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.

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, $F_{\text{rem}}$, 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, $F_{\text{rem}}$, 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, $ED$. $F_{\text{rem}}$ is in the range of 0 to 1. Other exposure equations can be similarly modified.

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, $\delta$, and the parameter, $\sigma$, 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, $L_s$. 
### Table 1. Equations for estimating screening levels for surficial soil as modified from USEPA (2016) to include $F_{rem}$

| Noncancer: Residential | Carcinogenic: Residential |
|------------------------|---------------------------|
| **Ingestion**          |                           |
| $S_{L_{res-soil-ing-c}} = \frac{\text{THQAT}_{\text{ing, c}}}{\text{BW} \cdot \text{RD}_{\text{soil}} \cdot \text{Frem}}$ | $S_{L_{res-soil-ca-ing}} = \frac{\text{TRAT}_{\text{ing, c}}}{\text{MW}_{o} \cdot \text{IUR}_{\text{ing, c}}}$ |
| $S_{L_{res-soil-ing-a}} = \frac{\text{THQAT}_{\text{ing, a}}}{\text{BW} \cdot \text{RD}_{\text{soil}} \cdot \text{Frem}}$ | $I_{FS_{adj}} = \frac{\text{EF}_{\text{pred}} \cdot \text{ED} \cdot \text{IRS}_{\text{pred}} + \text{EF}_{\text{MRI}} \cdot \text{ED} \cdot \text{IRS}_{\text{MRI}}}{\text{BW} \cdot \text{MW}_{o}}$ |
| **Dermal**             |                           |
| $S_{L_{res-soil-der-c}} = \frac{\text{THQAT}_{\text{der, c}}}{\text{ED_{r}} \cdot \text{RD}_{\text{soil}} \cdot \text{Frem}}$ | $S_{L_{res-soil-ca-der}} = \frac{\text{TRAT}_{\text{der, c}}}{\text{MW}_{o} \cdot \text{IUR}_{\text{der, c}}}$ |
| $S_{L_{res-soil-der-a}} = \frac{\text{THQAT}_{\text{der, a}}}{\text{ED_{r}} \cdot \text{RD}_{\text{soil}} \cdot \text{Frem}}$ | $D_{FS_{adj}} = \frac{\text{EF}_{\text{pred}} \cdot \text{SD} \cdot \text{IRS}_{\text{pred}} + \text{EF}_{\text{MRI}} \cdot \text{SD} \cdot \text{IRS}_{\text{MRI}}}{\text{BW} \cdot \text{MW}_{o}}$ |
| **Inhalation**         |                           |
| $S_{L_{res-soil-inh-c}} = \frac{\text{THQAT}_{\text{inh, c}}}{\text{TRAT}_{\text{inh, c}} \cdot \text{ET}_{\text{inh}} \cdot \text{Frem}}$ | $S_{L_{res-soil-ca-inh}} = \frac{\text{TRAT}_{\text{inh, c}}}{\text{MW}_{o} \cdot \text{IUR}_{\text{inh, c}}}$ |
| $S_{L_{res-soil-inh-a}} = \frac{\text{THQAT}_{\text{inh, a}}}{\text{TRAT}_{\text{inh, a}} \cdot \text{ET}_{\text{inh}} \cdot \text{Frem}}$ | $D_{FS_{adj}} = \frac{\text{EF}_{\text{pred}} \cdot \text{SD} \cdot \text{IRS}_{\text{pred}} + \text{EF}_{\text{MRI}} \cdot \text{SD} \cdot \text{IRS}_{\text{MRI}}}{\text{BW} \cdot \text{MW}_{o}}$ |
| **Total**              |                           |
| $S_{L_{res-soil-tot-c}} = \frac{1}{\text{TRAT}_{\text{ing, c}} \cdot \text{ET}_{\text{inh}} \cdot \text{ET}_{\text{inh}} \cdot \text{Frem}}$ | $S_{L_{res-soil-tot-a}} = \frac{1}{\text{TRAT}_{\text{ing, a}} \cdot \text{ET}_{\text{inh}} \cdot \text{ET}_{\text{inh}} \cdot \text{Frem}}$ |

