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MEMORANDUM

TO: Mr. Rich Smith
Law Office of John K. Dema

DATE: 11/2/94

FROM: P. Fahrenthold
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SUBJECT: Evaluation of Geraghty & Miller Remedial Investigation Report

I received a copy of selected pages from the Geraghty & Miller Report identified above. I have review the report for technical validity of the observations presented therein.

I placed particular emphasis on Section 5.0, addressing comments on Pages 5-18 and 5-19. The results of my review are provided in the following discussion.

General Comments

This Section of the report is devoted to the "Nature and Extent of Contamination". In reality, it attempts to explain the transport of contaminants from the sources identified in Section 5.1 and known to exist, to the groundwater and soils in the area.

It is my opinion, supported by the calculations provided in this memo, that the document is seriously flawed in its presentation and has no technical foundation for the statements made. The portions of the document with which I find flawed are identified below.

Paragraph 1, last 7 lines: ".....One exception noted for this indication of contaminant release is the detection of low levels (less than 10 ppb) of chlorinated VOCs in soil. Due to the presence of chlorinated VOCs in groundwater throughout most of the site, these low concentrations are attributed to volatilization and adsorption from the contaminated groundwater. This has been shown to occur in areas that are not suspected source areas (as discussed below), so low values of chlorinated VOCs (less than 10 ppb) in soil are not indicative of a release near the sampling source."

This paragraph is apparently written to remove from consideration all soil samples which contain less than 10 ppb of a VOC[1].

The above statement is supplemented by the first sentence of the second paragraph. It states that "....If impacted soils are identified and a corresponding groundwater impact originates in the same area, then a source of groundwater contamination has been identified."

This statement appears to be rather obvious and potentially contradictory to the previous statement that soil contamination less than 10 ug/kg does not indicate a source of contamination.

Both of these statements are necessary to set up the interpretative comments on Page 5-18. The discussion on that page, using the foundation previously laid which would prove that VOCs can only originate from soils to groundwater if the soils contain greater than 10 ppb of VOCs, is the grounds for stating that low level soil contamination due to VOCs north of the oil/water separator originated from contaminated groundwater.

The problem with all of this is that it's wrong, full of half truths, etc. The real story is far more complicated but easily demonstrated. The remainder of this memo is a scientific explanation of what the data in the report and simple engineering calculations say and how they should have been combined for interpretation of the data in the report.

Background

First some background. Like most technical discussions there is an element of truth in many of the statements made in the G & M document. They are not the entire truth, however. The real situation is like this: all VOCs near the ESSO Tutu station exist in three phases, oil, water and gaseous. There are two constants which describe the mathematical relationships among the contaminant concentrations in all of the phases: Henry's Law constant and the octanol-water partition coefficient. The relationship between the VOCs in oil and VOCs in air is

[1] The implication of this statement is not clear in the portion of the text I have reviewed. The authors of the document are eliminating from consideration as a potential source any areas which contain less than 10 ug/kg of PCE in soil. The text of this memo will show that to be an invalid criterion for selection of potential contaminant sources.

given by Raoult's Law, using vapor pressure of the compound to calculate the vapor composition of the VOC above the oil phase.

Henry's Law constant describes the relationship between the concentration of VOCs in water and their concentration in air (vapor). The octanol-water partition coefficient provides the relationship between VOCs in oil and water.

As a result of the property of VOCs to distribute themselves between water and the air space above the water (vadose zone), and between an oil phase and a water phase, we have the situation where VOCs dissolved in oil in an oil/water separator will be simultaneously dissolved in the water in the separator. If that water leaks into the soil it will contaminate the soil, allow the VOCs to volatilize into the vadose zone and also percolate to the ground water and contaminate the groundwater.

Similarly, if groundwater is contaminated with VOCs, from whatever source, the soil vapor above the groundwater will contain some level of VOC contamination. If there is an oil phase around the area, some of the VOCs will also be transported to the oil phase and dissolve in it.

