

Public Discussion Draft
RSR Wave 2 - Potential Changes to RSRs
Class B2 Cleanup
Alternative Pollutant Mobility Criteria
February 18, 2014

The Department of Energy and Environmental Protection is developing “public discussion drafts” of ideas for potential future amendment to DEEP regulations, or new provisions for regulations, to address remediation of releases and sites where hazardous substances and/or oil have been released. Many of the subject matters for these drafts grew out of the Cleanup Transformation workgroup recommendations from November 2012. The purpose of the public discussion drafts is to provide more detail to the concepts set forth in the November 2012 Workgroup reports and the February 2013 Cleanup Transformation draft report. As a discussion draft, the language is not structured to read exactly as regulation language would, and does not attempt to propose section and subsection outline format. Also, this discussion draft is not a public hearing draft of a proposed regulation; DEEP will further shape and refine the discussion draft, after considering public feedback, before initiating the formal regulation adoption process.

Purpose:

This proposal is intended to allow self-implementing site-specific fate and transport adjustments to pollutant mobility criteria (PMC) to derive alternative criteria. This self-implementing derivation of alternative soil PMC is intended to result in groundwater which meets the applicable risk based criteria in Section 22a-133k-3 of the Remediation Standard Regulations (RSRs). These site-specific alternative PMC options are proposed to allow a site to achieve a Tiered Class B2 cleanup exit. In accordance with the Draft Proposal for a Transformed Cleanup Program (2/7/2013), a Class B2 exit in relation to PMC means soil meets an alternative PMC based on risk or site conditions.

These alternative PMC would work to prevent the need for remediation of contaminants which exceed default soil cleanup criteria but can be shown to be sufficiently immobile, based on site conditions, to be at levels that do not pose a risk to human health or the environment, protect existing water uses, and do not significantly degrade groundwater quality.

Technical Principles:

For the proposed PMC options and sections below, "soil concentration" means soil concentration that will not cause an exceedance of the applicable RSRs risk based criteria in groundwater.

These PMC options allow evaluation of a site’s soil-leaching-to-groundwater pathway using methodologies that are more sophisticated approaches for estimating contaminant mobility than

those incorporated in the default RSRs PMC. These methodologies include using soil-water partition (SWP) equations with default values, using SWP equations with measured site-specific parameters, and using unsaturated zone fate-and-transport models. Proper use of these methods with adequate site-specific data (i.e., supported by site-specific groundwater data, etc.) results in site-specific estimates of soil concentrations (leaching-based site-specific levels/PMC), considered to be **protective** of the leaching to groundwater or surface water pathway for the site under evaluation. Each one of the methods is detailed in separate sections presented below.

General Requirements and Limitations:

To determine if soil meets acceptable criteria, one of the three methodologies specified in “Acceptable Methodologies to Determine an Alternative PMC” below may be used. They are:

- (1) SWP Equation: Fixed Parameter Three-Phase Partitioning Model,
- (2) SWP Equation: Variable Parameter Three-Phase Partitioning Model, and
- (3) Unsaturated Zone Leaching Models.

The specific requirements for deriving a soil concentration under a particular method may also depend on the substance. The SWP equation(s) can be modified using site-specific soil physical and chemical parameters. Unsaturated zone fate-and-transport modeling (SESOIL/VLEACH models) employing site-specific data can be used to account for contaminant distribution and attenuation in the unsaturated zone.

The SWP equation approach assumes that the soil column is contaminated throughout, from the source area or land surface to the water table. Thus, the SWP equation approach allows that there may be measurable, but not significant (i.e., below RSR groundwater criteria), impact from each substance to groundwater over time. The unsaturated zone fate and transport models may alternatively be used to incorporate consideration of additional potential attenuation where there is uncontaminated soil between the source area and water table; the models add complexity and provide no significant added value in areas where there is known contamination in soil extending to the water table. The unsaturated zone fate and transport modeling approach expects that measurable impact to groundwater may be absent if attenuation is sufficient, or may be sustainably present at concentrations less than applicable RSR groundwater criteria.

Using these alternative PMC options would not be applicable for soil constituents that are leaching into groundwater causing exceedances of groundwater, above the applicable risk based criteria, for each substance. If site groundwater and site-specific soil leaching data are inconsistent, the site conceptual model may need to be re-evaluated.

