
VADOSE ZONE NATURAL ATTENUATION OF HYDROCARBON VAPORS:

AN EMPIRICAL ASSESSMENT OF SOIL GAS VERTICAL PROFILE DATA

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A SUMMARY OF RESEARCH RESULTS FROM API'S SOIL & GROUNDWATER TECHNICAL TASK FORCE

1.0 Introduction

Gaining a better understanding of the subsurface migration of chemical vapors is important if we are to have confidence in our ability to identify those settings where vapor transport leads to unacceptable safety and human health risks. It is also important if we are to understand the role of these processes in the natural attenuation of residual hydrocarbons in the subsurface. In recent years, much effort has gone into developing screening-level risk assessment algorithms for the former (e.g. Johnson and Ettinger 1991, API 1998) as well as more advanced general transport codes primarily used for the latter (e.g. R-UNSAT, USGS 1997). While most published studies have focused on soil gas profiles at individual sites, little effort has gone into a broader empirical review of available field data. This type of approach should not be overlooked as it provides the opportunity to identify the range of behaviors that occur and how these might be affected by site characteristics. This approach also provides a broader basis for validating the appropriateness of different modeling approaches and the significance of different transport and fate mechanisms. With respect to the latter, confirming the occurrence of biodegradation and its attenuation of vapor fluxes at petroleum hydrocarbon impacted sites is important.

Thus, the focus of this work was an empirical assessment of available soil gas profile data with an emphasis on petroleum hydrocarbon release sites. The objectives included the following: i)

identify data sets with sufficient detail (i.e., hydrocarbon and oxygen soil gas profiles and lithologic information at a minimum), ii) review the data and identify the range of behaviors observed, iii) assess whether or not the data was consistent with the occurrence of aerobic biodegradation, and iv) assess the significance of aerobic biodegradation on soil gas profiles and hydrocarbon fluxes.

This was accomplished by: a) compiling a database of published and unpublished data from hydrocarbon spill sites where soil gas profiles had been monitored, b) collecting field data at three additional sites, and then c) conducting a data analysis. At most sites, moisture content, effective diffusion coefficient, subsurface characterization data, and vapor concentration profiles of oxygen, carbon dioxide, and petroleum hydrocarbon were measured. Complete details of the site characteristics, and data compilation and initial analysis can be found in Roggemans (1998).

In brief, four general categories of soil gas profiles were identified. In each case the data supported the hypothesis that aerobic biodegradation was an important factor in the development of the measured soil gas profiles; however, the significance of biodegradation to ongoing vapor transport varied across the categories. Estimates of upward hydrocarbon flux attenuation relative to the case of no biodegradation ranged from a high of 99.99% flux reduction to a low of 0% flux reduction. An attempt was made to correlate soil gas profile categories and

flux reductions with site characteristics; however, no clear correlation was observed. In particular, there was no clear correlation of behavior with depth to vapor source, lithology, or surface cover.

2.0 Approach and Methods

Soil gas profile data compiled from the literature included that presented by Ostendorf and Kampbell (1991), Lahvis and Baehr (1996), Fischer et al (1996), Hers et al. (1998), and Lahvis et al. (1999). In addition, data was obtained from non-published reports provided by British Petroleum (BP) for the vapor profile characterization studies conducted at five of their service station sites (referred to as Paulsboro, Conneaut, Kent, Akron, and Columbiana). Finally, soil gas data profiles were also measured at Port Hueneme, CA and at one former refinery site. At Port Hueneme, soil gas profiles were measured at four locations: a) above residual NAPL and beneath pavement, b) above residual NAPL and beneath an open grassy area, c) above the dissolved plume and beneath pavement, and d) above the dissolved plume and beneath an open grassy area. Specifics of each site are given in Roggemans (1998). A brief summary of site characteristics is given below in Table 1.

As a first attempt at data normalization, the data were condensed to plots of (z/L) vs. C/C_{\max} where z is the distance measured down from the upper boundary (i.e. ground surface or basement foundation), L is the distance from the upper surface of the vapor source and the upper boundary, C is the total hydrocarbon concentration at each height z , and C_{\max} is the total hydrocarbon concentration in the source zone (z and L , and C and C_{\max} are expressed in consistent units; L is determined from all the available data). It is important to note that only data above the upper surface of the vapor source is plotted, and that professional judgement was used to determine the upper surface of the vapor source. The upper surface was selected based on consideration of soil gas and residual soil concentration data, and was either: a) the depth at which the maximum soil gas

concentration was measured, or b) the upper boundary of the smear zone as suggested by residual soil concentration and soil gas profile data. For this collection of sites, the upper boundary, was either: a) open (unpaved) ground surface, b) paved ground surface, or c) a building foundation. Total hydrocarbon concentration plots were compiled for two reasons – not all sites had component-specific information and also because individual component plots were very similar to the total hydrocarbon plots at the sites with sufficient component-specific data.

The initial data review was focused on identifying similarities and differences between the qualitative shapes of the normalized total hydrocarbon soil gas profiles. This was followed by an attempt to correlate the observed qualitative behaviors with site-specific factors. Then the data from each site was reviewed to identify if the data supported or refuted the hypothesis that aerobic biodegradation processes contribute significantly to the soil gas profile and estimated upward vapor flux at that site.

