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December 12, 2000

MEMORANDUM

SUBJECT: Review of Draft Final Study of Monitored Natural Attenuation at SWMU 15, NAS Oceana, Virginia Beach, Virginia, prepared for the Department of the Navy, Atlantic Division, Naval Facilities Engineering Command under LANTDIV CLEAN II Program, Contract N62470-95-D-6007, by CH2MHill, Herndon, Virginia. (98RC03-001)

FROM: John T. Wilson, Ph.D., Microbiologist
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TO: Robert W. Stroud
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U.S. EPA, Region 4

At your request, I have reviewed the subject document. I find that the site characterization data presented in the report is of adequate detail and completeness to allow an assessment of natural attenuation processes at the site. However, I disagree with the evaluation of the data and the conclusions that were reached in the report.

Errors in Calculation of Rate Constants

They calculated the rate of attenuation of benzene using the approach of Buscheck and Alcantar (1995). I feel that this is the most appropriate approach for the data set. This approach fits field data to an analytical solution for one dimensional flow along a flow path in ground water. The mathematics assumes a steady state plume, where the concentration at any one point is determined by biodegradation and dispersion, but not by advection. The mathematics assumes that the plume has "broken through" the portion of flow path that is being described. Using this approach, The monitoring wells are arranged in a flow path. The slope of a linear regression of the natural logarithm of the concentration of contaminant on distance from the source is used to extract a first order rate of attenuation with distance. The flow velocity of the ground water and an estimate of the coefficient of dispersivity is used to convert the rate of attenuation with distance to a rate of biodegradation with time of travel along the flow path

The data they used to estimate the rate are presented in Appendix I. Note that they mis-labeled Flow path A as Flow path B and vice versa. The flow paths extend in a southerly direction from the original source in the area excavated down to DW10. Examine the data in my Table 1

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below. The flow path from MIP3-25 down to DW07 is uniformly filled with methane at a consistent concentration. If methane is used as a conservative tracer of the plume, then the flow path from MIP3-25 to DW07 meets the assumptions of the mathematics in Buscheck and Alcantar (1995). However, the concentration of methane at DW-10 is less than one tenth the concentration in the monitoring well immediately upgradient (DW07). The plume has not broken through at location DW10. As a consequence, most of the reduction in concentration in benzene between wells DW07 and DW10 is due to the fact that plume has not arrived at DW10. This segment does not meet the assumptions of the mathematics of Buscheck and Alcantar (1995). However, the segment from DW07 to DW10 is the only segment they used to calculate a rate of natural biodegradation.

Table 1. Attenuation of Benzene and Methane in Flow Path A to A'				
Location	Distance	Time	Benzene	Methane
	feet	years	ug/l	ug/liter
MIP3-25	0	0	4340	8180
DW15	36	1.8	1120	5700
DW14	144	7.2	2870	6720
DW5	252	12.6	3410	7370
MW20	324	16.2	3010	7060
DW01	333	16.65	1800	6580
DW07	369	18.45	3840	10300
DW10	504	25.2	5.9	340
Benzene data for DW wells from Table 5-5				
Methane data for DW wells from Figure 6-4				
Benzene and Methane data for MW20 well from Table B-1				
Benzene and Methane data for MIP3-25 well from Table D-1,				
note I used MIP3-25 for the estimate of source				
while their Table Flowpath B (really flowpath A) in Appendix I used MIP3-20				
The estimate of travel time assumes a seepage velocity of 20 feet per year.				

The approach of Buscheck and Alcantar is supposed to be applied to all the wells in the flow path that meet the assumptions of the mathematics. For the flow path from DW07 to DW10 they report a slope of -0.0600 per foot and r^2 of 1.0000. My Table 2 presents the results of a linear regression of Ln [benzene] on distance in feet for wells MIP3 to DW07. The slope of the regression (+0.00058) indicates that the concentration of benzene is actually increasing slowly along the flow path away from the source. At 95% confidence, the rate can be no greater than -0.0030 per foot, which is roughly 1/20 of the rate extracted in the subject report.

