



## Appendix C. Characterization Parameters for In situ Treatment Remedies – Definitions and Descriptors for Table 2-2

NOTE 1-This table of “hover definitions” is to be used with Table 2-2. Each item in Table 2-2 has a corresponding definition here that is focused on the importance of the characteristic for in situ optimization.

NOTE 2-For additional technology-specific information, refer to Tables 4-2 through 4-6.

### Physical Properties

**Provenance and Mineralogy**–Provenance and mineralogy of a rock or soil matrix are the properties of its physicochemical formation–geologic structure, chemical composition, distribution, and occurrence. They are the governing factors for the physical, flow, and geochemical properties, discussed in Table 2-2, that are necessary to understand and quantify in order to design an optimal in situ approach.

**Stratigraphy**–Stratigraphy describes the geologic layering in a formation. Formations with more layers (e.g., gravels, sands, silts) and complex “fingering” of high permeability units within low permeability media will require detailed characterization so that amendments can be emplaced properly.

**Degree of Weathering of Geologic Formation**–Generally, more weathered rock will more readily conduct water, and there will generally be less fracture flow and a higher degree of porous media flow. This can also be measured by the rock quality designation (RQD) described below.

**Fracture Representative Aperture and Length**–Fracture characteristics define the extent of fracture flow in a rock formation. Aperture is the representative fracture perpendicular width, and length is the representative length.

**Fracture Connectivity/Rock Quality Designation (RQD)**–Fracture characteristics define the extent of potential fracture flow in a rock formation. The connectivity of the fracture network determines the overall hydraulic conductivity of a rock formation; a highly connected fracture network will allow more flow. Rock quality designation (RQD) quantifies the degree of jointing or fracture in a rock mass by percentage, with >75% considered good quality hard rock, and <50% considered weathered.

**Fracture Orientation**–Fracture characteristics define the extent of fracture flow in a rock formation. In many formations the fractures are directionally oriented from the faulting that produced them. Orientation can influence the flow direction, even if the gradient is not aligned with the fractures.

**Grain Size Distribution**–Grain size is the diameter of individual particles of sediment, ranging from coarse (boulders, on the order of 10 inches) to colloidal (on the order of  $10^{-8}$  to  $10^{-5}$  inches). A formation’s ability to conduct groundwater will increase with grain size. Additionally, well-graded distributions will generally be less conductive than well-sorted distributions. If hydraulic testing has not been performed, grain size distribution can be used to estimate K via correlations provided in textbooks and literature.

**Bulk Density**–Bulk density of soil, measured in weight per volume, is used with the soil’s fraction of organic carbon to provide/calculate the carbon-water partitioning coefficient, which describes the affinity an organic chemical or contaminant will have for the soil matrix. It provides a measure of how much contaminant may be immobilized on the soil, and is important for *in situ* designs considering the incorporation of surfactants to release and treat such contamination.

**Fraction of Organic Carbon**–Fraction of organic carbon ( $F_{oc}$ ), either unitless or in units of volume/weight, is used with the soil’s fraction of organic carbon to provide/calculate the carbon-water partitioning coefficient, which describes the affinity an organic chemical or contaminant will have for the soil matrix. It provides a measure of how much contaminant may be immobilized on the soil, and is important for in situ designs considering the incorporation of surfactants to release and treat such contamination.

**Primary, Secondary, and Total Porosity**–Primary porosity, measured as a fraction or percentage, is the volume of void space to total volume of soil or rock, and is considered a depositional feature. Secondary porosity is a post-depositional feature resulting from, for example, leaching of minerals or the generation of a fracture system. In remediation, a secondary porosity system can be developed using an engineered fracturing approach, which increases the available contact between amendments and the subsurface. Total porosity refers to the porosity resulting from both primary and secondary.

## Transport Properties

**Flow Regime**—Flow regime refers to whether groundwater is confined, unconfined, or primarily governed by fracture flow. Groundwater occurrence significantly affects amendment emplacement design. For example, injection pressures are readily accommodated within an unconfined unit, but back pressure may limit distribution in a confined unit, which is already under pressure. Additionally, if a confined unit is mischaracterized as unconfined, the design may incorrectly call for amendment to be distributed within the vadose zone. Fracture flow presents unique challenges in fracture characterization and the general difficulty/inability to predictably distribute amendment.