3.0 Results – Qualitative Soil Gas Behaviors and Conceptual Models

Based on qualitative aspects of the measured soil gas profiles, each was classified into one of the behaviors referred to below as “Behavior A”, “Behavior B”, “Behavior C”, and “Behavior D”. For each behavior, all data sets were plotted on the same normalized total hydrocarbon and oxygen concentration vs. distance plots. In addition, a conceptual model figure was prepared to help explain the differences between the different types of data sets. These are presented in Figures 1 – 9.

It is important to note that the conceptual soil gas profiles drawn in Figures 2, 5, 7, and 9 are only intended to convey general increases or decreases in hydrocarbon and oxygen concentration with depth; therefore, the appearance of linear sections of soil gas profiles in the conceptual model

Table 1. Site characteristics and observed qualitative behaviors

Site	Surface	Approximate Depth to Source [m]	Lithology	C_o^{max}/C_h^{max}	D_T^{eff}/D^{air} Estimate	Behavior
Former Refinery Site vw93	uncovered	18	sandy	2.8	0.170	A
Former Refinery Site vw96	uncovered	18	sandy	1.2	0.170	A
Former Refinery Site vw99	uncovered	18	sandy	1.3	0.170	A
Hers et al. (1998)	uncovered	1	silt/sand	5.5	0.110	A
Kent	pavement	6	clayey silt	1.4	0.002	A
Akron VMP-1 (Oct 97)	pavement	3	sand/silt/clay	2.5	0.013	A
Akron VMP-2 (Sept 97)	pavement	3	sand/silt/clay	10.3	0.004	A
Fisher et al. (1996)	pavement	1	sandy	12.3	0.069	A
Ostendorf and Kampbell (1991) PT4 Oct-89	pavement	2	sandy	12.4	0.200	A
Ostendorf and Kampbell (1991) DG109 Oct-89	pavement	2	sandy	12.4	0.200	A
Ostendorf and Kampbell (1991) DG280 Oct-89	pavement	2	sandy	10.9	0.200	A
Paulsboro 1A	pavement	6	sandy	3.4	0.068	A
Paulsboro 2A	pavement	6	sandy	4.2	0.045	A
Fisher et al. (1996)	basement	1	sandy	12.4	0.069	A
Hers et al. (1998)	basement	1	silt/sand	2.9	0.046	A
Lahvis et al. (1999)	uncovered	3	sandy	15.5	0.052	A
Port Hueneme dissolved, MP7, Aug-98	uncovered	3	silty	1100.0	0.001	B
Ostendorf and Kampbell (1991) M30	pavement	2	sandy	10.1	0.200	B
Port Hueneme dissolved, MP10, Aug-98	pavement	3	silty	5525.0	0.005	B
Akron VMP-1 (Sept 97)	pavement	3	sand/silt/clay	2.7	0.013	B
Akron Vmp-2 (Oct 97)	pavement	3	sand/silt/clay	5.9	0.004	B
Columbiana	uncovered	6	silt	0.4	0.004	C
Paulsboro D Basement	basement	6	sandy	0.0	0.120	C
Conneaut	pavement	2	sandy	1.0	0.120	C
Lahvis and Baehr (1996) vw8	uncovered	1	sandy	13.7	-	D
Lahvis and Baehr (1996) vw9	uncovered	1	sandy	13.0	-	D
Port Hueneme source B Aug-98	uncovered	3	silty	1.3	0.001	D
Port Hueneme source MP7 Jul-98	pavement	3	silty	1.8	0.005	D

schematics is not meant to imply that linearity of the data should be observed as well.

In interpreting the data and creating the conceptual models it has been assumed that the systems have reached near-steady conditions with respect to vapor migration and source strength. Seasonal changes in soil gas profiles were observed in some of the data sets.

3.1 Behavior A: Transport-Limited Biodegradation Settings

Data sets classified as Behavior A are shown in Figures 1a and 1b. The defining characteristic of a Behavior A soil gas profile is the shape of its oxygen soil gas profile. As seen in Figure 1a, oxygen concentrations decrease in moving down through the subsurface and somewhere between about $z/L=0.5$ and $z/L=0.8$ the soil gas oxygen concentrations have declined to about 2% v/v oxygen. Beyond that depth, oxygen concentrations remain relatively constant with depth. In looking at Figure 1b, total hydrocarbon concentrations decrease by less than an order of magnitude across the lower oxygen

concentration region, and then they decrease by several orders of magnitude across the higher oxygen concentration region. The similarity in normalized profiles is interesting given the wide range of depths and geologic settings represented by this data; while this behavior might be expected mainly at deeper sites (e.g., the former refinery site), it is also observed at some of the relatively shallow sites (e.g., Fischer et al. 1996, and Ostendorf and Kampbell 1991).

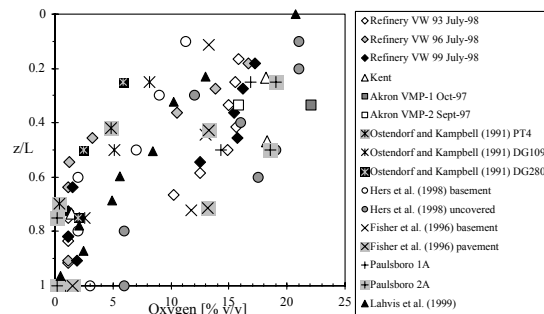


Figure 1a. Oxygen soil gas profiles for qualitative Behavior A.