Descriptions and values are available in USEPA (1996a, 1996b, 2016), ASTM (2015a, 2015b), and the Supplemental Data. Parameter definitions for residential exposure: $SL$ (mg/kg), screening level for soil; subscripted: a, adult; c, child; ca, carcinogen; der, dermal route; ing, ingestion route; inh, inhalation route; nc, noncancerous; res, residential; tot, summed total exposure. $ABS_{a}$, dermal relative absorption factor; $AF$, skin adherence factor (mg/cm²); $AT_{r}$, residential averaging time ($AT_{r} = ED$ for noncarcinogens, $AT_{r} = LT$ for carcinogens); $BW$, body weight (kg); $CSF_{o}$, oral carcinogenic slope factor (1/(mg/kg day)); $DFS_{adj}$, age-adjusted soil dermal factor (mg/kg); ED, exposure duration (years); $EF_{r}$, residential exposure frequency (days/year); $EF_{max}$, residential exposure frequency to soil (child) (days/year); $EF_{max}$, residential exposure frequency to soil (adult) (days/year); $ED_{r}$, residential exposure time (h/day); $F_{rem}$, time- and depth-averaged fraction of initial chemical remaining (0–1); $GIABS$, gastrointestinal absorption factor, relative to the applied toxicity data; $I_{FS_{adj}}$, age-adjusted soil ingestion factor (mg/kg); IRS, soil ingestion rate (mg/day); $IUR_{r}$, inhalation unit risk; LT, exposure lifetime (years) normalized for carcinogenic toxicity factors; $PEF_{w}$, wind particulate emission factor (m³ air/kg soil); RFC, inhalation reference concentration (mg/m³); $RD_{soil}$, oral reference dose (mg/kg day), chemical specific; $SA$, exposed skin surface area (cm²/day); THQ, target hazard quotient (−); $TR_{r}$, target cancer risk (−); $VF_{aw}$, wind volatilization factor (m³ air/kg soil).

### Soil matrix partitioning

Partitioning of chemical within the soil matrix is generalized from prior work (Jury et al. 1983) to include an immiscible organic (oil) phase. The total soil porosity, $\theta_{T}$ (cm³ void/cm³ soil), sums to its component fractions, $\theta_{i} = \theta_{o} + \theta_{h} + \theta_{d}$, with volume fractions for soil moisture, $\theta_{o}$ (cm³ water/cm³ soil); soil pore air, $\theta_{h}$ (cm³ air/cm³ soil); and a residual immiscible organic phase, $\theta_{d}$ (cm³ oil/cm³ soil). The oil phase is presumed immobile within the soil matrix (Brost and DeVaull 2000). Equilibrium partitioning occurs between the soil saturation limit, soil moisture, pore air, and immiscible phase. Partitioning between soil pore air, $c_{o,i}$ (mg/g soil), and the total soil concentration, $c_{T,i}$ (mg/g soil), per dry mass weight, $\rho_{o}$ (g/cm³), for chemical i is

$$R_{a,i} = \frac{c_{o,i} \cdot \rho_{o}}{c_{T,i} \cdot \rho_{o}} = \frac{H_{i} \cdot c_{o,i}}{H_{i} \cdot c_{T,i} \cdot \rho_{o} \cdot \theta_{o} \cdot \theta_{d}}$$

(1)

For nonpolar organic compounds, soil-sorbed to water partitioning, $K_{d,i}$ (cm³ water/g soil) follows a linear isotherm, $K_{d,i} = f_{oc} \cdot K_{oc,i}$, with the mass fraction of organic C in soil, $f_{oc}$ (g oc/g soil), and organic C-water partition coefficient, $K_{oc,i}$ (cm³ water/g oc). Henry’s law coefficient is $H_{i}$ (cm³ water/cm³ air). Raoult’s law is applied for air to organic phase partitioning, as defined by the immiscible phase density, $\rho_{o}$ (g/cm³); the average molecular weight of immiscible phase, $MW_{o,T}$ (g/mol oil); molecular weight of chemical i, $MW_{i}$ (g/mol); vapor pressure, $P_{v,i}$ (atm), ideal gas constant, $R$ (atm L/mol K), and temperature, $T$ (K). For fractionally water-miscible chemicals, the immiscible phase term in Equation 1 can be approximated as $(S/MW) = (P_{v,i}/R \cdot T) / H_{i}$, with pure chemical aqueous solubility limit, $S_{i}$ (mg/cm³ water). In the partitioning estimate of Equation 1, pore air concentrations reach an asymptotic upper limit for

