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Pilot Study of an *In situ* Reactive Zone for Perchlorate Treatment
Jet Propulsion Laboratory Test Area

Contract # N4740B-02-C-7314

March 4, 2004

Pilot Study of an *In situ* Reactive Zone for Perchlorate Treatment
Jet Propulsion Laboratory Test Area

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EXECUTIVE SUMMARY

This report describes an *in situ* perchlorate bioremediation demonstration implemented by ARCADIS through the Naval Facilities Engineering Service Center (NFESC) Broad Agency Announcement (BAA) program. During the demonstration, ARCADIS applied its *In situ* Reactive Zone (IRZ) technology at the National Aeronautics and Space Administration's (NASA) Jet Propulsion Laboratory (JPL), Pasadena CA.

Based on the data generated during this demonstration, the IRZ technology and specifically the application of corn syrup injections can be optimized for the cost effective remediation of perchlorate at the JPL facility. The laboratory and field data contained in this report technically support the subsurface application of corn syrup to stimulate perchlorate bioremediation in anaerobic reactive zones. This conclusion is supported primarily using measured reductions in perchlorate concentration in both the injection and monitoring wells. The inclusion of bromide in the corn syrup solutions that were injected permits the calculation of an injection solution dilution factor. This dilution factor is not sufficient to account for the noted reductions in perchlorate concentration over the demonstration interval. These reductions can be compared to both baseline perchlorate concentrations in the subject wells and to perchlorate concentrations during the demonstration in IRZMW-3, which proved to be a side gradient well and was thus minimally influenced by corn syrup injections. In addition, as a second line of evidence, biogeochemical conditions, particularly ORP, support the existence of anaerobic conditions necessary for perchlorate bioremediation during key sampling events over the length of the demonstration. Lastly, the decreases in perchlorate over the course of the demonstration followed a logical time sequence from beginning to end.

The corn syrup injection scheme during this demonstration did not result in attaining the interim closure standard for perchlorate in the three months of field testing but did result in substantial reductions in perchlorate concentration. IRZ systems typically require a period of injection adjustment and biological acclimation. Adjustment to the injection scheme for this demonstration was suggested but made impractical due to other work planned for the portion of JPL where this demonstration was sited. The need for additional injection scheme adjustment in this case is attributed to the variable and much increased flux of groundwater through the treatment zone during the demonstration. Adjustments to the injection scheme including increases in the mass of corn syrup delivered and potentially a continual low-load injection system or recirculation system to enhance DOC distribution could be designed to accommodate the additional, unexpectedly high flux of groundwater through the treatment zone. Such alterations in the injection scheme would result in the establishment of a more extensive and stable anaerobic reactive zone. This would extend the length of time that the perchlorate plume in this area of the site spends under anaerobic conditions and thus improve the percent reduction resulting in more complete, consistent perchlorate treatment.

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1.0 Introduction

1.1 Background

The oxy-anion perchlorate is a naturally occurring and anthropogenic oxidizer utilized in solid fuels for rockets and missiles, military and commercial munitions, pyrotechnic devices, fireworks, explosives, blasting agents, matches, nuclear reactors, electronic tubes, additives in lubricating oils, tanning and finishing leather, fixers for fabric and dye, electroplating, aluminum refinishing, rubber manufacturing, paint and enamel production, automobile air bag inflators, and pharmaceutical and analytical chemicals (U.S. EPA, 1998). During the last 50 years, it is estimated that 15.9 million kilograms (kg) of perchlorate has entered the environment as a function of the periodic replacement of perchlorate in solid rocket fuels and once accepted but now improper disposal techniques (Motzer, 2001). Perchlorate salts are highly soluble in water. Thus, sites contaminated with perchlorate are characterized by large masses of perchlorate readily entering the saturated zone from the vadose zone through percolation. Perchlorate is then transported laterally to form large groundwater plumes. Perchlorate is persistent in the environment under aerobic conditions (Chaudhuri et. al., 2002). Perchlorate has been added to the Contaminant Candidate List (U.S. EPA, 1998) and both U.S. EPA and various states are endeavoring to develop and ratify clean-up standards to guide remediation efforts.

The most common perchlorate remediation approach applied at full-scale to date is pump and treat (P&T) (ITRC, August 2002). Ion exchange or *ex situ* bioreactors are typically implemented on the recovered, contaminated groundwater. P&T coupled with ion exchange or *ex situ* bioremediation is demonstrated to be effective and will occupy a prominent position in the nation's remedial response to perchlorate. However, *in situ* bioremediation also represents a technically plausible and fiscally desirable alternative to P&T. *In situ* bioremediation through the injection of innocuous substrates such as corn syrup into the saturated zone is a logical response to some of the daunting challenges that are a part of the large perchlorate environmental "fingerprint" that is found repetitively in the United States. Due to its chemical characteristics, perchlorate has the tendency to form very large, diffuse plumes in groundwater (Xu et al, 2003). The application of P&T to a constituent of concern with this pattern of influence will prove to be a formidable undertaking because of the volume of perchlorate impacted groundwater delineated to date that would require extraction. In contrast, *in situ* bioremediation can be cost effectively utilized in a timely manner to more surgically attack perchlorate near source areas to preserve of human and ecological health. Therefore, ARCADIS is applying its *In situ* Reactive Zone (IRZ) technology at sites requiring perchlorate remediation. In this document, we report on a IRZ perchlorate remediation demonstration performed at the National Aeronautics and Space Administration's (NASA) Jet Propulsion Laboratory (JPL), Pasadena CA. Briefly, IRZ involves the injection of a food grade carbon source (substrate) into groundwater to enhance the anaerobic microbial degradation of perchlorate, nitrate, energetics and/or chlorinated hydrocarbons. The technology can also be used for the precipitation of metals and radionuclides.

1.2 Objectives of the Demonstration

The specific objectives of the pilot study were as follows:

1. Conduct a microcosm study to verify that corn syrup is an appropriate electron donor to support perchlorate bioremediation in the aquifer at JPL and in JPL vadose zone soils that are found to be contain elevated levels of perchlorate.
2. Create a reactive reducing zone for perchlorate bioremediation within groundwater in an area directly upgradient and near monitoring well MW-7 at the JPL site.

3. If perchlorate is detected in vadose zone soils, create a reactive reducing zone for perchlorate bioremediation in soil overlying the perchlorate groundwater plume upgradient and near monitoring well MW-7.
4. Monitor the hydrogeochemical changes in groundwater that occur over the course of treatment. Specifically, note the change in oxidation-reduction potential (ORP), dissolved oxygen (DO), hydrogen ion concentration (pH), and conductivity.
5. Monitor changes in specific inorganic compounds—nitrate, perchlorate, ferrous iron, and sulfate.
6. Monitor potential changes in the concentrations of specific organic compounds—chlorinated volatile organic compounds (CVOCs to include carbon tetrachloride, chloroform, trichloroethene, 1,2-dichloroethene, and vinyl chloride) and dissolved organic carbon (DOC).
7. Obtain hydrologic transport information using an inorganic tracer (bromide). This information will be used to determine appropriate well spacing for full-scale implementation.
8. Determine the overall rate of perchlorate removal within the reactive zone.
9. Determine the organic loading rate necessary to create reducing conditions amenable to perchlorate degradation.

The IRZ demonstration for *in situ* perchlorate remediation and addressing these goals was carried out by ARCADIS during the months of June through early September 2003.

1.3 Regulatory Drivers

The Office of Environmental Health Hazard Assessment in California EPA has proposed a Public Health Goal of 6 µg/L for perchlorate in drinking water (OEHHA, 2002). USEPA has proposed a draft reference dose that could produce a drinking water equivalent level of 1 µg/L for the protection of human health. California's Department of Health Service decreased the drinking water action level from 18 µg/L to 4 µg/L (DHS, 2002). Both California regulatory agencies and USEPA continue to move closer to the promulgation of a definitive perchlorate regulatory standard while other states such as New Mexico and Massachusetts have set action levels of their own. At JPL, the California Department of Toxic Substance Control (DTSC), the Regional Water Quality Control Board (RWQCB) and USEPA Region 9 are overseeing compliance with an interim action level enacted in January of 2002 by the California Department of Health Services of 4 micrograms per liter (µg/L).

1.4 Stakeholder/End-User Issues

Stakeholders and end-users of perchlorate remediation are concerned foremost with timely, economical, certain perchlorate cleanup. Under appropriate conditions, IRZ offers significant advantages over conventional P&T technology, including lower cost and reduced treatment time. The advantages and limitations of the technology are discussed in detail in Section 2.4. Perchlorate bioremediation in general and the IRZ technology in particular convert perchlorate to innocuous end products including chloride and oxygen through sequential reduction reactions (Xu et. al., 2003).

Secondary water quality impacts from IRZ implementation can occur due to the by-products of substrate consumption as measured by parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS), taste, odor, and sulfides. However these impacts are typically limited to the reactive zone itself. These byproducts, which are typical of many natural processes in which bacteria anaerobically consume a food source, are generally rapidly mitigated when the conditions become more aerobic on the edges of the reactive zone. Secondary water quality impacts can

also occur from mobilization of metals naturally occurring in the solid phase into the groundwater. Although enhanced anaerobic *in situ* bioremediation processes will, in general, reduce the mobility of many metals (indeed it has been successfully used for the treatment of many), it will solubilize some other naturally occurring metals in the reactive zone (e.g., iron, manganese, and arsenic). However, even in solubilized form under anaerobic conditions, metals such as arsenic are substantially retarded by adsorption to the aquifer matrix. Furthermore, it is generally believed that they will be reprecipitated/immobilized downgradient of the reactive zone when the conditions return to their preexisting state (which, for the purposes of this discussion, is assumed to be aerobic). Similarly, reprecipitation/immobilization will occur within the IRZ area some time after system shutdown. These reducing conditions are by no means unique to IRZ systems – they occur, for example, at sites of total petroleum hydrocarbon (TPH) releases and landfills as well. The potential for secondary water quality impacts needs to be fully identified and addressed during design and in consultation with all applicable regulatory agencies and the public. No noteworthy secondary water quality impacts were measured during this demonstration.

2.0 Technology Description

2.1 Technology Development and Applications

IRZ technology developed from *ex situ* biological reactor and precipitation technology, which has been routinely used for decades to treat a broad range of inorganic and organic compounds. However, some of these *ex situ* processes involve addition of reagents, such as sulfide salts, which would be difficult to use *in situ*. Efforts over the last 15 to 20 years have demonstrated that similar treatment approaches can be engineered *in situ* while using only food grade additions. For instance, biotransformation of chlorinated aliphatic hydrocarbons (CAHs) under anaerobic conditions has been studied for two decades at various scales (Vogel and McCarty, 1985; Freedman and Gossett, 1989, Maymo-Gatell et al, 1995 and references cited therein). Researchers and remediation practitioners at ARCADIS recognized that biochemically-induced changes could be achieved without the need to inject potentially controversial reagents, and that naturally occurring mechanisms of attenuation could be enhanced.

In early 1994, when a commercial client requested an innovative remedial solution for chromate-impacted groundwater at a CERCLA site in Pennsylvania, ARCADIS injected a carbohydrate solution (molasses) as a reagent to enhance these processes. In this case the technical, regulatory, safety and economic concerns associated with sulfide injection were avoided by using molasses to achieve reducing conditions. The Pennsylvania project clearly demonstrated that carbohydrate IRZs could effectively produce controlled conditions required to remediate heavy metals. Subsequent projects have demonstrated the effectiveness of IRZs for remediation of CAHs and other organic and inorganic contaminants (Suthersan, 2002). Our experience has shown that molasses is not the only water soluble carbohydrate material that can be used for this purpose; other carbohydrates such as high fructose corn syrup and whey can also be effective. This approach has been accepted by regulators and has since been demonstrated in a wide variety of geological conditions with both high and low groundwater velocities. Enhancing CAH degradation using IRZ technology has become an accepted practice in the last several years, but we continue to improve the design and optimize performance of IRZ systems under varying conditions and for other contaminants.

In addition to CAHs and perchlorate, anaerobic biological IRZ processes have demonstrated or potential application to a wide spectrum of contaminants and co-contaminants such as:

- Chlorinated cyclic hydrocarbons, e.g., pentachlorophenol (PCP)
- Chlorinated pesticides, e.g., chlorinated propanes, lindane
- Metals, e.g., Cr^{+6} to Cr^{+3}; metal sulfide complexes of nickel and copper; metal-humic complexes of beryllium and other metals
- Other halogenated organic contaminants including chlorinated phenols and chlorinated pesticides
- Radionuclides (uranium)
- Energetics (TNT, RDX)
- Nitrate

2.1.1 General Technology Description for Perchlorate Bioremediation

IRZ technology is founded on the concept of enhancing natural processes in a subsurface system to create conditions more conducive to degradation of the targeted compound of concern (COC). As such, it can be classified as an anaerobic enhanced bioremediation process.

IRZ technology relies on enhancing biologically mediated reactions by supplying additional organic carbon as an energy substrate to the subsurface and driving ORP to a lower, more strongly reduced state. This is accomplished by supplying the naturally occurring microorganisms in the subsurface with an organic substrate in the form of a common carbohydrate solution that serves as an electron donor. ARCADIS has utilized multiple carbohydrate substrates during IRZ implementation including molasses, high fructose corn syrup (corn syrup), and cheese whey. These water soluble substrates have proven to function as cost-effective, innocuous amendments for groundwater and have been accepted for injection by multiple state and national regulatory agencies.

Indigenous heterotrophic microorganisms readily degrade the carbohydrate solution, which consists mostly of simple sugars. The rapid degradation process depletes the available dissolved oxygen contained in groundwater and the vadose zone, and drives the system to a more anaerobic and reduced state. In most cases the conditions in the groundwater prior to implementation are aerobic or anoxic, but not strongly anaerobic. Limited amounts of degradable organic carbon typically limit microbial populations and thus metabolic rates. The make-up of the bacterial community present in the subsurface prior to carbohydrate injection is shifted to bacterial species adapted to the changed anaerobic aquifer condition. Bacteria from the initial community remain and metabolize the carbohydrate solution to the extent that oxygen recharge permits. However, in the low oxygen environment, bacteria that are capable of utilizing alternate electron acceptors begin to occupy a more prominent role than in the previously aerobic subsurface environment. Bacterial processes such as nitrate reduction, iron reduction, and manganese reduction become increasingly dominant in the subsurface environment during this phase of IRZ development. With increasing amounts of injected electron donor, the ORP of the system can be driven further down into the –250 millivolt (mV) to –300 mV range. In this range, methanogenesis and sulfate reduction begin to co-occur as bacterial processes with carbon dioxide and sulfate being utilized as the predominant electron acceptors. Methanogenic and sulfate reducing conditions are necessary for efficient treatment of CAHs and metals (Suthersan, 2002). Perchlorate reduction on the other hand occurs in the same mildly reducing ORP range as nitrate reduction. It is thus ARCADIS' intent at sites where perchlorate is the primary issue to control ORP to a range characteristic of nitrate reduction through appropriate electron donor dosing and subsequent monitoring. In the event that the dose needed to achieve nitrate/perchlorate reduction is locally exceeded, sulfate reduction and subsequent hydrogen sulfide release will be minimal due to the lack of sulfur in the electron donor chosen for this demonstration. This is important in this case since the production of hydrogen sulfide in a drinking water aquifer in proximity to supply wells is discouraged.

Research has demonstrated that many nitrate reducing bacteria can also utilize perchlorate as a terminal electron acceptor with more than thirty microorganisms having been identified from diverse environments that are capable of degrading perchlorate (Coates et al., 1999). Chlorate-reducing microorganisms have been identified as falling primarily into two groups: the *Dechlorimonas* group and the *Dechlorisoma* group. Members of these groups have been identified in nearly all environments screened in bench-scale studies, suggesting that these organisms may represent the predominant perchlorate reducing bacteria in the environment.

Bacterial reduction of perchlorate occurs as a result of anaerobic respiration. Anaerobic respiration couples the oxidation of an electron donor, such as an organic substrate (e.g., carbohydrates), or an inorganic molecule (e.g., hydrogen), to the reduction of a final electron acceptor (e.g., perchlorate). Under anaerobic conditions, oxidation of an electron donor requires the use of an alternative electron acceptor in place of oxygen, such as nitrate, manganese (IV), iron (III), or sulfate. As a highly oxidized compound (+7 oxidation state), perchlorate (ClO_4^-) has high potential for utilization as an alternate electron acceptor. For example, Rikken et al., (1996) provided equations for the stoichiometric reaction of acetate with either oxygen or perchlorate as electron acceptors follows:

$$CH_3COO^- + 2O_2 \rightarrow 2\ HCO_3^- + H^+ \ (\Delta G^\theta = -844 \text{ kilojoules/mole or kJ/mol})$$

$$CH_3COO^- + ClO_4^- \rightarrow 2\ HCO_3^- + H^+ + Cl^- \ (\Delta G^\theta = -966 \text{ kJ/mol})$$

Comparing the Gibbs free-energy changes (ΔG^θ, kJ/mol acetate), it is evident that perchlorate reduction is energetically favorable. The reduction of perchlorate under anaerobic growth conditions has revealed that perchlorate can be completely reduced to chloride and oxygen (Rikken et al., 1996; Attaway and Smith, 1993; Wallace et al., 1996). Rikken et al., (1996) proposed a pathway for perchlorate reduction. The environmental science community has now largely accepted this pathway. The chlorate and chlorite are generally accepted as transient daughter products:

$ClO_4^- \rightarrow$	$ClO_3^- \rightarrow$	$ClO_2^- \rightarrow$	$Cl^- + O_2$
Perchlorate	chlorate	chlorite	chloride

Through subsurface electron donor amendments, ARCADIS encourages this biological process in the field by altering existing aerobic or mildly anoxic aquifer to an anaerobic reactive zone. This creates suitable conditions for the biodegradation of perchlorate. Because perchlorate remediation occurs along with nitrate reduction under mildly reducing conditions, ARCADIS intends to dose the electron donor in a conservative manner initially at sites where perchlorate is the primary concern. The intent of conservative electron donor dosing is to avoid the development of undesirable bacterial processes such as excess fermentation, which will result in the production of organic acids and potentially lower aquifer pH unless a buffer is also used.

The reactive zone performance following carbohydrate enhancement is measured by evaluating changes in the subsurface environment such as DO, ORP, pH, organic carbon, and specific conductance as well as changes in concentration of the target chemicals and degradation products.

When properly applied, ARCADIS has had only very limited challenges associated with biofouling near the injection well. Proper IRZ implementation results in the formation of an anaerobic zone within the aquifer. Due to the reduction in energy available under anaerobic conditions, the growth of bacteria under anaerobic conditions is greatly curtailed. Nonetheless, if biofouling is encountered, it can be addressed by injecting a hydrogen peroxide solution or by simply “surging” the water in the injection well.

When remediation is complete, as the carbohydrate in the subsurface is depleted, the bacteria enter a phase of endogenous metabolism, in which subsurface biomass is decreased to background levels. The end products of endogenous metabolism are water, carbon dioxide, mineralized nitrogen (N_2), and limited amounts of methane.

In practice, IRZ can be operated as an *in situ* bioreactor as a curtain that forms downgradient from a line of substrate injection wells placed in a line perpendicular to groundwater flow. Alternately, it can be injected in a broad area to remediate a source zone or a whole plume. A conceptual design of the process has been provided as Figure 2-1. Substrate delivery can be implemented in a variety of ways, including fixed, automated systems and mobile, manually controlled systems. The particular system used in this demonstration was located at JPL and was stationary consisting of standard equipment such as tanks, mixers, and pumps (see Figure 2-2 for a schematic of this system).