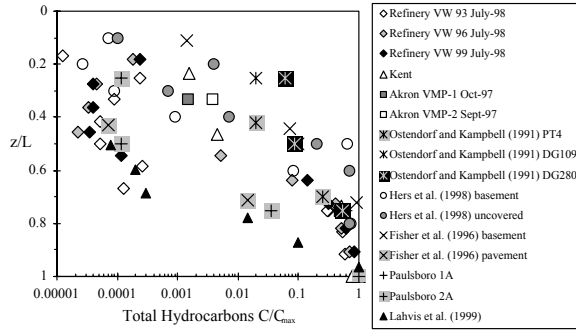


Figure 1b. Total hydrocarbon soil gas profiles for qualitative Behavior A.

We can conceptualize the subsurface and the processes occurring in the Behavior A settings as shown in Figure 2, and then use this to develop a hypothesis that explains the observed soil gas profiles. First, all of these settings have two relatively distinct subsurface regions: a) an aerobic region where oxygen concentrations are >2% v/v and decreasing with depth, and b) an anoxic region where oxygen concentrations are relatively constant with depth at about 2% v/v.

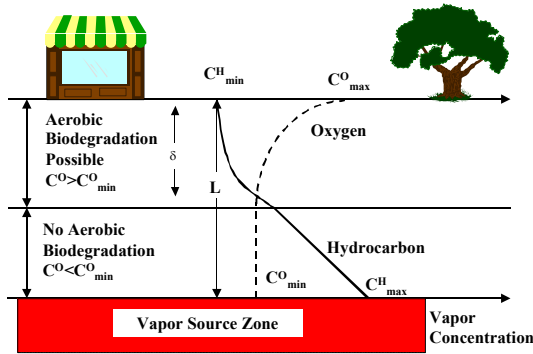


Figure 2. Conceptual model for Behavior A.

Published data from bioventing respirometry studies (i.e., Leeson and Hinchee, 1997) suggest that aerobic biodegradation of hydrocarbons ceases, or slows to very low rates when oxygen soil gas concentrations decline below the 2% v/v range. Considering that this soil gas concentration corresponds to dissolved oxygen (DO) concentrations <1 mg/L, one could argue that this data is also consistent with dissolved hydrocarbon aerobic

microcosm studies showing that rates of aerobic biodegradation typically decline significantly when DO <1 mg/L.

Thus, it can be hypothesized that aerobic biodegradation is occurring in the upper aerobic zone, and it is not occurring to any appreciable extent in the lower anoxic zone. Furthermore, the profiles are also consistent with “large” potential reaction rates relative to the maximum transport rate of oxygen; consequently, the rate of degradation in these systems is limited by transport and not reaction. This hypothesis can be tested by writing simplistic oxygen and hydrocarbon balances for the limiting case of a nearly instantaneous reaction at the aerobic/anoxic interface:

$$D_o^{eff} \left[\frac{C_o^{max} - C_o^{min}}{\delta} \right] = \beta D_h^{eff} \left[\frac{C_h^{max}}{L - \delta} \right] \tag{1}$$

where:

- D_o^{eff} = overall effective diffusion coefficient for oxygen transport across the aerobic region [cm²/s]
- D_h^{eff} = overall effective diffusion coefficient for hydrocarbon transport across the anaerobic region [cm²/s]
- δ = distance from ground surface to the anaerobic/aerobic interface [cm]
- C_o^{max} = maximum oxygen concentration in aerobic region [mg/cm³]
- C_o^{min} = oxygen concentration in anoxic region [mg/cm³]
- C_h^{max} = maximum hydrocarbon concentration in anoxic zone [mg/cm³]
- β = stoichiometric conversion factor [mg-O₂/mg-Hydrocarbon]
- L = distance from upper surface to the hydrocarbon vapor source [cm]

This equation can be rearranged to provide an expression for δ/L , the depth where the anoxic zone is expected to occur:

$$\frac{\delta}{L} = \frac{1}{1 + \beta \left[\frac{D_h^{eff}}{D_o^{eff}} \right] \left[\frac{C_h^{max} / C_o^{max}}{1 - C_o^{min} / C_o^{max}} \right]} \quad (2)$$

For the purposes of rough approximation, consider the case where $\beta=3 \text{ mg-O}_2/\text{mg-hydrocarbon}$, $(D_h^{eff}/D_o^{eff})=(D_h^{air}/D_o^{air})=0.6$, $(C_o^{min}/C_o^{max})=(2\%/20\%)=0.10$, and $(C_h^{max}/C_o^{max})=0.08 \text{ to } 0.8$ (based on Table 1). For these inputs $0.4 < (\delta/L) < 0.9$, and this range compares favorably with the data in Figure 1a where anoxic regions are first encountered from about $z/L=0.5$ to $z/L=0.8$. Equation (2) has been plotted in Figure 3 as a function of (C_o^{max}/C_h^{max}) and the values given above. Also plotted are field derived (δ/L) values for data sets having sufficient vertical resolution to reasonably estimate (δ/L) within ± 0.1 .