$$c_{o,i} = \frac{P_{v,i} \cdot MW_{o,T}}{R \cdot T} \cdot c_{T,i}$$

or

$$c_{o,i} = \frac{P_{v,i} \cdot MW_{i}}{R \cdot T} \cdot y_{o,i}$$

(2)

for which $c_{o,i}$ (mg/g soil) and $y_{o,i}$ (mol/mol oil), respectively, are the mass concentration and mole fraction of chemical i in the immiscible organic phase. For 3-phase partitioning, $\theta_{o} = 0$. The effective soil saturation limit, or concentration level for a

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Chemical vapor transport within surface soil

The evolution of soil vapor concentration over time and depth is found in solution of the transport equation. One-dimensional transient vapor diffusion of a chemical constituent in a homogeneous soil matrix is governed by

$$\frac{1}{R_{a,i}} \frac{\partial c_{a,i}}{\partial t} - D_{eff,i} \frac{\partial^2 c_{a,i}}{\partial z^2} = 0. \quad (6)$$

Chemical degradation, advective soil gas flow, and aqueous leaching are neglected. The partition coefficient, $R_{a,i}$, is defined by Equation 1. An effective diffusion coefficient, $D_{eff,i} \, (\text{cm}^2/\text{s})$, is applied (Jury et al. 1983; Millington and Quirk 1961).

$$D_{air,i} = \frac{\theta_a 10^{3}}{\theta_r \varepsilon} \cdot D_{air,i} \cdot \frac{1}{\theta_w 10^{3}} \cdot D_{water,i} ^{7} \quad (7)$$

$D_{air,i}$ and $D_{water,i}$ are, respectively, molecular diffusion coefficients in air and water. Diffusion through the residual phase is neglected. For a semi-infinite layer of soil with a uniform initial soil vapor concentration of $c_{a,i} = c_{a,i,0}$ for $0 \leq z \leq \infty$, a fixed surface boundary condition [$c_{a,i}(z = 0, \ t > 0) = 0$], and constant coefficients, the vapor concentration profile is

$$c_{a,i}(z, t) = \frac{z}{\sqrt{2 \pi \cdot \sigma}} \exp \left(- \frac{z^2}{2 \cdot \sigma^2}\right) \quad (8)$$

where erf is the error function. For a surface-impacted layer of soil with a uniform initial soil vapor concentration of $c_{a,i} = c_{a,i,0}$ for $0 \leq z \leq L_0$ at $t = 0$, and $c_{a,i} = 0$ for $z > L$ at $t = 0$,

$$c_{a,i}(z, t) \bigg|_{c_{a,i,0}} = \frac{z}{\sqrt{2 \pi \cdot \sigma}} \exp \left(- \frac{z^2}{2 \cdot \sigma^2}\right) - \frac{1}{2} \exp \left(- \frac{z + L_0}{\sqrt{2 \cdot \sigma}}\right). \quad (9)$$

Surface flux

Surface vapor emission flux is found from the soil vapor concentration profile. Chemical vapor flux through soil is defined by Fickian diffusion.

$$J_i(z, t) = D_{eff,i} \cdot \frac{\partial c_{a,i}(z, t)}{\partial z} \quad (10)$$

From Equations 8 and 10, for an initial concentration of $c_{a,i} = c_{a,i,0}$ for $0 \leq z \leq \infty$ at $t = 0$,

$$J(z, t) = D_{eff,i} \cdot c_{a,i,0} \sqrt{\frac{2 \cdot 1}{\pi \cdot \sigma}} \exp \left(- \frac{z^2}{2 \cdot \sigma^2}\right). \quad (11)$$

The normalized instantaneous surface emission flux ($z = 0$), with $c_{a,i} = R_{a,i} \cdot c_{T,i} \cdot \rho_b$, is

$$J(z = 0, t) = \sqrt{\frac{R_{a,i} \cdot D_{eff,i}}{\pi \cdot t}} \cdot \frac{\sigma}{\sqrt{2 \cdot \pi}}. \quad (12)$$

