TASK 1.16 – ENHANCED MOBILITY OF DENSE NONAQUEOUS-PHASE LIQUIDS (DNAPLs) USING DISSOLVED HUMIC ACIDS

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DISCLAIMER

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1.0 BACKGROUND

Chlorinated solvent contamination is widespread across the U.S. Department of Energy (DOE) complex and other industrial facilities. Because of the physical properties of dense nonaqueous-phase liquids (DNAPLs), current treatment technologies are generally incapable of completely removing contamination from the source area. Incomplete removal means that the residual DNAPL will persist as a long-term source of groundwater contamination. When DNAPLs occur in the subsurface, they resist remediation, owing to low water solubility, high viscosity and interfacial tension, and microbial recalcitrance. Because of their high density and polarity, they are usually found sorbed to aquifer solids or in pools on impermeable materials. Surfactants have been used with some success to reduce interfacial tension between the aqueous and organic phases and improve solubility of DNAPLs. However, surfactants are expensive and toxic and exhibit an oxygen demand. An alternative is the use of dissolved humic acids in improving DNAPL mobilization and solubilization. Humic acids, a natural form of organic carbon, are abundant, inexpensive, and nontoxic; biodegrade slowly (low oxygen demand); and have excellent mobilization properties. The present work is to establish the feasibility of using humates for enhancing DNAPL remediation.

2.0 OBJECTIVES

The specific objectives of this subtask are as follows:

- Evaluate the suitability of using humic acids to enhance the solubility and mobility of DNAPL contaminants sorbed to soils.

- Evaluate the toxicity and bioavailablity of the DNAPLs to biodegrading microorganisms.

3.0 STATEMENT OF WORK

To meet the first objective, the Energy & Environmental Research Center (EERC) evaluated a set of humic acids (two) with different chemical compositions and polarities for the following:

- Ability of the humates to mobilize/solubilize selected (three) DNAPLs

- Mobilization/solubilization in batch soil–water experiments (one soil)

- Removal rate via biotreatment with a well-established active microbial culture

The second objective was met by evaluating the inhibiting effects of a leonardite-derived humic acid on active microbial populations.

4.0 METHODS

4.1 Humic Acid Preparation

Humic acid solutions were obtained from leonardite coal and Carex peat material using the following extraction method. 50 grams of dry material was blended at high speed for 10 minutes with 500 mL of a 10% sodium hydroxide (NaOH) solution. The suspended material was allowed to settle, and the remaining solution was centrifuged at 3000 rpm for 10 minutes to remove any additional suspended material. The supernatant was then poured into a large beaker and labeled as the humate solution. The suspended material was dried and weighed to calculate the concentration of the humate, which was approximately 9% by weight. This batch solution was then diluted with distilled water to the desired humate concentrations ranging from 0.1–3.0 wt%. The distilled water contained sodium acetate which would allow for a constant Na^+ ion ratio within the varying solutions.

4.2 Batch Water and Humate Experiments

4.2.1 Water vs. Humate Partitioning

These experiments were conducted in 60-mL glass jars using Teflon stoppers. The tests were completed using different variations of the two humate solutions and one artificial surfactant and four different contaminants: trichloroethylene (TCE), tetrachloroethylene (PCE), *4*-bromobiphenyl ether (BPE), and carbon tetrachloride (CT). The jars were filled with distilled water or the desired concentration of humate solution, with no headspace, and allowed to equilibrate on a stir plate for 2 hours with the same amounts of the selected contaminant. The amount of contaminant added to each jar was the maximum solubility for each at the given room temperature of 70°F. After equilibration, an internal standard was added to each jar and allowed to mix for 1 minute. A solid-phase microextraction (SPME) fiber was introduced to the sample for exactly 1 minute and then injected into a gas chromatograph with a 1-minute holding time in the injection port. The resulting area ratio of contaminant to internal standard was compared to a previously constructed calibration curve to determine the contaminant concentration. The SPME fiber, which is coated with a 100-µm-thick polydimethylsiloxane coating, will adsorb only the contaminant that is not bound to the humate micelles. The amount of contaminant adsorbed or partitioned into the humate vs. the amount of humate or surfactant in the solution can then be plotted.

4.2.2 Water/Humate vs. Liquid Phase

This set of experiments used basically the same protocol for testing as the water-vs.-humate partitioning tests except that the amount of contaminant in the sample was 3 to 4 times the solubility levels, and the sample was injected directly into the gas chromatograph rather than using the SPME fiber, allowing for evaluation of the amount of contaminant in solution with the

humate. The samples were also centrifuged before being analyzed to pellet out any free-phase contaminant.

4.3 Batch Soil–Water Experiments

These experiments were completed using 5–30 grams of a selected sediment with a low level of organic matter, leonardite humate, and TCE as the contaminant. The solution was mixed for 24 hours, and the sediment was allowed to settle. The dissolved phase contaminant was then analyzed by taking a 1-mL sample of the solution and adding it to a 2-mL scintillation vial containing the internal standard solution. The sample was mixed for 1 minute, and then 2–3 µL were injected into the gas chromatograph with a syringe. The area ratios of the contaminant and internal standard were compared to a calibration curve, and concentrations of the amount of contaminant remaining in solution were derived.

The sediment used in these experiments was obtained from a gravel pit near Rader, North Dakota. The sample, which was light brown in color when dry, consisted of a fine to medium sand, with quartz and feldspar minerals composing approximately 90% and 5% of the material, respectively. Clay content was approximately 2%–3%, with very little organic material present.

