Including Volatilization in Risk-Based Surficial Soils Criteria

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26th National Tanks Conference & Exposition

September 11-13, 2018 | Louisville, KY.

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June 2018

Outline and Overview

- Soil Screening Levels
  - Application
  - Background Information
- Model Revisions
  - Depletion Factor
  - Residual Phase
- Data Comparisons
  - Pure Chemicals, Mixtures
  - With and Without Residual Phase
- Example Screening Levels
  - Benzene / Petroleum in Soil

What are Surficial Soil Criteria?

Chemical Concentrations in Soil, at and below which Risks and Hazards are Negligible

- **Includes:**
  - **Current Conditions**
  - **Remediation Targets**
  - **Potential future conditions**
    - **such as excavated soils (current risk versus potential future risk)**

'Human Health Risk-Based'

Applications:

Undisturbed: 0 to 5 cm

Tilled / root depth: 0 to 45 cm

typical excavation depth (buried utilities, basements)

Risk-Based Soil Criteria

- **Surficial Soil Screening Levels – Available Examples**
  - **USEPA Regional Screening Levels and ASTM E1739 'RBCA'**
  - **Chronic (Long-Term) Exposure Assumptions (25 ~ 70 yrs)**
  - **Summed Exposure: Soil Ingestion, Dermal Uptake, Volatile & Dust Inhalation**
  - **Applied: Current Use or Potential Future Use**

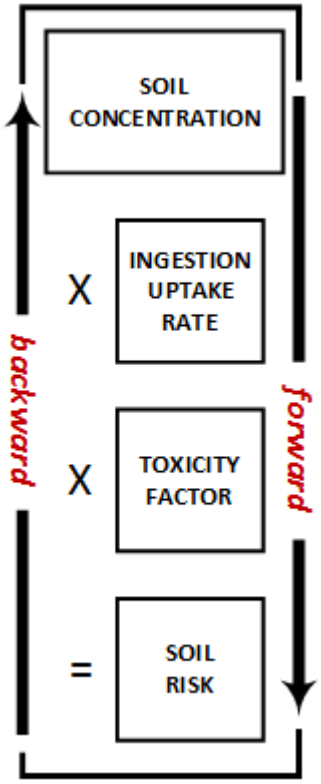
Look-up Tables, Calculators, Software, etc. …

USEPA 'Regional Screening Levels'
http://www.epa.gov/risk/risk-based-screening-table-generic-tables

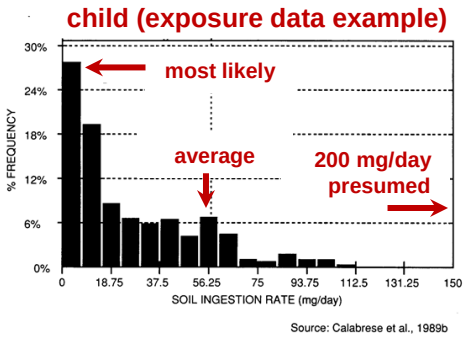
Observations:

- **Criteria for many volatile chemicals is dominated by 'inhalation of vapors from soil'.**
- **For direct ingestion, the chemical is presumed present at the initial concentration for the entire exposure duration.**

Soil Screening Levels – Conservatism & Protectiveness



- **Soil Concentration**
  - Choose peak versus area average
  - No depletion over exposure time
- **Exposure: Soil Uptake**
  - Long-term (26 years) and frequent (350 days/year)
  - Choose upper range uptake (but low frequency of high exposure)
- **Toxicity Factors**
  - Sensitive sub-populations, sensitive effects, hi-to-low extrapolation
  - Applied safety factors / upper bound confidence
    - 2 to 5 orders of magnitude below no-effects levels or point-of-departure (benzene, toluene, ethylbenzene, xylenes)