The time-averaged surface emission flux is

$$J(t) = \frac{1}{c_{T,i,0} \cdot \rho_b} \cdot \frac{1}{t} \int_{t=0}^{t} J(t) \, dt = \sqrt{\frac{4 \cdot R_{a,i} \cdot D_{eff,i}}{\pi \cdot t}} \cdot \frac{\sigma}{\sqrt{2 \cdot \pi}} \cdot \frac{1}{t}. \quad (13)$$
For a finite-depth initial concentration, \( c_{a,i} = c_{a,i,0} \) for \( 0 \leq z \leq L_D \) and \( c_{a,i} = 0 \) for \( z < L_D \) at \( t = 0 \), the instantaneous surface emission flux at the surface, \( z = 0 \), with \( \sigma = \sqrt{2 \cdot R_{a,i} \cdot D_{\text{eff}} \cdot t} \) is

\[
J(z = 0, t) = \frac{(\sigma/t)}{\sigma} = \frac{\sqrt{2 \cdot \pi}}{\sigma} \left( 1 - \exp \left( - \frac{L_D^2}{2 \cdot \sigma^2} \right) \right).
\]  
(14)

The time-averaged surface emission flux is

\[
\frac{J(0)}{\rho_b} = \frac{\sqrt{2 \pi \cdot \sigma}}{\rho_b} \cdot \left( 1 - \exp \left( - \frac{L_D^2}{2 \cdot \sigma^2} \right) \right) + \text{erfc} \left( \frac{L_D}{\sqrt{2 \cdot \sigma}} \right).
\]  
(15)

Equation 16 indicates complete depletion of chemical from soil, for \( \sigma/L_D \geq \sqrt{\pi/2} \), whereas Equation 15 approaches complete depletion for \( \sigma/L_D >> \sqrt{\pi/2} \). Equating the 2 limits from Equations 16a and 16b with Equation 8, an effective depth is found.

\[
L_D(\text{eff}) = \sqrt{2 \pi \cdot \sigma} = \frac{\sqrt{4 \pi \cdot \sigma \cdot R_{a,i} \cdot D_{\text{eff}} \cdot t}}{\sqrt{\pi/2}}.
\]  
(17)

This equates the initial total mass of chemical in a soil layer of depth \( L_D(\text{eff}) \) to the time-integrated total surface mass flux from time \( 0 \) to \( t \). An instantaneous drying front depth, \( \delta \), is defined by presuming a linear vapor concentration gradient from Equation 10, partitioning from Equation 1, and the instantaneous surface flux of Equation 12.

\[
\delta = \frac{\pi \cdot R_{a,i} \cdot D_{\text{eff}} \cdot t}{\sqrt{\pi/2}}.
\]  
(18)

### APPLICATION FOR SURFACE SOIL EXPOSURE ESTIMATES

Volatilization from soil

Consistent with the USEPA (2016), a volatilization factor, \( V_{F_s} \) (Table 1), relates soil concentrations to ambient air concentrations.

\[
V_{F_s} = \frac{c_{a,i}}{c_{a,\text{air}}} = \frac{DF_{\text{amb}}}{J/\rho_b}
\]  
(19)

The ambient air dispersion factor, \( DF_{\text{amb}} \), relates surface emission flux to ambient air concentrations, \( DF_{\text{amb}} = J/\rho_b \). This is in the approximate range of \( DF_{\text{amb}} = 6.881 \text{ cm/s} \) (USEPA 1996a, 1996b) to \( DF_{\text{amb}} = 30 \text{ cm/s} \) (ASTM 2015a, 2015b) based on air dispersion estimates. For a semi-infinite surface soil layer, from Equation 13,

\[
V_{F_s} = \frac{DF_{\text{amb}}}{\rho_b} \sqrt{\frac{4 \cdot R_{a,i} \cdot D_{\text{eff}} \cdot t}{\pi}} = \frac{DF_{\text{amb}}}{\rho_b} \sqrt{\frac{\pi}{2} \cdot (t/\sigma)}.
\]  
(20a)