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Table 2. Regression of LN [benzene] on distance in feet from location MIP3 to DW07

SUMMARY OUTPUT						
<i>Regression Statistics</i>						
Multiple R	0.1821					
R Square	0.0332					
Adjusted R Square	-0.1602					
Standard Error	0.5124					
Observations	7.0000					
ANOVA						
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>	
Regression	1.0000	0.0450	0.0450	0.1715	0.6959	
Residual	5.0000	1.3126	0.2625			
Total	6.0000	1.3576				
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>
Intercept	7.77232	0.35010	22.20048	0.00000	6.87237	8.67227
X Variable 1	0.000580	0.001400	0.414128	0.695946	-0.003020	0.004179

An examination of their Figure 6-2 shows a sharp reduction in concentration of methane along Flow path ~~B~~^D between locations DW12 and DW11. In Appendix I, they report a rate of attenuation of -0.0387 for Flow path B (mis-labeled ~~A~~), where the attenuation was calculated from wells DW12 to DW11 to DW27. When the attenuation is calculated for the wells from DW17 to DW12 where the assumptions of the mathematics of Buscheck and Alcantar are met (see Table 3), the rate is -0.00452 per foot. However, this rate is also not different from zero at 95% confidence.

Table 3. Attenuation of Benzene in Flow Path B to B¹

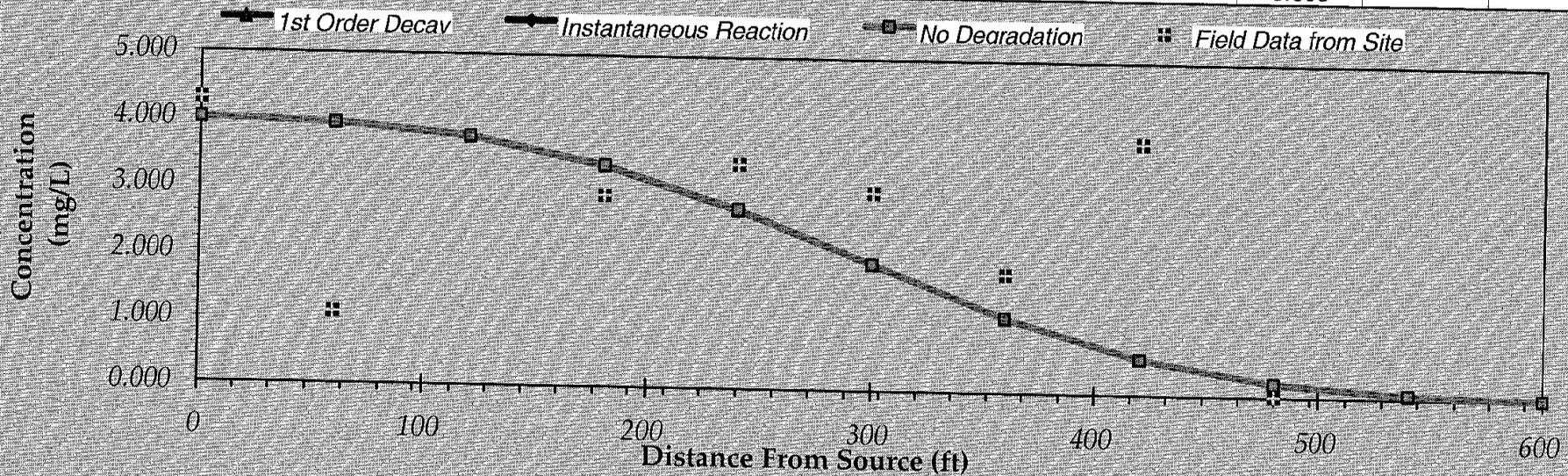
Location	Distance feet	Benzene ug/l	Time years
DW17	0	3350	0
DW13	126	6910	6.3
DW06	234	2500	11.7
DW03	315	261	15.75
DW12	378	2118	18.9
DW11	468	73	23.4
DW27	576	1	28.8
Benzene data for DW wells from Table 5-5			

Appendix I also has some curious tables where they estimated attenuation along transects labeled Flowpaths C,D, and E that are perpendicular to ground water flow (compare Figures 5-6 and Figure 3-3). These rate estimates have no physical meaning.