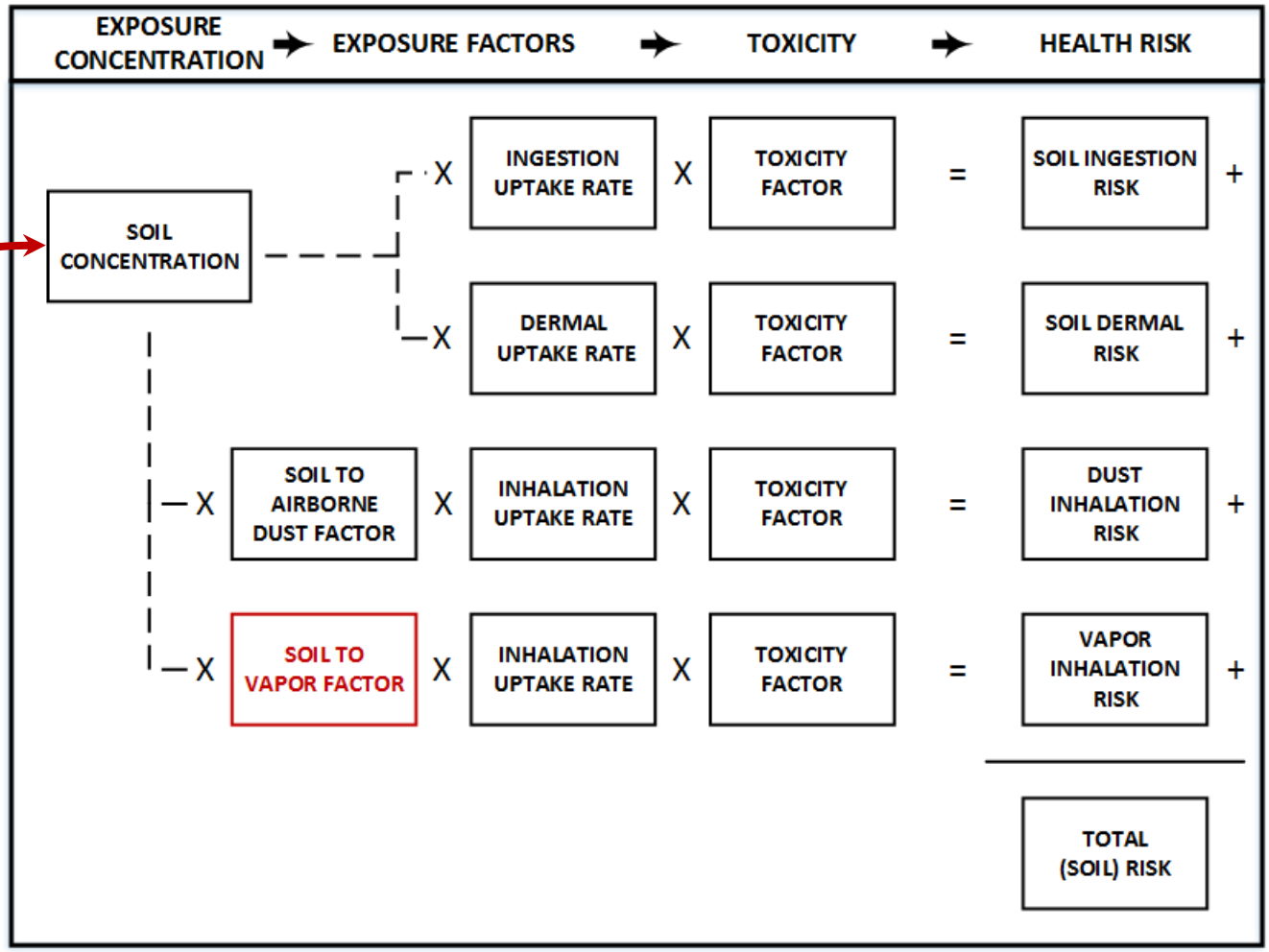


- Conservative but uncertain
- Parameter assumptions tend to compound the conservatism

