Volatile organic compounds (VOCs), petroleum hydrocarbons, perchlorate and fumigants have impacted groundwater at numerous sites within the Central Valley Region and cause or threaten adverse impacts to existing and potential beneficial uses of groundwater resources. Those sites are being required to clean up the pollution and restore the beneficial uses of the groundwater. This cleanup can take many forms. The two most common methods of cleanup of groundwater pollution are pump and treat, and in-situ remediation. The operation and discharge of a pump and treat system is generally regulated under site-specific or general waste discharge requirements. Prior to this General Order, in-situ groundwater remediation projects have had site-specific waste discharge requirements issued. The process to develop and adopt site-specific waste discharge requirements can be lengthy. Many in-situ treatment processes have common components and issues that can be regulated under general waste discharge requirements.

In-situ remediation of groundwater pollution at most sites includes the use and application of biological, chemical, and/or physical treatment processes. These processes include addition of oxygen, chemical oxidation/reduction, and the addition of nutrients, carbon and/or bacteria to enhance biodegradation. The method of delivery can be via injection to soil or groundwater insitu, or via groundwater recirculation (extraction and treatment with return of treated groundwater to the impacted aquifer zone). In most instances the in-situ remediation processes will cause reducing or oxidizing conditions within the aquifer in order to either reduce or oxidize the target pollutant. The remediation processes can result in exceedances of water quality objectives that are generally limited in duration and/or in a relatively small portion of the aquifer. These waste discharge requirements allow exceedances of water quality objectives to occur while oxidation/reduction processes are taking place, but only within the treatment zone.

Oxidation/reduction reactions take place when an electron is transferred from one compound to another. The electron donor becomes oxidized, and the electron receptor becomes reduced. These are always coupled reactions. If a compound is reduced, another must necessarily be oxidized to provide the electron. Reducing environments are typified by the absence of oxygen and are also referred to as anaerobic environments. Oxidative environments contain oxygen and are also referred to as aerobic environments.

Reducing Environment Processes

The primary reduction processes that are effective on perchlorate and VOCs are anaerobic in nature as aerobic processes are generally not effective on most highly chlorinated VOCs. Aerobic dechlorination or aerobic cometabolism of perchloroethylene (PCE) and trichloroethylene (TCE) has not been successful at most sites. Therefore, reductive dechlorination of VOCs requires development of anaerobic conditions within the groundwater contaminant plume. PCE can be sequentially reduced to TCE, thence to cis1,2-dichloroethylene, vinyl chloride and finally to ethane. Along the way the rate of reduction, consortium of bacteria involved in the process, and groundwater conditions may change. Reduction of VOCs may even stall at a stage if the correct conditions and bacteria are not present. Perchlorate reduction appears to occur more readily than VOCs and stalling at a particular stage in the dechlorination process does not occur

In order to develop a reducing environment to achieve reduction of chlorinated hydrocarbons and perchlorate, concentrations of oxygen and nitrate need to be significantly depleted. Oxygen and nitrate are more easily reduced than the chlorinated compounds and will utilize the electrons preferentially over the chlorinated compounds. Elevated concentrations of dissolved iron and manganese may also inhibit reduction of the chlorinated hydrocarbons by being electron acceptors.

There are three types of anaerobic reduction that may be occurring:

- **Direct Anaerobic Reductive Dechlorination** is a biological reaction in which bacteria gain energy and grow as one or more chlorine atoms on the chlorinated hydrocarbon molecule are replaced with hydrogen. In this reaction, the chlorinated compound serves as the electron acceptor, and the hydrogen serves directly as the electron donor (USEPA, 2000a).

- **Cometabolic Anaerobic Reductive Dechlorination** is a reaction in which a chlorinated compound is reduced by a non-specific enzyme or co-factor produced during microbial metabolism of another compound (i.e., the primary substrate) in an anaerobic environment. For the cometabolic process to be sustained, sufficient primary substrate is required to support growth of the transforming microorganisms.

- **Abiotic Reductive Dechlorination** is a chemical degradation reaction, not associated with biological activity in which a chlorinated hydrocarbon is reduced by a reactive compound. Addition of an organic substrate and creation of an anaerobic environment may create reactive compounds, such as metal sulfides, that can degrade chlorinated aromatic hydrocarbons (ITRC, 2007).