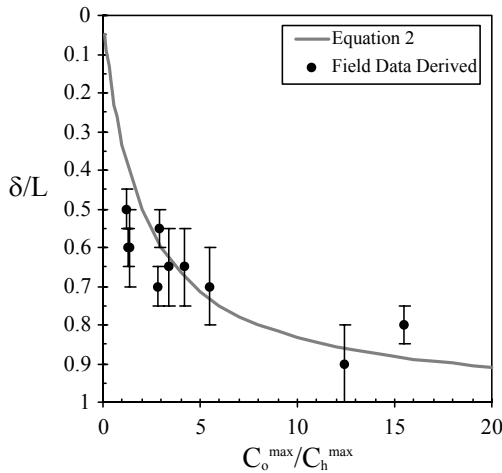


Figure 3. Theoretical and field-derived (δ/L) vs. (C_o^{max}/C_h^{max}) for the Behavior A profiles [inputs for Equation (2) are: $\beta=3 \text{ mg-O}_2/\text{mg-hydrocarbon}$, $(D_h^{eff}/D_o^{eff})=(D_h^{air}/D_o^{air})=0.6$, and $(C_o^{min}/C_o^{max})=(2\%/20\%)=0.10$]

3.2 Behavior B – Aerobic Biodegradation Rate-Limited Settings.

Behavior B soil gas profiles are shown in Figures 4a and 4b, and the conceptual model is presented in Figure 5. These profiles share some similarities to Behavior A plots in that hydrocarbon vapor concentrations decrease in moving up from the source zone, and oxygen soil gas concentrations decrease in moving down from ground surface. However, Behavior B differs from Behavior A because the oxygen soil gas concentration is everywhere $>5\%$ v/v, and there is no anoxic region across which oxygen soil gas concentrations are relatively constant.

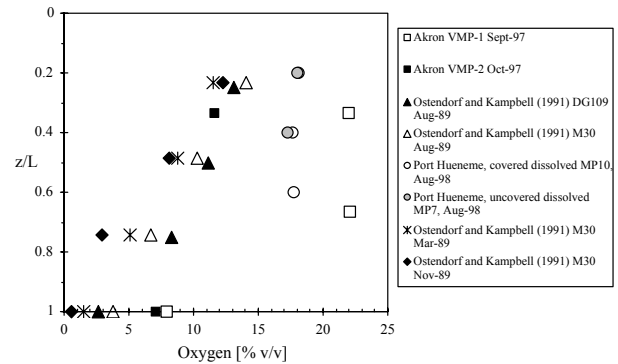


Figure 4a. Oxygen soil gas profiles for qualitative Behavior B.

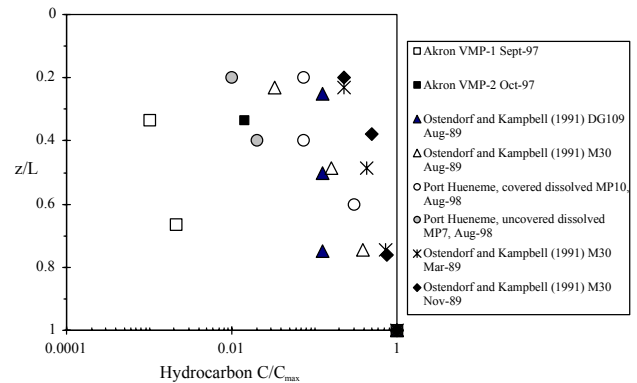


Figure 4b. Total hydrocarbon soil gas profiles for qualitative Behavior B.

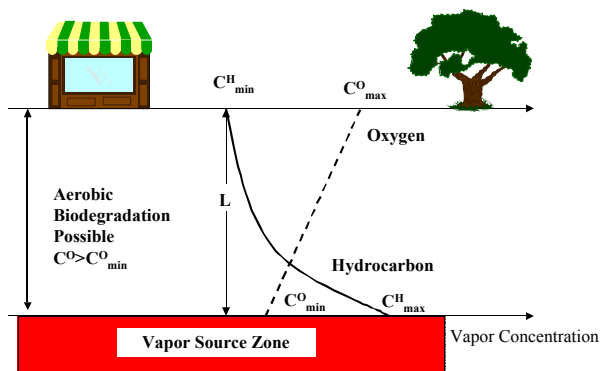


Figure 5. Conceptual model for Behavior B.

The conceptual model for Behavior B is presented in Figure 5. It is similar to that for Behavior A, except that in this case aerobic biodegradation may occur throughout the entire soil column. Furthermore, oxygen concentrations are high enough that biodegradation is limited only by the biodegradation rate and not the oxygen supply rate (as in Behavior A). Relative to the settings in which Behavior A occurs, it is anticipated that Behavior B might occur at sites with “low” source zone hydrocarbon vapor concentrations relative to atmospheric oxygen concentrations, or at shallower sites having hydrocarbon concentration gradients and fluxes that are high enough that hydrocarbon vapor transport from the source to upper surface is “fast” relative to possible biodegradation rates.

3.3 Behavior C – Oxygen Deficient Subsurface Settings

The Behavior C soil gas data profiles are shown in Figure 6a and 6b. These are easy to identify by their anoxic oxygen soil gas profiles, which are relatively uniform, and for which oxygen soil gas concentrations are less than about 2% v/v throughout the entire vadose zone.

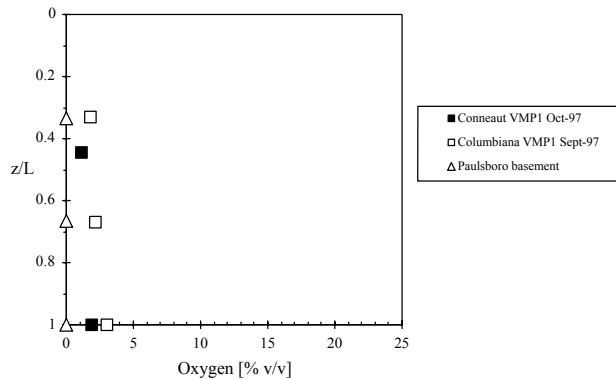


Figure 6a. Oxygen soil gas profiles for qualitative Behavior C.