For a finite depth impacted surface soil layer, from Equation 15,

\[
V_{F_s} = \frac{DF_{\text{amb}}}{\rho_b} \sqrt{\frac{\pi}{2} \cdot (t/\sigma)} \left( 1 - \exp \left( - \frac{L_D^2}{2 \cdot \sigma^2} \right) \right) + \text{erfc} \left( \frac{L_D}{\sqrt{2 \cdot \sigma}} \right).
\]  
(20b)

Time and vertically averaged surface soil concentration

The mass fraction of chemical remaining in the surface soil layer, \( F_{\text{rem}} \), is an average over both time, from \( 0 \) to \( t \), and depth, from \( 0 \) to \( L_s \).

\[
F_{\text{rem}} = \frac{c_{a,i}(L_s, t)}{c_{a,\text{air}}} = \frac{1}{L_s} \int_{0}^{L_s} \int_{0}^{t} c_{a,i}(z, t) \frac{dz}{\sigma}.
\]  
(21)

Soil vapor concentration profiles are presented in Equations 8 and 9. In estimating total soil concentration from vapor concentration, the applied partitioning factor, \( R_{a,i} \), is presumed constant and equal to its initial value, with \( c_{a,i}(z, t)/R_{a,i} \). This relationship is valid either with absence of residual (\( \theta_r = 0 \)) or with residual (\( \theta_r > 0 \)) if the volatilized fraction of residual is small. If residual is reduced or disappears from soil after volatilization, the actual value of \( R_{a,i} \) in shallow soil will increase at later times. In these cases, using the initial value for \( R_{a,i} \) yields a conservative overestimate of total soil concentration.

From Equation 8 and applying the constant initial \( R_{a,i} \) assumption, for a semi-infinite impacted soil layer, time-averaged soil concentration is

\[
s = \frac{c_{a,\text{air}}}{2} = \frac{1}{t} \int_{0}^{t} \int_{c_{a,i}(z, t)} \frac{dz}{\sigma}.
\]  
(22)

where \( s \) is the signum or sign function, \( \text{sgn}(x) = |x|/x \). For a finite surface-limited layer of soil depth \( L_D \), with \( f \) as defined in Equation 23 and using Equation 9,

\[
\frac{c_{a,i}(z, t)}{c_{a,\text{air}}} = f(z/\sigma) - \frac{1}{2} \cdot f \left( z - \frac{L_D}{\sigma} \right) - \frac{1}{2} \cdot f \left( z + \frac{L_D}{\sigma} \right).
\]  
(23)

Vertically averaged soil concentrations are found for a semi-infinite soil layer by integrating Equation 8 over a surficial soil layer, \( L_s \).

\[
\frac{c_{a,i}(z, L_s)}{c_{a,\text{air}}} = g \left( \frac{L_s}{\sigma} \right) = \int_{0}^{L_s} \int_{0}^{t} \frac{dz}{\sigma} = \frac{1}{2} \cdot \int_{0}^{L_s} \int_{0}^{t} \left( z + \frac{L_D}{\sigma} \right) \frac{dz}{\sigma}.
\]  
(24)
For a finite surface-impacted layer of soil of depth $L_D$, with $g$ as defined in Equation 25 and using Equation 9,

$$\frac{c_T(L_D, z, t)^{L_s}}{c_T,0} = g\left(\frac{L_s}{\sigma}\right) - \frac{1}{2} g\left(\frac{L_s - L_D}{\sigma}\right) - \frac{1}{2} g\left(\frac{L_s + L_D}{\sigma}\right).$$

(26)

For a semi-infinite impacted soil depth, the time- and depth-integrated average is found from Equation 23 for a surficial soil layer, $L_s$.

$$F_{rem} = \frac{c_T(L_s, t)^{L_s}}{c_T,0} = F\left(\frac{\sigma}{L_s}\right) = \frac{1}{L_s} \int_0^{L_s} \left(\frac{z}{\sigma}\right) dz$$

(27)

$$F_{rem} = F\left(\frac{\sigma}{L_s}\right) = \sgn\left(\frac{\sigma}{L_s}\right) \left\{ - \frac{2}{\sqrt{3}} \frac{\sqrt{\pi}}{\sigma} \left( 1 - \exp\left( -\frac{1}{2} \left(\frac{L_s}{\sigma}\right)^2\right) \right) - \frac{1}{\sqrt{3}} \left(\frac{L_s}{\sigma}\right)^2 + \frac{1}{3} \sqrt{\frac{\pi}{\sqrt{2}}} \frac{L_s}{\sigma} \exp\left( -\frac{1}{2} \left(\frac{L_s}{\sigma}\right)^2\right) + \frac{1}{3} \sqrt{\frac{\pi}{\sqrt{2}}} \left(\frac{L_s}{\sigma}\right)^3 \right\}$$