Overall $1 - [\,(1-0.95)\cdot(1-0.95)\cdot(1-0.95)\cdot(1-0.95)\,] = 0.999994$

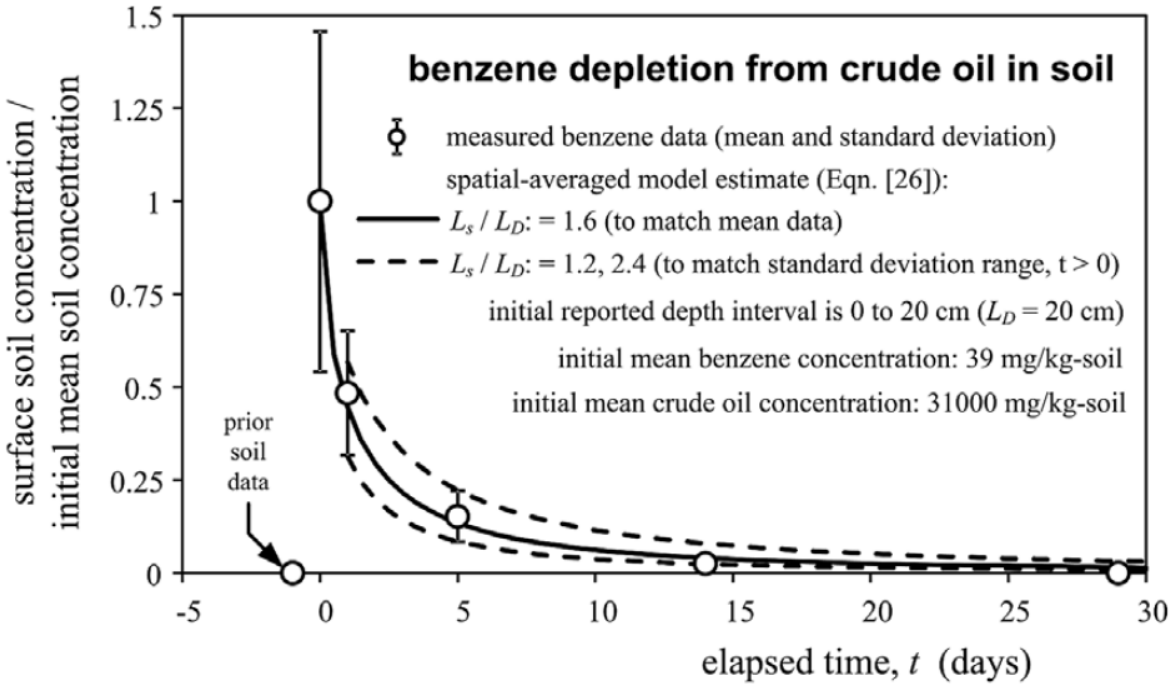
Soil Criteria Calculation

- **Multiple Summed Exposure Routes (As Applied)**



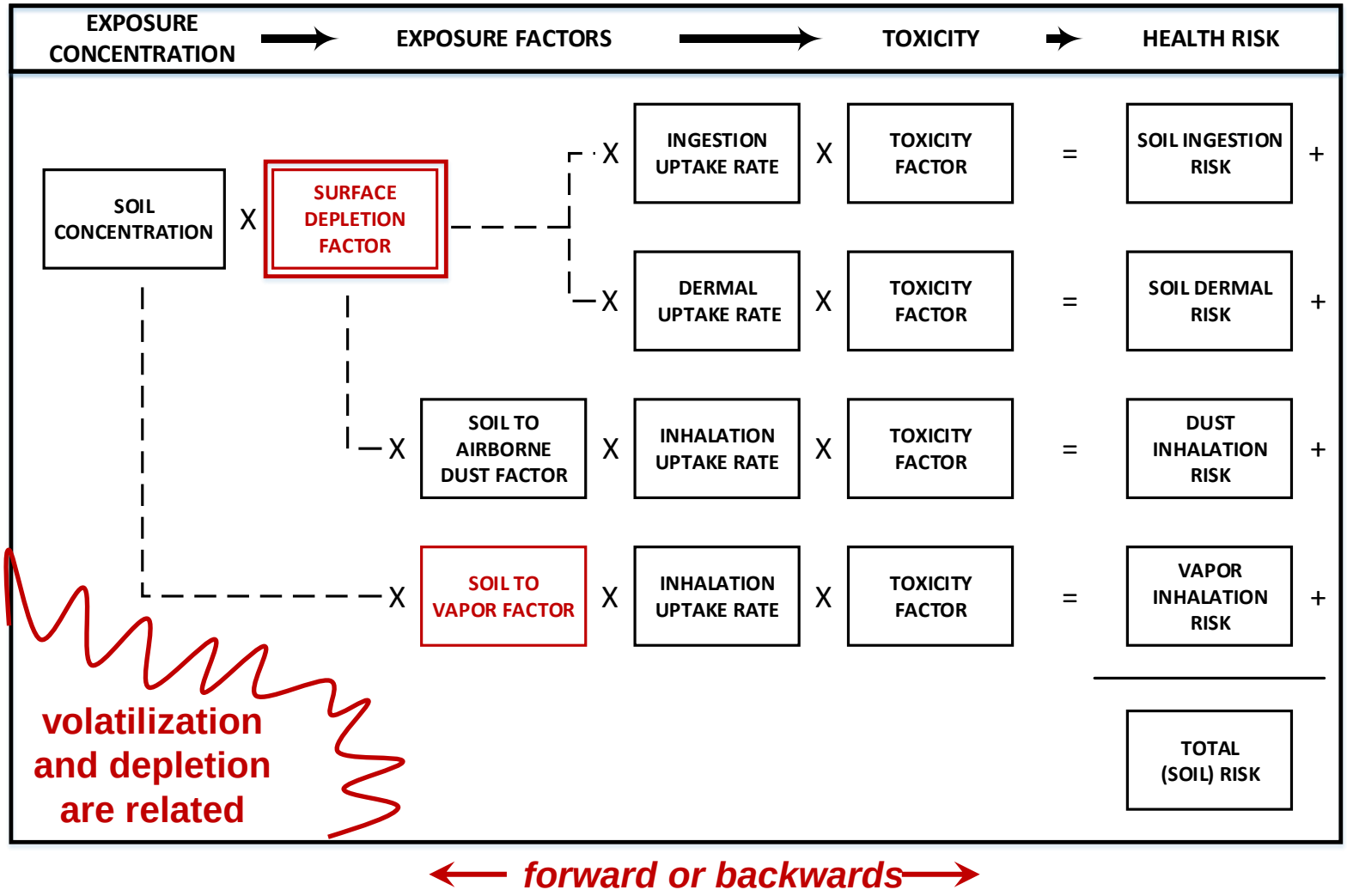
Measured Depletion - example

- 3200 L Petroleum Crude Oil – Niagara (Michigan, USA)
- 15 m x 15 m area, mixed to 20 cm deep (3% oil in soil)
- Benzene
  - Initial: 39 mg/kg, non-detect (< 0.005 mg/kg) after two months



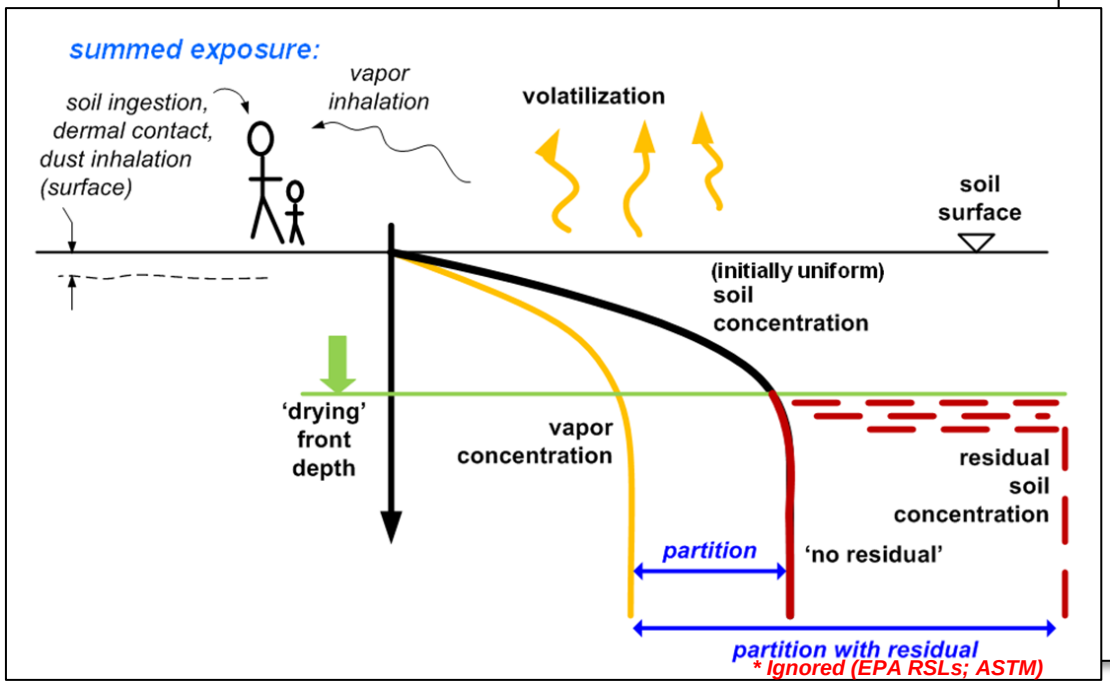
Soil Criteria Calculation – Modify and Revise

