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Evolving Conceptual Models for Natural Source Zone Depletion: Methanogenesis, Gas Transport, and Sequenced Biodegradation

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Background/Objectives. There has been a quiet revolution in the groundwater community's thinking about attenuation of light nonaqueous phase liquid (LNAPL) source zones over the past 10 years, largely due to the development of natural source zone depletion (NSZD) as a viable remediation alternative. First, there has been an increased appreciation of the importance of methanogenesis, ebullition, off-gassing, and gas dynamics in and above LNAPL source zones. Second, this new conceptual model has enabled new field methods to emerge that better quantify NSZD rates for bulk LNAPL. Third, application of these measurement techniques indicate that NSZD rates at petroleum release sites are typically hundreds to thousands of gallons per acre per year, a rate that can match or exceed LNAPL removal rates from active LNAPL extraction systems at some sites. Despite this strong interest in measuring and applying NSZD, many practitioners and regulators are not sure what this rate represents, leading to several important questions such as:

- *How can NSZD rates inform timeframes to meet regulatory criteria, e.g., groundwater and soil concentration?*
- *Why are most site-wide NSZD rates within a relatively tight range?*
- *How can NSZD rates be enhanced?*

Approach/Activities. A concerted effort involving multi-disciplinary literature review and fieldwork was undertaken to enhance the current conceptual model for NSZD. We researched (i) anaerobic process analogs from other systems (e.g., anaerobic digesters, peat, wetlands, landfills, petroleum reservoirs) in an attempt to better understand methanogenic processes at LNAPL sites, (ii) identified potential key factors that might be controlling NSZD rates to help explain the relatively tight range of NSZD rates and could be possibly manipulated to enhance them, (iii) biodegradability information about key LNAPL constituents and chemical classes, and iv) available biodegradation and/or NSZD rate models. The ongoing fieldwork includes NSZD rate measurement at a dozen locations with different LNAPL architectures, saturations and compositions.

Results/Lessons Learned. This work has led to several preliminary hypotheses, observations, and conclusions about NSZD, such as:

- There is considerable intra-site variability (temporal and spatial) in surface carbon dioxide efflux NSZD measurements; this may be in part due to a "signal shredder" effect that has been used to describe methane ebullition in peat systems (Ramirez, 2015);
- Methane oxidation is an important process for NSZD measurement techniques, and research from landfills and climate studies can provide important insights about this process;
- NSZD is a process where methanogenic bacteria consume different LNAPL constituents/chemical classes in a semi-sequential basis due to inhibition and other effects, which may cause a quasi-zero order NSZD rate over long time periods;
- The Ng et al. (2015, 2016) model provides a useful foundation for exploring how NSZD works on a long-term composition change basis.

Results from the extensive fieldwork, which is in progress, will also be presented.