Natural Attenuation Review

July 2006

July 28, 2006

MEMORANDUM

TO: Steve Hampson, Assistant Director, UK-KRCEE
FROM: Alan Fryar, Associate Professor, UK Earth & Environmental Sciences
RE: Review of "Derivation of the Dissolved Trichloroethene Degradation Factor for the
            Regional Gravel Aquifer at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky"
            (BJC/PAD-757, Appendix F)

I have read the aforementioned report and, although I have not checked all of the calculations, I have several concerns about the approach used. In particular, I think (1) the assumption that trichloroethene (TCE) biodegradation occurs in the Regional Gravel Aquifer (RGA) is not well supported, and (2) the approach used in the calculations (assuming one-dimensional flow, linear sorption, and a single value for the fraction of organic carbon [f_{OC}]) is simplistic. I address these issues as follows.

(1) The argument for aerobic biodegradation in the RGA is based on Clausen et al. (1997) and Sorenson et al. (2000) (by analogy with a TCE plume in the Snake River Plain aquifer beneath the Idaho National Engineering and Environmental Laboratory). Evidence of TCE biodegradation is inferred from (a) above-background Cl^- concentrations, (b) dissolved O_2 concentrations less than would be expected for equilibrium with air and elevated dissolved CO_2 concentrations, and (c) $^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$ ratios of RGA ground water (this report, p. 10). However, there are errors in all of these arguments.

(a) Fryar et al. (2000, Table 4) reported Cl^- concentrations of 59.9 to 62.1 mg/L but no detectable TCE in monitoring well LB7Y, located on the east bank of Little Bayou Creek just north of McCaw Road. This well appears to be southeast of the northeast plume but downgradient of PGDP. Sturchio et al. (1998, p. 3039) stated "we are aware of no major sources of groundwater Cl^- input, other than TCE degradation, in the study area". Those authors eliminated road salt, salt piles, landfills, evaporite deposits, sea water effects, water softeners, and septic systems as possible sources. However, industrial activities at PGDP could have generated Cl^- without involving TCE. For example, considering that Cl^- tends to be chemically conservative, it could have been concentrated by evaporation of cooling water or waste water, which then infiltrated beneath lagoons or ditches. (Note that the background Cl^- concentration reported in this report for well MW103, upgradient of PGDP, should be 3 to 7 mg/L, not 0.003 to 0.007 mg/L [p. 6].)

(b) Dissolved O_2 concentrations less than air-saturated water and dissolved CO_2 concentrations greater than air-saturated water indeed indicate microbial respiration. Such respiration commonly occurs during infiltration through the soil zone and is not necessarily indicative of biodegradation in the saturated zone.

(c) Clausen et al. (1997, p. 30) noted that "$\delta^{13}C$ values for TCE were obtained…using an untested sampling method…and therefore should be used with caution, because of the possibility of isotopic fractionation by interaction with the container materials. The data is not considered further in this report." Sturchio et al. (1998, p. 3039) stated that the $\delta^{13}C$ values of dissolved inorganic carbon "are not uniquely diagnostic of a particular source". Sturchio et al. (1998, p. 3039) did contend that Cl-isotope data could indicate TCE biodegradation, but conceded that "(s)imple closed-system models of TCE degradation are generally inconsistent with the data shown". Those authors suggested that "TCE degradation may have been more extensive within the UCRS [Upper Continental Recharge System] early in the site's history" (p. 3041). Therefore, this report's contention that "isotopic ratios…of RGA groundwater are consistent with microbial degradation of TCE *within the main contaminant plumes*" (p. 10; emphasis mine) is inaccurate.

Moreover, the analogy with the INEEL plume is flawed. Biodegradation depends on the bioavailability of organic matter and not simply the amount (as stated on p. 8–9). At Test Area North at INEEL, TCE and other wastes were co-injected with sewage into the Snake River Plain aquifer (Sorenson et al., 2000). Organic matter in sewage is likely to be more readily metabolized than aged sedimentary organic matter, such as would occur in the Continental Deposits. Alternatively, methane in the Snake River Plain aquifer (Chapelle et al., 2002) could drive TCE oxidation by methanotrophic bacteria. Although bacterial groups capable of microaerophilic oxidation of TCE have been identified in the Snake River Plain aquifer, I am not aware of such bacterial analyses for the Continental Deposits. Likewise, I am unaware of analyses of compounds capable of sustaining microaerophilic activity (such as methane, propane, and phenols) or of daughter products of TCE oxidation in RGA ground water.

(2) Both the method used to derive the apparent TCE degradation factor (EPA, 1998) and BIOCHLOR assume a 1-D ground-water flow field. However, the plume trajectories shown in figures 1 and 2 of this report depict a non-linear (multidimensional) flow field. As Aziz et al. (2002, p. 1–2) note, "BIOCHLOR is an appropriate model at sites where simplifying assumptions (e.g., uniform ground-water flow, a vertical plane source, first-order decay) can be made so that the resulting simulations provide useful information for the problem being addressed. At other sites, where these assumptions do not hold, a more sophisticated numerical model such as RT3D (Clement, 1997) would be appropriate."

Sensitivity analyses conducted during calculations and modeling appear to have been limited to varying ground-water velocity (between 1 and 3 ft/day), the apparent degradation rate, and the retardation factor. The range of ground-water velocities seems reasonable *if unidirectional flow can be assumed*. My estimates based on lengths of the northwest and northeast plumes and the range of possible release dates yield a velocity range of 0.99 to 2.4 ft/day for the northwest plume and 0.54 to 7.8 ft/day for the northeast plume (Fryar, 1997). Estimates of seepage velocity into Metropolis Lake (following the inferred trajectory of the northeast plume), modified from Fryar et al. (1999), range from 1.8 to 5.1 ft/day. However, the use of the median f_{OC} value to calculate the apparent degradation factor is insufficient. The median and mean f_{OC} values listed in Table 4 (354,500 and 228,500 µg/kg, respectively) appear to be correct, but the range (29,000 to 2,530,000 µg/kg) is much broader than that cited on p. 5 (100,000 to 500,000 µg/kg) or the "typical" value of 200,000 µg/kg mentioned on p. 11. The standard deviation (423,500 µg/kg) is larger than either the median or the mean. The sensitivity analysis using BIOCHLOR did consider a range of retardation factors for an apparent degradation rate of 0.083 yr^{-1}, but not for an apparent degradation rate of 0 (compare Figures 17 and 19). Finally, it is worth noting that sorption to

sedimentary organic matter may be non-linear, rather than linear, as assumed in this report (see Allen-King et al. [2002] for a review).

References
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