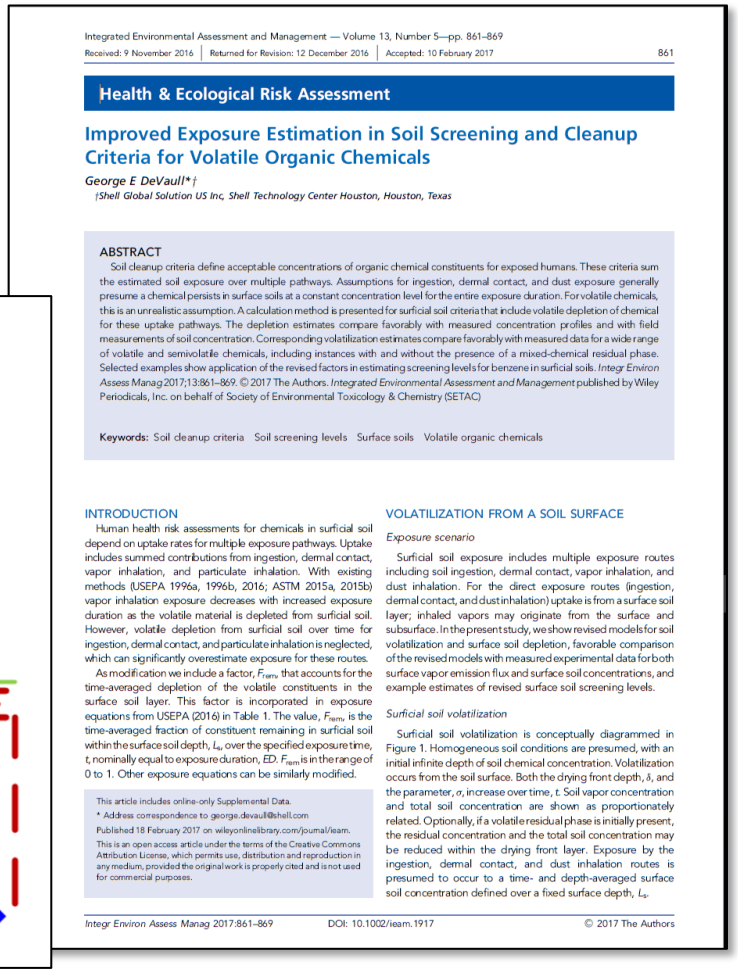
- **Include Soil Depletion Factor for Volatile Chemicals**



Physical Model: Surficial Soil Exposure

- **Initial concentration from surface downward**
- **As vapors evolve (over time), 'drying front' descends**





Integrated Environmental Assessment and Management — Volume 13, Number 5—pp. 861–869
Received: 9 November 2016 | Returned for Revision: 12 December 2016 | Accepted: 10 February 2017 861

Health & Ecological Risk Assessment

Improved Exposure Estimation in Soil Screening and Cleanup Criteria for Volatile Organic Chemicals

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ABSTRACT
Soil cleanup criteria define acceptable concentrations of organic chemical constituents for exposed humans. These criteria sum the estimated soil exposure over multiple pathways. Assumptions for ingestion, dermal contact, and dust exposure generally presume a chemical persists in surface soils at a constant concentration level for the entire exposure duration. For volatile chemicals, this is an unrealistic assumption. A calculation method is presented for surficial soil criteria that include volatile depletion of chemical for these uptake pathways. The depletion estimates compare favorably with measured concentration profiles and with field measurements of soil concentration. Corresponding volatilization estimates compare favorably with measured data for a wide range of volatile and semivolatile chemicals, including instances with and without the presence of a mixed-chemical residual phase. Selected examples show application of the revised factors in estimating screening levels for benzene in surficial soils. *Integr Environ Assess Manag* 2017;13:861–869. © 2017 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals, Inc. on behalf of Society of Environmental Toxicology & Chemistry (SETAC)

Keywords: Soil cleanup criteria Soil screening levels Surface soils Volatile organic chemicals

INTRODUCTION

Human health risk assessments for chemicals in surficial soil depend on uptake rates for multiple exposure pathways. Uptake includes summed contributions from ingestion, dermal contact, vapor inhalation, and particulate inhalation. With existing methods (USEPA 1996a, 1996b, 2016; ASTM 2015a, 2015b) vapor inhalation exposure decreases with increased exposure duration as the volatile material is depleted from surficial soil. However, volatile depletion from surficial soil over time for ingestion, dermal contact, and particulate inhalation is neglected, which can significantly overestimate exposure for these routes.

