Technology integration for contaminated site remediation: clean-up goals and performance criteria

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Abstract There is a need to develop and field-test *integrated* remediation technologies for cost-effective treatment of contaminated sites to achieve risk-based and rational endpoints. Aggressive technologies designed for rapid source-zone remediation must be linked to technologies for achieving enhanced clean up of the dissolved plume. Remediation technology integration should minimize the cost of achieving risk-based endpoints by selecting treatment trains or technology combinations that, when coupled together, work in a synergistic manner. Contaminant *flux* across a control plane immediately downgradient from the source, rather than contaminant *concentration*, should be used as the basis for evaluating the effectiveness or success of remediation. The acceptable threshold contaminant flux should be set equal to, or less than, the natural attenuation capacity within the dissolved plume. Simulation results show that significant contaminant-flux reductions can be achieved by partial removal of contaminant mass from DNAPL source zones.

Key words contaminant flux; contaminant mass removal; DNAPL source zones; risk reduction; treatment trains

INTRODUCTION

Technology performance and integration

The primary goal of any remediation activity is site closure by achieving the required risk reduction for regulatory compliance or liability reduction at the least cost. In some

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cases, this goal is simply achieved by installation of some type of institutional controls to limit access (e.g. deed restrictions, fencing off the area). In other cases, either source control (e.g. containment, stabilization) or plume cut-off (e.g. hydraulic capture, permeable reactive barriers) or both can be used to achieve the goal. At sites where some type of remediation technology is to be implemented, the *rate* of risk reduction achieved per unit cost determines the *efficiency* with which site closure is achieved. In this context, risk-reduction efficiency can be defined in terms of risk reduction achieved per unit of resources expended or unit time required. Thus, remediation technologies providing the most efficient risk reduction are preferred over less-efficient technologies. Some technologies may be very inefficient in contaminant mass removal (e.g. pump-and-treat), but are accepted by regulatory agencies as providing compliance in terms of plume management. On the other hand, aggressive technologies (e.g. *in situ* extraction or destruction) that offer high efficiency in terms of reduction in contaminant mass or flux are not always found acceptable since they are viewed as having failed to provide regulatory compliance or reduce risks to desirable levels. Rao (1999) has examined the factors influencing the evolution of remediation technologies.

In this paper, we focus on sites contaminated with DNAPLs. We define two spatial domains of interest: the *source zone* and the *dissolved plume*. The source zone is defined as the groundwater region in which DNAPL is present as a separate phase, either as randomly distributed sub-zones at residual saturations, or "pools" of accumulation above confining units (Mackay & Cherry, 1989; Cohen & Mercer, 1993; Feenstra *et al.*, 1996). The plume contains only the dissolved constituents of the DNAPL and their degradation products, always at concentrations substantially lower than the solubility limits. Following Sale & McWhorter (2000), we use the term *source-zone architecture* to collectively refer to the geometry (shapes, sizes, interconnections), spatial distribution, and DNAPL content of the sub-zones. Thus, the term architecture implies both the form and function of the sub-zones as they impact the source strength (flux), the evolution of the dissolved plume, and the efficiency of remediation.

Certain technologies might reduce risks in a very efficient manner but soon reach a point of diminishing returns (asymptotic approach to some minimum risk above that is acceptable) where continued use of that technology is ill advised. For example, aggressive treatment of NAPL source zones using *in situ* destruction or extraction technologies may result in a large reduction in contaminant mass in a short period (Fiorenza *et al.*, 2000; Lowe *et al.*, 2000; Wood & Enfield, 2000). But, contaminant concentrations within the source zone might still be above the regulatory limits, and further attempts to remove or destroy the remaining contaminant mass often prove to be very difficult and costly. Thus, partial mass removal from the source zone is judged to be inadequate using the concentration-based performance metrics. However, an assessment based on a reduction in source strength (i.e. contaminant flux) would be different, as we show below. Contaminant flux is defined as the contaminant mass leaving the source zone across a control plane orthogonal to the mean groundwater flow, and may vary widely at different sites. Feenstra *et al.* (1996) discussed the use of contaminant flux as a measure for risk assessment at DNAPL sites. Einarson & Mackay (2001) used this concept more recently to evaluate the impacts of source zones on downgradient water-supply wells.