The extent to which any of this occurs depends on the concentration of VOCs in any of the media. The following tables should help calibrate your thinking on the matter.

First, lets look at the relationship between VOCs in oil and VOCs in water. The tables below provide the basic data. The term $K_{o/w}$ represents the logarithm of the ratio of concentrations of a VOC in oil to that in water.

Table 1. Log $K_{o/w}$ for VOCs

Compound	Log $K_{o/w}$
TCE	2.29
TCA	2.17
1,2-DCE	1.48
PCE	2.88

Using the values for $K_{o/w}$ and making calculations, we can produce the following table containing the correct relationships.

Table 2. Concentration of VOCs in Water and Oil

	Conc. of VOC in Water, ppm			
Conc. of VOC in Oil	TCE	TCA	1,2-DCE	PCE
400 ppm	2.06	2.72	13.24	0.527
200	1.03	1.36	6.62	0.263
100	0.515	0.68	3.31	0.132
10	0.0515	0.068	0.331	0.0132
1	0.00515	0.0068	0.0331	0.0013

The way to read the table is as follows: for PCE (perchloroethylene or tetrachloroethylene) when the concentration of PCE in oil is 400 ppm the concentration in water is 527 ppb. For comparison purposes you will note that 1,2-DCE (1,2-dichloroethylene) is distributed much greater to the water than is PCE. This result is due to its much greater volatility than PCE.

I did not calculate values higher than 400 ppm for any of the compounds in oil. You can do it by ratio of the values in the table.

Similarly, we can look at the relationship between the VOCs in water and the vapor space above groundwater (the vadose zone). The following table provides the basic data, calculated using a Henry's Law constant of 567 atm/mole fraction at 25°C (the EPA published value).

Table 3. Vapor Concentrations of PCE Above Water

ppb PCE in Water	ppb PCE in Vadose Zone Air
1	134
2	269
4	538
8	1077
12	1615
30	4039
50	6732
100	13,465
300	40,397

The table shows that for a groundwater concentration of 300 ppb in water there will be a vapor concentration of PCE of 40.4 ppm(v) in equilibrium with it.

Similarly, the values for the vapor concentrations for VOCs in the vapor phase above oil with the VOCs dissolved in it are provided in the following table.

Table 4. PCE and DCE Concentrations in Air Above Oil

Oil Conc. ppm	1,2-DCE, Conc. ppm	PCE, Conc. ppm
10	22.63	0.669
30	67.89	2.00
50	113.15	3.34
100	226.3	6.69
300	6778.9	20.07
700	1584	46.87

You will see from the table that the concentration of 1,2-DCE is very much larger than that of PCE due to its greater volatility.

Interpretation of the Data

Based on the information provided above we can interpret the data in the vicinity of the Four Winds Center and the Esso Tutu station to determine if there is a source or sources in the area.

Lets start with groundwater. The groundwater concentration of PCE in MW-8 is approximately 40 ppb, indicating that if its source was the water in the north oil/water separator, the oil in the separator would have contained about 40 ppm (40,000 ppb) of PCE. If you have concentration values for the other VOCs in the oil phase of the separator (particularly 1,2-DCE which is found in rather high concentration in MW-8), you can make the appropriate comparisons with the groundwater data in the Geraghty & Miller tables.

At the low end of the concentration range we can easily determine that the concentration in the soil will be approximately 3 to 42 ug/kg if the concentration of PCE in the water from the separator is between 13.2 and 263 ppb (corresponds to 10 and 200 ppm PCE in the oil phase in the separator). This calculation assumes that we take 1 kilogram of soil which is saturated with water from the separator (20% of the soil volume) as the basis of the calculation[2].

It is clear from the monitoring data that there is a potential relationship between the measured concentration of PCE in groundwater at MW-8 and the possible concentation of

[2] This calculation is based on a material balance which considers the only source of contamination to be the contaminated water in the pores of 1 kilogram of soil of 20% porosity.