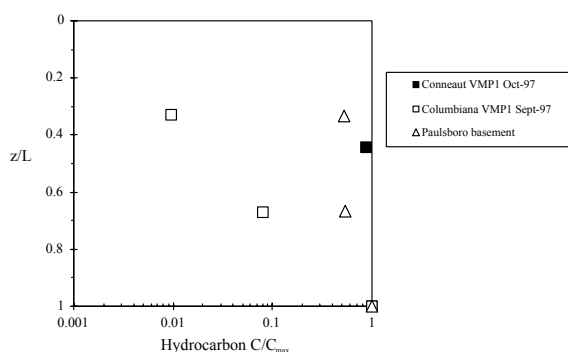


Figure 6b. Total hydrocarbon soil gas profiles for qualitative Behavior C.

A conceptual model for Behavior C is given schematically in Figure 7. It is hypothesized that at some time in the past, aerobic biodegradation consumed the usable oxygen in soil gas (>2% v/v), and at this time the oxygen re-supply to the subsurface through the upper boundary is slower than the oxygen consumption rate. Thus, if degradation is occurring, it is only happening very near the upper surface where oxygen recharge occurs. Relative to Behavior A and B sites, it is expected that Behavior C behavior would be observed below pavement, buildings, very wet surface soils, or other cases where oxygen re-supply might be limited. However, there are sites in the Behavior A and B groups that have surface covers, and some are beneath buildings. The three Behavior C profiles were observed beneath an open surface, a building, and a paved surface.

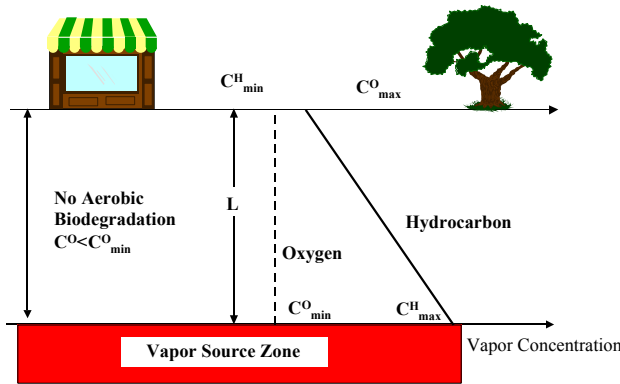


Figure 7. Conceptual model for Behavior C.

3.4 Behavior D: Near-Source High Diffusion Resistance Soil Gas Profiles

Figures 8a and 8b show Behavior D soil gas profiles; these are somewhat similar to Behavior B, except that they are distinguished by the hydrocarbon concentration profiles; unlike Behavior B, the Behavior D hydrocarbon vapor concentrations decrease by several orders-of-magnitude immediately above the hydrocarbon vapor source. Oxygen concentrations may decrease or remain relatively unchanged throughout the soil column for Behavior D; however, they generally decline in moving down through the subsurface, and in some cases have reached the anoxic level of about 2% v/v at the lower boundary.

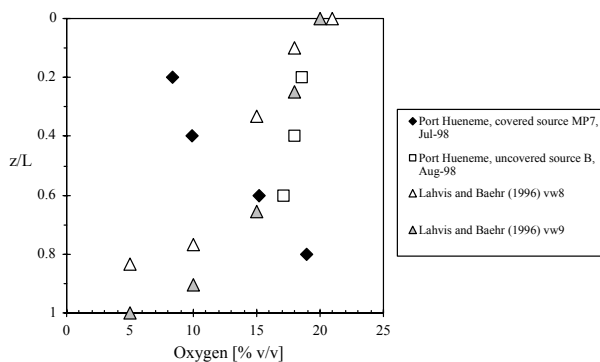


Figure 8a. Oxygen soil gas profiles for qualitative Behavior D.

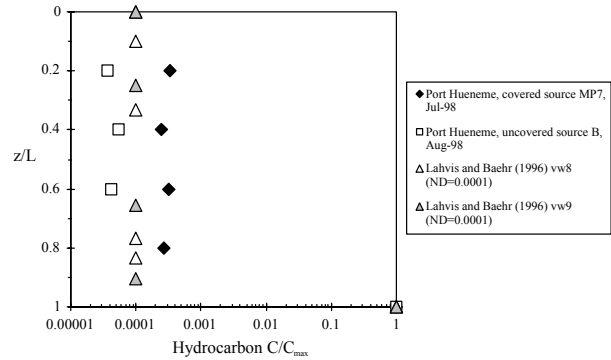


Figure 8b. Total hydrocarbon soil gas profiles for qualitative Behavior D.

