

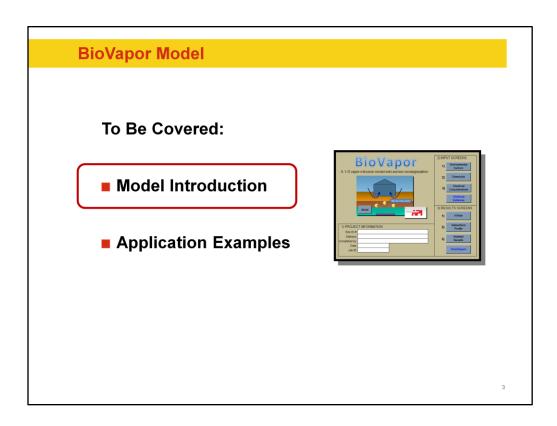
⁺ This section is a presentation on the BioVapor model, which was specifically developed for petroleum vapor intrusion estimates.

Workshop Agenda

- Welcome, Introductions, Safety Issues
- Petroleum Vapor Intrusion Conceptual Model
- Updates: EPA, ITRC, Training
- BioVapor Model, Exclusion Criteria
- Natural Attenuation and Recommended Screening Criteria
- Sampling and Analysis
- Case Studies
- Methane
- Lessons Learned

Summary

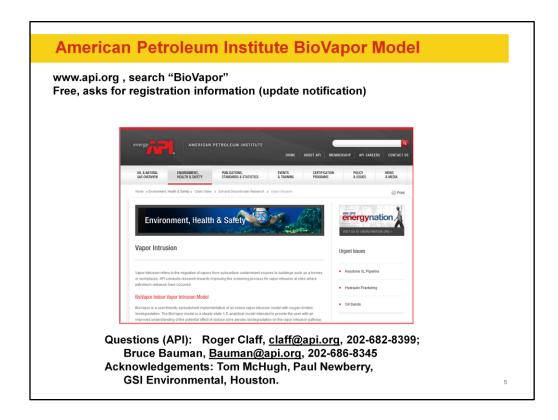
25 minutes



- + The talk includes:
- + A brief introduction and overview.
- + Several applied examples of the model use.
- + It does not include details of the model theory (which you can find in the model documentation)
- + And does not include running case examples.

J&E Model: Subsurface Vapors to Indoor Air Vapor Intrusion

- Johnson and Ettinger (1991): Heuristic model for predicting the intrusion rate of contaminant vapors into buildings, Environ. Sci. Tech., 25:1445-1452.
 Applied: ASTM E2081-00; E1739-95; USEPA, 2003; others
- USEPA OSWER Subsurface Vapor Intrusion Guidance (2002):
 - "The draft guidance recommends certain conservative assumptions that may not be appropriate at a majority of the current 145,000 petroleum releases from USTs. As such, the draft guidance is unlikely to provide an appropriate mechanism for screening the vapor pathway at UST sites."
- Tillman, F.D. and J.W. Weaver, 2005, Review of recent research on vapor intrusion, EPA/600/R-05/106
 - "While caution would require the evaluation of the soil-to-indoor air pathway for all subsurface contamination, there are, in fact, not many cases of proven vapor intrusion documented in the scientific literature. This is particularly true for organic vapors subject to aerobic biodegradation, such as gasoline compounds (petroleum hydrocarbons).



- + The BioVapor model is available from API. It's a free download.
- + Registration is requested for communication of updates and a download count.
- + If you have questions, talk to me or contact API staff.
- + And I acknowledge Tom McHugh and Paul Newberry of GSI who put together the software and user guide.

API website updated February 2012. Navigate www.api.org to Environment, Health & Safety > Soil & Groundwater Research > Vapor Intrusion

BioVapor: Intended Application ■ Improved understanding of Petroleum **Vapor Intrusion** ■ Calculate oxygen concentration / flux ye required to support aerobic S biodegradation ■ Identify important model input parameters and output variables – and their sensitivity Available, free ■ Predict hydrocarbon concentrations in indoor air within a factor of 10 no ■ Site complexity ■ Temporal variability Indoor background