As modification we include a factor, F_{rem}, that accounts for the time-averaged depletion of the volatile constituents in the surface soil layer. This factor is incorporated in exposure equations from USEPA (2016) in Table 1. The value, F_{rem}, is the time-averaged fraction of constituent remaining in surficial soil within the surface soil depth, L_s, over the specified exposure time, t, nominally equal to exposure duration, ED. F_{rem} is in the range of 0 to 1. Other exposure equations can be similarly modified.

This article includes online-only Supplemental Data.
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Published 18 February 2017 on wileyonlinelibrary.com/journal/ieam.

VOLATILIZATION FROM A SOIL SURFACE

Exposure scenario

Surficial soil exposure includes multiple exposure routes including soil ingestion, dermal contact, vapor inhalation, and dust inhalation. For the direct exposure routes (ingestion, dermal contact, and dust inhalation) uptake is from a surface soil layer; inhaled vapors may originate from the surface and subsurface. In the present study, we show revised models for soil volatilization and surface soil depletion, favorable comparison of the revised models with measured experimental data for both surface vapor emission flux and surface soil concentrations, and example estimates of revised surface soil screening levels.

Surficial soil volatilization

Surficial soil volatilization is conceptually diagrammed in Figure 1. Homogeneous soil conditions are presumed, with an initial infinite depth of soil chemical concentration. Volatilization occurs from the soil surface. Both the drying front depth, δ, and the parameter, σ, increase over time, t. Soil vapor concentration and total soil concentration are shown as proportionately related. Optionally, if a volatile residual phase is initially present, the residual concentration and the total soil concentration may be reduced within the drying front layer. Exposure by the ingestion, dermal contact, and dust inhalation routes is presumed to occur to a time- and depth-averaged surface soil concentration defined over a fixed surface depth, L_s.

Details:

DeVaull, GE. Improved Exposure Estimation in Soil Screening and Cleanup, Criteria for Volatile Organic Chemicals, Integrated Environmental Assessment and Management. 13, 5, 2017, 861–869. https://setac.onlinelibrary.wiley.com/doi/10.1002/ieam.1917 (open access)

Math

- **Vapor in Soil:**

$$\frac{1}{R_{a,i}} \cdot \frac{\partial c_{a,i}}{\partial t} = D_{eff,i} \cdot \frac{\partial^2 c_{a,i}}{\partial z^2}$$

