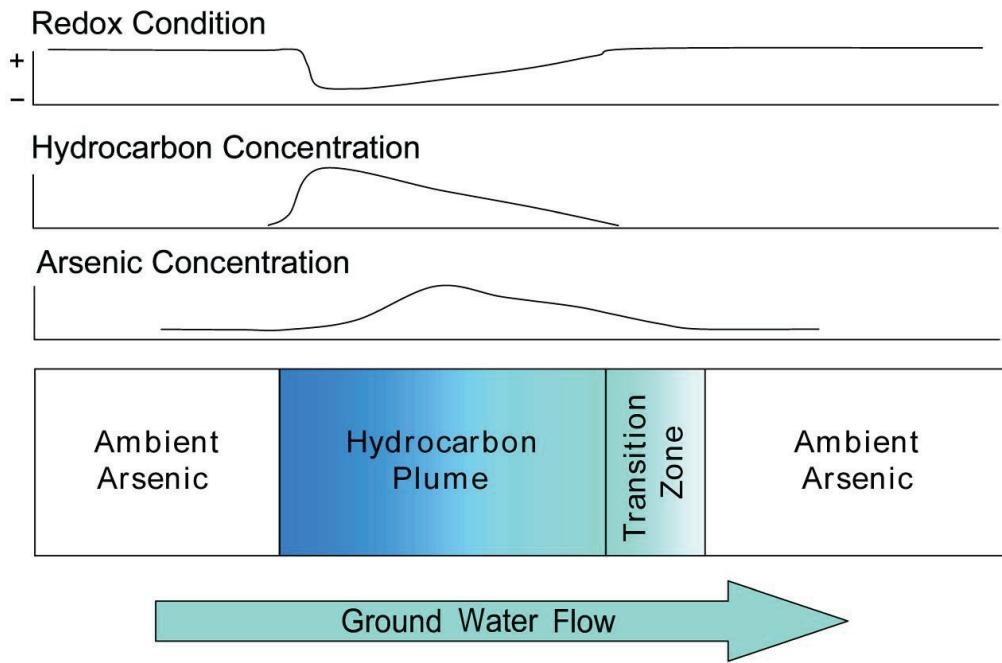
Figure 2-7: Change in Hydrocarbons, Arsenic and Redox in Reactive Zones Expanding Plume

Table 2-4: Factors Affecting Arsenic Mobilization for Plume Expansion Stage

Stage	Plume Expansion
Driving forces	Reducing conditions created by hydrocarbon degradation. The areal extent and the reducing potential of the metabolic zones (i.e., iron reduction, sulfate reduction, methanogenesis, etc.) continue to change as the terminal electron acceptors are depleted in different areas.
Mobilization processes	Reductive dissolution of metal adsorption sites; direct reduction of arsenate to arsenite
Limiting factors	Amount of hydrocarbons present, amount of terminal electron acceptors
Mitigating factors	Downgradient sorption of arsenate/arsenite on metal (Ca, Fe) sites. Formation of arsenic sulfides and arsenopyrite in sulfate reducing zone.
Duration of Stage	Once hydrocarbon input has ceased most plumes will stabilize in 3-10 years.

2.4.2   *Steady-State Plume*

After a period of time, the processes of sorption, transport, and biodegradation, achieve a steady state. The flux of hydrocarbons into groundwater is balanced by the removal due to biodegradation and volatilization. Plume expansion ceases and the redox zones remain spatially constant. At the plume source, the strongest reducing conditions of methanogenesis are present. Downgradient and laterally away from the plume source, the other TEAs can be present, such as sulfate reduction and iron reduction, depending on the available mass of the TEAs. Because many aquifers contain large amounts of iron minerals and iron oxyhydroxides, the iron reducing condition is expected to be dominant in the downgradient part of the plume, and arsenic is expected to be present in the aqueous phase in the footprint of the hydrocarbon plume. Figure 1-3 depicts plume conditions at steady state.

Although the hydrocarbon plume expansion has ceased in this scenario, arsenic enriched groundwater flows from the hydrocarbon plume area into a transition zone, where more oxidizing geochemical conditions similar to the ambient aquifer condition are present. A case study of an Oklahoma refinery (Section 5.1) describes steady-state conditions. Any reduced iron in the transition zone will react with available oxygen and precipitate onto the aquifer matrix. Arsenite will also be re-oxidized to the less soluble arsenate. The precipitated ferric iron oxyhydroxides form new sorption surfaces adsorbing aqueous arsenic oxyanion. Arsenic that was mobilized and transported in the reduced biogeochemical zones of the hydrocarbon plume is attenuated into the solid phase in the downgradient aerobic zone of the unaffected aquifer. Table 2-5 summarizes the factors affecting arsenic mobilization for this stage.

Figure 2-8 depicts the steady-state conceptual model and includesredox, hydrocarbon and arsenic concentrations for a steady state plume. Redox values are spatially stable and transition from highly reduced conditions at the plume source to aerobic conditions downgradient of the transition zone. The maximum arsenic concentrations have moved downgradient (as compared to the expanding plume in Figure 2-7) as the arsenic in the soil in the hydrocarbon plume is leached out and accumulates with groundwater flow. The arsenic concentrations drop as groundwater flows through the transition zone and finally reach ambient concentrations.

2.4.3   *Retreating Plume Conditions*

When the residual non-aqueous phase liquid (NAPL) and adsorbed hydrocarbons in the source area are sufficiently depleted due to natural attenuation, and the rate of degradation exceeds the rate of dissolution of residual hydrocarbons, the plume will begin to shrink. The redox zones will subsequently recede, extending the transition zone back towards the former hydrocarbon source area. Arsenic may be mostly depleted within the footprint of the residual hydrocarbon plume. Within the transition zone, reduced iron will react with available oxygen and precipitate onto the aquifer matrix. Arsenites may also be re-oxidized to the less soluble arsenates. As with the steady-state

conceptual model, beyond the distal end of the plume, the aquifer is at the ambient geochemical conditions and arsenic concentrations will return to ambient concentrations. Table 2-6 summarizes the factors affecting arsenic mobilization for this stage. Figure 2-9 depicts the conceptual model for a retreating plume and includes the redox, hydrocarbon and arsenic concentrations.

Table 2-5: Factors Affecting Arsenic Mobilization for the Steady State Stage

Stage	Steady State
Driving forces	Continued degradation of hydrocarbons. Stable Redox Zones are established based on TEA availability, hydrocarbon availability. The most likely stable redox processes within the hydrocarbon plume are iron reduction, sulfate reduction and methanogenesis.
Mobilization processes	Reductive dissolution of metal adsorption sites; direct reduction of arsenate to arsenite; and migration of arsenite down gradient
Limiting factors	Amount of hydrocarbons present, amount of terminal electron acceptors, and amount of arsenic available in different zones. The source area and the hydrocarbon-rich ground water zone could become depleted of arsenic.
Mitigating factors	Downgradient sorption of arsenate/arsenite on metal (Ca, Fe) sites. Formation of arsenic sulfides and arsenopyrite in sulfate reducing zone. Depletion of arsenic in source area.
Duration of Stage	Without intervention the steady state plume area can persist for multiple decades. Arsenic mobilization would hit a peak and then decrease over time even if the hydrocarbon plume is steady state.
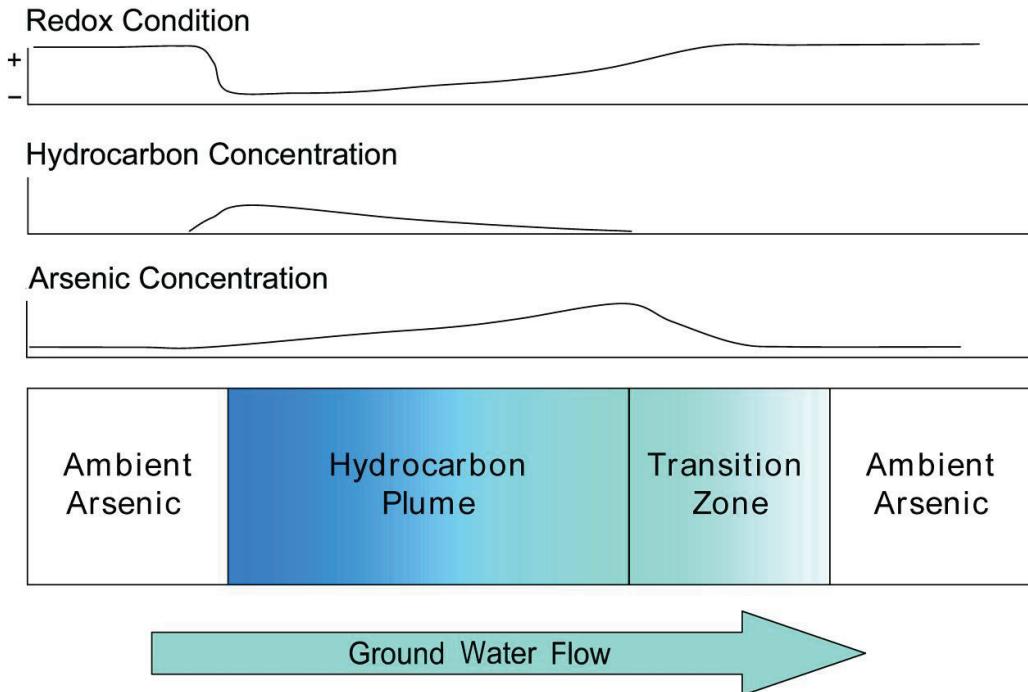
*Figure 2-8: Change in Hydrocarbons, Arsenic and Redox in Reactive Zones –
Steady State Plume*

Table 2-6: Factors Affecting Arsenic Mobilization for Retreating Plume Stage

Stage	Retreating Plume
Driving forces	Continued degradation of residual hydrocarbons. TEA availability, arsenic availability. Redox potential will start increasing. The most likely stable redox process within the hydrocarbon plume is iron reduction.
Mobilization processes	Reductive dissolution of metal adsorption sites; direct reduction of arsenate to arsenite. Migration of arsenite down gradient
Limiting factors	Amount of arsenic available in different zones. Availability of sorption sites. The hydrocarbon plume area would be depleted of arsenic.
Mitigating factors	Downgradient sorption of arsenate/arsenite on metal (Ca, Fe) sites. Oxidation of arsenite to arsenate
Duration of Stage	As the residual hydrocarbons are depleted, the redox potential will gradually increase. This stage may last 5-15 years.

Redox Condition

Hydrocarbon Concentration

Arsenic Concentration

Ambient Arsenic	Hydrocarbon Plume	Transition Zone	Ambient Arsenic

Ground Water Flow
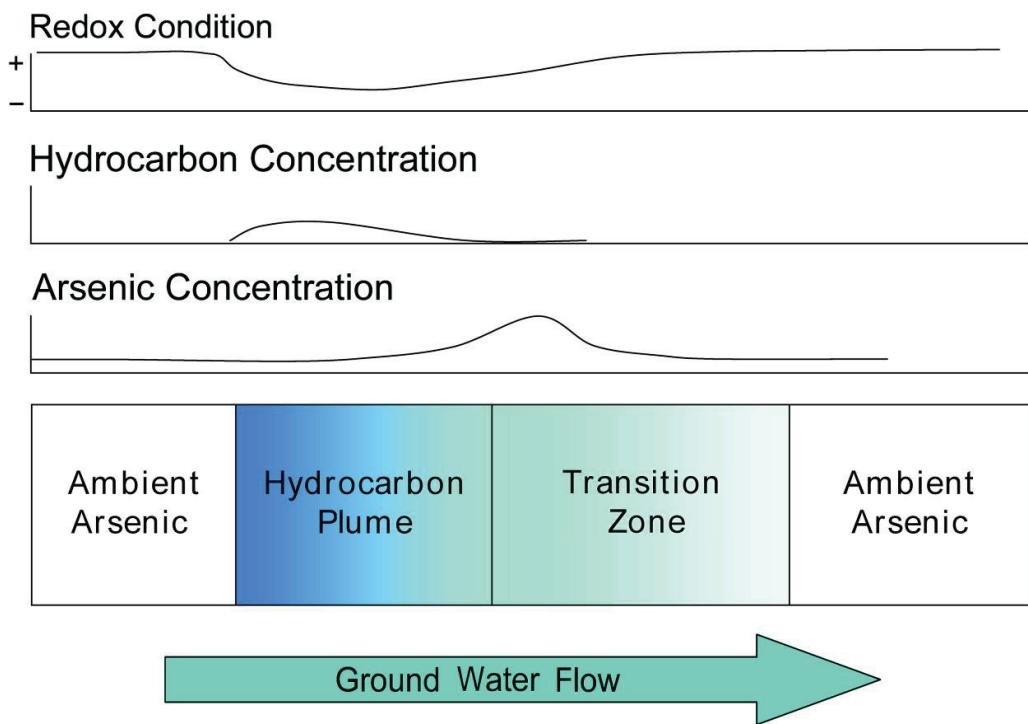
*Figure 2-9: Change in Hydrocarbons, Arsenic and Redox in Reactive Zones –*
Retreating Plume

3.0   *ASSESSMENT AND SITE CHARACTERIZATION TO EVALUATE ARSENIC NATURAL ATTENUATION*

As discussed in the previous sections, arsenic can be mobilized by the input of hydrocarbons to a shallow aquifer. When mobilized into groundwater, the arsenic will eventually attenuate to ambient concentrations as groundwater flows away from the petroleum impacted area. The question is whether this occurs within the time frame and distances needed to mitigate unacceptable impacts and risk. This section discusses how to assess the efficacy of natural attenuation at sites impacted by petroleum. When is natural attenuation of arsenic sufficient to mitigate human health or ecological risks?

Key to assessing the efficacy of natural attenuation is understanding the biogeochemistry of the site. Section 2.4, "Conceptual Models for Arsenic Natural Attenuation" describes two reaction zones on arsenic-containing sites that have been impacted with petroleum. The two reaction zones are the hydrocarbon plume and the transition zone (Figures 2-7 to 2-9). The groundwater conditions upgradient and downgradient of these two zones are governed by the ambient, background biogeochemistry.

Evaluating the natural attenuation of arsenic at petroleum impacted sites requires five areas of assessment, which may be addressed qualitatively or quantitatively, within the framework of this conceptual model:

1. Ambient arsenic - the background biogeochemical conditions that control the ambient concentrations of arsenic,

   - Are background dissolved arsenic concentrations above the MCL?