2.1.2 Design Criteria

The key parameters considered in an IRZ system design include:

- Formation geochemistry (including the concentrations of electron acceptors such as dissolved oxygen [DO], nitrate, and sulfate; pH and buffering capacity)
- Site-specific hydrogeology (including depth to water, saturated thickness, hydraulic conductivity,average horizontal linear velocity and any vertical gradients)
- Contaminant form (dissolved, sorbed or free phase) and concentration or mass.

Ultimate design goals include contaminant removal rates and closure requirements typically expressed as concentrations. Interim design goals are set to ensure the creation of appropriate conditions for perchlorate biodegradation and may typically include the following ranges for field parameters (in this context, monitoring wells are 1 to 3 months downgradient of injection wells):

- pH - greater than 4.0 s.u. at injection wells; greater than 5.0 s.u. at monitoring wells
- DO – less than 1.0 mg/L at both monitoring and injection wells
- Oxidation-reduction potential (ORP) – greater than -250 mV and less than -100 mV at injection wells; less than -100 mV at monitoring wells. Note however that these ORP values should not be taken as absolutes since ORP is pH dependent. For sites where reducing environments are identified in the groundwater prior to initiation of reagent injections, a target goal of lowering the ORP by 200 mV at injection wells and 100 mV at monitoring wells should be employed.
- Total organic carbon (TOC) – greater than 500 mg/L and less than 9,000 mg/L at injection wells and greater than 50 mg/L at monitoring wells
- Specific conductance – order of magnitude increase at injection wells; 20 to 50% increase at monitoring wells

To achieve those goals, parameters that must be specified during system design include:

- Substrate to be used and initial dose rate
- Intended radius of influence/injection well spacing
- Injection and monitoring well layout (which may be a barrier, source zone or plume treatment system)
- Injection system type (manual vs. automated, conventional well vs. direct push, etc.)
- Systems to handle byproducts (which may require injection of buffers or the use of ventilation systems under structures).

Pilot testing is usually required to refine design estimates, and adjustment or "tuning" of the dosage size and frequency during operation is critical in achieving and maintaining optimum biogeochemical conditions.

2.2 Previous Testing of the Technology

As of November 2003, ARCADIS has been involved with more than 170 IRZ sites, across eight countries and 32 U.S. states. Fifty of these sites are full-scale implementations, six of which have achieved closure. The other sites are ongoing pilot applications, or Interim Remedial Measures, or they are completed pilot projects that are now in the full-scale design phase. The technology has successfully been applied to the following chlorinated compounds and metals:

- PCE, TCE, DCE, VC, CT, chloroform (CF), chlorinated propanes, PCP, pesticides, trichlorofluoromethane, and perchlorate;
- Hexavalent chromium, nickel, lead, cadmium, mercury, and uranium.

ARCADIS' CAH IRZ protocol document (Suthersan et al., 2002) includes information on specific IRZ sites for a variety of contaminants, as well as 15 case studies. An extensive bibliography of papers and book chapters published on this technology is also available in the protocol document.

2.3 Factors Affecting Cost and Performance

Although application of IRZ using soluble carbohydrates can occur in a variety of hydrogeologic settings, there are certain conditions that are better suited for cost-effective use of the technology. Existing conditions that are anaerobic or borderline aerobic/anaerobic but with insufficient TOC can be most rapidly treated. Conditions that are anaerobic and already have sufficient degradable TOC may not be aided substantially by addition of soluble carbohydrates. One of the most important criteria is hydraulic conductivity. Generally, hydraulic conductivity of the aquifer needs to be greater than 1 ft/day and when coupled with hydraulic gradients, groundwater velocities on the order of 30 ft/year, or greater, are desirable. Another important criterion is the pH, which should be initially in the range from about 5 to 9 in order to ensure the presence of an active microbial population (if initial pH is outside this range an initial microbial population screening should be done before pilot testing).

Implementation of an IRZ project is a dynamic process which requires a detailed understanding of the site geochemistry and hydrogeologic conditions before implementation and as they change as a result of pilot or full-scale implementation. The technology is most likely to be successful when there is considerable process monitoring during the initial deployment of the pilot test that allows for adjustment of reagent deliverability (strength and frequency). Where IRZ technology has failed, or has required longer than expected treatment periods, it is usually the result of improper monitoring (the wrong parameters or the wrong frequency) or data evaluation in the early stages of the pilot test. TOC loading and induced gradients must be reviewed early in the pilot process to allow delivery rates to be increased (for greater spreading and greater TOC levels within the treatment area) or reduced (or a buffering agent added), if pH levels drop too quickly.

Similarly, the effects of reagent injections must be reviewed in the context of how the addition of aqueous solutions affect hydraulic gradients (i.e., mounding) and flow directions. Groundwater flow directions and gradients should be viewed both in a macro- and micro-scale before and during the demonstrations.

Once a preliminary determination has been made that IRZ is an appropriate technology option to consider for the site, a more detailed data set needs to be gathered. Information required to fully review a site for IRZ includes:

- Site-specific geology and hydrogeology, including: boring logs, predominant aquifer lithology, aquifer hydraulic characteristics, horizontal and vertical hydraulic gradient, groundwater velocity, and depth to water
- Contaminant concentrations and distribution, both current and historical, if available
- If available, data on general groundwater quality such as TDS, specific conductance, pH, DOC, carbonate and bicarbonate alkalinity, and general cation/anions (calcium, magnesium, sodium, potassium, chloride, sulfate, and nitrate)

- Any previously gathered biogeochemical data, including ORP, nitrate, sulfate/hydrogen sulfide, ferric/ferrous iron, DO, and trace gases (including methane, hydrogen, carbon dioxide, ethane, and ethene)
- The site's situation (regulatory drivers, stage in the investigation/remediation process, clean-up goals and time frames, future plans for the site)
- Brief historical information on the site (source of contaminant, estimated date of release, and duration of release events)
- Maps showing the relationship of active operational areas (buildings, etc.) and impervious surfaces (roads and parking lots) to the contaminant plume(s).

Table 2-1 provides a comprehensive overview of cost elements associated with an IRZ project.
In a general sense, with an IRZ system, the cost of the reagent material itself is relatively insignificant. A goal should be to minimize overall project cost by minimizing the number of required injection points, the number of injection events, and reagent cost (Harkness, 2000). The physical characteristics of the substrate (i.e., phase and solubility) may make certain substrates more suitable than others in particular applications.

The majority of the costs related to reagent injection include the labor associated with preparing the reagent mixture and injecting the material into the wells/points along with related costs (mobilization to the site, record keeping, preparation, etc.) Temporary equipment required for the injections includes a solution mixing/holding tank, a portable mixer, a transfer pump, and injection piping/hose. This equipment should be sized and consistent with use at the pilot test site and can be mobilized to each site in a conventional pick-up truck or by trailer. The mixer can be simple as a paddle, or agitation of the tank through truck movement. A nontoxic, non-reactive tracer or pH buffers may also be included in the reagent solutions. Permanent equipment at the various injection wells includes a removable well seal for the injection wellhead, removable perforated diffuser tubing (to assure even reagent distribution along the screened interval of the well), and quick-disconnect fittings to allow easy attachment of the injection piping/hose to the diffuser tubes for the injection itself.

Budgetary limitations can often directly or indirectly affect design decisions such as source reduction versus plume-wide treatment. ARCADIS' IRZ protocol document (Suthersan et al., 2002) contains specific information regarding the technology application cost (capital and operation and maintenance) at a variety of sites in which IRZ has been successfully applied. Based on ARCADIS' experience and analysis, the two largest cost factors for IRZ implementation are the injection well installation and the O&M associated with reagent injections. Three other factors that need to be given special consideration during design in order to develop the most cost effective approach for site remediation are:

1. Plume Size to be Treated – This is the primary factor driving the cost of the technology as the larger the plume area to be treated, the more wells are needed (drilling costs) and the more time it takes for reagent delivery.
2. Depth of Target Zone – Drilling costs are the primary factor affecting technology cost for all in-situ technologies not just IRZ. Therefore, deep contaminant settings and/or those requiring specialized drilling techniques (bedrock drilling, multiple conductor casings, etc.) can significantly increase costs. The depth to groundwater will define well design and contribute significantly to the capital cost of a full-scale system. The saturated thickness can also have an influence on cost, since there are practical limits on the maximum screened interval that can effectively be used in an injection well. Based on our experience, a 40-foot screened interval represents a practical limit for a conventionally designed injection point. Of course, this limit will be impacted by the heterogeneity of the subsurface lithology, depth of the screened interval,

hydraulic conductivity, and the resulting effects on groundwater flow characteristics. For example, if the lithology and resultant groundwater flow characteristics are such that there are variations in the flow characteristics within the target saturated interval, the use of multiple screened zones or multiple well points should be considered – even if the interval is less than 25 feet.

3. Groundwater Flux through Zone of Treatment – Reagent injections also play a large role in overall technology costs. At sites at which there is a high groundwater flux, more substrate will be required, thereby increasing costs (note that high flow raises the cost of all remediation technologies – not only IRZ). In faster groundwater flow systems, the limited transverse dispersion in groundwater can limit the extent of the reactive zone created by an individual injection point. This is of particular importance in settings where drilling costs may be high, i.e., deep settings or complex geology. In such cases, an *in situ* recirculation well can yield considerable cost savings over use of direct injection wells. The *in situ* recirculation well concept aims primarily at delivering reagents in a cost-effective manner while remediating larger, deeper contaminant plumes at sites with relatively high groundwater velocities.

2.4 Advantages and Limitations of the Technology

The most well-established remediation option for sites contaminated with perchlorate involves groundwater extraction followed by treatment using ion exchange, or aboveground bioreactors. This approach is also known as pump-and-treat, where impacted groundwater is removed to the surface for treatment and discharge. P&T is a conventional groundwater containment technology with well-documented limitations (of the effectiveness of the extraction system) due to the tendency of pollutants to remain behind in the aquifer in adsorbed phases or in low water mobility zones within the aquifer. This in turn means the systems incur long-term operation-and-maintenance costs, which can be prohibitively expensive. Perchlorate, because it is minimally adsorptive and water soluble, does not present the mass transfer limitations on pump-and-treat that other contaminants (notably CAHs) do. However, it is subject as is any dissolved contaminant to inefficiencies in extraction due to subsurface heterogeneities. The treatment technologies for perchlorate are also expensive to build and operate. The primary advantages of IRZ over pump-and-treat approaches can be summarized as follows:

- The *in situ* process eliminates the need for transferring contaminant mass to other media (such as groundwater extraction and subsequent treatment with ion exchange does)
- IRZ processes have a potential application to a wide spectrum of contaminants and co-contaminants
- No *ex situ* waste is generated
- The process uses electron donor sources that are typically easily accepted by regulators and the public
- The biologically-mediated reactions involved can generally be driven by indigenous microflora
- The technology is flexible in application, yielding a spectrum of contaminant mass treatment options from passive/containment barrier applications to aggressive source area applications
- IRZ enhances natural perchlorate attenuation processes
- IRZ is applicable to various geological settings and aquifer conditions
- The electron donor source is highly soluble and can move through both diffusive and advective processes into difficult lithologies such as fractured bedrock

- Systems can be designed with flexible operation approaches ranging from automated systems to manual bulk application
- The technology can be used in tandem with existing remediation systems to optimize performance
- Systems can be designed for minimal disturbance to site and facility operations

All *in situ* remediation technologies have an inherent limitation associated with subsurface conditions. The geology in which the technology is being applied will exert considerable control over remediation efficacy. This can be compensated for to a great extent by a complete understanding of the geochemical and hydrological conditions of the aquifer system to be treated. A good conceptual model of the aquifer will produce a more effective IRZ design. Potential limitations to the application of the IRZ technology as applied to perchlorate can be summarized as follows:

- An excessive depth of contamination tends to raise costs
- Low permeability aquifers require more injection points
- High permeability aquifers with high groundwater flows require a large amount of reactant to establish a reducing environment due to dilution and oxygen recharge
- Heterogeneous lithology, which incorporates preferential flow paths, can limit the distribution of the injected substrate
- A medium of limited porosity, such as fractured bedrock, minimizes the propagation of the reactive zone
- Biological fouling of injection wells resulting from reagent injection is theoretically possible but is rarely observed in practice
- Systems with large amounts or influxes of electron acceptors such as oxygen, nitrate or soluble iron can require large doses of substrate; however, substrate cost is typically a small fraction of the total project cost
- The production of excessive quantities of reduced gases such as methane can be problematic in the vicinity of confined structures. Also, the production of byproduct organic compounds containing reduced sulfur or nitrogen, including hydrogen sulfide, is possible.
- Highly brackish aquifers can pose problematic microbial ecology requiring more careful microbial evaluation before project implementation
- Fermentation effects of carbohydrate loading can create conditions conducive to formation of aldehydes, ketones and mercaptans, which, however, can then be further degraded biologically. Excessive fermentation can also decrease pH and potentially mobilize naturally occurring metals.

These potential limitations are general guidelines to be considered when evaluating potential sites for IRZ treatment. Site-specific constraints should be considered for all remediation technology options.

3.0 Facility Description and History

JPL is a federal facility under the jurisdiction of the National Aeronautics and Space Administration (NASA). The facility is a research and development (R&D) laboratory primarily used for aeronautics, space technology, and space transportation programs. JPL is located along the southern edge of the San Gabriel Mountains and at the northern edge of the metropolitan Los Angeles area. JPL encompasses approximately 176 acres, of which approximately 156 acres are federally owned. The term "JPL" is used throughout this document to refer to the facility located at 4800 Oak Grove Drive, Pasadena, California. The location and boundaries of the JPL site are shown on Figure 3-1.

Testing of liquid propellant rockets by a California Institute of Technology (CalTech) professor began in the Arroyo Seco in 1936. The United States Army developed and contracted with JPL between 1939 and 1958 as an R&D laboratory for ordnance activities. In July 1940, CalTech and U.S. Army Air Corps, entered into a contract under which CalTech agreed to study jet propulsion for airplanes. This contract was the first of a series of JPL contracts between CalTech and the United States that span the last 59 years for research and development work at JPL.

By 1944, the facility officially became known as the Jet Propulsion Laboratory. In 1958, jurisdiction was transferred to NASA at which time R&D efforts at JPL began to focus on aeronautics, space technology, and space transportation. During historic operations at JPL, various chemicals (including chlorinated solvents, solid rocket fuel propellants, cooling tower chemicals, sulfuric acid, Freon™, and mercury) and other materials were used at the site.

In 1992, JPL was placed on the National Priority List (NPL) of sites subject to regulations under CERCLA. The JPL Superfund site has been divided into 3 operable units (OUs). OU-1 is on-facility groundwater at JPL; OU-2 is on-facility vadose zone soil at JPL; and OU-3 is off-facility groundwater adjacent to the JPL property.

A final Remedial Investigation (RI) report was completed in 1999 at JPL. The RI report identifies 40 seepage/disposal pits, 5 waste pits, 4 discharge points at the site, and chemicals of concern from past site operations that have been detected in JPL soil and groundwater (Foster Wheeler 1999). Perchlorate is believed to have been released to the environment through discharges to seepage/disposal pits or discharge pits in either as a solid or dissolved in process water. The RI concludes that there appears to be more than one perchlorate source at JPL.

Some of the seepage pits received VOCs and other waste materials that are currently found in vadose zone soil and groundwater at JPL. In the late 1950s and early 1960s, a sanitary sewer system was installed at JPL to handle sewage and wastewater, and the use of seepage pits for sanitary and chemical waste disposal was discontinued. Today, laboratory chemical wastes are either recycled or sent off-site for treatment and disposal at regulated facilities.

In 1980, analyses of groundwater from Pasadena water-supply wells located in the Arroyo Seco, near JPL, revealed the presence of VOCs. Around the same time, VOCs were also detected in two Lincoln Avenue Water Company (Lincoln) supply wells. As a result, the Pasadena and Lincoln wells near JPL discontinued pumping between 1985 and 1989. In 1990, NASA funded the installation of a water treatment plant in the Arroyo Seco to treat these VOCs and allow the Pasadena wells to resume normal operations.

The groundwater beneath and downgradient of the JPL facility has been divided into two operable units, Operable Unit 1 (OU-1) for groundwater beneath JPL and extending to the east across the Arroyo Seco,

and Operable Unit 3 (OU-3) for groundwater off-facility to the south of JPL and east of the Arroyo Seco. Operable Unit 2 (OU-2) is the designation for the on-facility source investigation in soils.
The site of the ARCADIS IRZ demonstration was within OU-1. During the first half of 1997, the California Department of Health Services (CDHS) began an extensive screening for perchlorate in several hundred drinking water wells around the state (http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/earlyfindings.htm). As a result of the perchlorate detections that occurred during this screening, CDHS developed and released an improved analytical methodology for perchlorate on June 3, 1997 (http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/clo4meth.pdf). Based on the timing of JPL perchlorate analyses discussed in the OU-1/3 Remedial Investigation Report (RI) dated August 1999, ARCADIS anticipates that the bulk of early perchlorate analysis at JPL was conducted using the improved analytical methodology (Foster Wheeler Environmental Corporation, RI Report) and its associated lower detection limit of 4 µg/L.

3.1 Facility Characteristics

JPL is located along the southern edge of the San Gabriel Mountains and the northern edge of the metropolitan Los Angeles area. JPL encompasses approximately 176 acres, of which approximately 156 acres are federally owned. The Arroyo Seco, an intermittent stream, lies immediately to the east of JPL. A series of surface impoundments, used for groundwater recharge, lie along the eastern margin of the Arroyo Seco stream channel. The Arroyo Seco continues south of JPL to the Los Angeles River.
The JPL facility is located within the northeastern segment of the San Gabriel Valley in the eastern portion of Los Angeles County. It is bounded on the south by east-to-west trending hills including the Repetto, San Raphael, Puente, and San Jose Hills (RWQCB 1994). This local hill system rises about 500 feet from the valley floor separating the southern edge of the San Gabriel Valley from the coastal plain of Los Angeles.

The JPL facility is bounded to the north by the San Gabriel Mountains. The San Gabriel Mountains range from about 1,500 feet in elevation along their base to a maximum elevation of more than 10,000 feet above sea level. The San Gabriel Valley is a broad plain that slopes generally to the south, downward from the base of the San Gabriel Mountains. The average slope of the valley floor is about 65 feet per mile. The rivers and tributaries that traverse the valley floor generally flow in a southerly direction. Almost all natural surface outflow from the San Gabriel Valley passes through the Whittier Narrows to the south (Foster Wheeler 1999).

The JPL facility was constructed on an alluvial fan system originating from the southern slope of the adjacent San Gabriel Mountains. As a result, the facility is terraced from north-to-south with most buildings leveled by jacks, supports, columns, or construction cuts into soil to provide horizontal grade.

3.2 JPL Site Geology and Hydrogeology

The general local and regional geology of the JPL area and the previous geologic and hydrogeologic investigations at the facility are summarized in the RI report (Foster Wheeler 1999). The RI report was reviewed along with geologic maps of the area from Dibblee (1989) and DMG (1969), and the geologic study and maps from Smith (1986) to extract information relevant to the pilot study objectives.

Groundwater is present primarily in the unconsolidated alluvial sediments in the JPL area and these units range in thickness up to about 1,100 feet. At depth is the conglomerate, gravel, arkosic sand (derived from the disintegration of granite or gneiss, and characterized by feldspar fragments) and boulders of the Pacoima Formation, which overlies crystalline rock below most of the JPL area (Foster Wheeler 1999). Overlying the Pacoima Formation throughout the study area is the Older Fanglomerate Series. This water-

bearing alluvial unit consists of arkosic sands with abundant gravel and boulders, and is faulted by the JPL Fault trending roughly east-west just south of Building 299.