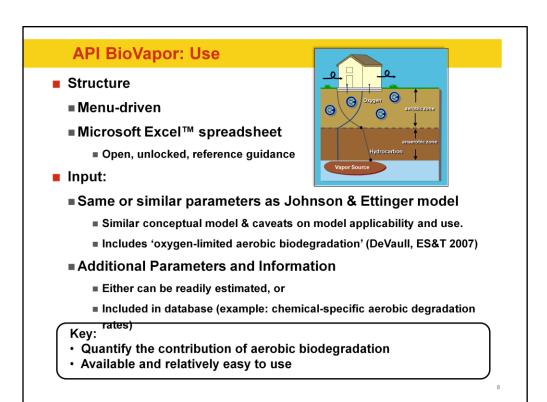
Model Use Comparison

Many models are available ... tradeoffs

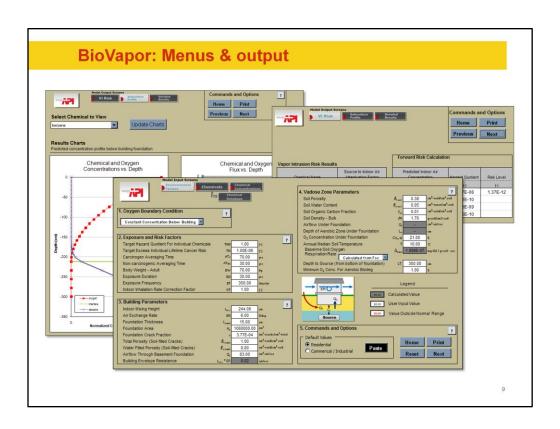
- Complex: numerical, multi-dimensions, time-dependent
 - intensive computation, potentially few users
 - Explore building / foundation interaction details
 - Lateral building / foundation to source separation
 - Can be 'stiff' (numerically unstable)
- Simple: analytical, semi-analytical, one-dimension
 - Very fast calculations
 - Multiple chemicals, oxygen sinks, no problem
 - Sensitivity estimates are realistically possible
 - Insight into trends, sensitivity, key parameters
 - Easily coded and run

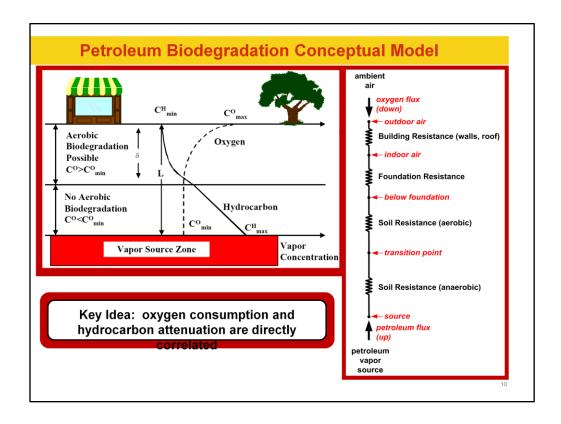
Yao and Suuberg, 2013: A Review of Vapor Intrusion Models, ES&T

2B.7



- + BioVapor is not the only model available, but the intent here was to have a model that was simple-to-use, run, and apply.
- + The model includes relatively simple defined input menus and output tables and plots.
- + If you want to check, the model is open and can be unlocked.
- + Parameters are same as for many implementations of the Johnson and Ettinger model, but the model includes oxygen limited chemical biodegradation.
- + So therefore there are a few more model parameters. These are either easy to estimate, or included in the model database (like degradation rates).





- + The BioVapor conceptual model follows the diagram on the left.
- + It includes a building, a soil layer, and a petroleum vapor source at depth.
- + A shallow aerobic soil layer is included where degradation occurs. If oxygen is limited there is a deeper anaerobic layer where degradation is neglected.
- + The key idea there is that oxygen consumption is directly linked to petroleum biodegradation and attenuation.
- + I've included another conceptual model on the right, as a flow-resistance diagram. As in the other figure we have oxygen at the top and petroleum vapor at the bottom, and reaction of both in the middle. This diagram helps illustrate that the flow resistances for oxygen and other gases, through the building, foundation, and soil, as well as petroleum vapors are substantially similar. So if we have resistance parameters for one chemical, we have or can estimate the parameters for any and all of the gasses or vapors.

Oxygen below Buildings: Basis

- Aerobic Biodegradation
 - Hydrocarbon to Oxygen use ratio: 1:3 (kg/kg)
 - Atmospheric air (21% Oxygen; 275 g/m³ oxygen) provides the capacity to degrade 92 g/m³ hydrocarbon vapors (92,000,000 ug/m³)
- Oxygen below a Foundation: can it get there?
 - Through the foundation
 - Equate to same transport parameters as other VI chemicals
 - Around the foundation edges (bonus)
 - Additional oxygen

Key: Oxygen below a foundation

- · Can oxygen get there?
- Is there enough oxygen to support significant aerobic

biodegradation?

