N00639.AR.002322
NSA MID SOUTH
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LETTER REGARDING EXPLANATION OF F CONCENTRATION AT UNDERGROUND STORAGE TANK SITE N-12 MILLINGTON SUPPACT TN
03/27/1998
ENSAFE

ENSAFE FAX COVER SHEET

March 27, 1998

TO
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FROM
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SUBJECT
Explanation of f_{oc} concentration
UST N12 Investigation, Memphis, Tennessee

PAGES
5, including this cover sheet.

COMMENTS

Attached is part of a document that defines f_{oc} and also presents the Soil-Water Partition Equation for Migration to Groundwater Pathway for organic contaminants. The f_{oc} concentration detected at N12 (0.008) is considered significant and would indicate the potential for sorption of the contaminants to the soil. However, all the contaminants detected in soil are below their respective action levels.

Please call if you have any questions.

Thank you,

Allison L. Dennen
Task Order Manager

Equation 22 is used to calculate SSLs (total soil concentrations, C_t) corresponding to soil leachate concentrations (C_w) equal to the target contaminant soil leachate concentration. The equation assumes that soil water, solids, and gas are conserved during sampling. If soil gas is lost during sampling, θ_a should be assumed to be zero. Likewise, for inorganic contaminants except mercury, there is no significant vapor pressure and H' may be assumed to be zero.

The User's Guide (U.S. EPA, 1996) describes how to develop site-specific estimates of the soil parameters needed to calculate SSLs. Default soil parameter values for the partition equation are the same as those used for the VF equation (see Section 2.4.2) except for average water-filled soil porosity (θ_w). A conservative value (0.15) was used in the VF equation because the model is most sensitive to this parameter. Because migration to ground water SSLs are not particularly sensitive to soil water content (see Section 2.5.7), a value that is more typical of subsurface conditions (0.30) was used. This value is between the mean field capacity (0.20) of Class B soils (Carsel et al., 1988) and the saturated volumetric water content for loam (0.43).

K_d varies by chemical and soil type. Because of different influences on K_d values, derivations of K_d values for organic compounds and metals were treated separately in the SSL methodology.

2.5.2 Organic Compounds—Partition Theory. Past research has demonstrated that, for hydrophobic organic chemicals, soil organic matter is the dominant sorbing component in soil and that K_d is linear with respect to soil organic carbon content (OC) as long as OC is above a critical level (Dragun, 1988). Thus, K_d can be normalized with respect to soil organic carbon to K_{oc}, a chemical-specific partitioning coefficient that is independent of soil type, as follows:

$$K_d = K_{oc}\, f_{oc} \tag{23}$$

where

K_{oc} = organic carbon partition coefficient (L/kg)
f_{oc} = fraction of organic carbon in soil (mg/mg)

Substituting into Equation 22:

Soil-Water Partition Equation for Migration to Ground Water Pathway: Organic Contaminants

$$C_t = C_w \left((K_{oc}\, f_{oc}) + \frac{\theta_w + \theta_a H'}{\rho_b} \right) \tag{24}$$

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Parameter/Definition (units)	Default	Source
C_s/screening level in soil mg/kg)	–	–
C_w/target leachate concentration (mg/L)	(nonzero MCLG, MCL, or HBL) × 20 DAF	Table 1 (MCL, nonzero MCLG); Section 2.5.6 (DAF for a 0.5-acre source)
K_{oc}/soil organic carbon-water partition coefficient (L/kg)	chemical-specific	see Part 5
f_{oc}/organic carbon content of soil (kg/kg)	0.002 (0.2%)	Carsel et al., 1988
θ_w/water-filled soil porosity (L_{water}/L_{soil})	0.3 (30%)	U.S. EPA/ORD
θ_a/air-filled soil porosity (L_{air}/L_{soil})	0.13	$n - \theta_w$
n/total soil porosity (L_{pore}/L_{soil})	0.43	$1 - \rho_b/\rho_s$
ρ_b/dry soil bulk density (kg/L)	1.5	U.S. EPA, 1991b
ρ_s/soil particle density (kg/L)	2.65	U.S. EPA, 1991b
H'/dimensionless Henry's law constant	H × 41, where 41 is a conversion factor	U.S. EPA, 1991b
H/Henry's law constant (atm-m³/mol)	chemical-specific	see Part 5

Part 5 of this document provides K_{oc} values for organic chemicals and describes their development.

