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To: Interested Parties

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Subject: Additional notes on HDOH report *Field Investigation of the Chemistry and Toxicity of TPH in Petroleum Vapors*

The following notes respond to general comments received on a draft copy of the TPH vapor report. The final report was prepared in August 2012 (HDOH 2012).

1. Is it appropriate to use USEPA Provisional Peer-Reviewed Toxicity Values (PPRTV) for development of TPH action or screening levels when TPH toxicity factors have not yet been posted to the IRIS database? USEPA PPRTVs are one of several sources used to develop risk-based screening levels when toxicity factors have not been posted to the USEPA IRIS database. Five separate reviews of TPH aliphatic and aromatic carbon range compounds are referenced in the HDOH report, including USEPA PPRT, inhalation Reference Concentrations for aliphatic and aromatic carbon ranges (USEPA 2009). The HEER office elected to use the PPRTV Reference Concentrations to develop indoor air and soil gas action levels for specific carbon ranges and ultimately for TPH action levels. The latter represents the toxicity-weighted sum of the individual carbon ranges. In part this was because the USEPA guidance is the most recent and the authors had the opportunity to review the four, earlier publications as well as other data.

The review of appropriate toxicity factors for aliphatic and aromatic carbon ranges is ongoing. Full consensus is rarely if ever reached on toxicity values for specific chemicals, including toxicity factors posted to USEPA's IRIS database – considered to be the most supportable and defensible database available (e.g., witness the ongoing debates over arsenic, dioxins and TCE). States as well as USEPA routinely draw on available information for assessment of the health risk posed by chemicals that are not currently listed in IRIS. Indeed, USEPA RSLs for over one-hundred of the chemicals listed in USEPA's guidance document are based at least in part on PPTV toxicity factors (refer to USEPA 2012). The USEPA RSLs are widely used across programs within that agency and beyond Superfund, as well as across programs within state agencies. As discussed in the HDOH report, a number of states, including Hawai'i, have published risk-based screening levels for TPH carbon ranges in soil and groundwater, although California (first published in 2001; CalEPA 2008) and Hawai'i (first published in 2005; HDOH 2011) are the first states to formerly publish screening/action levels for TPH indoor air and soil gas.

Although there is certainly room for debate over the specific toxicity factors that should be applied to individual carbon ranges, it would be technically indefensible for the HEER office to ignore potential vapor intrusion concerns posed by the TPH component of petroleum vapors given the dominance of non-BTEX compounds in vapors associated with petroleum-contaminated soil and groundwater. The results of the HDOH soil vapor study support the need for TPH action levels. Alternative toxicity factors can be proposed and supported in site-specific risk assessments, as outlined in the HEER office EHE guidance. The use of a less stringent, total noncancer Hazard Index greater than 1.0 to determine when actual mitigation is required to address vapor intrusion problems identified at a site might also be appropriate but would require a thorough review of the studies used to develop the toxicity factors.

2. The draft USEPA Petroleum Vapor Intrusion (PVI) report (March 2012) states that “...data indicate benzene is the primary risk driver (for vapor intrusion associated with petroleum-contaminated soil and groundwater).” Why does the HDOH report state that TPH can drive risk over benzene in some circumstances? Field data collected as part of the HDOH study suggest that TPH can drive vapor risk over benzene and other individual compounds, depending on the type of fuel released and the target cancer risk used to assess individual compounds. Benzene and other individual compounds (e.g., TEX) made up a very small percentage of the total petroleum vapors at the sites included in the HDOH study, with the average TPH:Benzenes ratio ranging from approximately 1,000:1 to greater than 10,000:1. The study intentionally targeted sites contaminated with diesel and other low-BTEX fuels, due to the lack of published data on vapors associated with releases of middle distillate fuels. Relatively high ratios of TPH:Benzenes were also observed at reported gasoline-only release sites, however (e.g., 100: 1 to greater than 1,000:1).

Although “less toxic” with respect to toxicity factors and action levels, the higher proportion of TPH aliphatics in the vapors causes these compounds to be the primary risk driver with respect to potential vapor intrusion concerns. In risk assessment terms, this means that the noncancer Hazard Quotient for TPH can still exceed 1.0 even though the risk posed by benzene is less than 10^{-6} .

To our knowledge, a risk-based evaluation of TPH in soil vapors was not included in the studies referenced in the draft, USEPA guidance. If TPH was quantitatively considered, is the conclusion that benzene (always) drives vapor intrusion risk based on modeling or actual field data? Without such a review, the suggestion that benzene (or any other individual compound) is the primary risk driver for vapor intrusion at petroleum-contaminated sites is not supportable.

It is anticipated that ongoing evaluations of soil gas field data will help address the lack of published information on the relative risk of vapor intrusion posed by TPH versus benzene and other individual compounds. Additional field studies of this issue by the USEPA and other parties would be welcomed.

3. Discuss biodegradation of petroleum vapors in the subsurface and the reduced threat of vapor intrusion in comparison to chlorinated solvents, including “exclusion distances”. A brief discussion of this issue will be included with updates to Section 7 of the HEER office Technical Guidance Manual (HDOH 2009). Current HEER office guidance recommends a focus on subslab, soil gas data for final decisions regarding potential vapor intrusion risks from both chlorinated solvents and petroleum. This is intended to target vapors at the point that they could

enter a building and take into account attenuation from the source area, due to physical barriers (e.g., low-permeability strata) and/or biodegradation.