- + In aerobic biodegradation, disappearance of oxygen and hydrocarbons are proportionately related. On a mass basis, this is about a 1 to 3 ratio.
- + Using the concentration of oxygen in air, we can see that there is significant capacity for aerobic petroleum degradation. On a concentration basis, about 92 million micrograms per cubic meter.
- + The question in our conceptual model is whether oxygen can get below the foundation and into the soil.
- + It can go through the foundation (similar to chemical vapors, which move both ways), and it can also go around the edges of a foundation.
- + there are provisions in the model for including both, or conservatively neglecting the airflow around the foundation, either way.

Oxygen in the BioVapor Model

- Three Options:
 - 1. Specify Aerobic depth
 - Measure vapor profile
 - 2. Specify Oxygen concentration under a foundation
 - Measure oxygen
 - 3. Let the model balance hydrocarbon & oxygen consumption
 - Specify vapor source composition (gasoline vapor, etc.)

Key: Estimate or measure hydrocarbon source

- Pick one method; the others are related (and predicted)
- Relatively unique to this model (particularly #3)

1.

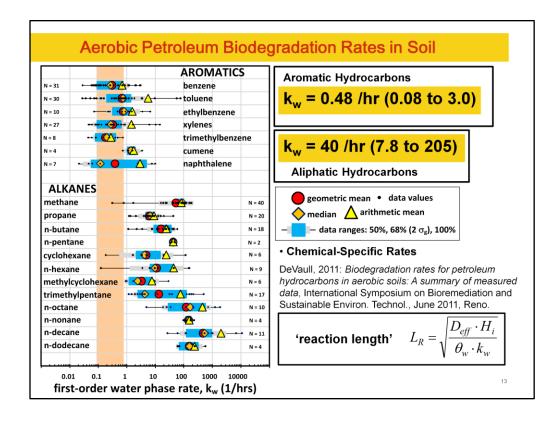
- + Now in the model, oxygen (or the contribution of degradation) can be specified three ways:
- 1) Directly specify the aerobic depth comes from a measurement.
- 2) Specify oxygen concentration under a foundation.

or

3) Specify the source vapor concentration (either measured or conservatively estimated). Then the model estimates the oxygen consumption and the aerobic depth.

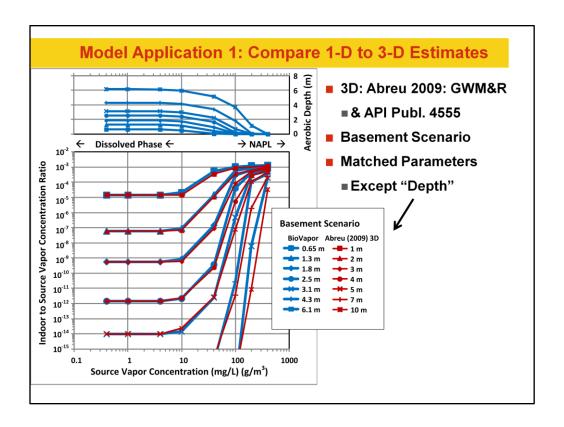
The third method is fairly novel. It means we can conservatively make these estimates based on existing data.

All three of the methods are related in a given scenario. If one oxygen value is specified, the other two are directly related and predicted.



- + Another part of the model is in estimating aerobic biodegradation rates in vadose zone soil.
- +I am showing a figure from a recent presentation this summer at the Battelle conference of 'first-order water phase degradation rates' for a range of petroleum hydrocarbon chemicals. Based on field and laboratory measurements.
- + These values are consistent with what is in the BioVapor model and in the 2007 E&ST paper. Not exactly matching, but consistent.
- + What is shown gives us more granularity on the data more chemical-specific rates, shows comparisons between different chemicals, and distributions of rates across a wide range of empirical data sets.
- + The last point on this slide is that the 'first-order water phase rates' are not applied directly, but are combined in the model with soil-specific parameters (soil moisture) and chemical-specific properties (Henry's law coefficient). In combination with a soil diffusion coefficient, this gives a 'diffusion reaction length' for each chemical in soil.

