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STATE OF MISSOURI
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DEPARTMENT OF NATURAL RESOURCES
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MEMORANDUM

DATE: December 29, 2004

TO: Missouri Risk Based Corrective Action (MRBCA) Vapor Subgroup Members

FROM: Edward Galbraith, Director
Hazardous Waste Program (HWP) *(original signed by Edward Galbraith)*

SUBJECT: Technical Memorandum to Vapor Pathway Subgroup: Update and Recommendations

When the MRBCA for Petroleum Storage Tank Sites guidance document was released in February 2004, some members of the Risk-Based Remediation Rule Workgroup expressed concern that the Tier 1 Risk-Based Target Levels (RBTLs) for the indoor inhalation vapor pathways for soil and groundwater were very low. Of particular concern were the RBTLs for benzene: 0.042 mg/kg (residential soil), 0.177 mg/L (residential groundwater), 0.222 mg/kg (non-residential soil), and 0.928 mg/L (non-residential groundwater). There was also concern about TPH-GRO vapor intrusion RBTLs.

In response, the Department of Natural Resources (department) agreed to convene a "vapor subgroup" consisting of interested parties from the Workgroup. Over the summer of 2004, the Vapor Pathway Subgroup met on three occasions to discuss various issues related to the vapor pathway.

This memo outlines areas of agreement and provides the HWP's decisions on other areas where, despite much discussion, complete consensus could not be reached. While there are a number of important details to be worked out, this memo is to clarify discussions to date and establish a platform upon which some of those details can be worked out.

This memo addresses the following issues that were discussed in the Vapor Pathway Subgroup (many of these pertain to both the Tanks RBCA documents and the RBCA document under development for VCP, Superfund, RCRA, etc.):

- Area fraction of cracks in foundation/walls (i.e., crack fraction)
- Tier 1 default residential and non-residential air exchange rates (AER)

- Consideration of Soil Type Specific Fate and Transport Parameters at Tier 1
- Capillary Fringe Thickness
- Considering the Indoor Vapor Pathway at Active Gas Stations
- Use of Bioattenuation Factor
- Comparison of Missouri Tier 1 RBTLs for Benzene and TPH-GRO with Other State's Tier 1 Levels

In addition, this memo addresses a correction in toxicity data for certain carbon fractions and TPH-GRO, DRO, and ORO.

Area Fraction of Cracks in Foundations/Walls (i.e., Crack Fraction)
In the February 2004 MRBCA guidance document, the crack fraction was assigned a default value of 0.01 cm^2/cm^2. However, Environmental Protection Agency (EPA) guidance, in particular the draft *Subsurface Vapor Intrusion Guidance*, indicates the 0.01 cm^2/cm^2 value to be overly conservative. Therefore, the subgroup agreed to use the crack fraction proposed by EPA, 0.001 cm^2/cm^2, as the Tier 1 default value. **This change alone increases the Tier I target levels for the indoor vapor pathway by a factor of 10.**

Therefore, the program recommends that the default value for crack fraction of 0.001 cm2/cm2 be used as the default parameter in both the RBCA documents.

Tier 1 default residential and non-residential air exchange rates (AER)
During discussions with the Vapor Pathway Subgroup, the department proposed the use of AERs lower than those in the February 2004 Tanks MRBCA guidance used to develop Tier 1 RBTLs. The department proposed lower AERs of 6 exchanges every 24 hours for residential structures and 12 exchanges every 24 hours for non-residential structures. However, a member of the Subgroup researched the literature further and found that different default values are appropriate to different regions of the country and that the department's proposed new values were not the most representative of this region. In fact, the literature demonstrates that the most appropriate values to this region are very close to the original values in the February 2004 guidance.

Therefore, the program recommends retaining the original values, which are 12.096 exchanges per 24 hours for residential structures and 19.872 exchanges per 24 hours for non-residential structures, as the Tier 1 AER defaults.

Consideration of Soil Type Specific Fate and Transport Parameters at Tier 1
In response to stakeholder concerns regarding the relatively low vapor pathway RBTLs in the February 2004 Tanks MRBCA guidance, the department proposed to develop soil type specific Tier 1 RBTLs. Under this proposal, a set of Tier 1 RBTLs would be developed for each of three soil types: sand, silt and clay. Each set of RBTLs would reflect soil type specific fate and transport parameter inputs for total soil porosity, volumetric water content, and, as originally proposed, capillary fringe thickness. However, as discussed below, we have not made the capillary fringe thickness values soil type specific because of a limitation of the Johnson-Ettinger

vapor model used in the MRBCA process. Also, note that, because the volumetric air content of soil is a function of the volumetric water content, the air content changes when the water content is changed. Therefore, by default, the volumetric air content value becomes soil type specific.