They used the rate constants extracted by the approach of Buscheck and Alcantar as input data for a BIOSCREEN model. I consider this to be appropriate. However, they only modeled the segment of the flow paths for which they calculated the rate constants, and not the entire flow path. Their Figure 1A is the input screen for a calibration of BIOSCREEN that is based on their assumptions, but that models the entire flow path A from MIP3 to DW10. I increased the model length to 600 feet to include the data in my Table 1. The Seepage Velocity in their Appendix J is reported as 6.2 feet per year. This is an error. They may have failed to "Recalculate This Sheet" before they entered "Run Centerline." I used their values of Hydraulic Conductivity, Hydraulic Gradient, and Porosity to estimate a Seepage Velocity of 10.6 feet per year. The next two pages (Pages 5 and 6) are the input screen for BIOSCREEN and the Run Centerline output screen from my calibration of BIOSCREEN. I set the rate of biodegradation to an arbitrarily low number (0.001 per year) to calibrate the model for no biodegradation. As you can see, there is a good correspondence between these assumptions (their assumptions of flow and my assumption of biodegradation kinetics) and the field data along Flow path A. There is no evidence that benzene has been biologically degraded in the aquifer. There is no evidence that the benzene plume has come to a steady state. If past is prologue, the benzene plume will continue to advance slowly along Flow path A.

DISSOLVED HYDROCARBON CONCENTRATION ALONG PLUME CENTERLINE (mg/L at Z=0)

TYPE OF MODEL	Distance from Source (ft)										
	0	60	120	180	240	300	360	420	480	540	600
No Degradation	3.997	3.951	3.768	3.361	2.722	1.923	1.140	0.550	0.211	0.063	0.015
1st Order Decay	3.997	3.948	3.763	3.354	2.715	1.918	1.137	0.548	0.210	0.063	0.015
Inst. Reaction	3.997	3.951	3.768	3.361	2.722	1.923	1.140	0.550	0.211	0.063	0.015
Field Data from Site	4.300	1.100		2.900	3.400	3.000	1.800	3.800	0.006		



Calculate Animation

Time:

40 Years

Return to Input

Recalculate This Sheet

Errors in Use of Expressed Assimilative Capacity

They state on page 6-7 that the stoichiometric calculations indicate that the ground water at SWMU 15 has more than sufficient assimilative capacity to degrade the dissolved BTEX that partitions from the residual phase into the groundwater before the plume migrates to potential receptors off site. This evaluation came from a comparison of the BTEX concentration in the plume at the source and the expressed assimilative capacity as calculated from the geochemical changes in the water. Expressed assimilative capacity is assimilative capacity that has already been used, not capacity remaining to degrade new contaminants.

Most of the expressed (used) assimilative capacity is associated with methane produced in the water. There is little or no toluene in the groundwater at SWMU 15, probably because it has been biologically degraded. The concentration of toluene in fresh spills of JP-4 is usually about twice that of benzene. The highest benzene concentration is near 4 mg/liter, which would predict an initial toluene concentration of 8 mg/liter. If the toluene were fermented to methane it would produce near 6 mg/liter of methane. Examine my Table 1. The amount of methane in the water corresponds to the methane that would have been produced from the amount of toluene is missing. The calculation of expressed assimilative capacity describes the fate of the missing toluene. It can not be used to predict the future fate of the benzene remaining in the water.

Uncertainty in their Time to Cleanup (TTCU) model

They used values for benzene degradation of 0.55 per year and 0.29 per year in their two phase modeling approach (page 7-3). As discussed above, there is no evidence in the field data that biodegradation of benzene is occurring at all. If it is occurring, the rate is less than 10% of the rates they used in their TTCU model. The estimate of time to cleanup would increase by ten fold if more realistic estimate of the upper boundary for biodegradation were used in their spread sheet.

