Strawman on approach to evaluate SCIR data on TCE to evaluate biodegradation, or a process to get to a decision estimation statement

For the wells sampled and sent to OU for analysis in Paul Philp's lab, DOD will provide a calculation of the apparent extent of removal of TCE (measured concentration divided by original concentration) based on concentrations of TCE normalized to concentrations of ^{99}Tc. The up gradient well will be the well with the highest concentration of TCE that is in a plausible flow path to the down gradient well. The up gradient well must be one of the wells sampled and sent to Paul Philp.

$$C/C_o = TCE_{\text{down gradient}} / (TCE_{\text{up gradient}} * [\,{}^{99}Tc_{\text{down gradient}} / {}^{99}Tc_{\text{up gradient}}\,])$$

Then, based on the results of the carbon isotopic analysis, C/Co will be independently calculated from the following formula

$$C/Co = e^{((\delta^{13}C_{downgradient} - \delta^{13}C_{upgradient})/\varepsilon)}$$

Where $\delta^{13}C_{upgradient}$ is the carbon isotopic ratio in TCE in the up gradient well, where $\delta^{13}C_{downgradient}$ is the carbon isotopic ratio in TCE in the down gradient well, and ε, the isotopic fractionation factor for aerobic biodegradation of TCE through co-metabolism (subject to revision based availability of more literature), will be -1.1 ‰. This value of ε is provided by Chu, K.-H., Mahendra, S., Song, D.L., Conrad, M.E., and Cohen, L.A. (2004) Stable carbon isotope fractionation during aerobic degradation of chlorinated ethenes. *Environmental Science & Technology* 38: 3126-3130.

The stable isotope analyses will be evaluated by comparing the rate of TCE transformation as predicted from the analyses to the rate of TCE transformation extracted from the field monitoring data. If the rate of TCE transformation predicted from the extent of removal of TCE based on stable isotope measurements is at least one third the rate extracted from the field data, then the stable isotope analyses will be considered to provide a third line of evidence for MNA processes as defined in United States Environmental Protection Agency. 1999. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*. Office of Solid Waste and Emergency Response, Directive 9200.4-17P. http://www.epa.gov/swerust1/directiv/d9200417.htm.

Assuming pseudo first order kinetics:

$$C/Co = e^{-kt}$$

Where k is the first order rate constant for attenuation and t is time of travel from the up gradient to the down gradient well. Taking the natural logarithm of both sides:

$$\ln(C/Co) = -kt$$

Because t is the same for the estimate based on TCE concentrations or the estimate based on stable isotope ratios, it can be scaled as "one travel time." The value of t in both cases is one.

If the natural logarithm of the value of C/Co provided from the analysis of stable isotope ratios is more negative than natural logarithm of the value of C/Co as calculated from measured concentrations of TCE as normalized to the measured concentrations of ^{99}Tc, or if the natural logarithm of the value of C/Co provided from the analysis of stable isotope ratios is no more than a factor of 0.33 more positive than the natural logarithm of the value of C/Co as calculated from measured concentrations of TCE as normalized to the measured concentrations of ^{99}Tc, the stable isotope analyses will be considered to provide a third line of evidence for MNA processes.

As an example:

Assume the normalized value of C/Co for measured TCE concentrations is 5.5 µg/L down gradient and 200 µg/L upgradient. The value of C/Co is 0.0275 and the value of ln(C/Co) is -3.59. Multiplying -3.59 by 0.33 produces a criterion of -1.18. The stable isotope data will be considered to provide the third line of evidence if the value of ln(C/co) estimated from the stable isotope ratios is less than -1.18.

Assume the value of $\delta^{13}C_{upgradient}$ is -30.20‰ and the value of $\delta^{13}C_{downgradient}$ is -28.10‰. If ε is -1.1‰, the value of C/Co predicted from the stable isotope ratios is 0.148 and the value of ln(C/C0) is -1.91. Because -1.91 is less than -1.18, the criterion would be satisfied and the stable isotope data would be considered to provide the third line of evidence.

If the natural logarithm of the value of C/Co provided from the analysis of stable isotope ratios is more than a factor of 0.33 more positive than the natural logarithm of the value of C/Co as calculated from measured concentrations of TCE as normalized to the measured concentrations of ^{99}Tc, the stable isotope analyses will be considered to provide no interpretable information, and will not be used to support a decision.

Assume the value of $\delta^{13}C_{upgradient}$ is -30.20‰ and the value of $\delta^{13}C_{downgradient}$ is -29.00‰. If ε is -1.1‰, the value of C/Co predicted from the stable isotope ratios is 0.336 and the value of ln(C/C0) is -1.09. Because -1.09 is greater than -1.18, the criterion would not be satisfied and the stable isotope data would be considered to provide no interpretable information, and will not be used to support a decision.

To allow for statistical uncertainty in the determination of $\delta^{13}C$ analyses, the value of $\delta^{13}C_{upgradient}$ will be replaced with $\delta^{13}C_{upgradient}$ plus the sample standard deviation of the analysis, and $\delta^{13}C_{downgradient}$ will be replaced with $\delta^{13}C_{downgradient}$ minus the sample standard deviation of the analysis.

If the natural logarithm of the value of C/Co provided from the analysis of stable isotope ratios is not more than a factor of 0.10 more positive than the natural logarithm of the value of C/Co as calculated from measured concentrations of TCE as normalized to the measured concentrations of ^{99}Tc, the stable isotope analyses will be considered to provide a third line of evidence for

MNA processes. If the natural logarithm of the value of C/Co provided from the analysis of stable isotope ratios is more than a factor of 0.1 more positive than the natural logarithm of the value of C/Co as calculated from measured concentrations of TCE as normalized to the measured concentrations of ^{99}Tc, the stable isotope analyses will be considered to provide no interpretable information, and will not be used to support a decision.

The value of ln(C/Co) for the normalized TCE field data was -3.59. Multiplying -3.59 by 0.10 produces a criterion of -0.359.

Assume the value of $\delta^{13}C_{upgradient}$ is -30.2‰ and the value of $\delta^{13}C_{downgradient}$ is -28.1‰. Also assume the sample standard deviation is 0.25‰. The values modified by the standard deviation are -29.95‰ and -28.35‰. If ε is -1.1‰, the value of C/Co predicted from the stable isotope ratios is 0.234 and the value of ln(C/C0) is -1.45. Because -1.45 is less than -0.359, the criterion would be satisfied and the stable isotope data would still be considered to provide the third line of evidence, despite its measured uncertainty.

If the parties choose to accept this outline to negotiate a decision estimation statement, they should negotiate the factors of 0.33 and 0.01, and the value for ε.