Dilution Factors (DF):

The Department recognizes that contaminant fate and transport in the unsaturated zone is complex. The use of unsaturated zone fate and transport models incorporates the processes that attenuate pollution during transport. As soil leachate moves through soil

and enters groundwater, contaminant concentrations are attenuated by physical, chemical, and biological processes, acting in both the saturated and unsaturated zones that tend to reduce the eventual contaminant concentration at the point where compliance is evaluated. The reduction in concentration can be expressed succinctly by a dilution-attenuation factor (DAF), which is defined as the ratio of contaminant concentration in soil leachate to the concentration in ground water at the compliance point. When calculating soil concentration, a DAF is used to back-calculate the target soil leachate concentration from an acceptable ground water concentration. For example, if the Groundwater Protection Criteria (GWPC) or Surface Water Protection Criteria (SWPC), depending on the resource that is being protected, is 0.05 mg/L and the DAF is 10, the target leachate concentration would be 0.5 mg/L.

The SWP equation calculates the concentration of contaminant that may remain in soil so that the aqueous phase concentration of a contaminant will, at a defined compliance point, not exceed an applicable risk based criteria. The SWP equation does assume that contaminants in soil exist in equilibrium between the soil matrix (sorbed), aqueous (soil pore water), and vapor (soil gas) phases. The conceptual model for migration of contaminants from soil to groundwater includes two steps: (1) release of contaminant into soil leachate; and (2) transport of this leachate containing the contaminant through unsaturated and saturated soil to a groundwater compliance point. The SWP equation, however, does not account for attenuation process such as degradation, cation exchange, hydrolysis, and metal complexation (i.e., biological or chemical degradation) during transport through the unsaturated soil zone. The SWP addresses only the physical process of contaminant leachate dilution in groundwater. Therefore, a dilution factor (DF) rather than a DAF is included in the equation.

The default RSR PMC GA criteria implicitly incorporate a combined partitioning and dilution-attenuation factor of 20.

Distribution Coefficient (K_d):

The distribution coefficient is a measure of the tendency of a pollutant to migrate from solid to dissolved phase. K_d values are affected by a variety of soil and groundwater conditions including, but not limited to: pH, oxidation-reduction conditions, iron oxide content, soil organic matter content, cation exchange capacity, and major ion chemistry. The methodologies proposed allow for use of site specific values that allow this variability to be incorporated in the evaluation of a soil. U.S. EPA Soil Screening Guidance (1996a) provides pH-specific K_d coefficients for a selected listed of metals including silver (Ag), barium (Ba), beryllium (Be), cadmium (Cd), chromium⁺³ (Cr⁺³), copper (Cu), mercury (Hg), nickel (Ni), and zinc (Zn). Site-specific soil pH measurements should be used to select appropriate K_d values for these metals.

ACCEPTABLE METHODOLOGIES TO DETERMINE AN ALTERNATE PMC:

(1) SWP Equation: Fixed Parameter Three-Phase Partitioning Model.

- a. Overview:** A three-phase partitioning model with fixed input parameters may be used to establish or calculate unsaturated zone soil concentrations for any substance. Site-specific data are not required for use of this model.

The three phases considered are soil, water, and air so this model is not applicable when non-aqueous phase liquid (NAPL) is present. The partitioning model is a simple linear soil/water partitioning equation (SWP) that relates the concentration of a contaminant in soil to soil leachate concentrations in the contamination zone, based on simplified assumptions.

- b. Description of the model:** Input parameter descriptions and DEEP approved default values for the SWP equation are provided below and in Tables 1 through 4.

