

Attenuation of Naturally Occurring Arsenic at Petroleum Hydrocarbon-Impacted Sites

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ABSTRACT: 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 has heightened public and regulatory awareness of dissolved arsenic in groundwater.

Arsenic occurrence at petroleum-impacted sites 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, petroleum impacts will not cause arsenic impacts to groundwater. Arsenic is not a major contaminant in petroleum hydrocarbons;
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. If the background level of arsenic naturally exceeds the new MCL, then the MCL is unachievable as an attenuation or remediation goal;
3. The introduction of petroleum hydrocarbons (or other degradable organics) may cause a perturbation to the existing geochemistry, resulting in the mobilization of existing naturally occurring arsenic at concentrations above the ambient level;
4. The perturbation of the ambient arsenic geochemistry (and related arsenic mobilization) will persist until the soluble hydrocarbons are attenuated; and
5. Once the hydrocarbons are attenuated, the arsenic will revert to its pre-existing stable geochemistry, which may be above or below the arsenic drinking water MCL of 0.010 mg/L, it depends on the background geochemistry and background arsenic concentrations.

Proper management of a petroleum-impacted site at which arsenic has become mobilized requires an understanding of the site-specific ambient conditions and how petroleum impacts affect arsenic chemistry and mobility in the subsurface. This understanding can be refined by developing a site-specific conceptual model incorporating background and site data to guide further investigation and remedial actions concerning arsenic.

INTRODUCTION

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 has heightened public and regulatory awareness of dissolved arsenic in groundwater.

While petroleum hydrocarbons, themselves, are not a source of arsenic, naturally-occurring arsenic may be mobilized into shallow groundwater by inputs of biodegradable organic carbon, including petroleum hydrocarbons. “Naturally-occurring arsenic” refers to arsenic that is present in the solid phase prior to impacts by degradable organic carbon, including petroleum hydrocarbons. Arsenic may be present as specific minerals, as an amorphous phase, or adsorbed onto iron oxyhydroxides and other soil constituents, either as a natural trace metal in native rocks and soils or from human activity such as agriculture or waste disposal. Hydrocarbons can mobilize arsenic by creating reduced conditions.

When a petroleum release occurs, the more soluble hydrocarbon fractions can dissolve into groundwater, stimulating biological activity. Bacteria degrade the dissolved hydrocarbons and consume the available terminal electron acceptors (TEAs), creating 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.

When the petroleum hydrocarbons are attenuated, the natural attenuation of arsenic will occur as the aquifer is restored to its original aerobic conditions. Arsenite is re-oxidized 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. The natural attenuation of arsenic is coupled to the attenuation of hydrocarbon plumes.

NATURALLY OCCURRING ARSENIC

One of the fundamental principles of arsenic mobilization and attenuation at hydrocarbon-impacted sites is that arsenic has to be present in the soil prior to the release of the hydrocarbons.

As shown in Table 1, crude oils and therefore, petroleum products, are not a source of arsenic. Arsenic can, however, be present at a site due to either natural site mineralogy or geochemistry, or due to anthropogenic activity.

TABLE 1. 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.

Arsenic is 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 [FeS₂]). 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.

There are broad areas of the United States where arsenic in groundwater already exceeds the old MCL (50 µg/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 due to naturally occurring arsenic minerals.

Arsenic also has many industrial uses. 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 mining and mineral processing sites. It is also found as a constituent of municipal landfills and leachate.

Industrial and agricultural uses of arsenic can result in both point source and non-point source contamination. Of greatest interest are non-point sources of arsenic. Typically, these uses involve application of industrial chemicals (e.g., pesticides) over wide areas resulting in diffuse, low-level arsenic contamination. Nonpoint source arsenic has the greatest potential to overlap with areas of petroleum impact.

PRINCIPLES OF ARSENIC MOBILITY

The mobility of arsenic is controlled by redox conditions (Eh), by the pH and by the presence of metal oxyhydroxides that can adsorb and bind arsenic. With 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 (AsO₄⁻³), 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.

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. Site characterization should 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. The ambient dissolved arsenic concentrations are a function of the site mineralogy, hydrogeology and redox conditions.

Figure 1 (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, aquifers that are in contact with the

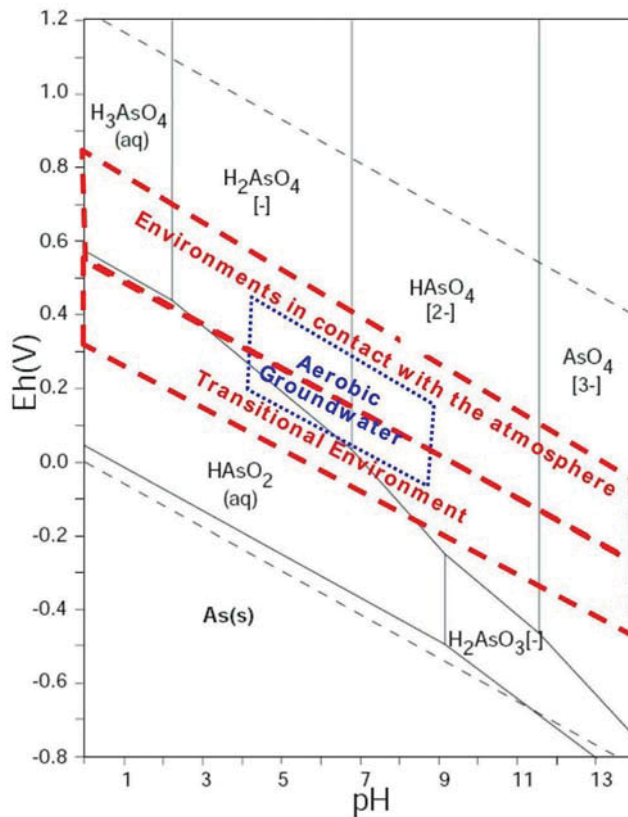


FIGURE 1. Arsenic speciation in groundwater regimes.

atmosphere (unconfined conditions) will be mostly aerobic, and arsenic will be predominately in the pentavalent (As+5; arsenate) valence state. The solubility of arsenic under aerobic conditions is determined by the pH and mineralogy, particularly the presence of iron oxy hydroxides (FeO(OH)).

The primary forms of inorganic arsenic in both oxidizing and reducing groundwater are oxyanions. Oxyanions of arsenic readily sorb to solid phase metal oxyhydroxides such as goethite. (Wilkin, 2003) Adsorption of arsenic at mineral surfaces occurs as a result of a set of chemical reactions generally referred to as sorption.

The most important reactive surface phases for arsenic attenuation in many soils 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

IMPACT OF PETROLEUM HYDROCARBONS ON ARSENIC MOBILITY

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 groundwater system. The progression is, in decreasing order of redox potential, aerobic respiration, followed in sequence by nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and finally, methanogenesis. 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 levels 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. 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 shows that the relative areas of metabolic activity vary in the direction of groundwater flow. The most reduced conditions are found in the source area. The aquifer conditions become less reducing in the direction of groundwater flow. Aerobic conditions generally bound the plume in both directions.

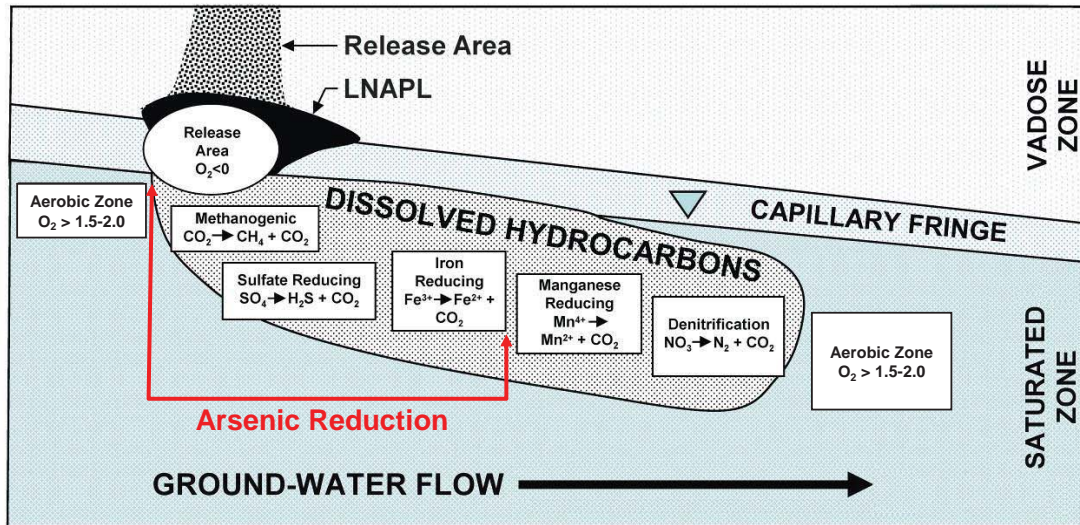


FIGURE 2. Conceptual model of biodegradation of a petroleum-hydrocarbon plume.

If microbial activity is high and there is sufficient dissolved hydrocarbon, the aquifer environment will progress rapidly through these different anaerobic metabolic conditions. Once the microbial conditions reach iron reduction or below, arsenic will be reduced and mobilized.