The conceptual model of Behavior D is given schematically in Figure 8. The dramatic reduction in hydrocarbon vapor concentrations is likely the result of having a higher diffusion resistance zone immediately above the source (i.e. a capillary fringe above a smear zone) in combination with aerobic biodegradation. It could also be accounted for by a narrow region across which very rapid biodegradation occurs. The Behavior D profiles are for sites where the vapor source is a dissolved hydrocarbon plume or residual hydrocarbons in soil beneath the water table. In these cases, a significant concentration drop would occur anyway in the absence of aerobic biodegradation, but most of the oxygen profiles (except Port Hueneme – covered source zone) show decreasing oxygen concentrations with depth. Therefore, it is likely that aerobic biodegradation is occurring immediately above, or within, the high diffusion resistance zone. Behavior D shares similarities to the Behavior A profiles in that they are vapor transport-limited; in fact, the profiles are consistent with the assumptions used in deriving Equation (2) and the condition that $(D_h^{eff}/D_o^{eff}) \ll 1$.

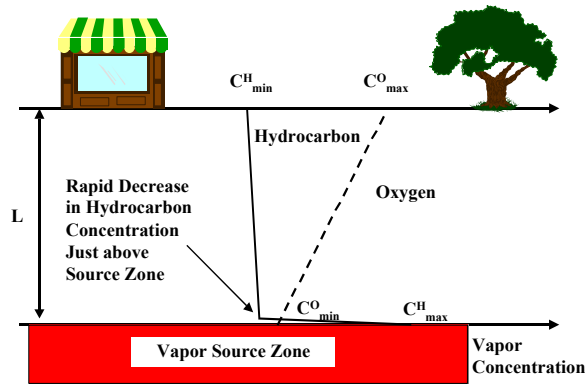


Figure 9. Conceptual model for Behavior D.

4.0 Assessment of the Significance of Aerobic Biodegradation

It is clear from the soil gas profiles and discussions above that the measured soil gas profiles are consistent with the occurrence of aerobic biodegradation at all of the sites. What is not clear from the soil gas profile plots is whether or not aerobic biodegradation has a significant impact on vertical hydrocarbon vapor migration at each site. Two approaches were taken in an attempt to assess “significance”. In the first, measured hydrocarbon vapor profiles were compared with predicted steady-state hydrocarbon vapor profiles, assuming no biodegradation. If a hydrocarbon vapor profile was reasonably predicted without allowing for biodegradation, then biodegradation was judged to be insignificant. The layered-system equations presented in API (1998) and Johnson et al. (1999) were used along with available site-specific data (soil texture, soil moisture, total porosity, etc.). Complete details of this exercise are given in Roggemans (1998), and the results are briefly discussed here.

While discrepancies could also be due to poor characterization data, or non-steady conditions, the argument for significant aerobic biodegradation is strengthened by the observation of decreasing oxygen concentrations with depth. Also, good agreement between modeled and measured profiles does not necessarily indicate a lack of biodegradation at a

particular site; rather, it only means that the observed profiles can be adequately predicted by models that do not include biodegradation terms.

Of the hydrocarbon soil gas profiles reviewed, only the following were reasonably predicted by the diffusion-only model:

- Ostendorf and Kampbell (1991) locations: DG280 March-88, M30 March-89, M30 Nov-89
- Port Hueneme locations: covered dissolved MP10, uncovered dissolved MP7, uncovered source B
- BP Site Locations: Paulsboro (D) Basement

When considering both hydrocarbon and soil gas profiles, all other model-data comparisons suggested significant influence of aerobic hydrocarbon biodegradation. The comparisons were done visually (and not statistically), for the reason that in all of the profiles not listed above, the measured hydrocarbon concentrations were consistently less than predicted values in moving up from the source.

A second approach focused on assessing the significance of biodegradation on attenuation of the upward hydrocarbon vapor flux. To do this, an estimate of the vapor flux attenuation was made using the following approach:

- An approximate expression was written to estimate the upward hydrocarbon vapor flux F_{\max} that would occur in the absence of biodegradation:

$$F_{\max} = \frac{D_T^{\text{eff}}}{L} C_h^{\max} \quad (3)$$

where C_h^{\max} denotes the maximum measured vapor concentration [mg/cm^3] at a depth $z=L$ [cm], and D_T^{eff} [cm^2/s] is the overall effective diffusion coefficient between the maximum measured vapor concentration and the upper surface.

- Next, an estimate for the vapor flux near the upper surface was written:

$$F_{\text{surface}} = \frac{D_{\text{up}}^{\text{eff}}}{Z_{\text{up}}} C_h^{\text{up}} \quad (4)$$

where C_h^{up} [mg/cm³] denotes the vapor concentration measured closest to the upper surface at a depth $z=Z_{\text{up}}$ [L], and $D_{\text{up}}^{\text{eff}}$ [cm²/s] is the effective diffusion coefficient between that depth and the upper surface.

- The expression for the vapor flux attenuation factor A_{flux} was then defined to be the ratio of these two fluxes:

$$A_{\text{flux}} = \frac{F_{\text{surface}}}{F_{\text{max}}} = \left[\frac{D_{\text{up}}^{\text{eff}}}{D_{\text{T}}^{\text{eff}}} \right] \left[\frac{C_h^{\text{up}}}{C_h^{\text{max}}} \right] \left[\frac{L}{Z_{\text{up}}} \right] \quad (5)$$

The values for C_h^{max} , C_h^{up} , L and Z_{up} come directly from the data sets, while $D_{\text{T}}^{\text{eff}}$ and $D_{\text{up}}^{\text{eff}}$ are estimated from measured moisture contents using the Millington empirical correlation as described in API (1998) and Johnson et al. (1999).