Soil-Water Partition (SWP) Equation:

$$C_s = RBC \times DF \left(K_d + \frac{(\theta_w + \theta_a H')}{\rho_b} \right) \quad \text{(Equation 1)}$$

Where:

- C_s = Soil concentration (mg/kg)
RBC = Risk Based Criteria (GWPC/SWPC) established under RSRs (mg/L)
DF = Dilution factor (dimensionless: 20 for unsaturated zone soil, see c.)
 K_d = Distribution coefficient, for inorganic contaminants, (L/kg, chemical-specific, see d.) (see below for organic contaminants)
 θ_w = Water-filled soil porosity (L water/L soil; 0.28 see RSRs, p. 24)
 θ_a = Air-filled soil porosity (L air/L soil; 0.15 for unsaturated zone soil, see RSRs, p. 24)
 H' = Henry's law constant (dimensionless, chemical-specific, see e.)
 ρ_b = Dry soil bulk density (1.5 kg/L, see RSRs, p. 24)

and, for organic contaminants :

$$K_d = K_{oc} f_{oc} \quad \text{(Equation 2)}$$

Where:

- f_{oc} = Soil fraction of organic carbon (0.6% or 0.006 kg/kg, see RSRs, p. 24)
 K_{oc} = Soil organic carbon-water partitioning coefficient (L/kg; see d.(i))

- c. Dilution Factor (DF):** The SWP equation assumes that contaminants in soil exist in equilibrium between the soil matrix (sorbed), aqueous (soil pore water), and vapor (soil gas) phases, and that there is dilution as this soil water is transported to the point where

compliance is determined. A default DF of 20 is selected to account for the water mass balance effects that reduce contaminant concentrations that occur in the subsurface flow system. At most sites, this adjustment will more accurately reflect a contaminant's threat to ground water resources than assuming a DF of 1 (i.e., no dilution or attenuation).

d. Distribution coefficient (K_d): The default K_d values for organics and metals used in Equation 1 are as follows:

(i) **Organics:** The K_{oc} (soil organic carbon-water partition coefficient) parameter specified in Equation 2 shall be derived as follows:

(A) **Nonionic organics:** For individual nonionic organic substances (e.g., benzene and naphthalene), the K_{oc} values in Table 1 shall be used. For substances not listed in Table 1, K_d values may be developed as provided in Section (2) (variable three-phase partitioning model).

(B) **Ionizing organics:** For ionizing organic substances (e.g., phenol and benzoic acid), the K_{oc} values in Table 2 shall be used. Table 2 provides K_{oc} values for three different pHs. To select the appropriate K_{oc} value, a representative soil pH must be determined. The K_{oc} value for the corresponding soil pH shall be used. If the soil pH falls between the pH values provided, an appropriate K_{oc} value shall be selected by interpolation between the listed K_{oc} values.

(ii) **Metals:** For metals, the K_d values in Table 3 shall be used. For metals not listed in Table 3, K_d values may be developed as provided in Section (2) (variable three-phase partitioning model).

e. Henry's law constant: For petroleum fractions, the values for Henry's law constant in Table 4 shall be used in Equation 1. For individual organic hazardous substances, the value shall be based on values in the scientific literature (for example, Table A4 of March 2003 Connecticut's RSRs Volatilization Criteria). For all metals present as inorganic compounds except mercury, zero shall be used. For mercury, either 0.47 or a value derived from the scientific literature shall be used.

(2) SWP Equation: Variable Parameter Three-Phase Partitioning Model.

a. Overview: The three-phase partitioning model with variable (site-specific) input parameters may be used to establish or calculate unsaturated zone soil concentrations for any substance.

The method allows for the substitution of representative site-specific values for the default values in Equation 1 for one or more of the following five input parameters:

- Distribution coefficient, K_d
- soil bulk density, ρ_b

- soil volumetric water content, θ_w
- soil air content, θ_a
- dilution factor, DF

The methods that may be used and the requirements that shall be met to derive site-specific values for each of the five input parameters are specified in (b) through (g) of this subsection.

b. Methods for deriving a distribution coefficient (K_d): To derive a site-specific distribution coefficient, one of the following methods shall be used:

(i) Deriving K_d from soil fraction of organic carbon (f_{oc}) measurements: Site-specific measurements of soil organic carbon may be used in Equation 2 to derive distribution coefficients for organics, using the tabulated values for K_{oc} and, as appropriate, a site specific pH. Soil organic carbon measurements shall be based on uncontaminated soil below the root zone that is representative of site conditions or in areas through which contaminants are likely to migrate.

U.S. EPA (2002) methods for the determination or measurement of soil organic carbon may be used. All laboratory measurements of soil organic carbon shall be based on methods that do not include inorganic carbon in the measurements.