PCE in the oil phase of the separator which would have been in equilibrium with the water leaked from it. To further elaborate on this statement; if the oil in the separator contained 400 ppm of PCE the water would have contained 527 ppb (see Table 2). This separator water could have been diluted by water migrating to the Four Winds wells from the east and west to provide the dilution to about 40 ppb as observed in the groundwater at MW-8. [This analysis relies, in part, on my recollections that the groundwater under the Esso station migrated to the Four Winds wells during pumping.]

Similarly, if the oil in the separator contained low concentrations of PCE (less than 10 ppm, for example), it would be reasonable to expect that concentrations in soil around the area where water leaked from the separator could have migrated, could contain concentrations of PCE in the 10 ug/kg range. This is clear from the data in Table 2.

In conclusion, the monitoring data and the calculations strongly suggest that the north oil/water separator at the Esso Tutu was a potential direct source of PCE to groundwater in the area through the distribution of PCE between the aqueous and oil phases present in the device and migration of the aqueous phase directly to groundwater. Further, the soil analysis data indicate that there could have been saturation of soils with water from the separator, diluted or undiluted, which produced concentrations of 10 ug/kg PCE in the soils in the area.

The above analysis relied upon the migration of water containing PCE from the separator into the pore spaces of the soil in the area. The other possibility for distribution of contamination is volatilization of PCE from groundwater or the oil phase from the separator into the pores of the soil and resulting detection and quantification in soil analyses.

The following table provides all of the relevant information to evaluate transport from either oil or water to the vadose zone and the resulting concentration of PCE in a soil sample.

Table 5. Concentrations of PCE in Soil Derived from Volatilization from Oil or Water[3]

PCE in Water in ppb	PCE in Oil in ppm	PCE in Air in ppm	PCE in Soil in ug/kg
0.496	1	0.0669	0.0707
14.9	30	2.00	2.12
24.84	50	3.34	3.53
49.68	100	6.69	7.07
198.73	400	26.78	28.28
347.7	700	46.78	49.49

As can be seen from the table, values of 10 ug/kg in soil could be observed as the result of vapor phase migration of PCE from oil, at approximately 250 ppm PCE concentration, or of PCE from water at approximately 150 ppb PCE concentration.

Conclusions

The major flaw in the Report is its reliance on qualitative information to reach quantitative conclusions. Unfortunately, logic and reason alone are not adequate to assess the extent to which transport pathways are available and have been operating in an environment. This erroneous approach renders any interpretative comments contained in the report subject to serious question.

First, the values provided in the table above as well as in tables previously presented in the text indicate that values of PCE in the range identified by Geraghty and Miller of 31 to 3,200 ug/kg could be derived from the various products in the north separator at the Esso Tutu station (Geraghty and Miller, Page 5-18).

It follows from the calculations and discussions provided in this memo that the 10 ug/kg value is without any scientific and engineering foundation as a criterion for selection of sources of contamination and is invalid for elimination of the north oil/water separator as a source.

There is another instance of a conclusion without a scientific basis in the document which is worth noting.

[3] The values in this Table are also based on a material balance assuming the porosity of the soil is 20% and that the pores are filled with air at the VOC concentrations indicated. The mass of VOC in the air is considered to be quantified in the analysis of the soil sample.

The statement "....This is confirmed by soil samples collected by BB&L (see Figure 5-10). The deepest soil sample collected by BB&L, SS-1 from 9.0 feet bls, had no detections of chlorinated VOCs." is made on Page 5-18 of the document supporting the hypothesis that there is limited migration of VOCs from the north oil/water separator.

This statement alone is inadequate to support the hypothesis proposed. There are numerous factors, primarily the geologic conditions and sampling technique which could have impacted the detection of chlorinated VOCs in the sample. A responsible technical presentation would describe the validity of the sample, its geologic tentativeness, and sampling and analytical representativeness prior to making such a sweeping conclusion.