ATTENUATION OF HYDROCARBONS AND ARSENIC

Migration of the dissolved hydrocarbons and the resulting microbial activity creates overlapping hydrocarbon and arsenic plumes. As pictured in Figure 3, the hydrocarbon impact reduced the redox. Arsenic is initially mobilized by the change in redox. The hydrocarbons attenuate due to biological activity. The arsenic plume commonly extends beyond the hydrocarbon plume, with arsenic remaining above background concentrations until aquifer redox conditions return to aerobic. This downgradient portion of the plume is a transition zone where dissolved arsenic concentrations decrease as the aquifer becomes more oxidizing, the arsenic is reabsorbed and 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. 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.

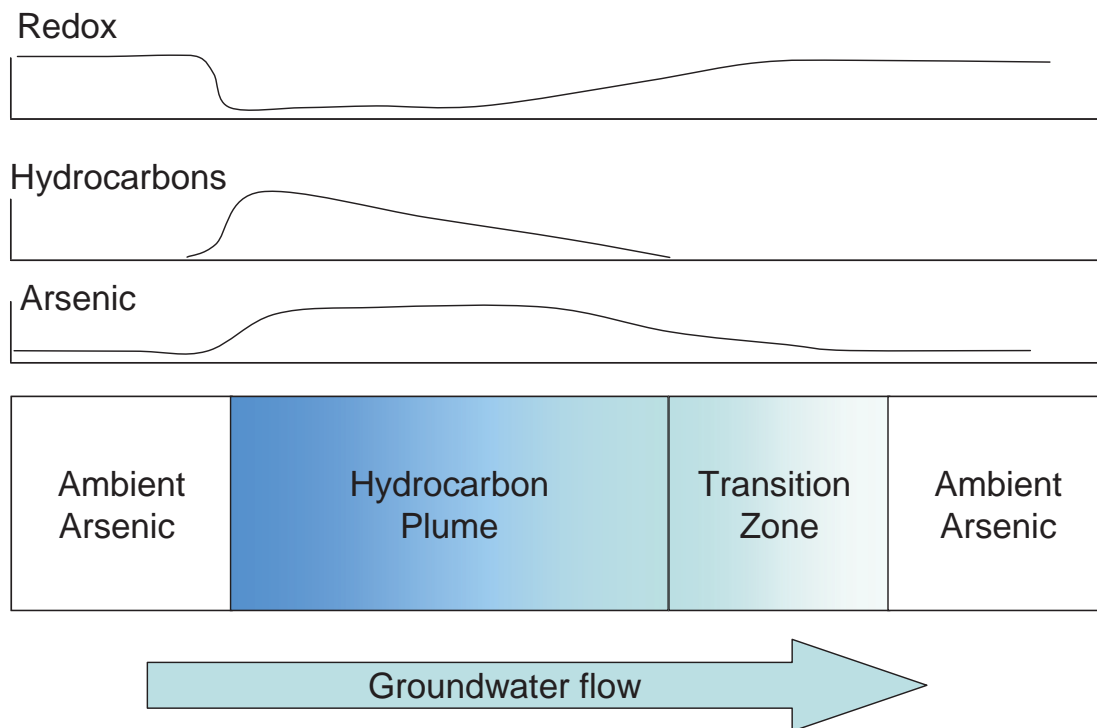


FIGURE 3. Change in hydrocarbons, arsenic, and redox with distance.

CASE STUDIES

Four case studies illustrate the basic principles of arsenic mobilization and attenuation discussed above.

1. **An Operating 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, as the hydrocarbon plume migrates down gradient, aerobic conditions are re-established and the arsenic is re-oxidized and re-adsorbed onto the soil matrix when DO is observed to be ~ 1.5 to 2 mg/L.

2. **A Former 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. The arsenic concentrations correlate to dissolved iron.
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 naturally occurring reduced conditions that exist at the site.

CONCLUSIONS

Five basic principles 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.

NOTE

This work is a combined effort of the American Petroleum Institute (API), The Petroleum Environmental Research Forum (PERF) and ERM. The API will be publishing a document, "API Arsenic Manual: Attenuation of Naturally Occurring Arsenic at Petroleum Impacted Sites" in 2010.

RECOMMENDATIONS

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

1. The general site geology and hydrogeology of the groundwater bearing units (GWBU) that have 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 has been 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.

REFERENCES

- Boulding, Russell and Ginn. 2004. Practical Handbook of Soil, Vadose Zone, and Ground-Water Contamination: Assessment, Prevention, and Remediation. CRC Press, Figure 3.3, pp. 98.
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- Wilkin, R.T., D. Wallschlaeger, and R.G. Ford. 2003. Speciation of arsenic in sulfidic waters. *Geochemical Transactions*. Vol. 4, pp. 1-7.



Arsenic Occurrence at Petroleum Hydrocarbon Impacted Sites

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Context for Talk

- API Manual: “Attenuation of Naturally-occurring Arsenic at Petroleum Impacted Sites”
 - Cooperative effort of ERM, API and PERF
- Purposes of Manual
 - 1) Identify potential sources of arsenic at petroleum impacted sites,
 - arsenic contained in native rock and soils, and
 - arsenic resulting from anthropogenic sources,
 - **petroleum hydrocarbons are not a source of arsenic;**
 - 3) Present the fundamentals of arsenic biogeochemistry; and
 - 4) Provide validated tools for the assessment of arsenic at petroleum impacted sites and its management through natural attenuation.



Problem Statement

- In January, 2006 the United States Environmental Protection Agency (USEPA) lowered the maximum contaminant level (MCL) for dissolved arsenic in groundwater from 50 µg/L to 10 µg/L due to long-term chronic health effects of low levels of arsenic in drinking water.
- Are petroleum hydrocarbon releases a source of arsenic in groundwater?



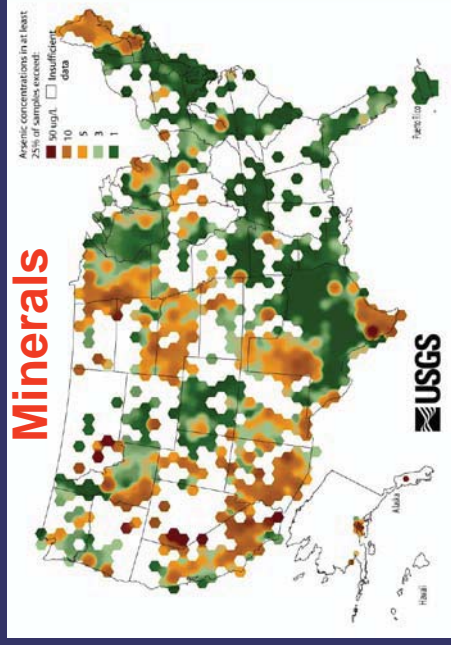
Five Principles of Arsenic Mobilization at Petroleum Impacted Sites

- Arsenic mobilization can only occur if arsenic is present as a soil mineral or from its use on site.
- Sites with sources of arsenic have a stable arsenic geochemistry controlled by Eh, pH and minerals able to adsorb, complex, or precipitate arsenic (e.g. Fe^{+3}).
- Petroleum hydrocarbons (or other degradable organics) perturb the existing geochemistry, mobilizing arsenic above the ambient level, by lowering the redox state through anaerobic biological activity.
- This perturbation of the ambient arsenic geochemistry persists until the soluble hydrocarbons are attenuated.
- 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 depending on the background geochemistry.

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Sources of Arsenic



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

Use/Application	Form of Arsenic Used
Fruit Trees, Nut Trees	Arsenates (AsO_4^{3-})
Golf Courses	Monosodium Methyl Arsenate (MSMA)
Animal Feed (Chickens)	Arsenates
Rat Poison Manufacturing	Arsenates
Flame Retarding Plastics Manufacturing	Arsenates
Phosphate Fertilizer Manufacturing	Arsenates
Wood Treating (Historic)	Arsenates
Animal Dips (Sheep and cows for lice and hoof diseases)	Arsenates
Pigments	Copper Arsenate, Arsenic Sulfides
Semiconductors	Arsenic Metal
Herbicide Application	Arsenate
Defoliant	Arsenic trioxide