   - What is the source of the arsenic? Is arsenic present in site mineralogy and/or adsorbed to the soil matrix, or was arsenic released by prior human activity?

   - What is the ambient, background level of arsenic in groundwater?

   - How do Eh and pH control the ambient groundwater concentration of arsenic?

2. Overall site conditions – the basic stratigraphic and hydrogeologic framework affecting transport and fate of chemicals of concern at the site,

3. Petroleum hydrocarbons and redox processes - the extent of the hydrocarbon source and plume and the biological and geochemical processes within the hydrocarbon plume that both cause and mitigate the mobilization of naturally-occurring arsenic,

   - What is the areal extent of petroleum impacts in groundwater?

   - What is the areal extent of elevated arsenic concentrations (i.e., above background or MCL, whichever is higher)?

   - How do redox conditions vary across the elevated arsenic plume and within the hydrocarbon plume?

4. Arsenic attenuation processes - the geochemical processes within and surrounding the hydrocarbon plume that attenuate the arsenic and

restore arsenic concentrations to the ambient conditions, such as oxidation and sorption onto HFO, and

5. Exposures and Risks – the receptors and potential exposure pathways for arsenic that could present risk to human or ecological receptors,

- Where are potential or actual receptors in relation to the elevated arsenic plume and the hydrocarbon plume?

- Is natural attenuation sufficient to be protective of human or ecological receptors?

These assessment areas are best addressed through the development of a SSCM (Figure 3-1).
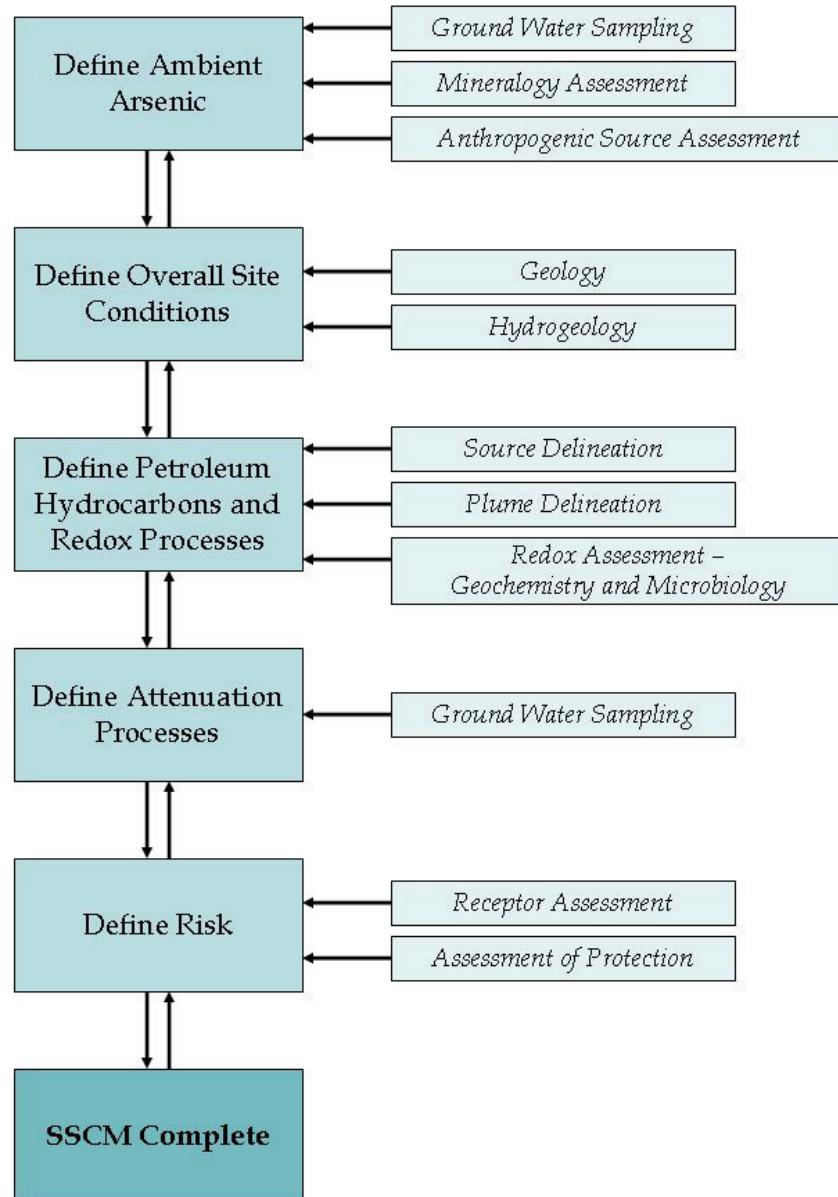
Figure 3-1: Site-Specific Conceptual Model (SSCM) Development Path

3.1   *DEVELOPMENT OF A SITE-SPECIFIC CONCEPTUAL MODEL*

At simple sites where 1) no arsenic is mobilized, 2) arsenic mobilization is limited in extent or concentration, 3) the hydrocarbon plume is stable or decreasing, or 4) no probable or actual risk exists to receptors, an understanding of the site is straight forward and further development of an SSCM to address arsenic concentrations is likely not necessary. At more complex sites, with arsenic concentrations significantly above the MCL, where arsenic mobilization exists to a large areal extent (especially with offsite impacts), where the hydrocarbon plume is expanding, or where there is probable or actual risk to a receptor, a SSCM can be developed. In the cases where it is deemed necessary, a SSCM should be developed following the process depicted in Figure 3-1. The development of the SSCM should incorporate basic assumptions for petroleum impacted sites, as discussed in Section 1.5 of this document, such as:

- Petroleum impacts typically occur in a shallow aquifer open to the atmosphere;

- The ambient (background) redox conditions are generally aerobic; and

- Reducing conditions are induced by the petroleum hydrocarbon release.

Initial detection of arsenic often occurs as a result of an existing groundwater monitoring program. Simple monitoring over time of selected wells from the previous hydrocarbon release investigation (with some downgradient additions, if necessary) and/or via compliance monitoring wells, can verify that arsenic mobilization is increasing, stable or subsiding. The normal groundwater monitoring data may provide a benchmark for future seasonal or annual monitoring. Groundwater monitoring data from compliance well monitoring may adequately assess the current arsenic attenuation zone and rate. Each site is unique in this regard and monitoring network and specific needs should be assessed. An SSCM may be beneficial to fully understand and communicate the behavior of arsenic at a site. The process of developing the SSCM is sequential and iterative. Figure 3-1 presents a general sequence for addressing the five assessment areas. However, these areas may need to be re-addressed multiple times depending on site-specific factors.

3.1.1   *Defining Ambient Arsenic*

3.1.1.1   Determining Sources of Arsenic

If groundwater arsenic becomes an issue at a site, one of the first steps in developing a SSCM for arsenic concentrations at petroleum impacted sites is to identify all potential point sources of arsenic at the subject site. Point sources may be due to disposal of arsenic containing wastes, or the use of topical pesticides.   If there are no identifiable point sources of arsenic, then the observed arsenic level may be from naturally-occurring arsenic or historical arsenic use, mobilized by the petroleum impact. The two most common sources of arsenic are the natural site mineralogy or prior human activity (agricultural, mining, industrial).

Petroleum and refined products are not a significant source of arsenic. Arsenic concentrations in petroleum were described in Table 1-2 and are generally considered insignificant.

Arsenic detections in groundwater may be false positives, and need to be verified. Several circumstances should be considered that can lead to a false positive. Sampling techniques and other data quality issues should also be considered when evaluating potential sources of arsenic at a site.

- Arsenic may be associated with drilling methods. Groundwater samples could be contaminated by drilling mud that contains low concentrations of arsenic (arsenic is a trace element in barite);

- Potable water used in the drilling process may contain arsenic;

- Arsenic detections at low concentrations may be due to matrix interference, depending on the analytical methods used; and

- Elevated arsenic may be due to turbidity present in groundwater samples. Even low concentrations of turbidity (<5-10 nephelometric units) can affect the total arsenic concentration due to colloidal facilitated transport. The colloids are frequently a mixture of clays and/or freshly precipitated Fe-oxide minerals which, as discussed previously, have a strong affinity for arsenic. If turbidity is an issue, filtration of the sample should be considered. While 0.45 micron filter membranes are often used for dissolved concentrations, the appropriate filtration protocol should be assessed for site-specific characteristics and the data requirements (USEPA, 2007a). If filtered samples cannot be negotiated, low flow sampling techniques may off-set the false positive to some extent.

Good use of laboratory and field quality assurance methods and data quality review (discussed in Section 3.1.6) will ensure that detections of arsenic accurately portray site conditions.

3.1.1.2   *Background Arsenic in Soil and Groundwater*

A site-specific background concentration range for arsenic should be established through an assessment of background soil and groundwater concentrations. This should address the vertical variation, as well as lateral, since the changing redox conditions with depth can readily influence arsenic concentrations in soil and groundwater (Cherry, et al, 1986). Multiple sampling locations should be used because there will be variability in both soil and groundwater arsenic concentrations. Assessment of background concentrations of arsenic in soils and aquifer material can (if necessary) include a more in-depth investigation into mineralogy and phases of arsenic (present within arsenic-rich pyrite, sorbed onto iron oxyhydroxides, etc.). There are instances where the arsenic in ambient (background) soil or aquifer media can exceed soil media action concentrations. Related background geochemistry should also be assessed. Ambient arsenic behavior is dependent on the background redox conditions and the presence of metals (especially iron). The evaluation of site geochemistry and its relation to arsenic mobility is further discussed in Section 3.1.3.

The background geochemistry should be included in an assessment of background arsenic concentrations. The background conditions of redox, pH, organic carbon, and other geochemical parameters discussed here will constrain the effects of hydrocarbon impact on arsenic mobility. The majority of this assessment can be done in conjunction with existing monitoring programs for hydrocarbon plumes.

Without determining a background arsenic concentration, it is impossible to determine if naturally-occurring arsenic has actually been mobilized or attenuated. The methods for determining background concentrations in groundwater are often prescribed by the regulatory entity in the state where the site is located, or by federal guidelines (USEPA, 1989a; USEPA, 1992a).

It is common to have vertical variation in arsenic concentrations in the vadose and saturated zone over a short vertical distance (Cherry, et al, 1986) due to natural heterogeneity. The importance of understanding the spatial variability of naturally-occurring arsenic is illustrated by a recent case example. The USEPA recently recognized that lower portions of the saturated zone at an arsenic site contain dissolved arsenic in excess of the MCL (prior or current) due to natural variations in geochemical conditions, not related to arsenic released through site activities (MWH, April 2006). As a result, USEPA acknowledged that arsenic concentrations up to 25 micrograms per liter are naturally-occurring in a portion of the saturated zone.

3.1.2 *Defining Overall Site Conditions*

Another element of the SSCM is a thorough understanding of the site geological and hydrogeological conditions. These provide the context and limits for the chemical of concern distribution. The data requirements for the SSCM are largely the same as those required for any hydrocarbon-impacted site.

3.1.2.1 *Geology and Hydrogeology*

The development of the SSCM should incorporate an understanding of the hydrogeologic framework within which the mobilization and/or attenuation of arsenic occurs. The hydrogeology will guide understanding of the fate and transport of all chemicals of concern (COCs) at the subject site, and will partially determine potential exposure pathways and receptors.

Identification and delineation of the major shallow groundwater bearing units (GWBU) should be done through a combination of literature research on area geology, and collection of site-specific data, often through a drilling program. Only those GWBU that can receive hydrocarbon impacts should be considered. These are generally shallow, unconfined aquifers. In conjunction with describing the GWBU at the site, the lithology can be examined for potential zones of critical mineralogy, such as iron-oxide or iron-sulfides, carbon-rich zones, or other potential matrix influences to arsenic distribution and mobility.

Once the appropriate GWBUs are determined for the SSCM, the potentiometric surface and flow direction should be examined for each GWBU. Groundwater flow direction also helps to define the site background (i.e. upgradient of potential source), and identify potential exposure pathways and receptors. Groundwater/surface water interactions should be considered within the hydrogeologic model, as well. An understanding of the groundwater hydraulics in comparison to plume transport will be important for selecting monitoring locations for a potential monitored natural attenuation remediation approach (USEPA, 1998a, USEPA, 1999, USEPA, 2007a, USEPA, 2007b).

Because naturally-occurring arsenic is common in some regions of North America (and worldwide) and in certain depositional environments (Welch, et al., 2000), an investigation of the GWBU matrix, and that of surrounding units, can help to determine if arsenic sources are present in soil and sediments from the site. Arsenic present in the solid phase at the site can be determined using the appropriate methods usually executed in conjunction with subsurface delineation and well installation efforts. Color of the soil/rock is often an empirical indicator of overall redox state and should be noted when logging drill core or collecting samples. Generally, tan to red colors indicate overall oxidizing conditions, while green to gray and/or black indicate reducing conditions. Following completion of well drilling activities, aqueous geochemical information can be collected for nature and extent of chemicals of concern and geochemical data pertinent for further refinement of the SSCM. Although not typically conducted, nor a routine component of the SSCM, elemental analysis by portable X-ray fluorescence (XRF) in the field (USEPA SW-846 Method 6200), and X-ray diffraction (XRD) can provide additional information on chemical composition and crystallographic structure of aquifer materials. Further discussion of possible aquifer material and soil assessment techniques can be found in USEPA reference documents (USEPA, 2007a; USEPA, 2007b).

Hydrogeologic conditions can change with time, therefore, a temporal site monitoring plan is recommended. Temporal site monitoring should be designed at a frequency sufficient to identify seasonal changes to the flow regime, large-scale recharge events, and hydraulic, geochemical, and microbial responses to on site remediation activities. Temporal changes in the flow regime can alter the COC plumes, including transport of arsenic. Changes in the redox conditions due to changes in potentiometric surface or flow direction can also affect arsenic mobility and concentrations in groundwater. Likewise, on site or nearby remediation activities, such as pumping or excavation, can bias investigation results and evaluation of the potential for natural attenuation of arsenic and other COCs. Development of a SSCM could require temporary suspension of other remediation activities to achieve steady-state hydrogeologic conditions for assessment, if sufficient historical data are not available.

3.1.2.2   *Geochemistry*

Analysis and interpretation from specific geochemical data gathered from the site helps to build the conceptual model. Geochemical information will help to identify mobilization mechanisms and provide information on the natural

attenuation of arsenic at the site. Much of the geochemical data needed to make an assessment can be gathered from routine groundwater monitoring, including or in addition to existing delineation or compliance monitoring of the associated hydrocarbon plume. The need for additional data gathering can be considered after review of key geochemical parameters discussed below.