5.0 RESULTS

5.1 Partitioning of TCE Between Aqueous Humate (solubilized TCE) and TCE Liquid Phase

In these experiments, the partitioning between the aqueous phase containing various concentrations of dissolved humate vs. liquid DNAPL was investigated. Thus the three phases are actually present: the liquid DNAPL, the dissolved free DNAPL, and the dissolved humate-bound DNAPL. This partitioning is of critical importance in determining the effectiveness of the humate in solubilizing DNAPL and, therefore, in remediating a contaminated area by pump-and-treat methods. The sum of the dissolved free DNAPL and the dissolved humate-bound DNAPL in the total aqueous phase after equilibration is easily determined by addition of a known amount of internal standard to a sample and direct injection in the gas chromatograph. This determination of the solubility in the humate solution in µg/L is called SW*. The ratio of SW* to the solubility of the DNAPL in pure water (called SW) represents the partitioning for that concentration of humate. The values of SW*/SW vs. humate concentration (Hum) are plotted, and the slope gives the partition coefficient (K_{doc}) for the compound in the particular humic acid. This coefficient can be compared for various humates or other surface active reagents. The humates or surfactants with the highest values for K_{doc} will have the greatest increase in solubilities and the most success in removing DNAPLs.

The plot of SW*/SW for TCE in leonardite humate solutions gave a linear plot with a high R^2, and the intercept was very close to the expected value of 1.00 (see Figure 1). The value for K_{doc} from the slope is relatively large. Thus the 1.5% humate solution will increase the solubility by a factor of 3. The linear plot is typical of surfactant systems that feature micellular structures

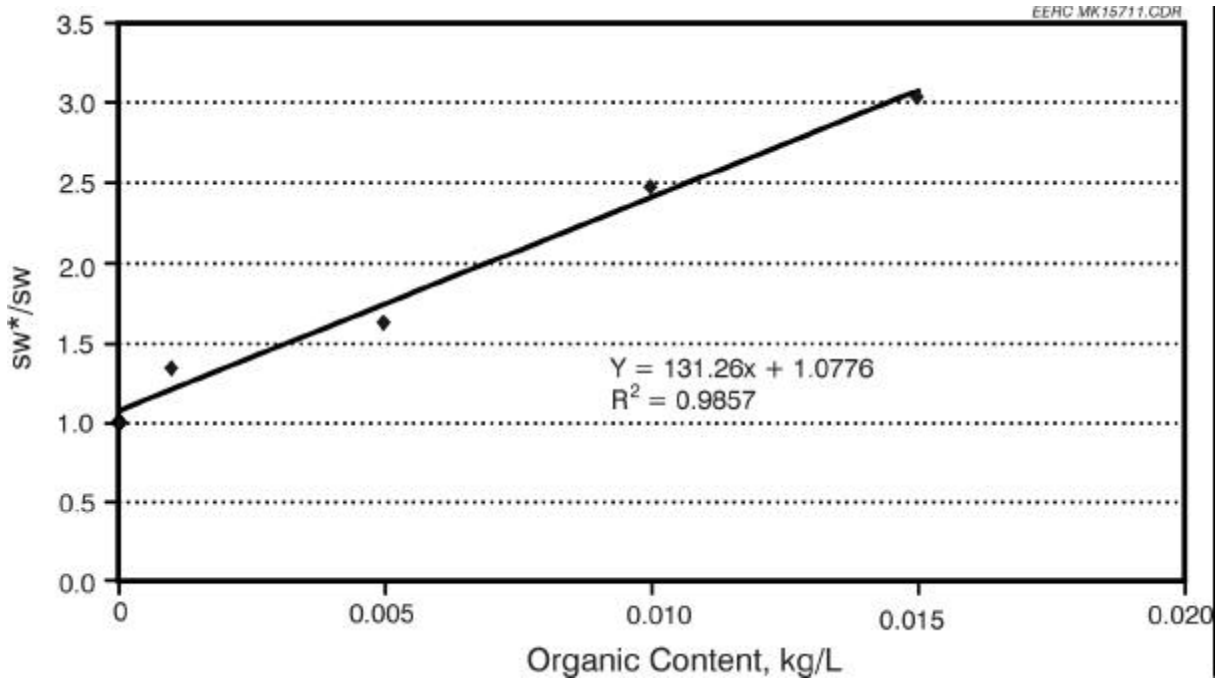

Figure 1. The plot of SW*/SW for TCE in leonardite humate solution.

for binding nonpolar organic species. Thus the model of humate macromolecules containing a hydrophobic interior binding site consisting of regions of aliphatic and aromatic groups is consistent with these data. The value obtained for K_{doc} for the TCE–leonardite system (131 L/kg) is much larger than that (3.6 L/kg) determined for TCE–Aldrich humic acid. The humate solutions used in this study are obtained freshly from the leonardite samples and may be less oxidized than the Aldrich humate. This would result in a more hydrophobic macromolecule and perhaps higher-molecular-weight distribution. How these factors affect the K_{doc}s for humates from various sources remains to be studied.

$$SW^*/SW = K_{doc}(Hum) + 1$$

$$K_{doc} = 131 \text{ L/kg}$$

5.2 Partitioning of DNAPLs Between Water (dissolved DNAPLs) and Humate (bound DNAPLs)

Experiments were performed to determine the partitioning of DNAPLs between the humate macromolecules in a solution and the water solvent. In these experiments, there was no undissolved DNAPL phase as in the above case. These tests were performed similarly to the isotherm tests used to evaluate adsorption of organic compounds on sorbents. An identical amount of DNAPL (less than the solubility limit) is equilibrated with a series of concentrations of humate solutions, and the concentrations of the DNAPL in the water or dissolved state are determined by SPME and gas chromatography (GC) analysis. The difference between initial and

dissolved concentrations represents the humate-bound concentration. The bound humate concentrations are plotted vs. the humate concentrations, and the type of curves are indicative of the binding process. The data will indicate the relative affinity of the humate for various organic solutes.

