



Chemical Engineering & Applied Chemistry
UNIVERSITY OF TORONTO

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1001 I Street
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**Re: PEER REVIEW OF SCIENTIFIC BASIS OF THE TECHNICAL
JUSTIFICATION FOR THE PROPOSED LOW-THREAT UNDERGROUND
STORAGE TANK (UST) POLICY**

Dear Dr. Bowes,

Below please find my peer review of the above-stated proposed policy, as requested. Overall I found the policy to be based on sound science where possible or extensive practical experience and field data in other cases, and is generally conservative when considering uncertainty. This policy is designed to increase overall cleanup efficiency by making sure that funds are not spent where the efforts would have minimum incremental benefit and thereby make funds available for the most threatening releases.

Moreover, the general criteria (a-h) that must be satisfied to be even considered as a candidate site are very conservative with respect to ensuring that drinking water has no chance of being impacted by the proposed policy.

I was asked to review specifically the technical aspects of the justifications, particularly focusing on the ten assertions arranged into three groups (Groundwater, Vapor Intrusion, Direct Contact). My review addresses these assertions in order. I do not address the last group (Direct Contact) as this is outside my area of expertise.

Assertions for Groundwater

The three assertions for groundwater come from the justification presented in Appendix 5. The focus on three specific components, Benzene, MTBE, and TPHg as representative measures of 1) toxicity (Benzene), 2) mobility (MTBE), and 3) mobile hydrocarbon fingerprint (TPHg) is a logical choice to span the range of contaminant types and properties at these sites.

Overall, Appendix 5 culminates in a valid justification for the development of plume classes, but I would recommend that this appendix be presented with a more logical structure to be more specific and to make a stronger rationale.

As currently written, the first part talks about plume length (without any heading); next

there is a heading entitled “Diesel”, but is really more about analytical challenges (i.e. what constituents do you measure and how) and how they relate to defining plume length. The next section is the definitions of plume classes. A final section speaks about free-product removal. These sections are a little disjointed and could flow more logically to culminate in the proposed plume classes.

I would suggest that Appendix 5 be structured first with a section on the measurement of plume concentrations and appropriate methods to delineate the plume (including analytical challenges and approaches associated with free product and other heterogeneities), then present the use of plume lengths as a site-specific, in situ measure of the rates of attenuation relative to groundwater flow, and finally the integrated view presented as rationale for defining plume classes. I elaborate on my reasons for this suggestion below.

The ability to clearly and sufficiently accurately delineate a given plume, with appropriate measurement and sampling strategy, is absolutely key. Practical guidelines for establishing a sufficiently accurate Site Conceptual Model (SCM) need to be clearly referenced in this proposal. A SCM can include varying degrees of extrapolation and interpretations that may compromise the accuracy of the model. Since the groundwater plume classes are defined based on specific plume lengths and separation distances, it is imperative that more detail be provided on how to adequately practically measure these distances given the challenges related to heterogeneity and seasonal variations (e.g., such as changes water table depths and flow patterns). A set of consistent guidelines and methodology are needed to clearly define how a plume length is measured in practical terms. Often plumes are not clear ovals, and length can also be a function of depth. Determinations of plume length can be quite arbitrary and are subject to error and subjectivity. What if the source area is not known, or there are multiple source areas? How then is plume length determined? What concentration limit is used to define the edge of a plume? I think these should be clearly set and explained to minimize chance of error or misinterpretation.

Assertion 1. It has been well established that natural attenuation processes tend to stabilize the spreading of petroleum plumes in groundwater. Biodegradation reduces dissolved petroleum concentrations over time and ultimately can restore groundwater to below regulatory objectives.

I agree with this assertion. However, paragraph 6 of Attachment 5 states speaks to the body of work demonstrating biodegradation and attenuation of petroleum hydrocarbons and oxygenates, but only one reference from 1990 is cited (Howard, 1990). There is indeed a tremendous body of work on this subject, many of the citations are provided, and should be cited explicitly to reflect that the statement includes work more recent than 1990.

Moreover, the following statement: “the rate of biodegradation/attenuation depends on

the constituent and the plume bio/geochemical conditions” is vague. While I don’t disagree with this statement, really what is needed is a measure of confidence that the attenuation rate will be always greater than zero for the chemicals of concern at sites that meet the criteria defined in this policy. The challenge is that in the literature, the reported rates of biodegradation and natural attenuation are all over the map because every single experimental system or site is different and everyone picks a different measure of rate, so what numbers do you pick?

