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Review of Proposed Low-Threat UST Closure Policy

The proposed policy for low-threat UST closure is an important effort to alleviate resource allocation challenges and preserve mitigation and remediation resources for higher priority sites. The policy is based on 10 assertions, all of which are based on broadly accepted axioms and best practices such as conservative assumptions about bioattenuation and generally safe separation distances. The assertions are also consistent with existing California statutes and regulations. Overall, the document is well written, but it could be improved by providing additional information and clarification as detailed in the following comments.

- The policy should explicitly recognize that biodegradation of vapors in the unsaturated zone significantly depends on moisture content. The modeling efforts seem to have ignored moisture content. Whereas the assumed bioattenuation rate coefficients (e.g., 0.79 h^{-1}) might be appropriate for most of the state of California, they may be optimistically high for arid areas where lack of soil moisture may preclude biodegradation. What attenuation factors would be predicted by models assuming dilution/dispersion alone? Would dilution alone in arid areas support the presumed 1,000-fold attenuation factor? What do field studies show for arid areas?

- In principle, I agree that stable or shrinking plumes tend to be low risk, but there should be some minimum data requirements (e.g., number of monitoring wells and time span considered for data analysis) to reliably establish that the plumes are indeed stable or shrinking. What statistical tests or other data analysis tools will be used to ascertain that a groundwater plume has stabilized?

- A clear definition of the criteria for establishing plume length, specifically what dissolved phase concentration of benzene or MTBE defines the leading edge of the plume (1 ug/L, 5 ug/L or some other value?) is needed. As the term "defined plume boundary" is used in the document (Attachment 4, p. 16 for example) a definite guideline for determining plume length should be provided.

- When referring to the oxygen gas concentration minimum threshold criteria, clarify what does % mean in 4%. Does this mean 40,000 ppm_v? Or, recognizing that pure air has about 21% O_2, is 4% $0.04 \times 210,000$ ppm_v = 8,400 ppm_v? Also, while very conservative, no justification (or reference to an authoritative literature source) is given for this arbitrary threshold.

- Attachment 4, page 15 needs a transition statement to provide context for the criteria beginning on p. 16

- The technical arguments are often based on conference papers and other literature that has not been rigorously peer-reviewed. This does not imply the studies are wrong, but points to the potential need for greater scrutiny. For example, there are several figures showing probability of exceeding a given concentration as a function of distance (e.g., Attachment 6, page 12 & 17). However, no assurances are given that the correct probability distribution function was used (as opposed to using the normal distribution as a default).

- For Appendices 1-4 in Attachment 4: Guidance for determining the soil TPH concentrations in the separation/bioattenuation zones should be provided. Language on the minimum acceptable

number of soil samples that are representative of the entire depth of the separation distance is desirable. Also, to avoid confusion, guidance should be included on deriving the TPH < 100 mg/kg criteria. Is this an average, maximum, geometric mean or some other statistical descriptor based on a prescribed minimum of samples?

- For Appendix 3 in Attachment 4: How and where should the representative dissolved phase concentration be determined? Is this concentration representative of the nearest monitoring location sampling results, is this a concentration based on multiple sampling points, if historical monitoring data exists would this be the highest dissolved phase concentration ever detected (assuming a current worst case scenario), or is this criteria to be determined by other means? Guidance on acceptable statistical analysis for developing a representative dissolved phase concentration should be provided.

- Criteria for Groundwater (Attachment 4, page 16): Similar to the previous comments, guidance for determining dissolved phase criteria need to be clarified (e.g., 3,000 ug/L benzene). The number of representative groundwater samples, location of the samples within the plume, minimum number of sampling events (i.e., historical data) and adequate/allowable statistical methods for determining the representative dissolved phase concentration should be addressed.

- The document should provide criteria for qualifying a site as a Low-Threat UST site when another nearby source(s)/site(s) (not associated with the potential Low-Threat site in question) also poses risks to common receptor(s). Although the Policy as written should provide the majority of the necessary guidance, cases such as commingled plumes or risk contribution from nearby sources should be addressed. If a potential Low-Threat site cannot be considered by default as such due to the presence of other (unassociated) impacts, the Policy should include specific language addressing this potential scenario.

- In Attachment 5, page 2, only Howard (1990) is cited to support the statement that "*biodegradation/natural attenuation of petroleum hydrocarbons and MTBE occurs under aerobic and anaerobic conditions*". This is not an authoritative literature source to support this statement. More literature review and discussion is needed regarding MTBE biodegradability in the saturated zone (consider for examples see, Martienssen et al., 2006; Rasa et al., 2011; Schirmer et al., 1999; Shah et al., 2005; Wilson et al., 2005). Note that there is still significant debate on the significance of the reported MTBE biodegradation rates.