Optimal use of resources for site clean up will be possible only when combinations of technologies or technology treatment trains are utilised. In some cases, a combination of two technologies might result in more efficient risk reduction (e.g. coupling abiotic and biotic transformations). In other cases, a sequential application of successively less aggressive technologies might be the best approach (e.g. aggressive *in situ* treatment, followed by less aggressive engineered bioremediation, then natural attenuation). The major challenge is to know when to switch from one technology to the next in a treatment train. It would seem logical that the timing of such sequencing should be based on achieving the maximum risk-reduction efficiency throughout the remedial project period. However, little information exists on the rate of risk reduction achieved during applications of specific technologies. Also, little is known about the compatibility of the technologies to be used either in sequence or simultaneously. What are the unintended or unforeseen consequences of an aggressive technology that are either beneficial or detrimental to another less aggressive technology that might be selected in a treatment train? How can such adverse effects be minimized to improve technology coupling? How can the beneficial effects be taken advantage of in improving the overall remediation performance? What factors control the compatibility of technologies that are to be applied either sequentially or in conjunction with each other? These types of questions are crucial to: (a) integration and design of new remediation technologies that provide optimal site clean-up efficiency; and (b) development of new computational codes that couple source remediation to plume behaviour.

Certain technologies implemented for source-zone treatment have secondary, long-term benefits in enhancing contaminant degradation within the source zone and the dissolved plume. For example, long-term monitoring data collected subsequent to *in situ* ethanol flushing of DNAPL source zone at the Sages site (Jacksonville, Florida) indicate that the residual ethanol in the source zone serves as an electron donor in promoting reductive dechlorination of PCE (Mravik *et al.*, 2000). Field tests we conducted at the Hill AFB, and Utah and Dover AFB (Delaware), show that microbial activity was increased after *in situ* alcohol or surfactant flushing, most likely because contaminant concentrations had been reduced to negate toxicity effects. Thus, aggressive source-zone remediation technologies can be designed not only to remove substantial DNAPL mass, but also to promote contaminant attenuation in the plume.

Risk assessment and risk reduction

Remediation technology development must explicitly integrate risk-reduction goals into the evaluation of individual and combined treatment technologies, and recognize that the evaluation of risk includes human health, and ecological considerations (Suter *et al.*, 1993; EPA-SAB, 1999). We recognize that risk assessment methodology should be used to evaluate the benefits accruing from site remediation. It is possible to estimate the probabilities of contaminant concentrations exceeding some critical value (e.g. MCL) in groundwater to evaluate risks to human health (see Anderson & Destouni, 2000). However, similar analysis for ecosystem impacts is much more complex, at least because there are multiple receptors that have different sensitivities to type, magnitude and duration of exposure to contaminants (Suter *et al.*, 1993).

An important element of our assessment is an analysis of the impacts of source-zone remediation on the dissolved plume. We will define risk in terms of two features of the dissolved plume: the spatial extent (defined by length or area or shape), and the average contaminant concentration. Our measures for risk reduction then are based on whether: (a) the spatial extent of the existing dissolved plume is stable or decreases; (b) the total contaminant mass within the plume is constant or diminishing; (c) both the average concentration and the range in concentrations is diminishing; and (d) contaminant fluxes decrease at succeeding control planes along the dissolved plume. The linkage between source-zone and plume assessments is that to achieve a stable or shrinking plume, the contaminant fluxes leaving the source zone must be equal to or less than the intrinsic potential within the plume zone to attenuate the contaminants of interest. Such conditions ensure that the dissolved plume is either stable (source strength equals attenuation capacity) or will in fact shrink (source strength less than attenuation capacity). Protocols for estimating such potential exist for many contaminants (Thornton *et al.*, 2001), based on a plume-scale electron and carbon balance approach.