The result of this effort is three sets of Tier 1 RBTLs, each reflective of a specific soil type. See attached Tables 1 and 2, *Comparison of Tier 1 RBTLs for Benzene and TPH-GRO for Three Soil Types*. This approach increases the Tier 1 RBTLs for the vapor pathway significantly. Tables 1 and 2 show values only for benzene and TPH-GRO because most stakeholder concerns focused on these two chemicals of concern. The new soil type specific Tier 1 RBTLs will replace the RBTLs found in the February 2004 version of the Tanks MRBCA guidance. The default target levels (DTLs) will change accordingly.

Note that the attachment containing Tables 1 and 2 also presents information regarding development of the soil type specific RBTLs, including corrections made to several TPH parameter values (which are further discussed below).

Soil type specific RBTLs will also be used in the draft departmental MRBCA. Because there are over 300 chemicals of concern in that document, more tables may be required to provide lookup values for all constituents. Therefore, the Workgroup may want to reconsider this from an "ease of implementation" perspective, i.e. whether to include tables for all constituents or merely make the process available. The important point is that both MRBCA documents will provide the ability to consider specific soil types at Tier 1.

Capillary Fringe Thickness

In developing the Tier 1 soil type specific RBTLs, department staff initially changed the default value representing the capillary fringe thickness from 5 centimeters to soil type specific values. The soil type specific values were 20 cm for sandy soils, 79 cm for silty soils, and 100 cm for clayey soils. Using the Johnson and Ettinger model (JE Model), an increase in the thickness of the capillary fringe results in an increase in the allowable target level. This is due to the fact that the JE Model assumes that the capillary fringe is uncontaminated. Under this assumption, the capillary fringe creates a hindrance to upward vapor migration; the thicker the capillary fringe, the more significant the hindrance. In reality, however, the capillary fringe is usually contaminated at petroleum release sites. Research shows that petroleum released into the soil will migrate vertically until coming into contact with the top of the capillary fringe. At that point, the petroleum will spread out over the capillary fringe, with some product migrating into voids in the capillary fringe. Petroleum COCs will then slowly dissolve into water in the capillary fringe and the underlying saturated zone. In addition to this mechanism, variations in the elevation of the saturated zone can cause contaminant "smearing" that can result in soil and capillary fringe contamination.

For these reasons, the department found that, when applied to petroleum release sites, the JE Model is not accurate in assuming the capillary fringe is uncontaminated. In addition, our preliminary analysis indicates that the JE model assumption would also be inaccurate for all

other contaminated sites. Therefore, rather than assign a soil type specific value for the capillary fringe thickness associated with each soil type, the department recommends that the capillary fringe be set at the ASTM default of 5 cm. The RBTLs were derived using a capillary fringe of 5 cm for each soil type.

Considering the Indoor Vapor Pathway at Active Gas Stations

Although the program agrees that decreasing the crack fraction, retaining the AERs and considering soil type are defensible means to change the Tier I numbers, the program does not find it reasonable or advisable, as a policy decision, to exempt active gas stations from considering the indoor vapor pathway. The arguments, advanced by some members of the Subgroup, in favor of this exemption are:

1. Common sense would say that operating gas stations and C-stores would reasonably be expected to have elevated benzene levels; therefore,
2. Any additional risk from subsurface benzene contamination would be negligible and; therefore,
3. The costs associated with assessing and addressing the vapor pathway cannot be justified.
4. Furthermore, it is impossible to delineate between benzene from subsurface contamination as opposed to ambient sources.
5. Finally, employees at locations such as gas stations where harmful chemicals are present understand that they are accepting additional risks.

Response to #1 The program observes that there are no available data or studies documenting indoor air benzene concentrations at operating stations, despite efforts by Subgroup members to locate such studies. Furthermore, a survey sent to fifty states on this question yielded some surprising results. The survey asked two questions: 1) Does your state consider the vapor pathway at tank sites? and, 2) If so, is the vapor pathway considered at active gas station sites? Of the 17 states responding to the survey, 15 require evaluation of the vapor pathway at tank sites and, of those 15, 13 (87%) require evaluation of the vapor pathway at active gas stations sites. Those states are:

Indiana
Kansas
Oklahoma
Ohio
New York
New Jersey
Vermont
Massachusetts
South Carolina
New Hampshire
Arizona
California
Oregon

The results of this survey suggest that this pathway is an important part of other states' RBCA processes.