Discussion of their Conclusions and Recommendations

They state in the third paragraph of Conclusions and Recommendations (page 9-1) that "... dissolved phase contaminants released into the sand aquifer from the adjacent silts are apparently biodegrading rapidly and being flushed out, as evidenced by the limited contamination detected in the aquifer. Therefore, the migration potential of a dissolved phase plume is limited." My Table 1 and their Figure 5-7 for Flow path A show little or no evidence that the contaminants have been flushed out. Some of the highest concentrations are found in MIP3 and MIP4, near the ponded excavation.

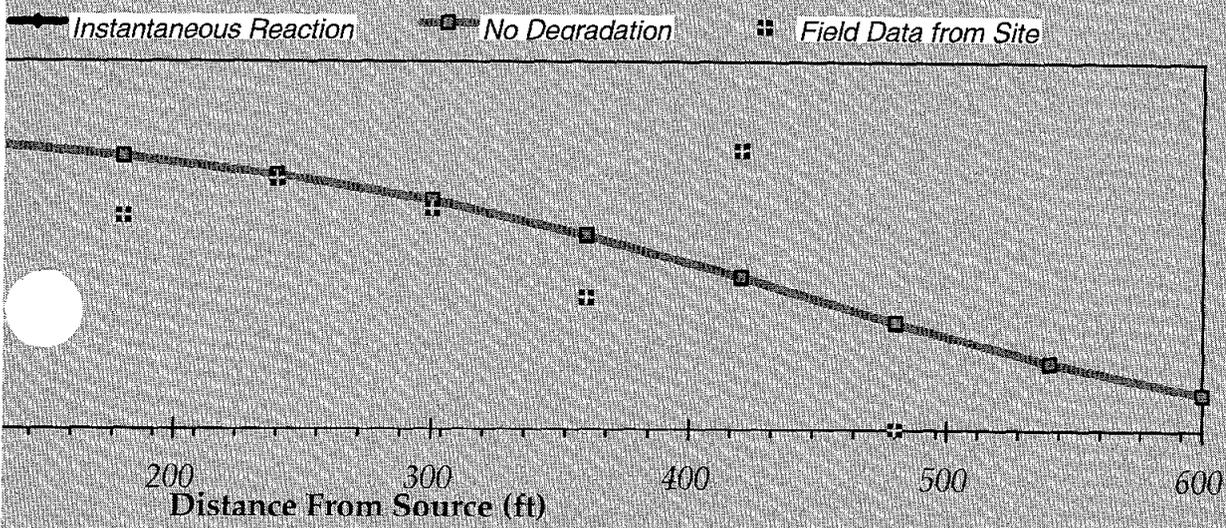
The note that "Without biodegradation, the BIOSCREEN model predicts that benzene would have been observed at relatively high concentrations more than 200 feet downgradient, which is not indicated in the field data." BIOSCREEN was correct but their interpretation of the field data is in error. Relatively high benzene concentrations were observed at location DW07, which is 369 feet downgradient of MIP3 (see my Table 1), and even further downgradient of the original source.

They note that "Modeling with BIOSCREEN supports the conclusion that the plume is stable and shrinking." When BIOSCREEN is used to model the entire flow path, and not just the short segment where concentrations are declining with distance, the model indicates that benzene is not degrading, which indicates that the plume will continue to expand. The following page is a BIOSCREEN calibration for 60 years, showing changes to be expected over the next 20 years.

Please call me at 580 435 8534, or e-mail at wilson.johnt@epa.gov if I can provide any further

HYDROCARBON CONCENTRATION ALONG PLUME CENTERLINE (mg/L at Z=0)

<i>Distance from Source (ft)</i>								
120	180	240	300	360	420	480	540	600
3.902	3.723	3.466	3.115	2.649	2.079	1.471	0.920	0.500
3.897	3.714	3.456	3.105	2.638	2.070	1.465	0.916	0.498
3.902	3.723	3.466	3.115	2.649	2.079	1.471	0.920	0.500
	2.900	3.400	3.000	1.800	3.800	0.006		



Time:

Return to Input

Recalculate This Sheet

assistance.

cc: