In situ remediation of contamination has arrived as a robust technique for treatment of both petroleum and chlorinated hydrocarbons. In situ remediation is typically categorized as chemical or biological. Either of these types of in situ remediation involves injecting chemicals that directly treat the contaminant or promote reactions that treat the target contaminant. The chemical that is injected depends upon whether the in situ treatment involves chemical oxidation, chemical reduction, or anaerobic or aerobic bioremediation.

There are two important factors in the selection of the chemical to be injected. One factor is selecting a chemical that will readily promote the degradation of the target contaminant. For example, if the target contaminant is a chlorinated alkane, chemical oxidation via potassium permanganate injection is eliminated because it does not oxidize most chlorinated alkanes. As another example, tetrachloroethene is not treated directly via aerobic bioremediation.

The second important consideration is the current biogeochemical state of the aquifer. The current biological and geochemical state of the aquifer should be carefully examined before selecting the chemical to be injected. For example, if the geochemical state of the subsurface system is highly reducing (or biologically anaerobic), it will require injecting significant quantities of chemical oxidant in order to bring the aquifer sufficiently oxic for treatment of the target contaminants. As a second example, if there is elevated dissolved oxygen (DO), then an anaerobic biodegradation approach may not be the proper approach, because it will be working against the natural tendencies of the aquifer and might require substantial chemical. If a cost-effective approach is to be developed, the geochemistry must be examined carefully.

Fortunately, there are relatively inexpensive analytical measurements of the groundwater that indicate the biogeochemical state of the aquifer. These parameters include: pH, dissolved oxygen, alkalinity, dissolved iron and manganese, sulfate, nitrate (or ammonium), and dissolved hydrocarbons such as methane, ethene and ethane. Ethene and ethane are important when the target contaminant is chlorinated alkenes, such as TCE plus daughters. This suite of analyses is often called the MNA (monitored natural attenuation) parameters for chlorinated compounds. These same measurements can be used to determine whether chemical oxidation or reduction **may** be appropriate for the site. For chemical oxidation, an additional test called a total oxidant demand (TOD) test is often required to better estimate the oxidant required. The TOD test will be discussed later.

In general, the geochemical state of the aquifer changes from background conditions in response to microbiological activity associated with the released contaminants and other materials. Typically, for sites with some petroleum material released, oxygen is the first element that is consumed during microbial processes. Microbes gain energy from the consumption (oxidation) of electron donors coupled to the utilization (reduction) of electron acceptors. Contaminants will either serve as electron donors or electron acceptors. For example, a common biodegradation activity is the aerobic metabolism of fuel contaminants. In this case, oxygen is the electron acceptor, while the fuel hydrocarbon is the electron donor which may be oxidized completely to CO_2 by this process. After the oxygen is consumed, alternative electron acceptors, such as nitrate and sulfate, may be

utilized in contaminant oxidation in the absence of oxygen. In general, the electron acceptor will be used in the following order: $O_2 > Mn^{+4} > NO_3^- > Fe^{+3} > SO_4^{2-} > CO_2$. Thus, the presence of absence of these compounds will indicate how reducing nature of the groundwater. This can also be measured by an oxidation-reduction potential measurement in the field, but ORP measurements have proved to be less reliable than measurement of the MNA parameters. If nitrate where depleted and sulfate was present at high levels, it **may** be concluded that the system is moderately reducing (somewhere around iron-reducing conditions). If sulfate was not present at elevated levels and methane was present, the system would even be more reducing, past sulfate-reducing conditions and onto methanogenic conditions. Methanogenic is generally the most reducing that an aquifer can naturally sustain.

As previously stated, the presence or absence of MNA parameters in comparison to background levels can be used to infer the geochemical state of the subsurface environment (sometimes called ORP). In relative order, as previously presented above. Absence of DO (less than 2-3 ppm) indicates anaerobic or anoxic conditions. The presence of dissolved manganese (greater than 10 ppm) may indicate manganese-reducing conditions. As the manganese (+4) is accepts electron it is converted to the generally more soluble manganese (+2). Nitrate depletion, may indicate denitrification (the reduction of nitrate to N_2) or nitrate reduction. Nitrite, an intermediate in denitrification, may also be an indicator of this process. Elevated ammonia/ammonium measurements can also indicate nitrogen-reducing conditions. The presence of dissolved iron (great than 10 ppm or so) may indicate iron-reducing conditions where generally insoluble ferric iron has been reduced to more soluble ferrous iron. However, under sulfate reducing conditions, hydrogen sulfide is produced which readily precipitates ferrous iron. Sulfate depletion (relative to background) or the presence of sulfide gas may indicate sulfate reducing activity. The presence of dissolved methane gas (10 to 100 ppb or so) in groundwater indicates methanogenic conditions Elevated concentrations of these gasses will also indicate microbial activity in groundwater samples. Chapelle *et al.* (2002) has recently shown that sulfate may be present at 10's of ppm and methanogenic conditions may still be present.