While useful from a qualitative standpoint, model-based evaluations of petroleum vapor fate and transport and attenuation away from source areas discussed in the draft USEPA guidance appear to be limited in scope and not sufficiently backed up by field data. For example, the models referenced imply that the TPH aliphatic component of petroleum vapors is unlikely to migrate more than two to three feet from the source area before degrading below levels of potential concern. This does not match our observations in the field. The model also predicts a clear, *decreasing* ratio of TPH to BTEX away from a source area and over time, due to the higher degradation rate for aliphatics vs aromatics. This is likewise not supported by the results of the HDOH study. As currently presented in the draft USEPA guidance, this perpetuates the fallacy that the bulk of petroleum vapors is made up of BTEX. A better field understanding of both the chemistry and toxicity of petroleum vapors, including TPH, is required to properly evaluate vapor intrusion risk and educate regulators and consultants on this important issue.

4. Clarify the use of critical ratio of TPH to individual compounds, since this ratio can vary by product type and weathering and in itself does not necessarily indicate that a vapor intrusion problem exists. As discussed in the report, the ratio of TPH to an individual compound such as benzene provides initial information on the potential for TPH to drive potential vapor intrusion risks over individual compounds. As discussed in the Executive Summary and in Section 4: “Note that exceeding the critical ratio does not in itself imply that the TPH in soil vapors poses an actual vapor intrusion risk, since this will be governed by the concentration (as well as total mass) of TPH and individual VOCs present in the soil vapors, the location of the vapor plume with respect to nearby or future buildings, building design and related factors (refer also to HDOH 2011).”

5. Why does the ratio of TPH to individual compounds in soil vapor samples vary within the study sites and between sampling events? Both spatial and temporal differences in TPH and BTEX ratios were observed at the study sites, as well as data from other sites reviewed during the study. For example, TPH:Benzene ratios observed at some sites seem to suggest the presence of both gasoline (low ratio) and diesel (high ratio) contamination. Alternatively, this could reflect natural heterogeneity within the vapor plume due to differences in weathering and biodegradation. Variations over time could similarly reflect the effects of natural, biodegradation, subsurface migration and small-scale heterogeneity within the plume, as well as remediation. The data highlight the potential problems associated with one-time sampling events and a limited number of vapor points. Ongoing studies are planned to further investigate sampling related variations and issues.

6. What is the best laboratory method to test for TPH in soil vapors? This question was not fully answered by the study. As discussed in the report, selected samples were tested for TPH and individual carbon ranges using multiple methods (see Section 9 of report). This included:

Summa canister samples:

- TO-3 (GC/FID);
- TO-15 (GC/MS);
- Sum of individual, MA-APH carbon ranges (GC/MS);

Sorbent tube samples:

- TO-17 (GC/MS);
- Sum of individual, MA-APH carbon ranges (GC/MS).

Although limited in scope, the study results suggest that a combination of Summa canister samples and TO-15 analysis for TPH provides the most conservative (i.e., highest) estimate of TPH concentrations in soil vapor. Discussions with the laboratory, however, suggest that calculation of TPH as the sum of individual carbon ranges using TO-15 or TO-17 methods is probably the most accurate. Although TO-3 data correlated reasonably well with the other methods, the laboratory cautioned that the TO-3 method was far less sensitive than TO-15 and TO-17.

It is important to note that longer chain aliphatics (e.g., >C12) cannot be reported using Summa canister methods. If heavier hydrocarbons could be present in soil gas, as was the case for several of the diesel-contaminated sites included in the HDOH study, then sorbent tube methods must be used to collect the samples and accurately report TPH. This is important, since longer-chain hydrocarbons (C9+) are more toxic than shorter-chain hydrocarbons and their presence can significantly increase the vapor intrusion risk. These compounds made up greater than 75% of the TPH at one diesel site included in the study. Longer-chain hydrocarbons make up only a very small proportion of the overall TPH at gasoline-contaminated sites. Gas chromatographs can be used to help evaluate the presence of longer chain hydrocarbons in soil vapors. The volume of high-concentration vapors that can be drawn through a sorbent tube without saturating the tubes can be very limited (e.g., maximum 50mls required by the laboratory for the HDOH study). When utilizing sorbent tubes for sample collection, Summa canister samples are also recommended for comparison.

Laboratories must also be specifically instructed to report TPH in soil vapors at diesel-contaminated sites as the sum of C5 to *at least* C16 and preferably C24 compounds. Laboratories traditionally report TPHd as the sum of C10-C24 compounds for diesel in soil or groundwater, since these compounds make up the bulk of the actual, liquid fuels. This is not necessarily the case for vapors associated with the fuels, however. The study identified high proportions of C5-C8 aliphatic compounds in vapor samples collected over fresh diesel fuel and JP-8 jet fuel as well as at sites where releases of middle distillate fuels were known to have occurred. This isn't surprising, since these compounds represent the most volatile fraction of the fuels. Reporting TPH as only the sum of C10 to C24 compounds would have significantly underestimated the total concentration of TPH in the vapors, and subsequently underestimated the potential vapor intrusion risk. If C5-C12 compounds make up the majority (e.g., >90%) of the hydrocarbon vapors based on initial sorbent tube data, then Summa canisters can be used to collect future samples, as needed (HDOH 2011; to be discussed in updates to Section 7 of the HEER office Technical Guidance Manual, HDOH 2009).

7. Why were auto exhaust samples collected? A limited number of auto exhaust samples were collected to determine if petroleum vapors associated with exhaust have a distinct, chemical signature in comparison to vapors from fresh fuel. Based on the few samples collected, it appears that the TPH:BTEX ratio for exhaust could be significantly higher than typically observed for vapors from pure fuels (i.e., greater proportion of TPH aliphatics consumed during combustion).

In the future, this could assist in determining the origin of petroleum vapors identified in the shallow subsurface or indoor or ambient air.

References:

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