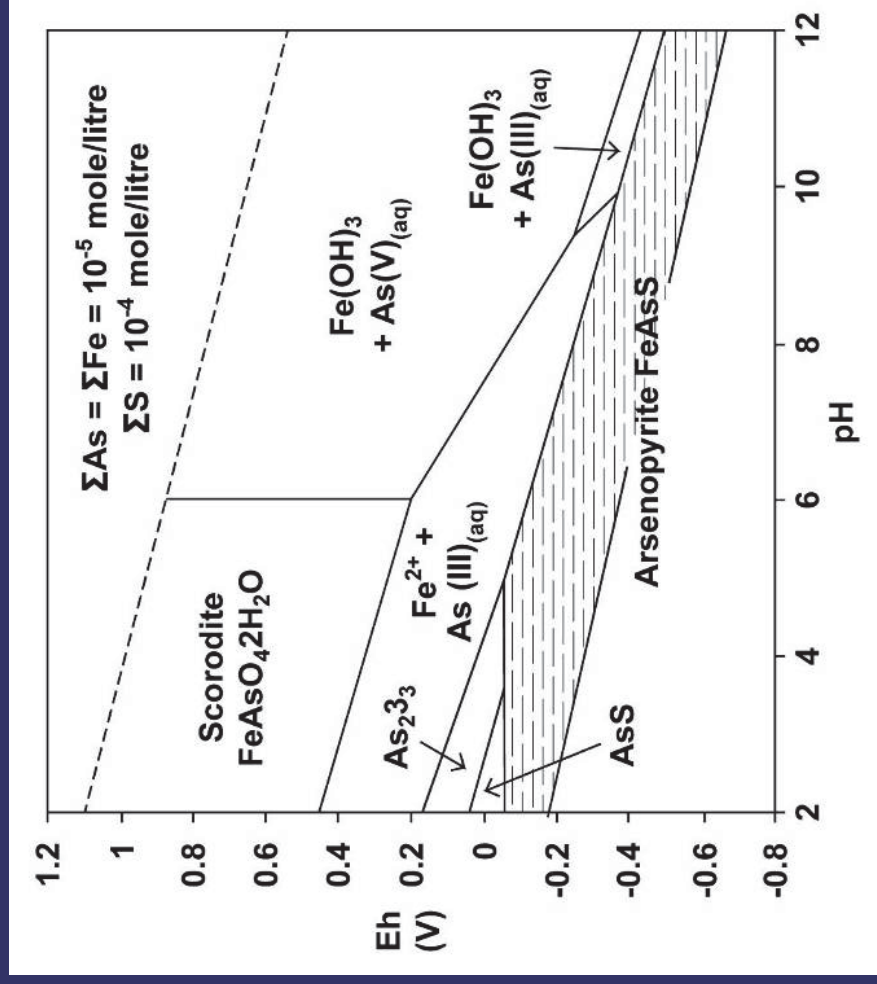
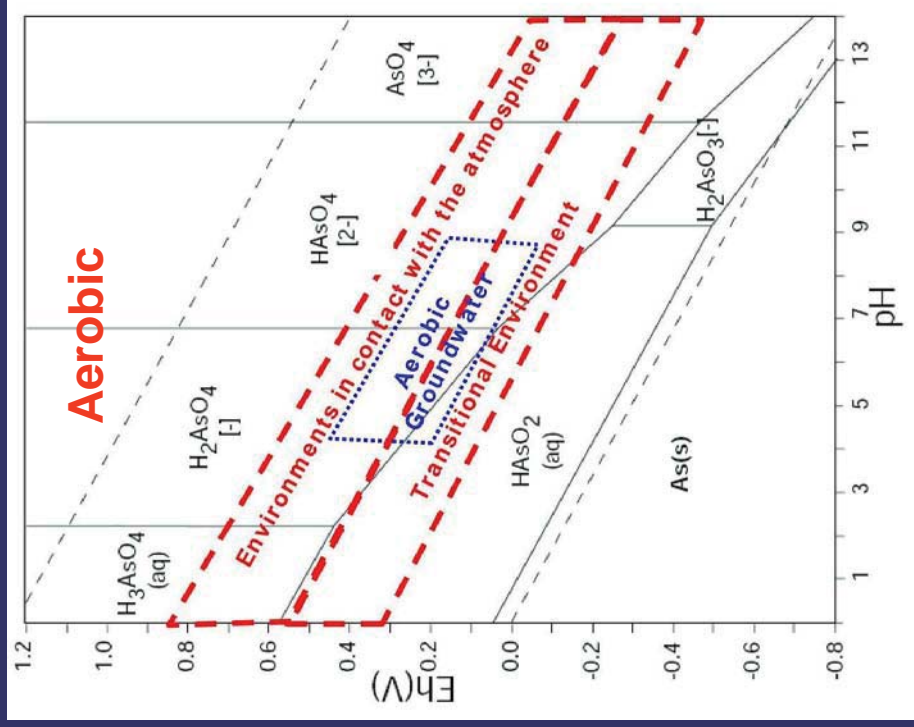
Source: www.wikipedia.com, 2009)



Mobilization

- Mobilization of arsenic from natural or anthropogenic sources can occur in the presence of petroleum hydrocarbons
- Perturbation of the ambient conditions increases arsenic solubility as a result of changes to redox conditions and pH

Arsenic in Groundwater



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Geochemical influences on arsenic solubility

- **Minerals and dissolved-phase constituents affect the solubility of arsenic**
 - Formation of complexes
 - Stability of metal-arsenic phases
 - Sorption of arsenic onto/into solid phases
- **Background or ambient conditions**
 - Are metal-arsenic phases present?
 - Are sorptive phases present?



Arsenic Solubility vs. Valence

Table 2-1: Relative Solubilities of Arsenite and Arsenate

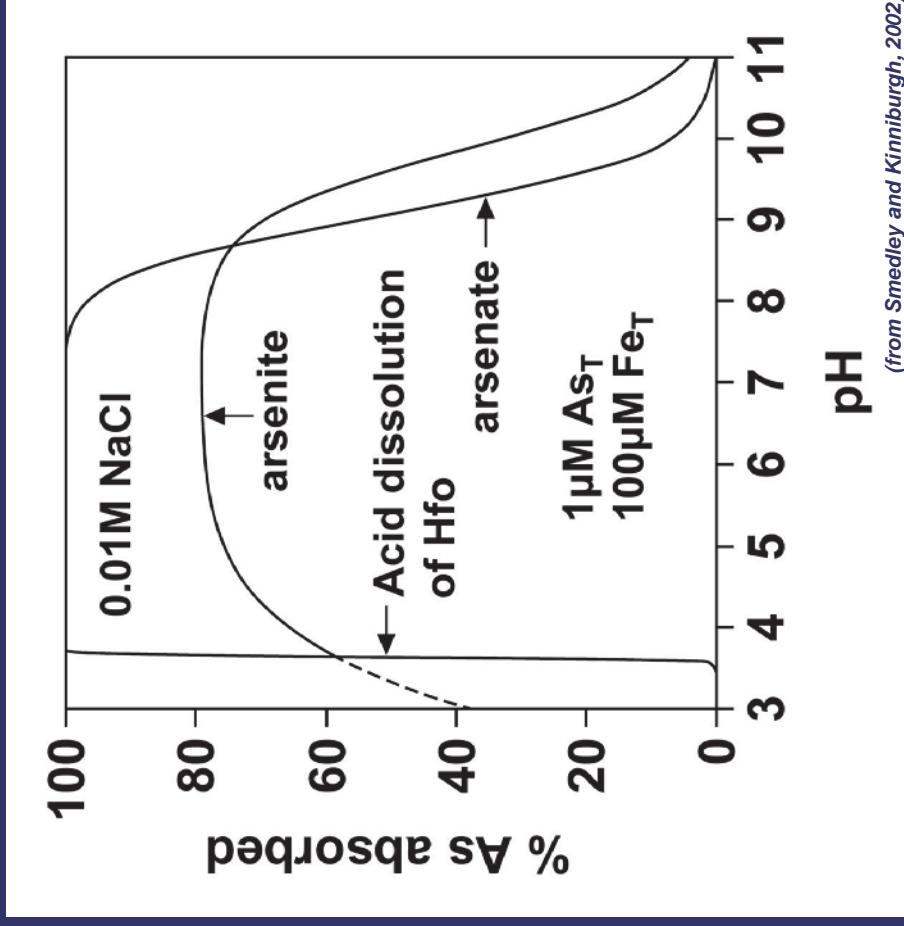
Cation Added	Initial As Conc.	Final Concentration	
		Arsenate	Arsenite
Ferric Iron	350 µg/L	6 µg/L	140 µg/L
Ferric Iron	300 µg/L	6 µg/L	138 µg/L
Aluminum (Alum)	350 µg/L	74 µg/L	263 µg/L
Aluminum (Alum)	300 µg/L	30 µg/L	249 µg/L
Aluminum (Alumina)	100 µg/L	4 µg/L	~100 µg/L
Calcium	2 mg/L	20 µg/L	160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

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



Absorption of Arsenate and Arsenite on Hydrous Ferric Oxide



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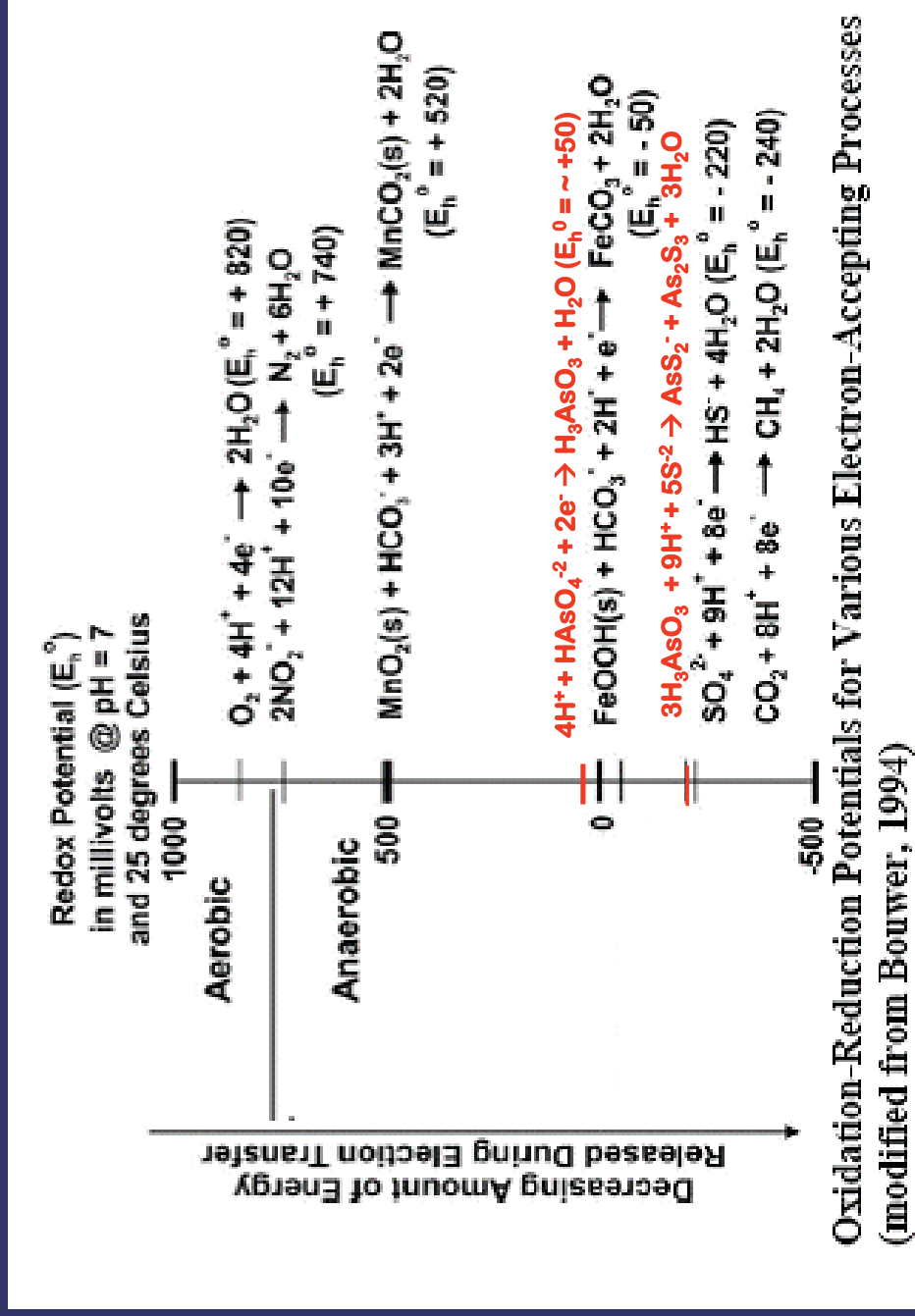