(28)

For the finite-depth impacted soil, $L_D$, with function $F$ as defined in Equation 28,

$$F_{rem} = \frac{c_T(L_D, t)^{L_s}}{c_T,0} = F\left(\frac{L_s}{\sigma}\right) - \frac{1}{2} F\left(\frac{L_s - L_D}{\sigma}\right) - \frac{1}{2} F\left(\frac{L_s + L_D}{\sigma}\right).$$

(29)

For residential exposure, the USEPA (2016) presumes single pure chemicals and no residual phase in soil and tabulates $V_F$ for 261 volatile chemicals ranging from $6.5E+5$ to $4.4E+9$ cm$^3$/g. With the applied USEPA parameters ($t = 26$ years, $D_{amb} = 6.818$ cm/s, $\rho_0 = 1.5$ g/cm$^3$, $L_D \to \infty$) from Equation 20a this corresponds to a range of $\sigma$ from 1 to 7200 cm. Substituting into Equation 28 with $L_s = 5$ cm, the corresponding calculated values of $F_{rem}$ range from 0.89 to 5.5E–4. The USEPA model equations (Table 1) actually presume no depletion, with $F_{rem} = 1$. This indicates that there may be a conservative bias in the USEPA exposure estimates for ingestion, dermal contact, and dust inhalation by factors ranging up to 1800 (or 1/$F_{rem}$) for volatile chemicals. The estimated bias may be even greater if a finite contamination depth, $L_D$, is applied.

**Experimental data and model comparisons**

**Surface emission flux.** Comparisons are made between surface vapor emission flux models and measured data. Measured surface emission flux from soil for a range of pure and mixed chemicals is available from laboratory and field measurements (Farmer et al. 1972; Jury et al. 1980; American Petroleum Institute 1989; Johnson et al. 1990; Kang and Oulman 1996; Saterbak et al. 1997). Transient surface emission flux of pure carbon dioxide gas and 1.9 mg/m$^3$ (319 ppbv) sulfur hexafluoride gas in air from a 110-cm-long, 7.7-cm-diameter glass column packed with clean, dry, 10-μm glass beads was measured in the present study. Further descriptions of these data sets are included in the Supplemental Data along with relevant summary parameters. The measured data are plotted in Figure 2 and compared with the instantaneous surface flux models. This comparison shows that 95% of the measured data fall below a factor of 1.33 greater than the flux estimate of Equation 12. The comparison is improved using Equation 14, particularly for measurements in which depletion of chemical over the finite depth of impacted soils is significant. The measured data are within a factor of 0.3 to 1.7 (95% error bounds) of Equation 14. Slightly increased error is evident for cases in which the chemical is nearing complete depletion from the finite impacted soil depth.

A number of chemicals (benzene, toluene, ethylbenzene, and n-heptane) and mixtures (gasoline and diesel fuel) in the data are amendable to aerobic biodegradation. The effect of

![Figure 2. Comparison of measured surface flux data with the instantaneous surface emission flux models.](image-url)
biodegradation on surface emission flux is apparently insignificant. Aerobic biodegradation would be more significant for larger drying front depths, \( \delta \), and lower initial soil concentrations than included within the range of these data.

Selected data in this comparison include a residual phase. With residual phase neglected, the emission estimate would be biased high proportional to the ratio \( J(t, \theta_0 = 0)/J(t, \theta_0) \), or from Equation 12, \( \sqrt{R_{a,i}(\theta_0 = 0)/R_{a,i}(\theta_0)} \). Using the ranges for \( R_{a,i} \), tabulated in the Supplementary Data, this high bias is within the approximate range of 4 to 200.