DeVaull, 2011: Biodegradation rates for petroleum hydrocarbons in aerobic soils: A summary of measured data, International Symposium on Bioremediation and Sustainable Environmental Technologies, June 27-30, 2011, Reno, Nevada



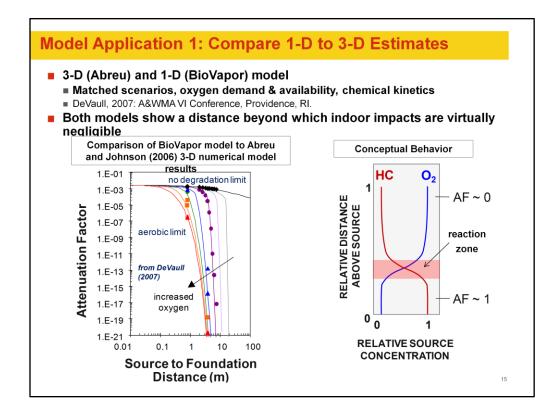
3-D model parameters from:

Lilian D. V. Abreu, Robert Ettinger, and Todd McAlary, 2009: Simulating the Effect of Aerobic Biodegradation on Soil Vapor Intrusion into

Buildings: Evaluation of Low Strength Sources Associated with Dissolved Gasoline Plumes, API Publication 4775, April 2009, American Petroleum Institute, Washington, DC. http://www.api.org/ehs/groundwater/vapor/api-4775.cfm

Lilian D.V. Abreu, Robert Ettinger, and Todd McAlary, Simulated Soil Vapor Intrusion Attenuation Factors Including Biodegradation for Petroleum Hydrocarbons, Ground Water Monitoring & Remediation 29, no. 1/ Winter 2009/pages 105–117.

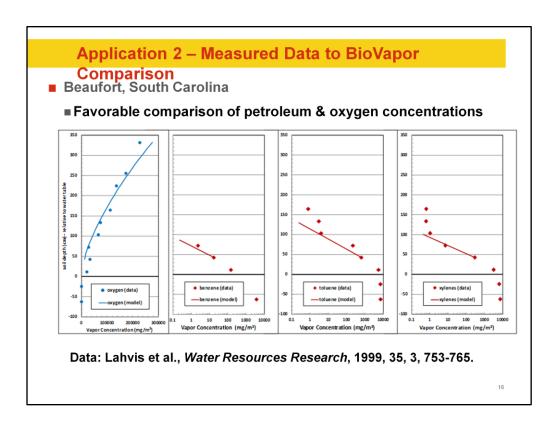
Match BioVapor attenuation at aerobic limit to 3-D Abreu estimates to get effective total depth



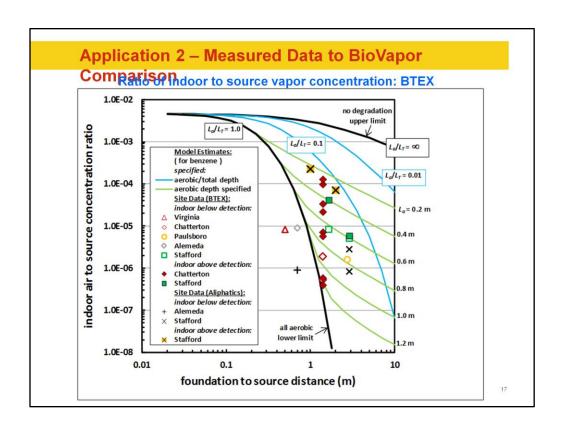
- + I'm going to jump to several applied examples of results from this BioVapor model.
- + The first is a comparison of the 1-D BioVapor model to the 3-D Lillian Abreu model, where we're matching model parameters. The results (plot on the left) are reasonably consistent.
- + The interesting part is that both models show a distance, which we're calling an exclusion distance, beyound which the occurrence of petroleum vapor intrusion is virtually negligible.
- + The cartoon on the right illustrates the soil layer; what we have is a case when the significant reaction zone is far from the building, petroleum vapors are attenuated to negligible levels. And if the source is too close (or too high a concentration) the reaction zone is much shallower and attenuation is less.

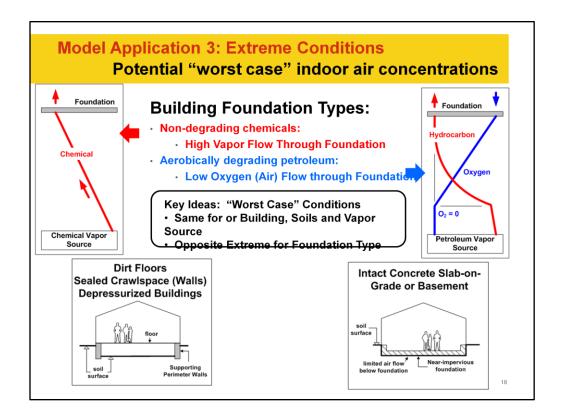
DeVaull, 2007: A&WMA VI Conference, Providence, RI.