Natural Attenuation of Arsenic

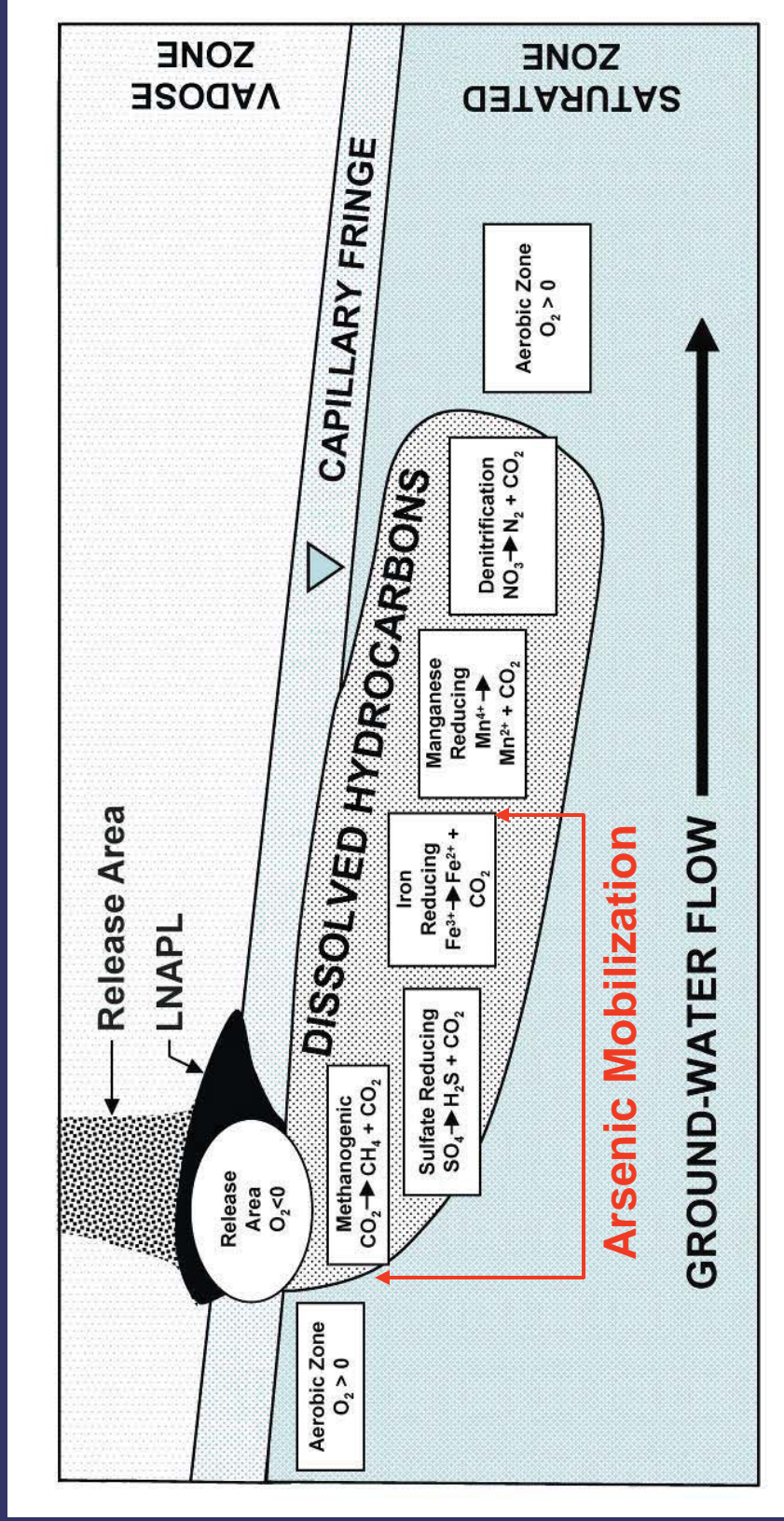
- **As conditions in groundwater become more reducing, arsenic is mobilized**
- **Attenuation of petroleum impacts by biodegradation allows ambient conditions to return**
- **As ambient conditions return, redox state of arsenic is reversible**



Arsenic Redox versus Biodegradation



Petroleum Hydrocarbon Degradation



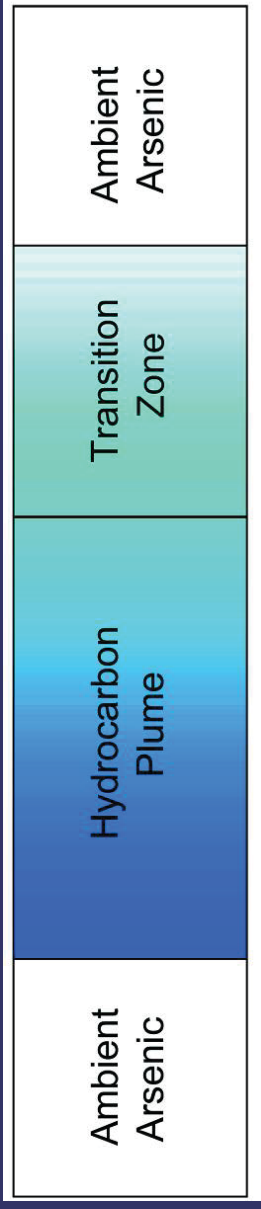
The Arsenic Plume Conceptual Model

- A plume of arsenic mobilized by petroleum hydrocarbon impacts will mimic the hydrocarbon plume
- Stages of arsenic mobilization can be related to the hydrocarbon plume conditions (expanding, stable, or shrinking)