**Groundwater Occurrence and Variability**—Groundwater occurrence is tied to a flow regime and can refer to groundwater depth, groundwater recharge from upgradient baseflow or precipitation, groundwater discharge boundaries such as lakes, rivers, and the ocean. These boundaries, in turn generally define the hydraulic gradient. For in situ design, deep groundwater can be a challenge for emplacement. In unconfined units, groundwater levels that fluctuate widely over the seasons or during droughts result in variability in the thickness of the saturated zone, and seasonal injection/reinjection events may be warranted. Finally, in heterogeneous or layered formations, groundwater may occur in separate hydrostratigraphic units, which must be identified during characterization and treated, possibly individually, during emplacement.

**Hydraulic Conductivity**—Hydraulic conductivity is a measurement of the rate at which a fluid (in our case, groundwater) will move through a permeable unit. Regardless of test methods (field or laboratory) or empirical data based on grain size, hydraulic conductivity is only an average representation of the overall unit's ability to transmit groundwater. For robust in situ design, hydraulic conductivity must be taken in context and bolstered by knowledge of stratigraphy and groundwater occurrence, for example, so that permeable layers or stringers separated by less permeable layers will be appropriately targeted, and the unit will not be assumed to be homogeneous.

**Degree of Heterogeneity**—Heterogeneity refers to the variability in soil types within an aquifer (gravels, sands, silts, clays, bedrock/fractures). Heterogeneity is related to a unit's provenance and conditions of formation, for example, alluvial units are more heterogeneous than fluvial units. Understanding and mapping the more permeable zones is a critical step in characterization, because these zones are more likely to be saturated with groundwater and contain contaminants. The less permeable units are more likely to have sorbed contaminants that will be slowly released over time via back-diffusion.

**Anisotropic Orientation**—Anisotropy refers to the directionality of physical aquifer properties. Layered units are generally isotropic, with continuity of properties and flow in the lateral direction, limited in the vertical direction by low permeability layers.

**Effective Porosity**—Effective porosity, a smaller number than total porosity, is the void space available for groundwater flow and injected amendment. "Unavailable" void space results from non-interconnected voids (e.g., as in some volcanic rock) or groundwater under surface tension (negative pressure) between soil grains, which prevents flow. For in situ design, effective porosity, not total porosity, should be used to estimate parameters such as seepage velocity and injected radius of influence. Further discussion of porosity and its effects on flow and transport are provided by ITRC ([2015](#)).

**Velocity/Flux**—Seepage velocity is calculated using Darcy's Law ( $v_s = Ki$ ), where  $i$  is the hydraulic gradient. Discharge velocity, or effective velocity, is the actual velocity of groundwater moving through soil pores ( $v_e = Ki/n_e$ ), where  $n_e$  is the effective porosity. Flux is the velocity (seepage or discharge) through a vertical unit area of aquifer, which has the same units as velocity.

## Aqueous Geochemistry

**pH**—The optimum pH range for aerobic or anaerobic biological activity is between 6 and 8, and certain amendments are prone to a reducing aquifer pH below the optimum range (see alkalinity). Some chemical oxidants (e.g., hydrogen peroxide/Fenton's amendment) require low pH (i.e., 2.4) to be effective. During alkaline-activated persulfate oxidation and calcium or magnesium peroxide reactions, pH is expected to increase, typically above 10.

**Temperature**—For bioaugmentation, each microbial species has an optimal range of temperature for growth and survival; this optimal range should be obtained from the vendor and compared with the aquifer temperature during the selection process. Groundwater temperature can increase during the active injection period of many amendments. This depends on factors such as the difference in temperature between ambient air and subsurface, and whether the remediation process is exothermic. For example, during chemical oxidation reactions, temperature can increase notably and can be used, in part, to assess injection ROI.