DNAPL SOURCE ZONE TREATMENT

A reduction in the DNAPL mass from a source zone is expected to provide the following benefits: a reduction in risk; a decrease in source longevity; a shorter period for plume management; and an increase in natural attenuation (Sale & McWhorter, 2001). However, there is a disagreement in the technical and regulatory communities as to whether the aggregate benefits of partial DNAPL mass removal are sufficient to reduce risks to an acceptable level, and if the costs associated with partial DNAPL mass removal are justified. Furthermore, there is no consensus on appropriate risk measures that should be used to evaluate the derived benefits from partial mass removal from DNAPL source zones. The question we address here is: what are the impacts of partial DNAPL source removal in *heterogeneous* aquifers on the extent of migration and the longevity of the contaminant plume compared to no source removal?

In our analysis, we assume that some aggressive remediation technology is implemented within the source zone to achieve a rapid reduction in DNAPL mass, either via *in situ* extraction or destruction. The endpoint for our risk assessment is not based on a reduction of the contaminant concentrations in groundwater within the source zone. Rather, our analysis is predicated on a reduction in the DNAPL content (total mass or average saturation), and, more importantly, the alteration in source zone architecture as a result of remediation. The nature of the expected changes in the source-zone architecture depends on the processes underlying the remediation technology and how it is implemented at a site. We are specifically interested in how remediation modifies the hydrodynamic contact with the remaining DNAPL mass, which, in turn, determines the contaminant flux leaving the source zone in response to groundwater flow under induced gradients (as in pump-and-treat) or natural gradients. Thus, different technologies might achieve similar levels of mass reduction, but may result in very different source-zone architecture and yield different reductions in contaminant fluxes. Limited field evidence is currently available to evaluate such differences.

Benefits of partial remediation of DNAPL source zones

Based on modelling analysis of contaminant transport in *uniform flow fields* with a non-uniform distribution of DNAPL sub-zones, Sale & McWhorter (2001) reached two primary conclusions: (a) the dominant process limiting mass transfer is advective–dispersive transport in the aqueous phase, not the internal rate of DNAPL dissolution within the sub-zones; and (b) source-zone remediation efforts that reduce DNAPL content, by decreasing either the size or the number of sub-zones, are likely to have little beneficial effects on the near-term groundwater quality. This supports earlier conclusions that significant mass removal from source zones is ineffective unless some impractically large mass removal is achieved (Travis & Doty, 1990). It is our contention that different conclusions will be reached for *heterogeneous flow fields*, and we present the following in support.

Berglund (1997) conducted stochastic modelling of the "clean-up time" (defined as 99% mass removal from source zone) under pump-and-treat scenarios for three-dimensional heterogeneous (random fields of hydraulic conductivity) aquifers having a source zone with either uniform or variable distribution of DNAPL and dissolution mass-transfer rate constants. He concluded that compared to the base case of uniform DNAPL distribution in the source zone, the clean-up times actually decrease when a positive correlation is assumed between the spatial variability of hydraulic conductivity and DNAPL content. We surmise from his analysis that for aggressive remediation scenarios (not simulated by Berglund), such effects on flux reduction are likely to be even more evident. The analysis presented by Enfield (2000) also supports this expectation.