For the RI, the Older Fanglomerate Series was divided into an upper and lower section, each representing a groundwater flow model layer (Layers 1 and 2). The layers were identified with geophysical log features, geochemical signature, and the variation in water levels with nearby potable well pumping. The variable water level response to pumping stress was related to low permeability units between the model layers that appear to inhibit vertical groundwater flow (Foster Wheeler 1999).

Groundwater elevation has been measured in JPL monitoring wells from approximately 22 to 270 feet below grade in both Layers 1 and 2. This relatively wide range of groundwater depths is due to terraced topography, geologic structure, hydrogeologic boundaries, variable natural and artificial recharge, and historical production well pumping in the vicinity of JPL (Foster Wheeler 1999).

Groundwater flows generally to the southeast at JPL down the alluvial fan system. However, localized flow components are in a more easterly direction. Site wide flow reversals have been recognized. Flow reversals are a result of the effects of nearby significant hydrogeologic boundaries, such as the recharge basins at the eastern facility boundary, where groundwater mounding is typical. Additionally, to the south and southeast of the JPL facility, active groundwater production wells can influence hydrogeology at the site.

In the location where JPL was built [within the Monk Hill Sub basin of the larger Raymond Basin, within the San Gabriel Valley (RWQCB 1994)], several cities and water companies installed supply wells for potable water extraction. As noted in the RI, groundwater elevations and flow direction at JPL fluctuate significantly with supply well pumping, primarily from the City of Pasadena wells in the nearby Arroyo Seco to the east of JPL. However, these wells have been deactivated since January 2002.

3.3 Pilot Study Area Geology and Hydrogeology

The focus of this demonstration is *in situ* perchlorate remediation. Associated in part with advances in perchlorate analytical chemistry, perchlorate was detected in groundwater during the RI and traced back to several potential upgradient vadose zone source areas.

The pilot test demonstration detailed in this report was completed in the parking area just north of JPL Building 288 and south of Buildings 299 and 117, where existing monitoring well MW-7 is located. A map showing the demonstration location on the JPL facility is provided as Figure 3-2.

This area was selected for the pilot study based on site accessibility and the detected concentrations of perchlorate in MW-7 groundwater (i.e., MW-7 is located within the current contour of 500 µg/L perchlorate in groundwater).

The lithology logged in the four main pilot test boreholes is consistent with the lithology of the terrigenous clastic, alluvial, depositional environment described and reported in the RI report: The subsurface between grade and about 375 feet below grade at the MW-7 area consists of unconsolidated detrital sand of varying grain size, commonly angular, with varying amounts of silt, clay, cobbles and boulders in a thick, massive sequence with little or no typical correlating stratigraphic markers, such as distinct contacts, beds, layers, or lenses. The following details are evident in the pilot test area boring logs:

- Perched groundwater was not encountered;

- Distinct, correlating clay beds or lenses were not encountered;
- The screened intervals of wells IRZMW-1 and IRZMW-3, along the west side of the pilot test area, are relatively more clay-rich than adjacent borings, although gravels and cobbles are common;
- The screened intervals of wells IW-1 and IRZMW-2, along the east side of the pilot test area, are relatively less clay-rich than adjacent borings, while gravels and cobbles are common;
- Isolated boulders were encountered and cored in each borehole at shallow, intermediate, and deep depths within the boring;
- Cobbles and coarse gravel were commonly encountered in each boring;
- Slickensides1 were observed and logged in boring IW-2 at 110 feet, and interpreted to be indicative of the JPL thrust fault; and
- Minor slickensides were encountered in boring IW-2 at 36 feet that were interpreted to be indicative of a minor, perhaps normal, fault associated with the larger JPL thrust fault.

Based on earlier investigation efforts, ARCADIS believed that the vadose zone structure in the demonstration area might contain geology supportive of the generation of perched groundwater scenarios. Extensive effort was expended looking for vadose zone perchlorate source areas during the installation of each of the wells involved in the pilot study. Though perchlorate is extremely soluble, previous investigation suggested the possibility that perchlorate might accumulate in geology supportive of perched groundwater. Accumulation of perchlorate in a hypothetical perched groundwater setting would represent a continuing subsurface perchlorate source at the JPL site. Consequently, careful planning had been conducted to facilitate remediating any perchlorate detected in the vadose zone using the IRZ technology. Despite the assessment by ARCADIS and NFESC that vadose zone perchlorate was likely to be found in the demonstration area, extensive soil analysis did not result in perchlorate detection. Next, with supplemental funding approved by NFESC and JPL, ARCADIS installed one borehole in the former Pit No. 30 area in an effort to locate vadose zone perchlorate so as to support the implementation of the portion of the workplan dealing with vadose zone perchlorate remediation. Again, vadose zone perchlorate was not detected in the former Pit No. 30 area. Therefore, the portions of the work plan addressing the remediation of vadose zone perchlorate were not implemented due to a general lack of conditions supportive of this portion of the planned demonstration.

During drilling, saturated sediments were encountered at approximately 245 to 255 feet below grade in each boring except IRZMW-3 where saturated sediments were first encountered at about 300 feet below grade. In late February and early March 2003, once the pilot test wells were installed and developed, groundwater had stabilized at a higher elevation within the test area at approximately 209 feet below grade or about 1,006 feet above mean sea level.

Water levels were measured several times over the course of the pilot test. Groundwater elevation contour maps constructed with the data indicate that groundwater flow direction is oriented largely to the southeast with minor flow components oriented south and oriented east. Coupled with the 7.8 feet per day hydraulic conductivity estimate from the December 1994 MW-7 aquifer test (Foster Wheeler 1999), the groundwater gradient of 0.02 measured from the March 2003 water level data indicates that groundwater flows at approximately 0.58 feet per day across the test area.

By May 2003 and prior to the first pilot test injection, groundwater levels had increased about 20 feet to about 188 feet below grade or 1,028 feet above mean sea level. This water level increase may be due to

[1] A slickenside is a polished rock surface with distinct step-like striations indicative and diagnostic of faulting.

increased local recharge from periods of rain recorded during the first and second quarters of 2003 in the JPL area or potential activity on the adjacent JPL fault. The fluctuations are not interpreted to be due to local supply well pumping because the Pasadena Water and Power supply wells are inactive and other area wells did not significantly affect JPL water levels during RI pumping tests (Foster Wheeler 1999).

Thereafter, duration of the pilot test from May to September 2003, groundwater levels slowly declined about 20 feet to about 1,008 feet above mean sea level. These water level changes, with corresponding changes in groundwater gradient and flow velocity, are discussed further in Section 7.3.3.

3.4 Distribution of Perchlorate in Groundwater

The perchlorate anion has been detected in Aquifer Layer 1, Layer 2, and Layer 3 during the RI (Foster Wheeler 1999). The plume shape and extent suggests that dissolved perchlorate originates from multiple vadose zone source areas in the north central portion of JPL. Research into the health impacts of perchlorate continues. In addition, analytical chemistry improvements are lowering the perchlorate detection limit. Both of these factors have the potential to influence perchlorate remediation at JPL.

For the purposes of the pilot study, the portion of the site that will be evaluated for full-scale treatment is that area within the 500 μg/L isoconcentration contour for perchlorate developed from the most-recent groundwater-monitoring event. This area includes three monitoring wells (MW-7, MW-16, and MW-24) located in OU-1. In addition to elevated levels of perchlorate, groundwater in this area also includes elevated levels of CVOCs; primarily carbon tetrachloride. A comprehensive discussion of the nature and extent of chemicals in this area can be found in the RI report (Foster Wheeler 1999).

The RI concludes there are multiple vadose zone perchlorate source areas located in the northeast portion of the JPL facility in and around monitoring wells MW-7, MW-16, and MW-24. The perchlorate source area contour, currently defined at 500 μg/L in the OU-1/3 RI, is contained within the facility boundaries making the search for source areas widespread geographically.

Figure 3-3 provides quarterly perchlorate groundwater monitoring data from MW-7, which is a monitoring well sampled repeatedly during this demonstration. Perchlorate concentrations in MW-7 were seen to rapidly increase in the spring of 2001 and have remained consistently above 2 milligrams per liter (mg/L) since that time. ARCADIS is uncertain of what sequence of events resulted in this increase in perchlorate levels in MW-7 groundwater starting in early 2001. The answer to this question could assist with the location of any remaining vadose zone perchlorate source areas at JPL.

4.0 Pre-Demonstration Administrative Activities

4.1 Permitting

Section 121 (e)(l) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) exempts EPA from having to obtain permits (local, state, or federal) for any Remedial Action (RA) conducted entirely o*n-site*; however, the "substantive requirements" of such permits must still be met. This applies to all permits, including environmental and building permits. However, the formal permitting process must be completed for any off-facility activities, as they are not exempt under CERCLA.

ARCADIS abided by the substantive permitting requirements associated with Los Angeles County for well installation. In addition, ARCADIS contacted the Los Angeles Regional Water Quality Control Board (RWQCB) to confirm the CERCLA exemption for this project and to discuss the applicable sampling and monitoring required under the Waste Discharge Requirements General Approval Permit (WDR permit). Health and safety during the pilot study were conducted in accordance with the OSHA and Cal-OSHA requirements.

4.2 Facility Access

ARCADIS worked within the guidelines set forth by JPL to obtain access for personnel and equipment as detailed below.

Several weeks prior to performing field activities, ARCADIS submitted a technical memorandum to NASA, which provided detailed discussion of the proposed fieldwork dated August 22, 2002. NASA then coordinated field activities with Caltech to ensure that the demonstration did not have any direct impacts on sensitive JPL operations. The ARCADIS field manager conducted a site walk identifying work areas, equipment staging areas, and other coordination concerns that needed to be addressed.

Two weeks prior to the start of field activities, a final technical memorandum was submitted to NASA. The revised memorandum addressed issues and/or concerns that were raised to NASA by Caltech. The following items were addressed in the technical memorandum.

- Proposed field activities,
- Objective of field activities,
- Pre-fieldwork preparation (i.e. site drawing review, geophysical survey, etc.),
- Work area space requirements,
- Field activity schedule, and
- Scaled drawing identifying number of parking spaces needed, any road blockages.

4.3 Site Drawing Review

Prior to commencement of field activities, available site drawings of the immediate work area were reviewed to determine if any underground or overhead utilities were present that would conflict with our activities. ARCADIS personnel visited Mr. Paul Kulkarni and Mr. Manuel Mendez of the JPL Facilities Engineering and Construction Section on July 22 and November 26, 2002. ARCADIS personnel examined engineering plans for utilities that were likely to be present in the pilot test area. These included domestic water, natural gas, sanitary sewer storm drains, compressed air, cooling tower water, nitrogen or

other gaseous systems, electrical primary or secondary power lines, fire protection, and/or instrumentation cables. The information gathered during the document review was used to focus the subsequent geophysical investigation. Only one area of potential concern was identified during the document review along the northern edge of the pilot test area. Underground electrical lines for the parking lot lights were noted in the vicinity; however, the geophysical investigation identified that their specific location and confirmed that they did not conflict with the ARCADIS pilot test.

4.4 Employee Clearance

ARCADIS included the names of its employees and those of authorized subcontractors in an email communication to Ms. Leticia Woodard of JPL on June 18, 2002. After this initial communication was reviewed, the listed ARCADIS employees and subcontractors were granted unescorted access to the portion of the JPL facility where the demonstration was sited. ARCADIS kept in communication with Ms. Leticia Woodward throughout the duration of field activities, and updated this authorization list in accordance with JPL visitor procedures.

5.0 Pre-Demonstration Field and Laboratory Activities

5.1 Geophysical Survey

ARCADIS enlisted the service of Spectrum Geophysics (Spectrum) to conduct geophysical investigations at the test area. Spectrum employed both surface and electromagnetic geophysical methods to determine subsurface structures as specified below.

Surface geophysical techniques included, but were not limited to, ground penetrating radar (GPR), magnetic, and electromagnetic techniques. The objectives of these techniques are to locate the boundaries of suspected or known underground metallic objects, electrically-conductive materials or volumes of disturbed soil. The areas that were surveyed were the work areas shown on site maps presented in Figures 5-1 and 5-2.

The surface geophysical survey was conducted within predetermined grids defined by transect lines crossing each site or area of interest. The spacing of the grids was determined from the approximate dimensions of the features to be located. Specifically, the areas of interest include the well boring locations as well as the former Pit No. 30 area. Qualified individuals conducted the surveys and a California Registered Geophysicist (RGP) supervised them. Location data, instrument numbers, calibration information, geophysical interpretation, and maps for all geophysical surveys are stored in the project files.

Electromagnetic utility location methods are commonly employed techniques to detect utilities constructed of electrically conductive materials. Examples of these utilities include water, natural gas, telephone, electric, and fuel lines.

Typically, a radio frequency (RF) signal is induced into the electrically conductive conduit. This signal is propagated along its length and is detected above ground with a matched-frequency receiver. Often, underground water, electrical, oil-transmission, and telephone utilities radiate their own electromagnetic field and this field can be detected using an RF receiver alone. By detecting the signal maxima at several locations, the surface trace and burial depths of the underground utility can be determined. Non-electrically conductive conduits, such as storm drains and sewers, are generally more difficult to detect with these methods. One technique to determine their surface trace is to insert a small RF transmitter. An RF receiver is then used at the surface to detect an area of maximum signal strength. A series of these areas or points yields the surface trace of the conduit.

A variety of utility locating instruments were utilized to locate the utilities in the proposed work areas. The geophysical surveys were implemented solely for location and avoidance of underground utilities during well installation and did not have specific investigational goals relative to perchlorate contamination. On November 4, 2002, the geophysical subcontractor located an electrical conduit for the overhead parking lights in the MW-7 parking lot area. Numerous utility lines were located in the area of Pit No. 30 on December 7, 2002. Despite the dense utilities in this area, ARCADIS was able to choose a well location that did not conflict or obstruct any underground utilities.

5.2 MW-7 Area Investigation

One injection well (directly upgradient of MW-7) and five monitoring wells were originally proposed for the pilot area. During the course of the installation of the injection well, IW-1, the number and configuration of pilot test wells was revised according to information gained in the field. Laboratory analytical results from soil collected in the vadose zone during the installation of IW-1 did not indicate

the presence of perchlorate. The lack of perchlorate in the vadose zone of the test area caused ARCADIS, with the approval of JPL and the Navy, to revise the well configuration and the pilot test objectives such that only the saturated zone and groundwater were targeted during this pilot demonstration. Another attempt to isolate perchlorate in the vadose zone was conducted by the drilling and sampling of a well in the area of former Pit No. 30. Well installation is described below.

5.3 Pit No. 30 Area Investigation

Since perchlorate was not detected in the vadose zone in the area of MW-7, an additional attempt to locate perchlorate in the vadose zone in the former Pit No. 30 area with the permission of NFESC and JPL. Pit No. 30 was an area known to be a previous repository for perchlorate waste products and a primary source of perchlorate contamination at the facility. ARCADIS submitted a separate cost and scope of work to JPL for this additional phase of investigation. Well installation is described below.

5.4 Well Installation

5.4.1 Drilling Technology

Sonic drilling was selected for two of its fundamental advantages: speed and continuous core output. Sonic drilling is also referred to as vibratory drilling and rotasonic drilling. A sonic rig uses an oscillator or head with eccentric weights driven by hydraulic motors to generate high frequency sinusoidal force in a rotating pipe drill. The top-mounted hydraulically powered drill head transmits the rotary power, hydraulic down pressure and vibratory power directly to the dual line of pipe. The frequency of vibration (generally between 50 and 120 cycles per second) of the drill bit and core barrel could be varied to allow for optimum penetration of subsurface materials. The dual string assembly allowed advancement of casing with the inner casing used to collect samples. The inner drill pipe contained a core bit and represented the core barrel sampler while the outer pipe was used to prevent the collapse of the borehole and was used in the construction of monitoring wells.

The combination of forces advanced the inner core barrel sampler through unconsolidated deposits and most consolidated deposits without the use of water, mud, or air. During the drilling of the wells in the pilot test area, the sonic rig drilled through and sampled both unconsolidated material and boulders up to 5 feet in diameter. Small amounts of air and water can be used to remove the material between the inner and outer casing. The inner drill pipe was always advanced in front of the outer drill pipe (typically 2 to 3 meters). Once the inner drill pipe was set, the outer drill pipe was advanced down over the inner drill pipe to hold the boring open. The inner drill pipe was then mechanically lifted by the drill head to the surface for core sample recovery. The core sample was vibrated out of the inner drill pipe into plastic sheaths approximately 2 feet in length. Typical core recovery ranged from 2 feet to 10 feet of material. After the core barrel was emptied, the inner drill pipe was then advanced to the next sample interval. The continuous core recovery allowed our field geologist to view the cuttings from each boring in their entirety.

5.4.2 Well Design

The injection well (IW-1) was constructed as a single casing with a single screen in the upper saturated zone. The injection well was constructed using 4-inch Schedule 40 PVC casing and stainless steel wire wrapped screen from 223 to 253 feet below surface. Low-carbon stainless steel was proposed for the injection well in the work plan, assuming that there would be multiple screen intervals in the well. However, since this well was constructed with the same design as a monitoring well, ARCADIS made the decision to use similar materials as other monitoring wells on the facility and to utilize SCH 40 PVC as

casing material. The saturated zone was screened from 10-feet above the potentiometric water surface, at the time of well installation, to a total depth of 253 feet below grade (approximately 30 feet of screen). If perched groundwater was encountered during the installation of the injection well, it was to be sampled and analyzed for perchlorate. However, neither perched water nor perchlorate in soil samples was detected during the installation of IW-1. This well was finished with standard, traffic rated, flushmount well box.

The vadose zone monitoring wells originally proposed in the work plan (clusters VMW1 and VMW2) were not installed after the injection well, due to the lack of perchlorate in the vadose zone. As a replacement, three groundwater monitoring wells (IRZMW-1-3) were installed in both cross and downgradient directions to monitor the effectiveness of injections into IW-1 (see Figure 5-2). Each monitoring well consists of a single 4-inch PVC casing with a single stainless steel screened interval. The screen was placed approximately 10 feet above the potentiometric surface of groundwater at the time of drilling. Monitoring well IRZMW-2 was completed after the installation of IW-1 and is located halfway between IW-1 and MW-7. IRZMW-2 was completed with the same screened interval as IW-1 (223 to 253 feet below surface). IRZMW-3 was located approximately 20 feet west of IRZMW-2. IRZMW-1 was subsequently utilized as an injection well rather than a monitoring well as a strategy to adjust for the unexpectedly high groundwater velocity. IRZMW-1 served as an injection well for the duration of the demonstration. These wells were finished with standard, traffic rated, flushmount well boxes.

Results of grab groundwater samples obtained while drilling IRZMW-3 indicated that perchlorate concentrations in the saturated zone increased with depth. ARCADIS, with the approval of JPL, elected to continue drilling and sampling IRZMW-3 in order to vertically profile perchlorate concentrations in the pilot test area. ARCADIS drilled and sampled the boring for IRZMW-3 to total depth of 375 feet below surface. Laboratory analytical results indicated that the optimal interval for a well screen for this well was 225 to 280 feet below surface. IRZMW-3 was subsequently screened between 235 and 280 feet below surface (See Appendix A for Boring Log). IRZMW-3 was backfilled with a series of layers of clean filter sand and bentonite pellet layers in order to prevent potential vertical migration of perchlorate. ARCADIS followed the same drilling and sampling procedure while installing the last monitoring well, IRZMW-1. This boring was drilled and sampled to 280 feet below grade and the screen was installed from 225 to 280 feet below grade. This well was finished with standard, traffic rated, flushmount well box.

