Groundwater Monitoring&Remediation

Special Issue: Diagnostic Tools to Assess In Situ Remediation System Performance

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While substantial progress has been made in the development of in situ remediation technologies for petroleum hydrocarbon sites such as multiphase extraction, air sparging (AS), soil vapor extraction (SVE), and in situ chemical oxidation (ISCO), their field application is often associated with considerable uncertainty. Most remediation methods are implemented to invoke a specific contaminant removal process, either physical, chemical, or biological. However, other processes act on contaminant concentrations as well, in addition to naturally occurring variability. Some physical processes (e.g., dilution, diffusion, and dispersion) may lead to short-lived reductions in dissolved hydrocarbon concentrations, but post-treatment "rebound" can occur. Destructive processes, such as biological and chemical transformation, are more likely to result in sustainable, long-term reductions in dissolved concentrations. Based on concentration data alone, which is the most common performance indicator, it is difficult to separate treatment-induced effects from unrelated changes. As a result, the treatment efficacy might be over- or underestimated, remediation systems operated longer than required, or alternatives sought prematurely. There is a need for diagnostic tools to assess the effectiveness of the intended removal process. Diagnostic tools are particularly valuable for remediation strategies that increasingly rely on combinations of treatment technologies making it necessary to evaluate the expected sequential occurrence of contaminant removal processes over time.

Evaluating contaminant removal processes during engineered in situ remediation is arguably more challenging than for monitored natural attenuation (MNA). The treatment introduces additional transience and multiple removal processes often occur in parallel, while for MNA, biodegradation is usually the most dominant process. For MNA, systematic approaches have been developed to demonstrate contaminant removal and it is widely accepted that multiple lines of evidence should be combined for a robust assessment (e.g., US EPA 1999). However, comparable approaches for evaluating the efficacy of engineered in situ remediation are lacking. In the case of MNA, methods that unequivocally differentiate biodegradation from physical attenuation processes are usually preferred, such as compound-specific isotope analysis (CSIA) and biomarkers. While some of these diagnostic tools have also been applied to engineered in situ treatment systems, it is not clear if they are widely applicable in this context and, if so, what are their relative strengths and weaknesses. For example, CSIA is commonly used to demonstrate biodegradation during MNA (US EPA 2008), but it is not clear if dual carbon and hydrogen isotope plots can distinguish between chemical and biological contaminant removal of BTEX, or how dynamic conditions during contaminant mass removal influence isotope ratios.

This special issue reports results from a major research program that systematically evaluated the performance of diagnostic tools in an engineered in situ treatment context. The 7-year program included three academic research partners, University of Neuchâtel, University of Waterloo, and Cornell University. The selected diagnostic tools shared some common features. Similar to MNA applications, a key requirement was that the tools provide insight into a specific contaminant-removal process. In addition, the information should be available on a compound-specific basis. Based on these criteria, a series of isotope tools and biomarkers were selected. The isotope tools include (1) CSIA (e.g., $\delta^{13}C$ and $\delta^{2}H$ of carbon and hydrogen, respectively in target contaminants) that can be used to discriminate between a broad range of contaminant-specific removal processes and (2) isotope analysis of electron acceptors (e.g., $\delta^{34}S$ for sulfate) and degradation end products (e.g., $\delta^{13}C$ of dissolved inorganic carbon) to assess overall transformation of hydrocarbons. The biomarkers include signature metabolites for specific degradation pathways and functional genes on a mRNA level to understand biological activity. mRNA was preferred to DNA to assess the active microbial participants rather than simply those that are present. While in previous studies often only one type of diagnostic tool was evaluated, the diagnostic tools were applied side-by-side, which makes it possible to demonstrate their relative strengths and weaknesses.

The research included testing and development of the diagnostic tools, starting with laboratory experiments to derive controlling parameters (e.g., isotope fractionation factors) and moving to three controlled-release field

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experiments conducted at the University of Waterloo Groundwater Research Facility at the Canadian Forces Base in Borden, ON, Canada. After validating the diagnostic tools using laboratory and field experiments, they were applied at two full-scale remediation sites; one site was being actively treated by SVE, and the other was being treated by the application of sulfate (as agricultural gypsum) on the land surface. The controlled-release experiments provide a crucial link between the laboratory and the full-scale. In such experiments, the initial conditions (e.g., released contaminant mass and its isotopic signature) are known. Furthermore, the removal processes can be constrained with independent information, and thus the diagnostic tool response can be "validated" to a greater degree than at full-scale remediation sites. Therefore, the controlled-release experiments are in the foreground in this special issue. Results from the three field experiments are reported in separate papers. In the first one, an AS system was implemented and the relative role of aerobic biodegradation, anaerobic biodegradation, and physical contaminant removal of BTEX and alkanes was evaluated (Bouchard et al. 2018b). In a second field experiment, the relative importance of ISCO of BTEX by persulfate vs. anaerobic biodegradation stimulated by the resulting release of sulfate was investigated (Shayan et al. 2018). This field study was complemented by a laboratory study to constrain isotope fractionation for chemical oxidation of BTEX by persulfate (Solano et al. 2018). In the third experiment, the effect of surface application of a sulfate solution on BTEX biodegradation was evaluated (Wei et al. 2018). The outcome from these three controlled-release experiments and the application of the diagnostic tools at two full-scale remediation sites was integrated into a technical note that outlines their use in a tiered approach for remediation process assessment (Bouchard et al. 2018a).

Diagnostic tools will likely see increased application to monitor contaminant mass removal progress and assess effectiveness of treatment systems at field sites. These tools can be used to evaluate processes contributing to concentration reductions and optimize remediation system performance. In addition, these tools can help demonstrate when contaminant treatment is no longer effective, recommend transition to an alternative remedial technology, and support regulatory requests to terminate active remediation and transition to MNA. Overall, these tools can improve remediation decision quality, design, and performance optimization, leading to lifecycle cost reductions.

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