The partitioning of TCE in humate solutions was determined for two types of humate, that is, humate obtained from leonardite and from peat. The plot of humate-bound TCE concentration (shown in Figure 2) vs. leonardite humate concentration was prepared over the concentrations tested (0.05% to 4%). The R^2 was 0.89 for the linear regression. The slope was not as high as expected, and thus the proportion of bound TCE was not as high as desired. The Freundlich isotherm plot of $\log_{x/m}$ vs. $\log_c$ was much less linear, however. Thus even though the bound TCE concentrations may be lower than expected at high humate concentrations, the partitioning observed is consistent with surfactant behavior. One explanation for the curve falling off at high humate concentrations is that the SPME phase is actually pulling substantial amounts of organic solute out of the humate during the sampling period. This would be less likely to occur at low humate concentrations.

The plot of humate-bound TCE vs. peat humate concentration (Figure 3) gave a similar curve, but the linearity was substantially worse, with greater flattening out at higher concentrations. The slope was higher at low concentrations, however, indicating that the peat humate has a greater affinity for the organic phase. This is consistent with our earlier studies

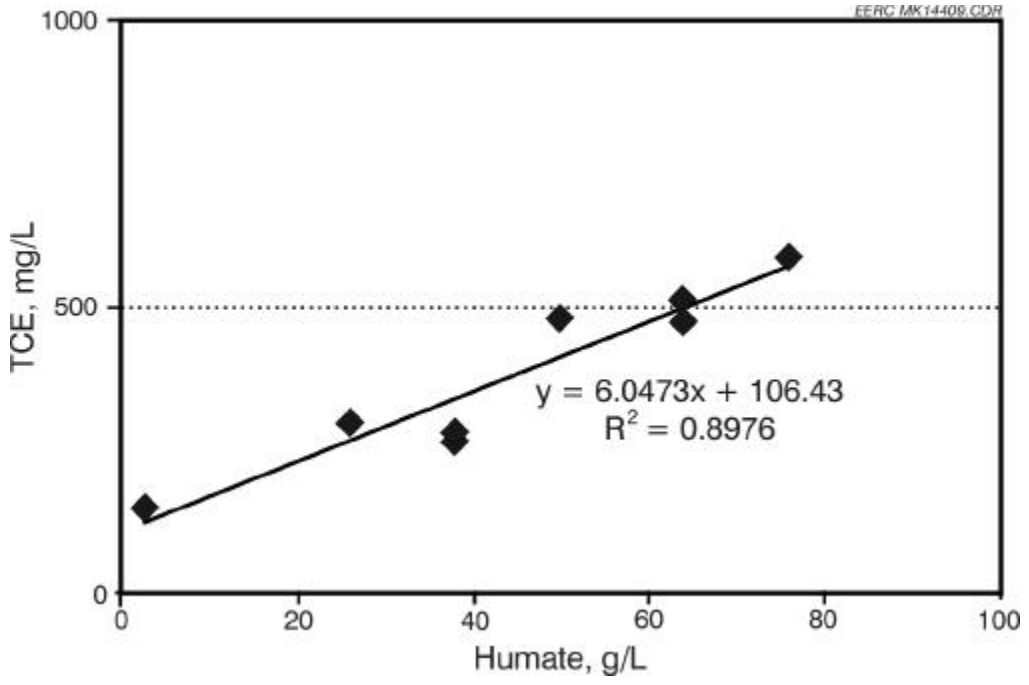

Figure 2. The plot of humate-bound TCE concentration vs. leonardite humate concentration.

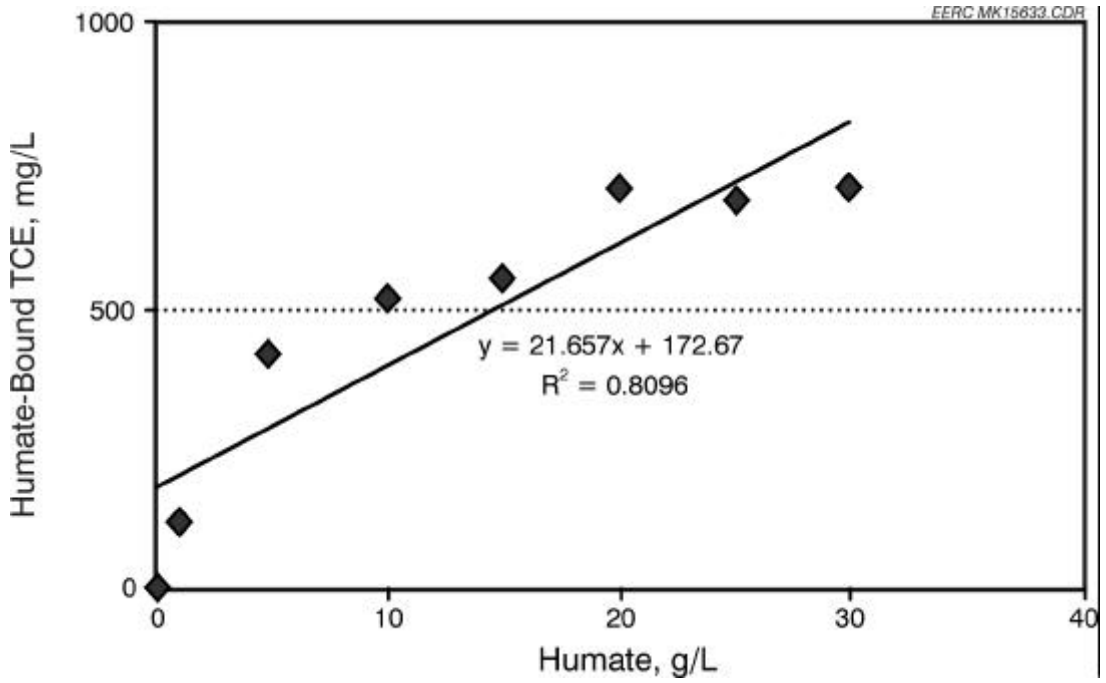

Figure 3. The plot of humate-bound TCE concentration vs. peat humate concentration.

which determined that Carex peat contains a large proportion of aliphatic groups derived from microorganism residues captured during peat diagenesis.