The potential injection well labeled IW-2 was installed in the Pit No. 30 area in an attempt to locate vadose zone perchlorate and would have been used as a vadose zone injection well had perchlorate been detected in the vadose zone at this location. The well design for IW-2 was similar to that of IW-1. The well IW-2 was constructed as a single casing with a single screen in the upper saturated zone. This injection well was constructed using 4-inch SCH 40 PVC casing and stainless steel wire wrapped screen. Low-carbon stainless steel was proposed for an injection well in the work plan, assuming that there would be multiple screen intervals in the well. However, since this well was constructed with the same design as a monitoring well, ARCADIS made the decision to use similar materials to other monitoring wells at the facility and to utilize SCH 40 PVC as casing material. The boring for IW-2 extended to approximately 351 feet below surface. The results of expedited perchlorate soil sampling indicated that there was no perchlorate present in the vadose zone. Therefore, the boring was backfilled with a series of clean filter sand and hydrated bentonite chip intervals in order to inhibit any potential vertical migration of contaminants. Then, the saturated zone was screened from 249 to 299 feet below grade. This well was finished with standard, traffic rated, flushmount well box.

5.4.3 Soil Sampling and Logging

As the injection well (IW-1) was being drilled, soil samples were collected at ten-foot intervals as well as intervals that appeared to be potential repositories for perchlorate. All injection soil samples were sent to

the analytical laboratory, although not all samples were analyzed. While injection well soil samples were collected every ten feet, initially the injection well soil samples collected every twenty feet and those with suspected potential perchlorate were analyzed for perchlorate concentration. Soil samples were subjected to an aqueous extraction procedure prior to analysis by USEPA Method 314.0. The resulting extract was subjected to perchlorate analysis using Method 314.

Based upon the results of the analyses from the injection well, soil samples were collected at ten-foot intervals from the other four monitoring wells for analysis to try to isolate perchlorate in the vadose zone and fill in data gaps. Soil samples initially selected for analysis were every 20 feet or those with suspected potential perchlorate concentrations or based upon other factors decided in the field. All well soil samples were run on a 24-hour to 48-hour basis to provide data prior to constructing the well.

During the drilling and sampling, additional soil samples were collected at the same intervals as perchlorate samples in wells IW-1 and IRZMW-2 in an attempt to perform a microcosm study on native soil naturally infused with perchlorate. As mentioned previously, significant concentrations of perchlorate were not isolated in the vadose zone and therefore these samples were not used for a microcosm study.

Lithologic samples were examined in the field and logged according to the Unified Soil Classification System (USCS). Boring logs can be found in Appendix A.

As the injection well (IW-2) was being drilled, soil samples were collected at ten-foot intervals as well as intervals that appeared to be potential repositories for perchlorate. All injection soil samples were sent to the analytical laboratory, although not all samples were analyzed. While injection well soil samples were collected every ten feet, initially the injection well soil samples collected every twenty feet and those with suspected potential perchlorate were analyzed for perchlorate concentration. Soil samples were subjected to an aqueous extraction procedure prior to analysis by USEPA Method 314.0. The resulting extract was subjected to perchlorate analysis using Method 314.

Based upon the results of the analyses from the injection well, it was determined that the former Pit No. 30 was not an optimal place for a vadose zone pilot test. Significant concentrations of perchlorate in the vadose zone were not found in the area of former Pit No. 30. Therefore, the investigation of this area was not expanded and only IW-2 was installed.

During the drilling and sampling, soil samples were collected at the same intervals as perchlorate samples in an attempt to perform a microcosm study on native soil naturally infused with perchlorate. As mentioned previously, significant concentrations of perchlorate were not isolated and therefore these samples were not used for a microcosm study.

At approximately 39-feet below ground surface, a minor fault zone was encountered. This fault zone appeared to be approximately 6-inches thick. Soil encountered on either side of the fault appeared to be consistent with the typical local lithology. At approximately 112 feet bgs, a significant fault zone (approximately 3-4 feet thick) was encountered and identified by characteristic “slickensides” and metamorphic deformation typical of fault zones. The fault encountered at 112 feet bgs was interpreted to be the JPL Thrust Fault.

Boring logs for all wells installed can be found in Appendix A. Figure 5-3 is a scaled drawing that illustrates how the screened intervals of the five wells involved in the demonstration compare to one another with regard to the vertical profiles of the screened intervals.

5.4.4 Well Development

Once the wells were installed, they were developed by surging, bailing, and/or pumping. The objectives of well development were to remove sediment that may have accumulated during well installation, to consolidate the filter pack around the well screen, and to enhance the hydraulic connection between the target zone and the well. Well development began on February 11, 2003. In most of the wells, a bailer was used to remove sediment and turbid water from the bottom of the well. A surge block was then used within the screened interval to flush the filter pack and screen. The well was bailed again to remove sediment drawn into the well by the surging process until suspended sediment was minimized. Following the bailing and surging steps, the well was further developed using pumping methods. The well was developed at a higher pumping rate than the anticipated rate of future pumping for sampling. During development, the turbidity of the water was monitored and the pH, specific conductance, and temperature of the return water were measured. Drawdown and recovery were measured during and at the end of the development process, respectively, using an electric sounder. Well development proceeded until the following criteria were met:

- The return water was visibly clear or turbidity visually declined to a stable level.
- The sediment thickness remaining within the well was less than one percent of the screen length.
- A minimum removal of five well volumes was completed. One well volume consists of standing water within the well as well as the saturated filter pack (assuming 30 percent porosity).
- Potable water used during well installation was removed. A volume equal to five times the volume of water used during well installation was removed in addition to the five well volumes described above.
- Stabilization criteria were three consecutive measurements for which the specific conductance was within 10%, pH is within 0.1 units, and temperature was within 1 degree C.

Significant variations were not encountered from these criteria. However, during the attempted development of injection well IW-1 an obstruction was noted between 210 to 215 feet below ground surface. The drilling company, Boart Longyear, dispatched a down hole camera in order to view the obstruction prior to selecting a remedy. The camera revealed damage to the well casing at ~ 209 feet below ground surface (bgs). The damage to the well casing consisted of a swollen, warped section of the PVC pipe. This damaged section of well casing constituted an obstruction that prevented ARCADIS from installing a pump into IW-1.

Monitoring well IW-1 was repaired on May 14, 2003. The well, which is a 4-inch casing, was reamed out at the depth of the damaged area using a diamond core auger drill rig. The damaged area appeared to be about 2 feet in length and it is uncertain what caused the PVC casing to swell and obstruct the well. It is likely a defect in the PVC casing. After the well was reamed, a 3-inch diameter well casing was installed inside of the existing 4-inch casing. Stainless-steel well screen (0.060 slot size) was installed from 225 to 255 feet bgs and schedule 40 PVC casing was installed from 225 feet bgs to ground surface. Packers were installed above and below the damaged area. Additional centralizers were installed at multiple depths to centralize the inner well casing. After completing the repairs, the well was then developed using the same criteria as the other wells.

5.4.5 Surveying

ARCADIS contracted Guida Surveying Inc. to locate the wells in the pilot test area along with IW-2 and select other JPL wells on February 27, 2003. The wells coordinates are California Coordinate System 83, Zone 5, based upon GPS observation and post-processed to CORS Stations JPLM & CIT1. Elevations are

based on L.A. County Benchmark Y 12255 (La Canada Quad) Datum: NAVD 88 (1995 Adjustment) Elevation: 113.623 Feet. Refer to Appendix B for a copy of the surveyor's data.

5.4.6 Drilling Rig Demobilization

Following the installation and development of the pilot test wells, the size of the fenced-off work area in the MW-7 parking lot was reduced such that only the immediate area surrounding the wells was within the enclosure. All fencing material was removed from the former Pit No. 30 area and well IW-2. Demobilization also included the removal and disposal of all solid and liquid waste generated as part well construction activities. Refer to Section 3.4.4 for a discussion of residuals handling.

5.4.7 Residuals Handling

Waste generated during the drilling activities included solid and liquid waste. Solid waste consisted of the soil cuttings generated during drilling activities and it was sampled for waste characterization during the drilling activities. Soil was stored on site in labeled Department of Transportation (DOT) roll-off bins in a secure storage area. Liquid waste generated during the drilling activities consisted of decontamination waters generated as part of the decontamination procedures associated with drilling and sample collection. Additionally, there was water removed from the wells during the well development. The liquid waste was collected and temporarily stored in labeled DOT approved 55-gallon drums on-site within the same secure storage area as the solid waste. Due to the large quantity of water generated during decontamination and sampling of the deeper borings, ARCADIS, with the approval of JPL, elected to store the wastewater in several poly tanks already present at the site. The poly tank was labeled and stored in a secure area. A composite sample of liquid waste from each waste stream was collected and characterized for disposal.

Upon review of the analytical results for the wastes, the wastes were classified as nonhazardous, and transportation and disposal was arranged. ARCADIS secured ARTS Disposal, a licensed waste disposal contractor, for all off site transportation and disposal of solid wastes. ARCADIS secured Nieto and Sons, a licensed waste disposal contractor, for all off site transportation and disposal of liquid wastes. ARCADIS prepared manifests, scheduled the removal of the waste. Disposal activities were conducted on January 3, 2003, January 7, 2003, February 27, 2003 and February 29, 2003 and were coordinated with the authorized representative from JPL, Mr. Mark Araki. All of the Non Hazardous Waste Manifests were be submitted to the JPL representative for review and signature at the time off-site disposal of the contaminated material. Refer to Appendix C for a copy of the non-hazardous waste manifests.

5.5 Laboratory Microcosm Study

A previous research project funded through the Department of Defense Strategic Environmental Research and Development Program (SERDP) performed by Envirogen, (currently Shaw Environmental) collected soil and groundwater samples from the JPL monitoring well MW-7 and performed laboratory microcosm testing to confirm the presence of perchlorate reducing bacteria (Note that ARCADIS was supplied a version of this report by NFESC staff. As far as ARCADIS knows, this data has not been formally published). The results of microcosm testing suggested that indigenous bacteria capable of degrading perchlorate were present in the subsurface at JPL and that carbohydrate electron donors could be used to stimulate perchlorate reduction. The laboratory studies further suggested that perchlorate could be treated to below 5 µg/L in groundwater. ARCADIS was asked to confirm that the performance of its chosen carbohydrate, corn syrup, would compare favorably with data from this previous laboratory microcosm study that was conducted with yeast extract, acetate, methanol, and molasses. Corn syrup was chosen due to the relative lack of dissolved inorganic constituents found in it. The addition of inorganic species in the carbohydrate is counter indicated because it is undesirable to increase the total dissolved solids loading in

groundwater destined to be utilized as drinking water. Therefore, molasses was avoided and corn syrup was selected.

Using methods similar to the previous study, ARCADIS collected a saturated zone soil sample. Vadose zone soil samples were not considered since perchlorate was not detected in the vadose zone during extensive investigation concurrent with well installation. The sample was asceptically homogenized and soil and groundwater were mixed together in sterile, 280-ml serum bottles at a 1:6 weight-to-weight (wt/wt) ratio to create fourteen replicate microcosms. Each of the fourteen replicate serum bottles was amended with a sterile stock of diammonium phosphate to provide nitrogen (5 mg/L as NH_4) and phosphorus (4.5 mg/L as P) as nutrients for bacterial growth. Four of the replicate microcosms were amended with corn syrup to achieve a concentration of 150 mg/L. Four of the replicate microcosms were incubated with no electron donor amendment. Four microcosms were amended with corn syrup to achieve a concentration of 150 mg/L and 1% formaldehyde on a volume-to-volume basis (v/v) to inhibit biological activity. The thirteenth and fourteenth replicate microcosms were sacrificed immediately to provide duplicate analyses for the establishment of the perchlorate starting concentration.

After distribution of soil, groundwater, corn syrup, and formaldehyde, the headspaces of all microcosms were purged out with argon gas and the serum bottles were crimp-sealed with sterilized Teflon-lined septa and incubated at room temperature (~ 20°C). At 7, 14, and 21 days of incubation, a serum(s) bottle from each treatment will be sacrificed and analyzed for aqueous phase perchlorate. Microcosms were sacrificed in duplicate at the 21-day sampling point to provide a measurement of variability. P & Ch Laboratory in Chino, California will perform the perchlorate analyses according to USEPA Method 314.0.

The average perchlorate concentration of replicate microcosms sacrificed and analyzed at set-up was 7,220 µg/L. By Day 30, the perchlorate concentration in the corn syrup amended microcosm had fallen to below the detection limit (3.3 J). The perchlorate concentration in the unamended microcosm at Day 30 was 7,230 µg/L. The perchlorate concentration in the abiotic microcosm at Day 30 was 7,350 µg/L. Thus, the ARCADIS microcosm study confirmed the applicability of corn syrup to stimulate perchlorate biodegradation in the JPL saturated zone.

6.0 Pilot Test and Evaluation Plan

6.1.1 Demonstration Installation and Startup

Pre-demonstration activities were covered in Section 5 above.

6.1.2 Period of Operation

Baseline sampling for wells IRZMW-1-3 and MW-7 was conducted on February 21, 2003. Baseline sampling for IW-1 was completed after it was repaired and developed on June 4, 2003. The first injection event was June 4, 2003. The first progress monitoring was June 6, 2003. Four total injections were completed throughout the pilot test as well as numerous progress monitoring events. Refer to Table 6-1 for a tabulation of injection events,, an injection event formulation summary and progress monitoring records. The last injection was August 15, 2003 and the last progress monitoring event was September 4, 2003. While a continuation of the pilot test was requested to refine the injection scheme, additional time was not available due to JPL's plans for the implementation of another technology for perchlorate remediation in the same area of the site in which this IRZ demonstration was being implemented.

During the demonstration interval, ARCADIS conducted a baseline monitoring event, 14 process monitoring events and 4 performance monitoring events. The spacing between monitoring events was determined following review of data generated during process monitoring events. Perchlorate sample collection was triggered by process monitoring events where DO was found to be near zero and ORP was found to be negative. Under the expected groundwater flow rate, ARCADIS expected each injection event to influence all the downgradient monitoring wells. Downgradient monitoring wells were installed with spacing that took expected groundwater velocity into account. The increased groundwater velocity that was actually noted in the treatment zone caused by the greater than expected quantity of groundwater in the aquifer (as demonstrated by vastly elevated groundwater table) led to process monitoring rounds being more closely spaced over time that was originally expected.

6.2 Sampling Plan

The *in situ* reactive zones formed in the saturated zone are dynamic because of the continuing lateral groundwater. Multiple corn syrup injection events were planned for this zone. Prior to the first saturated zone corn syrup injection event, ARCADIS collected a round of groundwater samples that was intended to establish the baseline biogeochemical conditions within the aquifer. Downgradient sampling of the monitoring wells identified in Figure 5-2 for non-pollutant analytes was necessary to "tune" the injection schedule and provide feedback on the appropriateness of the corn syrup dosing within each injection event. In addition, previous bench-scale research suggested that perchlorate, the primary compound that this demonstration focused on, has the potential to biodegrade rapidly after the onset of anaerobic conditions within the aquifer. Therefore, the sampling strategy for the saturated zone demonstration remained flexible and was adapted to changing microbiological conditions in the subsurface that were initiated by the corn syrup injection event(s).

6.2.1 Sample Collection

This section discusses collection and analysis of samples to meet the project objectives during the pre-demonstration activities. The potential for deviation was determined based on review of analytical data for samples collected in the first days following the beginning of the drilling and based upon conditions encountered in the field.

Vadose Zone Soil Sampling

Vadose Zone sampling was performed during well installation. Soil samples were collected every ten feet during the installation of the injection well (IW-1), injection well IW-2, and IRZMW-2. Soil samples were collected at 20-foot intervals in IRZMW-1 and IRZMW-3. All soil samples collected during the well installation were sent to the analytical laboratory. Selected soil samples were analyzed while others were held pending the release of analytical results. Samples that were held were to be analyzed in the event that perchlorate was detected in order to further delineate the perchlorate profile with depth. While injection well soil samples were collected every ten feet, initially the injection well soil samples collected every twenty feet and those with suspected potential perchlorate were analyzed for perchlorate concentration. Similarly, IRZMW-1 and IRZMW-3 well soil samples were collected every twenty feet, initially the soil samples collected every forty feet and those with suspected potential for perchlorate presence based on geology supportive of perching groundwater were analyzed for perchlorate concentration. Soil samples were subjected to an aqueous extraction procedure prior to analysis by USEPA Method 314.0. The resulting extract was subjected to perchlorate analysis using Method 314. Based upon the results of the analysis, other injection well soil samples were selected for analysis to fill in data gaps. Injection well soil samples were run on a 24-hour to 48-hour basis to provide data prior to constructing the well.

The procedures followed during soil sample collection included collecting soil samples at ten-foot intervals. The inner drill pipe and core barrel sampler were advanced to the desired sampling interval. The inner drill pipe was always advanced in front of the outer drill pipe.

1. Once the inner drill pipe is set, advance the outer drill pipe down over the inner pipe to hold the borehole open.
2. Mechanically lift the inner pipe and core barrel sampler to the surface using the drill head for core sample recovery.
3. Vibrate the core barrel manually with a hammer and extrude the sample into a casing of visqueen and record the lithology on the log of boring.
4. Collect grab soil samples from the core barrel at the required depths.
5. Transfer the sample from the core barrels to pre-cleaned, 4-ounce glass jars using a pre-cleaned trowel.
6. Cap the jar(s) and wipe any moisture or soil from the outside of the jar(s).
7. Place a sample label, completed with the information described in Section 8.2 of the SAP, on the jar.
8. Place the jar in a resealable bag.
9. Place the resealable bag containing the sample in a cooler with bagged ice and packing material for shipment to the analytical laboratory.

Vadose zone soil sampling also included filling one-liter glass sample jars for the microcosm study. Samples were mechanically collected utilizing similar methodology as described above, however, the samples were held in their coolers on ice until confirmation of perchlorate concentration was received from the local analytical laboratory. Since significant amounts of perchlorate were not isolated in the vadose zone, the sample containers for the microcosm study were eventually emptied into the soil bins with the drill and the glass jars were decontaminated for reuse.

Saturated Zone Soil Sampling

Sampling in the saturated zone was completed utilizing the same methodology as described above during discussion of vadose zone soil sampling. The saturated zones of IW-1, IRZMW-2, and IW-2 were sampled with the same frequency as their respective vadose zones. Microcosm samples of these same intervals were also acquired.

Groundwater Sampling

Grab groundwater samples were collected at discrete depths during the well installations. Single grab groundwater samples were taken from IW-1 and IRZMW-2 approximately at the point where the first groundwater was encountered. Results of grab groundwater samples obtained while drilling IRZMW-3 indicated that perchlorate concentrations in the saturated zone increased with depth. ARCADIS, with the approval of JPL, elected to continue drilling and sampling IRZMW-3 in order to vertically profile perchlorate concentrations in the pilot test area. ARCADIS drilled and sampled the boring for IRZMW-3 to total depth of 375 feet below surface. Grab groundwater samples were not taken from IRZMW-1 because they were not needed to further characterize the area. Additionally, during the course of drilling the pilot test wells, ARCADIS dispatched a technician to sample existing well MW-7 at discrete intervals within the screened interval to verify any layering of perchlorate concentrations within the saturated zone. These results were used finalize well constructions during the pilot test area construction phase.

Additionally, several 1 gallons amber jugs of water were sampled from IRZMW-1 during the drilling process. These samples were taken with a new disposable bailer from the boring when it was cased to 275 feet below grade. This water was then packed in sample containers and placed in coolers on ice for shipment to the ARCADIS laboratory in Raleigh, North Carolina to be used in the microcosm bench test study. Refer to Section 3.3.3 for a further discussion of the laboratory bench test.