I think that perhaps one could turn the argument around to make a more compelling case for the approach proposed in the policy. Rather than using literature values of rate for rationale, (i.e., picking a conservative rate range and then running scenarios) it should be emphasized that the measurement of plume stability is in effect akin to taking a site-specific approach. The plume criteria are essentially a site-specific and “in situ” measure of the overall attenuation/biodegradation rate relative to groundwater flowrate. In other words, if a plume meets the criteria to put it into one of the groundwater classes defined in the policy, then biodegradation and natural attenuation are definitively occurring at the site and most importantly are occurring fast enough to prevent contaminant migration. These criteria essentially define site conditions where rates of natural attenuation and biodegradation are clearly sufficient to protect downstream receptors.

The additional advantage to presenting plume lengths and plume stability as an in situ measurement of relative attenuation rate means that site-specific conditions that are known to very much affect the rate of biodegradation, such as presence of ethanol blends are inherently considered.

Assertion 2. The Policy requires a separation distance from the edge of a stabilized petroleum plume to an existing well that is more protective than Department of Water Resources (DWR) well standards.

This use of separation distances is consistent with other State and local practices regarding impacts to groundwater caused by other anthropogenic releases.

This assertion provides additional confidence in the approach and the feasibility to practically implement a policy based on separation distances and attenuation (because this has been done before, and is easy to understand – which is very important). Again though, as mentioned previously, the definitions of the points that define the distances (plume boundaries) are critical. These have not been specified and in my opinion ought to be.

Assertion 3. The required separation distances from the edge of a plume to an existing well combined with the requirement for plume stability will protect existing wells from impacts unless unique site specific conditions exist.

This second part of this assertion is vague. I'm not sure what site specific conditions would change the assertion. Who is going to be responsible for determining that "unique site specific conditions exist". It seems like this would be a way to easily disqualify any site at the slightest uncertainty, which may be counter-productive to the goals of the policy.

Other miscellaneous comments regarding Attachment 5:

Table of plume length measurements (Tables should have a title and a number).

The rationale by Shih et al, 2004 for using 5 ug/L rather than 1 ug/L for plume edge is a practical one. What will be implemented in the proposed policy?

Oxygenates (MTBE, TBA, DIPE, TAME, ETBE). Acronyms should be defined.
Ethanol should be added to this list as it is going to be very relevant.

Acronym for Silica Gel Cleanup (SGC) should be defined on first use, and it is misspelled later in the paragraph "non-SCG laboratory quantified" change to SGC.

It is inconsistent that the policy attachment does not specify specific concentration measurement guidelines except for this SGC step...At some point the policy needs to state that EPA (or whatever is deemed appropriate) approved methodology for measurements and site characterization are used throughout. I'm not sure why this specific attention to Silica Gel Cleanup was necessary. Perhaps additional details on all measurement methods and sampling plans should be provided? (or reference to approved standard practices?)

Low threat groundwater classes:

The proposed policy needs to provide a clear definition of how safety factors are defined and implemented to come up with separation distances. For example the last sentence of the first paragraph relating to ethanol gasoline blends "... by applying separation distance safety factors of 100% to 400%." I don't find this statement clear. What are the safety factors applied to (i.e. 100% of what)? Why would these values for safety factor be adequate for ethanol blends? I recommend that different wording be used (or a figure would be good) to show what these safety factors clearly represent and what literature was used to support their use. Rather than say "a SF of 100%", it seems to be clearer to say "twice the length of the plume from the source", or "an additional distance equal to the length of the plume from the edge"? I thus suggest being more direct.

Class 2: wording of sentence: "Solubility of MTBE in water in contact with unweathered gasoline" (rather than solubility of MTBE in unweathered gasoline).

References: check that website accession dates are provided, and that acronyms are written out in full (e.g. SFRWQCB)

Assertions for Vapor Intrusion

The assertions for vapor intrusion are also based on separation distances. Just as the definition for separation distance is important in the context of a groundwater plumes, it is also very important in defining distances in the context of vapor intrusion. Given that the distances are actually quite small (as low as 5 ft), the accuracy with which these distances are defined becomes more all the more important (see comments below under Assertion 4).

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.

