## Current Models of Vapor Production and Mass Recovery at Thermal Remediation Sites And Their Implications for Appropriate Heating Strategies

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The efficiency and performance of in situ thermal remediation (ISTR) is primarily due to the significant enhancements in chemical volatility, increased tendency for chemicals to partition into a vapor phase, and the generation of large volumes of mobile vapor during DNAPL-water co-boiling and steam generation. Heating and extraction strategies that result in the effective transport and removal of the vapor phases containing the chemical mass being targeted from the subsurface, leads to the rapid, uniform, and predicable cleanup of sites. Given the uncertainties in the distribution of contaminant mass within a treatment volume, it is necessary to implement comprehensive and robust heating strategies that result in uniform and sufficient generation and maintenance of vapor phase to reliably remove the mass from the soil and/or rock matrix.

Identifying appropriate and adequate heating and extraction strategies for a site requires a clear understanding and careful consideration of the mechanisms of vapor phase formation and mass recovery. Vapor production mechanisms that are enhanced or initiated with ISTR at sites containing chlorinated volatile organic chemicals (CVOCs) DNAPL below the water table include: 1) degassing of dissolved gasses (e.g., O2, N2, CO2, etc.), 2) co-boiling at the DNAPL-water interface, and 3) generation of steam within the pore space at water boiling temperatures. All three mechanisms can result in connected vapor channels that mobilize mass from the pore space, barring unwanted phase changes (i.e., condensation), to extraction systems and ex situ treatment processes.

This paper introduces and examines current models of vapor production and mass transport at CVOC DNAPL ISTR sites. Uncertainties with the models and research needs are noted. The importance of various heating strategies are evaluated with respect to these models, including: 1) uniform heating of the treatment volume to the target temperature (e.g., 100°C); 2) heating of the vadose zone to the ground surface and use of an insulated vapor cover; 3) heating outside and around the perimeter of the treatment zone (i.e., heated zone larger than the treatment zone); 4) partial heating of the vadose zone at deep sites where the upper portion of the vadose zone is below cleanup goals; and 5) heating only to the DNAPL-water co-boiling point; and 6)The use of ISTR in saturated confined systems.

Co-boiling at the DNAPL-water interface is the primary mass removal mechanism at CVOC DNAPL sites. For common CVOCs such as PCE and TCE, the co-boiling point is well below the boiling point of water (e.g., 88°C and 76°C, respectively) and the vapor phase generated consists of ~90% by mass of the CVOC. Approximately 85 to 90% of the total mass present will be removed during co-boiling within the first 3 months of heating before water boiling substantially commences (achievement of 100°C). Insufficiently heated treatment volumes, either laterally or vertically, results in the condensation of the CVOC vapor streams in the cool zones and can lead to re-formation of DNAPL and / or failure to meet the remedial objectives. Heating and extraction systems have to be designed with a clear understanding of the vapor formation and mobilization mechanisms in order for ISTR to reliably and predictably achieve performance goals.