The redox and pH conditions are important to the potential mobilization and sequestration of arsenic at the subject site (release mechanisms described in Section 2.2). Arsenic redox and pH conditions change along the extent of the hydrocarbon plume and arsenic geochemistry changes should be considered as well. Sample data locations should include background, plume center (or source zone), and points along the plume axis (USEPA, 1999). These sample locations should be monitored to provide information on changes in geochemistry and plume geometry over time. The SSCM should consider redox and arsenic geochemistry and it can be further refined from this information.

Assessments of redox potentials from field measurements can be difficult and the results can be confusing or misleading. Problems with field probes used to measure Eh or oxidation-reduction potential (ORP) frequently arise from equipment instability or operator error that lower the quality of the field-measured Eh (YSI, 2005). In addition, much discussion in the literature has taken place regarding the usefulness of a field-measured ORP/Eh. Natural or impacted water bodies can contain multiple redox couples (for example Fe^{+3}/Fe^{+2}, Mn^{+4}/Mn^{+2}, SO_4^{-2}/S^{-2}) that are not at equilibrium in the solution. Thus, a thermodynamically meaningful value of Eh cannot be easily assigned from a field measurement (Thorstenson, 1984). A more accurate measure of Eh is the quantitative measurement of the concentrations of the species that make up each of the redox couples that are present in the solution. However, field measured ORP can be considered a useful qualitative indicator of the overall redox state if proper attention is given to calibration and operation of the field equipment.

3.1.3   Defining Petroleum Hydrocarbons and Redox Processes

3.1.3.1   Hydrocarbon and Arsenic Distribution

Since the hydrocarbon plume provides the impetus for arsenic mobilization, the SSCM should include the distribution of the hydrocarbons and the dynamics of the hydrocarbon plume (i.e., expanding, stable, or retreating). Delineation and assessment of hydrocarbon plumes are discussed in API (API, 1996) and USEPA literature (USEPA, 1998a; USEPA, 1999). In general, these documents illustrate that sample locations should be distributed sufficiently to delineate the plumes of petroleum hydrocarbon and dissolved arsenic in groundwater. Soil borings, cone penetrometers, deployed sensors, temporary wells and permanent wells are all tools that can be utilized to gather data for delineation. Arsenic impacts should be delineated to background or compliance concentrations (e.g., MCLs, groundwater standards), whichever is higher. In general, soluble components of petroleum hydrocarbons should also be delineated.

If significant areas of elevated dissolved arsenic do not correspond with the plume of petroleum hydrocarbons, the downgradient transition zone or with the ambient, background level of arsenic, further assessment may be necessary, and the SSCM should be re-evaluated. It is possible, under such circumstances, that an undefined source of arsenic could be present, or that the actual hydrology differs from the current SSCM.

Geochemical parameters pertinent to plume conditions and arsenic mobilization have been previously discussed. Table 3-1 lists the principal parameters necessary to refine the SSCM along with recommended methods and usefulness of the data gathered. Pertinent references for sampling methods include *Standard Methods for the Examination of Water and Wastewater* (APHA, 1992) and *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (USEPA SW-846), which includes USEPA SW-846 Method 7061A; USEPA SW-846 Method 6020 or Method 6010, inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). In-depth discussion of sampling methods and approaches for geochemical parameters listed in Table 3-1 are provided in USEPA documents on the subject (USEPA, 1998a; USEPA, 2007a). Specific discussion of arsenic species sampling methods, techniques, and sensitivities is presented in USEPA, 2007b.

3.1.3.2   *Microbiology*

Further refinement of the SSCM can include an examination of the conditions for microbial activity. The biodegradation of hydrocarbons is the primary driving force for the mobilization of arsenic. The extent and persistence of arsenic mobilization is therefore tied directly to the attenuation of the hydrocarbon plume. The attenuation of petroleum hydrocarbon and arsenic is largely dependent on the ability of native subsurface bacteria to adapt and metabolize or co-metabolize petroleum and the availability of TEAs. Table 3-2 lists some of the microbiological parameters that can help to determine the extent of reducing conditions that are present at the site. In-depth discussion of sampling method and approach for natural attenuation parameters listed in Table 3-2 is provided in USEPA documents on the subject (USEPA, 1998a; USEPA, 2007a).

Hydrogen (H_2) concentration in groundwater (Lovely and Goodwin, 1988) can be used to indicate the TEAP which dominates within the plume. Hydrogen concentrations for the various TEAPs are shown in Table 3-3 (Chapelle et al., 1996; USEPA, 1998a). This approach is often used when other geochemical lines of evidence are unclear regarding the redox status of an aquifer.

Table 3-1: Key Ground Water Geochemical Parameters for Assessment of Natural Attenuation of Arsenic at Petroleum Hydrocarbon Sites

Parameter	Approach	Method Reference	Assessment
pH	Flow-through cell or down-hole measurement; pH probe	Follow the pH probe or multi-parameter probe manufacturer's instructions	Master variable – affects arsenic mobility, particularly in terms of surface reaction, sorption
Eh (ORP)	Flow-through cell or down-hole measurement; probe can measure ORP; measure redox pair concentrations for reaction-specific E^0	Standard Methods (APHA, 1992) 2580B	ORP provides relative data for assessing redox conditions and can calibrate dissolved oxygen values. If more reaction/mechanism specific redox information is necessary, redox pair concentrations should be assessed (see arsenic speciation or TEA)
Alkalinity	Field titration or colorimetric kit, such as Hach	Hach Alkalinity test kit; Chemetrics; field titration (digital or use Standard Methods (APHA, 1992))	Field alkalinity measurements aid in geochemical facies identification and measure buffering capacity
Dissolved Oxygen (DO)	Low-flow sampling or down-hole measurement; oxygen probes (preferably optical) can be used; field colorimetric kits can be more accurate; proper technique critical	Follow the DO probe/meter manufacturer's instructions; CHEMetrics DO test kit; refer to Standard Methods (APHA, 1992) 4500	Determines whether ground water conditions are aerobic or anaerobic, which indicates the potential abiotic and biological mechanisms for arsenic fate and transport
Iron	Dissolved iron can be measured in the field with colorimetric kits; samples can be collected for Fe^{2+}/Fe^{3+} species or total dissolved iron (Fe_T can be used as an approximation of Fe^{2+} for many Eh/pH conditions)	Standard Methods (APHA, 1992) 3500-Fe B; ASTM D 1068-77, Iron in Water, Test Method A; CHEMetrics or HACH kits (8146)	Care must be taken with samples collected for Fe2+/Fe3+ to preserve speciation; the presence of iron (and its speciation) indicates current redox condition of GWBU, as well as attenuation capacity for sequestration of dissolved arsenic
Arsenic Speciation	Low-flow sampling; sampled and preserved in the field (reference methods) to analyze for total arsenic (As_T), As^{3+} and As^{5+}	EPA Method 1632A; Standard Method (APHA, 1992) 3500-As B or C (Hach Method 8013); total arsenic by SW-846 6020B; see further discussion of methods in USEPA, 2007b	Preservation of arsenic speciation requires special sampling method; various sampling and field preservation methods are available; arsenic speciation provides information specific to redox potential for arsenic as it relates to mobility

Table 3-2: Key Microbiological Parameters for Assessment of Natural Attenuation of Arsenic at Petroleum Hydrocarbon Sites

Parameter	Approach	Method Reference	Assessment
Alternate Terminal Electron Acceptors (TEA)	Low-flow sampling; alternate TEA include Fe^{3+}, SO_4^{2-}, NO_3^-, and CO_2, measured by collecting and preserving samples according to appropriate method; CO_2, or other gases, should be sampled by gas stripping method for laboratory analysis.	Methods depend on analyte – metals by SW-846 6020B, anions by EPA 300; nitrate by Standard Methods (APHA, 1992) 4500-NO_3 D (Hach Method 8324) or EPA 353.2/353.3; sulfate by Hach Method 8051; CO_2 by CHEMetrics Method 4500	Investigate alternate TEA as appropriate for aquifer mineralogy and ambient ground water conditions; TEA concentrations provide information on redox conditions, degradation of hydrocarbon, and attenuation capacity of the aquifer.
Total Organic Carbon	Low-flow sampling; collect sample for laboratory analysis.	SW-846 9060	Total organic carbon indicates presence of energy source for microbial processes.

Table 3-3: Molecular Hydrogen Concentrations Characteristic of Reducing Zones in Ground Water

Terminal Electron Accepting Process	H_2 Concentration Range (nM/L)
Denitrification	0.1
Fe^{2+} reduction	0.2 - 0.8
SO_4^- reduction	1.0 - 4.0
Methanogenesis	>5.0

From USEPA, 1998a; Chapelle et al., 1996.

3.1.4   *Defining Attenuation Processes*

Part of SSCM development involves evaluating the fate and transport of arsenic at the site to identify the attenuation of arsenic as concentrations approach ambient conditions. Fate and transport comprises the hydrogeology, the geochemistry, and the microbiology at the site to determine zones where arsenic will expand in extent, is currently stable, or has begun to decline, as occurs in the transition zone. The extent of degradation of petroleum hydrocarbon, fate of the source area, and possible return to ambient conditions all determine the future fate of arsenic concentrations in groundwater. Investigation should include groundwater sampling to determine the extent to which arsenic and iron concentrations are declining and to determine whether the redox conditions are progressing towards ambient conditions. Investigation of the downgradient conditions, including changes in hydrogeology, chemistry, and aquifer materials, can also aid development of the SSCM and prediction of downgradient arsenic mobility. It should be noted that the lateral extent of arsenic in groundwater beyond the hydrocarbon plume boundary may be limited due to the rapid attenuation of arsenic under aerobic conditions.

3.1.5   *Defining Risk*

The last element in the SSCM is determining potential exposure pathways, human and ecological receptors and the associated estimates of current or future risks. According to the Risk-Based Corrective Action (RBCA) method (ASTM, 1995; ASTM, 2002), in order for risk to be present, there must be both the chemical of concern and an exposure pathway between that source and a potential receptor (human or ecological). The exposure pathway considered here is the groundwater transport pathway. A generalized exposure pathway assessment is shown in Figure 3-2 to establish potential human and ecological exposure pathways and risk related to mobilization of arsenic in groundwater. The figure is used to document the potentially complete exposure pathways between affected physical media and possible receptors. An exposure pathway is not considered complete unless all four of the following elements are present:

- A source and mechanism for hydrocarbon release;

- An environmental transport/exposure medium;

- A receptor exposure point; and

- A receptor and a likely route of exposure at the exposure point.

The hydrocarbon release and transport mechanisms to freshwater aquifers were discussed in Section 2. In some cases, unconfined aquifers are in hydraulic communication with nearby rivers. Potential exposure points for receptors include freshwater aquifers used for water supply but also the surface water bodies in hydraulic communication and their ecosystems. Potential receptors are defined as human and ecological populations that could encounter arsenic in environmental media. Consistent with USEPA 1989 guidance (USEPA, 1989b), reasonably anticipated future groundwater uses should be considered when selecting potential receptors. The following potential human receptors are considered in the exposure pathway assessment (Figure 3-2):

- Future domestic water users;

- Future irrigation/agricultural water use; and

- Future surface water recreational users.

In this exposure pathway assessment, the ecological receptors are organisms, populations, or communities that could be exposed to chemicals of concern as a result of discharge to surface water. All wildlife and plant species occurring in the vicinity of the potentially affected surface waters are potential ecological receptors. The following general ecological receptors are considered in the exposure pathway assessment (Figure 3-2):

- Primary producers (e.g., plants);

- 1st consumer (e.g., invertebrates);

- 2nd consumer (e.g., wading birds, rodents); and

- 3rd consumer (e.g., fish-eating and small animal eating birds).

Primary Sources	Primary Release Mechanism	Secondary Source	Secondary Release Mechanism	Exposure Media	Exposure Route	Human			Ecological[1]			
						Residents	Worker	Recreational	P	1	2	3
Naturally Occuring Arsenic	Arsenic Mobilization	Freshwater Aquifer		Domestic Water Use	Direct Contact	✓						
					Ingestion	✓						
			Irrigation		Direct Contact		✓					
					Ingestion		✓					
			Bio Uptake	Food Items	Ingestion	✓						
TPH Release			Surface Water Discharge	Surface Water	Direct Contact	✓		✓	✓	✓	✓	✓
					Ingestion	✓		✓		✓	✓	✓
					Root Contact				✓			
				Sediment	Direct Contact	✓		✓		✓	✓	✓
					Ingestion	✓		✓		✓	✓	✓
					Root Contact				✓			

(1) Trophic Level: P= Primary producers (e.g., plants); 1=1st consumer (e.g., invertebrates);
   2=2nd consumer (e.g., wading birds, rodents); 3=3rd consumer (e.g., fish-eating and small animal eating birds)
✓ Potentially complete exposure pathway.

Figure 3-2: Exposure Pathway Flow Diagram

Sensitive species are not identified as part of this exposure pathway assessment, and should be considered as appropriate for a site. Identification of sensitive species occurring near potentially affected surface waters would be carried out as part of a site-specific risk assessment. The exposure pathway assessment presented (Figure 3-2) is a generalized example for assessment of arsenic impacted sites. Each site risk assessment should include an exposure pathway assessment considering the specifics of that site. Guidance on applicable risk assessment procedures can be found in the USEPA documents (USEPA, 1989; USEPA, 1992b; USEPA, 1998b). State requirements on risk assessment may be different, so the appropriate state rules and guidance should be consulted, as well.

The appropriate benchmark concentrations should be considered as part of an ecological risk assessment. These concentrations can vary from the human-health MCL, depending on the identified exposure pathways and receptors, and the applicable agency standards. Examples of ecological benchmark concentrations for various media (primarily from Oklahoma and Texas) are presented in Table 3-4.