I agree that different exclusion distances are needed for the two source scenarios, because the thickness of the bioattenuation zone required to degrade hydrocarbons to below levels of concern are indeed different for low- and high concentration sources. However, in this and subsequent Assertions, exclusion distances are defined as source-to-building separation distances. And while the distances proposed seem justified in the context of a static source, they do not seem to consider complications related to changing water table elevations to the determination of these distances. Some specific clarity on this point is required, to show how the determination of the distance in a real situation (with inherent variability) is achieved.

In addition I suggest that the document clearly distinguish aqueous and gas phase concentrations for compounds like benzene. In section 3.1.1, benzene gas phase concentrations are reported as “< 10 mg/L”, units typically applied to liquid phase concentrations and therefore easily confused. Elsewhere, concentrations are reported in units of $\mu\text{g}/\text{m}^3$, which is probably a better way to consistently express gas-phase concentrations to avoid confusion (even though they are technically equivalent). If ambiguity is possible, always specify “in the gas phase” or “in the liquid phase”.

I suggest a table of aqueous and equilibrium gas phase concentrations would very much help the reader. The Henry’s law constant is cited several times throughout the document in various forms. This should be consistent. For example at the bottom of Attachment 6 page 5 footnote, a Dimensionless Henry’s law constant for benzene is provided (0.25). It is also provided at the bottom of page 10 with units of m^3 per m^3 (the units are atypical). Moreover, it is nowhere noted that this constant is a strong function of temperature, and that this value is for 25°C (I think). Was the effect of temperature considered in the development of exclusion distances?

Similarly, biodegradation constants are also a strong function of temperature. Some discussion on the effects of temperature changes on the assumptions in the model should be elaborated on. As temperature decreases, volatility decreases (good), but biodegradation rates decrease (bad), so the potential for vapor intrusion depends on the slope of the temperature dependencies of these two competing processes.

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]

This assertion is based on both modeling and field soil gas data, and both sources agree in that the attenuation of benzene above an LNAPL is significant, and thus from the data presented the assertion is valid. However, as mentioned above, there should be some analysis to show that the temperature effects would not significantly change the results. I don't think they would, but it would be important to run through the scenarios, much like different oxygen concentrations were considered.

Another comment would be to consider the effect of soil moisture. Biodegradation only occurs if there is sufficient moisture in the soil. For arid sites where the LNAPL is not on the water table (i.e. as in Assertion 7), biodegradation rates may be significantly slower, and a correction or test for low moisture content should be considered.

I agree that the 30-ft. exclusion distance is conservative based on both modeling results and field data analysis. However, another way to look at the modeling would be to determine what biodegradation rate you would need to achieve the desired attenuation in the given scenarios. And then show that this value is readily achieved.

In Section 3.1.1 Model studies – the value of the aerobic biodegradation rate of 0.79 per hour is referred to as the mean of published rates. In fact it is the geometric mean of published rates, and should be accurately referred to as such. The geometric mean is always lower than the arithmetic mean, and is the appropriate measure here.

Other minor comments

-Appendix 2 of the policy, Scenario 2. I wondered what the dotted fill in the figure signifies (I don't think anything really).

-In general, I do think that the figures reproduced in Attachment 6 should be properly named with the title of the figure (from the original source) and proper legends. In some cases the axes are not evident, for example the figure on page 12 from Lahvis (2011), the probability presented on the Y-axis is not defined, and forces the reader to go to the original source to understand what the probability really means. A proper legend would remedy this easily, and give the reader an easier task.

-Replace all uses of ug and use proper symbol: μg (e.g. p 11)

-Spelling of receptor on P. 15

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 agree with Assertion 6, that the rates of biodegradation of such low concentrations of benzene in the dissolved phase will be sufficient given the proposed exclusion distances. I agree with the statement that the field data indicate that the water table would have to essentially be in contact with a building foundation for there to be a potential concern for vapor intrusion at low concentration sites.

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]

I am less confident in (and my ability to comment on) the predictions of the vadose-zone biodegradation from vapor sources. As mentioned before, I would be concerned about moisture content in these situations. The proximity to the water table and precipitation record would be a factor that should be considered (monitored).

Assertions pertaining to Direct Contact

Assertions 8, 9 and 10 are too far outside my expertise to comment

8. The equations used to develop the soil screening levels are appropriate.

9. The Input parameters used to develop the soil screening levels are appropriate.

10. The use of benzo(a)pyrene (BaP) toxicity to represent all of the polyaromatic hydrocarbons (PAHs) is conservative.

Thus concludes my review at this time. If there are any further points of clarification or if additional revision is required, please let me know. I would be happy to be of further assistance.

Yours sincerely,



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