**Alkalinity**—Alkalinity, measured in mg/L, refers to the capability of water to neutralize acid without changing the pH appreciably (also called buffering capacity). For acidic aquifers with low alkalinity, buffering may be required to neutralize

the pH if a biological approach is selected. Even in a neutral aquifer, acids that may be generated from fermentation of organic substrates during biological activity could also lead to the need for buffering. Conversely, if magnesium or calcium peroxide is being added, the alkalinity of the groundwater can help determine the amount of a buffer or acid to add to mitigate the pH increasing to above the desired level (generally 8). Standard laboratory alkalinity tests can underestimate the base or acid demand.

**Conductivity, Salinity, and Total Dissolved Solids (TDS)**–Conductivity is a field measurement that can be converted to approximate salinity and TDS concentrations. Groundwater conductivity will typically increase during the active injection period of any amendment that introduces ions. In this way, increases in conductivity can be used, in part, to assess injection ROI. Elevated TDS can inhibit microbial activity in some cases. In the case of surfactant flushing, many surfactants will perform poorly unless the groundwater is at their optimal conductivity/salinity level; this needs to be screened prior to designing a flushing program.

**Oxidation-Reduction Potential (ORP)**–ORP in natural groundwater will range as high as 800 mV (highly oxidizing) to as low as -400 mV (highly reducing) and is a measure of oxidizing potential of a groundwater system. In contaminated groundwater, ORP often has decreased over time via natural degradation processes, especially if there is no groundwater recharge. Very generally, groundwater systems with high ORP may be candidates for chemical oxidation or aerobic biostimulation, while groundwater systems with low ORP may be candidates for anaerobic biostimulation or abiotic reduction. These remediation approaches will increase or decrease ORP during implementation, respectively. Note that pH and ORP values are inversely related, and dependent on the reference electrode used. ORP measurements alone, without integrating pH and metals concentrations into the analysis, can be misleading. ORP changes, not absolute ORP readings, are generally most instructive when examining the impacts of in situ remediation.

**Dissolved Oxygen (DO)**–Related to ORP, DO can range from close to zero to approximately 14 mg/L (at full saturation and cold water temperatures), and possibly higher in deeper wells. DO is a measure of the oxidizing potential of available oxygen. Groundwater is usually considered reducing if DO is less than 0.5 mg/L, and reasonably oxidizing at concentrations of 2 mg/L or more. In contaminated groundwater DO may typically have decreased over time via natural degradation processes, especially if groundwater recharge is slow. Very generally, groundwater systems with high DO may be candidates for chemical oxidation or aerobic biostimulation, while groundwater systems with low DO may be candidates for anaerobic biostimulation or abiotic reduction. These same remediation approaches will create an increase or a decrease in DO during implementation. For anaerobic bioremediation projects, higher doses or more frequent injection of electron donor can overcome an elevated DO. Dissolved oxygen is often difficult to measure in the field. If the ORP is negative, and there is evidence for anaerobic microbial activity (reduction of nitrate or sulfate, or production of methane), then elevated DO levels should be evaluated carefully. As with ORP, changing and controlling DO over a long time frame may be difficult and costly.

**Nitrate ( $\text{NO}_3^-$ )**–Nitrate can be naturally present in groundwater as a product of geologic formations and their naturally occurring minerals. It is also a widespread agricultural contaminant and may in fact be a target compound for in situ remediation. Natural or preremediation nitrate acts as a competitor for electrons during biological in situ reduction, and will typically react with carbon amendments more readily than typical target compounds such as chlorinated solvents. Nitrate concentrations as low as 1 mg/L can indicate competition and need to be taken into considered during amendment dosing.

**Nitrite ( $\text{NO}_2^-$ )**–Nitrite is the first product of nitrate reduction and its presence typically indicates a reducing groundwater environment. Nitrous oxide (NO) and nitrogen gas ( $\text{N}_2$ ) are also produced during nitrate reduction. These compounds may be present at low concentrations or transitory. Oxygen will typically be reduced prior to nitrate; this is a generality, as this complicated process also depends on the microbial populations present and the relative concentrations of electron acceptors and electron donors in the groundwater.