The critical organic carbon content, f_{oc}^*, represents OC below which sorption to mineral surfaces begins to be significant. This level is likely to be variable and to depend on both the properties of the soil and of the chemical sorbate (Curtis et al., 1986). Attempts to quantitatively relate f_{oc}^* to such properties have been made (see McCarty et al., 1981), but at this time there is no reliable method for estimating f_{oc}^* for specific chemicals and soils. Nevertheless, research has demonstrated that, for volatile halogenated hydrocarbons, f_{oc}^* is about 0.001, or 0.1 percent OC, for many low-carbon soils and aquifer materials (Piwoni and Banerjee, 1989; Schwarzenbach and Westall, 1981).

If soil OC is below this critical level, Equation 24 should be used with caution. This is especially true if soils contain significant quantities of fine-grained minerals with high sorptive properties (e.g., clays). If sorption to minerals is significant, Equation 24 will underpredict sorption and overpredict contaminant concentrations in soil pore water. However, this f_{oc}^* level is by no means the case for all soils; Abdul et al. (1987) found that, for certain organic compounds and aquifer materials, sorption was linear and could be adequately modeled down to $f_{oc} = 0.0003$ by considering K_{oc} alone.

For soils with significant inorganic and organic sorption (i.e., soils with $f_{oc} < 0.001$), the following equation has been developed (McCarty et al., 1981; Karickhoff, 1984):

$$K_d = (K_{oc}\, f_{oc}) + (K_{io}\, f_{io}) \qquad (25)$$

where

K_{io} = soil inorganic partition coefficient
f_{io} = fraction of inorganic material
$f_{io} + f_{oc}$ = 1.

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Although this equation is considered conceptually valid, K_{io} values are not available for the subject chemicals. Attempts to estimate K_{io} values by relating sorption on low-carbon materials to properties such as clay-size fraction, clay mineralogy, surface area, or iron-oxide content have not revealed any consistent correlations, and semiquantitative methods are probably years away (Piwoni and Banerjee, 1989). However, Piwoni and Banerjee developed the following empirical correlation (by linear regression, $r^2 = 0.85$) that can be used to estimate K_d values for hydrophobic organic chemicals from K_{ow} for low-carbon soils:

$$\log K_d = 1.01 \log K_{ow} - 0.36 \qquad (26)$$

where

K_{ow} = octanol/water partition coefficient.

The authors indicate that this equation should provide a K_d estimate that is within a factor of 2 or 3 of the actual value for nonpolar sorbates with $\log K_{ow} < 3.7$. This K_d estimate can be used in Equation 22 for soils with f_{oc} values less than 0.001. If sorption to inorganics is not considered for low-carbon soils where it is significant, Equation 24 will underpredict sorption and overpredict contaminant concentrations in soil pore water (i.e., it will provide a conservative estimate).

The use of fixed K_{oc} values in Equation 24 is valid only for hydrophobic, nonionizing organic chemicals. Several of the organic chemicals of concern ionize in the soil environment, existing in both neutral and ionized forms within the normal soil pH range. The relative amounts of the ionized and neutral species are a function of pH. Because the sorptive properties of these two forms differ, it is important to consider the relative amounts of the neutral and ionized species when determining K_{oc} values at a particular pH. Lee et al. (1990) developed a theoretically based algorithm, developed from thermodynamic equilibrium equations, and demonstrated that the equation adequately predicts laboratory-measured K_{oc} values for pentachlorophenol (PCP) and other ionizing organic acids as a function of pH.

