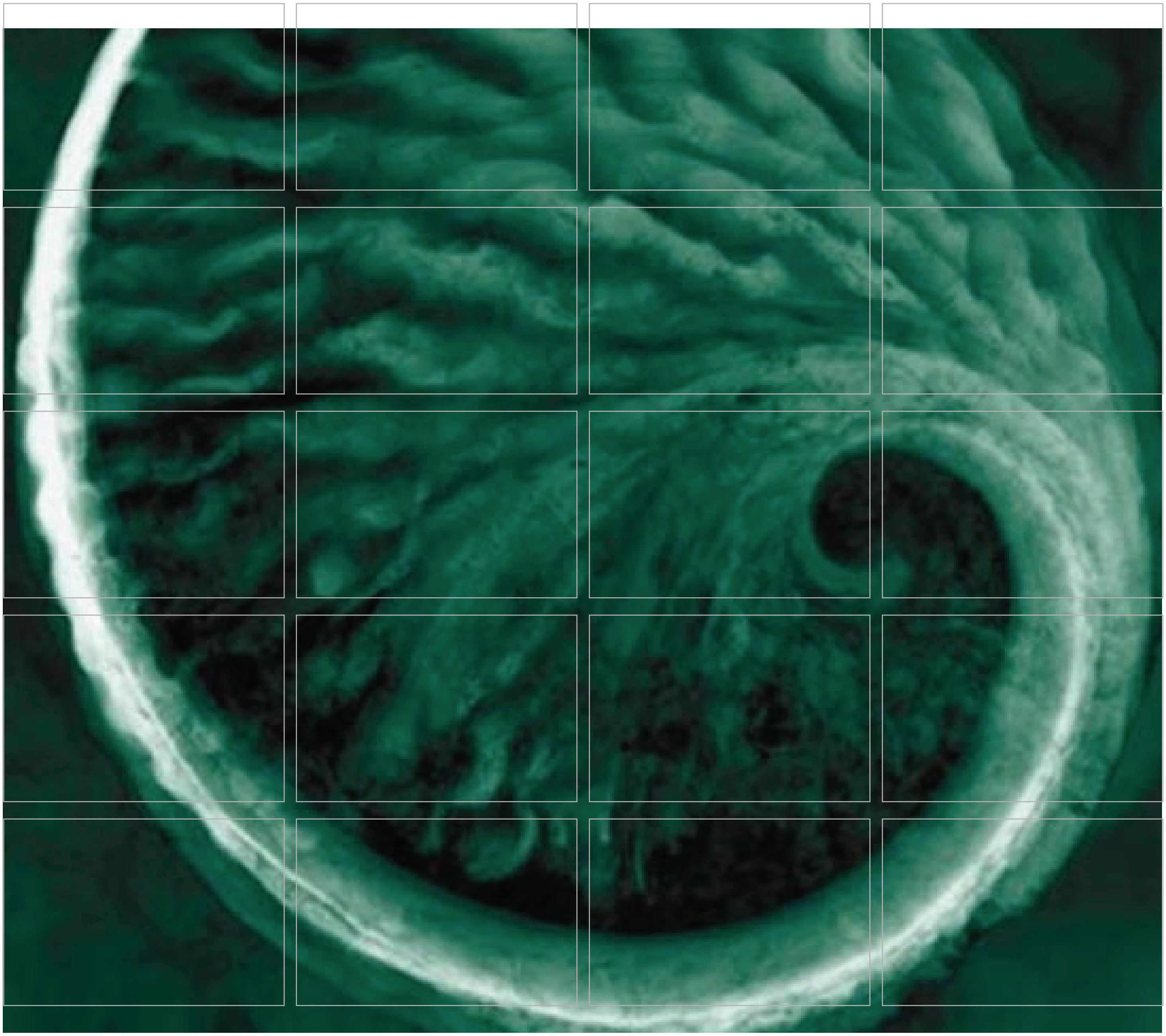

API Groundwater Arsenic Manual

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, $M\text{-}OH \rightarrow M\text{-}O^- + H^+$.

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: $6Fe^{+3} + \text{-}CH_2\text{-} + 3H_2O \rightarrow HCO_3^- + 7H^+ + 6Fe^{+2}$.

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.