Both models show a distance beyond which indoor impacts are virtually negligible DeVaull, G., 2007: Indoor Air Vapor Intrusion: Predictive Estimates for Biodegrading Petroleum Chemicals, Air and Waste Management Association (A&WMA) Specialty Conference: Vapor Intrusion: Learning from the Challenges, Providence, Rhode Island • September 26-28, 2007.



Lahvis, M. A., A. L. Baehr, and R. J. Baker: Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions, *Water Resources Research*, **1999**, 35, 3, 753-765. March.





- This second example is qualitative, and looks at 'worst case' conditions.
- •That is we define reasonable ranges for all the model parameters, then finding the conditions which produces the highest indoor air concentrations.
- We're doing this for 'non-degrading' chemicals (PCE, TCE, etc) and aerobically-degrading chemicals like petroleum.
- The interesting part is where these two case differ, which is in the worst-case building foundation.
- For non-degrading chemicals, worst-case is for foundations which pass the most vapors (low resistance). This would be, typically, a dirt floor, or a dirt floor in a sealed crawlspace.
- •For degradable chemicals, a worst-case foundation keeps oxygen out of the subsurface (high resistance). This is typically an intact concrete foundation.
- So this type of result has implications in site assessment (what types of houses to examine), and, if needed, in mitigation measures.
- •Figure to start: \\houicvfc006\george.devaull\$\Cached\My Documents\VI paper\Screening Level Development\Shell-Internal\tables and files for review: Figure bldg.vsd

Model Application 4: Sensitivity Analysis Is a proposed exclusion distance okay for varied buildings? ■ Base Case 'Exclusion Effective Foundation Airflow (L/min) Distance': 0.1 10 100 ■ 5 ft separation, water-dissolved Indoor Air Benzene Concentration (ug/m³) 10 1 mg/L benzene, 10 mg/L BTEX ■ Robin Davis (2010) Without Biodegradation 0.1 Higher foundation airflow, ■ Higher indoor air concentration 0.001 ■ With Aerobic Biodegradation Soil Layer Higher foundation airflow, 0.000 0.2 0.4 0.6 0.8 1.0 0.1 Lower indoor air concentration Aerobic depth fraction Model His (infrages)(Fie Mation iteal).api.org/vi) Residential default parameters, varied foundation airflow

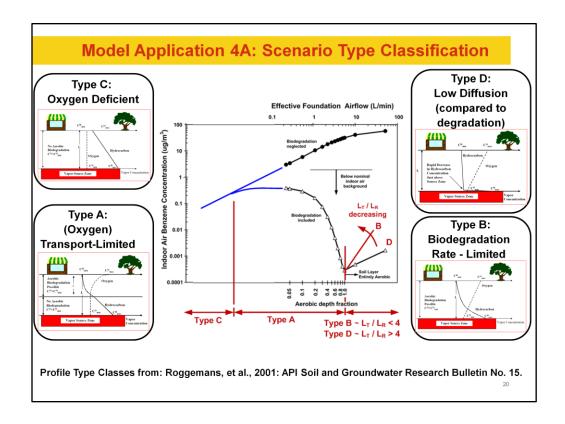
- + This example application is a variation on the last case.
- + We define a base case consistent with proposed 'exclusion criteria'
- + Then look at varied foundation conditions to see if the 'exclusion criteria' are protective (they are, when biodegradation is included).
- + The illustrated trends (including and neglecting biodegradation) are consistent with the prior slide.
- + Up to the case when oxygen is not limited below the building foundation; at this point the soil layer is entirely aerobic, oxygen is not limited, and a more permeable foundation lets more oxygen into the subsurface, but also more chemical into indoor air.
- + This case also illustrates something that can be done with this modeling; we can make estimates for future land development (buildings that are not yet constructed).

Base Case: 5 ft (152.4 cm) of clean overlying soil; Source strength of 1 mg/L benzene, 10 mg/L dissolved TPH (as 1-3-3-3 BTEX).

Re. Davis (2010); Hartman (2010)

Check effect of 1-D foundation resistance (0.2 L/min to 60 L/min).