The partitioning of PCE in solutions of various leonardite humate concentrations were investigated. Results of the graph can be seen in Figure 4. The plot of PCE concentration vs. humate concentration gave a mediocre R^2 for the linear regression. A flattening out at higher humate concentrations was observed. The attempted Freundlich plot gave an even lower R^2 and did not seem to represent an acceptable solution. A linear curve is expected for a straight partitioning effect between two phases. Thus this type of behavior is more likely the case than an adsorption such as occurs in an activated carbon.

Nevertheless, the data indicate that at 1%–2% humate concentrations, a substantial proportion of the PCE is bound to the humate. The plot cannot be directly compared with the TCE–humate system because of the different amounts of organics used (different water solubilities). If we compare the percentage of organics bound, the two cases are similar.

The partitioning of PCE in synthetic (dioctyl sodium dulfosuccinate [AOT]) surfactant was also investigated. Although the AOT is very expensive, it serves as a comparison model for binding of the organic solutes. Below 0.5%, the surfactant is ineffective in binding PCE, owing to the inability to form micelles at this low concentration. At AOT concentrations of 1%–2%, linear behavior was exhibited. Comparison of the AOT curve (Figure 5) with that obtained above for leonardite humate showed similar values for the slope. Thus the inexpensive humate should be as effective as the surfactant for solubilization of PCE.

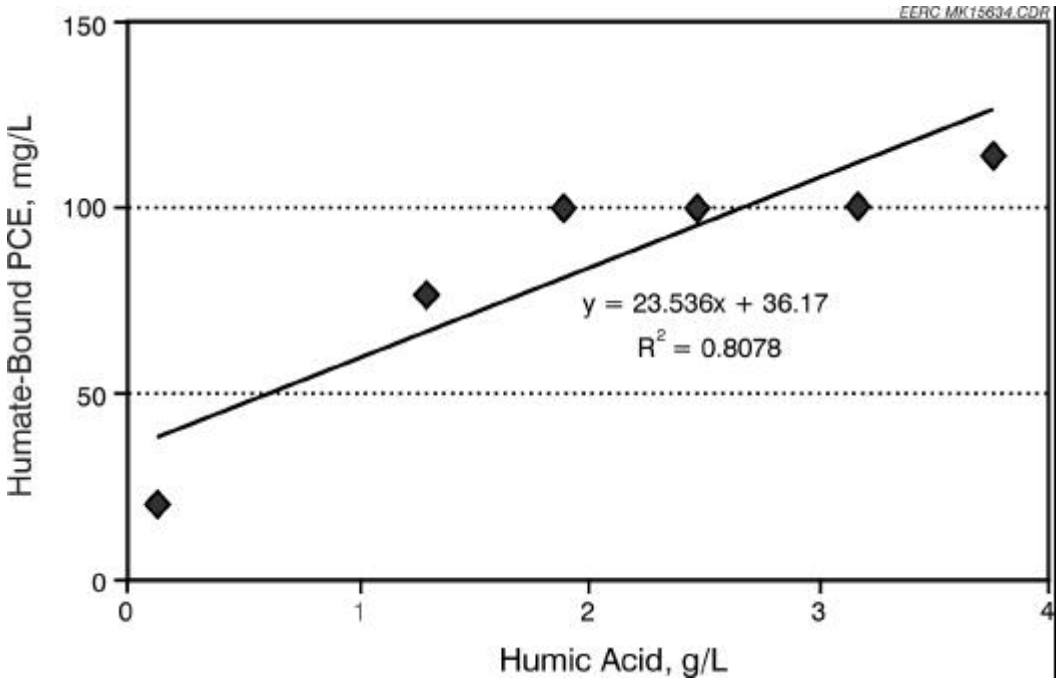

Figure 4. The plot of humate-bound PCE vs. leonardite humate concentration.

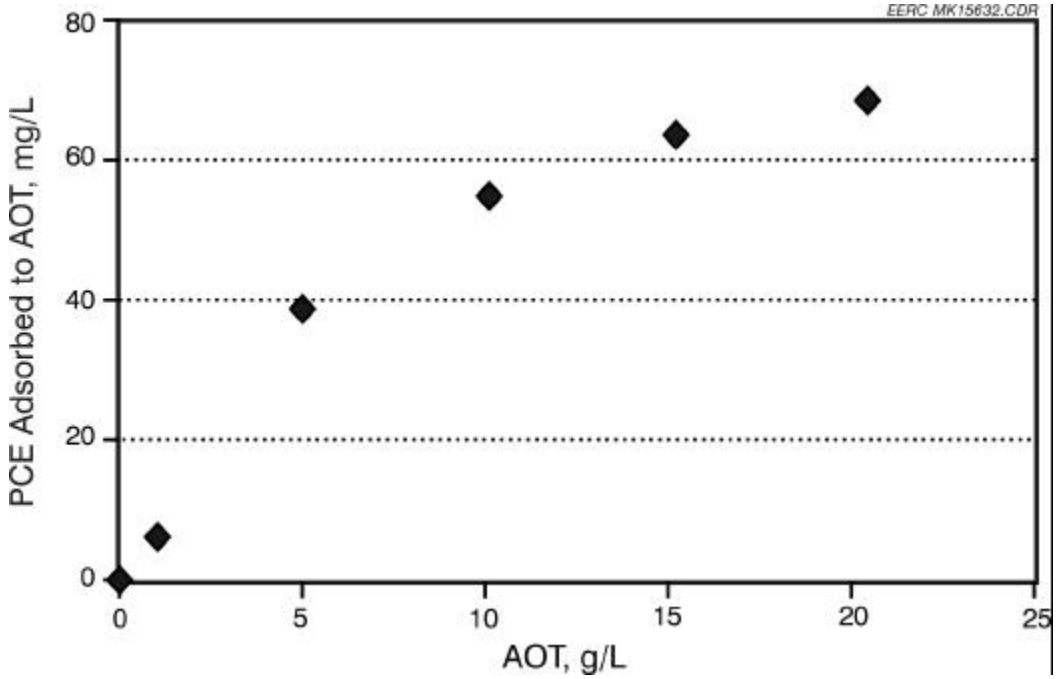

Figure 5. The plot of humate-bound AOT vs. leonardite humate concentrations.