Prior to initiating the pilot test, a baseline-sampling event was conducted in the test area to determine a basis for which the results of IRZ pilot test could be compared. Baseline sampling was conducted within 14 days of the development of each respective well and prior to carbohydrate injection. The following procedures were used for the collection of groundwater samples:

1. The intake of the sampling tubing was placed approximately half way into the saturated screen interval of each well during the purging and sampling intervals.
2. A dedicated submersible pump was used to purge the wells at a low flow rate (typically, not to exceed 1.0 liter/minute) to produce minimal drawdown and turbidity during pumping. Purge water was stored and disposed of appropriately based on procedures approved by NASA.
3. Groundwater parameters were measured and recorded on a Groundwater Sampling Log. Groundwater samples for analyses were collected when specific conductance, pH, and temperature had stabilized. DO and ORP were not used as stabilization parameters. Stabilization criteria was three consecutive measurements for which the specific conductance was within 10%, pH is within 0.1 units, and temperature is within 1 ºC. Water quality parameters were recorded on the Groundwater Sampling Log.
4. Hydrogen sulfide and ferrous iron were measured in the field using colorimetric methods. The conductivity, pH, and turbidity meters were calibrated per manufacturers instructions prior to the beginning of each day of sampling. In the event of an anomalous reading, the calibration of the given meter was checked immediately and recorded on the field sheet.

Note: Please refer to Appendix E, the demonstration work plan, for specific analytical methods utilized during the project.

Soil Sampling during Well Installation

Soil samples and groundwater were collected during the drilling of the injection well and the monitoring wells. Selected samples were run on a quick turnaround basis to provide data prior to constructing the well so that appropriate screened intervals could be chosen. Refer to Section 3.3.2.3 and 3.4.7.1 for a description of soil and groundwater sampling conducted during the well installation.

Sample Shipment and Labeling

Immediately after sample collection, sample labels were affixed to each sample container. Sample labels were filled out with indelible, waterproof ink, and were affixed to each sample container that was shipped to an off-site laboratory for analysis. Each off-site sample was labeled with the following information:

- Sample identification number;
- Sample collection date (month/day/year);
- Time of collection;
- Site location;
- Project number;
- Sampler's initials; and
- Analyses to be performed.

Off-site samples were transported to the analytical laboratory at the end of each day for analyses consistent with the project's needs and the specific holding times of individual analytes. Samples were transported on ice in coolers to the Applied P & Ch Laboratory in Chino, California by a laboratory supplied courier.

6.2.2 Sample Analysis

Analytical methods that were used for each type of sample collected for this project included the following:

- Soil samples collected during the drilling of the new injection and monitoring wells were extracted with deionized water in a ratio of 5:1. The extract was passed through a 20-micron filter press and analyzed for perchlorate using EPA Method 314.
- Groundwater samples collected during the demonstration were analyzed using EPA method 8260B for volatile organic compounds and EPA 314 for perchlorate.

6.3 Selection of Analytical/Testing Methods

To establish baseline conditions within the aquifer (i.e., groundwater conditions prior to the start of the demonstration), an initial round of groundwater elevation measurements and groundwater analytical samples was collected from the injection well and the groundwater monitoring wells in the demonstration area (See Table 6-2). During this sampling event, groundwater samples were collected and analyzed for a variety of organic and inorganic parameters in order to characterize the existing biogeochemical environment in the aquifer. Analyses included field parameters, electron acceptors, potential

biodegradation byproducts and end products, other biogeochemical indicators, and laboratory analyses that focus on perchlorate and the USEPA Method 8260 analytes carbon tetrachloride, chloroform, trichloroethene, 1,2-dichloroethene, vinyl chloride, 2-butanone (methyl ethyl ketone), and 4-methyl-2-pentanone (methyl isobutyl ketone). Details regarding the various analyses performed are presented below:

- Field Parameters - These parameters were measured at each of the wells in the field, and used to assist with the assessment of groundwater conditions for the biodegradation of the perchlorate. The field parameters included DO, ORP, pH, temperature, and specific conductance.
- Electron Acceptors and their products - Analysis for the presence of electron acceptors provided an indication of the relative levels of inorganic compounds present in the groundwater that act as alternate electron acceptors. An understanding of the cycling of alternate electron acceptors permitted ARCADIS to infer the dominant bacterial processes within the aquifer as the demonstration proceeded. Concentrations of electron acceptors in the facility groundwater before and after reagent injection were compared to manage for an optimal reducing environment was maintained in the subsurface. Electron acceptor analyses included nitrate, sulfate, total and dissolved iron, and total and dissolved manganese. Lastly, reduced inorganic species such as ferrous iron and sulfide are often produced from the reactions of these alternate electron acceptors under anaerobic conditions. Thus they are an expected part of the changed aquifer chemistry associated with the creation of strongly anaerobic zones. Their presence and concentration during IRZ implementation can depend both on the type and amount of electron donor substance used and the background availability of iron and sulfur in the aquifer.
- Potential Degradation Byproducts and End Products - Analysis for the degradation byproducts and end products provided an indication of the relative levels of compounds formed through biodegradation and therefore were used as an indicator of perchlorate degradation and reductive dechlorination together with other observations. Byproducts and end products fall into several categories. Transient byproducts from the bacterial reduction of perchlorate include chlorate and chlorite. Also, depending on the electron donor loading, metabolic byproduct molecules such as alcohols and aldehydes can be formed within an IRZ as a result of natural fermentation processes. These species are then subsequently metabolized downgradient. Small quantities of chloride are expected to be liberated as a final breakdown product of perchlorate. However since chloride concentrations in natural aquifers are normally much higher then perchlorate concentrations the appearance of chloride may not be detectable even if perchlorate is successfully treated.

Although heavy metals are not “products” of IRZ implementation, care was taken when dosing the IRZ not to encourage excess fermentation of electron donor sugars as this could lead to the formation of low molecular weight organic acids which can lower pH values in poorly buffered aquifers. Lower pH values can correlate with the dissolution and release of heavy metals from aquifer solids where they are naturally present in the groundwater. Although most metals become less soluble under reducing conditions, other metals such as iron and manganese can be released under geogenic conditions but are normally rapidly reprecipitated at the edges of the reactive zone.

Each type of laboratory-based QA sample (including method blanks) was analyzed at a rate of 5 % or one per batch (a batch is a group of 20 samples analyzed together), whichever was more frequent. QC samples consisted of laboratory duplicates, laboratory blanks, matrix spike/matrix spike duplicates (MS/MSDs), and laboratory control sample/laboratory control sample duplicate (LCS/LCSDs), whichever was applicable, and any other method-required QC samples.

6.4 Selection of Analytical/Testing Laboratory

The analytical laboratory selected to analyze samples for this project was certified by the California Department of Health Services through the Environmental Laboratory Accreditation Program (ELAP) for all the analytical methods required for the project. In addition, the selected off-site laboratory, Applied P & Ch Laboratory in Chino, CA, has successfully completed a NFESC laboratory evaluation program prior to sampling activities and maintained that status throughout the project. The laboratory was selected for the project because it was capable of providing the required turnaround times, project QC, and data deliverables required by the SAP.

7.0 Performance Assessment

This section will first discuss QA/QC confirmation methods including analytical data quality parameters, analytical data quality indicators, calibration procedures, and quality control checks. Following the QA/QC discussion, Section 7 will move to data analysis, interpretation, and evaluation. Interpretation of perchlorate results will be pursued using multiple lines of evidence supporting the conclusion that perchlorate was bioremediated during the demonstration.

7.1 Performance Criteria

The performance criteria or goals of the demonstration are covered in Section 1.2. Assessments of the attainment of these goals follow in Section 7.4.5.

7.2 QA/QC Confirmation Methods

7.2.1 Data Quality Parameters

Definitions of QC criteria are presented in this section.

Precision - a measure of the reproducibility of a set of replicate results or the agreement among repeat observations made under the same conditions. Analytical precision is the measurement of the variability associated with duplicate or replicate analyses. Total precision is the measurement of the variability associated with the entire sampling and analysis process. It is determined by analysis of duplicate field samples and measures variability introduced by both the laboratory and field operations. Field duplicate and matrix spike duplicate (MSD) samples were used to assess field and analytical precision, and the precision measurement was determined using the relative percent difference (RPD) between the duplicate sample results. The formula for calculating the RPD is as follows:

RPD = ((Result A – Result B)/Average of A and B) x 100

Accuracy - the nearness of a result or the mean of a set of results to the true or accepted value. Analytical accuracy is measured by comparing the percent recovery of analytes spiked into a laboratory control sample (LCS) against a control limit. Surrogate compound recoveries are also used to assess accuracy and method performance for each sample analyzed. The formula for calculating accuracy uses the following equation to determine percent recovery (%R) of specific analytes.

%R = 100 x (spiked sample result - un-spiked sample result) / amount of spike added

Representativeness - the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition. Representativeness is a qualitative parameter mostly concerned with the proper design of the sampling program.

Completeness - the percentage of measurements made that are judged to be valid measurements. The completeness goal is to generate a sufficient amount of valid data to meet project needs. Completeness is calculated and reported for each method, matrix, and analyte combination. The number of valid results divided by the number of possible individual analyte results, expressed as a percentage, determines the completeness of the data set. For completeness requirements, valid results are all results not qualified with an "R" flag. The requirement of completeness is 95 percent for aqueous samples and 90 percent for soil samples, and is determined using the following equation:

Percent completeness = 100 x (number of valid analyte results/number of possible results)

Comparability - A qualitative parameter expressing the confidence with which one data set can be compared with another. Sample data should be comparable with other measurements for similar samples and sample conditions. The objective for the quality assurance/quality control (QA/QC) program is to produce data with the greatest possible degree of comparability. The number of matrices that are sampled and the range of field conditions encountered are considered in determining comparability. Comparability is achieved by using standard methods for sampling and analysis, reporting data in standard units, normalizing results to standard conditions, and using standard and comprehensive reporting formats.

7.2.2 Data Quality Indicators

Precision and accuracy QC limits for each method involving regulated contaminants are identified in Table 7-1.

For the Volatile Organic Compound analyses, the surrogate, internal standard, and LCS recoveries were within the established laboratory control limits. In most cases, these limits were more stringent than those originally established for this project. It should be noted that because the laboratory included a Matrix Spike (MS)/Matrix Spike Duplicate (MSD) analysis with each batch of samples, LCSD were not run.

For the Perchlorate analyses, the LCS recoveries or LCS/LCSD recoveries and RPD (lab report 03-5027 only) were within the established laboratory control limits. Each batch of samples included either a sample-specific or batch sample MS/MSD analysis.

For the Metals, Formaldehyde, Alcohols, and Methane analyses, the LCS/LCSD recoveries and RPD were within the established laboratory control limits.

7.2.3 Calibration Procedures, Quality Control Checks and Corrective Action

Portable instruments were used in the field to analyze pH, conductivity, temperature, dissolved oxygen (DO), oxidation/reduction potential (ORP), ferrous iron, and sulfide. Where used, the portable instruments were calibrated according to manufacturer's recommendations. Calibration standards were utilized for this purpose for pH, conductivity, and dissolved oxygen. These calibration standards were also periodically used as quality control check standards. Calibration events were noted in the field notebook for the JPL project. No corrective action was necessary for the field parameters listed below.

7.2.4 Technical Systems Audit

On Friday, August 22, 2003 Mr. John Dodge, senior geologist with ARCADIS' Los Angeles office conducted an internal technical systems audit (TSA) of a JPL groundwater sampling event. A checklist prepared from the project's QAPP by the project's QA Project Officer was utilized to guide the audit and the checklist was filled out during the audit. There was a single findings during the audit involving the calibration check performed on the DO meter. The meter calibrated to 112% of the 100% standard. This exceeds the stated objective that the meter calibration standard fall within 5% of the expected value. Subsequent probe conditioning led to improved DO meter performance. The checklist filled out during the audit by Mr. John Dodge is presented as Appendix G.

7.3 Data Analysis, Interpretation and Evaluation

The following sections detail the analysis of data collected during the pilot test. The data is evaluated in terms of the overall objectives of the test and additional observations that may prove useful for future development of remediation approaches at the site.

7.3.1 Performance Overview6

Monitoring of performance was divided into two categories: Process monitoring and Performance monitoring. Process monitoring including measurement of key field parameters such as Oxidation Reduction Potential (ORP), pH, dissolved oxygen (DO), nitrate, and iron. Process monitoring data is used to determine if the desired reducing conditions are being established in the subsurface and to adjust the frequency and strength (organic concentration) of injection. Reducing conditions are evaluated by field measurement of ORP. ARCADIS believes that, for optimum perchlorate degradation to occur, the ORP should range between 0 and –100 mV. In addition, the DO content of the groundwater should be less than 1 mg/L. The pH of the groundwater is measured to determine if carbon loading is leading to excessive fermentation. The optimal pH range for bacterial degradation for this pilot test was expected to be between 5.5 and 7.5 standard pH units. The pH was monitored to ensure that optimal conditions were maintained. If pH dropped below the desired range, injection strength and frequency were reduced. Nitrate and iron were monitored using field test kits to provide an indication as to the overall efficiency of treatment. Nitrate was expected to be consumed in the treatment process. The efficiency of nitrate reduction would be impaired due to the instability of the anaerobic zone formed during the demonstration. Iron had the potential to be released under reducing conditions and therefore the concentration of iron was potentially expected to increase slightly in the area of treatment.

Performance monitoring includes measurement of specific target analytes such as perchlorate and other regulated compounds that were present in the groundwater such as CVOCs using certified laboratory analytical procedures. Performance monitoring data is used to determine the overall effectiveness of treatment and monitor for secondary water quality effects that may occur as a result of treatment. Perchlorate and CVOCs were monitored in the wells in the study area to determine the effectiveness of treatment. To account for potential dilution effects related to the injected solution, a bromide tracer was added to each injected volume. Bromide was monitored in each well and compared to background levels (bromide concentration prior to commencing the test). An observed increase in bromide concentration would have been attributed to spiked bromide introduced along with injection solution. Perchlorate concentrations could then be adjusted to account for the relative contribution from the injected solution for each well.

In general, injection events carried out during the demonstration resulted in measurable decreases in perchlorate concentration in the injection wells. Later in the demonstration interval, after ARCADIS adjusted the injection scheme to increase the volume of injected solution, some downgradient monitoring wells also displayed some decreases in perchlorate concentration. These perchlorate data will be iteratively reviewed in detail in the next section.

7.3.2 Changes in Groundwater Flow Direction and Velocity

The elevation of the groundwater potentiometric surface increased approximately 20 feet at the early part of the test (after the baseline monitoring but prior to injections), then slowly decreased about 16 feet from late May to early September 2003. The change in groundwater elevation is shown in Figure 7-1 with

rainfall data[2] for before and during the pilot test period. Groundwater gradient and velocity also varied over the test. While rainfall is a contributor, ARCADIS does not believe that rainfall alone can account for the elevation in groundwater table that was documented during the demonstration. Likewise, the volume of injected corn syrup solution can not possibly explain measured elevations in the water table. ARCADIS investigated the possibility that the release of water upgradient of the demonstration zone and off of JPL property to achieve aquifer recharge may have contributed to the elevated water table documented during the demonstration. While no conclusive evidence of aquifer recharge was immediately evident, this possibility still cannot be ruled out.

The flow direction and gradient in the May 29 map are broadly typical of the pilot test period although this was markedly different from the March 6th map as well as markedly different from the assumptions based on MW-7 slug test data from RI and utilized to price and design this demonstration. ARCADIS used the k value of 7.8 feet per day based on 1994 MW-7 slug test data and a gradient value of 0.02 to calculate an expected groundwater velocity of 0.58 feet per day that was based upon the March 6 flow map (See Figure 7-3).

Most of the flow maps created from the water level datasets during the pilot test appear roughly similar to the May 29 map although groundwater elevations varied (Figures 7-2 thru 7-12):

- On the May 29 map (Figure 7-5), flow is oriented southeast in the northern part of the test area with a slightly more southerly component in the southern part of the test area. The groundwater gradient between wells IRZMW-1 and MW-7 is about 0.07 to 0.09, and using the average hydraulic conductivity value from the December 1994 slug test in well MW-7 (7.8 feet per day) (Foster Wheeler 1999), groundwater velocity in the test area calculates at about 2.1 to 2.8 feet per day with an effective porosity estimate of 0.25.

The typical gradient and velocity are higher than first estimated for the test area using the March 6 data, which show a gradient of 0.02 and a velocity of 0.58 feet per day. By May 29 groundwater elevations had increased from the March 6 data, mostly in well IRZMW-1, and so gradient steepened with a corresponding increase in velocity.

Variations in flow direction and gradient were mapped when water levels in wells IRZMW-2 or MW-7, at the southeast corner of the test area, were relatively elevated or when the water level in well IW-1, at the northeast corner, was relatively depressed. Variations were also mapped when water levels in wells IRZMW-1 and IRZMW-3 were similar. Water level datasets from the following dates show variations from the broadly typical May 29 map (Figures 7-2 thru 7-4, 7-7, and 7-9):

- February 27, March 6, May 27, June 12, and July 16.

These dates correspond to anomalous periods of decreased groundwater gradient, velocity, and discharge in the pilot test area, occurring about once every 3 to 4 weeks on average, in between more typical periods of higher discharge and groundwater flow directed mostly to the southeast between about 2 and 3 feet per day. The piezometric groundwater elevations measured in the test area monitoring wells are complicated by relatively long well screens used for potentiometric data measurement with variable and interbedded sand, silt, and clay lenses that likely generate composite heads over the well screen intervals.

[2] Rainfall data from: U.S. Department of Commerce, National Oceanic & Atmospheric Administration, National Climatic Data Center, Annual Climatological Summaries, Station 046719/99999, Pasadena, California.

In an attempt to understand and explain these anomalous periods of increased groundwater gradient, velocity and discharge, ARCADIS looked at maps, talked to the Battelle modeler, and re-read the RI. Battelle indicated that the Valley Water Co. wells are active, but they are to the southwest and therefore do not represent a complete explanation. The RI indicates that only Pasadena wells caused JPL water levels to fluctuate with pumping and the Pasadena wells were known to be inactive during the demonstration interval. USGS maps and geologic maps show no features that could be implicated in this phenomenon to the north or northwest of JPL. ARCADIS also looked at MWD operations and found no suitable explanation. The most likely explanation remains localized injection for aquifer recharge but no such location or activity has been detected to date.

7.3.3 Performance and Process Monitoring Results and System Operational Adjustments

The initial design injection rates and carbon loading rates were calculated based on estimates of various electron acceptor (dissolved oxygen and nitrate) concentrations and groundwater velocity in the treatment area. The Process Monitoring Events were designed to determine the extent of the reactive zone following each injection event. As the data from Process Monitoring Events was collected, adjustments were made to the frequency of injection and the carbon loading rates in order to optimize reducing conditions within the treatment zone.

Following the initial injection of 210 gallons of a 10% volume per volume (v/v) corn syrup and water solution into well IRZMW-1 on June 4, 2003, Process Monitoring was conducted on June 6, 2003 with little change noted in pH, ORP and DO in the injection well or the monitoring wells associated with the pilot test. A second Process Monitoring event was conducted on June 12, 2003 and changes ORP were noted in wells in the test area. The injection well (IRZMW-1) had a much lower ORP (-49.4) and a stable pH and DO. Monitoring wells IRZMW-2 and IRZMW-3 displayed ORP levels believed to be comparable to the baseline with stable pH and DO. A third Process Monitoring event was conducted on June 18, 2003 prior to the second injection. This monitoring event found that ORP in all of the wells had returned to the pre-injection highly oxidative levels and pH and DO remained stable (see Table 7-2a).

A second injection event was conducted on June 18, 2003 using the same ratios of corn syrup and water as the initial injection. However during this event, 210 gallons of carbohydrate was added to both IW-1 and IRZMW-1 for a total volume of 420 gallons.

