Virginia Tech
College of Engineering

The Charles Edward Via, Jr. Department of Civil and Environmental Engineering
200 Patton Hall (0105)
Blacksburg, Virginia 24061
(540) 231-6635 Fax: (540) 231-7532

TO: Gerald W. Bowes, Ph.D.
Manager, Cal/EPA Scientific Peer Review Program
Office of Research, Planning and Performance
State Water Resources Control Board

FROM: Mark A. Widdowson, Ph.D., P.E.
Professor of Civil & Environmental Engineering

John C. Little, Ph.D., P.E.
Professor of Civil & Environmental Engineering

DATE: February 29, 2012

SUBJECT: Scientific Peer Review of the Technical Justification for Proposed Low-Threat UST Closure Policy

Enclosed you will find the scientific peer review regarding the subject noted above that was requested in your letter dated January 17, 2012. As instructed, we have reviewed the scientific basis and scientific portion of the technical justification for the proposed Policy.

Please note that the scope of our review is limited to issues related to Item 2 of the Media Specific Criteria, listed as “Petroleum Vapor Intrusion to Indoor Air” (Attachment 4, proposed Policy).

As per instructions in a memo dated December 8, 2011 from Kevin Graves, Manager of the UST Program Section, Division of Water Quality, State Water Resources Control Board, our review addresses technical justification of pertinent assertions. In this case, Assertions 4 through 7 (assertions related to vapor intrusion) were specifically addressed in determining whether the scientific portion of the proposed rule is based upon sound scientific knowledge, methods and practice. In addition, we included recommendations that we believe will assist in implementation of the proposed Policy in the screening of UST sites.

Scientific Peer Review of the Technical Justification for the Proposed Low-Threat UST[1] Closure Policy

Mark A. Widdowson, Ph.D., P.E. and John C. Little, Ph.D., P.E.
The Charles E. Via, Jr. Department of Civil & Environmental Engineering
Virginia Tech; Blacksburg, VA

The focus of this review is the scientific basis of and technical justification for *Low-Threat UST Closure Policy*, 11-10-11 (Policy) proposed by the California State Water Resources Control Board. The scope of this review is limited to issues related to Item 2 of the Media Specific Criteria, listed as "Petroleum Vapor Intrusion to Indoor Air" (Attachment 4, proposed Policy). As reviewers of the Policy, we are charged with determining whether the technical justification and literature cited are based on sound scientific knowledge, methods and practices.

Instructions from the State Water Resources Control Board dated December 8, 2011 (Attachment 2, "Findings, Assumptions and Conclusions to be Reviewed") list ten assertions to be addressed by reviewers. Assertions 4 through 7 were identified as "Assertions for Vapor Intrusion". Associated with assertions related to vapor intrusion is Attachment 6, "Technical Justification for Vapor Intrusion Media-Specific Criteria", which summarizes the scientific literature and state-of-the-science used as the basis for Assertions 4 through 7.

Assertion 4. The framework for the petroleum vapor intrusion evaluation, which considers the effect of vadose-zone bioattenuation processes, is appropriate for use at UST release sites.

It is well established that naturally-occurring subsurface microorganisms are active in degrading petroleum hydrocarbon vapors in the unsaturated region above the water table (i.e., vadose zone or unsaturated zone). Microorganisms utilize petroleum hydrocarbon compounds (PHCs) as a food source (carbon/energy source) in the presence of oxygen. Under natural conditions, the composition of dissolved gas in the vadose zone is nearly identical to the earth's atmosphere which contains approximately 21% oxygen. PHCs have the propensity to volatilize from gasoline and other fuels. As a result, PHC vapors are commonly detected in soil gas at UST sites. The movement or transport of these vapors is primarily a diffusive process driven by concentration gradients where molecules of PHCs are capable of transport through interconnected pore spaces in the vadose zone. Oxygen in the vadose zone is also subject to diffusion along with advective transport driven by pressure gradients. Because conditions required for the biodegradation of PHC vapors in the vadose zone are common, it is correct to use the term "conservative" if biodegradation is not considered in any site screening methodology. Given the state-of-the-science pertaining to bioattenuation of petroleum vapors in the vadose zone, the proposed framework for evaluating vapor intrusion evaluation at UST release sites is appropriate.

The phenomenon of aerobic biodegradation in the vadose zone has been observed at UST sites for over 20 years including field research supported by the U.S. Environmental Protection Agency[2,3]. An outcome

---

[1] UST = underground storage tank
[2] Ostendorf and Kampbell, *Water Resources Research*, 27(4), 453-462, April 1991
[3] Deyo et al. *Ground Water Monitoring Review*, 31(4), 598-604, Jul 1993.

of aerobic biodegradation of PHC vapors in soils at UST sites is the reduction in PHC vapor concentrations as the vertical distance from gasoline/fuel source increases (i.e., closer to the ground level). At sites where an adequate distance for attenuation of PHC vapors exists, naturally-occurring biodegradation can be sufficient to reduce concentrations to a level that will prevent harmful intrusion of vapors into buildings. Therefore, the notion of using an exclusion distance as a means for a site-screening methodology for PHC vapor intrusion is scientifically sound.