**Manganese (manganic,  $\text{Mn}^{4+}$ )**–Manganese is naturally present in many groundwaters as a product of geologic formations and their naturally occurring minerals or from sodium or potassium permanganate ISCO injections.  $\text{Mn}^{4+}$  acts as a competitor for electrons during in situ reduction, particularly at concentrations of approximately 50 mg/L or more. Conversely, during in situ oxidation,  $\text{Mn}^{4+}$  can be formed and mobilized from  $\text{Mn}^{2+}$ , inadvertently creating manganese plumes that can be of concern to regulators. When used to assess electron acceptor competition, total manganese should be measured by the laboratory.

**Manganese (manganous,  $\text{Mn}^{2+}$ )**– $\text{Mn}^{2+}$  is the product of  $\text{Mn}^{4+}$  reduction, and its presence typically indicates a reducing groundwater environment.  $\text{Mn}^{2+}$  is almost exclusively present in dissolved form in groundwater, and it should be analyzed in a filtered sample. For projects undergoing in situ oxidation, an  $\text{Mn}^{2+}$  baseline should be established to assess the potential for manganese mobilization, if this is a regulatory concern. Following electron donor injections,  $\text{Mn}^{2+}$  can increase.

**Iron (ferric, Fe<sup>3+</sup>)**–Iron is naturally present in many groundwaters as a product of geologic formations and their naturally occurring minerals. Fe<sup>3+</sup> acts as a competitor for electrons during in situ reduction. When used to assess electron acceptor competition, total iron (which will almost always be present as Fe<sup>3+</sup> and other oxidized forms) should be measured by the laboratory. When used to assess the oxidative-reductive environment, an additional dissolved Fe<sup>2+</sup> (filtered sample) should be analyzed.

**Iron (ferrous, Fe<sup>2+</sup>)**–Fe<sup>2+</sup> is the product of Fe<sup>3+</sup> reduction, and its presence typically indicates a reducing groundwater environment. Fe<sup>2+</sup> is almost exclusively present in dissolved form in groundwater, and it should be analyzed as a filtered sample. Iron will accept electrons with approximately the same competitiveness as many chlorinated solvents. Following electron donor injections, Fe<sup>2+</sup> generally increases. In the presence of some oxidants (e.g., persulfate) where localized acidification following oxidant decomposition may occur, Fe<sup>2+</sup> may also increase temporarily.

**Sulfate (SO<sub>4</sub><sup>2-</sup>)**–Sulfate is naturally present in many groundwaters as a product of geologic formations and their naturally occurring minerals and is often elevated in saline waters. It can also be a manufacturing or agricultural contaminant and a byproduct of persulfate used in some ISCO treatments. Sulfate needs to be carefully considered when selecting a remedial approach, as it can be beneficial and impeding, depending on the technology selected. Natural or preremediation sulfate at elevated concentrations can inhibit reductive processes such as reductive dechlorination, because sulfate, at elevated concentrations, is a powerful competitor for electrons. Typically, approximately 400 mg/L or greater sulfate at preremediation conditions can be a potential cause for concern (for reductive dechlorination) and special consideration for dosing. On the other hand, sulfate can react in situ with iron to form iron sulfides, which can provide long-term anaerobic chemical reduction. Sulfate reduction is yet another process, where sulfate is used as the primary electron acceptor, that can degrade specific contaminants (i.e., petroleum hydrocarbons).

**Sulfite (SO<sub>3</sub><sup>2-</sup>) and Sulfide (S<sup>2-</sup>)**–These are the products of sulfate reduction, and their presence typically indicates a strongly reducing groundwater environment. Oxygen, nitrate, manganese, and iron will typically be reduced prior to sulfate. This is a generality, as this complicated process also depends on the microbial populations present and the relative concentrations of the electron acceptors in the groundwater. Sulfide can react in situ with ferrous iron to form ferrous sulfide precipitates and little free sulfide will be detected. Some aquifers, such as limestone or other fractured bedrocks, may have little bioavailable iron and sulfides, which may facilitate long-term anaerobic chemical reduction capacity. If hydrogen sulfide is formed, this can be toxic to microbes.