Response to #2 Incremental excess lifetime cancer risk is a bedrock principal of the entire RBCA process. When exposure to a carcinogen increases, the incremental risk of cancer increases, however slightly. How much increased risk is acceptable? In Missouri, the members of the Risk-Based Remediation Rule Workgroup agreed that, when addressing contamination, the acceptable incremental excess cancer risk is 1 in 100,000.

The increased risk from an exposure to benzene is the same for a C-store employee as it would be for a neighboring bank employee. To exclude the C-store employee from the risk assessment process because he or she already has elevated risk is a departure from the RBCA philosophy. We are all at elevated risk. The current lifetime risk of cancer for Americans is about one in three. A risk-based process that excludes a pathway on the basis of a preexisting risk is a contradiction in terms.

Response to #3 We recognize that evaluating the vapor pathway will involve some additional costs on the part of tank owners and Petroleum Storage Tank Insurance Fund (PSTIF). However, the cost of a Tier I analysis is very small. A Tier II evaluation, when necessary, will involve some additional costs. In some cases it may be possible to demonstrate that, based on site-specific conditions, one or more of the default assumptions are conservative, such as the crack factor or air exchange rate. Finally, in the rare cases where some corrective action is needed to protect human health, public welfare, and the environment, there are usually alternatives to removing contamination from beneath an active C-store.

Response to #4 The program recognizes that it is practically impossible to delineate between benzene from two different sources. For this reason, indoor air assessment is conducted entirely by modeling. The program would not approve indoor air sampling for contamination from subsurface contamination unless all other sources could, in fact, be eliminated.

Response to #5 The program does not have any legal or technical information to support or refute the idea that certain workers accept increased risks in return for the compensation that they receive.

Use of Bioattenuation Factor

Bioattenuation (sometimes called biodegradation) of benzene in the uncontaminated soil horizon was the subject of much discussion among the Subgroup members. Some members argued that the vapor cleanup numbers at Tier I should be increased by a factor of 10 or 100 in order to account for biodegradation. The Subgroup agreed that bioattenuation "happens", but beyond that very little is understood about what conditions contribute to bioattenuation. Data indicates that, while bioattenuation does occur at virtually every petroleum site, the rate and degree of bioattenuation varies significantly from site to site.

The program believes that the state of understanding is best summarized in a report prepared by the American Petroleum Institute's (API) Soil and Groundwater Technical Task Force. In its summary, the report, entitled *Vadose Zone Natural Attenuation of Hydrocarbon Vapors,* states that of 28 soil gas profiles studied, biodegradation ranged from "0% at some sites and as much as 99.99% at other sites." The report goes on to state that the "attempt to correlate observed soil gas profiles and …attenuation with basic site characteristics did not reveal any obvious relationships."

The report does argue that predictive models (such as the model used in the MRBCA) could overestimate the risks from vapor by up to 10,000 times. However, in attempting to understand the conditions favorable to biodegradation and determine a scientifically defensible bioattenuation factor, the report states that more work remains.

> "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…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.[1] (emphasis added)

Members of the Subgroup spoke by conference call with the study's authors and concluded that the state of the science still does not yield sufficient information to establish a generic bioattenuation factor applicable to all sites. Therefore, recognizing that the guidance provides cleanup numbers that are conservative in many if not most cases, the guidance also provides for the collection of soil gas data where modeling suggests that there is unacceptable risk. The department is currently reviewing a draft standard operating procedure for collecting soil gas profile data and will make that procedure available shortly.

Realizing that collecting soil vapor data costs resources, the program will stay at the table on this issue. Many groups are studying this issue and collecting data in order to build a scientifically defensible case for bioattenuation factors that do not involve site specific soil gas sampling. We are confident that, in the not too distant future, the mechanisms of bioattention will be better understood and documented in the peer-reviewed literature. We recognize that data from sites that are PSTIF insured will be available. However, any changes that the department may recommend must be validated by peer-reviewed or otherwise scientifically defensibly studies.

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[1] Sophie Roggemans, Cristin L. Bruce, Paul C. Johnson, and Richard L. Johnson. *Vadose Zone Natural Attenuation of Hydrocarbon Vapors: An Emperical Assessment of Soil Gas Vertical Profile Data.* American Petroleum Institute, December 2001, No. 15.