Table 3-4: Examples of Ecological Benchmark Screening Levels for Arsenic in Various Media

Applicable Standard	Benchmark Screening Value for Arsenic
Ground and Surface Water	
ORNL preliminary remediation goal for surface water [a]	0.190 mg/L
Oklahoma Water Quality Standard for Fish & Wildlife Propagation (Chronic) [b]	0.190 mg/L
Texas Ecological Benchmark for Water [c]	0.190 mg/L
Sediment	
ORNL preliminary remediation goal for sediments [a]	42 mg/kg
Soils	
EPA Ecological Soil Screening Levels [d]	
Plants	18 mg/kg
Wildlife: Avian	43 mg/kg
Wildlife: Mammalian	46 mg/kg

Source:
[a] ORNL, 1997
[b] OWRB, 2008
[c] TCEQ, 2008
[d] EPA, 2005

3.1.6 *Arsenic Data Quality and Gaps Review*

Arsenic data should be reviewed and qualified based on quality assurance and quality control principles as specified in data quality objectives (DQOs). These DQOs are often established within the context of the regulatory programs applicable to the site (Resource Conservation and Recovery Act (RCRA), state agency, etc.) and the site management objectives of the site stakeholders.

Guidance on appropriate data qualification can be found in the USEPA documents (USEPA, 2000a; USEPA, 2000b). State requirements on arsenic sampling and analyses may vary, so the appropriate state rules should be consulted, as well.

Data quality also should be assessed for all critical parameters in addition to arsenic, such as the petroleum hydrocarbon COCs, and transient parameters, DO, Eh and pH. DO, Eh and pH sampling and measurement results are sensitive to technique. These methods can greatly affect DO, Eh and pH values (which are critical for determining arsenic mobility) and how well they represent actual conditions; therefore, it is important to review the applicability of sampling methods for the site as part of a data quality review, and to maintain proper technique.

In addition to data quality review, a complete assessment of arsenic attenuation at petroleum impacted sites may include a data gaps assessment. There are a number of potential data gaps that could be encountered. Data gaps for a site may consist of either missing chemical analyses of soil and groundwater, poor quality data, or inadequate spatial information needed to determine nature and extent of arsenic in soil or groundwater in the impacted area of the hydrocarbon release. Data gaps should be identified and addressed at all stages in the SSCM development process.

3.2   *USES OF THE SSCM*

Site managers should be able to use the SSCM to support stakeholder discussions and decision-making. Hydrogeological, geochemical, biological, and fate and transport information acquired during site assessment are provided in the SSCM. The SSCM can be used to explain the mobilization and attenuation of arsenic at petroleum impacted sites.

Computational modeling can aid site visualization and further enhance the value of the SSCM at complex sites. Individual components, such as hydrologic flow, can be modeled, or these components can be taken into consideration for evaluating future site conditions and remedial alternatives. Many model codes are available from the US Geological Survey, USEPA websites, and commercial vendors to aid in site assessment. Geochemical modeling of arsenic behavior using these models is also discussed in the literature (Allison, et al., 1990; USEPA, 1991; Parkhurst and Appelo, 1999).

Once a SSCM has been developed, strategies for site closure can be considered. If supported by the SSCM, natural attenuation of arsenic can be incorporated into the remediation strategy in the form of an MNA approach. The SSCM should also help determine appropriate locations for long-term monitoring. Key parameters to monitor the effectiveness and status of natural attenuation at the site should be determined from the SSCM and associated data and information. The MNA plan should include remediation goals and timelines, as well as contingencies to enact if the remedial goals are not met. At most petroleum hydrocarbon release sites, arsenic attenuation and attainment of cleanup goals should correlate with attenuation of hydrocarbon compounds in the plume. If source control or removal of hydrocarbon-impacted soils is required, arsenic concentrations should eventually return to near-ambient conditions. If site remedial actions and monitoring have taken place, any new data and information should be used to validate and refine the SSCM as needed.

4.0   *REMEDIATION TECHNOLOGIES FOR ARSENIC IN GROUNDWATER IMPACTED BY PETROLEUM HYDROCARBONS*

Arsenic concentrations in groundwater at petroleum impacted sites that are above the natural background concentrations are generally a result of microbial activity caused by the presence of the hydrocarbons. In response to the availability of degradable carbon, biological activity consumes any oxygen present and then, successively, other TEAs. Once the groundwater redox conditions are at or below iron reduction, arsenic will be mobilized. The presence of petroleum thus changes the arsenic geochemistry from ambient conditions, to more reduced conditions, generally causing it to be more mobile. This condition is reversible. If and when the petroleum impact is remediated and background redox conditions are re-established, the arsenic will revert back to its background level.

As discussed in Section 2.4, hydrocarbon plumes will achieve a stable condition and then attenuate over time. Likewise, the arsenic plume will achieve stable conditions and then attenuate over time. Both the hydrocarbon plume and the concomitant arsenic plume will not and do not continue to migrate. Over time, both stabilize and both attenuate.

If, however, there is a need or a desire to accelerate the attenuation of the mobilized arsenic, two remedial approaches can be considered. The focus of remediation can be the removal/mitigation of the hydrocarbons or the focus can be the direct stabilization of the arsenic. In general, remediating the hydrocarbon impact can have the greatest, most lasting effect on the arsenic concentrations. If the hydrocarbons are remediated, the arsenic concentrations will, over time, revert to their ambient concentrations throughout the area that had been impacted by the hydrocarbons.

There are, however, situations under which the attenuation or remediation of the hydrocarbon plume may not be not adequate, and additional measures are necessary to address the dissolved arsenic. In particular, if groundwater receptors are impacted or threatened, additional methods of arsenic remediation may be necessary. These techniques are generally focused on specific receptors and are mostly barrier technologies. If, however, the hydrocarbon plume is also not attenuated or remediated, then there is an ongoing risk that arsenic can re-mobilize. Ultimately, the attenuation of the hydrocarbons and the attenuation of arsenic are integrally linked. Hydrocarbons are the causative factor for arsenic mobilization; their attenuation is the determinative factor in the re-stabilization of the arsenic.

4.1   *HYDROCARBON REMEDIATION TECHNOLOGIES*

Natural attenuation of hydrocarbons can address arsenic mobilization. The key question about the sole use of natural attenuation to address hydrocarbons is time. If hydrocarbons need to be more rapidly addressed, there are a number of technologies which are well proven and can be applied (Table 4-1). As shown in the table, most of these also have a beneficial impact on dissolved arsenic concentrations as well. For more detailed information on hydrocarbon remediation, the API has extensive publications available on their website (www.api.org).

4.2   *ARSENIC TREATMENT TECHNOLOGIES*

Direct treatment of arsenic at hydrocarbon impacted sites has limited utility; as long as there are residual hydrocarbons present, arsenic may continue to be present. Plume-wide arsenic remediation, if warranted, should be coordinated with hydrocarbon remediation, including MNA.

There are, however, situations where arsenic may need to be specifically addressed. The primary situation is where a receptor is or may be adversely impacted by the arsenic. In such cases, an approach can be to use a barrier or adsorptive technology. The following sections describe some of the technologies that can be considered for use to address impacts to receptors.

Table 4-1: Hydrocarbon Remediation Technologies

Hydrocarbon Remedial Process	Short Term Effect on Arsenic	Long Term Effect on Arsenic
Natural Attenuation	Arsenic attenuation at plume boundaries	Arsenic attenuates plume-wide
Separate Phase Removal	No Effect	Accelerates attenuation by removing mass
Pump and Treat	Removal of arsenic; arsenic attenuation at plume boundaries	Accelerates attenuation by removing mass
In Situ Aeration – Soil Vapor Extraction (SVE); Air Sparging (AS); Dual-Phase Extraction (DPE):	Plume shrinkage; Stabilization of arsenic	Stabilization of arsenic
In Situ Chemical Oxidation (ISCO)	Stabilization of arsenic	Stabilization of arsenic
In Situ Aerobic Biodegradation	Plume shrinkage; Stabilization of arsenic	Stabilization of arsenic
In Situ Biodegradation – Sulfate Reduction	Mixed, can stabilize arsenic by forming arsenic sulfides; can mobilize arsenic through reduction and/or formation of thioarsenates.	Sulfides can re-oxidize and re-mobilize arsenic

4.2.1 Phytoremediation

Phytoremediation is designed to use plants to degrade, extract, contain, or immobilize chemicals of concern in soil, sediment, or groundwater. A number of species are known to be able to accumulate or hyperaccumulate metals including arsenic. For example, Porter and Petersen (1975) have documented arsenic accumulation of up to 100 mg/kg of dry weight in plant material.

Typically, trees with deep roots are planted in areas with the affected shallow groundwater. Other species, including ferns have been used to reduce arsenic concentrations in soils and in the treatment of industrial waste water (Ma et al., 2001)

The types of plants that are used in phytoremediation to treat arsenic include:

- Poplar;

- Ferns;

- Cottonwood;

- Sunflower; and

- Indian mustard.

Phytoremediation is an emerging technology. Experimental research into identifying appropriate plant species for phytoremediation is ongoing. It is generally applicable only to soil and relatively shallow groundwater (less than 20 feet) that can be reached by plant roots. In addition, the plants used in phytoremediation can accumulate high concentrations of arsenic during the process, and might require additional treatment prior to disposal or disposal as hazardous waste.

4.2.2 Precipitation/Coprecipitation

Precipitation uses chemicals to transform dissolved chemicals of concern into an insoluble solid. In coprecipitation, the target chemical of concern can be dissolved or in a colloidal or suspended form. Dissolved chemicals of concern do not precipitate, but are adsorbed onto other species that are precipitated. Colloidal or suspended chemicals of concern become enmeshed with other precipitated species, or are removed through processes such as coagulation and flocculation. Many processes to remove arsenic from water involve a combination of precipitation and coprecipitation. Arsenic precipitation/coprecipitation can use combinations of the chemicals and methods listed below.

Chemicals and methods used for arsenic precipitation/coprecipitation:

- Ferric salts, (e.g., ferric chloride), ferric sulfate, ferric hydroxide;

- Alum (aluminum hydroxide);

- Manganese sulfate;

- Copper sulfate; and

- Sulfide.

Precipitation/coprecipitation has been one of the most frequently used methods to treat arsenic impacted water, including groundwater, surface water, leachate, mine drainage, drinking water, and wastewater in numerous pilot- and full-scale applications. This technology can reduce arsenic concentrations to less than 0.050 mg/L and in some cases has reduced arsenic concentrations to below 0.010 mg/L. As previously stated, this process can only reduce dissolved arsenic concentrations to pre-existing ambient concentrations.

The limitation of precipitation is that it may need to be repeated. If, however, iron salts are used, a secondary benefit is that the excess iron also acts as a sorbent as described below.

4.2.3   *Adsorption*

In adsorption, solutes (chemicals of concern) concentrate at the surface of a solid phase, typically an iron oxyhydroxide, thereby reducing their concentration in the bulk liquid phase. Most of the application of this process is as a treatment technology for a pump and treat system. The process can be used *in situ* to create new sorption sites in the affected part of the aquifer to remove arsenic from the aqueous phase.

Types of sorbent used in adsorption to treat arsenic are:

- Activated alumina (AA);

- Hydrous Ferric Oxide (HFO);

- Geothite; and

- Surfactant-modified zeolite.

Adsorption has been used to treat groundwater and drinking water containing arsenic. It is often used to treat groundwater and drinking water ex situ, or as a polishing step for other water treatment processes. Based on the information collected for this report, this technology typically can reduce arsenic concentrations to less than 0.050 mg/L and in some cases has reduced arsenic concentrations to below 0.010 mg/L. Its effectiveness is sensitive to a variety of untreated water chemicals and characteristics. If redox potentials are lower than iron-reduction, this approach will not work without additional technology. While HFO, or other iron material, will also adsorb arsenite, this technology can be supplemented by aeration to further improve adsorption.

4.2.4   *Permeable Reactive Barriers*

Permeable reactive barriers (PRBs) are trenches containing reactive media that are installed in the ground across the path of a contaminated groundwater plume to intercept the plume. The barrier allows water to pass through while

the media removes the chemicals of concern by precipitation, degradation, adsorption, or ion exchange.

Chemicals and reactive media used in PRBs to treat arsenic:

- Zero valent iron (ZVI);

- Limestone;

- Basic oxygen furnace slag;

- Surfactant modified zeolite; and

- Activated red mud.

PRBs have been used to treat arsenic in groundwater at full scale. Although many candidate materials for the reactive portion of the barrier have been tested at bench scale, ZVI and limestone have been used at full scale most often. The installation techniques for PRBs are established for depths of up to 100 feet, and require innovative installation techniques for deeper installations. Success is highly dependent on site specific aspects of hydrology and geochemistry.

5.0   *CASE STUDIES FOR ARSENIC MOBILIZATION AND ATTENUATION AT PETROLEUM IMPACTED SITES*

The following case studies illustrate the principles of arsenic mobilization and attenuation at petroleum hydrocarbon release sites, and illustrate examples of site assessment.

5.1   *AN OPERATING OKLAHOMA REFINERY*

5.1.1   *Site Description*

This refinery manufactures fuels from crude oil and has operated continuously for about 80 years. Hydrocarbon-impacted groundwater in the alluvial terrace sand aquifer above shale and limestone bedrock has been pumped and treated at the facility since 1968, with major pumping efforts initiated in the early 1990's. As of 2008, there are about 30 dual pumping recovery wells used to achieve hydraulic containment of dissolved and LNAPL plumes, with 500 monitoring wells at the site. Presently, the site is under a RCRA Part B permit. Dissolved and LNAPL plumes at the site have remained stable, and in some areas plume extent has decreased (Figure 5-1).

5.1.2   *Ambient Conditions*

The site is underlain by about 20 to 40 feet of a silty clay unit. Beneath this layer is the principal impacted aquifer, a fine to coarse sand with thin gravel lenses at depth that occurs in three sand terrace deposits. The present day alluvial fine to coarse sand aquifer, comprising these terrace deposits, is approximately 5 to 25 feet in saturated thickness. Depth to groundwater ranges from zero feet below ground surface (ftbgs) (where it issues as springs) to 60 ftbgs, but is generally about 10 to 40 ftbgs. Underlying the coarse sand is bedrock consisting of shale and limestone. The terrace aquifer is present on site as a predominantly unconfined aquifer, but can also behave as confined, depending on the location and water level elevation at the time. The site area is approximately 6.5 square miles. Groundwater flow direction is generally from north to south across the site but is heavily influenced by the containment pumping wells.