(ii) Deriving K_d from site data: Site-specific measurements of the substance concentrations in the soil and the soil pore water or groundwater may be used to derive a distribution coefficient. Distribution coefficients that have been derived from site data shall be based on measurements of soil and groundwater substance concentrations from the same depth and location. Soil and groundwater samples that have substances present as a NAPL shall not be used to derive a distribution coefficient and measures shall be taken to minimize biodegradation and volatilization during sampling of organic pollutants, or transport and analysis of these samples.

(iii) Deriving K_d from batch tests: A site-specific distribution coefficient may be derived by using batch equilibrium tests, such as ASTM Method C1733 for metals or ASTM Method E1195 for organics, to measure substance adsorption and desorption. The results from the batch test may be used to derive K_d from the sorption/desorption relationship between substance concentrations in the soil and water. Samples that have substances present as a NAPL shall not be used to derive a distribution coefficient and measures shall be taken to minimize biodegradation and volatilization during testing of organic pollutants.

Substance movement in soil water can generally be described as "mobile/immobile phase" partitioning. At equilibrium, the adsorption-desorption equilibrium constant or distribution co-efficient, K_d is defined as:

$$K_d = C_s/C_w$$

Where, C_s (in mg/kg) and C_w (in mg/L) are equilibrium concentrations in soil and water, respectively.

- c. **Deriving soil bulk density:** ASTM Method 2049 may be used to derive soil bulk density values that are representative of the soil being evaluated.
- d. **Deriving soil volumetric water content using laboratory methods:** ASTM Method 2216 may be used to derive soil volumetric water content values that are representative of the soil being evaluated.
- e. **Estimating soil air content:** An estimate of soil air content may be determined by calculating soil porosity and subtracting the volumetric water content.
- f. **Deriving a dilution factor from site-specific estimates of infiltration and groundwater flow volume:** Site-specific estimates of dilution factor may be derived using the following equation (U.S. EPA, 1996):

$$DF = 1 + \frac{Kid}{IL} \quad \text{(Equation 3)}$$

Where:

- i = gradient (m/m)
- d = mixing zone depth (m), calculated below (Equation 4)
- I = infiltration rate (m/yr)
- L = length of area of concern parallel to ground water flow (m)
- K = aquifer hydraulic conductivity (m/yr)

Equation for calculating the aquifer mixing zone depth, d:

$$d = (0.0112L^2)^{0.5} + d_a \{1 - \exp[(-LI)/(Kid_a)]\} \quad \text{(Equation 4)}$$

Where:

- d_a = aquifer thickness (m)
- and calculated d may not exceed d_a

The Department seeks input on whether the self-implementing alternative PMC should incorporate any lower boundary on the value of the Length of the area of concern because the EPA soil screening guidance suggests the use of extremely small values for L can result in very large DF values (similarly for Infiltration). Alternatively, should an upper bound on the value of the DF be specified for the self-implementing option, with higher values subject to review and approval?

- g. **Other Site Data Collection Requirements and Methods:** Equation 1 is used to calculate site-specific estimates of soil concentrations (leaching-based site-specific levels/PMC). 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.

Determination of comprehensive physical properties for vadose zone soils is needed for site-specific evaluations of soil leaching to groundwater. A minimum of five subsurface soil samples must be collected and analyzed for physical and chemical properties that are representative of the soil type in the area of contamination and leaching pathway. In addition to the above methods, the following laboratory methods are necessary:

- Soil dry bulk density – ASTM D2937;
- Soil moisture content (volumetric) – ASTM D2216;
- Soil pH – ASTM D4972; and
- Fraction organic carbon (f_{oc}) – ASTM D2974.

(3) Unsaturated Zone Leaching Models:

a. **Applicability:** This section specifies the procedures and requirements for establishing site-specific soil concentrations through the use of fate and transport models other than those specified in the sections above. These models may be self-implementing at GB groundwater classification areas. The Commissioner's review and approval will be required for GA groundwater classification areas. These models, SESOIL and VLEACH, add the greatest value when clean soil exists between the soil contamination and the seasonal high water table. In the simplest use of models, this approach incorporates the assumption that no measurable impact to groundwater has yet occurred, at any concentration. When there is already measurable impact to groundwater additional evaluation and departmental review and approval will be required. Additional restrictions on the use of these models include:

- With the exception of VOCs, the SESOIL model may be used to establish a soil concentration for any substance. The VLEACH model may be used to establish soil concentration for VOCs;
- These models are not applicable when non-aqueous phase liquid (NAPL) is present;
- If soil pH has been significantly altered beyond the natural pH for the soil, the SESOIL model may not be used for metals; and,
- Use of the SESOIL model should be limited to sites without fill material.