**Concentration versus depth.** Soil vapor profiles have been compared with measured soil gas concentrations. Transient diffusion tests using sulfur hexafluoride gas (SF6) were conducted on three 1.1-m-long by 7.5-cm-diameter homogeneous soil-packed columns. Constant SF6 gas concentrations averaging 1.8 \( \mu \)g/m\(^3\) (300 pptv) in air were swept across the open tops of the soil columns. Diffusion of SF6 into the soil was quantified by analysis of syringe samples taken from septum ports spaced at 10-cm intervals along the sides of the columns. For SF6, we have negligible partitioning to water (\( H_i \rightarrow \infty \)), low soil sorption (\( K_{d,i} \rightarrow 0 \)), and no residual phase (\( \theta_0 = 0 \)). From Equation 1, \( R_{a,i} = 1/\theta_0 \) and soil concentration is directly proportional to soil vapor concentration, \( c_{\text{a,i}}(z, t) = c_{\text{a,i}}(z) \). For \( c_{\text{a,i}}(z, t = 0) \), \( c_{\text{a,i}}(z = 0) = c_{\text{a,i},0} \) Equation 8 is

\[
\frac{c_{\text{a,i}}(z, t)}{c_{\text{a,i},0}} = 1 - \text{erf} \left( \frac{z}{\sqrt{2} \cdot \sigma} \right) \quad \text{with} \quad \sigma = \sqrt{\frac{2 \cdot \theta_0^{7/3}}{\theta_i^2} \cdot D_{\text{air}} \cdot t}
\]

Equation (30)

Results are compared in Figure 3 for the vapor concentration profile and the transient change in \( \sigma \). Both are well represented by Equation 30. Comparison of air-filled porosity based on direct measurement and best-fit estimates from the diffusion tests are also reasonably consistent.

**Soil concentration versus time.** Modeled soil concentrations in a case with high residual levels have been compared with measured soil concentrations. In 1 of the surface emission flux tests (Saterbak et al. 1997), independent measurements of benzene concentrations in undisturbed shallow soils were included. A plot of the measured benzene concentrations normalized by the initial mean benzene concentration (39 mg/kg soil) is shown in Figure 4 and compared with \( c_{\text{T,i}}(L_{\text{d}}, z, t)^{\text{meas}}/c_{\text{T,i}}(L_{\text{d}}, 0) \) calculated with Equation 26. At \( t \geq 1 \) day, the model and data agreement is reasonable. Variation in model estimates is shown using Equation 26 with a range of \( (L_{\text{d}}/L_{\text{s}}) \) values selected to match the 1- and 5-day SD of the measured concentration data. Variation could also be attributed to other parameters in Equation 26. The significance of this comparison is that: 1) the soil data are reasonably well represented by the model, and 2) these measurements indicate near-complete depletion of benzene from surface soils (>99.99%) in less than 30 days, whereas existing methods of estimating soil screening levels would have presumed complete persistence of benzene over much longer time periods.

**Applied parameter estimates**

Risk evaluation using the revised volatilization and depletion models requires specification of additional parameters.

**Surficial soil depth.** The surficial soil depth, \( L_{\text{s}} \), is an averaging depth over which direct exposure (ingestion and/or dermal contact) is expected. For direct exposure to undisturbed soils, an estimate of \( L_{\text{s}} \) is taken as a 0- to 5-cm (0- to 2-inch) surface interval, based on studies of surface deposition of relatively immobile lead near roadways and smelters (USEPA 1986; ATSDR 1992). Deeper surficial soil depths may be appropriate for disturbed soil or, if site-specific conditions dictate, up to 45 cm for gardening (USEPA 2016).
Subsurface vapor source: Finite source depth. Volatile vapors deplete from impacted surface soil over time. At later times exposure is dominated by inhaled vapors originating from remaining subsurface chemical at greater depth. A finite contamination depth, $L_D$, may be specified in some cases from assessment data. For petroleum chemicals, $L_D = 1.5$ or 4.6 m (5 or 15 feet), respectively, for low and higher level (residual) source concentrations could be applied. At these depths volatile exposure from subsurface petroleum chemicals has been found to be negligible (Lahvis et al. 2013; USEPA 2015).