air concentration

distance

air / soil partition

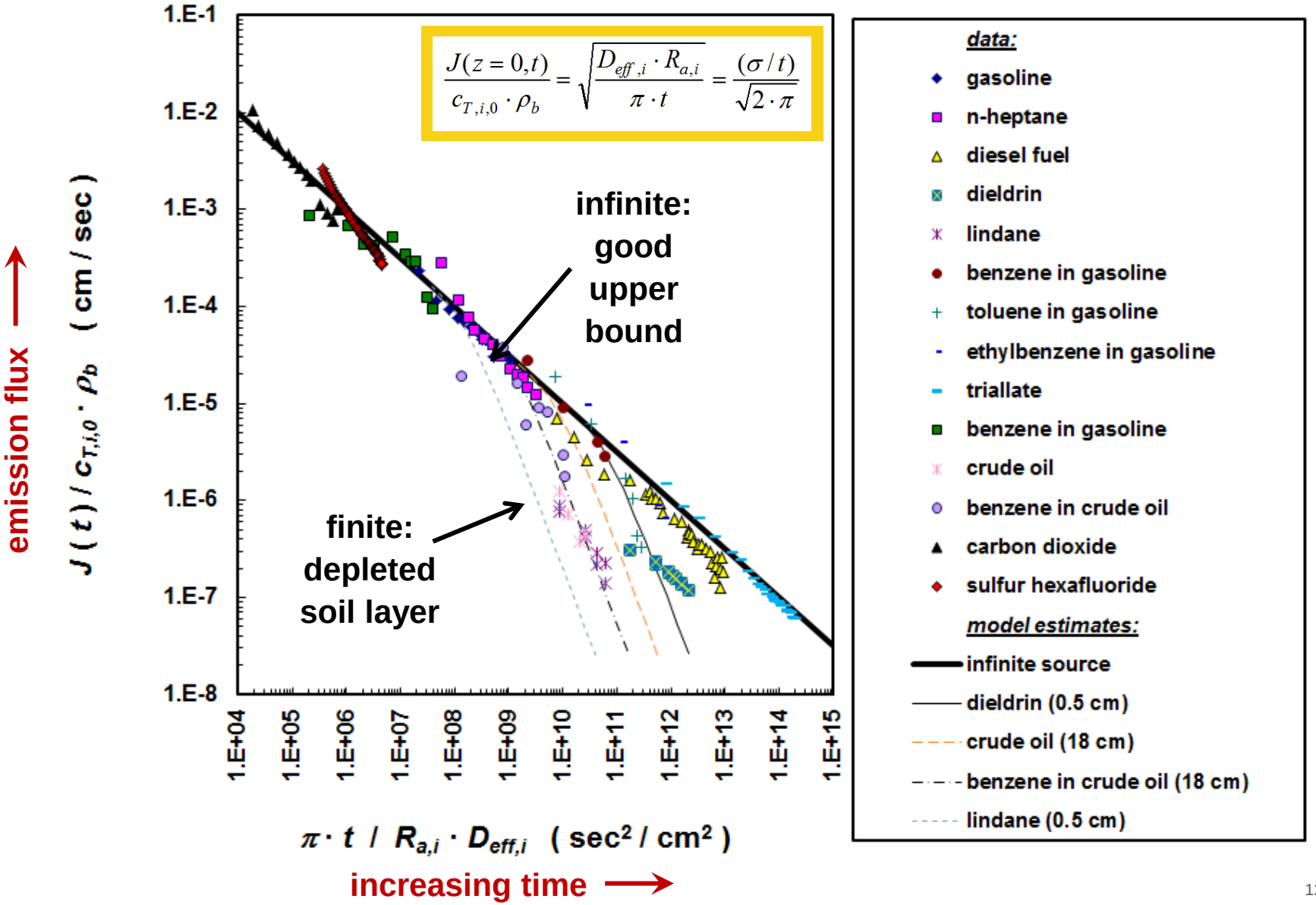
time

effective diffusion coefficient in soil

- **Solve:**
  - **Uniform finite soil profile, porous media, specified soil parameters**
- **Get estimates of instantaneous and time-averaged:**
  - **Surface Emission Flux**
  - **Soil Concentration Profiles**
- **Compare to Measured Data**
  - **Model equations, data comparisons:**

DeVaull, GE. Improved Exposure Estimation in Soil Screening and Cleanup, Criteria for Volatile Organic Chemicals, Integrated Environmental Assessment and Management. 13, 5, 2017, 861–869. https://setac.onlinelibrary.wiley.com/doi/10.1002/ieam.1917 (open access)

Volatilization: Surface Flux model to data

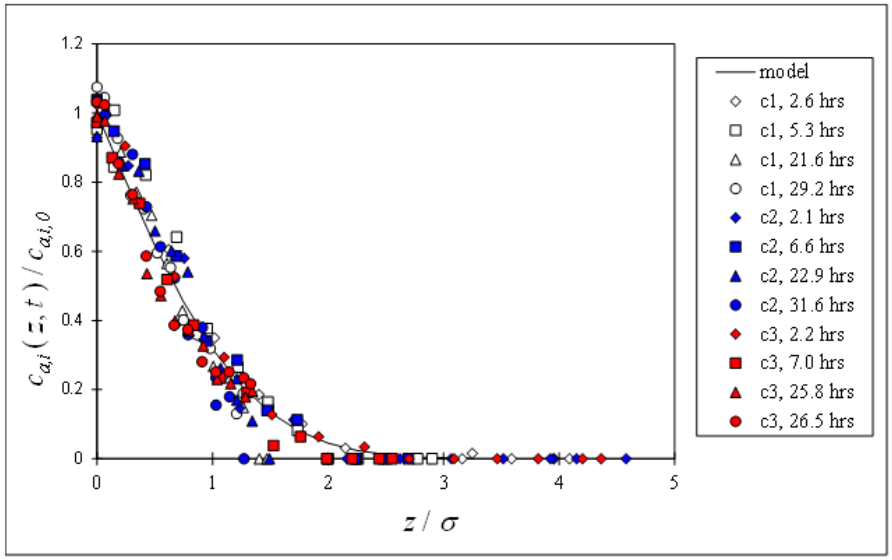


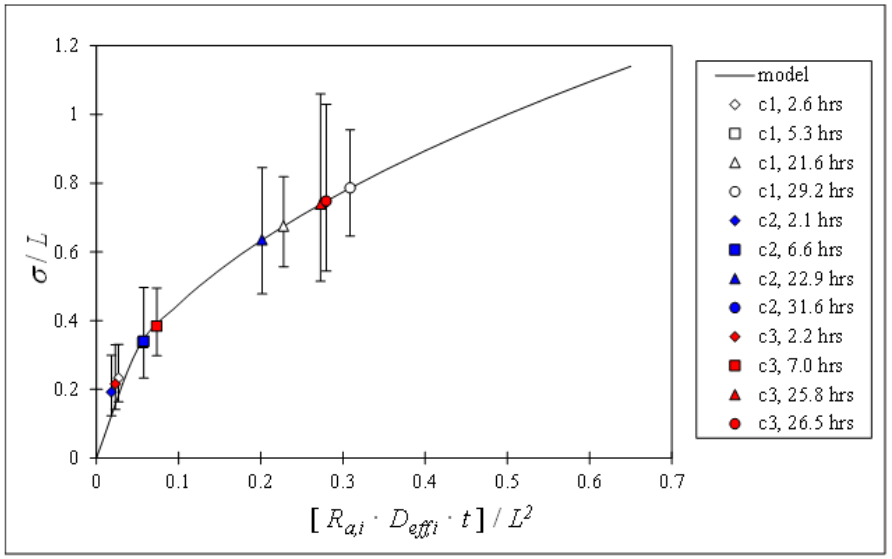
Soil Concentrations: Profile

- **Measured concentration profiles in a soil column**
  - **Gas (SF_6) diffusion into the top of a uniform soil-packed column**
  - **Measure profile & penetration depth is well predicted by parametric estimates:**

$$\frac{c_{a,i}(z,t)}{c_{a,i,0}} = 1 - \mathrm{erf}\left(\frac{z}{\sqrt{2}\cdot\sigma}\right) \quad \text{with} \quad \sigma = \sqrt{2\cdot R_a \cdot D_{eff}\cdot t} = \sqrt{2\cdot\frac{\theta_a^{\,7/3}}{\theta_T^{\,2}}\cdot D_{air}\cdot t}$$