We conducted three-dimensional particle-tracking model simulations for heterogeneous flow fields to examine contaminant-flux reduction achieved from partial DNAPL mass reduction. Demmy *et al.* (1999) described details of the particle-tracking numerical simulations in exponentially correlated, isotropic random fields to obtain travel-time ensemble statistics. We assumed an isotropic, lognormal hydraulic conductivity (K) field ($\mu_{\ln K} = 0$; $\sigma_{\ln K} = 1.0$) with the following dimensions: 46 correlation lengths, λ, in the mean flow direction, and 36λ in the transverse direction, with five grid blocks per correlation length (230×180 blocks). For a flux-proportional injection of particles, the arrival times and travel distances were recorded to estimate the velocity (v) distribution. Note that the resulting velocity probability density function (pdf), $f(v)$, was lognormal. Here, we examined three cases of correlation between the hydraulic conductivity field and the DNAPL saturations: zero, positive and negative correlations. We also assumed equilibrium dissolution of DNAPL. Thus, dissolved DNAPL concentrations were equal to the solubility limit (C_{sol}) as long as there was any residual DNAPL present within the particle trajectories; otherwise, the dissolved DNAPL concentration was set to zero. Contaminant advective flux (J) was estimated as: $J = \Sigma v_i C_i$ where C_i is either equal to C_{sol} (when DNAPL is present) or zero (no DNAPL). Given the average velocity and DNAPL content along a trajectory, the level of DNAPL removal was then estimated for specified injection periods. Contaminant flux reductions are achieved as a result of complete mass removal from certain particle trajectories; note that complete mass removal occurs first in the highest-velocity trajectories, while the lowest velocity trajectories are the last to experience complete mass removal. Thus, with increasing DNAPL mass removal with
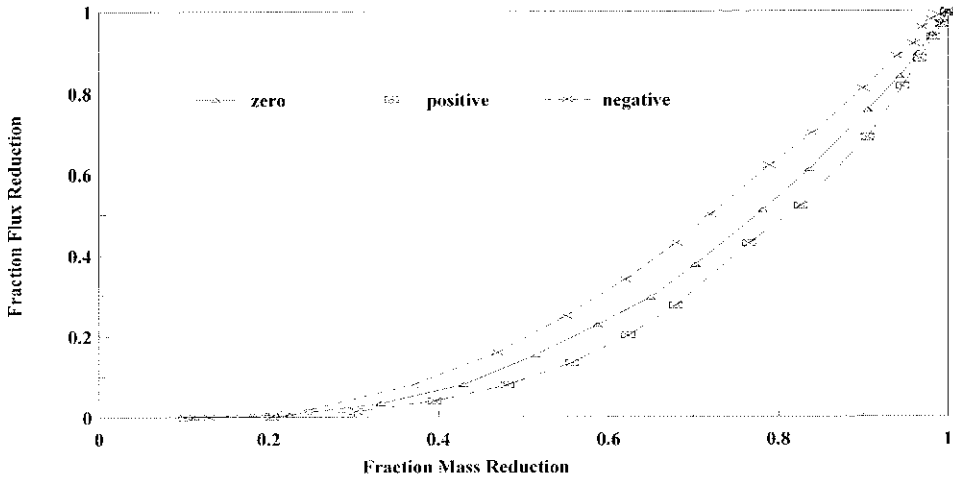
Fig. 1 Particle tracking simulation results for contaminant flux reduction achieved as a function of DNAPL mass reduction in the source zone.

progressively longer flushing, contaminant flux is expected to gradually decline and diminish to zero. The pdf statistics for the velocity field and the correlation between DNAPL content and velocity should then determine the efficiency with which DNAPL mass reduction can be achieved, and the expected rate of contaminant flux reduction in heterogeneous flow fields.

Our simulation results show that significant reductions in contaminant flux are likely for partial DNAPL mass removal (Fig. 1). Note that for a given reduction in DNAPL mass, the largest flux reduction is achieved for the case of negative correlation between hydraulic conductivity and DNAPL saturation. That is, since most of the DNAPL mass is located in the low-velocity streamtubes, removal of the relatively small fraction of DNAPL mass resident in the high-velocity streamtubes provides a large reduction in contaminant flux. Note that due to constraints on hydrodynamic access, DNAPL mass removal is less efficient for the negative correlation case. While for the positive correlation case, a larger fractional mass reduction is required to achieve the same level of flux reduction; but doing so is easier since a much larger fraction of the DNAPL mass is located in the high-velocity zones. We are further examining these effects using simple analytical approaches (Rao & Jawitz, 2002), three-dimensional particle-tracking simulations, and three-dimensional numerical simulations using the T2VOC model for source-zone remediation in heterogeneous flow domains.