Monitor wells installed at the upgradient (northern) boundary of the refinery contain arsenic concentrations that range from below the detection limit, to above the MCL of 0.01 mg/L (Figure 5-2). Also, arsenic has been detected in soil core samples from the site, along with iron, indicative of naturally-occurring arsenic associated with the iron mineral phases (Figure 5-3).
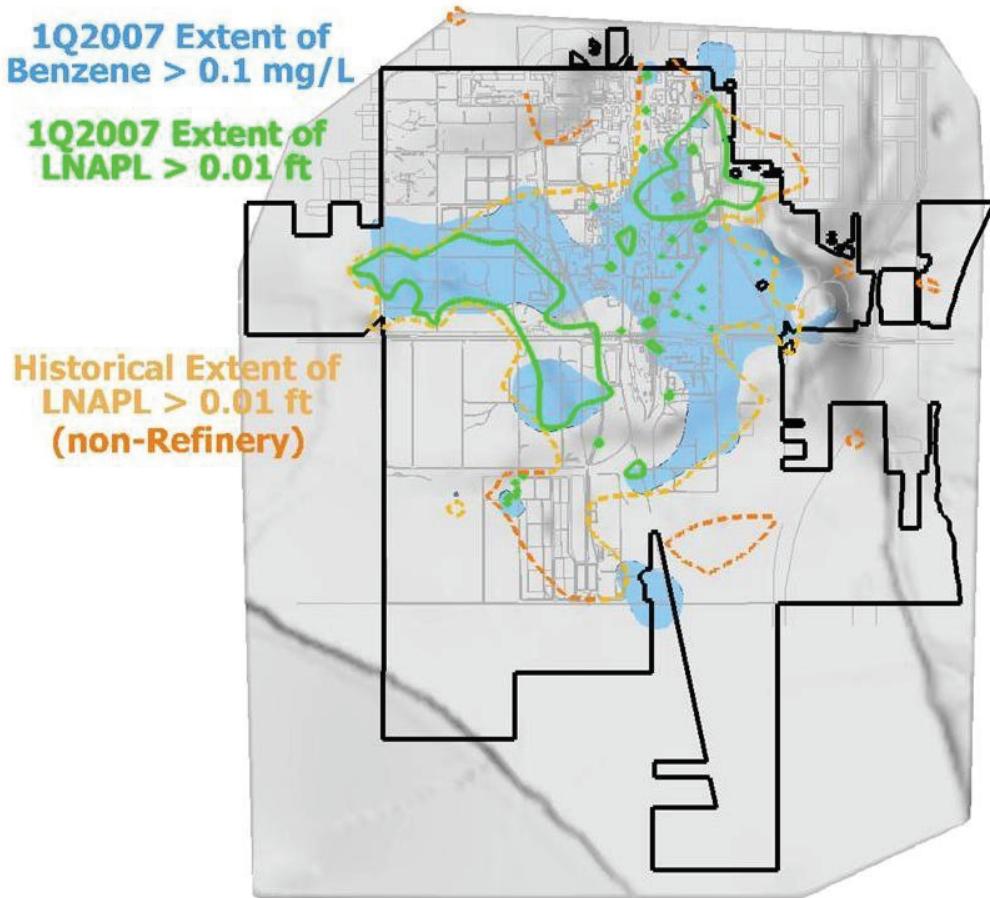
Figure 5-1: Current (2007) Extents of Hydrocarbons in the Shallow Aquifer at the Oklahoma Refinery
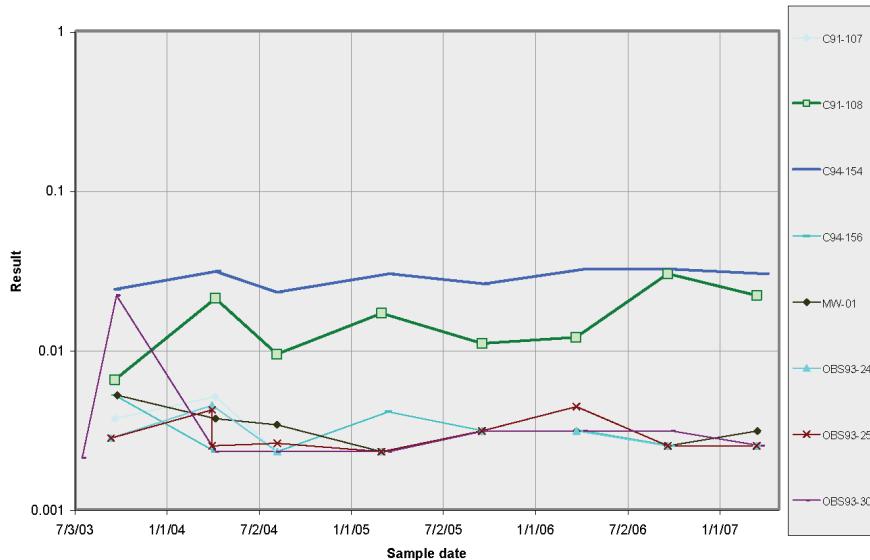

Figure 5-2: Arsenic Concentration in Ground Water from Background Wells

$$y = 0.000187x + 0.682743$$
$$R^2 = 0.613142$$
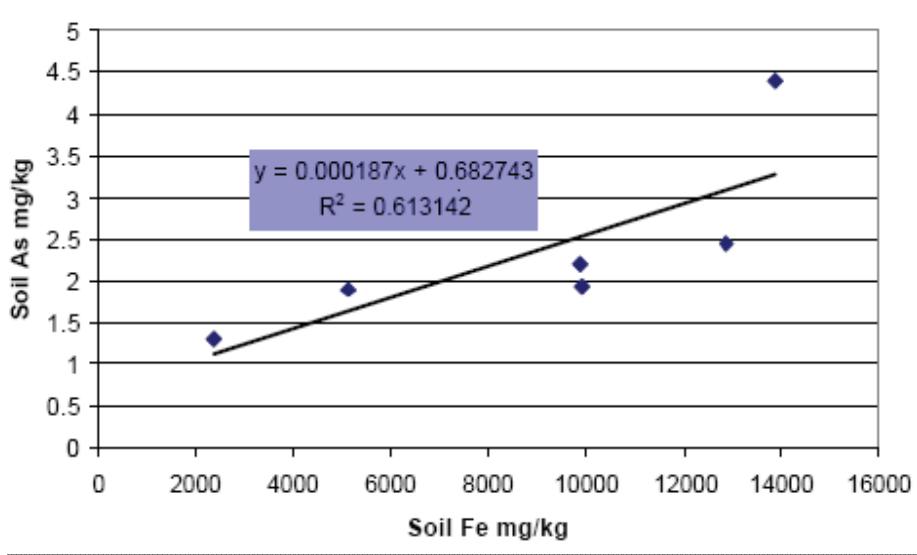
Figure 5-3: Soil Arsenic Concentration versus Soil Iron Concentration

5.1.3 Hydrocarbon Impacts

The terrace aquifer is impacted with hydrocarbon LNAPL, with LNAPL and dissolved phase hydrocarbon plumes extending south from the source area as shown in Figure 5-1. Hydrocarbon impacts have affected the groundwater geochemistry, creating reducing conditions and slightly increased pH but which is generally circumneutral; conditions that are amenable to arsenic mobilization. Remedies including pump and treat, monitored natural attenuation, and phytoremediation have served to stabilize the dissolved and product plumes at this site, and in some areas plume extent has decreased.

5.1.4 Arsenic Mobilization

Arsenic has appeared in affected groundwater at a maximum dissolved concentration of 0.170 mg/L, with other elevated concentrations generally detected around 0.020 to 0.100 mg/L, exceeding the MCL of 0.010 mg/L. Data analyses show that groundwater arsenic concentrations are correlated with dissolved iron (Figure 5-4).

Based on strong correlations of iron in soils with arsenic in soils (Figure 5-3), it is clear that in unaffected areas, arsenic is sorbed to the iron oxyhydroxides present in the aquifer. Biodegradation and lowered redox states in the hydrocarbon impacted parts of the terrace aquifer have led to reduction of ferric iron in the iron oxyhydroxides to the more soluble ferrous iron. The loss of sorption sites in the aquifer has resulted in release of sorbed arsenic to groundwater, and transport as a solute by groundwater.
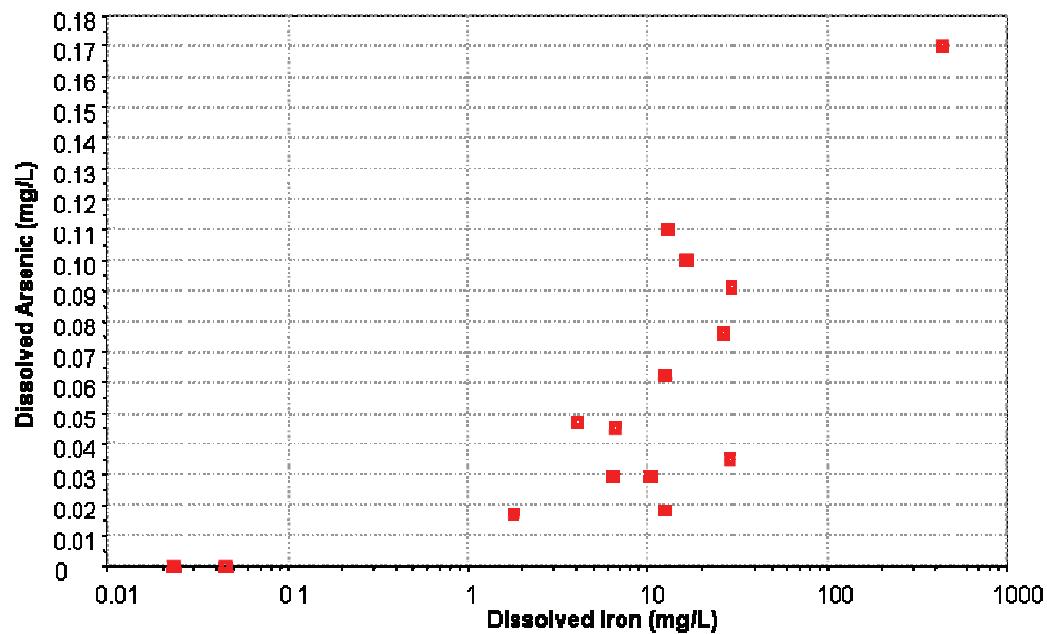
Figure 5-4: Dissolved Arsenic versus Dissolved Iron in Terrace Aquifer Water, Second Half of 2004

RCRA monitoring wells on-site along the southern extent of the hydrocarbon impacted area show elevated dissolved arsenic concentrations (approximately 0.05-0.1 mg/L) in groundwater (Figure 5-5). This is in part due to a co-mingled hydrocarbon plume from another petroleum company's source area in the south. The concentrations of arsenic in groundwater further downgradient, south and outside the hydrocarbon impact areas, (i.e. <0.005 mg/L BTEX), indicate that groundwater is at ambient aerobic conditions (DO >2.0 mg/L) and that the arsenic is not mobile in these perimeter monitoring areas.

Although the extent of this refinery's hydrocarbon and arsenic impacts extends further than many documented sites, the data demonstrate well the principles of arsenic attenuation presented in this document. With the hydrocarbon source area and plume controls actively in place since 1992, this site demonstrates arsenic stabilization around a petroleum hydrocarbon plume, with both plumes shrinking or at steady state.
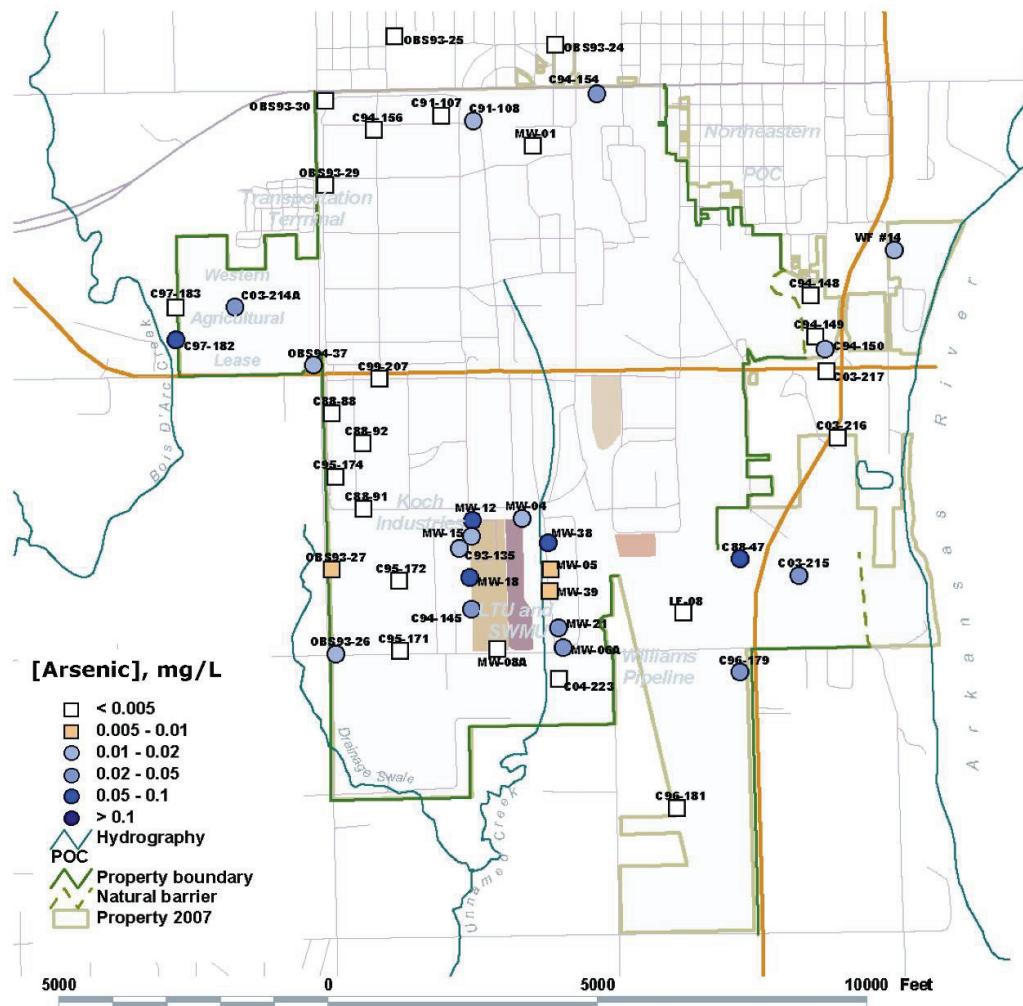
Figure 5-5: Average Total Arsenic Concentration in RCRA Monitoring Wells (2003-2007)

5.2   WEST TEXAS REFINERY

5.2.1   Site Description

The former refinery site is located on the south side of the Colorado River in West Texas, and is situated both inside and outside of the river valley, which is bordered by a steep bluff approximately 80 feet in height that separates the floodplain from an upper plateau (Figure 5-6). The former tank farm area, and subject of this case study, is located on the bluff, where depth to groundwater in the upper unit is less than 5 ftbgs in some areas and as deep as approximately 40 ftbgs in others. The Dockum Group of Triassic age underlies the site, where it outcrops along the Eastern Caprock Escarpment (Eifler et al. 1994; Johns 1989; McGowen et al. 1979). The Dockum Group is composed of fluvial, deltaic and lacustrine deposits of mudstone, siltstone, sandstone and conglomerate (Bradley and Kalaswad 2001; Johns 1989; Granata 1981). The Dockum Group at the site is composed of three major sandstone sequences, separated by mudstone/siltstone intervals (Figure 5-7). These sequences include, from the base of the Dockum:

the Santa Rosa Sandstone, the Lower Trujillo Sandstone (LTS), and the Upper Trujillo Sandstone (UTS) (Bunting 1994).