$$R_{a,i} = c_{a,i} / c_{T,i}\cdot\rho_b$$

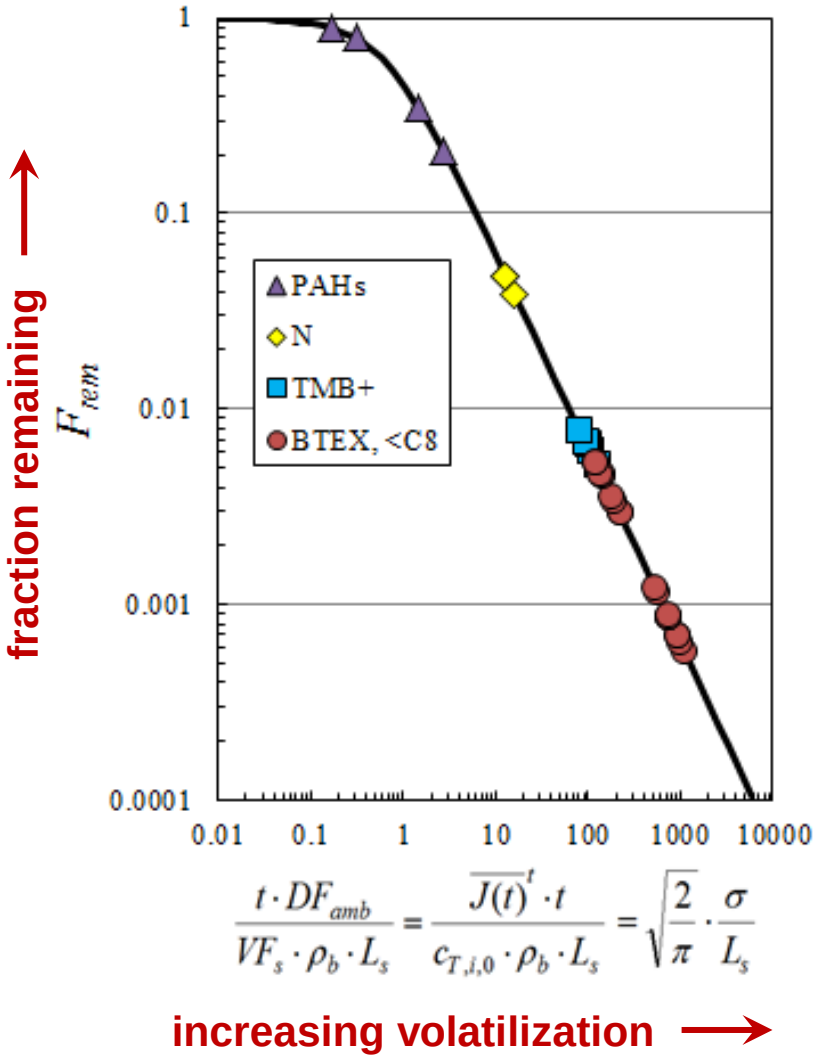




Volatilization & Depletion Are Directly Related

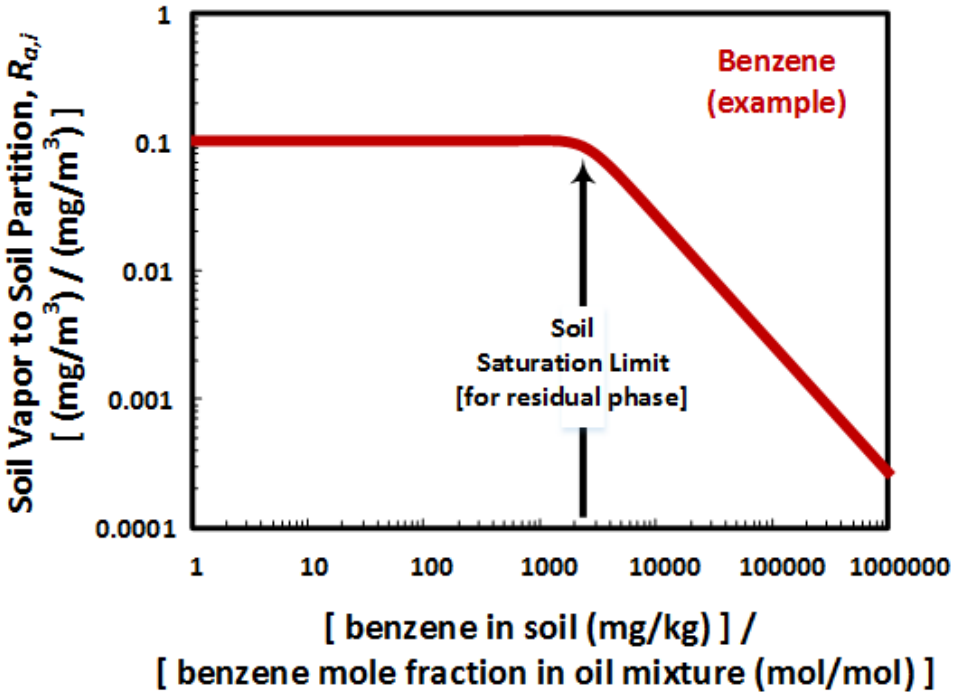
- VF_s (volatilization factor)
  - directly from USEPA Regional Screening Level Tables
  - (and other scenario parameters)
- F_{rem} (fraction remaining)
  - For infinite depth of soil contamination, L_s = 5 cm surface depth
  - Selected chemicals indicated