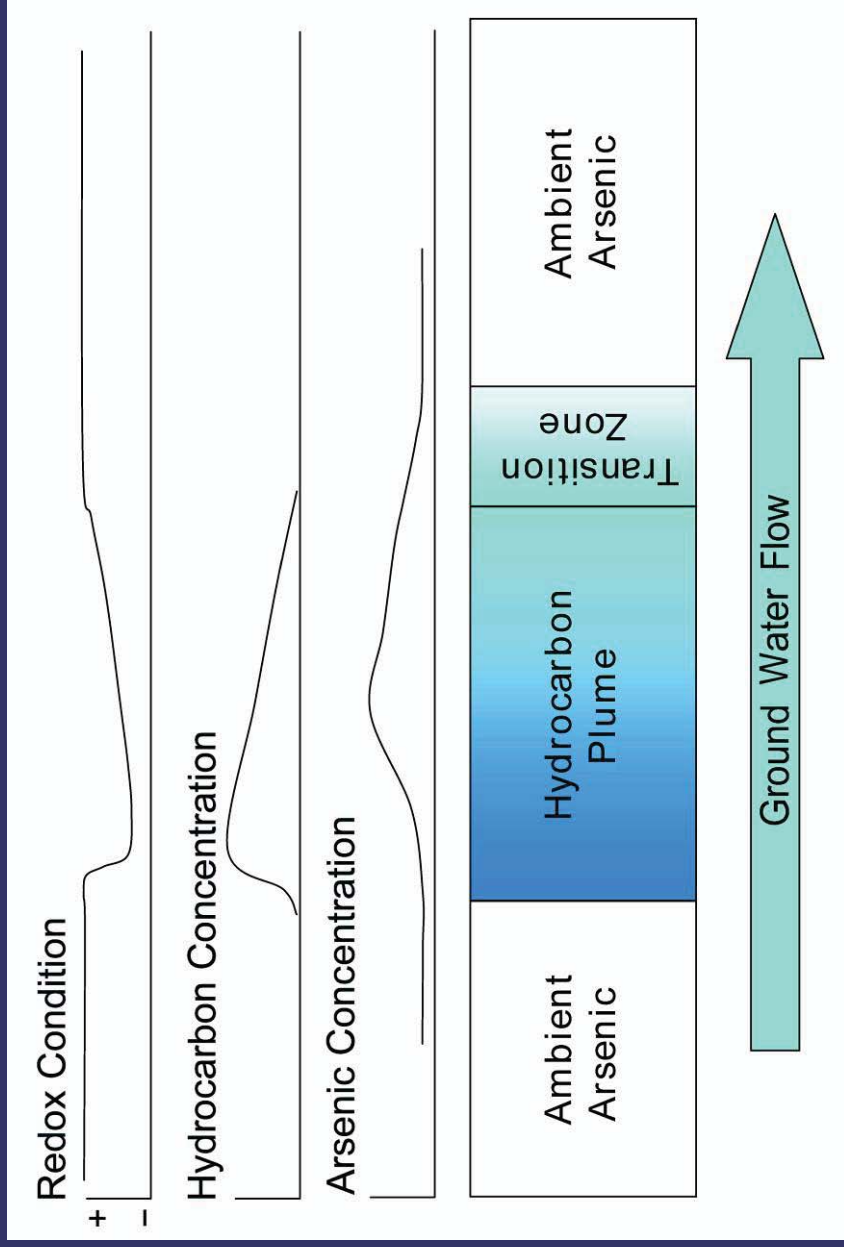


Stages of Arsenic Mobilization

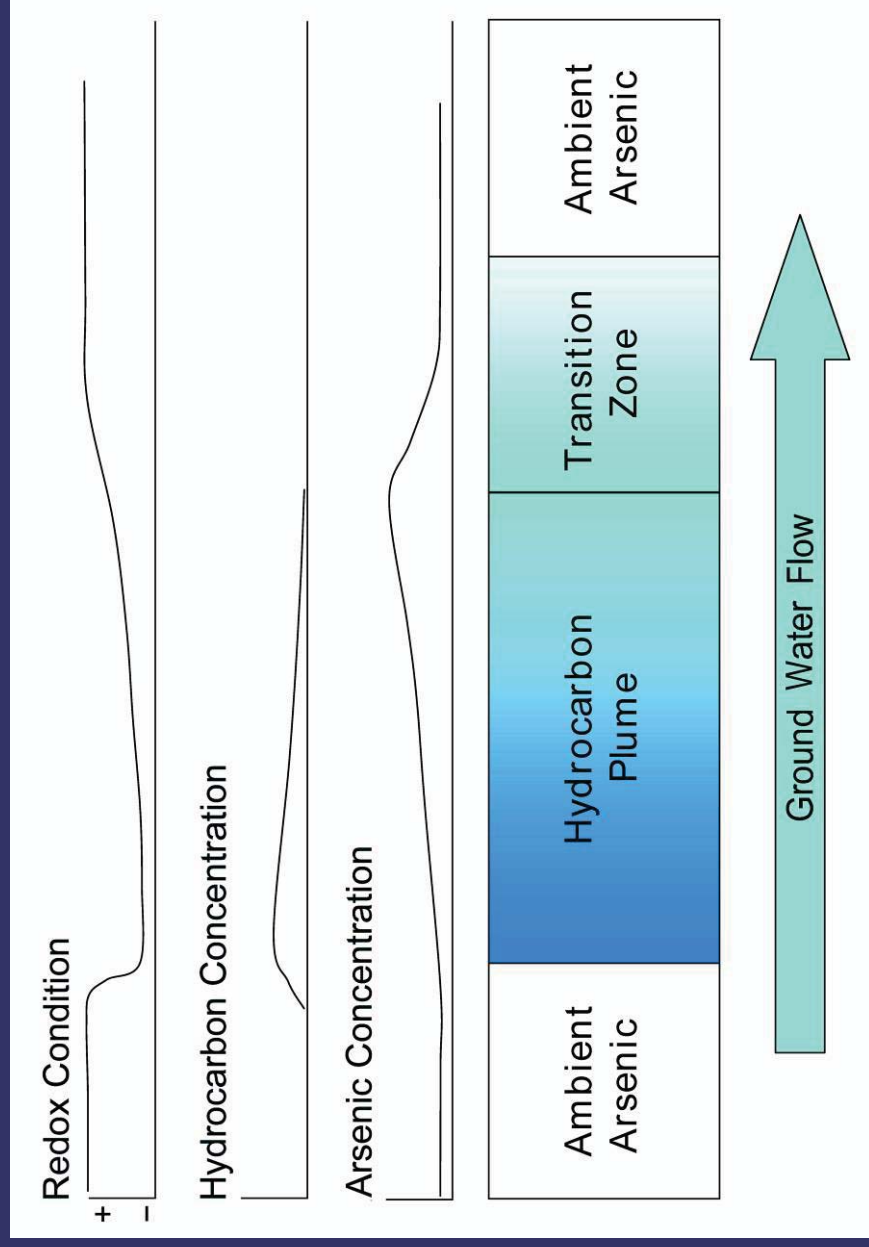
- **Expanding plume**
 - Influx of HC >> Attenuation
- **Steady State**
 - Influx of HC = Attenuation
- **Shrinking plume**
 - Influx of HC << Attenuation