Query: Under what conditions will oxygen demand be limiting? [foundation]

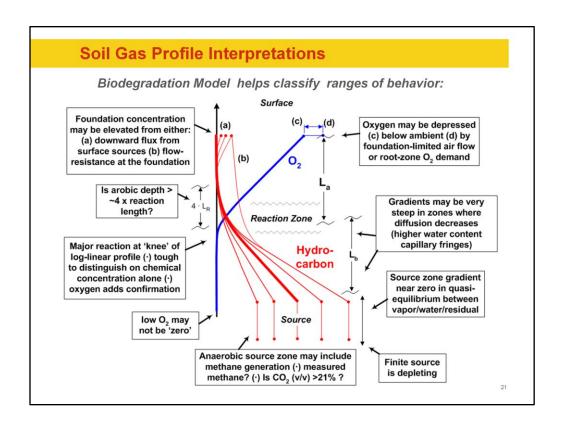


As a final case example,

- + I'm using the plot from the last case, and adding the four 'Scenario Types defined by Sophie Roggemans and others in an API Technical Bulletin.
- + In this example, all four of the case types are included through the range of foundation conditions (defined by foundation airflow).
- + Similar plots and an overlay of these types can be put together for sensitivity analyses on other parameters (such as: varied source vapor concentration or varied source-to-foundation separation distance). On which the varied type classes can also be identified.
- + This illustrates that the model is fairly robust; it can estimate a wide range of cases and further it can tie the identified conditions to values or ranges for key parameters.

Roggemans, et al.; Vadose Zone Natural Attenuation Of Hydrocarbon Vapors: An Empirical Assessment Of Soil Gas Vertical Profile Data,

API Soil and Groundwater Research Bulletin Number 15, American Petroleum Institute, December 2001



Sensitivity Analysis 1:

BioVapor User's Guide:

- "Some required or optional model inputs parameters such as oxygen concentration below the building foundation and baseline soil oxygen respiration rate are not commonly measured during site investigation. ...the user should conduct a sensitivity analysis in order to evaluate the effect of input parameter value uncertainty on the model results"
- "Users of this model should not rely exclusively on the information contained in this document. Sound business, scientific, engineering, and safety judgment should be used in employing the information contained herein."
- Neither API nor any....

Weaver, J. (2012). BioVapor Model Evaluation, For 23rd National Tanks Conference Workshop St. Louis, Missouri, March 18, 2012

Sensitivity Analysis 2:

BioVapor versus Johnson and Ettinger:

- Parameter importance ranking
 - Primary
 - Depth, source concentration
 - Oxygen content, biodegradation rate, foundation air flow, soil moisture content
 - Secondary
 - Air exchange rate, other factors in J&E
 - Results will be more strongly dependent on source depth and strength than analogous J&E, and unless the source is right below foundation, less dependent on building

parameters.

Weaver, J. (2012). BioVapor Model Evaluation, For 23rd National Tanks Conference Workshop St. Louis, Missouri, March 18, 2012.

Picone, S. et al., 2012: Environmental Toxicology and Chemistry, Vol. 31, No. 5, pp. 1042–1052, 2012.

BioVapor Model: Forward Plan

- Use:
 - Improved Understanding, Oxygen Requirements, Sensitivity
 - Baseline Site Screening, Sample Plan Development, Training
 - What-if Analysis (foundation / no foundation, etc.)
 - It is .. a model
- Review and Plans:
 - Validation and sensitivity analysis (EPA OUST, ORD)
 - EPA: recoding
 - API Workshop: Interactive Demonstration / Case Studies
 - Fixes and Updates: Very Few 'Bugs' or Model Issues to Date

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Finally

- + I've gone through an introduction for this Biovapor model and shown a few case examples.
- + Currently EPA (Jim Weaver) is looking at a sensitivity analysis of the model; a contractor for EPA has previously validated the math.
- + We have not run the model; API does have a workshop which includes hands-on running through a number of case examples.
- + So far on the first model revision; no significant bugs or model issues have been identified.

American Petroleum Institute BioVapor Model

Download at: www.api.org/pvi
OR Navigate www.api.org to
Environment, Health & Safety > Soil & Groundwater Research > Vapor Intrusion
Free, asks for registration information (update notification)

Questions (API): Roger Claff, claff@api.org, 202-682-8399; Bruce Bauman, Bauman@api.org, 202-686-8345 Acknowledgements: Tom McHugh, Paul Newberry, GSI Environmental, Houston.