Aquifers are present at two separate intervals in the Trujillo Sandstone, each corresponding to the UTS and LTS. The uppermost aquifer is found in the UTS interval under the bluff and is the subject of this case study. The Colorado River Valley escarpment truncates this unit, forming an outcrop (Figure 5-7). Groundwater in the UTS aquifer flows radially towards the bluff edge from a potentiometric high near the center of the former tank farm, discharging in surface seeps (Figure 5-8). Groundwater occurs in the UTS under unconfined conditions. Recharge to this unit is by local precipitation and infiltration to the subsurface through fractures.

5.2.2 Ambient Conditions

Upgradient of the former tank farm area, redox conditions are generally oxidizing, and ORP measurements of groundwater are above zero. Within the hydrocarbon plume on the bluff, ORP measurements are greatly below zero (<-500 mV in some areas) indicating reducing conditions. Likewise, dissolved oxygen concentrations are above 7 mg/L upgradient of the site, while dissolved oxygen concentrations within the plume decrease to below 0.01 mg/L. The pH of groundwater within the plume has also increased, due to additional historic impacts.

5.2.3 Hydrocarbon Impacts

In the former tank farm area, approximately 36 impoundments and multiple storage tanks were removed. The impoundments contained by-products of refining processes that impacted groundwater in the UTS with high total dissolved solids (10,000-20,000 mg/L), high pH (9.5-10.5), and high concentrations of benzene (>3 mg/L), phenol (>80 mg/L), various methylated phenols, pentachlorophenol and arsenic (>3 mg/L). The extent of dissolved hydrocarbons and arsenic in groundwater is depicted in Figures 5-9 and 5-10. The plume is truncated in the direction of groundwater flow by the bluff edge itself. Impacted groundwater discharges as seepage from the bluff face. Groundwater collection trenches have been installed that effectively stopped the seepage and the associated risk.
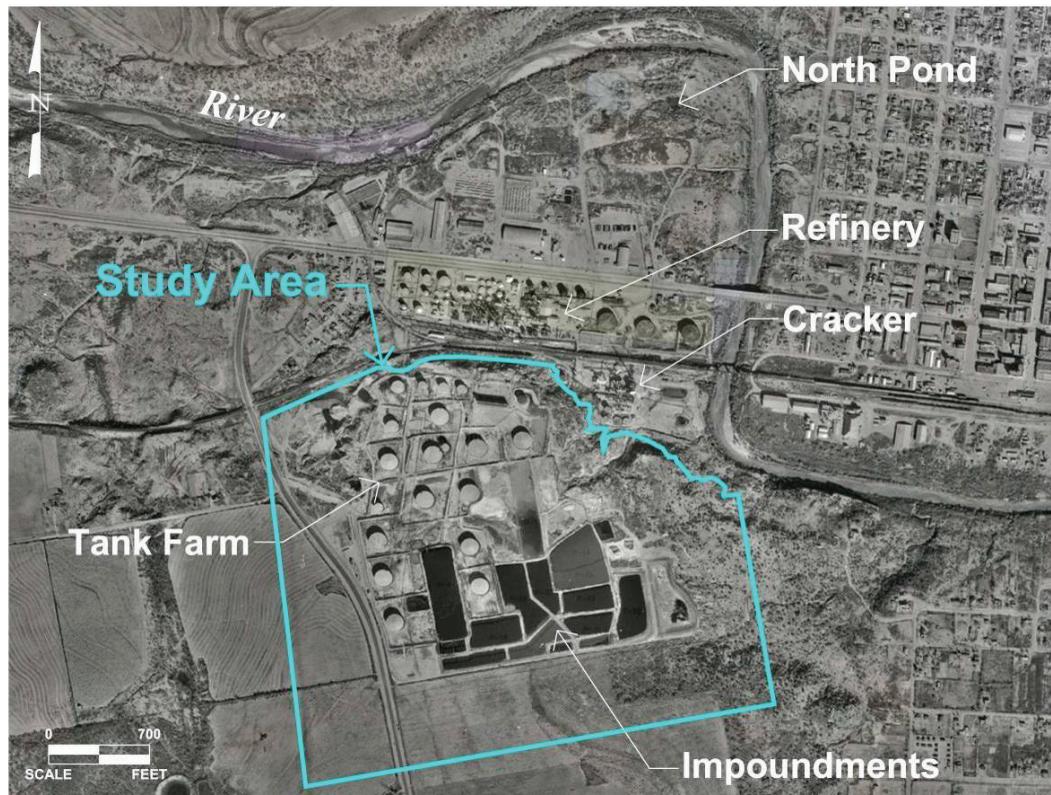
*Figure 5-6: Aerial Photo of Subject Refinery in West Texas When It Was Operating in the 1950's*
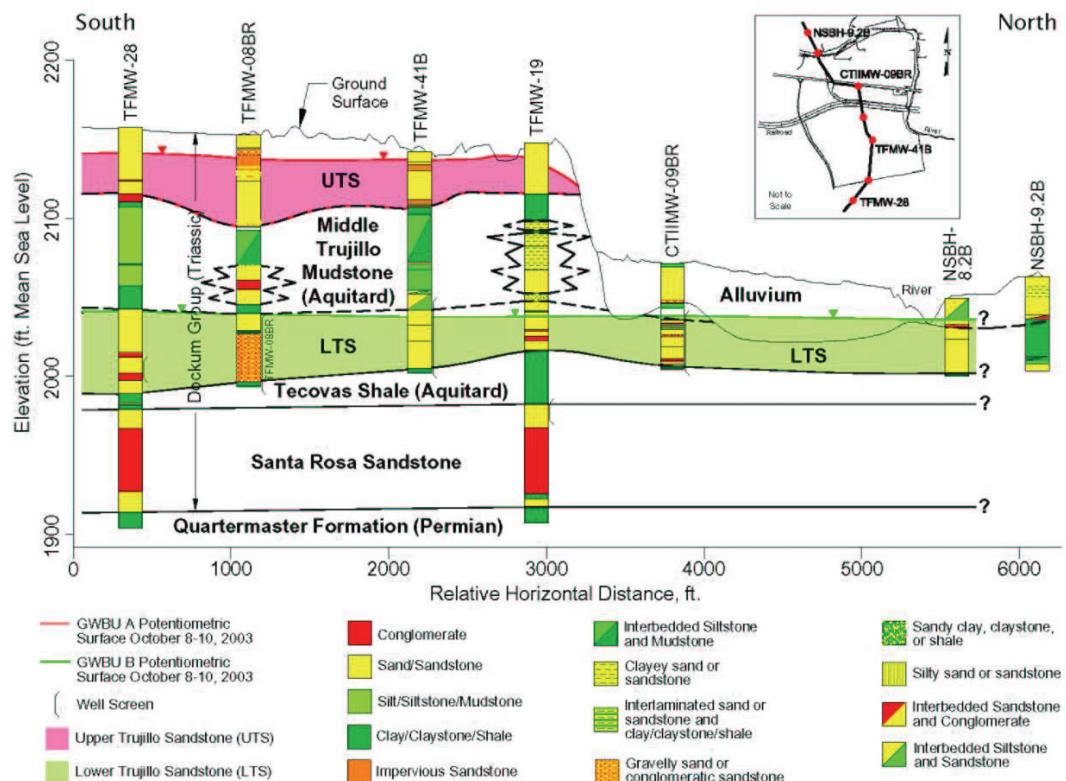
Figure 5-7: Cross-section of Upper Trujillo Sandstone (UTS) and Lower Trujillo Sandstone (LTS)
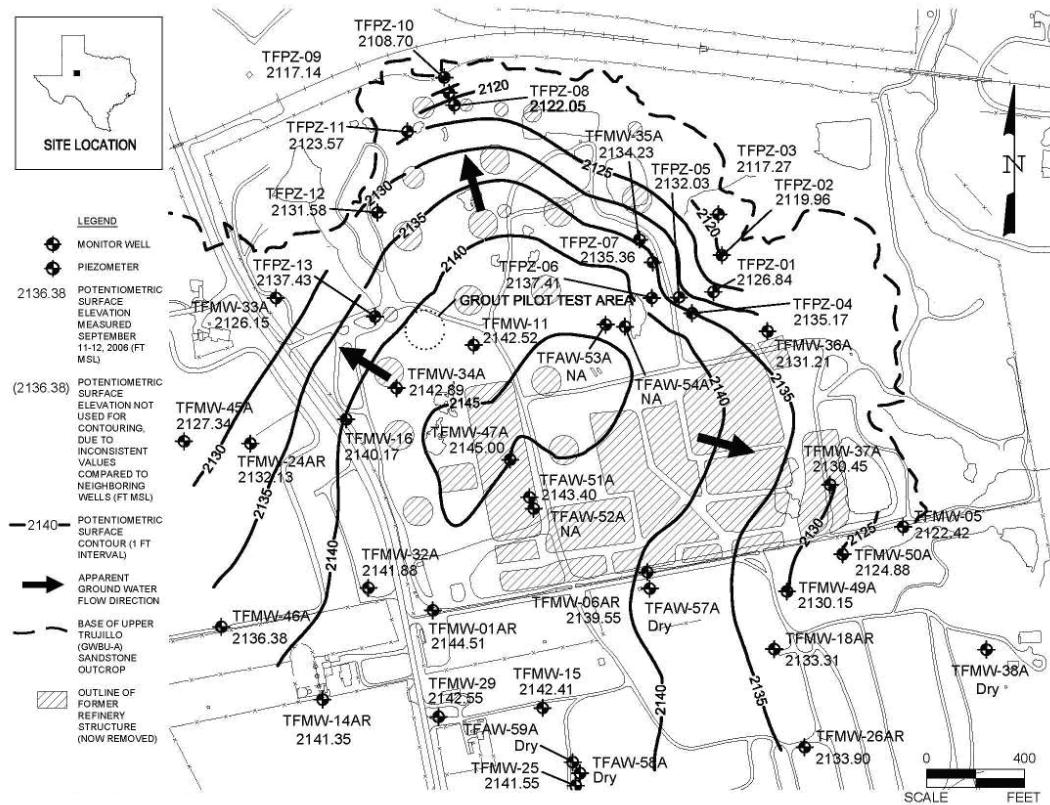
Figure 5-8: Potentiometric Surface Map of Ground Water in the UTS

5.2.4   *Arsenic Mobilization*

In the off site area upgradient of the former tank farm, sandstone coring shows the ambient geochemistry of the formation (Figure 5-11). The sandstone is orange to red in color, and analysis shows that the quartz grains are coated in ferric hydroxides that contain sorbed-phase arsenic. Groundwater samples collected in this area (e.g., TFMW-14A) do not contain arsenic above the detection limit of 0.01 mg/L (Figure 5-10). However, in the on site area, where groundwater is impacted with hydrocarbons, the reducing conditions resulting from biodegradation processes have mobilized both iron and arsenic. The sandstone cores in the hydrocarbon-impacted area are gray to black indicating primarily reducing conditions in the groundwater bearing zone. Arsenic and total organics in groundwater are strongly correlated (Figure 5-12). In general, when dissolved-phase organics are not detected in groundwater, neither is arsenic. Conversely, when dissolved-phase organic concentrations are high, so are dissolved-phase arsenic concentrations.

While there is geochemical evidence that biodegradation of hydrocarbon is occurring, hydrocarbon impacts extend to the edge of the unit, and hydrocarbons are detected in seeps from the bluff edge. Therefore, there is no downgradient transition zone in this scenario, where hydrocarbon concentration decreases and redox conditions become oxidizing (as in the conceptual models of Section 2.4); arsenic mobilization occurs to the edges of the unit.

The important points to consider in this case study are:

- Groundwater ingestion is not always the primary human exposure pathway at petroleum-impacted industrial sites with arsenic impacts. At this former West Texas refinery, the primary exposure pathway is sediment impact from surface seepage.

- Borings outside of the hydrocarbon-impacted zone can be beneficial in understanding the ambient, background geochemical conditions.

- Core coloring is a qualitative indicator of the presence of iron and manganese and the overall redox state of these metals.