Of those three, direct anaerobic reductive dechlorination is the primary process for biological reduction of VOCs. In order to accomplish the complete reduction to ethane, the appropriate species of bacteria must be present. Lacking the complete consortium of bacteria could cause the process to stall at cis-1,2-DCE and vinyl chloride. If this condition occurs, adding bacteria that are known to effectively reduce cis-1,2-DCE and vinyl chloride is an option to correct the problem.

Hydrogen has a lead role as a direct electron donor in the anaerobic dechlorination of chlorinated aromatic hydrocarbons. Hydrogen is generated by fermentation of non-chlorinated organic substrates, including naturally occurring organic carbon, accidental releases of anthropogenic carbon (fuel), or introduced substrates such as carbohydrates (sugars), alcohols, and low-molecular-weight fatty acids (lactates, acetates, etc.). As hydrogen is produced by fermentative organisms, it is rapidly consumed by other bacteria, including denitrifiers, iron-reducers, sulfate-reducers, methanogens, and dechlorinating microorganisms. For anaerobic reductive dechlorination to occur, dechlorinators must successfully compete against other microorganisms that also utilize hydrogen (ITRC, 2007).

Generally, there are not sufficient numbers of bacteria naturally present to conduct an effective anaerobic dehalogenation process. To increase the concentration of bacteria biostimulation is implemented by injecting a carbon source or substate into the groundwater. For the degradation of chlorinated ethenes, the injected carbon source provides for cell growth and ferments to produce products like hydrogen, providing an electron donor for the reductive dechlorination process. By adding electron donors, methanogenic and/or sulfate-reducing conditions can be achieved at a site, which can be used to dechlorinate cis-1,2-DCE and vinyl chloride. Complete reductive dechlorination to ethene without the accumulation of cis-1,2-DCE and vinyl chloride is most likely to occur under these strongly-reducing conditions (ITRC, 2007).

Biostimulation also may include injecting limiting nutrients, such as phosphorus or nitrogen. The advantage of biostimulation is that native populations present in the subsurface are already acclimated to the site, so enhancements such as the addition of nutrients will increase their biodegradation capacity. The disadvantage is that subsurface geology of a site may interfere with the introduction of nutrients, including the formation of preferential flow patterns due to fractures and impermeable lithology affecting the distribution of additives. Important subsurface characteristics to consider for biostimulation include velocity of the groundwater, and hydraulic conductivity of the soil. Pilot studies are usually conducted to provide additional site-specific information before full-scale implementation (ITRC, 2007).

Substrates added to promote reductive dechlorination come in many forms and may be soluble, low viscosity, high viscosity or solid. Soluble substrates, such as sugars, citric acid and lactic acid, may be applied in an aqueous phase offering uniform distribution throughout the aquifer. These dissolved substrates travel with advective groundwater flow and are typically applied continuously or periodically. The soluble substrates are consumed rather quickly and must be frequently replenished.

Substrates that are viscous are less mobile than soluble substrates, but they tend to last longer in the subsurface. Slow release materials such as vegetable oil or HRC^{TM}, which are intended to be long lasting, may require a single or limited number of injections. The low mobility of viscous substrates may lead to non-uniform distribution and require different application mechanisms to achieve the desired distributions. These substrates are relatively immobile and rely on advective and dispersive qualities of soluble compounds (lactic acid for the HRC and metabolic acids for the oil) to deliver them throughout the subsurface (ITRC, 2007).

Moderate viscosity fluids such as emulsions of vegetable oil have a relatively high mobility as compared to solid or highly viscous materials that allows more uniform distribution within the aquifer. Emulsified oils slowly release hydrogen through fermentation of fatty acids. Other moderate viscosity substrates that could be used include, chitin, whey and oleate.

Oxidative Environment Processes

As with reductive processes, oxidation processes can be either chemically or biologically induced. A chemical oxidant removes electrons from constituents in the vicinity of the oxidant and the oxidant becomes reduced. In a biological oxidation process, one compound is the electron donor and another compound is the electron acceptor. An example of biological oxidation happens with fuel contaminants in groundwater. In an aerobic environment, fuel can provide the carbon and the electrons for microbial metabolism, and the oxidizing agent is oxygen, which is the electron acceptor. In the absence of oxygen, nitrate also serves as an electron acceptor. The fuel becomes degraded as it is oxidized.