2

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Summary

25 minutes

Workshop Agenda

- Welcome, Introductions, Safety Issues
- Update on ITRC VI Workgroup
- Update on EPA OUST
- BioVapor and other models; and Introduction to Exclusion Criteria
- Evaluating the Vapor Intrusion Pathway Studies
- Regulatory updates effecting sampling and Analysis
- Case Studies/ Lessons
- Summary

State Summary

■ 35 States with Vapor Intrusion Guidance

Screening Values:

media values range

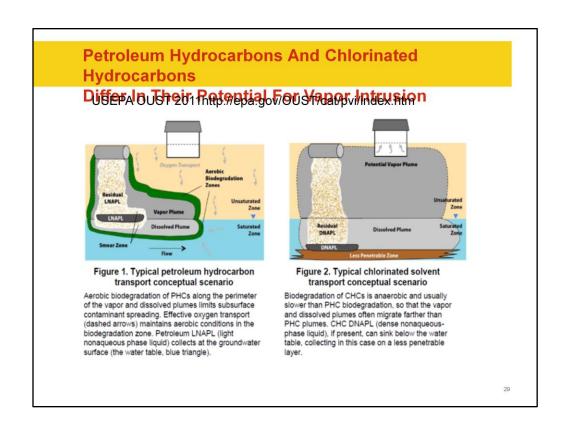
indoor air 0.084 to 4.98 ug/m³ 140x

groundwater 2.4 to 3500 ug/L 1500x

shallow soil gas 3.1 to 190,000 ug/m³ 61,000x

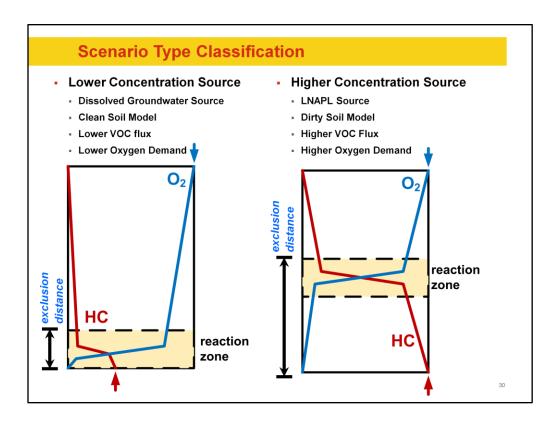
Clearly, a lot of variability

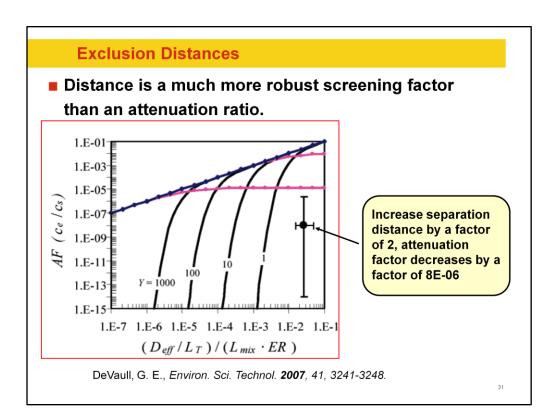
Eklund, B., L. Beckley, V. Yates, T. E. McHugh, Overview of State Approaches to Vapor Intrusion, Remediation, Autumn 2012, 7-20.



USEPA OUST is developing a compendium of information about petroleum vapor intrusion (PVI), available at www.epa.gov/oust.

Contact: white.hal@epa.gov or 703-603-7177





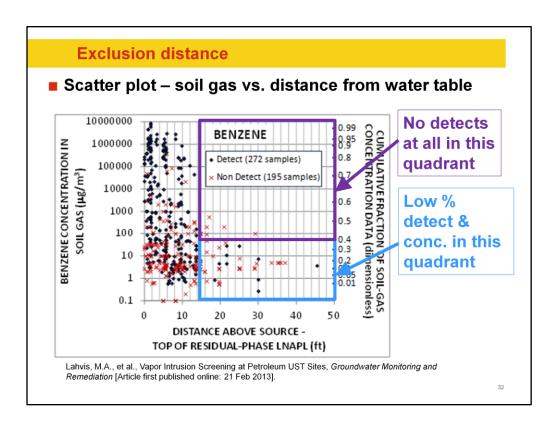


Figure 6. Plot of benzene concentrations in soil gas versus distance above a LNAPL hydrocarbon source. Non-detect values are plotted at the reporting limit. The plot includes 467 soil-gas samples collected at 73 UST sites and 204 vertical sampling locations. The cumulative fraction of all (detect and non-detect) benzene soil-gas concentrations is noted on the right vertical axis.