Using this approach, the vapor flux attenuation factor was estimated for some of the monitoring locations presented in Figures 1 through 9. The results are presented below in Table 2. Given the very approximate nature of this method, all results have been rounded off to the nearest order-of-magnitude. As the approach does not account for biodegradation above the shallowest monitoring point, these are expected to be conservative attenuation estimates and actual A_{flux} values are likely to be lower for all Behavior A, B, and D settings.

As can be seen, the most significant hydrocarbon vapor flux attenuation occurs in the Behavior A group, where vapor fluxes are estimated to be attenuated by two to four orders-of-magnitude (99 – 99.99% reduction in upward vapor flux relative to the case of no biodegradation). The significance of attenuation for the Behavior B and C monitoring locations is estimated to be much less than that for Behavior A sites, and in some cases the effect of

aerobic biodegradation is estimated to be insignificant ($A_{\text{flux}}=1$). As expected, biodegradation at the anoxic Behavior C sites is estimated to have little impact on the vapor flux.

Table 2. Estimated Vapor Flux Attenuation Factors (A_{flux})*.

* - rounded to the nearest order-of-magnitude

Site/Location	Behavior	A_{flux}
Former Refinery Site/VW-93	A	0.0001
Paulsboro/1-A	A	0.001
Fischer et al. (1996)/sub-slab	A	0.001
Lahvis et al. (1999)	A	0.001
Kent	A	0.01
Hers et al. (1998)/sub-slab	A	0.01
Akron/VMP-1	B	0.1
Akron/VMP-2 (Oct. 97)	B	0.1
Ostendorf and Kampbell (1991)/M30	B	1
Ostendorf and Kampbell (1991)/DG109	B	1
Port Hueneme/uncovered-dissolved source	B	1
Columbiana	C	0.1
Conneaut	C	1
Paulsboro/D basement	C	1
Port Hueneme/uncovered- source zone	D	0.001

5.0 Discussion: Correlation Between Observed Behaviors and Site Conditions

Having identified four different qualitative behaviors, an attempt was made to identify site characteristics that might dictate what behavior is observed at any given site. Based on theoretical considerations and the fact that all sites in this study were contaminated by similar petroleum compounds, it was postulated that the following might be relevant to dictating behavior:

- Type of surface cover (uncovered, pavement, basement)
- Soil type

- Maximum concentration of oxygen relative to the maximum concentration of hydrocarbon in the subsurface (C_o^{\max}/C_h^{\max})
- The overall effective diffusion coefficient between the source and upper surface relative to the diffusion coefficient in air ($D_T^{\text{eff}}/D^{\text{air}}$), as estimated from moisture content and porosity data.

Values for each site and their assigned behavior are listed in Table 1, and a relatively wide range of conditions is represented. However, no obvious correlation was discernable from this analysis. Of particular interest is the lack of a correlation between the soil gas profiles and the surface cover type. While it might have been expected that surface covers, such as pavement, would limit the oxygen flux to the subsurface, this appears not to be the case.

6.0 Summary

In summary, the following are key features of this work:

- Soil gas profiles were segregated into four general behaviors; in two of these (A and C) oxygen transport through or into the subsurface seemed to be the limiting factor for aerobic biodegradation, while in the other two (B and D), sufficient oxygen was present throughout the vadose zone.
- Aerobic biodegradation was an important mechanism in all of the hypothetical conceptual models that were presented to explain the observed behaviors; this was consistent with the data as all soil gas profiles exhibited some degree of oxygen depletion at depth.
- The significance of aerobic biodegradation was assessed by two different approaches; in the first, measured soil gas hydrocarbon profiles were compared against predicted profiles expected in the absence of biodegradation. In the second

approach, hydrocarbon vapor fluxes near the upper surface were compared with fluxes expected in the absence of biodegradation.

- Of the 28 soil gas profiles studied, six hydrocarbon profiles could be reasonably anticipated by steady-state predictive equations not including biodegradation; in all other the effect of biodegradation was deemed significant by the first assessment approach.
- Using the flux-estimate-based assessment approach, it was estimated that upward hydrocarbon vapor fluxes were attenuated relative to the base case of no biodegradation by as little as 0% at some sites and as much as 99.99% at other sites. In general, the highest attenuation occurred at sites exhibiting Behavior A profiles.
- An attempt to correlate observed soil gas profiles and vapor flux attenuation with basic site characteristics (surface cover, depth, soil type, hydrocarbon concentration, etc.) did not reveal any obvious relationships.

In summarizing these results, it is useful to revisit one of the key issues raised in the introduction – namely it is desirable to have confidence in our ability to identify those settings where vapor transport leads to unacceptable safety or human health risks. With respect to this issue there are two key findings in this work. First, the apparent lack of correlation of vapor profiles with simple site characteristics (i.e., depth to source, lithology, and surface cover) suggests that there are other as-yet-to-be-examined site properties of importance that need to be identified. It also implies that the collection of soil gas profile data (both hydrocarbons and oxygen) may need to be an important component of any method for assessing the significance of vapor migration, especially if one wants to account for the effects of aerobic biodegradation.

Second, aerobic biodegradation was deemed significant in determining the observed profiles at a

large proportion of the sites. This observation, along with the results presented in Table 2 can be used to argue that predictive models not accounting for biodegradation could overestimate the risks from upward vapor fluxes by 10 – 10000 times at some sites.

References and Bibliography

Acomb, L., C. Rea, T. Simpkin, R. Hoffman, and B. Elder. "Intrinsic Remediation of Shallow Vadose-Zone Petroleum Hydrocarbons". *The Proceedings of the API/NGWA Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Remediation*. Houston, TX. 13-15 November. 1996.