Remediation of groundwater pollution, including VOCs, benzene, toluene, ethylbenzene, xylenes, organic pesticides, munitions (i.e., HMX, RDX), petroleum hydrocarbons or MTBE can potentially be achieved using chemical or biological oxidation processes. This involves injecting oxidants directly into the source and the downgradient plume, or delivering oxidants by means of a groundwater recirculation system. The oxidant reacts with the pollutants, producing innocuous substances such as carbon dioxide, water, and chloride. The four main chemical oxidants used are permanganate, peroxide, persulfate and ozone.

The ability of the oxidant to react with a certain contaminant in the field depends on kinetics, stoichiometry, thermodynamics and delivery of the oxidant. On a microscale, kinetics or reaction rates are the most important. The rates of oxidation reactions are dependent on many variables, such as, pH, temperature, concentration of the reactants, catalysts, reaction by-products, and impurities (oxidant scavengers, organic matter, etc.) that all must be taken into consideration.

The oxidant needs to be delivered in such a manner that the oxidant comes into the contact with the pollutant to be oxidized. The delivery goal is to ensure that the oxidant is dispersed evenly throughout the groundwater needing to be remediated. The solubility and rate of reaction of the oxidant need to be considered when developing the method of delivery of the oxidant.

Treatment Zone

The treatment zone is the area where the oxidation/reduction processes take place. During oxidation, several changes in water quality parameters can occur. The oxidation process can cause trivalent chromium present in formation materials and dissolved in the aquifer to be converted to hexavalent chromium, a much more toxic form of chromium. In addition, chlorides will be liberated if the pollutants being oxidized are chlorinated compounds. Increases in salts can occur if the oxidant being used has a salt component such as sodium or potassium.

Reduction processes have similar concerns with chlorides and salts. Reducing conditions will remove dissolved oxygen from the water, and can liberate excess concentrations of dissolved iron and manganese from formation materials, and generate methane, causing secondary water quality problems. These waste discharge requirements recognize that water quality objectives for some parameters may be exceeded within the treatment zone. However, water quality objectives are not allowed to be exceeded outside of the treatment zone. Monitor wells are established downgradient of the treatment zone for use as compliance wells. The monitor wells are used to measure compliance with water quality objectives and groundwater limitations.

The size of the treatment zone should be made as small as feasible, but in most cases will be driven by the plume configuration and design of the treatment system. The treatment zone could include a transition zone where ambient groundwater mixes with the treatment zone, reestablishing ambient oxidative conditions. In contact with the oxygen of ambient groundwater, the elevated concentrations of ferrous iron and dissolved manganese are oxidized, removing them from solution. Methane concentrations return to ambient concentrations much more slowly, and travel further than other reduced species. Therefore, the formation of methane should be avoided to the extent practicable by minimizing the degree of reducing conditions generated by the project. It is not appropriate to significantly increase the size of the treatment zone to simply allow for methane concentrations to reduce back to ambient levels.

Amendment Delivery

The in-situ treatment system is usually one of three types. One type utilizes a groundwater recirculation consisting of extraction and injection wells and provides control of the injectants and treatment zone. The extracted groundwater is amended aboveground and the amended water recharged upgradient of the extraction well. The second type injects the amendments into the groundwater and allows the groundwater to flow though the treatment zone. The third type uses extraction and injection wells to create a barrier with the treatment zone being established within and downgradient of the capture zone of the injection well(s). In this type of system the injection tends to occur downgradient of the extraction wells. The use of extraction and recharge systems is preferred as it provides greater flexibility and control of the treatment zone, and can be operated to help restore the treatment zone to pre-project conditions after remediation of the initial pollution has been completed.