The CT–peat humate system was investigated. Results, as seen in Figure 6, reveal that again the curve flattens out severely. The slope at low concentrations, however, indicates that a substantial proportion of the CT is bound to the humate.

As a surrogate for polychlorinated biphenyls (PCBs), the partitioning of BPE in peat humate solutions was investigated. This organic phase exhibits quite low solubility in water, as can be seen in Figure 7. Again, the curve flattened out and even dropped at high humate concentrations, presumably owing to sampling problems. The initial slope is quite large, however, indicating promise for PCB remediation with humate solutions.

5.3 Batch Soil–Water Experiments

Experiments were conducted with soil added to the humate–TCE system to determine the effect of the soil on the partitioning. The results of the determinations of dissolved TCE with the SPME method indicate that the concentration of free-dissolved TCE decreased with increased humate concentrations as expected. The difference between the dissolved TCE and the original amount of TCE added represents the amount bound to the humate plus the amount bound to the soil. This sum is called bound TCE. Figure 8 shows the plot of bound TCE vs. humate concentration. This increases but flattens out as with previous SPME experiments. Thus the determinations at high humate concentrations may be erroneous.

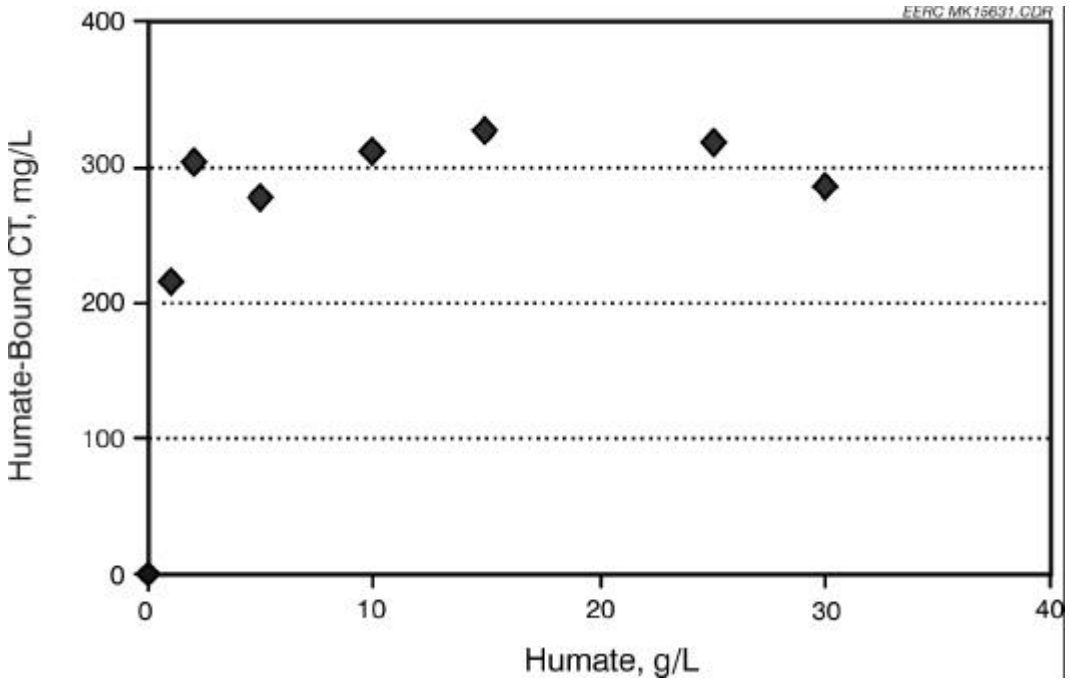

Figure 6. The plot of humate-bound CT concentration vs. peat humate concentration.