**Chloride (Cl<sup>-</sup>)**–As reductive dechlorination occurs chloride ions are released and the concentration of chloride may increase. However, natural and anthropogenic chloride may be present in groundwater at concentrations high enough that this change could be difficult to detect or attribute solely to remediation of the chlorinated solvents. In high chloride environments, such as landfills and areas subject to seawater intrusion, chloride can cause toxicity to microbes, typically at concentrations in the thousands of mg/L.

**Chemical Oxygen Demand (COD)**–COD in soil or water is the total measurement of all chemicals that can be oxidized. It is a measure of the total species, including the target contaminants, that will compete for an injected oxidant and is important in selection of oxidation as an appropriate approach, and dosing. It is important to include both soil and groundwater in COD testing, as both will be available to react with the injected oxidant. In addition to humic substances and dissolved organic matter, the presence of petroleum contaminants and reduced metals can contribute to the COD. In general, chlorinated solvents are in a more oxidized state and will not contribute appreciably to COD.

**Soil Oxidant Demand (SOD)**–SOD is the amount of a specific oxidant consumed by the soil. SOD tests are performed in the laboratory using site soil and the specific oxidant(s) under consideration for the site, and provide design data. In an SOD test, site groundwater is not used, and the site soil may or may not be from a contaminated portion of the site; therefore, SOD is a partial measure of Total Oxidant Demand (see TOD).

**Total Oxidant Demand (TOD)**–TOD is the amount of a specific oxidant consumed by all constituents (natural and contaminant) present in the soil and via the autodecomposition of the oxidant itself. Impacted groundwater may sometimes be used in the test. TOD tests are performed at varying oxidant concentrations using site matrix materials and the specific oxidant(s) under consideration to inform ISCO design. TOD may be the major component of chemical costs for a project.

**Natural Oxidant Interaction (NOI)**–NOI is a holistic term to describe the interactions among oxidant, oxidant dose, naturally occurring reductants and catalysts, multiple inorganic species in soil and groundwater, and the natural organic matter (NOM) and seeks to model the behavior of various oxidants under similar conditions by accounting for the concentration of the oxidant, catalyst, and NOM reactions. NOI is a comprehensive term, recognizing that the reaction

kinetics and persistence of the available chemical oxidants vary greatly, sometimes leading to confused use of NOD/SOD/TOD.

**Total Organic Carbon (TOC)**–TOC provides an indication of the potential for biological activity/degradation to occur. TOC includes both naturally occurring organic carbon (such as humus) and organic carbon contamination, e.g., benzene. TOC values above approximately 50 mg/L indicate carbon levels that, if biologically available, could foster cometabolism. TOC may be depleted in areas where such cometabolism has already occurred. During the addition of a carbon source for biostimulation, TOC is expected to increase and can provide a measure of the injection ROI. Over time TOC will decline again to preremediation levels. This, combined with aquifer flow and transport information, can indicate when the substrate is depleted. TOC also provides a general indication of the amount of oxidant that will be needed, if a soil sample cannot be collected for testing.

**Anions and Cations**–These are the species comprising conductivity, salinity, and TDS. These species can become oxidized or reduced in areas undergoing in situ remediation. The most important anions and cations are discussed individually within Table 2-2. Like conductivity, anions and cations may be used to document preremediation baseline groundwater conditions and changes subsequent to the addition of a remediation injectate.

**Arsenic (arsenite,  $As^{3+}$ , and arsenate,  $As^{5+}$ )**–Arsenic is naturally present in many soils and groundwaters as a product of geologic formations and their naturally occurring minerals. Arsenic has also been widely used as a pesticide for golf courses, orchards, wood treatment, and other uses. During in situ oxidation, arsenic can be mobilized, inadvertently creating an arsenic plume. The presence of arsenic both in soil and groundwater should be established prior to remediation of other compounds by oxidation, and laboratory testing can be used to assess the potential for transformation and mobilization. Many regulatory bodies require preremediation and postremediation testing for arsenic in groundwater. Arsenic concentrations may also increase after electron donor injections as arsenate is reduced to arsenite. Arsenic should be measured as an unfiltered sample. Amendments should also be assayed for arsenic by the batch, prior to use. Assessing arsenic presence and mobility should be combined with an evaluation of ferrous and ferric iron given the close geochemical interaction that occurs between the species.