- When iron is present in the oxidized ferric hydroxide form (under aerobic conditions), arsenic is sorbed and not dissolved in the groundwater.
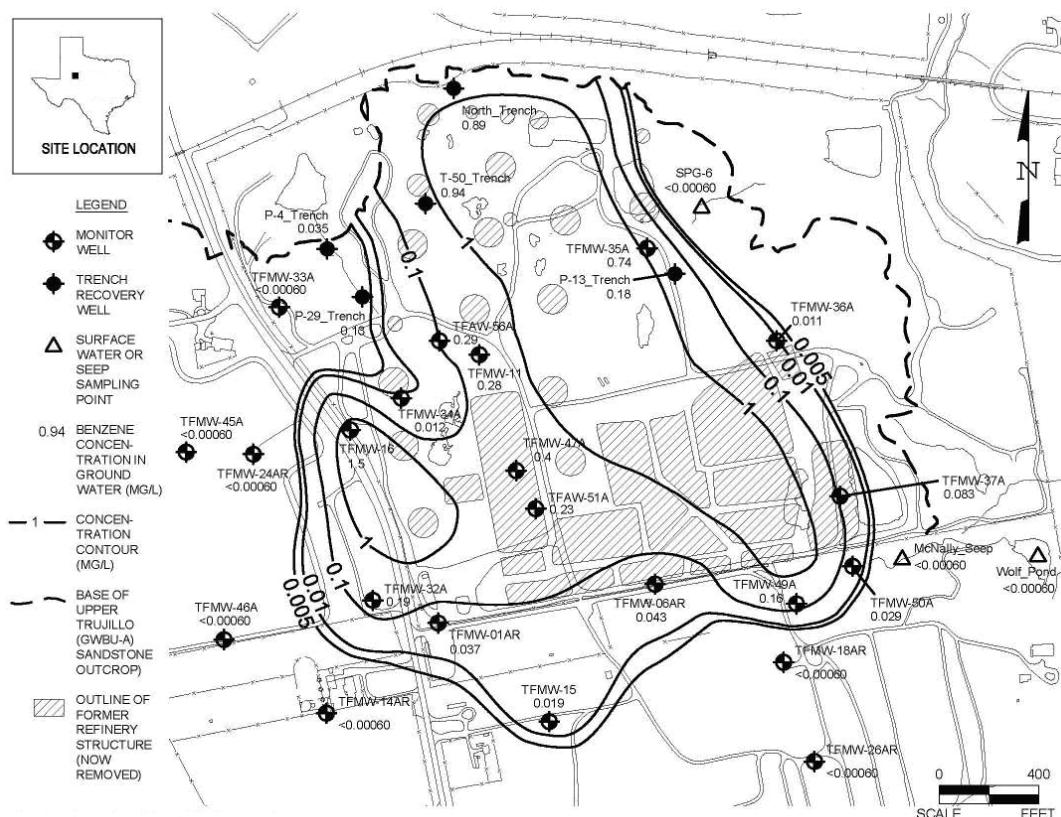
Figure 5-9: Concentration of Benzene in Ground Water of the UTS (The benzene plume is similar in size and shape to other dissolved-phase organics in ground water.)
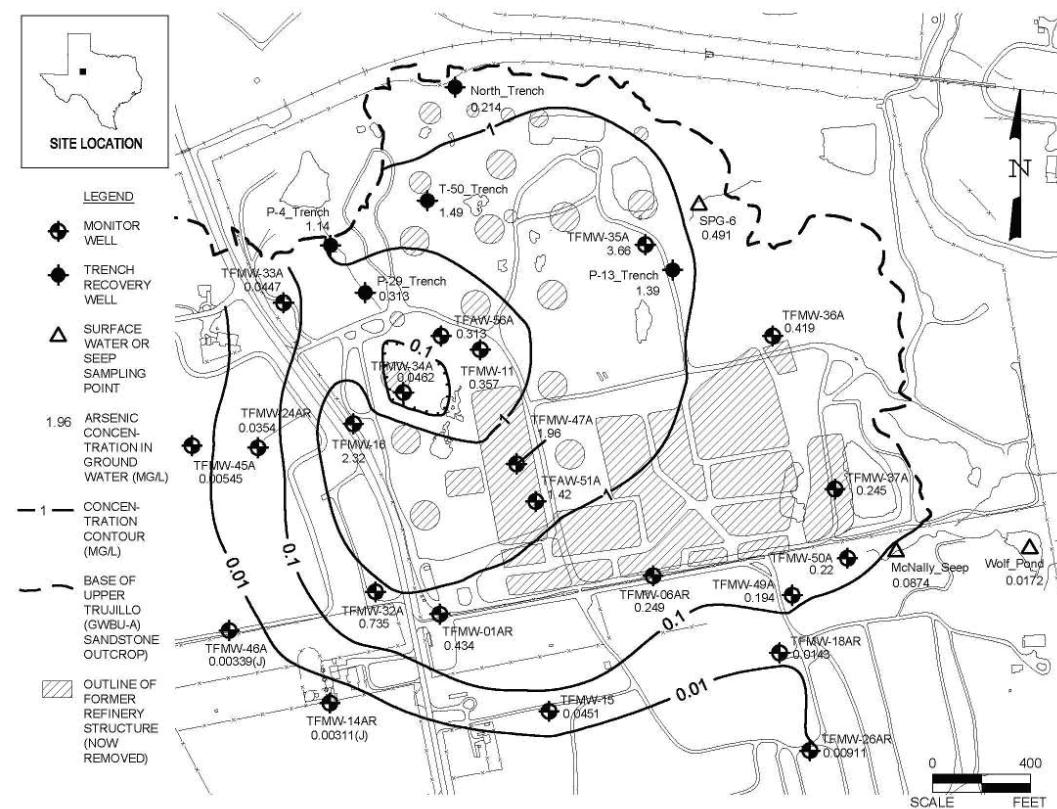
Figure 5-10: Concentration of Arsenic in Ground Water of the UTS

Figure 5-11: Sandstone Core From Outside of Petroleum-Impacted Zone Showing Orange to Red Coloring, Which Indicates High Iron Content and Oxidizing Ground Water Conditions

Arsenic vs. Total Organics
UTS Groundwater
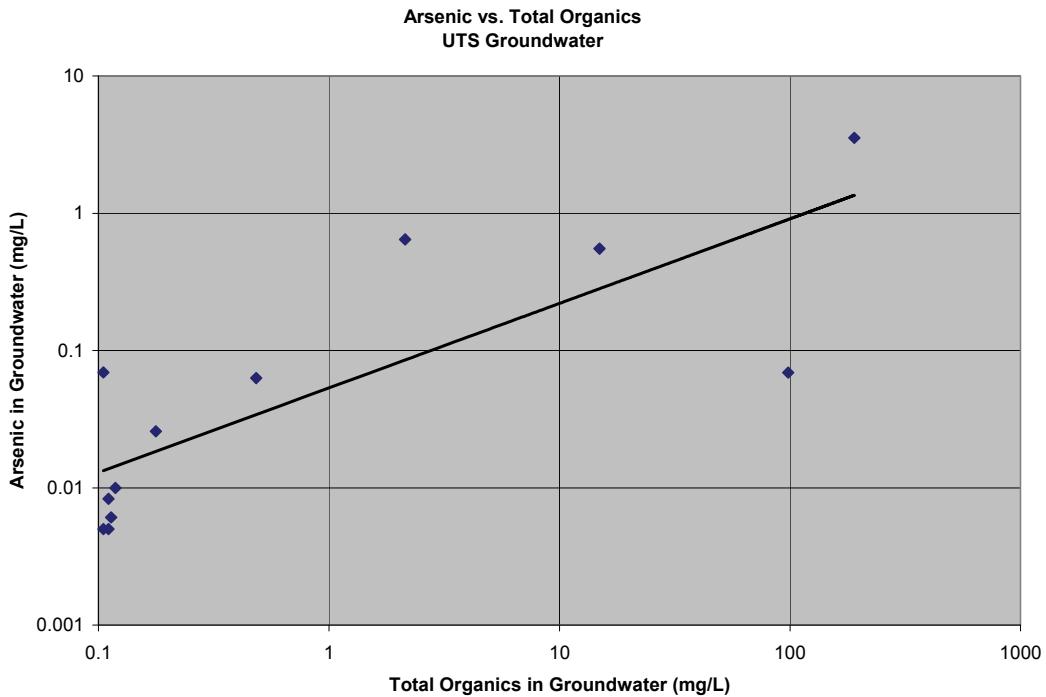
Figure 5-12: Graph of Arsenic versus Total Organic Concentrations in Ground Water at the West Texas Site

5.3   FORMER RESERVE PIT

5.3.1   Site Description and Geology

A former drill site reserve pit was constructed to receive drilling wastes from two wells located approximately 1.5 miles inland of the Beaufort Sea coastline on the North Slope of Alaska. This pit was approximately 220 feet by 250 feet in area and contained up to five feet of water. The elevation of the gravel pad surrounding the pit was approximately four feet above the surrounding tundra. The wells were plugged and abandoned in 1984 and 1992 and the reserve pit closed. Surface water samples collected during reserve pit closure studies contained elevated concentrations of some constituents, including arsenic. Visual inspection of areas around the pad and of sample locations included observation of iron staining, biogenic sheen, salt damage, drilling mud, and stressed tundra. Figure 5-13 is an aerial photo of the former reserve pit (before closure and corrective actions), and includes the sample locations discussed here.

Figure 5-13: Aerial View of Reserve Pit with Surrounding Sample Locations

5.3.2   Ambient Conditions

Tundra surrounds the former pad site, including scattered surface water features, thermokarst cracks, and vegetation. Ambient conditions (represented by sample location M2) include pH of 8.10, 11.17 mg/L dissolved oxygen (at 9.21 degrees Celsius) and a field ORP of 173.5 mV. Dissolved arsenic concentration at sample location M2 was below detection (1.00 ug/L) in 2004 (total arsenic was 1.38 ug/L). Ambient dissolved iron concentrations were 0.201 mg/L and total iron concentration was 0.401 mg/L. Some of the water quality exceedances and vegetation stress were attributed to naturally-occurring conditions at the site (e.g. wind, increased sediment load, natural North Slope water chemistry).

5.3.3   Hydrocarbon Impacts

Evidence of impact from former site activities at the pad was observed during site assessments. Stressed vegetation, iron staining, and increased biogenic sheen have been observed at certain locations surrounding the site. Potential hydrocarbon impact was identified primarily by the presence of sheen on surface water surrounding the former pit. Hydrocarbon compounds such as diesel range organics (DRO), benzene, toluene, ethylbenzene, xylenes, and total aromatic hydrocarbon were not detected or not detected above comparison standards in any of the surface water samples. Although the muds used to drill the wells were water-based, low-concentrations of diesel (generally less than 500 mg/kg DRO) were detected in the pit mud during pit excavation and site cleanup.

5.3.4 *Arsenic Mobilization*

Arsenic had been detected in surface water near the reserve pit and gravel pad during initial site assessment in 1996 and 2001. In 2004 nine of fourteen water samples from locations surrounding the reserve pit contained arsenic concentrations as high as 96.7 ug/L, well above the applicable marine water quality criterion. Arsenic concentrations were also elevated at similar concentrations in the reserve pit water. Arsenic concentrations at background location M2 did not exceed the criterion.

Further investigation in 2005 included collection and analysis of tundra samples, gravel pad borings, and drilling mud material. There was no statistically significant difference between arsenic concentrations in drilling mud (8-12 mg/kg), the gravel pad material (8-11 mg/kg), and background tundra (7-13 mg/kg).

5.3.5 *Remediation Actions and Arsenic Stabilization*

Corrective actions (removal of waste, placement of a reserve pit cap, and removal of the gravel pad) at the former reserve pit were completed in 2006. Surface water samples collected in 2006 did not contain arsenic concentrations above the applicable water quality criterion. The highest dissolved arsenic concentration measured in 2006 was 3.82 ug/L at location M9.

Results of soil and drilling waste analysis from 2005 indicate that there are likely multiple sources of arsenic at and around the site. The elevated dissolved arsenic concentrations in surface water in 2004 do not strongly correlate with geochemical parameters such as ORP, pH or dissolved iron. Within two years, dissolved arsenic concentrations had decreased dramatically, to below the applicable surface water quality criterion.

In 2006, as concentrations of arsenic decreased, evidence of attenuation became more apparent. A correlation between iron and arsenic was observed in 2006 water sample analyses (Figure 5-14) as well as a correlation between dissolved iron concentration and pH (Figure 5-15). In samples where pH is significantly below the background value of 8.24, elevated dissolved iron and arsenic are also detected. As conditions surrounding the former pad area return to ambient geochemistry, dissolved arsenic concentrations have decreased.

5.4 *FORMER FUEL STORAGE FACILITY*

Elevated concentrations of naturally occurring arsenic in groundwater at hydrocarbon release sites are commonly assumed to be the result of reducing redox conditions associated with the presence of hydrocarbons. However, this case study indicates that naturally occurring organic matter at certain sites can sometimes be the primary reason for reducing redox conditions and elevated concentrations of arsenic. Data presented here are a subset of data that were shared with regulators to demonstrate that arsenic concentrations were naturally elevated.
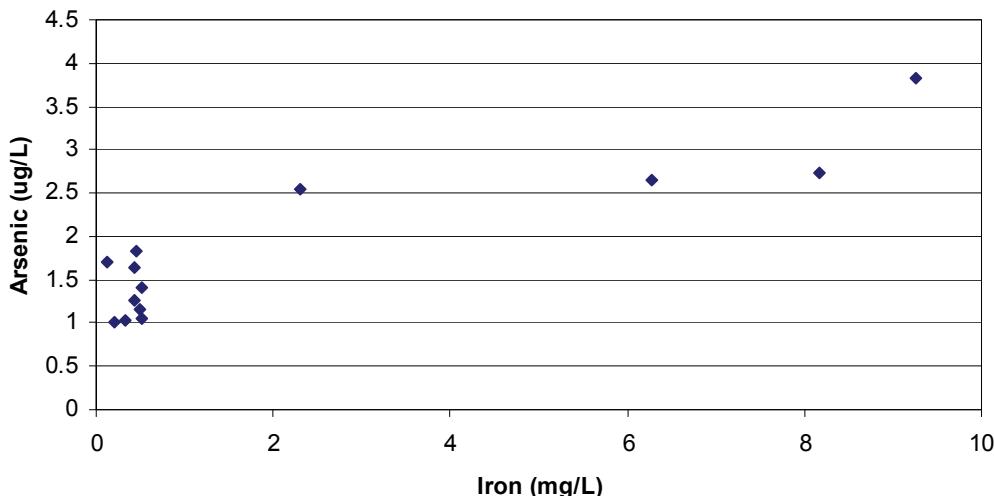
*Figure 5-14: Plot of Arsenic Concentration versus Iron Concentration in Water Samples from 2006*
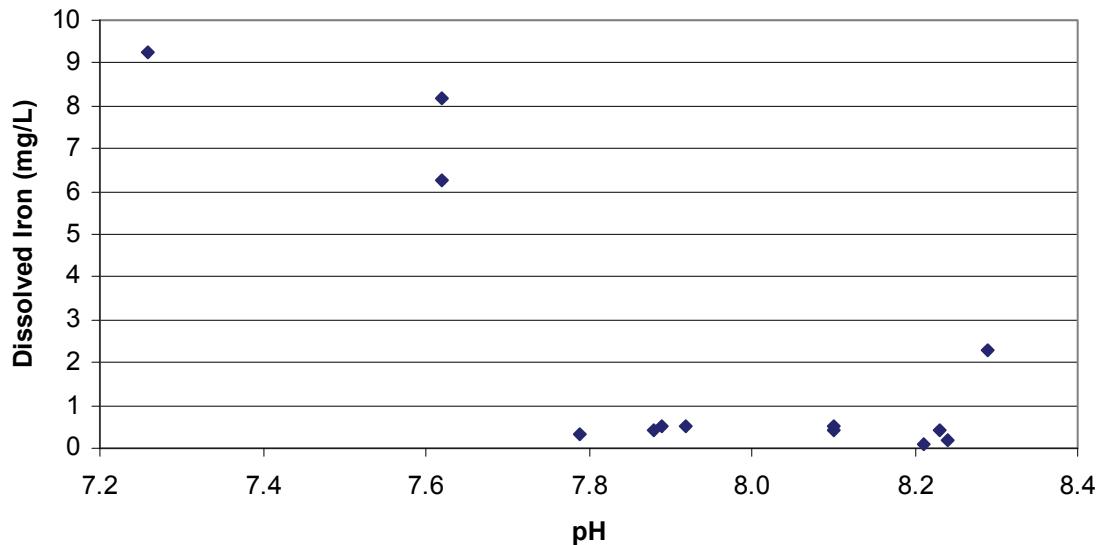
Figure 5-15: Plot of Dissolved Iron versus pH in Water Samples from 2006
(background pH is 8.24)

5.4.1   *Site Description*

Soil and groundwater at a former fuel storage facility have locally been impacted with fuel hydrocarbons during several decades of operation. Remedial actions performed at the site included removal of free product from the groundwater and targeted excavation of impacted soil. The site is approximately 25 acres and consists of surficial fill material underlain by native soil. Native fine- to medium-grained sand interbedded with layers of sand and silt forms an unconfined hydrostratigraphic unit, which is designated as the site-wide aquifer where saturated. Water samples have been collected from 30 groundwater monitoring

wells screened in the site-wide aquifer. Borehole logs reveal the presence of an organic clay unit at various locations.