The two source scenarios described in Assertion 4 represent the two most commonly encountered conditions at UST sites: low-concentration source (i.e., dissolved phase plumes) and high-concentration source (i.e, light non-aqueous-phase-liquids [LNAPLs]). The latter describes the condition where gasoline/fuel is present in a free-phase either floating on the water table or trapped in pore spaces above or below the water table. In PHC plumes present in groundwater at UST sites, the dissolved phase concentration of contaminants of concern such as benzene are controlled by solubility limits and the composition of the fuel. These values are unique for each compound and result in equilibrium concentrations in both aqueous (liquid) and vapor (gas) phases. Therefore, the maximum expected concentration of a volatile compound such as benzene at either high- or low-concentration sources can be predicted with confidence. Given the range of possible source concentrations based on these two common scenarios, it is reasonable to relate the required extent of an exclusion distance to the strength of the source.

General comments on the "Technical Justification for Vapor Intrusion Media-Specific Criteria" (Attachment 6).

The literature cited in Attachment 6 is pertinent to the question of petroleum vapor intrusion into buildings and is derived from reputable peer-review journals. The scientific evidence cited as justification for the proposed Policy relies on model simulation and field investigations. Model simulations are useful to visualize the spatial distribution of PHC vapor and oxygen concentrations with depth relative to the foundation of buildings and the location of low- and high-concentration sources. The simulation results are based on representative values of soil properties, biodegradation rates and building/foundation characteristics. While the results shown from the literature are not meant to represent the exact outcome at every UST site, these simulation studies are useful to determine the minimum required separation distance for these representative conditions.

The field studies provide supporting data that show the range of soil-gas concentrations for benzene, an expected risk driver for vapor intrusion at UST sites, with distance above the source. Site data are presented for both low- and high-concentration sources. This type of data analysis has been employed in the remediation field for other questions related to the efficacy of natural attenuation in soil and groundwater and has proven to be useful to understanding the bigger picture. However, the impact of site-specific parameters that could influence results is not always captured in this type of study.

The conceptual model for a generic UST site can incorporate a range of assumptions from relatively simple to overly complex. Assumptions are needed to fill in the details to allow calculations but should be meaningful for applicability to the real world. The conceptual model associated with the modeling investigation (i.e., Abreu et al. 2009) includes several assumptions that are known to vary among sites and may potentially impact on results. These include the assumptions of 1) a static water table, 2) no barriers to the replenishment of oxygen from the atmosphere to soil, and 3) a homogeneous sandy soil. The exact impact of these assumptions on the proposed Policy is unknown, but the following are raised as potential concerns in relation to Assertions 5 through 7.

1. **Static water table** – The elevation of a local water table is subject to increases with rainfall and decreases with drought. The extent to which a water table rises or falls over time is site specific depending on the intensity and duration of recharge events, land cover, and soil properties. At UST sites historical data from monitoring reports would provide data for determining temporal variation in the water table elevation. *Some consideration for a site-specific evaluation of the temporal variability in the depth to the water table is recommended to properly implement the proposed Policy*.

2. **Barriers to oxygen exchange at the land surface** – As noted previous, diffusive and advective transport of oxygen from the atmosphere is known to replenish soil-gas oxygen at UST sites. In the model simulations cited from the literature there is no substantial barrier to oxygen exchange at the land surface. It is known that the porosity[4] of asphalt and concrete is relatively low and will inhibit, but not completely prevent, the flow of gases or liquids. The presence of impervious land cover around a building will result in less oxygen replenishment and the potential trapping of PHC vapors. In addition, a 10 m × 10 m building footprint was used in the model simulations. For larger buildings, the peak concentration of PHC vapors and extent of oxygen depletion in soil gas would be greater than that depicted in the simulation results. *Sites with barriers to oxygen exchange at the land surface should be identified as part of the screening process and given consideration in implementation of the proposed Policy*.

3. **Soil properties** – Data analysis provided by Lahvis (2011) from numerous UST site provides a wealth of information on attenuation of PHC vapors due to aerobic biodegradation. It is noted that for less permeable soils (i.e., silt and silty clay), the mean rate of aerobic biodegradation for benzene decreased by as much as two orders of magnitude relative to UST sites with a sandy soil type. While this site condition suggests less attenuation potential, it is noted that soil porosity and moisture content in less permeable soils favors attenuation and is less conducive for transport of PHC vapors. *Therefore, the lack of consideration of soil properties is a conservative approach in site screening.*

Assertion 5. A 30-foot source-receptor separation distance used for LNAPL (high-concentration) source sites is conservative (Appendix 1 and 2 of the Policy).