We conducted field experiments at the Dover AFB, Delaware (Brooks *et al.*, 2002) to evaluate the performance of *in situ* ethanol flushing to solubilize and extract PCE from a source zone created by controlled release of DNAPL in a sheet-pile walled test cell. Preliminary analysis of data from these tests (Brooks, 2000) shows that an increase in PCE mass removal achieved via *in situ* alcohol flushing is manifested as a decrease in PCE flux (Fig. 2). Note the remarkable similarity of the shape of the predicted curves (Fig. 1) to that for field data (Fig. 2). These curves can be described by an empirical function, $Y = X^{1/\beta}$, where Y is the fractional contaminant flux reduction, X is
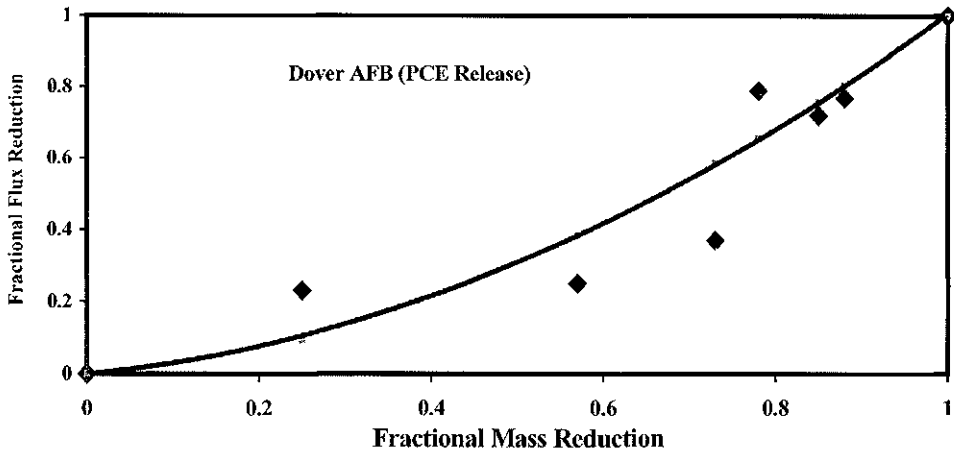
Fig. 2 Field data for observed PCE flux reduction achieved as a function of PCE mass reduction in the source zone.

the fractional DNAPL mass reduction, and β is an empirical parameter representing the *efficiency* of flux reduction. These data and model simulations also suggest that a minimum mass fraction, X_{min}, may need to be removed before any flux reduction is noted. The β and X_{min} values depend on the degree of heterogeneity of the flow field and the source-zone architecture (correlation with the K field), as well as the remediation technology and its implementation. Additional simulations and field data are needed to establish the specific nature of such inter-dependence. While our analysis focused on the *relative* reduction in contaminant fluxes, it is the value of the *absolute* contaminant flux, coupled with the likely fluxes of a suite of electron donors and competing electron acceptors, that will control the dissolved plume evolution (see Thornton *et al.*, 2001). Thus, the site geochemistry within the dissolved plume must also be explicitly considered in assessing the likely benefits of partial DNAPL mass removal from source zones.

SUMMARY

We need to emphasize the development of *linkages* among remediation technologies (either sequential implementation, as in treatment trains, or simultaneous implementation, as in technology combinations) to achieve appropriate flux-based endpoints in a cost-effective and timely manner. Such an integrated approach is the essential next step in remediation technology development, to make progress beyond the current expectation that a single technology will provide the desired site clean up. The acceptability of the target endpoints should be established within a human health and ecological risk framework, while the appropriateness of the technology combinations or sequence will be established based on compatibility and cost. The present analysis suggests that contaminant flux from a DNAPL source zones can be reduced by partial mass removal. Such contaminant flux reductions can be beneficial in reducing risks either by reducing contaminant concentrations at downgradient supply wells or by producing conditions that promote stable or shrinking dissolved plumes.

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