**Chromium (trivalent,  $Cr^{3+}$ )**–Trivalent chromium is naturally present in many soils and groundwaters as a product of geologic formations and their naturally occurring minerals. During in situ oxidation, hexavalent chromium ( $Cr^{6+}$ ) acts as a competitive electron acceptor and trivalent chromium can be transformed into the more mobile and toxic hexavalent chromium (see Chromium, hexavalent), inadvertently creating a chromium plume. The presence of chromium in both soil and groundwater should be established prior to remediation of other compounds by oxidation, and laboratory testing can assess the potential for transformation to the hexavalent form. Amendments should also be assayed for chromium by the batch, prior to use.

**Chromium (hexavalent,  $Cr^{6+}$ )**–Hexavalent chromium is the common oxidized form of trivalent chromium. Though naturally occurring in some locations worldwide,  $Cr^{6+}$  is of greatest concern as an anthropogenic compound, both as a byproduct of in situ oxidation and, importantly, as a contaminant source itself. Hexavalent chromium has had many applications in electroplating, wood treatment, etc. Indeed, in situ chemical reduction is often employed to remediate  $Cr^{6+}$  to its less mobile and less toxic  $Cr^{3+}$  form.  $Cr^{6+}$  is present almost exclusively in dissolved form in groundwater, and it should be analyzed as a filtered sample. (Note, however, that dissolved analyses may be acceptable for remediation design and monitoring, but in some states total metals may be required for regulatory site closure.) There are also specific colorimetric and ion chromatography methods for hexavalent chromium.

**Other Heavy Metals (e.g., lead, copper, selenium)**–Various metals may be naturally present in groundwater based on provenance and mineralogy. These should be assessed on a site-specific basis as part of in situ remediation planning. See Tables 4-2 through 4-6 for select discussion of some metals in relation to technology-specific applications.

**Stable Isotope Probing**–Stable isotope probing (SIP) tracks the environmental fate of a “labeled” contaminant of concern to assess whether biodegradation is occurring. The “label” serves as a tracer, which can be detected in the end products of biodegradation (e.g., new biomass or carbon dioxide). For a SIP study, test media (commercialized, for example, as Bio-Traps) are “baited” with a synthesized form of the contaminant containing  $^{13}C$  as the label. Since  $^{13}C$  is rare, carbon originating from labeled contaminant can be distinguished from  $^{12}C$  from other sources. If biodegradation is occurring, the  $^{13}C$  label from the synthesized contaminant will be incorporated into microbial biomass and  $CO_2$ . SIP studies can be performed for any compound that microbes use as a carbon source, e.g. BTEX.

**PLFA (phospholipid Fatty Acids)**–PLFA are a main structural component of the outer membrane of all microbes. The presence and ratios of certain PLFAs aid in identifying broad groupings of microbe types (e.g., iron reducers, sulfate

reducers, fermenters), that comprise a microbial community. Understanding can also be gained of the total biomass, functional groups, and relative health/activity before, in response to, and following an in situ remedy. PLFA is a useful tool to help identify whether biostimulation is an appropriate remedy for a site and whether bioaugmentation is needed. During remediation, the ongoing presence or increase in the biomass and changes to microbial community groups can be used to evaluate response to a remedy. PLFA cannot be used to determine if bioaugmentation will be helpful for chlorinated solvent impacted sites, as the test does not detect dehalogenators within the microbial community.