API. 1998. Assessing the Significance of Subsurface Contaminant Migration to Enclosed Spaces: Site-Specific Alternatives to Generic Estimates. American Petroleum Institute Publication No. 4674.

ASTM. *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*. E-1739-95; American Society for the Testing of Materials, West Conshohocken. 1995.

DeVaull, G. E., R. A. Ettinger, J. P. Salanitro, and J. B. Gustafson. "Benzene, Toluene, Ethylbenzene, and Xylenes [BTEX] Degradation in Vadose Zone during Vapor Transport: First-Order Rate Constants". *Proceedings of the 1997 Petroleum Hydrocarbon and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation Conference*. 12-14 Nov. 1997. Houston, Texas.

Fisher, M. L., A. L. Bentley, K. A. Dunkin, A. T. Hodgson, W. W. Nazaroff, R. G. Sextro, and J. M. Daisey. "Factors Affecting Indoor Air Concentrations of Volatile Organic Compounds at a Site of Subsurface Gasoline Contamination". *Environmental Science and Technology*. 30.10 (1996): 2448–2957.

Fitzpatrick, N. A., and J. J. Fitzgerald. *An Evaluation of Vapor Intrusion into Buildings through a Study of Field Data*. Massachusetts Department of Environmental Protection, 1997.

Garbesi, K., and R. G. Sextro. "Modeling and Field Evidence of Pressure-driven Entry of Soil Gas into a House through Permeable Below-Grade Walls". *Environmental Science and Technology*. 23.12 (1989): 1481-1487.

IST. *Report of Supplementary Field Activities Hydrocarbon Vapor Migration Research Project, BP Oil Test Site, Paulsboro, New Jersey*. November 1997.

IST^a. *Summary of Field Activities, Vadose Zone Natural Attenuation Study, BP Exploration and Oil, Conneaut, Ohio*. June 1998.

IST^b. *Summary of Field Activities, Vadose Zone Natural Attenuation Study, BP Exploration and Oil, Kent, Ohio*. August 1998.

IST^c. *Summary of Field Activities, Vadose Zone Natural Attenuation Study, BP Exploration and Oil, Akron, Ohio*. June 1998.

IST^d. *Summary of Field Activities, Vadose Zone Natural Attenuation Study, BP Exploration and Oil, Columbiana, Ohio*. June 1998.

Jin, Y., T. Streck, and W.A. Jury. "Transport and Biodegradation of Toluene in Unsaturated Soil". *Journal of Contaminant Hydrology*. 17 (1994): 111-127.

Johnson, P.C., R.L. Johnson, and M.W. Kemblowski. 1999. Assessing the Significance of Vapor Migration to Enclosed-Spaces on a Site-Specific Basis. *Journal of Soil Contamination*. 8 (3). 389 - 421.

Johnson, P. C., and R. Ettinger. "Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors into Buildings". *Environmental Science and Technology*. 25 (1991): 1445-1452.

Jury, W. A., D. Russo, G. Streile, and H. El Abd. "Evaluation of Volatilization of Organic Chemicals Residing Below the Soil Surface". *Water Resources Research*. 26.1 (1990): 13–20.

Lahvis, M.A., and A.L. Baehr. "Estimation of Rates of Aerobic Hydrocarbon Biodegradation by Simulation of Gas Transport in the Unsaturated Zone". *Water Resources Research*. 32.7 (1996): 2231-2249.

Lahvis, M.A. A.L. Baehr, and R.J. Baker. 1999. Quantification of Aerobic Biodegradation and Volatilization Rates of Gasoline Hydrocarbons Near the Water Table Under Natural Attenuation Conditions. *Water Resources Research*. 35 (3). 753 – 765.

Leeson, A., and R. E. Hinchee. *Soil Bioventing: Principles and Practice*. Lewis Publishers, 1997.

Little, J. C., J. M. Daisey, and W. W. Nazaroff. "Subsurface Transport of Volatile Organic Contaminants into Buildings". *Environmental Science and Technology*. 26 (1992): 2058-2066.

Loureiro, C. O., L. M. Abriola, J. E. Martin, and R. G. Sextro. "Three-Dimensional Simulation of Radon Transport into Houses with Basements under Constant Negative Pressure". *Environmental Science and Technology*. 24.9 (1990): 1338-1348.

Ostendorf, D. W., and D. H. Kampbell. "Bioremediated Soil Venting of Light Hydrocarbons". *Hazardous Waste and Hazardous Materials*. 7.4 (1990): 319-334.

Ostendorf, D. W., and D. H. Kampbell. "Biodegradation of Hydrocarbon Vapors in the Unsaturated Zone". *Water Resources Research*. 27 (1991): 453-462.

Roggemans, S.. 1998. Natural Attenuation of Hydrocarbon Vapors in the Vadose Zone. M.S. Thesis. Arizona State University.

Smith, J. A., A. K. Tisdale, and J. H. Cho. "Quantification of Natural Vapor Fluxes of Trichloroethylene in the Unsaturated Zone at the Picatinny Arsenal, New Jersey". *Environmental Science and Technology*. 30 (1996): 2243-2250.

USGS. 1997. Documentation of R-UNSAT, a computer model for the simulation of reactive, multispecies transport in the unsaturated zone. U. S. Geological Survey Open-File Report 97-630, 104 p.

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