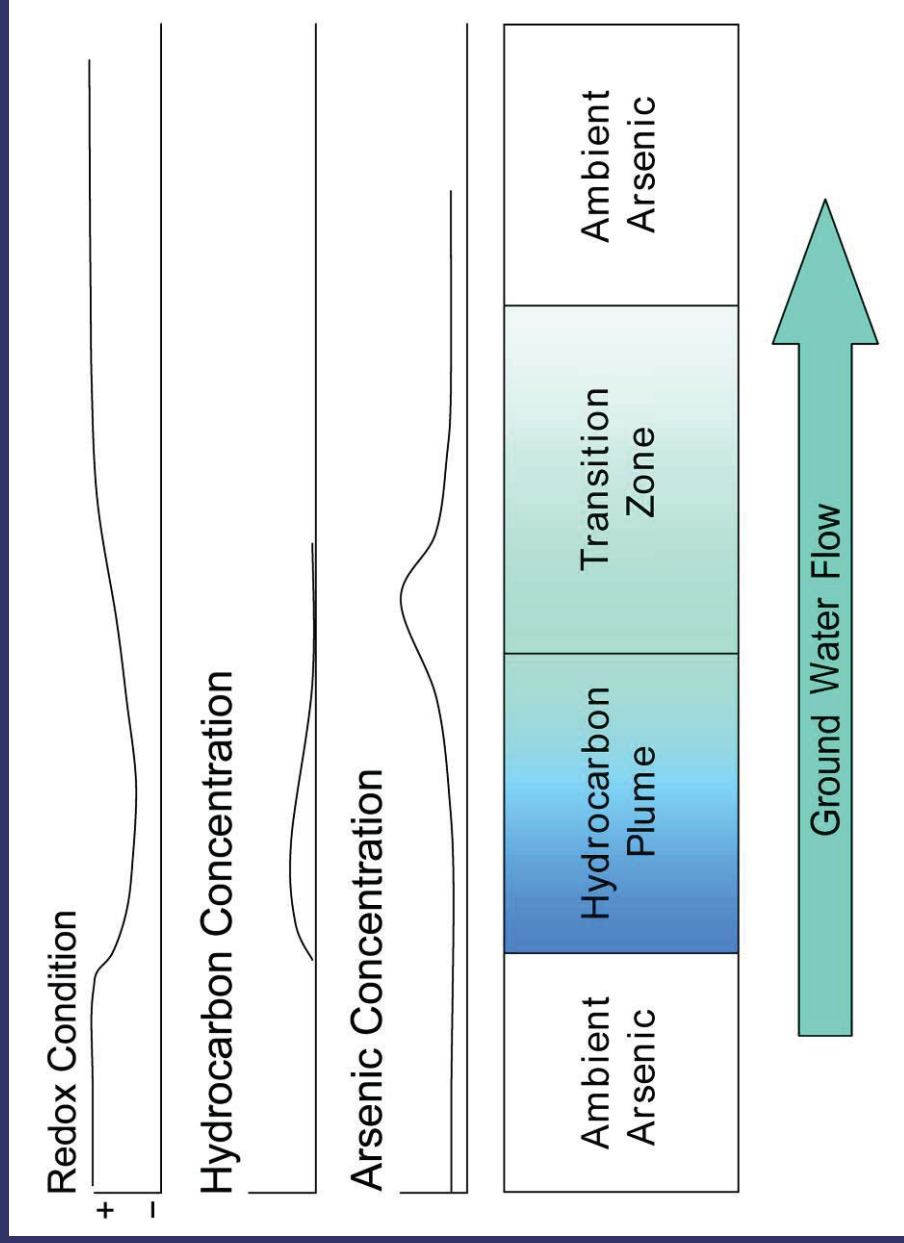
Expanding Plume



Steady State



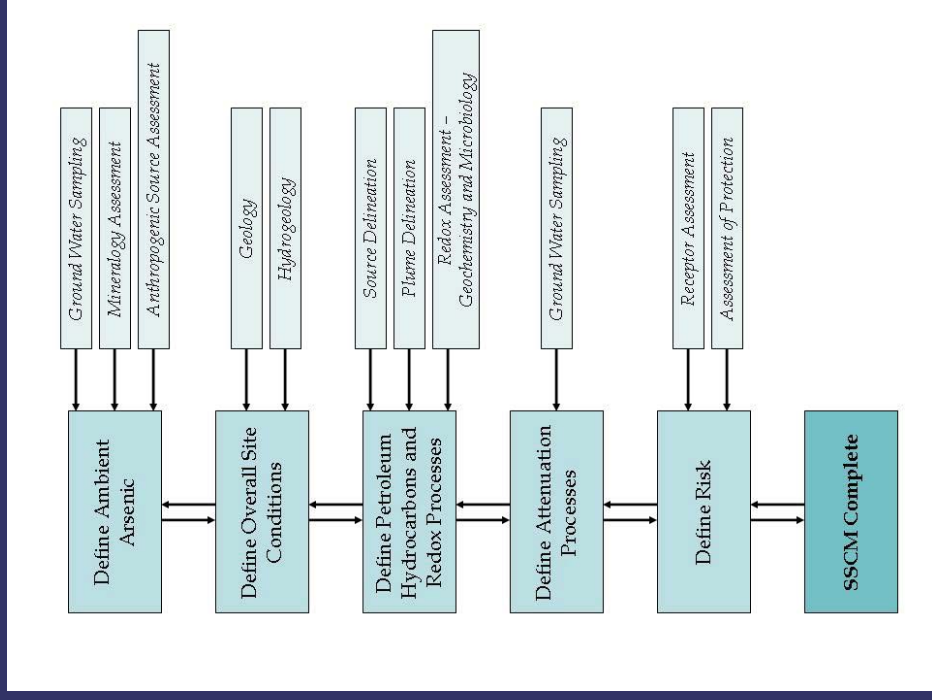
Shrinking Plume



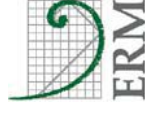
Creating a Site-Specific Model

- **Apply general model of arsenic mobilization within a hydrocarbon plume**
- **Understand the ambient conditions (will be the limit of natural attenuation)**
- **Understand the plume stage**
- **Determine attenuation indicators**
- **Understand risk (mobility → receptors)**

Site-Specific Conceptual Model

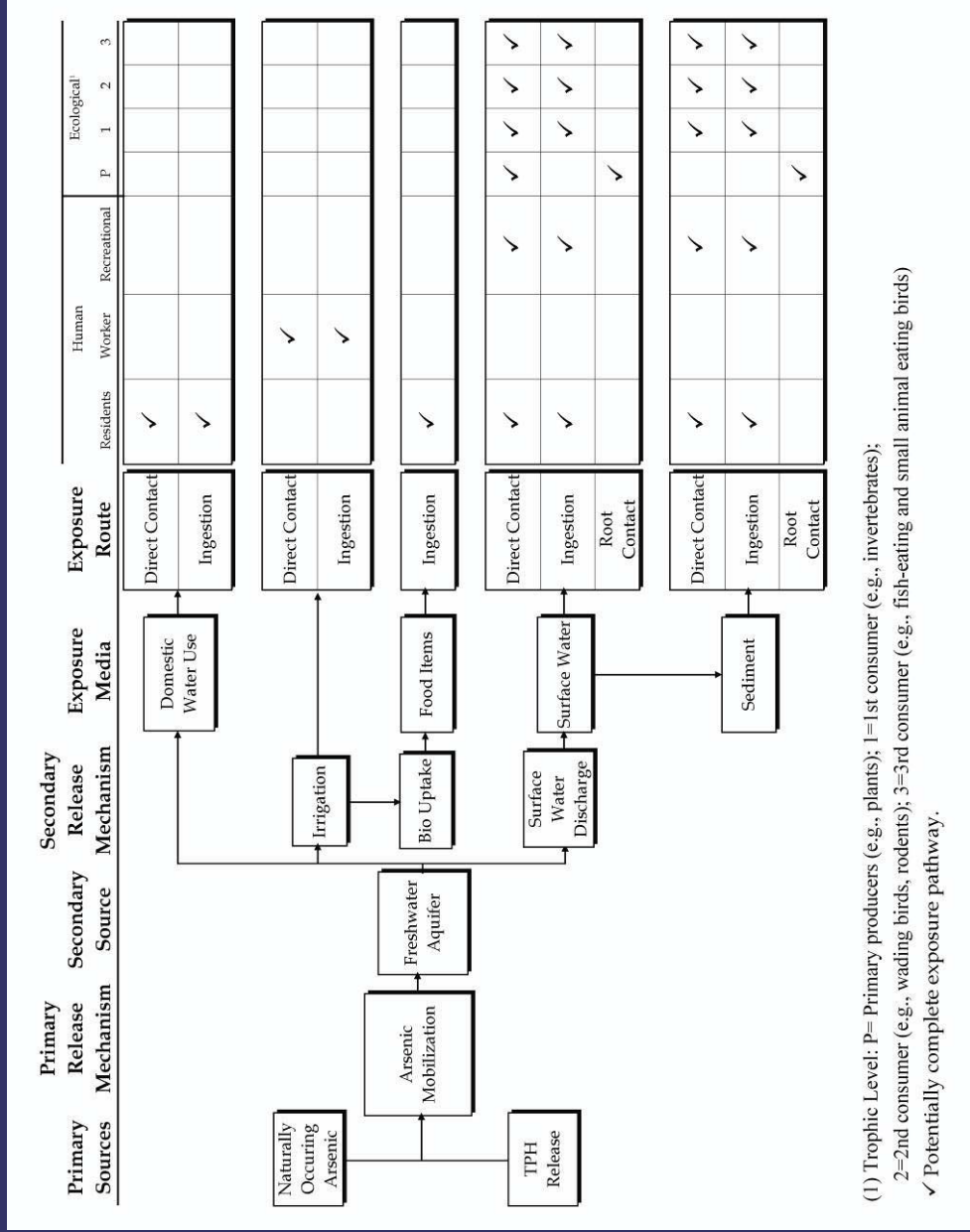


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Exposure Pathway Analysis



(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.



Applying a Site-Specific Model

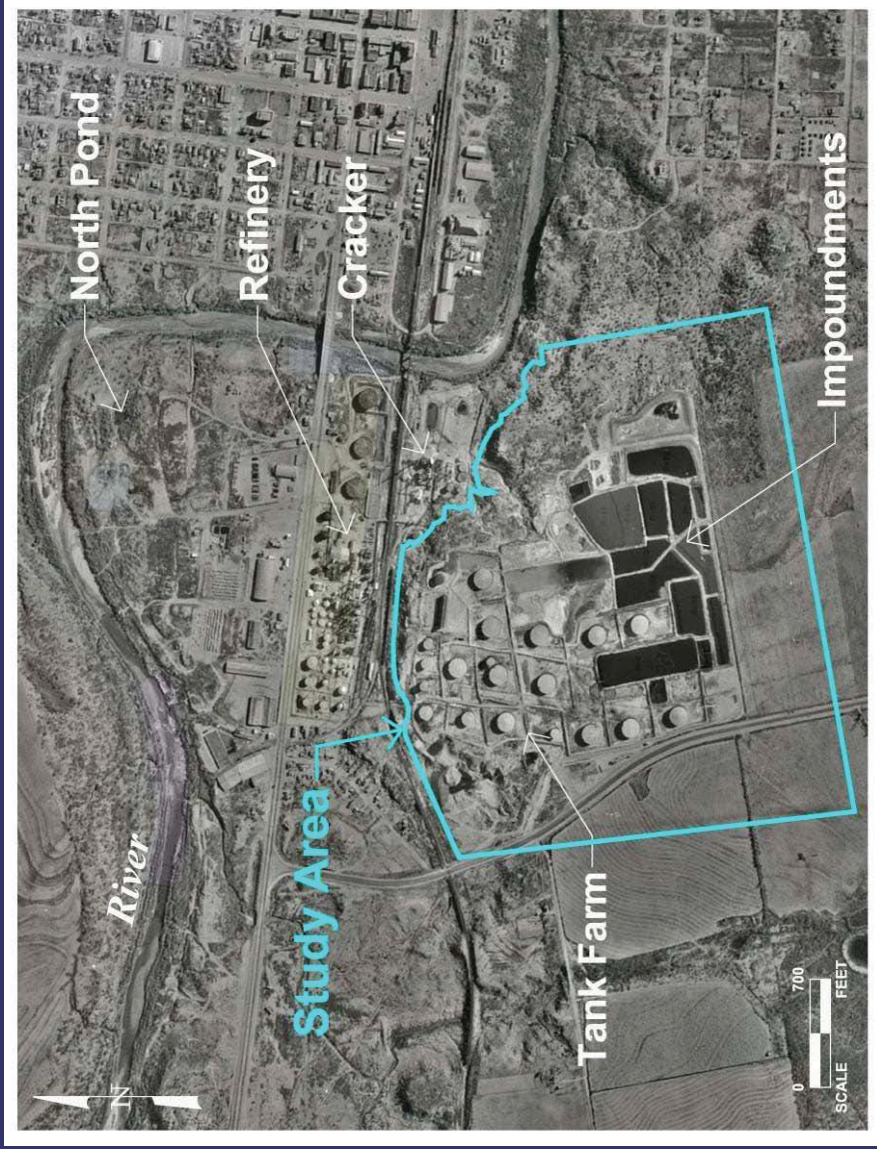
- **Understand the ambient conditions (will be the limit of natural attenuation)**
- **Understand the plume stage**
- **Determine attenuation indicators**
- **Understand risk (mobility → receptors)**