5.4.2   *Arsenic Mobilization*

Hydrous ferric oxides are common constituents of aquifer solids. These oxides, among other substances, are known to adsorb arsenic and can therefore accumulate naturally-occurring arsenic. Reduced redox conditions leading to iron reduction can cause dissolution of such ferric oxides, which can result in mobilization of the associated arsenic. At this site, dissolved arsenic concentrations in groundwater varied between 35 ug/L and below detection before remediation activities had occurred. Figure 5-16 shows dissolved arsenic concentrations in groundwater versus the redox potential (Eh) for samples with greater than 5 ug/L dissolved arsenic. Consistent with the anticipated behavior of arsenic, elevated dissolved arsenic concentrations at this site were generally associated with reduced redox conditions. The highest arsenic concentrations (> 10 ug/L) occurred under negative Eh conditions that would be expected in an iron reducing environment. Note that all arsenic is naturally occurring and that the hydrocarbon products did not introduce any arsenic into the environment.

5.4.3   *Hydrocarbon Impacts*

Total Petroleum Hydrocarbon (TPH) measurements in groundwater and soil samples indicate that the presence and extent of hydrocarbon impact varied strongly across the site. Groundwater TPH and arsenic concentrations are depicted in Figure 5-17. Although elevated arsenic concentrations are associated with low redox potentials, there is no clear relationship between TPH and arsenic concentrations at this site. Figure 5-18 compares site groundwater TPH concentrations to Eh before remedial action had occurred. The majority of the wells show TPH concentrations below 1 ppm, with many samples non-detect (indicating the detection limit in Figure 5-16). Groundwater TPH concentrations above 1 ppm (mg/L) correlate with a reduced groundwater environment. However, it appears that reduced conditions occurred even where TPH concentrations were low or below detection, suggesting that other carbon sources created reducing redox conditions across the site. The naturally occurring organic clay unit observed at the site is believed to be primarily responsible for creating reducing conditions and to be the main cause for mobilizing naturally occurring arsenic.

After soil excavation of a target area, groundwater arsenic concentrations and redox conditions remained consistent with historical values in three nearby compliance wells, while TPH concentrations were predominantly non-detect (data not shown). This observation supports the conclusion that elevated arsenic and depressed redox conditions are a result of natural causes and are not primarily caused by the presence of fuel hydrocarbons.
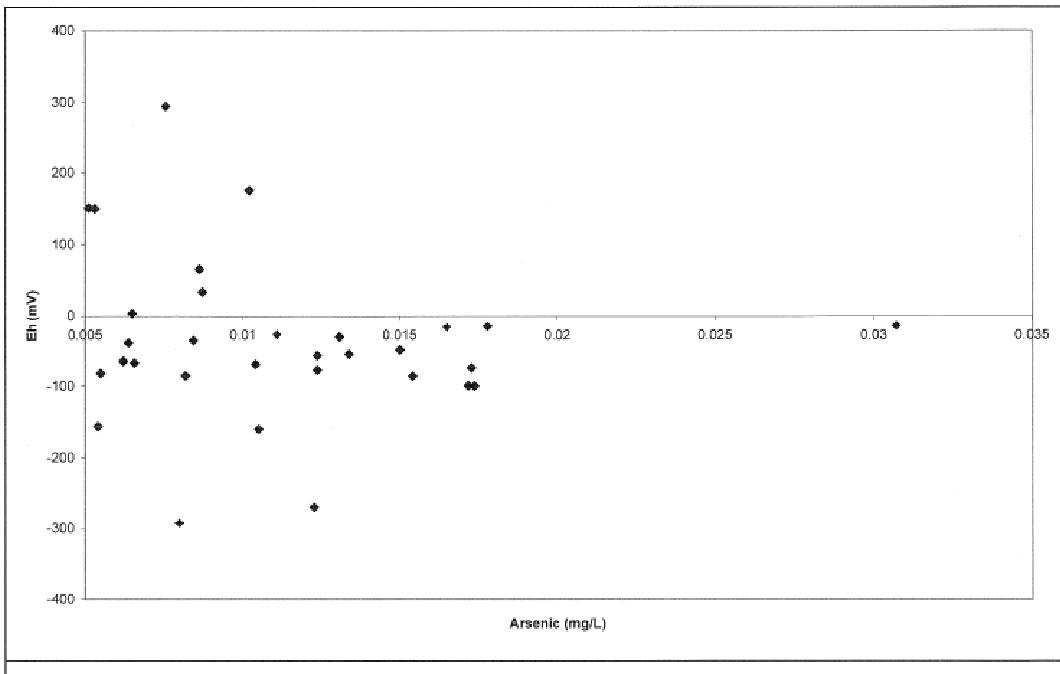
Figure 5-16: Eh versus Dissolved Arsenic Concentrations at the Former Fuel Storage Site
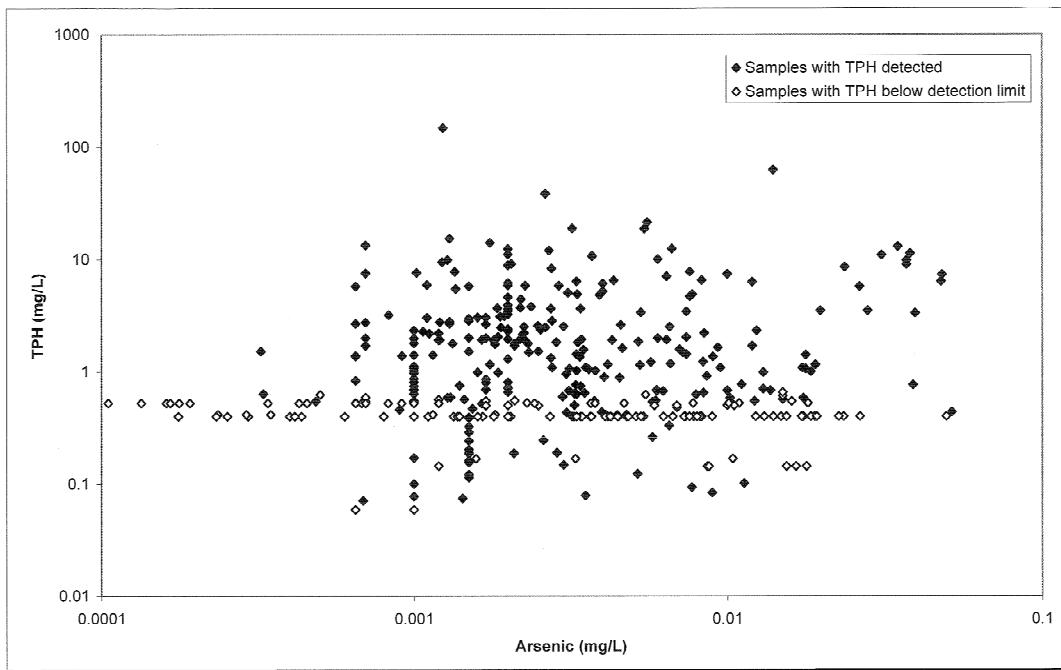

*Figure 5-17: TPH Concentrations versus Arsenic Concentrations at the Former Fuel Storage Site*
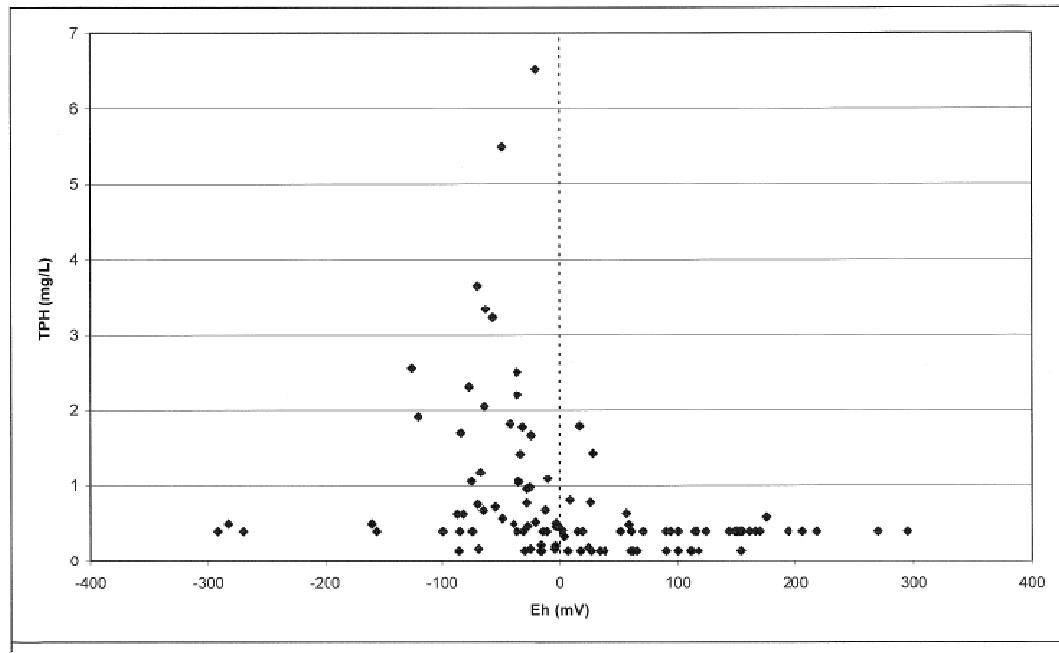
Figure 5-18: TPH Concentrations versus Eh at the Former Fuel Storage Site

6.0.   *CONCLUSIONS*

The new arsenic MCL of 0.01 mg/L has led to additional evaluation of arsenic in groundwater at petroleum hydrocarbon impacted sites. It is important to understand the mobilization, transport and attenuation mechanisms of naturally-occurring arsenic at these sites. This document was developed to facilitate the understanding and management of the fate and transport of arsenic in groundwater at sites impacted with petroleum hydrocarbons, when the arsenic is present at or above concentrations of concern. This document reviews the occurrence of arsenic in the subsurface and the major biogeochemical factors affecting arsenic mobility in groundwater. A general conceptual model of arsenic behavior and attenuation at petroleum-impacted sites is provided to guide assessment and site characterization strategies and techniques for the development of a SSCM.

An understanding of the ambient geochemistry at a site is crucial for assessment of mobilization of naturally-occurring arsenic and attenuation at petroleum hydrocarbon sites. The background Eh and pH in a site aquifer, along with existing site mineralogy, will determine the upgradient and ultimate downgradient arsenic mobility surrounding a hydrocarbon plume. The development of a SSCM should include an investigation of background (ambient) conditions. This not only allows a measure of the geochemical changes resulting from a hydrocarbon release, but also defines the downgradient and future arsenic attenuation as the hydrocarbon is attenuated.

The hydrogeological conditions most likely to be impacted by petroleum hydrocarbons (as discussed in this document) are aerobic, shallow, unconfined aquifers with a pH of 4 - 8. Such aquifers may have low soil organics. The release of a petroleum hydrocarbon perturbs these conditions. There are three primary factors that affect the fate and transport of arsenic in groundwater: the redox environment, pH, and adsorption/precipitation of arsenic onto aquifer solids. These factors are controlled by the hydrogeology and the mineralogy. All three of these factors may be affected by the presence of hydrocarbons.

The primary impact of petroleum hydrocarbons on arsenic mobility is that it changes the redox environment due to the biodegradation of petroleum hydrocarbons via microbial metabolism of oxygen or other terminal electron acceptors. The biodegradation of hydrocarbon also perturbs the pH and adsorption potential of the aquifer. This perturbation of the existing geochemistry may result in the mobilization of arsenic at concentrations above the ambient level, if arsenic bearing minerals are present in the aquifer, or if an arsenic source has been emplaced due to prior human activity. These changes to the ambient arsenic geochemistry, and its mobility, will persist within the impacted area, until the petroleum hydrocarbons are attenuated; or outside the hydrocarbon impacted area until ambient conditions are reestablished. Once ambient conditions return, the arsenic will revert to its pre-existing stable geochemistry, which may be above or below the new lower MCL of 0.01 mg/L for arsenic.

The general conceptual model of ambient arsenic stability, a perturbation to ambient geochemistry by a petroleum hydrocarbon release, resulting mobilization of naturally-occurring arsenic, the attenuation of the hydrocarbon leading to a downgradient geochemical transition zone, and return to ambient geochemistry and arsenic stability, can be applied for the development of a SSCM. The process of SSCM development should follow an iterative approach that investigates ambient arsenic concentrations and geochemistry, overall site conditions, hydrocarbon and arsenic plume delineation and redox processes, operable attenuation processes, and potential exposure pathways, receptors and risks.

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