The equation assumes that sorbent organic carbon determines the extent of sorption for both the ionized and neutral species and predicts the overall sorption of a weak organic acid ($K_{oc,p}$) as follows:

$$K_{oc,p} = K_{oc,n}\,\Phi_n + K_{oc,i}\,(1 - \Phi_n) \qquad (27)$$

where

$K_{oc,n}$, $K_{oc,i}$ = sorption coefficients for the neutral and ionized species (L/kg)
Φ_n = $(1 + 10^{pH - pKa})^{-1}$
pKa = acid dissociation constant.

This equation was used to develop K_{oc} values for ionizing organic acids as a function of pH, as described in Part 5. The User's Guide (U.S. EPA, 1996) provides guidance on conducting site-specific measurements of soil pH for estimating K_{oc} values for ionizing organic compounds. Because a national distribution of soil pH values is not available, a median U.S. ground water pH (6.8) from the STORET database (U.S. EPA, 1992a) is used as a default soil pH value that is representative of subsurface pH conditions.

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2.5.3 Inorganics (Metals)—Partition Theory. Equation 22 is used to estimate SSLs for metals for the migration to ground water pathway. The derivation of K_d values is much more complicated for metals than for organic compounds. Unlike organic compounds, for which K_d values are largely controlled by a single parameter (soil organic carbon), K_d values for metals are significantly affected by a variety of soil conditions. The most significant parameters are pH, oxidation-reduction conditions, iron oxide content, soil organic matter content, cation exchange capacity, and major ion chemistry. The number of significant influencing parameters, their variability in the field, and differences in experimental methods result in a wide range of K_d values for individual metals reported in the literature (over 5 orders of magnitude). Thus, it is much more difficult to derive generic K_d values for metals than for organics.

The K_d values used to generate SSLs for Ag, Ba, Be, Cd, Cr^{+3}, Cu, Hg, Ni, and Zn were developed using an equilibrium geochemical speciation model (MINTEQ2). The values for As, Cr^{6+}, Se, and Th were taken from empirical, pH-dependent adsorption relationships developed by EPA/ORD. Metal K_d values for SSL application are presented in Part 5, along with a description of their development and limitations. As with the ionizing organics, K_d values are selected as a function of site-specific soil pH, and metal K_d values corresponding to a pH of 6.8 are used as defaults where site-specific pH measurements are not available.

2.5.4 Assumptions for Soil/Water Partition Theory. The following assumptions are implicit in the SSL partitioning methodology. *These assumptions and their implications for SSL accuracy should be read and understood before using this methodology to calculate SSLs.*

1. **There is no contaminant loss due to volatilization or degradation.** The source is considered to be infinite; i.e., these processes do not reduce soil leachate concentrations over time. This is a **conservative** assumption, especially for smaller sites.

2. **Adsorption is linear with concentration.** The methodology assumes that adsorption is independent of concentration (i.e., the Freundlich exponent = 1). This has been reported to be true for various halogenated hydrocarbons, polynuclear aromatic hydrocarbons, benzene, and chlorinated benzenes. In addition, this assumption is valid at low concentrations (e.g., at levels close to the MCL) for most chemicals. As concentrations increase, however, the adsorption isotherm can depart from the linear.

   Studies on trichloroethane (TCE) and chlorobenzene indicate that departure from linear is in the **nonconservative** direction, with adsorbed concentrations being lower than predicted by a linear isotherm. However, adequate information is not available to establish nonlinear adsorption isotherms for the chemicals of interest. Furthermore, since the SSLs are derived at relatively low target soil leachate concentrations, departures from the linear at high concentrations do not significantly influence the accuracy of the results.

3. **The system is at equilibrium with respect to adsorption.** This ignores adsorption/desorption kinetics by assuming that the soil and pore water concentrations are at equilibrium levels. In other words, the pore-water residence time is assumed to be longer than the time it takes for the system to reach equilibrium conditions.

   This assumption is **conservative**. If equilibrium conditions are not met, the concentration in the pore water will be less than that predicted by the methodology. The kinetics of adsorption are not adequately understood for a sufficient number of chemicals and site conditions to consider equilibrium kinetics in the methodology.