The Department has encountered some instances of inappropriate use of models or indefensible selection of model inputs that raise concerns; the Department is still evaluating whether and to what extent self-implementation of a modeling approach would be permissible. Input on how to balance the apparent need for critical review oversight with a self-regulating and bounding regulatory approach is solicited; what level of supporting documentation, such as sensitivity analysis, should be submitted for review?

b. **Fate and Transport Models:** The Department has identified two fate and transport models that it considers widely applicable for determining a site-specific alternative

PMC. For certain pollutants, such as pesticides, other models may also be appropriate.

SESOIL: The Seasonal Soil Compartment Model (SESOIL) model was originally formulated by Arthur D. Little and Associates for the USEPA (Bonazountas and Wagner, 1984). Since that time it has been revised and updated several times (Bonazountas et al., 1997). SESOIL is a one-dimensional vertical transport and fate model for the unsaturated (vadose) zone. The SESOIL model is most useful when the contaminant has either low mobility, or has a higher mobility but is either present at low concentrations or has a low toxicity. If the contaminant has low mobility the contaminant will not migrate to the water table even under long simulation times. If the contaminant is present at low concentrations or has a low toxicity, then the contaminant may reach the water table, but concentrations in the leachate at the bottom of the unsaturated soil zone may not be sufficient to impact the ground water at levels that exceed the applicable risk based criteria. Under such conditions, existing soil contamination may be shown to not pose a threat to ground water quality demonstrating that the impact to ground water pathway is not of concern. SESOIL produces a leachate concentration at the base of the modeled unsaturated zone, not a groundwater concentration. Depending on the version of SESOIL employed the output contaminant concentration can be specified for selected depths versus time and/or selected time versus depth, however, it is a requirement that SESOIL model version 6.2 or later must be used.

VLEACH: VLEACH is a one-dimensional finite difference model that simulates fate and transport of volatile organic compounds (VOCs) sorbed in the unsaturated zone. The fate and transport processes are simulated in a vertical polygon that is represented by a stack of cells with constant thickness that reaches from the land surface to the groundwater table. The soil properties (e.g., dry bulk density, effective porosity, volumetric moisture content, and soil-water partition coefficient) and groundwater recharge rate are considered to be uniform within the vertical polygon. The program models four main processes: liquid-phase advection, solid-phase sorption, vapor-phase diffusion, and three-phase equilibration. In an individual run, VLEACH can simulate leaching in a number of distinct polygons, which may differ in terms of soil properties, recharge rates, depth of water, or initial conditions. Modeling results in an overall, area-weighted assessment of ground-water impact. The model assumes a steady state downward water flow. The processes of in-situ degradation and dispersion are neglected, making the VLEACH model more conservative.

- c. **Processing Unsaturated Zone Modeling Results:** The output of the models predicts the contaminant amount that is exiting the unsaturated zone and entering the saturated flow system, and how it varies over time. The peak estimated leachability must be used in evaluating a soil's PMC; if the model results do not exhibit a peak the value for a simulation of 100 years must be used. This output may be expressed as a concentration and then **divided** by a dilution factor (DF), either the default value of 20 or a site specific DF determined as described above for the Variable Parameter Three-Phase Partitioning Model, to derive an estimate of groundwater contaminant concentration at the compliance point. This concentration must be less than the applicable groundwater compliance criteria or soil remediation is necessary.

Note that if the groundwater has detectable concentrations of the contaminant being evaluated there may be a need to review the conceptual model to determine whether the soil pollution contribution to groundwater may cause an increase in groundwater pollution, or if the levels are controlled by a sustainable unsaturated zone attenuation process accurately depicted by the model and validated by monitoring. This is essential because the measured groundwater quality reflects past leaching history whereas the model prediction is for future leaching potential, and these are not immediately comparable, especially when the dynamics of the source are incompletely known.

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