- There should be consistency in choosing the additional safety factors applied to the separation distances, or at least provide the rationale/reference explaining why different safety factors are chosen for different cases (i.e., different plume classes, vapor intrusion scenarios, or plume versus vapor intrusion). For example, explain why the additional safety factors for plume edge separation distances range between 100% and 400% (i.e., 250% for Class 1, 400% for Class 2 and 3, and 100% for Class 4 plumes), whereas for vapor intrusion the safety factors range between 0% and 100% (i.e., 50% for scenario 1 and 2, 0 to 100% for scenario 3 and 0% for scenario 4 vapor intrusion). The rationale for choosing these wide ranges of safety factors and for choosing different safety factors for plume versus vapor intrusion is not provided.

- In Attachment 5, pages 4 and 5, do the separation distances consider the cases where the MTBE plume detaches from the source? If not, justify this decision. It seems that the separation distances are theoretically based on the plume lengths where the plume lengths are estimated from the source to the edge of the plume. What would be the base of plume length estimation and separation distances for sites where the plume is detached? There is an ongoing discussion

within the research community whether or not MTBE plumes detach from the sources and what may be the effect of plume detachment on their extent and associated environmental risk (for examples see, Durrant et al, 1999; Ellis, 2000; Rixey and Joshi, 2000; Weaver et al., 1999; Wilson and Kolhatkar, 2002).

- Is vapor intrusion significant in the case of MTBE volatilization? The significance (if any) of MTBE vapor intrusion should be addressed. While the Henry's Law Constant for MTBE is approximately 10 times lower than that for benzene and MTBE should not be readily volatilized from water, MTBE has a higher vapor pressure than benzene and it may volatilize more readily from the separate product phase or residual phase (LNAPL). Therefore, while MTBE vapor intrusion from a plume may not be significant, MTBE vapor intrusion from LNAPL source could pose risks.

- Explain why MTBE is not considered for vapor intrusion (Assertions 5-7) and direct contact (Assertions 8-10). As mentioned above, MTBE volatilization could be important if LNAPL source zones are present.

References:

Durrant, G.C., Schirmer, M., Einarson, M.D., Wilson, R.D., Mackay, D.M. (1999) Assessment of the Dissolution of Gasoline Containing MTBE at LUST Site 60, Vandenberg Air Force Base, California, Petroleum Hydrocarbons Conference, Houston, Texas.

Ellis, P. (2000) MTBE and BTEX Plume Behavior, Delaware Department of Natural Resources and Environmental Control, August 2000.

Martienssen, M., Fabritius, H., Kukla, S., Balcke, G.U., Hasselwander, E., Schirmer, M. (2006) Determination of naturally occurring MTBE biodegradation by analysing metabolites and biodegradation by-products, Journal of Contaminant Hydrology, 87, 37–53, doi:10.1016/j.jconhyd.2006.04.007

Rasa, E., Chapman, S.W., Bekins, B.A., Fogg, G.E., Scow, K.M., Mackay, D.M. (2011) Role of back diffusion and biodegradation reactions in sustaining an MTBE/TBA plume in alluvial media, Journal of Contaminant Hydrology 126 (2011) 235–247, doi:10.1016/j.jconhyd.2011.08.006

Rixey, W.G., Joshi, S. (2000) Dissolution of MTBE from a Residually Trapped Gasoline Source A Summary of Research Results, American Petroleum Institute, September 2000.

Schirmer, M., Butler, B.J. , Barker, J.F., Church, C.D., Schirme, K. (1999) Evaluation of Biodegradation and Dispersion as Natural Attenuation Processes of MTBE and Benzene at the Borden Field Site, Phys. Chem. Earth (B), Vol. 24, No. 6, pp. 557-560

Shah, N.W., Thornton, S.F., Bottrell, S.H., Spence, M.J. (2009) Biodegradation potential of MTBE in a fractured chalk aquifer under aerobic conditions in long-term uncontaminated and contaminated aquifer microcosms, Journal of Contaminant Hydrology, 103, 119–133

Weaver, J.W., Haas, J.E., Sosik, C.B. (1999) Characteristics of Gasoline Releases in the Water Table Aquifer of Long Island. Petroleum Hydrocarbons Conference and Exposition, November 1999.

Wilson, J.T., Kolhatkar, R. (2002) Role of Natural Attenuation in Life Cycle of MTBE Plumes, Journal of Environmental Engineering, Vol. 128, No. 9, September 2002, pp. 876-882, (doi http://dx.doi.org/10.1061/(ASCE)0733-9372(2002)128:9(876))

Wilson, J.T., Adair, C., Kaiser, P.M., Kolhatkar, R. (2005) Anaerobic Biodegradation of MTBE at a Gasoline Spill Site, Ground Water Monitoring & Remediation, 25, no. 3/ Summer 2005/pages 103–115