A process monitoring event was conducted on June 20, 2003. The only substantive change noted in the field parameters was the change in ORP and DO for IW-1. The ORP for IW-1 declined to –47.4 mV (slightly reducing) and DO declined to 1.11 mg/L (microaerophilic). The pH for IW-1 was slightly lower than previous monitoring events. All other wells had ORP, pH, and DO levels similar to previous monitoring events.

Another process monitoring event was conducted on June 23, 2003. Substantial declines in ORP were noted in three of the wells—the two injection wells (IW-1 and IRZMW-1) and monitoring well IRZMW-3. Dissolved oxygen concentrations declined in injection well IW-1 to <1 mg/L; a level consistent with anaerobic conditions but did not change substantially in the other wells.

The process monitoring event conducted on June 25, 2003 found that ORP remained reducing (<0 mV) in the injection wells and had remained strongly reducing in monitoring well IRZMW-3 (-284.6 mV) with essentially little change since the last process monitoring round. At the other two monitoring wells, the ORP was still oxidative and not dramatically changed. A significant decline in pH (3.81) was noted in IRZMW-1. The DO level in injection well IW-1 remained at <1 mg/L (anaerobic). The level in the other injection well (IRZMW-1) also went below 1 mg/L (0.25 mg/L). Samples were collected from the three

wells with ORP <-50 mV for analysis of perchlorate. Perchlorate concentrations for wells IW-1, IRZMW-1 and IRZMW-3 were reported at 802, 1,030, and 4,000 µg/L respectively (see Table 7-2a).

Five days after these widespread reducing conditions were detected, the process monitoring event conducted on June 30, 2003 found ORP levels had returned to oxidative levels (>0 mV) in all of the wells. However the ORP's in IW-2 and MW-2 appeared to be somewhat more reducing then baseline conditions. The DO changes were generally correlated. Aerobic conditions were measured in all of the wells with the exception of injection well IRZMW-01 which still had DO of <1 mg/L. The pH in injection well IRZMW-1 began to recover, but still was considerably lower that baseline conditions. Performance monitoring was also conducted at this time. Groundwater samples were collected from all wells for analysis of perchlorate. The results revealed that perchlorate concentrations had declined (from baseline levels) in both injection wells and in downgradient monitoring well IRZMW-2 to 1,810 µg/L. The cross gradient well IRZMW-3 and far downgradient well MW-7 had little or no change in perchlorate concentration. Since little or no direct effect of carbohydrate injection was observed in monitoring well IRZMW-2, the decline in concentration may be attributable to treated groundwater flowing through the point from an up gradient treatment zone. Note however that only mildly reducing conditions are needed for perchlorate consumption, so this result, coupled with a mildly reduce ORP is reasonable.

The process monitoring event conducted on July 3, 2003 reported results similar to the previous monitoring event. The pH in IRZMW-2 was still low (4.74) The ORP in the wells was showing an increasing trend towards the highly oxidative baseline conditions. Dissolved oxygen levels had returned to aerobic conditions in all wells. Thus, another injection event was scheduled to bring the site back to reduced conditions.

Prior to conducting the next injection event on July 9, 2003, another process monitoring event was conducted. The monitoring showed that pH had returned to above 5.0 in monitoring well IRZMW-2. The ORP and DO in IW-1 was substantially lower then measured on July 3rd. All other parameters were similar to those monitored previously.

On July 9, 2003 another injection event was conducted using an injection volume of 400 gallons in each of the two injection wells. The concentration of carbohydrate used in the injected solution was halved in an attempt to control fermentation in the subsurface and maintain the pH above 5.0. The volume was increased from previous injections to facilitate lateral transport from the injection wells.

The next process monitoring event was conducted on July 16, 2003. A pump problem prevented the sampling of IRZMW-1. All other wells were monitored for field parameters. The results of monitoring found that the ORP had decreased to reducing conditions in IW-1 (-76.8 mV) and cross gradient well IRZMW-3 (-70.9 mV). IRZMW-2 and MW-7 were still oxidizing in ORP and DO The pH in all of the monitored wells had returned to near neutral (7.0). Nitrate measured using a field test kit showed concentrations slightly less than in baseline laboratory samples. Groundwater samples were collected from IW-1, IRZMW-2, and IRZMW-3 for perchlorate analysis. Perchlorate concentrations in IW-1 and IRZMW-2 continued to decline while the concentrations in IRZMW-3 were similar to baseline conditions.

Performance and process monitoring was conducted again on July 23, 2003. Monitoring well IRZMW-2 could not be monitored because of biofouling of the sampling pump. Both injection wells (IW-1 and IRZMW-1) also had biofouling problems but samples were obtained from these wells. See Figure 7-13 for a photograph of the biofouling that was typical in these wells. Biofouling was found to cause in well pumps to overheat during operation. The remedy was to pull the pump(s) involved and clean the pump screen(s). Bailers were not employed due to the depth of the water table and the resulting inability to properly purge the wells with a bailer.

Results for the process monitoring on 7/23/2003 showed that ORP levels had declined significantly in injection well IW-1 (-278 mV) and considerably in IRZMW-1 (46.6 mV). The ORP levels in IRZMW-3 and MW-7 were still oxidative, but were lower than at any time during the pilot test. The pH in all of the monitored wells had remained stable in the 6 to 7 range. Dissolved oxygen concentrations had declined from the previous monitoring event in both injection wells and remained stable (aerobic) in IRZMW-3 and MW-7. The nitrate field monitoring showed that nitrate concentrations had declined from the previous monitoring event. Groundwater samples collected for perchlorate analysis reported nondetectable (<4 µg/L) concentrations from injection well IW-1; increased concentrations in injection well IRZMW-1 (4,070 µg/L); stable concentrations from IRZMW-3 and slightly declining concentrations from MW-7.

A process monitoring event was conducted on July 31, 2003. Both injection wells could not be sampled due to localized biofouling of the pumps. The ORP in the three monitoring wells remained oxidative. The pH continued to be stable between 6 and 7. The dissolved oxygen concentrations measured at this time in the monitoring wells is consistent with an aerobic aquifer. Nitrate concentrations were stable. Well redevelopment was performed on the injection wells and monitoring well IRZMW-2 on August 13, 2003.

Another injection event was conducted on August 15, 2003 using the same volume (400 gallons) and concentration as the July 9th event.

A process monitoring event was scheduled for August 22, 2003. Pump problems believed to be associated with localized biofouling again prevented the acquisition of samples from all but wells IW-1 and MW-2. The ORP in injection well IW-1 was –68.8 mV and the pH was 6.67. The ORP in monitoring well IRZMW-2 was 95.4 mV and the pH was 7.01 (see Table 7-2a). A follow up sampling event was scheduled for August 25th.

The follow up process monitoring event conducted on August 25, 2003 found that all of the wells had higher (oxidative) levels of ORP, stable pH (between 6 and 7) and aerobic levels of dissolved oxygen. Nitrate levels remained stable in the 6 to 9 mg/L range. Injection well IRZMW-1 could not be monitored because of a pump failure.

The final monitoring event was conducted on September 4, 2003. Process monitoring results reported that ORP levels had continued to increase in all wells from their previous lows. The pH is all wells remained relatively stable. Dissolved oxygen concentrations were elevated. Nitrate concentrations were increasing in all wells. Performance monitoring results for perchlorate concentrations in all wells indicated that injection well IW-1 still had much lower concentrations of perchlorate than initial baseline measurements; downgradient monitoring well IRZMW-2 reported it's lowest perchlorate concentration for the test period (850 µg/L); the far downgradient monitoring well MW-7 also reported decreased concentrations of perchlorate (2,050 µg/L). The cross gradient well IRZMW-3 reported slightly lower concentrations of perchlorate when compared with baseline, however the decline wasn't significant. Injection well IRZMW-2 had a lower concentration of perchlorate than the baseline sampling result, but had shown considerable rebound during the test.

7.3.4 Dissolved Organic Carbon, Oxidation/Reduction Potential, and Dissolved Oxygen as Measures of Reactive Zone Radius of Influence

Dissolved organic carbon (DOC), oxidation/reduction potential (ORP) and dissolved oxygen (DO) measurment are all means of assessing the range of influence of the injected corn syrup. While measuring the DOC directly quantifies corn syrup in downgradient monitoring wells, the ORP and DO

measurements detect bacterial responses to the injected corn syrup. DOC, ORP, and DO were analyzed as part of the baseline sampling. Below is a summary of the trends of these three constituents per well during the pilot test.

- IW-1: (operated as an injection well, but located roughly downgradient of another injection well):
  - Baseline DO (6/4/2003) 6.00 mg/L; seen to trend downward after the second injection event such as 1.11 mg/L on 6/20/2003, 0.39 mg/L on 6/23/2003, and 0.22 mg/L on 6/25/2003. DO was depressed from baseline conditions up until the third injection event on 7/9/2003. Recovery to baseline conditions was observed at the final sampling event.
  - Baseline DOC (6/4/2003) 0.99 mg/L; mid test event (6/30/2003) 2.7 mg/L, mid test event (7/23/03) 47.9 mg/L; final event (9/4/03) not detected above laboratory reporting limit (< 1 mg/L). These values are well below what would be expected for an injection well receiving this injection scheme. These trends in DOC are consistent with increased groundwater flux through the treatment zone.
  - Baseline ORP (6/4/2003) 168.9 mV; depressed following the first injection in this well (second injection event of the pilot test) on 6/18/2003 and dropping to a low point of –278.3 mV following the third injection event on 7/9/2003. During the final event (9/4/2003), the ORP had recovered to a positive value of 63.7 mV.

- IRZMW-1 (used as the most upgradient injection well):
  - Baseline DO (2/21/2003) 4.86 mg/L; some depression measured following the first injection event down to 2.24 mg/L on 6/18/2003. Though a recovery in DO was noted between the first and second injection events, the second injection event sustained the low DO values detected in this well. DO recovered towards the final event and was detected at 6.61 mg/L on 9/4/2003.
  - Baseline DOC (2/21/2003) 2.49 mg/L; mid test event (6/12/2003) 87 mg/L, mid test event (6/30/03) 536 mg/L; mid test event (7/23/03) 204 mg/L final event (9/4/03) not detected above laboratory reporting limit (1 mg/L). Again, these values are well below what would be expected for an injection well receiving this injection scheme. These trends in DOC are consistent with increased groundwater flux through the treatment zone.
  - Baseline ORP (2/21/2003) 82.1 mV; though an increase in ORP was noted until after the second injection event, ORP was –427 mV five days after the second injection event on 6/23/2003. ORP recovered between the second and third injection events to 127.4 mV on before the injection event on 7/9/2003. At the time of the final event (9/4/2003), ORP measured 149.7 mV.

- IRZMW-2: (downgradient monitoring well)
  - Baseline DO (2/21/2003) 5.77 mg/L; DO in this well never appeared to significantly decline in response to injection events during the pilot test.
  - Baseline DOC (2/21/2003) 2.1 mg/L; mid test event (6/30/03) 3.5 mg/L; final event (9/4/03) not detected above laboratory reporting limit (1 mg/L).
  - Baseline ORP (2/21/2003) 148.2 mV; ORP in this well never appeared to substantially decline in response to injection events during the pilot test, although the data on 8/22/03 and 8/25/03 as compared to the trend up to that point suggest a slight decline..

- IRZMW-3:
  - Baseline DO (2/21/2003) 4.31 mg/L; DO in this well remained aerobic throughout the pilot test with the lowest value of 3.03 mg/L being measured on 7/16/2003. The DO at the final monitoring event was 8.00 mg/L.

- Baseline DOC (2/21/2003) 2.0 mg/L; mid test event (6/30/03) 2.6 mg/L; mid test event (7/23/03) 2.4 mg/L; final event (9/4/03) not detected above laboratory reporting limit (1 mg/L).
- Baseline ORP (2/21/2003) at this well was 13.2 mV. The ORP in this well was generally stable although three monitoring rounds (2 after the second injection event and 1 after the third) showed substantially negative values.

- MW-7:
  - DO in this well remained positive throughout the pilot test with the lowest value of 6.77 mg/L being measured on 7/16/2003.
  - Baseline DOC (2/21/2003) 2.3 mg/L; mid test event (6/30/03) 2.1 mg/L; mid test event (7/23/03) laboratory estimated 4 mg/L; final event (9/4/03) not detected above laboratory reporting limit (1 mg/L).
  - The ORP at this well never went significantly below baseline.

7.3.5 Bromide Tracer Data

Bromide concentrations were evaluated as part of the baseline sampling, once during the pilot test, and as part of the final sampling. Below is a summary of bromide data trends per well.

- IW-1:
  - Baseline event (6/4/2003), bromide was not detected above laboratory reporting limits (< 1 mg/L).
  - Mid test event (6/30/2003), bromide was not detected above laboratory reporting limits (< 1 mg/L).
  - Final event (9/4/2003), bromide was detected at a laboratory estimated 0.83 mg/L (J value)

- IRZMW-1:
  - Baseline event (2/21/2003), bromide was not detected above laboratory reporting limits (< 0.48 mg/L).
  - Mid test event (6/30/03), bromide was not detected above laboratory reporting limits (< 1 mg/L).
  - Final event (9/4/2003), bromide was detected at a laboratory estimated 0.67 mg/L (J value).

- IRZMW-2:
  - Baseline event (2/21/2003), bromide was not detected above laboratory reporting limits (< 0.48 mg/L).
  - Mid test event (6/30/03), bromide was not detected above laboratory reporting limits (< 1 mg/L).
  - Final event (9/4/2003), bromide was not detected above laboratory reporting limits (< 1 mg/L).

- IRZMW-3:
  - Baseline event (2/21/2003), bromide was not detected above laboratory reporting limits (< 0.48 mg/L).
  - Mid test event (6/30/03), bromide was not detected above laboratory reporting limits (< 1 mg/L).
  - Final event (9/4/2003), bromide was detected at a laboratory estimated 0.57 mg/L (J value).

- MW-7:

- Baseline event (2/21/2003), bromide was not detected above laboratory reporting limits (< 0.48 mg/L).
- Mid test event (6/30/03), bromide was not detected above laboratory reporting limits (< 1 mg/L).
- Final event (9/4/2003), bromide was not detected above laboratory reporting limits (< 1 mg/L).

Dilution Calculations using Bromide as a Tracer

ARCADIS has assumed that the bromide tracer used is indeed conservative and flows along with and at the same rate as the injected liquids. Given the expected low TOC of these soils this is a reasonable assumption. Bromide was included in each injection event. Thus, the amount of dilution caused by the IRZ injections in a given well should be directly proportional to the amount of bromide that is observed in that well. As an extreme example, if 100 mg/L of bromide were injected into the injection well and then 100 mg/L bromide were withdrawn a week later at a monitoring well located one-week downgradient of the injection well, we would surmise that the monitoring well contains only injection fluid and is 100% diluted. If 0 mg/L bromide were measured in the monitoring well, none of the water from the injection well has made it to the monitoring well and there is thus 0% dilution.

Based on this logic, concentrations of constituents of concern determined through chemical analysis can be adjusted to correct for dilution effects. Measurements were corrected by calculating a dilution factor per the following equation:

$$DF \quad 1 - \frac{[Br]_{MW}}{[Br]_{Inj}}$$

Where,

DF = dilution factor (that is, the percentage of monitoring well sample that is not dilution water),

$[Br]_{MW}$ = the bromide concentration measured on a sample taken from a monitoring well on a given date, and

$[Br]_{Inj}$ = Injection fluid bromide concentration (an approximate running average of injection fluid bromide concentrations made around the assumed travel time of the injection well to the monitoring well). This takes into account both the molasses solution and the water "push" fluids.

Then, the concentration of the constituent of concern for a given monitoring well sample was corrected by calculating its actual concentration per the following equation:

$$VOC_{actual} \quad \frac{VOC_{measured}}{DF}$$

As an example, consider the Br concentration measured on a sample from IRZMW-3 on September 4, 2003 (final sampling event). The measured Br in IRZMW-3 was 0.57 mg/L (qualified as estimated). The average injection concentration of bromide was determined by averaging the reagent loading for all four injection events as follows:

- A total of 6.3 lbs KBr per 2,230 gallons of reagent, with a units conversion, is 338.56 mg/L KBr. Bromide accounts for 67% of the atomic weight of KBr, so the average bromide concentration in the reagent solution was 0.67 * 338.56 mg/L, or 227 mg/L

Thus the dilution factor was: 1 – 0.57/227 = 0.997. The perchlorate concentration from this sample was 3,640 mg/L. Therefore, the actual perchlorate concentration, corrected for the effect of dilution with the injection fluid should be 3640/0.997 = 3651 mg/L.

There were few bromide detections during the pilot test, and the detected levels were uniformly below 1 mg/l. Note that the concentration of bromide was below 1 mg/l *even in the injection wells*, when they were sampled 2-3 weeks after the previous injection. The low bromide levels at downgradient wells thus indicate that dilution by the injections in the reactive zone was a relatively insignificant factor. Given that dilution factors test-wide were above 99.5%, the perchlorate results used in evaluations elsewhere in this report have not been adjusted for dilution. Monitoring well data can then be accepted as not being significantly influenced by dilution. Caution should still be applied to injection well data, but injection well results should not be dismissed out of hand. Under these circumstances analysis of injection well data becomes broadly similar to the analysis of data from push-pull tests (see the publications of Istok and coworkers http://ccee.oregonstate.edu/research/grl/push-pull/literature.htm). The perchlorate data from injection wells on the dates when the bromide was analyzed can thus be interpreted with relative certainty as being attributable to biodegradation or the lack thereof, not dilution.

7.4 Perchlorate Treatment

7.4.1 Summary of Perchlorate Treatment Results

Perchlorate concentrations coupled with biogeochemical trends were evaluated as part of the baseline sampling, several times during the pilot test, and as part of the final sampling. Below is a summary of perchlorate data trends per well and a discussion of biogeochemical trends. Figure 7-14 graphically depicts perchlorate concentrations during the demonstration and the four corn syrup injection events.

- IW-1: (injection well, roughly downgradient of another injection well) - Baseline event (6/4/2003), the perchlorate concentration was 3,390 µg/L. Perchlorate decreased after the first and second injection events. Then, perchlorate concentrations increased slightly to 1910 µg/l prior to the third injection event (when a bromide sample was also analyzed, suggesting that dilution was minimal). After the third injection event, perchlorate decreased below laboratory reporting limits of 4 µg/L. After the fourth injection event, perchlorate concentrations increased to approximately 649 µg/L (when a bromide sample was also analyzed, suggesting that dilution was minimal). Taken together these results suggest a substantial treatment of perchlorate was observed in this well (81% removal at end of demonstration).
- IRZMW-1: (furthest upgradient injection well) - Baseline event (2/21/2003), the perchlorate concentration was 5,270 µg/L. Perchlorate decreased after the first and second injection events. In particular, perchlorate decreased dramatically after the second injection event. Then, perchlorate concentrations rebounded to nearly the same level 3260 µg/l prior to the third injection event (when a bromide sample was also analyzed, suggesting that dilution was minimal). After the third injection event, perchlorate concentrations increased further but then decreased to 2,810 µg/L in the final monitoring round (when a bromide sample was also analyzed, suggesting that dilution was minimal).
- IRZMW-2: (downgradient monitoring well) - Baseline event (2/21/2003), the perchlorate concentration was 9,340 µg/L. Perchlorate decreased after the first and second injection events to 1,810 µg/L. Then, perchlorate concentrations increased slightly prior to the third injection event. After the third and fourth injection events, perchlorate concentrations decreased to 850 µg/L. These results suggest a treatment effectiveness of up to 91% using the 2/21/2003 baseline data point and the final data point on 9/4/2003.