Illustrates potential omissions in the existing screening methods



Partitioning: air to soil, $R_{a,i}$: possible residual phase

- Low concentration soil phases: (vapor, moisture, soil-sorbed)
- Higher soil concentrations: plus a residual (oil) phase
  - Saturated soil vapor, air to soil partitioning is not constant
  - Mixture effects (Raoult's Law)



- With residual present:
  - Lower volatilization rates
  - Slower soil depletion
- Include residual in calculations

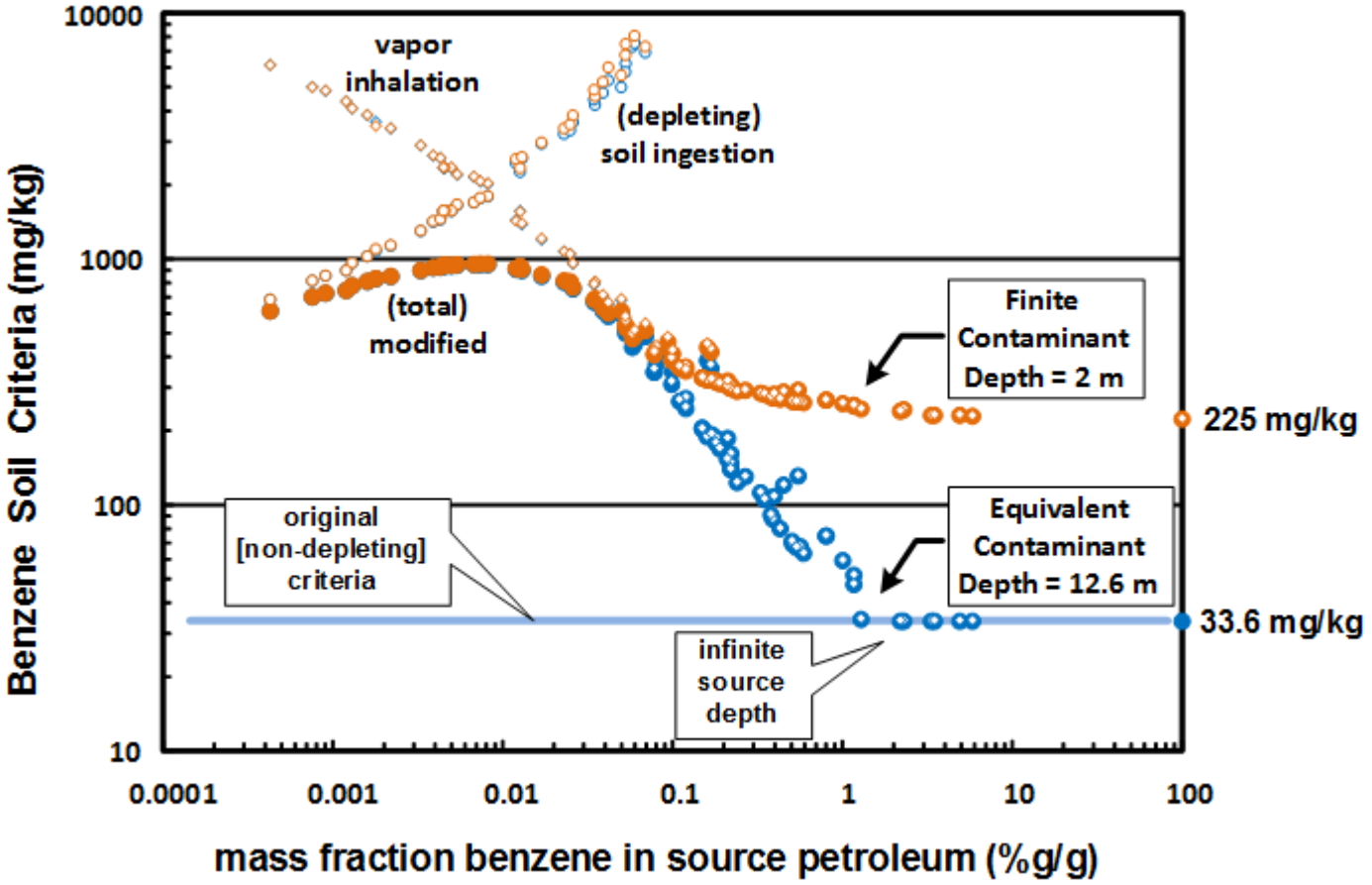
Example: Benzene in Petroleum Hydrocarbons

- Estimate screening levels for benzene in soil
  - Includes Potential Residual Oil Phase
  - Exposure for benzene is predominately summed soil ingestion and vapor inhalation

- Examine the effect of benzene depletion
  - Baseline (no depletion, no residual)
  - With depletion from surface soils,
  - Finite contamination depths, and
  - Petroleum hydrocarbon mixtures (products, crudes, condensates)
    - range: 4.3 mg/kg to 5.8% g/g benzene in oil

Benzene criteria; mass limit

- **Long-term exposure (risk = 1E-5, age-adjusted)**
  - **Contamination depths (infinite & 2 m)**



Summary

showed

- Modifications to surficial soil exposure estimates
  - Favorable comparisons to data
  - More realistic treatment for volatile chemicals

observations

- Over-conservatism in existing screening criteria
  - Varied contributions of presumed exposure pathways

model application

- Published technical paper
- In progress (API) spreadsheet model - planned for distribution

further efforts

- Examples shown
  - Sensitivity evaluations
  - Other exposure scenarios (including sub-chronic)
  - Biodegradation not included

End

Questions and Answers

Thank you

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