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Case History

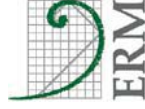
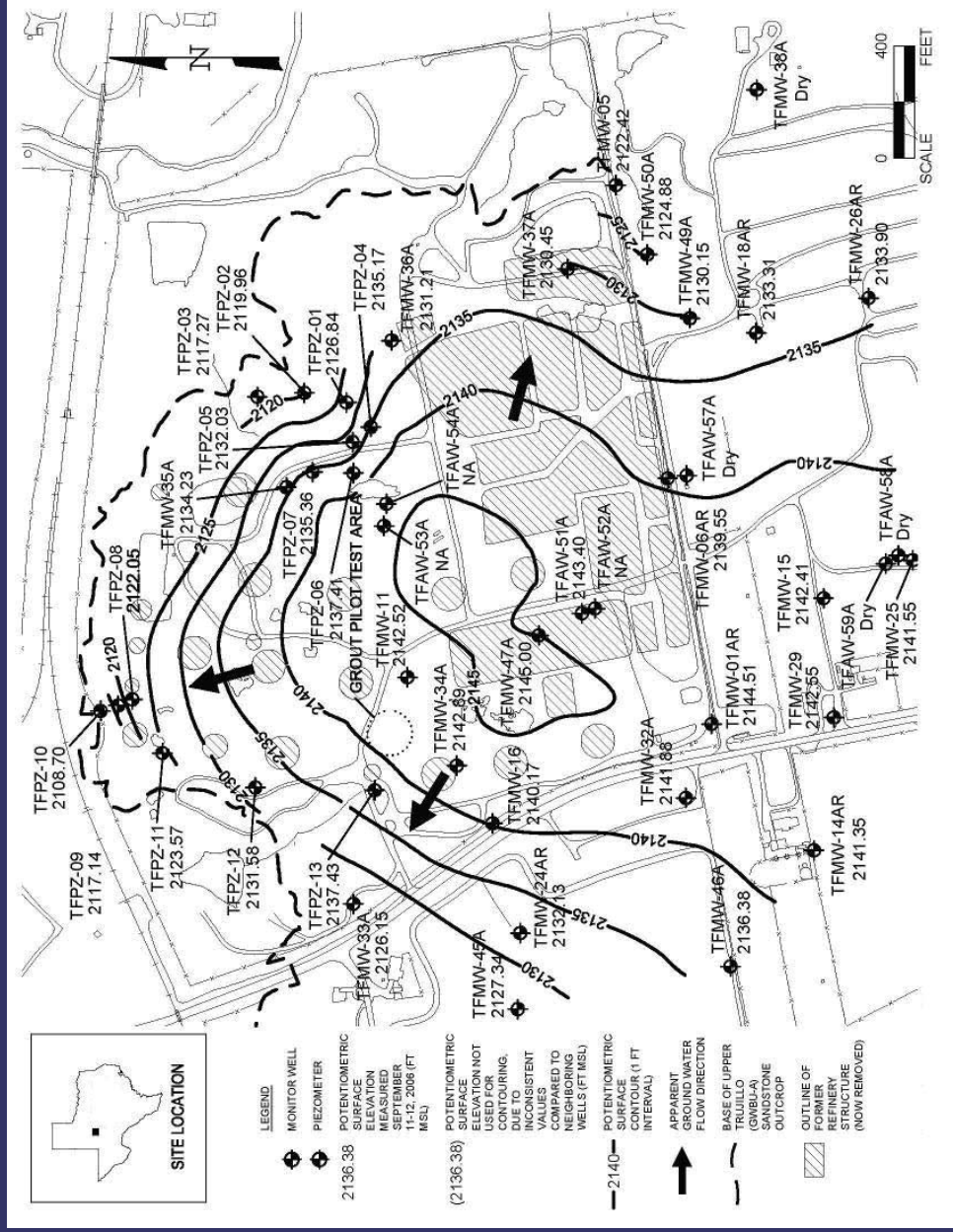


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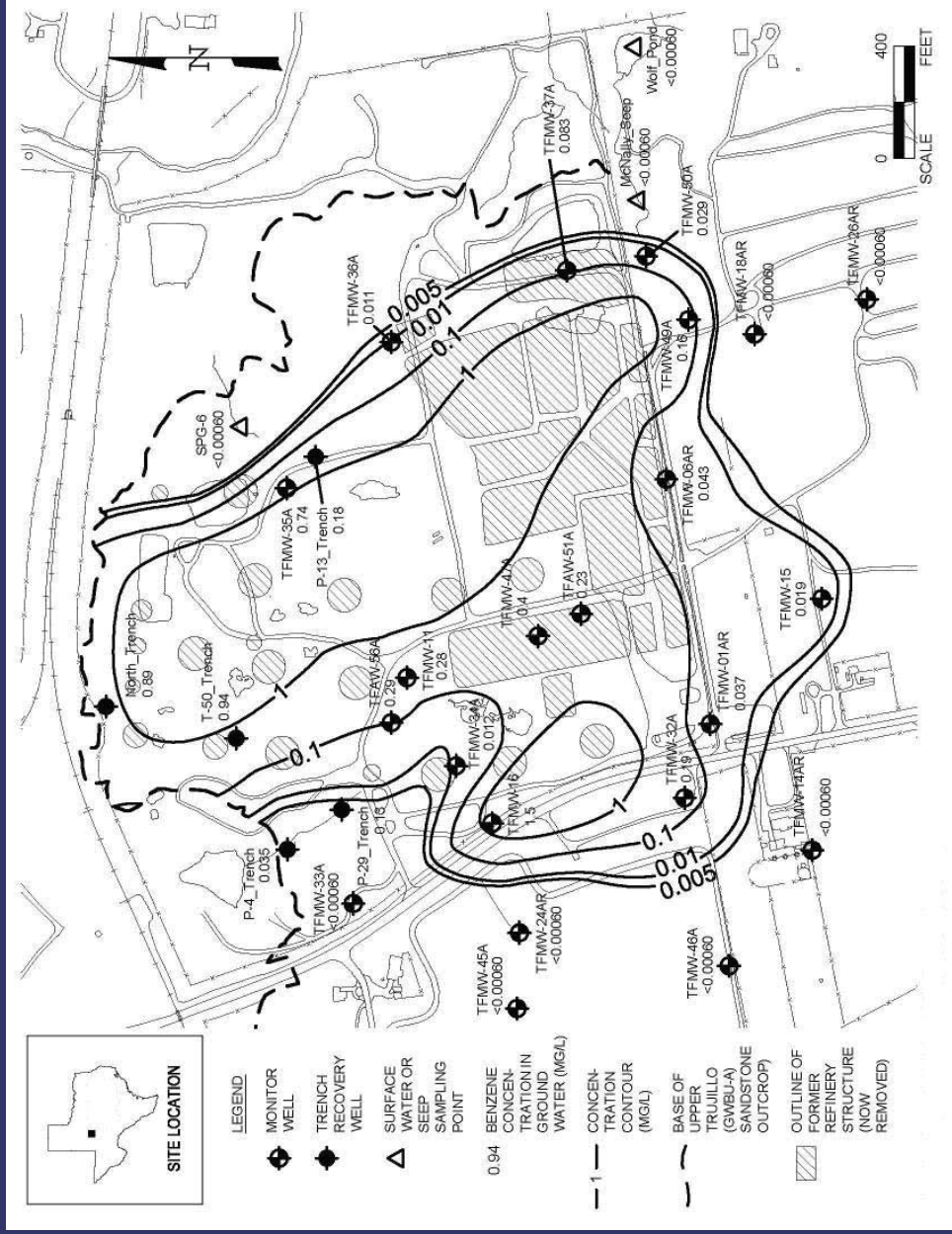
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Potentiometric Surface