Amendments

These waste discharge requirements require that the injectant materials be analyzed to determine the suitability of the materials to be used for in-situ remediation. Past analyses of various amendments, including corn syrup, molasses, HRC^{TM} and edible oils have shown elevated concentrations of sodium and other salts, and trace metals in some of them. As the groundwater in the Central Valley is in many places adversely impacted by salts, the use of salt-containing amendments is discouraged. A project that proposes using a salt-containing amendment is required to demonstrate that there is no cost-effective, salt-free amendment that can be utilized to achieve adequate remediation of the pollution before allowing the salt-containing amendment to be used. In addition, amendments containing other pollutants such as metals could contribute to exceedances of water quality objectives and/or degradation of the groundwater.

Basin Plan, Beneficial Uses, Background Groundwater Quality and Water Quality Objectives

The *Water Quality Control Plan for the California Regional Water Quality Control Board Central Valley Region, Fourth Edition* (Basin Plan), designates beneficial uses, establishes water quality objectives, and contains implementation plans and policies for all waters of the Basin. Beneficial uses often determine the water quality objectives that apply to a water body. For example, waters designated as municipal and domestic supply must meet the maximum contaminant levels (MCLs) for drinking waters. The Basin Plan sets forth the applicable beneficial uses (industrial, agricultural, and domestic supply in this instance) of groundwater, procedure for application of water quality objectives, and the process for and factors to consider in allocating waste assimilation capacity.

The antidegradation directives of Section 13000 of the California Water Code require that waters of the State that are better in quality than established water quality objectives be maintained "consistent with the maximum benefit to the people of the State." Waters can be of high quality for some constituents or beneficial uses and not others. Policies and procedures for complying with this directive are set forth in the Basin Plan (including by reference State Water Board Resolution No. 68-16, "Statement of Policy With Respect to Maintaining High Quality Waters in California," or "Antidegradation" Policy).

Resolution 68-16 is applied on a case-by-case, constituent-by-constituent basis in determining whether a certain degree of degradation can be justified. It is incumbent upon the Discharger to provide technical information for the Board to evaluate that fully characterizes:

- All waste constituents to be discharged;
- The background quality of the uppermost layer of the uppermost aquifer;
- The background quality of other waters that may be affected;
- The underlying hydrogeologic conditions;
- Waste treatment and control measures;
- How treatment and control measures are justified as best practicable treatment and control;
- The extent the discharge will impact the quality of each aquifer; and
- The expected degradation to water quality objectives.

In allowing a discharge, the Board must comply with CWC section 13263 in setting appropriate conditions. The Board is required, relative to the groundwater that may be affected by the discharge, to implement the Basin Plan and consider the beneficial uses to be protected along with the water quality objectives essential for that purpose. The Board need not authorize the full utilization of the waste assimilation capacity of the groundwater (CWC 13263(b)) and must consider other waste discharges and factors that affect that capacity.

The project proponent is required to determine background groundwater quality. The background data is used to determine compliance with water quality limitations at the points of compliance downgradient from the treatment zone. As stated above, salts can increase due to the dehalogenation of volatile organics or other pollutants or from salts present in amendments. Metals can be solubilized from aquifer materials by the reduction process, be released from amendments during reactions, or change to more toxic states during the oxidation process. These waste discharge requirements allow a slight increase (20% over background) in metals and salts, as long as water quality objectives are met. A value of less than 20% would be within the error of duplicate analysis comparability criteria and an exceedance not always verifiable. Water quality objectives for the anticipated pollutants that are found at these remediation projects are established in the Findings. The water quality objectives are established based on the numerical and narrative standards found in the Basin Plan.

Coverage Under the Order

To obtain coverage under the order, the project proponent must submit a Notice of Intent (NOI) and supplemental information listed in Attachment A. The information requirements are significant as these projects are complex and require a great deal of knowledge about the project site and remediation processes. Though the requirement for submittal of information is substantial, it should be information that has already been developed by the project in order to justify the remediation project to the appropriate regulatory agency.

In order for coverage to occur, the project proponent needs to demonstrate through laboratory-scale tests that the proposed project will adequately promote remediation of the pollution. The laboratory-scale tests will also be used to identify potential adverse water quality impacts with the project and help establish monitoring parameters. If there are data from projects sufficiently similar to the proposed project, the proponent can use that information in lieu performing the laboratory-scale testing, as appropriate. Once the project is completed, the project proponent will file for termination of coverage under the general order.

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