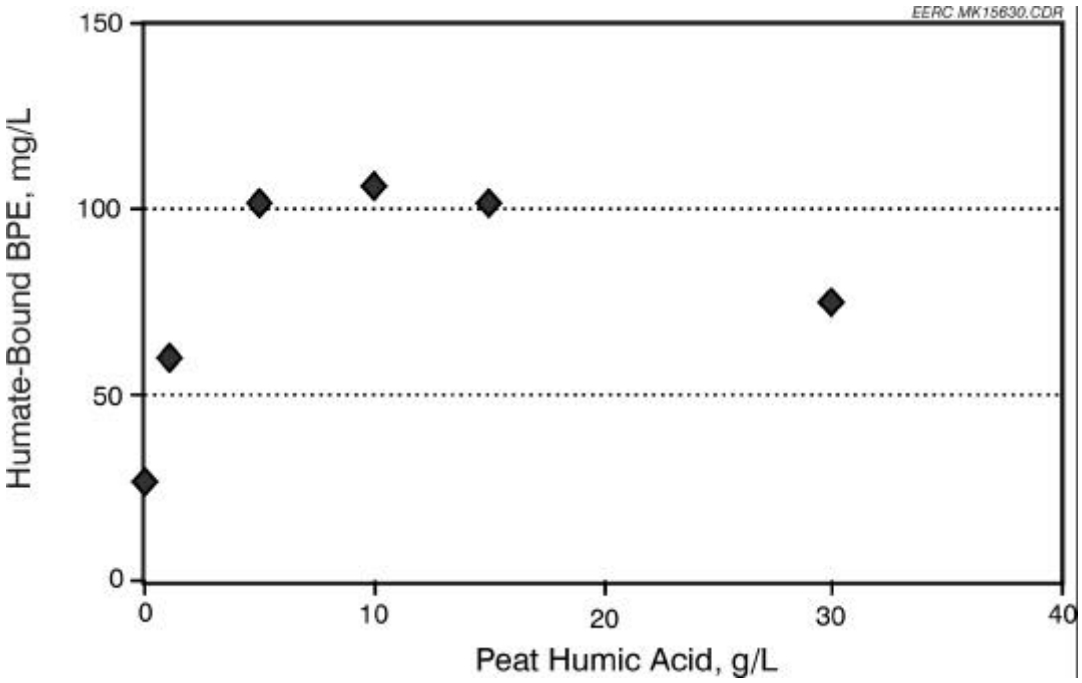

Figure 7. The plot of humate-bound BPE vs. peat humate concentration.

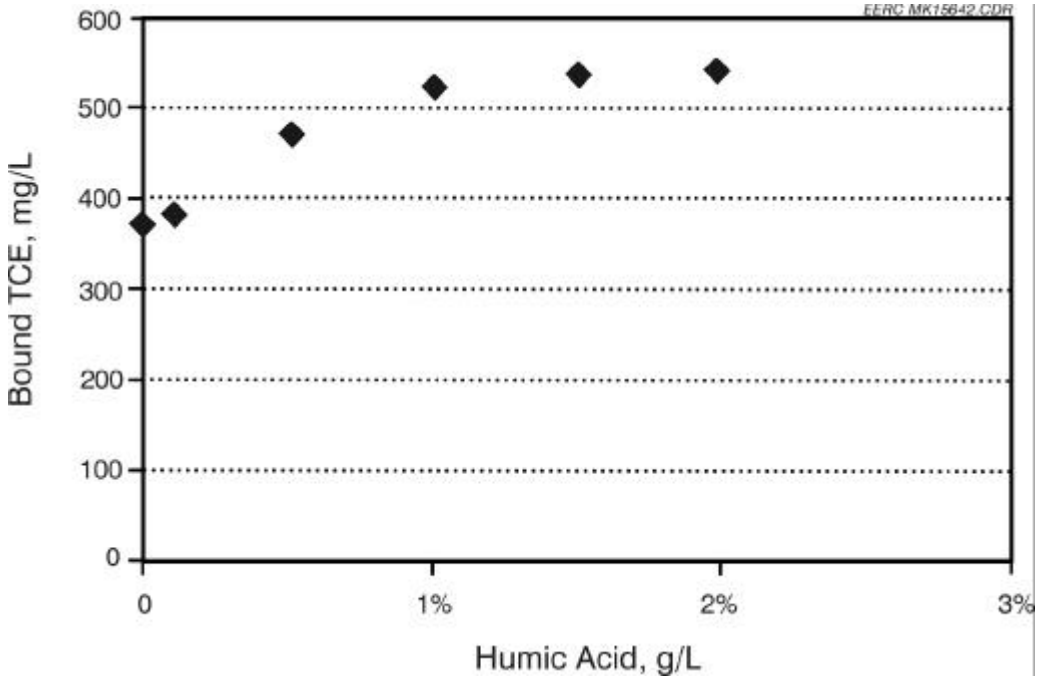

Figure 8. The plot of the sum of bound TCE vs. humate concentration.

In the same experiments, the total aqueous TCE (free-dissolved plus humate-bound) was determined by direct injection of the supernatant. The difference between the total aqueous TCE and the original amount of TCE is called the solid-phase TCE. This value remained constant (Figure 9) with increasing humate. This may be attributed to loss of humate containing bound TCE to the solid phase. The implication of this finding is that higher concentrations of humate are not useful for pump-and-treat applications. The excess of humate may be lost to the soil along with some of the organic contaminants.

5.4 Bioavailability Experiments

Figure 10 shows the oxygen uptake rate observed as a function of the concentration of leonardite-derived humic acid. This experiment was performed with microbial cells from the Moorhead, Minnesota, municipal wastewater treatment plant. This plant uses a pure oxygen activated sludge (POAS) system. The sludge was aerated for 72 hours to use up residual organic matter and diluted in 1.0M tris buffer, pH 8.0, and humic acid was added. The oxygen uptake rate was measured at 30°C using a YSI Model 25 apparatus. The data show an increase in oxygen uptake at very low concentrations, perhaps due to oxidizable organic matter, or it could be a toxic response. At higher concentrations, the oxygen uptake declines to a low, constant rate. This suggests that the humic acid inhibits but does not kill the cells.

Figure 11 shows the results of plate counts performed on two flasks. These flasks contained a simple mineral media (Organization for Economic Cooperation & Development