- IRZMW-3: (cross-gradient) - Baseline event (2/21/2003), the perchlorate concentration was 3,640 µg/L. Perchlorate increased slightly after the first and second injection events. Then, perchlorate decreased slightly prior to the third injection event. After the third injection event, perchlorate concentrations returned to exactly the starting concentration - 3,640 µg/L. The trend here indicates no biodegradation. No DOC was measured in this well. However, there were brief negative ORP excursions. At other IRZ sites, ARCADIS has observed that redox and DO changes occasionally propagate more widely than the influence of the substrate used in an IRZ system (ARCADIS, 2003; Lutes, 2002). Such effects have been observed in both downgradient and side-gradient directions from the injection point. Although the full mechanistic explanation for this phenomenon is not known, it likely explains the intermittently low ORP values at IRZMW-3. ARCADIS believes that the perchlorate concentration in this well was unaffected during the demonstration making a comparison of perchlorate concentrations in IRZMW-3 to the injection wells, IRZMW-1 and MW-7 perchlorate concentrations a useful tool. Such a comparison is useful to assist in addressing concerns that decrease in perchlorate in the treatment zone result from variable perchlorate concentration in groundwater rather than in situ bioremediation. ARCADIS is convinced that IRZMW-3 was not influenced substantially by injected corn syrup during the demonstration. Based on the perchlorate concentrations in IRZMW-3 through the project interval, ARCADIS is convinced that the declines in perchlorate concentration in other wells are the results of in situ bioremediation and not variations in the amount of dissolved perchlorate moving through the treatment zone.
- MW-7: (furthest downgradient well) - Baseline event (2/21/2003), the perchlorate concentration was 4,590 µg/L. Perchlorate decreased slightly after the first and second injection events. Then, perchlorate decreased more significantly after the third and fourth injection events. The final perchlorate concentrations decreased to 2,050 µg/L. Historic perchlorate concentrations in MW-7 during quarterly monitoring events had previously been greater than 2,000 µg/L since July of 2001 (see Figure 3-3).

The perchlorate analyses conducted on groundwater samples withdrawn from IRZMW-1, IRZMW-2, IRZW3, and MW-7 on 2/21/2003 provide an indication of the variability of perchlorate in the pilot study area prior to the demonstration (3,640-9,340 µg/l). The perchlorate analysis conducted on a groundwater sample from IW-1 on 6/4/2003 is indicative of the perchlorate concentration just prior to the first corn syrup injection. Figure 5-2 provides the lay-out of the wells involved in the pilot study.

Following the first two injection events, which occurred on 6/4/2003 and 6/18/2003, we noted significant decreases in the concentration of perchlorate measured in the two injection wells (IW-1 and IRZMW-1). Perchlorate in IW-1 decreased by 76% from 3,390 µg/L on 6/4/2003 to 802 µg/L on 6/25/2003. Perchlorate in IRZMW-1 decreased by 73% from 3,750 µg/L on 6/18/2003 to 1,030 µg/L on 6/25/2003. These measured decreases follow a logical time sequence thus substantiating that they resulted from previous corn syrup injection events. A lesser degree of perchlorate treatment was measured in the monitoring well IRZMW-2. During this same interval, the perchlorate concentration in the monitoring wells IRZMW-3 and MW-7 was relatively unaffected by the first two injection events (see the discussion of the use of bromide to establish the dilution factor associated with the corn syrup injection events in Section 7.3.5). Based on these calculations, the dilution factor caused by injections did not account for the degree of perchlorate disappearance in IW-1, IRZMW-1, and IRZMW-2 therefore it is reasonable to infer that biodegradation was successfully enhanced.

ARCADIS responded to the measured perchlorate treatment in the injection wells and of the observation of less then complete treatment in downgradient monitoring wells by increasing the volume of injected corn syrup solution and holding the quantity of corn syrup per injection constant. We hypothesized that:

- Given the higher then expected flow rate, a relatively narrow reactive zone would be expected to be formed at a given in injection volume
- Given that there was some variability in the groundwater flow direction, and that all aquifers are subject to preferential flow pathways, the reagent may have been "missing" some of the downgradient monitoring wells.

This adjustment to the injection scheme was intended to disperse the corn syrup more widely laterally so as to extend the size of the IRZ and maximize the chance of influencing additional monitoring wells. Therefore, on 7/9/2003, ARCADIS injected 20 gallons of corn syrup and 380 gallons of water into both IW-1 and IRZMW-1.

This third injection event resulted in a further decrease in perchlorate concentration in IW-1. On 6/25/2003, the perchlorate concentration in IW-1 was 802 µg/L. Following the third injection event, the perchlorate measured in IW-1 decreased to nondetect (ND). Further reductions in perchlorate concentration were measured in IRZMW-2, and MW-7 following the fourth corn syrup injection carried out on 8/15/2003.

Because perchlorate biodegradation occurs in anaerobic settings, ARCADIS looked at groundwater ORP values during the demonstration (See Figure 7-15). Despite higher than expected groundwater velocities, the ORP of IRZ treatment zone was seen to decline in response to corn syrup injection events. After the first injection event, ORP in the injection well IRZMW-1 declined to -49.4. Following the second injection event, ORP in IRZMW-1, IRZMW-3, and IW-1 all declined to significant negative values (See Figure 7-15). The third injection event resulted in measurable ORP declines in IRZMW-3 and IW-1. Had groundwater velocity been in the predicted range during this pilot test, ARCADIS believes that the ORP values detected in injection wells and downgradient monitoring wells would have been more stable and consistently negative. Nonetheless, the ORP data support periodic generation of anaerobic zones in response to corn syrup injection events that would be capable of sustaining perchlorate bioremediation.

Thus, evaluation of perchlorate reduction and biogeochemical data reveals that, the data set is consistent with enhanced perchlorate biodegradation. However the anaerobic character of the treatment zone and consequently the longevity of treatment was short lived due to the higher than anticipated flux of groundwater through the treatment zone. The strongest lines of evidence for this interpretation are:

- The very large dilution factors observed in the concentrations of bromide and corn syrup injected at both the injection and monitoring wells.
- Based on the changed gradient, one would expect limited changes in ORP and DO to be brought about following corn syrup injection.
- Limited changes in ORP and DO were observed in the monitoring wells.

For the reasons discussed above in Section 2.1.1, we designed this system to not go to deeply anaerobic conditions, so a mildly reducing, nitrate/perchlorate reducing zone was desired. These zones are necessarily subject to more rapid redox change when there is an influx of oxygen from upgradient than the deeply anaerobic (methanogenic) zones typically employed for high rate CAH treatment. Thus these zones are expected to be more short-lived and to have a smaller reserve of degradable organic carbon in the *in situ* system. Therefore more frequent injections should be employed in an IRZ system scaled up at this site or similar sites.

Though ARCADIS was willing to extend the demonstration at no additional cost to permit additional tuning of the injection scheme, which could have resulted in the formation of a more extensive, stable IRZ for perchlorate treatment, such a project extension was not possible in late September. JPL was

preparing the portion of the site surrounding the ARCADIS demonstration area to receive an alternate full-scale perchlorate remedy believed to be the most protective of the drinking water resource that this aquifer represents.

Previous Perchlorate Data in MW-7

Perchlorate concentrations in MW-7 have been monitored during quarterly groundwater monitoring events by SOTA Environmental Technologies, Inc. (SOTA) since the June/July 1997. From this first monitoring event until the beginning of a pilot test by Foster Wheeler in January/February 2001, perchlorate concentrations ranged from 120 µg/L to 740 µg/L. The average concentration for this time period was approximately 338 µg/L. Foster Wheeler collected perchlorate samples for the January/February 2001 event and the April 2001 event. The reported concentrations were 1,100 µg/L and 420 µg/l, respectively. Perchlorate was not sampled during the July and October 2001 groundwater monitoring events. SOTA resumed sampling and monitoring in January/February 2002 and continued through July 2002. Perchlorate concentrations for those three events were 4,090 µg/L, 6,770 µg/L and 2,590 µg/L, respectively. This perchlorate trend in MW-7 is graphically depicted in Figure 3-3.

Over the course of years it is reasonable to state that the concentrations at this well are highly variable, but seemed to be trending upwards prior to the pilot test. This suggests a continued source of contamination and likely an absence of effective natural attenuation processes.

7.4.2 Summary of CVOC Treatment

Although CVOC treatment was not a primary focus of this demonstration, the IRZ technology is well suited for *in situ* bioremediation of CVOCs. The major CVOCs present in the background samples at this site are carbon tetrachloride (CT) and chloroform (CF). The MCL for CT is 5 ppb and for CF is 100 ppb. Background CT levels in the wells used for this demonstration ranged from 19 to 244 ppb and CF from 9 to 28. Tetrachloroethene (PCE) was detected in some of the wells for the demonstration at concentrations from <5 to 25 ppb as compared to an MCL of 5 ppb.

There are multiple mechanisms of Carbon Tetrachloride (CT) degradation that occur under anaerobic conditions that have been reviewed by Faris (2002 http://www.engg.ksu.edu/HSRC/ag/2002/proceed/c02.pdf). *"Carbon tetrachloride biological destruction and its degradation products have been observed under denitrifying, sulfate-reducing, acetogenic, fermentative, and methanogenic conditions by a variety of organisms. These reductive processes do not solely follow a sequential reduction whereby a chloride ion is removed during each transformation. Research studies suggest that carbon tetrachloride destruction pathways may be both reductive and substitutional."* Thus these mechanisms include ones characterized by the temporary buildup of sequential degradation products such as chloroform (CF), methylene chloride and chloromethane as well as mechanisms in which little or no product buildup is observed. It is also important to note that the mildly reducing, conditions, such as denitrifying that were targeted in this demonstration, as discussed elsewhere, are amenable to CT biodegradation.

Although this field demonstration occurred for only three months, there is substantial evidence in the dataset that the degradation of CT was enhanced:

- The concentrations of CT decreased between 70-90% in most wells as compared to the background samples (see Table 7-2) were relatively little effected in IRZMW-2. Note also that bromide tracer data (discussed in Section 7.3.6) suggests that the dilution effect of the injected liquid should be negligible in the monitoring wells. Even for the injection wells the low concentrations of bromide

observed in the final round of samples (9/4/2003) suggests that dilution cannot explain changes in CAH concentration that occurred between the background and final rounds.

- Although as discussed above CT degradation can occur without substantial accumulation of CF, CF did appear to briefly accumulate and then degrade in well IW-1, which though it was used as an injection well was located downgradient of injection well IRZMW-1.
- A comparison of the time series in CT and CF concentrations in wells IW-1 and MW-1 and MW-7 is instructive (See figures A-C). In IW-1 the decrease in CT that occurs between the background round and the first post injection monitoring round is much more substantial on a percentage basis then the change in CF. In the second monitoring round, CT reaches a low point and CF peaks at a concentration more then twice its background concentration. This is suggestive of production of CF from degradation of CT. There is also marginal evidence of production of a trace of chloromethane in this well. The final round, which occurred several weeks after the last injection, may show signs that a rebound in concentrations was occurring at this well.
- In IRZMW-1, the most upgradient injection well the most significant decrease in CT appears to occur between the background and first post injection monitoring rounds but the change in CF appears to occur primarily between the first and second post injection monitoring rounds. Note that if dilution or many other nonbiodegradation processes were controlling the concentrations we would expect CT and CF to change concentrations roughly in parallel. Thus this suggests that the process occurring here is biodegradation. There is also marginal evidence of the transient production of methylene chloride in this well. At the furthest downgradient monitoring well, MW-7, the concentrations of CT and CF are roughly parallel.

The evidence regarding the biodegradation of PCE is less definitive. Although it appears to decrease in several wells, as does TCE, there is no detectable formation of cis-DCE and VC, which are typical products. Detectable product formation does not necessarily occur during all PCE/TCE degradation processes, especially when the starting concentrations are so low. A literature review suggests that degradation of these compounds under nitrate reducing conditions can occur, but not with all microbial consortiums (ITRC). In general PCE/TCE are less degradable under these conditions then CT is. Thus the absence of product formation, when coupled with the literature evidence, suggests that we should be cautious about concluding that PCE and TCE degradation occurred during this brief demonstration under mildly reducing conditions.

Thus, though only four rounds of monitoring data covering only three months of active treatment were available, this dataset does provide several lines of evidence that suggest that CT biodegradation was substantially enhanced. Some evidence of biodegradation of CF and PCE was also seen (see Table 7-3).

7.4.3 Hydrogeology Discussion

As previously discussed, ARCADIS utilized the average hydraulic conductivity value from the December 1994 slug test in well MW-7 (7.8 feet per day) along with an effective porosity estimate of 0.25 and a gradient of 0.02 to estimate groundwater velocity in the test area at 0.58 feet per day as the design basis for the demonstration. This calculation for groundwater velocity was applicable to the hydrogeological conditions present in the test area on March 6, 2003. Subsequently, hydrogeological conditions were altered following a substantial rise in the groundwater table elevation (See Figure 7-16 for graphic of groundwater elevation during demonstration). ARCADIS repeated groundwater velocity calculations reflecting the hydrogeological conditions as of May 29 (see Figure 7-5) and found a substantial increase in groundwater velocity driven by increased groundwater table elevation. Using the average hydraulic conductivity value for MW-7 from the RI, and the same porosity value of 0.25 along with a revised gradient of 0.07 to 0.09, groundwater velocity just eight days prior to the start of the demonstration was

calculated to be 2.1 to 2.8 feet per day across the demonstration zone. This alteration in hydrogeological conditions and its resulting influence on groundwater velocity played an important role in defining the outcome of the demonstration in that it led to the application of insufficient quantities of corn syrup to generate a stable, long-term anaerobic zone over the entire demonstration area. ARCADIS altered its injection scheme in an effort to correct for this alteration in hydrogeological conditions during the July 9 injection event by increasing the total volume of the injected solution to increase dispersion of the corn syrup in the aquifer. Increasing the total volume of injected solution while holding the corn syrup mass constant is the first, conservative step typically taken to widen the zone of influence of injected corn syrup during IRZ implementation.

7.4.4 Secondary Water Quality Issues

ARCADIS recognizes that, while corn syrup is nontoxic and does not contain any regulated organics or metals, its injection into the subsurface to enhance/facilitate perchlorate bioremediation could result in the temporary deterioration of secondary water quality characteristics. For example, by definition, any substrate used to enhance anaerobic bioremediation will elevate the BOD, a traditional measure of water quality. Based on past experience, ARCADIS realizes that overdosing of an organic substrate such as corn syrup into IRZ in an effort enhance bioremediation can result in excessive bacterial fermentation of the sugars present in the injection solution. Excessive fermentation can lead to secondary water quality issues with organics such as ketones.

It should be noted that, as expected in natural systems, the changes to secondary water quality characteristics sometimes seen during IRZ implementation are reversible. Over time as treated groundwater moves downgradient, baseline conditions associated with dissolved oxygen, ORP, pH, dissolved organic and inorganic content of groundwater are restored through natural attenuation mechanisms. This restorative process requires differing amounts of time and lateral space dependent on site hydrogeological characteristics and IRZ injection schedules and carbon source mass loading.

In addition to the normal performance monitoring parameters, groundwater samples were analyzed for additional parameters (similar to baseline sampling) to monitor potential secondary water quality effects of the treatment. At the conclusion of the demonstration, none of the wells contained measurable amounts of COD or DOC. Slight levels of BOD were measured in the injection wells, however the levels were much less than the baseline results. Nitrate concentrations were slightly less that baseline levels. Sulfate levels were similar to the baseline results. We also examined the potential mobilization of metals such as arsenic, iron and manganese. Results from this final sampling event reported that levels of all of these metals had declined from the baseline reported values. In addition, chromium had been reported in elevated levels during the baseline sampling event. Chromium concentrations were found to be reduced by more than an order of magnitude in the injection wells and more than half in the monitoring wells. This is an expected result since this technology has been used to successfully treat chromium at other ARCADIS site (Suthersan, 2002).

Inorganic impacts to secondary water quality can be caused by excessive fermentation, which results in the production of low molecular weight organic acids such as acetic acid and proprionic acid. The excessive production of these acids in an unbuffered aquifer can result in significant reductions in groundwater pH. While reduction in pH certainly represents a secondary water quality impact by itself, the lower pH, coupled with the reducing conditions within the reactive zone, will alter the geochemistry of the reactive zone. Altered geochemistry has the potential to make some soil mineral metals of regulatory significance more mobile (more dissolved) and others less mobile (more inclined to the solid phase).

Metabolism of high sugar concentrations can result in the production of ketones such as acetone, 2-butanone, 2-hexanone, and methyl isobutyl ketone along with alcohols, just as it does in organisms. If produced, these regulated organics are expected to be subsequently rapidly biodegraded within the reactive zone. Their formation can be minimized or eliminated through the use of downgradient monitoring to track the concentration of organic carbon that has been added to the aquifer. The experienced practitioner of the IRZ technology can observe the build-up of organic carbon resulting from the present injection strategy and make the decision to lessen the number/frequency/organic carbon loading or use buffer to control pH to control the formation of ketones and alcohols.

Regulated ketones generated by fermentation during IRZ implementation were largely absent with the exception of acetone found in the injection well IRZMW-1 (770 µg/L on 6/30/2003 and 1,480 µg/L on 7/23/2003) and 2-butanone found in the injection well IRZMW-1 (240 µg/L on 7/23/2003). No alcohols were detected in either the injection wells or the monitoring wells during the demonstration interval.

The implementation of in situ bioremediation using substrate additions could increase the total dissolved solids (TDS) present in the aquifer. Both the organic and trace mineral components of food grade carbohydrates contribute to elevated TDS values.

During the JPL project, ARCADIS periodically monitored the secondary water quality parameters discussed to evaluate decisions about the injection strategy for the perchlorate IRZ demonstration. Samples were collected and analyzed prior to the first injection to establish analyte specific baselines. Because it influences native metal related secondary water quality characteristics and because it indicates excessive fermentation, which is linked to the production of regulated organic molecules in an IRZ, pH has been graphed and presented as Figure 7-17. With the exception of one decline in the injection well IRZMW-1 following the second injection event, pH during the demonstration was above 6 s.u. in all monitoring and injection wells. Additional analytical results relevant to the assessment of secondary water quality parameters, including baseline data, have been assembled and presented in Table 7-2.

7.4.5 Comparison of Results with Objectives

The specific objectives of this pilot study as discussed in the workplan and Section 1.2 of this report are listed below in italics along with text discussing the individual degrees of success.

1. *Conduct a microcosm study to verify that corn syrup is an appropriate electron donor to support perchlorate bioremediation in the aquifer at JPL and in any JPL vadose zone soils that are found to be contain elevated levels of perchlorate.*

As discussed in Section 5.5, the laboratory microcosm study confirmed that corn syrup was an acceptable substrate to induce perchlorate bioremediation by microorganisms indigenous to the JPL saturated zone. Because there was no perchlorate detected in the JPL vadose zone, corn syrup was not confirmed as a perchlorate bioremediation inducing substrate in the JPL vadose zone.

2. *Create a reactive reducing zone for perchlorate bioremediation within groundwater in an area directly upgradient and near monitoring well MW-7.*

We typically utilize DO, ORP, and DOC measurements (as well as changes in alternate electron acceptors and their products) to assess the size and longevity of the reducing zone created following substrate injections. As discussed above we sought here to form only a mildly reducing zone so as to minimize secondary water quality impacts while still consuming perchlorate. Section 7.3.4 summarizes the DO, ORP, and DOC data for the pilot study. Close inspection of these data indicate

that, while the saturated zone microorganisms did respond to corn syrup injections as evidenced by marked decreases in DO and ORP in the injection wells, the volume and frequency of the injections, along with the mass of corn syrup injected did not result in the formation of a large permanent reducing zone. However, the data show the formation of a temporary reducing zone in and downgradient from the injection wells immediately following corn syrup injection events.