The field data provided by Lahvis (2011) for NAPL sites provides a compelling argument for the 30-ft source-receptor separation distance. Model simulation results provide meaningful justification for the observed data. Based on these findings, we agree that the vertical distance of 30 ft is conservative, and that the lateral exclusion distance of 30 ft is very conservative. Identifying the presence and location of LNAPL can be problematic at UST sites. However, the requirement that the TPH (total petroleum hydrocarbons) concentration in soils must be less than 100 mg/kg throughout the entire depth of the

[4] Porosity = volume of interconnected pores per total volume

bioattenuation zone (as defined in Appendix 1 and 2 of the Policy) is a conservative approach. *It is recommended to include technical guidance on evaluating TPH at sites (e.g., sufficient number of samples) and on determining LNAPL presence*. In addition, the concerns listed above, particularly #1 (site-specific analysis of the temporal variability in water table elevation), are applicable to Assertion 5.

Assertion 6. The dissolved phase concentrations and proposed exclusion distances specified in scenarios below are conservative (low-concentration sources) [Appendix 3 of the Policy].

- i. **A 5-ft bioattenuation zone is used for sites with benzene in groundwater concentration <100 μg/L, no soil impacts, and low (<4%) soil gas oxygen concentrations (or no soil gas oxygen measurements), or**
- ii. **A 10-ft bioattenuation zone is used for sites with benzene in groundwater concentration <1,000 μg/L, no soil impacts, and low (<4%) soil gas oxygen concentrations (or no soil gas oxygen measurements), or**
- iii. **A 5-ft bioattenuation zone is used for sites with benzene in groundwater concentration <1,000 μg/L, no soil impacts, and soil gas oxygen concentrations ≥4%.**

Studies citing data collected at various UST sites (Davis, 2010; Lahvis, 2011) for dissolved-phase sites (i.e., source derived from contaminant plume) provides ample data to suggest that i) and ii) are appropriate standards. For the case indicated by iii) the notion that benzene bioattenuation is associated with sites where soil gas oxygen concentrations are ≥4% is consistent with theory and observations at some UST sites. However, as noted in Lahvis (2011), oxygen concentration in soil gas is not necessarily a good predictor of benzene concentrations in the unsaturated zone. *It is recommended to incorporate technical guidance on the measurement of soil gas oxygen concentration in relation to the 4% threshold (e.g., number of samples and location of sampling locations) and on methods to verify benzene bioattenuation*. Again, the concerns listed above, both #1 and #2, are applicable to Assertion 6.

Assertion 7. Application of an additional attenuation factor of 1000x to risk-based soil-gas criteria (i.e., vapor sources) located 5 ft from a building foundation is conservative (Appendix 4 of the Policy).

In our opinion, Davis (2010) presents the most thorough study on the magnitude of attenuation factors (AF) at UST sites, which is based on soil gas data collected for over 400 sampling events. On p. 13, Davis (2010) provides three reasons for “insignificant” attenuation factors (<100-fold contaminant reduction): 1) no clean soil overlying the source; 2) low source strengths (e.g., low-concentration dissolved plume); and 3) rapid attenuation at the source. It is noted that over half of the events fell into this category. The majority of the remaining sampling events show 1,000-fold contaminant reduction (i.e., 1000x or greater). It is not clear what factors contributed to events where AF = 10^{-2} (i.e., only a 100-fold contaminant reduction). Also, the range in the distance of clean soil associated with the AF values is not clearly indicated. On p. 12, Davis (2010) notes “significant attenuation is observed when the petroleum contaminant source has 2 to 10 feet of clean overlying soil”. Written communication by Lahvis provided in Attachment 6 includes analysis of data derived from databases reported in Davis (2009) and Wright (2011). Specifically, Figure 5 (p. 33) shows AF values for benzene over 5 ft or less for 29 sampling events. On the basis of this more detailed analysis of AF values (compared to Davis, 2010) we concur that an AF of 1000x over 5 ft is conservative. However, an improved understanding of whether other site conditions, besides low source concentrations, would be beneficial to proper implementation of the proposed Policy.

In a paper[5] published 20 years ago (Little et al. 1992) a screening-level assessment showed that for a planar source located between 1 and 10 m below a building, an *abiotic* attenuation factor of between 0.003 and 0.0003 could be expected, based simply on contaminant diffusion through the unsaturated zone and subsequent dilution inside the building. The paper concluded with a recommendation that research be undertaken to investigate the rate of microbiological decay of the organic compounds diffusing through the unsaturated zone, noting that "biotic mechanisms could have a large impact on the concentration of petroleum hydrocarbons arriving at a building's zone of influence". In the intervening two decades, substantial field and laboratory research has shown that the aerobic biodegradation of gasoline vapors in the unsaturated zone is very rapid, and that attenuation factors that include these biotic transformations are orders of magnitude lower than those that account solely for abiotic conditions.

[5] Little, J. C., Daisey, J. M. and Nazaroff, W. W. "Transport of Subsurface Contaminants into Buildings," *Environmental Science & Technology*, Vol. 26, 2058-2066, 1992.