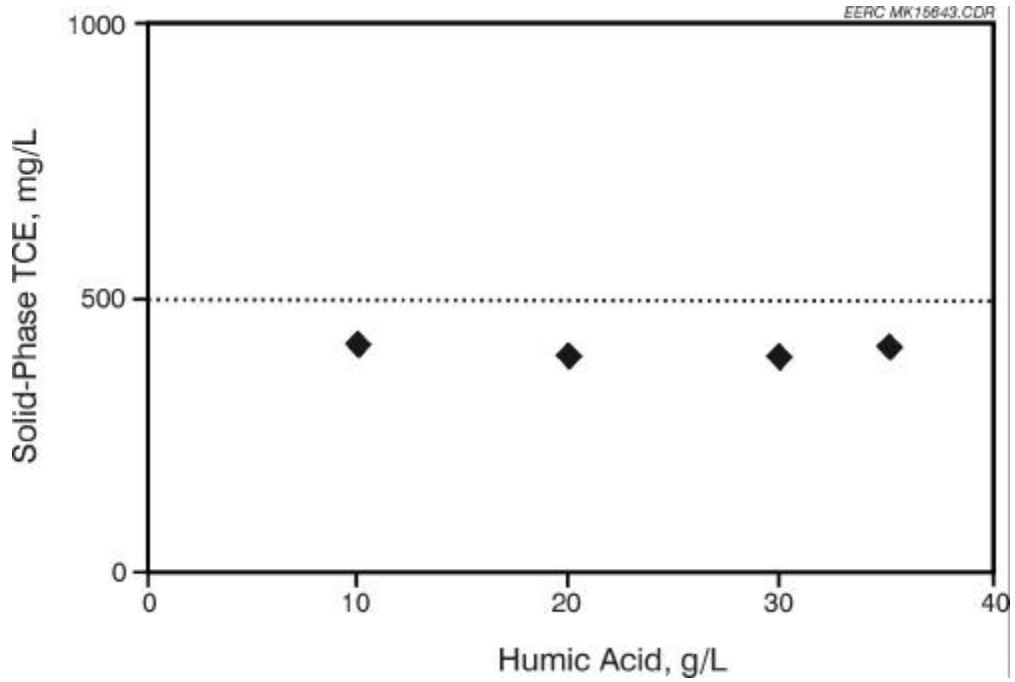

Figure 9. The plot of solid-phase TCE vs. humate concentrations.

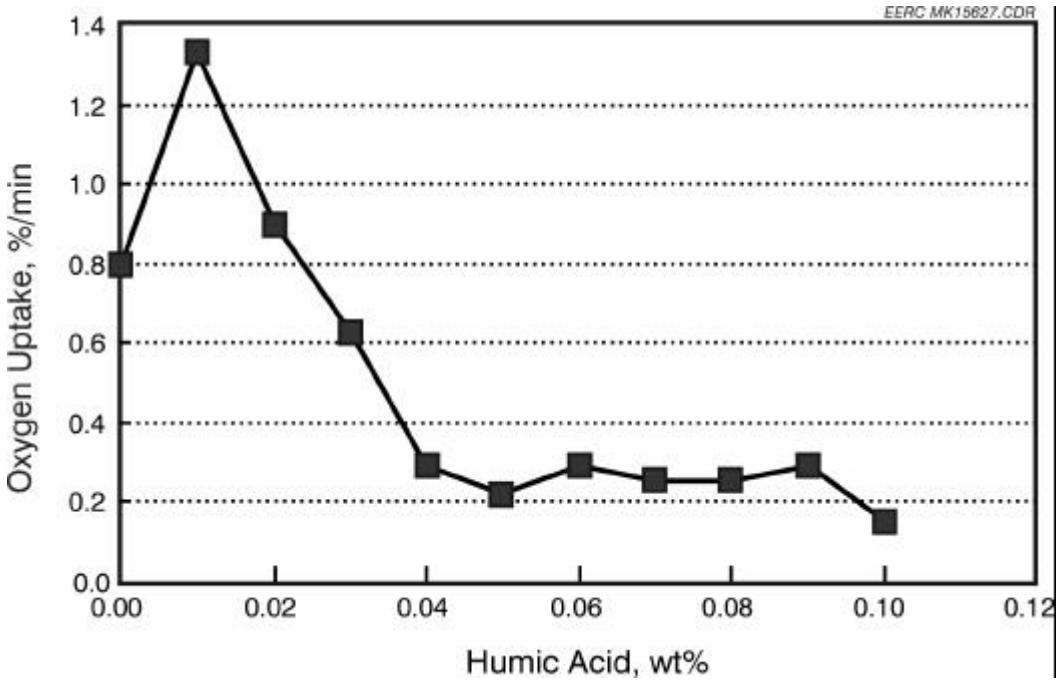

Figure 10. Microbiological inhibition studies (the plot of oxygen uptake vs. humate concentration).

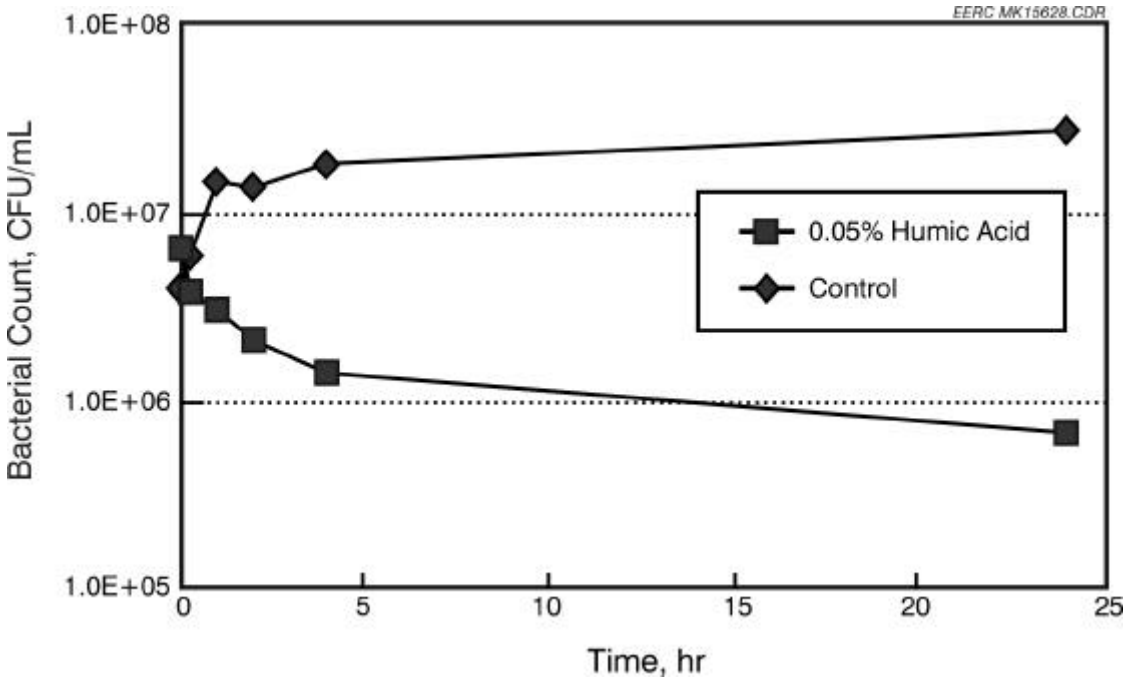

Figure 11. Microbiological inhibition studies (the plot of bacteria count vs. time).