**qPCR (Quantitative Polymerase Chain Reaction)**-qPCR, commercialized in various forms is a molecular biological tool that quantifies the number of genes present in a sample. CENSUS can establish the presence of: Dehalococcoides and Dehalogenimonas, the only known microbes to fully dechlorinate PCE or TCE to ethene; Dehalobacter, which degrades chlorinated ethanes and methanes; Dehalogenimonas, which degrades chlorinated propanes; and other functional reductase genes such as the tceA, vcrA, and bvcA that demonstrate the metabolic potential to degrade TCE and VC. Sulfate reducing bacteria nitrate reducing bacteria and methanogens can also be identified. The presence of these genes at a chlorinated solvent impacted site can help identify whether biostimulation is an appropriate remedy for a site and whether bioaugmentation with a dechlorinating enrichment is needed. During remediation, the ongoing presence or increase in the concentration of these genes can be used to demonstrate performance. Quantarray can also identify aerobic microorganisms useful for remediation of petroleum hydrocarbons or which may compete with anaerobic microorganisms. These concepts and tests are discussed in detail in ITRC (2013a).

## Degradation Potential

**CSIA (Compound Specific Isotope Analysis)**-Many elements of biological interest have two or more common stable isotopes, with the lighter isotopes present in much greater abundance than their heavier counterparts. For example, the abundance of the light isotope of carbon ( $^{12}\text{C}$ ) is 98.89 percent and the abundance of the heavy isotope of carbon ( $^{13}\text{C}$ ) is 1.11 %. Under conditions in which abiotic or biotic degradation of a compound is occurring, the parent compound gains a progressively higher content of heavy isotopes. This is because bonds between a heavier isotope and the atoms adjacent to it are stronger than the equivalent bonds of a lighter isotope. As a result, chemical or biologically mediated reactions of molecules that contain lighter isotopes occur more quickly than those that contain heavier isotopes. This process is called fractionation. Conversely, processes other than degradation that affect contaminant concentrations in groundwater, such as dilution, sorption, and volatilization, have very small or no isotopic fractionation effects. Thus, CSIA can be used to assess whether an in situ remediation program is successfully destroying contaminants. Evidence of degradation can be seen through spatial trends in isotope ratios. If multiple wells are sampled which are located consecutively downgradient of each other, and degradation of the contaminant of concern is occurring, the isotope ratio is expected to increase along the gradient. Evidence of degradation can also be seen through temporal trends in individual wells, again with an increase in the isotopic fractionation ratio over time. CSIA can also be applied to chlorine and hydrogen. CSIA is discussed in detail in (Allaire 2008).

**Dissolved Hydrocarbon Gases (methane, ethane, ethene, acetylene, propane, propene)**-Dissolved hydrocarbon gases are typical degradation products of reductive dechlorination of chlorinated ethenes (e.g., PCE), methanes (e.g., carbon tetrachloride), and propanes (e.g., 1,2-dichloropropane). Acetylene is thought to be primarily a byproduct of the abiotic reduction of chlorinated ethenes by reaction with ZVI or ferrous sulfide. The presence of these dissolved gases generally indicates that some complete reductive dechlorination is occurring. Methane can be produced from the contaminant(s), electron donor, other organics, or carbon dioxide. Methane is also the product of methanogenesis—that is, the reduction of carbon dioxide, and in that case is indicative of a significantly reducing environment. Natural gas contains many of these dissolved gases.

**Carbon Dioxide ( $\text{CO}_2$ )**-Carbon dioxide is the product of many degradation processes, as well as an electron acceptor in most reducing groundwater environments (methanogenesis). Because it can be simultaneously generated and consumed, it may not provide as good an indication of aquifer conditions as its product, methane.

**Magnetic Susceptibility**-The presence of magnetite in an aquifer matrix can be an indication of the potential for abiotic degradation, particularly of chlorinated ethenes, to occur via iron minerals. Magnetic susceptibility, given in volume per mass of soil (typically cubic meters per kg), can be measured with a laboratory instrument, or in-well, and the value correlated to a contaminant half-life (Wiedemeier 2017). Magnetic susceptibility can potentially guide a practitioner toward an abiotic remediation approach capitalizing on the naturally occurring iron to facilitate contaminant degradation. It can also be obtained remotely in some cases using geophysical techniques such as induced electromagnetics. Millivolt readings are usually higher in areas where abiotic degradation has occurred, demonstrating a shrinking plume, and may be the “shadow” left behind by a plume’s historic maximum extent.

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