Practical Applications of Chemical Reactivity Probes (CRPs) to Estimate Abiotic Reduction Rates

Chris M. Kocur (kocur@ohsu.edu), Paul G. Tratnyek (tratnyek@ohsu.edu),
Richard Johnson (rick.johnson.phd@gmail.com)
(Oregon Health & Science University, Portland, OR)

Background/Objectives. Understanding in situ abiotic degradation rates is essential to site management and ultimately site closure. Chemical reduction (redox) potentials determine if dechlorination of solvents is thermodynamically favorable. Lower (more negative) reduction potentials provide a stronger driving force for those reactions, which generally results in faster reduction kinetics. Reduction potential in aquifer systems is controlled by the mineral phases present in the soil, and as a consequence, reaction rates are expected to decrease as one moves along the sequence Zn > ZVI > FeS > Magnetite > Lepidocrocite > Pyrite > MnO_2 > Goethite. However, thermodynamics alone does not fully predict reduction kinetics, so more direct methods are needed. Unfortunately, most abiotic degradation rates are slow and, therefore, difficult to measure because the necessary experiments take too long to be useful for site decision making. Chemical reactivity probes (CRPs) represent an alternate approach to estimate reduction kinetics. CRPs can be selected to react more rapidly with mineral phases and, as a result, can be used to estimate abiotic reaction rates over time frames that are much shorter than for the actual contaminants, which and better suited to site decision making.

Approach/Activities. To assess the usefulness of CRPs, we are currently analyzing their reactions with a number of pure mineral phases, sulfate- and iron-reducing soils and field core samples. We are currently using a suite of four CRPs, including two redox active dyes (resazurin and indigo disulfonate, I2S) and two chlorinated contaminants (carbon tetrachloride, CT, and trichloroethene, TCE). The measurements are made in stainless steel reaction vessels with integrated sampling ports that allow repeat analyses for each of the CRPs for periods up to months while maintaining strictly anoxic environments. This approach also allows high soil to water ratios to be used, which facilitates shorter reaction times.

Results/Lessons Learned. Rapid screening of reduction rates, including in-the-field screening, can be accomplished with the redox-active dyes. For example, our preliminary tests indicate that samples capable of reducing I2S in one day can also rapidly reduce CT in a matter of days and can reduce TCE over longer periods. We are currently developing empirical relationships between the dye reduction rates and contaminant reduction rates which will provide improved estimates of contaminant reduction kinetics. This protocol for abiotic reaction rates, when applied to field samples, will support timely decision making before, during or after enhanced site remediation and to assess natural attenuation rates.