[OECD]) with glucose at 0.4% (w/v). One flask was a control with no humic acid added, and a second flask had humic acid added at 0.05% (w/v). The flask contents were inoculated with 100 µL of activated sludge mixed liquor from the Moorhead plant. The counts were performed by doing a serial tenfold dilution and plating onto plate count agar (standard methods, Difco). The plates were incubated at 25°C for 3 days. The data from this experiment failed to demonstrate any interpretable conclusions, and the experiment was duplicated.

The experiment documented in Figure 12 is identical to the experiment documented in Figure 10, but it was run for a longer time period and included a third flask. The three flasks contained a simple mineral media (OECD) with glucose at 0.4% (w/v). One flask was a control with no humic acid added, and a second flask had humic acid added at 0.05% (w/v). A third flask was set up with humic acid at 0.5% (w/v); however, the counts in this flask fell below detection (3.0×10^3/mL) after the initial count. The flask contents were inoculated with 100 µL of activated sludge mixed liquor from the Moorhead plant (see above). The counts were performed by doing a serial tenfold dilution and plating onto plate count agar (standard methods, Difco). The plates were incubated at 25°C for 3 days. The data show that the control had rapid growth, with a doubling about every 18 hours. Microbial growth in the 0.05% humic acid flask showed a quick decline, then remained constant during the remainder of the experiment. Once again, these data suggest that the humic acid inhibits growth, but is not especially lethal.

Another experiment was performed using a longer incubation period and higher concentrations of humic acid. However, the data were interpreted visually as relative turbidity because it is time-consuming and expensive to do plate counts and the color of the media precludes the usual inexpensive methods. The setup is the same as in Figure 11: OECD media with glucose, humic acid at several concentrations, and inocula from the POAS. These data

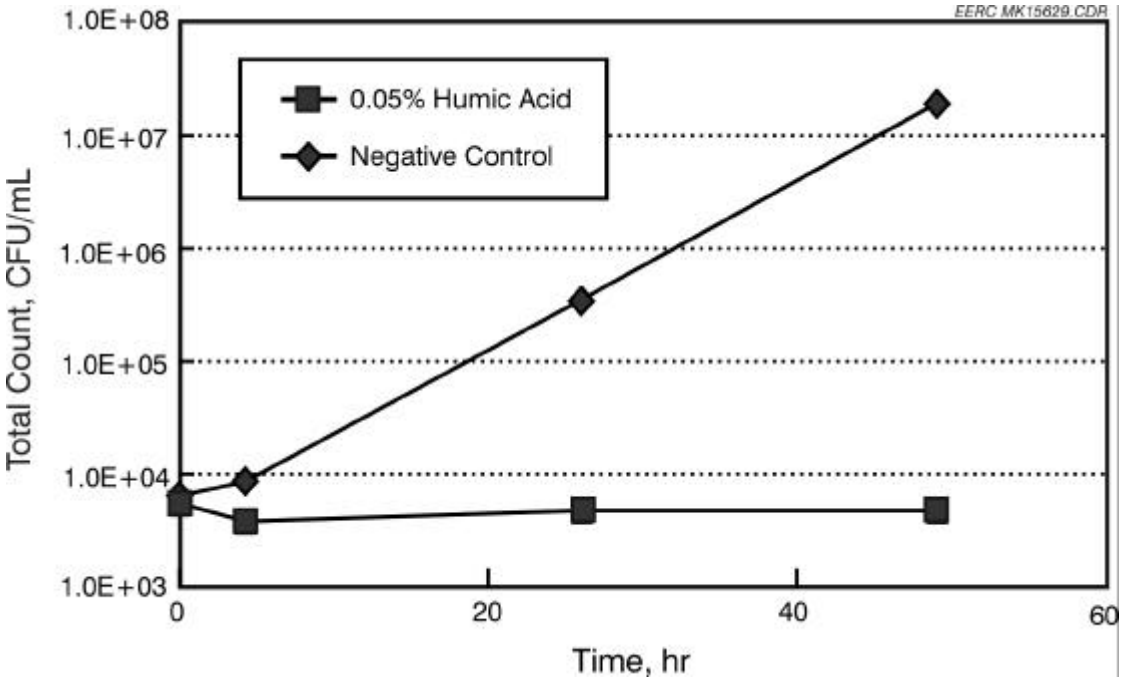

Figure 12. Microbiological inhibition studies (the plot of total count vs. time).

suggest that at doses of 0.005% and 0.010%, microbes are not inhibited (consistent with Figure 9. At doses from 0.015% to 0.050%, the microbes are inhibited but still capable of growth. At higher doses, inhibition of growth is complete. The implications for remediation is that growth is inhibited in the plume of humic acid, but as the humic acid is depleted or diluted, growth will resume.

6.0 CONCLUSIONS AND FUTURE PLANS

Humic acids have been shown to possess solubility- and mobilization-enhancing properties similar to those of artificial surfactants. These humic acids, because they are abundant and inexpensive, may prove to be an attractive alternative to using artificial surfactants to enhance pump-and-treat of various DNAPL compounds in the subsurface. Partition coefficients were determined for the TCE–leonardite humate system that indicate the potential for solubility enhancements of TCE using humates in the 1%–2% range.