Comparison of Missouri Tier 1 RBTLs for Benzene and TPH-GRO with Other State's Tier 1 Levels

The attached Tables 3 through 13, *State Comparison of Tier I RBTLs for Benzene and TPH-GRO*, compare Missouri's Tier 1 RBTLs for benzene and TPH-GRO with thirteen other state's Tier 1 levels for these COCs. The Missouri Tier 1 RBTLs used in the comparison reflect the following inputs: a crack fraction of 0.001 cm^2/cm^2, AERs of 12.096/24 hrs (residential) and 19.872/24 hrs (non-residential), values for porosity and water content specific to Type 3 (clay) soils, and capillary fringe thickness of 5 cm.

The tables show that, even with a capillary fringe thickness of 5 cm, Missouri's soil vapor pathway RBTL for benzene for adult resident and non-resident worker ranks 1st out of the 13 states (i.e., Missouri has the highest RBTL). The soil vapor RBTL for benzene for a resident child ranks 2nd. Missouri's groundwater vapor pathway RBTL for benzene for a resident adult and a resident child ranks 2nd out of 13. For a non-resident, Missouri's groundwater vapor pathway RBTL for benzene ranks 1st. For TPH-GRO, in every case, Missouri's residential and non-residential RBTLs for soil vapor and for groundwater vapor rank 1st. However, of the 13 states surveyed, only one besides Missouri, that being Washington, D.C., has developed RBTLs for TPH-GRO.

Correction of Toxicity Factors for Certain Carbon Fractions and TPH-GRO, DRO, and ORO

The RAM Group discovered a number of errors in the toxicity factors used to develop target levels for TPH-GRO, DRO, and ORO. These errors have been corrected and new RBTLs calculated. The errors and corrections are presented below. The Table 2 RBTLs for TPH-GRO reflect these changes and yield significantly higher values. **In light of the increased values, the program believes that a review of the adequacy of its nuisance policy may be in order.**

- Aliphatic carbon fractions
  - >C6-C8 - change inhalation reference dose (RfDi) from 1.514 mg/kg-day to 5.26 mg/kg-day;
  - >C8-C10 - change RfDi from 0.0857 mg/kg-day to 0.286 mg/kg-day;
  - >C10-C12 - change RfDi from 0.0857 mg/kg-day to 0.286 mg/kg-day;
  - >C12-C16 - change RfDi from 0.857 mg/kg-day to 0.286 mg/kg-day;
  - >C6-C8 - change dimensionless Henry's law constant (H) from 51 to 50;
  - >C8-C10 - change dimensionless Henry's law constant (H) from 82 to 80;
  - >C16-C21 - change solubility (S) from 1.3E-06 mg/L to 2.5E-06 mg/L;
  - >C21-C35 - change S from 1.3E-06 mg/L to 2.5E-06 mg/L;
  - >C6-C8 - change dermal RA factor (RAFd) from 0.1 to 0 or NA (unitless); and
  - >C8-C10 - change RAFd from 0.1 to 0 or NA (unitless).
- Aromatic carbon fractions
  - >C8-C10 - change RAFd from 0.13 to 0 or NA (unitless);
  - >C10-C12 - change RAFd from 0.13 to 0.1 (unitless); and

- >C12-C16 - change RAFd from 0.12 to 0.1 (unitless).

Moving Ahead

1. The program will implement changes identified in this memo in the Tanks RBCA process **effective immediately**. Those changes will be added to the next update of the guidance and will be included as part of the rulemaking process for Tanks RBCA.

2. The soil type dependent numbers for the leach to groundwater pathway are still under development but should be available shortly.

3. As previously mentioned, the department is currently reviewing a draft standard operating procedure for collecting soil gas profile data and will make that available shortly.

4. The program will be reviewing its nuisance policy under RBCA to determine whether, in light of the revised TPH values, the policy will be adequate to insure cleanup decisions that will yield productive reuse.

5. With respect to the MRBCA for VCP, Superfund and RCRA guidance under development, you can anticipate seeing the results of these recommendations, where applicable, on the MRBCA web site and you will have a chance to comment on their use in the month following release of the draft. The draft will be available in the very near future.

Finally, I apologize for the length of time this response has taken. The importance of this issue to stakeholders and the number and complexity of the issues has prevented us from moving as quickly as we all would have preferred. While there are still some unresolved issues, I believe this decision allows us all the opportunity to move forward in some key areas. Thank you all for the hard work that you have put into this process and for sticking with us as we work together to build an even better MRBCA process.

EG:tcp

Attachments

c: James D. Werner, Air and Land Protection Division
Scott B. Totten, Water Protection and Soil Conservation Division