AFCEE SOURCE ZONE INITIATIVE- TECHNICAL ASSISTANCE TO F.E. WARREN, NAS FORT WORTH & AFP 4

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Background

Chlorinated solvents in the form of Nonaqueous phase liquids (NAPLs) are found in contaminated soils at F.E. Warren, Air Force Plant 4, and Naval Air Station Fort Worth Sites. These organic liquids slowly dissolve into the flowing groundwater generating the downstream contaminant plume in which concentrations commonly exceed regulatory standards. Site cleanup involves the reduction in entrapped mass from the source zone with the expectation that the “emission” concentrations are at acceptable levels to meet regulatory standards. In general, four governing factors effect the emission concentrations downstream of the NAPL source zone, namely: (1) the entrapment architecture of NAPL, (2) the rate of dissolution of entrapped NAPL, (3) the attenuation of the plume resulting from diffusion of dissolved NAPL constituent into low permeability zones (matrix diffusion), and (4) retardation of the plume due to reactive and decay processes. A number of research studies are currently in progress to study these factors and associated processes. In this study, we have focused on matrix diffusion issues. Even after the complete removal of the free phase NAPL, the dissolved contaminants can diffuse back to the flow field from the low permeability zones producing long tailed emission curves. The longevity of the NAPL source depends on how long it takes for the concentrations in the tail of the emission curves to reach regulatory standards. The premise of this project is that an improved “a priori understanding” can be developed by conducting investigations of these governing processes at the three sites. Experimental and modeling studies that are designed to obtain this understanding are presented. Insights developed will be incorporated into site conceptual models and other decision tools with the net benefit of a better understanding of the potential benefits of selected remedial actions. The approach, progress to date and preliminary results from experimental and modeling studies are presented.

Methods

The methods used are a combination of field, laboratory and modeling studies. Two primary constraints have to be dealt with in conducting basic studies for process understanding at field sites. First, fundamental processes that determine the NAPL behavior cannot be studied in detail in the field. This is primarily due to our inability to fully characterize heterogeneous field sites where DNAPLs (denser than water NAPLs such as TCE, TCA and PCE) are entrapped under complex architecture. Also, it is difficult to conduct controlled experiments in the field where the velocity field can be accurately determined and strategies be developed to both monitor the depletion of NAPL source and sampling of the solute plume. The second constrain is associated with limitations on extrapolating findings from few field sites to other sites with different geologic and hydrogeologic conditions. To over come the first, we propose to conduct pilot scale tests in the laboratory under controlled conditions. Even though field heterogeneities cannot be reproduced exactly in the laboratory, features that are critical to field behavior can be created to obtain a fundamental understanding. In some of the experiments, soils collected at the field sites will be used in an attempt to capture some of the processes that occur at the pore scale and at soil-water interfaces. The extrapolation of results from the laboratory to the two field sites and then to other sites will be done using mathematical models that are validated using accurate laboratory generated data. At a later stage, any available field data from the three sites will also be used to further validate these models for field applications.

The methodology as presented involves the design and implementation of experiments conducted at the batch scale, in two-dimensional flow cells and intermediate-scale pilot tanks. Mathematical models based on both closed form analytical solutions and numerical methods will be used. The goal of this study is to design a set of experiments that provide data to obtain a fundamental understating of the governing processes and validate mathematical models. The experimental and modeling data are then used to answer a number of practical questions such as: (1) what is the significance of the process of diffusion of dissolved NAPL into low permeability zones in controlling the emission from the source zone? (2) what are the effects and significance of NAPL entrapment architecture on the emission curves during pre- and post- remediation in the source zone? (3) what features of the geologic heterogeneity (e.g. distribution of the low permeability zones, their volume fraction, stratification, among others) contribute to the emission curve, (4) what relationships exist between the rate of depletion of the free NAPL phase by dissolution and the role of low permeability zones in defining the time distribution of emission concentrations from the source zone. Other questions are expected to be raised during he progress of this study and in interaction with engineers and scientists involved in site cleanup. The experimental and modeling methods are presented briefly.

<u>Experimental Methods</u>: A set of batch tests were conducted to characterize the soil and the chemicals that will be used in proposed experiments in two dimensional cells and intermediate-scale test tanks. Analytical methods for MTBE, PCE, and TCE have been tested and validated. Silt and sand column studies have provided estimates of the porosity and hydraulic conductivity of the silt and sand collected from F.E. Warren. Six small tanks have been constructed for NAPL source studies. Dissolution of three NAPLs (MTBE, PCE, and TCE) will be evaluated with and without a silt layer.

Soil from NAS Fort Worth was collected and is being dried, pulverized, and sorted by particle size. Uniform quartz sands (F30 and F140) were also obtained. Both are currently being analyzed to obtain DCM sorption isotherms and hydraulic conductivities for the various particle size ranges. Construction of two tanks (one each at 16'x4' and 8'x2') has been completed. The smaller tank has been packed with the uniform quartz sands and is being used to develop and validate the following experimental methods: (1) X-ray measurement of porosity, water content, and DNAPL saturation; (2) Determination of pore velocity and dispersion by image analysis (moments) of dyed tracers; and (3) Measurement of DCM aqueous concentrations using a custom auto-sampler for the determination of emission curves and DNAPL mass transfer rates.

<u>Modeling</u>: A literature search has led us to an exact analytical solution for diffusive losses into stagnant layers adjacent to a sand layer. The solution provides an important step in developing tools that *a priori* analysis of the efficacy of source zone remedies. A modeling framework has been built within MODFLOW2000 and MT3D. Simulations of both mean behavior and sensitivity analyses have been performed for the tank scenarios pictured above. Model validation through comparison with analytical solutions is in progress.

Discussion

The experiments are currently in progress. Only the preliminary results are currently available.
In the soils that were collected at F.E Warren site, the contrast in hydraulic conductivity is ~ 3 orders of magnitude. Similar results are expected from the Soil from NAS Fort Worth. These contrasts in the properties will allow us to design experiments in the laboratory to create various packing configurations to evaluate matrix diffusion. Ongoing tests will resolve retardation and longitudinal dispersion values for MTBE, PCE, and TCE, in the sand and silt sediments. These are critical parameters for analysis of laboratory studies and development of site-specific predictive models.

Results from the small dissolution cells will provide a fundamental demonstration of how stagnant zones (associated with heterogeneity) initially attenuate, and subsequently sustain, contaminant discharge from subsurface source zones. Result will also be used to test predictive models and optimize future laboratory studies.

The tracer studies conducted in the 8'x2' tank have allowed us to determine the transport characteristics that will be used in the modeling. The experiment in this test tanks where the NAPL source depletion will be monitored during dissolution will allow us develop a mass transfer model that will be incorporated into the numerical model. The data from the break through curves will be used to obtain a qualitative understanding of the fundamental processes as well as in model validation.

The preliminary modeling results show that the model was able to capture the matrix diffusion process. Further refinement of the model is needed to simulate more complex architecture of NAPL entrapment, dissolution and matrix diffusion.

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