**EXAMPLE APPLICATION**

In this example, age-adjusted residential exposure of adults and children to benzene is presumed, and a lifetime excess cancer risk is specified ($TR_{tot} = 10^{-6}$). Exposure from soil ingestion and vapor inhalation is included. Dermal absorption and dust inhalation are assumed to be 0. Total surficial soil risk sums as $TR_{tot} = TR_{ing} + TR_{inh}$. Individual screening levels (mg benzene/kg soil) for soil ingestion and vapor inhalation combine to the total screening level as in Table 1.

$$SL_{res-soil-ca-tot}(TR_{tot}) = \frac{1}{SL_{res-soil-ca-ing}(TR_{ing}) + SL_{res-soil-ca-inh}(TR_{inh})}$$

(31)

Screening levels are calculated for benzene as a constituent in a petroleum hydrocarbon mixture, based on a range of chemical analyses for 90 different unweathered petroleum products, crude oils, and condensates (McMillen et al. 2001) in which the mass fraction of benzene ranged from 0.0000043 to 0.058 g benzene/g oil. Pure benzene is also included.

Soil screening levels that presume a semi-infinite soil contamination depth ($L_D \to \infty$) and include 4-phase partitioning but neglect depletion within surface soils for ingestion ($F_{rem} = 1$) are shown in Figure 5a. The screening level for ingestion is independent of the mass fraction of benzene in the source petroleum. The screening level for inhalation is a maximum at low-source benzene mass fractions and decreases to a minimum, constant value at benzene mass fractions equal to and greater than approximately 1.3% (g/g). At and above this level of 1.3% soil, screening levels are low enough that no residual phase is present; at and below 1.3%, residual oil is present in the soil, $R_a/R_s$ ($\theta_0 = 0$) > 1, and the inhalation screening criteria in soil are higher. The total screening level varies between the ingestion and inhalation-dominated values, respectively, at low and high benzene mass fractions in the source petroleum. Screening levels that neglect the residual phase (USEPA 1996a, 1996b, 2016; ASTM 2015a, 2015b) show no dependence on chemical mixture composition and are equal to the minimum values plotted in Figure 5a.

Soil screening levels determined for the same scenario with a depleting source ($F_{rem} < 1$) are plotted in Figure 5b. The screening levels for ingestion are higher than in Figure 5a, because $F_{rem}$ is always less than unity. The total and inhalation screening levels are also higher because the total lifetime excess cancer risk ($TR_{tot} = 10^{-6}$) is held constant. Within the plot, for a decreasing mass fraction of benzene in the source petroleum, benzene is depleted more slowly from surface soils and the screening level for benzene associated with ingestion decreases.

Similarly calculated screening levels for other volatile chemicals show trends similar to the plots of Figure 5, although the exposure pathway contributions and the resulting screening levels are, of course, different.
be significant for some volatile chemicals at time durations far shorter than a long-term scenario. More comprehensive evaluation, including evaluation of shorter subchronic or acute exposure duration scenarios, may be relevant.

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Data Accessibility—Data are available upon request from author George E DeVaull (devaull@shell.com).

SUPPLEMENTAL DATA

Supplemental Figure S1. Comparison of soil vapor partitioning calculated from Equations 4 and 5.

Supplemental Figure S2. Plot of normalized time versus the fraction of volatilized initial mass for Equations 13, 15, and 16.

Supplemental Figure S3. Depth- and time-averaged fraction of chemical remaining in surface soil layer versus surface soil averaging depth and initial chemical depth.

Supplemental Figure S4. Plot relating scaled volatilization factor, $VF_s$, to fraction remaining, $F_{rem}$, as a function of $L_D/L_s$.

Supplemental Figure S5. Relation of volatilization factor, $VF_s$, to the time-averaged fraction of chemical remaining in surface soil, $F_{rem}$, using the range of $VF_s$ applied by USEPA (2016).

Supplemental Figure S6. Comparison of measured flux data with the instantaneous surface emission flux model for a finite source depth.

Supplemental Figure S7. Risk for benzene-impacted surficial soils at the concentration levels and for the same scenario as plotted in Figure 5.

Supplemental Figure S8. Risk for benzene-impacted surficial soils at the concentration levels and for the same scenarios as plotted in Figure 6.

Supplemental Table S1. Summary parameters for the data in Figure 2.

Supplemental Table S2. Selected parameters for the example application.

Supplemental Table S3. Equations for estimating screening levels for the soil-to-vegetable uptake and vegetable ingestion exposure pathway.

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