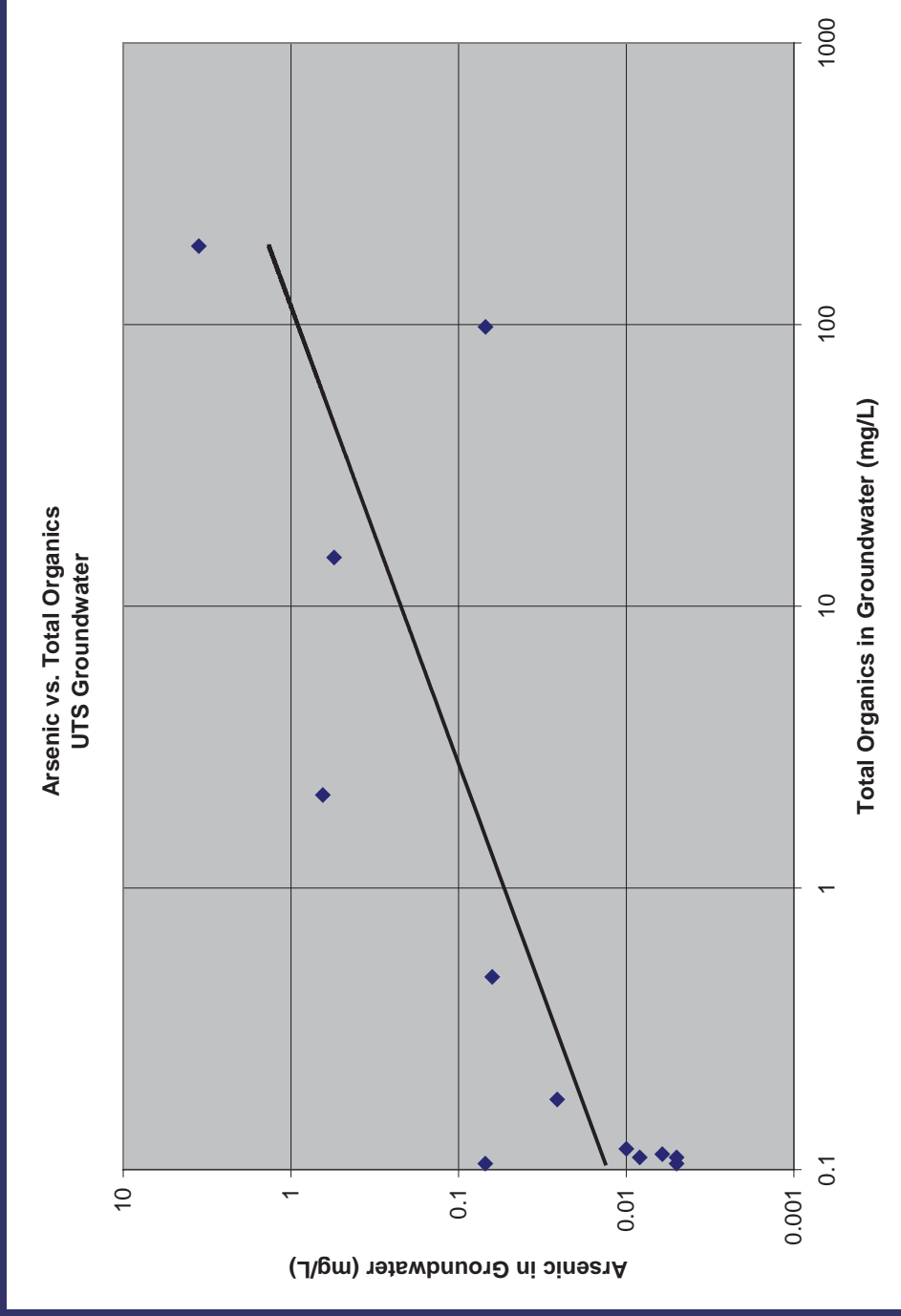
Benzene



Arsenic



Arsenic Versus TOC



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Assessment Tools

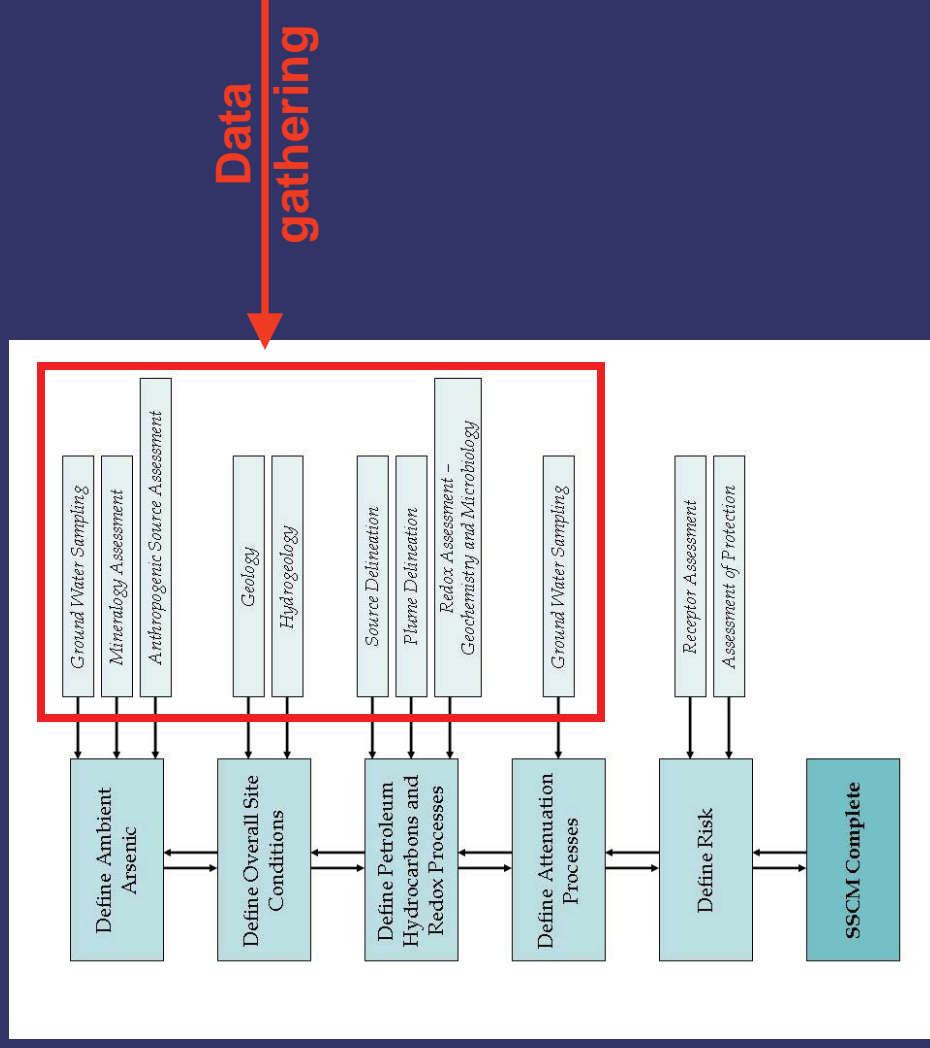


Table 3-1: Key Ground Water Geochemical Parameters for Assessment of Natural Attenuation of Arsenic at Petroleum Hydrocarbon Sites			
Parameter	Approach	Method Reference	Assessment
pH	Flow-through cell or down-hole measurement; pH probe	Follow the pH probe or multi-parameter probe manufacturer's instructions	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
Competing Ions	Low-flow sampling; sampled and preserved in the field (reference methods) to analyze for PO ₄ , SeO ₃ , SiO ₄ , HCO ₃	Standard Methods	Competing ions can desorb or displace arsenate and arsenite increasing their mobility. Bicarbonate can be produced biologically



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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 Fe ²⁺ /Fe ³⁺ 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

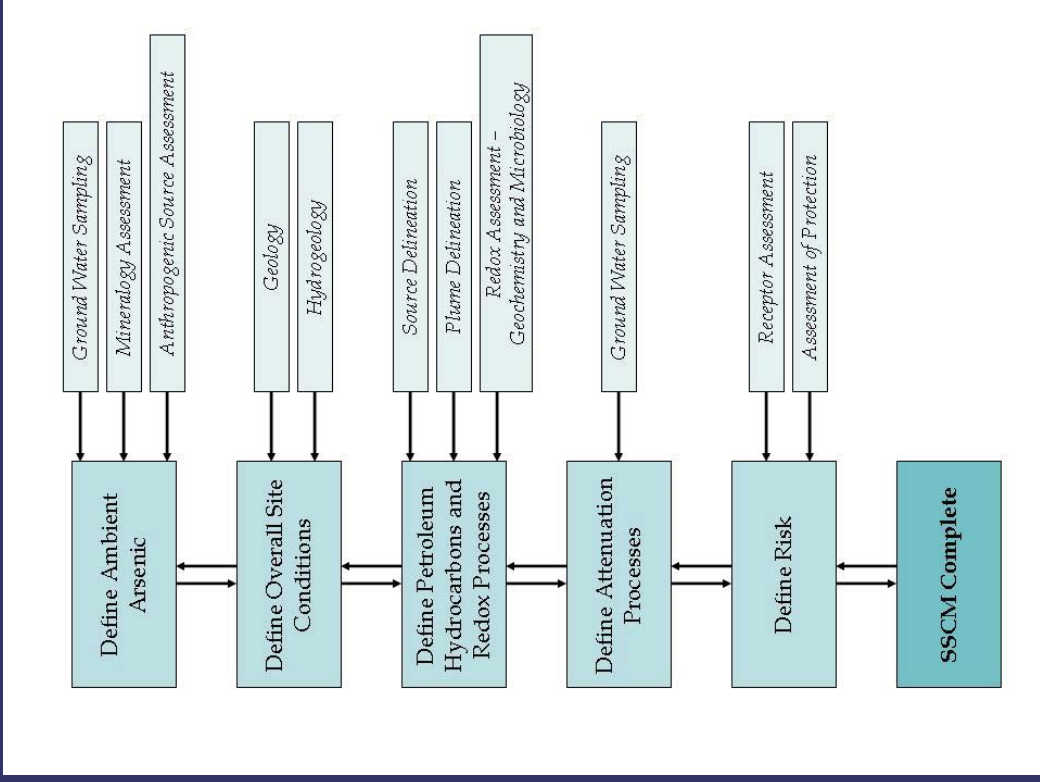


Table 3-2: Key Microbiological Parameters for Assessment of Natural Attenuation of Arsenic at Petroleum Hydrocarbon Sites

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.
Molecular Hydrogen, H ₂	Low-flow sampling; headspace equilibrium by “bubble-stripping” method.	Chapelle, et al., 1995, 1997; Weidemeier, 1998	Although difficult to collect, useful in determining specific redox state and primary TEA.



Site-Specific Conceptual Model



Managing Arsenic at Petroleum-impacted Sites

- Petroleum hydrocarbons perturb the existing geochemistry, mobilizing arsenic if it is already present (as a soil mineral or from anthropogenic sources).
- This perturbation of the ambient arsenic geochemistry persists until the soluble hydrocarbons are attenuated and the ambient redox condition is restored.
- Once the hydrocarbons are attenuated and the redox condition is restored, the arsenic will revert to its pre-existing stable geochemistry, which may be above the MCL.
- A site-specific conceptual model includes assessment of the ambient conditions and state of arsenic to determine the effect of petroleum hydrocarbon and the potential for natural attenuation of mobile arsenic.