Petroleum Vapor Exclusion Distances

- 23 states Range: 5 ft to 100 ft dissolved phase.
 - **■** Eklund, et al. 2012
- Site Vapor Database review:
 - Dissolved: 0 feet; 5 ft;
 - ■LNAPL: 15 ft
 - Lahvis et al., GWMR, online: 21 Feb 2013.
- Proposed:
 - LNAPL: 15 to 30 feet
 - Dissolved phase: somewhat less
 - Added factors of conservatism: ???

Inclusion Distances

■ USEPA: An Approach for Developing Site-Specific Lateral and Vertical Inclusion Zones, J. T. Wilson, J. W. Weaver, H. White, National Risk Management Research Laboratory, Cincinnati, OH, EPA/600/R-13/008. December 2012.

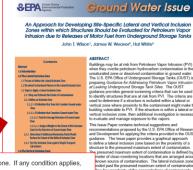


Table 4. Example conditions for a structure to be included in the Vertical Inclusion Zone. If any condition applies, the structure is in the Vertical Inclusion Zone.

These conditions are provisional and are for illustration purposes only. They are based on Davis (2009) and Cal EPA (2012). At such time as U.S. EPA Office of Underground Storage Tanks (OUST) issues the *Guidance for Addressing Petroleum Vapor Intussion at Leaking Underground Storage Tank Siltes*, the conditions for vertical separation in the Guidance will supersede the conditions in this table.

Media	Benzene Concentration	TPH Concentration	Vertical Separation Distance*		
Soil (mg/kg)	≤10	≤250		<6	
	>10 (LNAPL)	>250 (LNAPL)		<15	\
Groundwater (μg/L)	≤5,000	≤30,000		<6	
	>5,000 (LNAPL)	>30,000 (LNAPL)		<15	

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Petroleum Vapor Intrusion

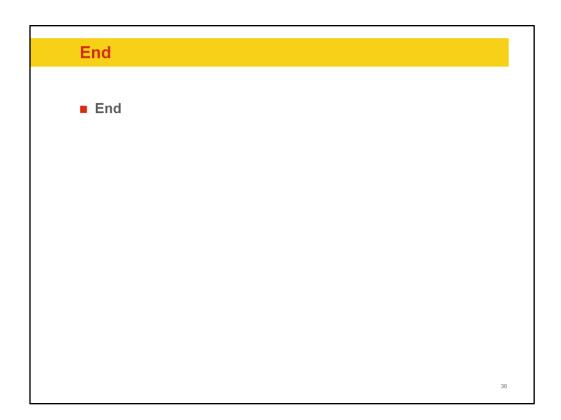
- USEPA OUST PVI Guidance
 - Exclusion distances
 - Biodegradation Modeling
- USEPA OSWER VI Guidance
 - Not USTs
- Each to WH OMB October 2014
 - Not too far off ... 90 days or so

References:

USEPA, 2013: Evaluation Of Empirical Data To Support Soil Vapor Intrusion Screening Criteria For Petroleum Hydrocarbon Compounds, U.S. Environmental Protection Agency, Office of Underground Storage Tanks, Washington, DC. January. EPA 510-R-13-001.

USEPA, 2012: An Approach for Developing Site-Specific Lateral and Vertical Inclusion Zones, J. T. Wilson, J. W. Weaver, H. White, National Risk Management Research Laboratory, Cincinnati, OH. December. EPA/600/R-13/008.

Lahvis, M.A., et al., Vapor Intrusion Screening at Petroleum UST Sites, Groundwater Monitoring and Remediation [Article first published online: 21 Feb 2013].



Oxygen Blow Buildings

- **■** Summary:
- Even modest oxygen transport yields sufficient aerobic biodegradation in most cases
- Oxygen demand (from high hydrocarbon source) can deplete oxygen below building foundations and capping

layers.

- Very Large Buildings ?
 - Refinery site: Perth, Australia (Patterson and Davis, 2009)
 - Measured Depleted Oxygen below Building Center
 - 35 to 40 g/m³ hydrocarbon vapor above LNAPL at 10 feet depth

Two key factors – both needed:

- 1. Limited oxygen transport below the foundation &
- 2. High oxygen demand

Conclusion: Introduction Overview

Subsurface source to indoor air vapor intrusion Actual Issues: Petroleum VI

- Occur very infrequently
- Occur (sometimes) with:
 - Very large releases of petroleum to the subsurface
 - Petroleum LNAPL very close, in contact with, or inside a basement or utility connected to an enclosure