3. *If perchlorate is detected in vadose zone soils, create a reactive reducing zone for perchlorate bioremediation in soil overlying the perchlorate groundwater plume upgradient and near monitoring well MW-7.*

Despite efforts to locate vadose zone perchlorate in the area of the saturated zone demonstration and in the Pit No. 30 area, no vadose zone perchlorate was detected. Therefore, this objective must be dropped from consideration.

4. *Monitor the hydrogeochemical changes in groundwater that occur over the course of treatment. Specifically, note the change in oxidation-reduction potential (ORP), dissolved oxygen (DO), hydrogen ion concentration (pH), and conductivity.*

This objective was attained as indicated by the generated and analyzed data set discussed above.

5. *Monitor changes in specific inorganic compounds—nitrate, perchlorate, ferrous iron, and sulfate.*

Decreases in perchlorate concentration during the course of the demonstration verify that perchlorate bioremediation did result during anaerobic conditions stimulated by corn syrup injection. Comparison of the nitrate, sulfate, and ferrous iron concentrations present as a baseline to those present at the conclusion of the pilot test reveal little change in these parameters.

6. *Monitor potential changes in the concentrations of specific organic compounds—chlorinated volatile organic compounds (CVOCs to include carbon tetrachloride, chloroform, trichloroethene, 1,2-dichloroethene, and vinyl chloride) and dissolved organic carbon (DOC).*

Small concentrations of carbon tetrachloride, chloroform, tetrachloroethene, and trichloroethene were detected at the beginning and conclusion of the pilot study. Although relatively limited concentrations of these CVOCs were detected, IRZ implementation at JPL appears to have had generated some CVOC treatment. CVOC treatment is discussed specifically in Section 7.3.2 above. Further we note that the mild reducing conditions targeted and achieved here are not those that have normally been associated with high rate treatment of CVOCs (Suthersan, 2002). However, the data set is adequate to address specific changes in the DOC during the demonstration. The DOC data is reviewed in Section 7.3.4 and shows substantial dilution.

7. *Obtain hydrologic dilution information using an inorganic tracer (bromide). This information will be used to determine appropriate well spacing for full-scale.*

While bromide was always added to each slug of injection solution delivered, bromide analyses mostly resulted in values below the detection limit. These results still contribute useful information about the injection scheme utilized during the demonstration and how it could be improved should full-scale implementation become desirable. They show that the groundwater flow and thus dilution in this system is substantially higher than was originally anticipated. This is expected to raise the scale up cost of all remediation technologies at this location in roughly equal proportions.

The bromide tracer data was also used to demonstrate that the observed reductions in perchlorate were not due to dilution by the injected fluids. An example dilution calculation using the bromide tracer data is presented in Section 7.3.5.

8. *Determine the overall rate of perchlorate removal within the reactive zone.*

The IRZ formed during this demonstration was of a transient nature due to the greater than expected flux of groundwater through the treatment zone. Because the entire treatment zone was not converted to anaerobic conditions by corn syrup injections, an estimate must be made as to the lateral and vertical extent of transient treatment zone that was formed to support this calculation. Though it is clear that substantial perchlorate treatment was acheived, ARCADIS believes that its ability to estimate the size of the treatment zone is too unscientific and fraught with error to support the calculation of a perchlorate removal rate of suitable accuracy for publication in this report.

9. *Determine the organic loading rate necessary to create reducing conditions amenable to perchlorate degradation.*

The organic loading rate necessary to generate a stable anaerobic reductive zone for perchlorate treatment is clearly greater than the highest loading rate under which this demonstration was conducted. While in would be necessary to increase the organic loading, engineering improvements to enhance distribution of the corn syrup injection solution laterally across the treatment zone are also likely to be required.

7.4.6 Technology Comparison

Groundwater Extraction (Pump & Treat) with Ion Exchange

Perhaps the most widely demonstrated and accepted technique for perchlorate remediation is pump and treat coupled with ion exchange resin. This technology is accepted for application to water supply systems and, when properly implemented, can achieve the current range of treatment standards (< 10 µg/L). Because it is highly influenced by the concentration of total dissolved solids, the distribution of competing anions in the water being treated, and the perchlorate concentration itself, ion exchange treatment cost is very site dependent. A range of cost from $0.31 to $1.53 per 1000 gallons was presented recently at the 2003 SERDP/ESTCP Symposium (Coppola Presentation entitled, "Available and Emerging Perchlorate Treatment Technologies for Drinking Water and Wastewater", http://www.serdp.org/symposiums/2003/2003SymposiumPresentations.cfm). This range in costs is said to include the capital cost of the treatment system hardware. One significant disadvantage of this remediation approach is its non-destructive nature. Additional technologies are currently being sought to destroy perchlorate in ion exchange regeneration brine.

Groundwater Extraction (Pump & Treat) with Ex-situ Fluidized Bed Bioreactors

While other bioreactor designs have been tested, perhaps the most accepted design for bioreactors intended to treat perchlorate is the fluidized bed bioreactor (FBR). Due to the size and typical geology associated with perchlorate plumes, relatively high flow rates are typical for perchlorate pump and treat systems. FBRs perform well at these high flow rates that are typical of perchlorate remedial systems and their design eliminates the formation of preferential flow pathways that are typical of packed bed bioreactors. Perhaps the most well known FBR currently in operation for perchlorate treatment is at the Aerojet Facility in Rancho Cordova, California. This FBR uses ethanol as a substrate and is reliably treating 5,000 gallons per minute for $0.17/1000 gallons (Hatzinger Presentation entitled "*In Situ* and *Ex Situ* Bioremediation Technologies for Perchlorate in Groundwater, SERDP/ESTCP Symposium, 2003, http://www.serdp.org/symposiums/2003/2003SymposiumPresentations.cfm). ARCADIS has confirmed that this figure does not factor in the substantial initial capitol cost of the treatment system but is in fact an operations and management (O&M) figure. While properly designed FBRs have a good track record of reliable performance, the acceptance of biologically based treatment for use on water supply systems is considerably lower than that afforded ion exchange systems.

8.0 Cost Assessment

8.1 Cost Reporting

A cost breakdown for a hypothetical case is provided as Table 2-1. Information is also presented regarding cost comparisons between IRZ and established perchlorate remediation technologies, based on ARCADIS' experience and that of others as presented in the literature.

8.2 Cost Analysis

In general, perchlorate plumes in groundwater take the form of pure dissolved phase contamination. IRZ can be applied to such a plume in at least three configurations – as a barrier, as a plume-wide treatment, and as a spot treatment of a source area. The choice of configuration for a given site depends on a variety of technical, economic, regulatory and risk factors. However, a common IRZ approach to an aqueous-phase contaminant like perchlorate is to treat the whole plume above a specified concentration, leaving low-concentration fringes to attenuate naturally. This approach is assumed for cost estimating purposes. Cost analyses presented in this section are based on a dissolved phase plume in groundwater, with no treatment of vadose contamination.

8.3 Cost Comparison

<u>Cost Comparison vs. Extraction and Above-grade Treatment (Pump and Treat)</u>

The best way to estimate the potential benefit of an innovative remediation technology is to evaluate its cost at sites where it has been demonstrated alongside more conventional technologies. ARCADIS has extensive experience in replacement of pump and treat systems with IRZ technology. Most of our examples are geared toward CAHs or metals rather than perchlorate plumes, but they provide a useful comparison. Differences in perchlorate and CAH remediation which would affect cost include sorption effects, which would be expected to prolong the extraction period required for a CAH plume relative to a perchlorate plume of the same initial size. Conversely, *ex situ* treatment systems for CAHs are generally less expensive to build and operate than those used for perchlorate. Furthermore perchlorate IRZ systems would use less substrate per unit volume then metals or CAH systems because a less reducing zone is required.

Examples of actual and projected savings associated with eleven sites are listed in Table 8-1. The geometries of the listed sites are inter-comparable, being generally plume-wide or multiple-transect applications (as opposed to single linear containment barriers) and not solely source area treatments. Actual or projected savings for replacement of the example pump and treat systems with IRZ systems ranged from $200,000 to over $6 million.

8.3.1 Cost Drivers

Section 2.3 provides a general discussion of cost factors associated with IRZ. Although a project-specific cost analysis has not been conducted, anticipated generic cost drivers are briefly summarized as follows:

The majority of the costs related to reagent injection are related to labor (including preparation and support), temporary and permanent equipment, type of application (source reduction vs. plume-wide treatment), etc. The cost of the reagent material is relatively insignificant.

Based on our experience and analysis, the two largest cost factors for IRZ implementation are the injection well installation and the O&M associated with reagent injections. Other factors that need to be given special consideration during design in order to develop the most cost-effective approach for site remediation are:

- Plume size
- Depth of target zone
- Magnitude of groundwater flux
- Geology

8.3.2 Life-Cycle Costs

A detailed breakdown of life-cycle costs for a hypothetical, typical IRZ site is provided in Table 8-2, using the Level 2 and 3 work breakdown structure from the U.S. Army Corps of Engineers (2001). The hypothetical site represents a whole-plume application. This approach is potentially appropriate for the JPL plume, where no vadose contamination has been located. Further, the hypothetical example assumes the following conditions:

> *The hypothetical site is a commercial property with a perchlorate plume. The perchlorate exists primarily in the dissolved phase; no residual source material remains. A combination of IRZ and monitored natural attenuation (MNA) will be used to achieve cleanup standards. The IRZ application is targeted for the portion of the plume where perchlorate concentrations exceed 500 µg/L. This area is approximately ____feet in length, ____feet in width, ____feet in thickness, and extends to a depth of ____feet. Groundwater velocity is ____feet/day. The portion of the plume targeted for IRZ technology is to be treated with a 10% molasses solution, injected through 25 injection wells. Injections are performed monthly for the first two years of treatment, using mobile, trailer-mounted injection equipment. The rate of injection is then reduced to bi-monthly for three additional years. The project duration is five years from the initiation of the IRZ program, including three years of MNA. MNA costs are not presented here.*

Table 8-2 includes estimated capital, operating and regulatory (permitting and reporting) costs. Since costs are based on complete destruction of perchlorate, no future liability costs are included.
The duration of IRZ injections and MNA are of course different for each site and dependent on site conditions. The example of five years of injections followed by three years of MNA is reasonable, based on ARCADIS' experience. Treatment at many sites is much faster. At least six ARCADIS IRZ sites for CAHs have succeeded in reaching MCLs for target CAHs or even obtaining closure certifications within 18 months to 2.5 years after the initiation of IRZ (Suthersan et al. [2002]; Panhorst et al. [2002]; and Payne et al. [2001]).

Based on ARCADIS' experience, actual project costs for CAH and metal applications have ranged from approximately $75,000 for a small-scale application and/or pilot study or demonstration-scale project to $2,000,000 for a large plume treatment with a fully automated reagent injection system. Table 8-3 presents a selection of cost examples with concentration and size information. The full-scale system for the automated site included installation of over 100 reagent injection wells to provide aggressive plume-wide treatment.

Operating costs (including reagent injection, monitoring and reporting) are generally on the order of $50,000 to $100,000 per year. The percentage of the total costs associated with the reagent injections is

typically greater than 50%. On the other hand, the actual cost of the reagent itself typically represents less than 10% of the total project cost.

The cost data presented in Table 8-3 illustrate the effective nature of the IRZ technology in addressing CAH contamination in groundwater. For example, two sites have been completed with “no further action” notifications from the regulatory agencies, for less than $500,000 each.

9.0 Conclusion

Based on the data generated during this demonstration, the IRZ technology and specifically the application of corn syrup injections can be optimized for the cost effective remediation of perchlorate at the JPL facility. The laboratory and field data contained in this report technically support the subsurface application of corn syrup to stimulate perchlorate bioremediation in anaerobic reactive zones. This conclusion is supported primarily using measured reductions in perchlorate concentration in both the injection and monitoring wells. The inclusion of bromide in the corn syrup solutions that were injected permits the calculation of an injection solution dilution factor. This dilution factor is not sufficient to account for the noted reductions in perchlorate concentration over the demonstration interval. These reductions can be compared to both baseline perchlorate concentrations in the subject wells and to perchlorate concentrations during the demonstration in IRZMW-3, which proved to be a side gradient well and was thus minimally influenced by corn syrup injections. In addition, as a second line of evidence, biogeochemical conditions, particularly ORP, support the existence of anaerobic conditions necessary for perchlorate bioremediation during key sampling events over the length of the demonstration. Lastly, the decreases in perchlorate over the course of the demonstration followed a logical time sequence from beginning to end.

The corn syrup injection scheme during this demonstration did not result in attaining the interim closure standard for perchlorate in the three months of field testing but did result in substantial reductions in perchlorate concentration. IRZ systems typically require a period of injection adjustment and biological acclimation. Adjustment to the injection scheme for this demonstration was suggested but made impractical due to other work planned for the portion of JPL where this demonstration was sited. The need for additional injection scheme adjustment in this case is attributed to the variable and much increased flux of groundwater through the treatment zone during the demonstration. Adjustments to the injection scheme including increases in the mass of corn syrup delivered and potentially a continual low-load injection system or recirculation system to enhance DOC distribution could be designed to accommodate the additional, unexpectedly high flux of groundwater through the treatment zone. Such alterations in the injection scheme would result in the establishment of a more extensive and stable anaerobic reactive zone. This would extend the length of time that the perchlorate plume in this area of the site spends under anaerobic conditions and thus improve the percent reduction resulting in more complete removal of perchlorate.

Adjustments to the injection scheme necessary to compensate for the greater than expected groundwater flux and achieve a more permanent, robust anaerobic zone were proposed toward the end of the demonstration interval. However, the possibility of refining *in situ* perchlorate treatment was eliminated as an immediate option in favor of a more widely demonstrated and accepted pump and treat approach. Therefore, the IRZ technology was not pursued further at this time at this site.

However this short field pilot program demonstrated:

- Successful reduction of perchlorate concentration of up to 81% in injection wells and 91% in monitoring wells
- That these perchlorate reductions could be achieved with only a mildly reducing environment, thus minimizing secondary water quality impacts
- Some removal of co-occurring CAHs.

10.0 References

ARCADIS (2003) Interim Demonstration Scale Test Report, In Situ Substate Addition to Create Reative Zones for Treatment of Chlorinated Aliphatic Hydrocarbons: Vandenberg Air Force Base. ESTCP Project CU-9920, Contract No. 41624-99-C-8032.

Attaway, H., and M. Smith (1993). Reduction of perchlorate by an anaerobic enrichment culture. *J. Ind. Microbiol.* 12:408-412.

Chaudhuri, S. K., S. M. O'Connor, R. L. Gustavson, L. A. Achenbach, and J. D. Coates. "Environmental Factors that Control Microbial Perchlorate Reduction", 2002. Applied and Environmental Microbiology Vo. 68, No. 9, p. 4425-4430.

Coates, J.D., U. Michaelidou, R.A. Bruce, S.M. O'Connor, J.N. Crespi, and L.A. Achenback. (1999). The ubiquity and diversity of dissimilatory (per)chlorate-reducing bacteria. *Applied and Environmental Microbiology*. V. 65:5234-5241.

Dibblee, Thomas W. Jr., 1989, Geologic Map of the Pasadena Quadrangle, Los Angeles County, California, edited by Helmut E. Ehrenspeck, published by the Dibblee Geological Foundation, Santa Barbara, California, Dibblee Foundation Map #DF-23, first printing May, 1989.

DHS. 2002 Perchlorate Drinking Water Action level and Regulation. Department of Health Services, Sacramento, California. http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/action-level.htm.

Division of Mines and Geology (DMG), State of California, Department of Conservation, 1969, Geologic Map of California, Olaf P. Jenkins edition, Los Angeles sheet, compilation by Charles W. Jennings and Rudolph G. Strand, sixth printing, 1991.

Faris (2002), http://www.engg.ksu.edu/HSRC/ag/2002/proceed/c02.pdf

Foster Wheeler Remedial Investigation Report, August 1999. Foster Wheeler Environmental Corporation.

Freedman, D.L., and J. M. Gossett. (1989) Biological Reductive Dechlorination of Tetrachloroethylene and Trichlororethylene to Ethylene under Methanogenic Conditions. Applied and Environmental Microbiology, Vol. 55, No. 9, p. 2144-2151.

Harkness, M.R. (2000). Economic considerations in enhanced anaerobic biodegradation. *Proceedings of. 2nd International Conference on Remediation of Chlorinated Recalcitrant Compounds, May 22-25, 2000.* Wickramanayake, G.B., et al. (Eds.). Columbus, OH: Battelle Press.

Maymo-Gatell, X., V. Tandoi, J. M. Gossett, and S.H. Zinder. (1995) Characterization of an H2-Utilizing Enrichment Culture That Reductively Dechlorinates Tetrachloroethene to Vinyl Chloride and Ethene in the Absence of Methanogenesis and Acetogenesis. Applied and Environmental Microbiology Vol. 61, No. 11. p. 3928-3933.

Motzer, W.E. (2001). Perchlorate: Problems, detection, and solutions. Environ. Forensics 2, 301–311.

U.S. EPA Office of Water, Office of Ground Water and Drinking Water. October 1, 1998, Perchlorate. http://www.epa.gov/ogwdw/ccl/perchlor/perchlo.html. (This Web page has been updated and no longer contains the information referenced in the report).

OEHHA. 2002 Public Health Goal for Perchlorate in Drinking Water. Office of Environmental Health Hazard Assessmentd (OEHHA) in California EPA, Sacramento, CA http://www.oehha.org/public_info/facts/perchloratefacts.html#down-load.

Istok, http://ccee.oregonstate.edu/research/grl/push-pull/literature.htm

ITRC, August 2002. "A Systematic Approach to In Situ Bioremediation in Groundwater Including Decision Trees on In Situ Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate. http://www.itrcweb.org/user/isb-8r.pdf

Panhorst, E.M., and G. B. Page (2002) Expedited Closure of a PCE/TCA Site Using IRZ Technology, Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 20-23, 2002, Monterey, California, Editors: Arun R. Gavaskar and Abraham S.C. Chen

Payne, F.C., S.S. Suthersan, F.C.Lenzo and J.S. Burdick. 2001. Mobilization Of Sorbed-Phase Chlorinated Alkenes In Enhanced Reductive Dechlorination. In: Anaerobic Degradation of Chlorinated Solvents. Proc. Internat. In Situ and On-Site Bioremediation Symp. 6(2):53-60.

Rikken, G.B., A.G.M. Kroon, and C.G. van Ginkel (1996). Transformation of (per)chlorate into chloride by a newly isolated bacterium: reduction and dismutation. *Appl. Microbiol. Biotechnol.* 45:420-426.

"RWQCB" - California Regional Water Quality Control Board. 1994: Water Quality Control Plan Los Angeles Region.

Smith, D. P., 1986, Geology of the North Half of the Pasadena Quadrangle, Los Angeles County, California, California Division of Mines and Geology Open File Report 86-4 LA.

Suthersan, Suthan, C.C. **Lutes**, P.L. Palmer, F. Lenzo, F.C. Payne, D.S Liles and J. Burdick. (2002). *FINAL: Technical Protocol for Using Soluble Carbohydrates to Enhance Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons*. Submitted to the Air Force Center for Environmental Excellence (AFCEE) and the Environmental Security Technology Certification Program (ESTCP) under Contract #1624-99-C-8032.

Vogel, T.M., and McCarty, P.L. (1985). Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. *J. Appl. Environ. Microbiol., 49*, 1080-1083.

Wallace, W., S. Beschear, S. Wyatt and S. Baxley (1995). Purification of the chlorite reductase from Wolinella succinogenes HAP-1. *American Society of Microbiology Annual Meeting, Abstract* O-53, p.3.

Xu, J., Y. Song, B. Min, L. Steinberg, and B. E. Logan, "Microbial Degradation of Perchlorate: Principles and Applications". 2003. Environmental Engineering Science, Vol. 20, No. 5. pp. 405-421.