Vadose Zone Modeling in RCRA Closure

" This Policy Does Not Have the Force of Law"

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Division of Hazardous Waste Management
Ohio Environmental Protection Agency

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Acronyms

ACL	Alternate Concentration Limit
ASTM	American Society for Testing and Materials
COC	Constituent of Concern
CPRG	Closure Plan Review Guidance (an Ohio EPA document)
DHWM	Division of Hazardous Waste Management
MCL	Maximum Contaminant Levels
NAPL	Non-Aqueous Phase Liquid
OAC	Ohio Administrative Code
ODNR	Ohio Department of Natural Resources
RCRA	Resource Conservation Recovery Act
REDOX	Reduction Oxidation Potential
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
UCL	Upper Confidence Limit

Variables

Parameter	Definition
A	Cross-sectional area perpendicular to flow
C_a	Upgradient concentration of the pollutant in the aquifer (if any) (µg/ml)
C_{gw}	Concentration of the contaminant in the saturated zone (µg/ml)
C_p	Contaminant concentration in the soil pore water (µg/ml)
C_{sat}	Soil saturation limit (mg/kg)
C_{sol}	Concentration of a metal dissolved in the soil solution
C_{solid}	Concentration of a metal absorbed to the solid material
CLF_{gw}	Critical Leaching Factor (kg/L)
DAF	Dilution Attenuation Factor
d	Depth of mixing zone (m)
d_α	Aquifer Thickness (m)
exp	Inverse of the natural log
f_{oc}	Fraction of organic carbon
g	Acceleration of gravity or grams
h	Pore water pressure head (cm)
h_2-h_1	Change in head per unit length
H’	Henry’s Law constant for the COCs (dimensionless)
i	Hydraulic gradient (m/m)
K	Horizontal hydraulic conductivity (m/yr)
K_d	Partitioning constant for the soil = K_{oc} X f_{OC} (cm^3/g)
K_h	Unsaturated hydraulic conductivity (cm/day)
K_{oc}	Organic carbon coefficient (Kg/L)
K_{ow}	Octanol-water partitioning coefficient
K_P	Partitioning coefficient

K_s	Saturated hydraulic conductivity
K_v	Vertical saturated hydraulic conductivity
L	Source length parallel to ground water flow (m)
LF_{gw}	Leaching factor (kg/L)
n_e	Effective porosity
q	Flux
Q_r	Volumetric flow rate of infiltration (soil water) to the aquifer (cm^3/d)
Q_{gw}	Volumetric flow rate of ground water beneath the contaminated area (cm^3/d)
r	Infiltration rate (meters/year)
S	Irreducible water content
S	Solubility in water (mg/L)
T	Temperature
v	Linear pore water velocity
w	Length of source perpendicular to ground water flow
ΔP	Change in hydrostatic pressure
κ	Intrinsic permeability (cm^2)
μ	Dynamic viscosity
ϕ	Porosity
ρ_b	Dry bulk density (gm/cm^3)
ρ_f	Fluid density
ρ_s	Particle density
θa	Fraction of air filled porosity
θ_m or θ_v	Water-filled porosity or water content
θ_r	Irreducible water content
θ_s	Volumetric water content
θw	Fraction of water filled porosity
$-\psi_A$	Air entry pressure
ψ_m	Matric potential, suction head, or pore water pressure
$\partial\theta/\partial t$	Change in volumetric water content through time (cm^3/cm^3)
$\partial h)/\partial Z$	Change in head with depth (cm)

Glossary

Absorption - Partitioning of a dissolved species into a solid phase.

Adsorption - Partitioning of a dissolved contaminant onto a solid surface.

Advection - Fluid migration induced by hydraulic gradients.

Albedo - Fraction of sun light reflected by the atmosphere (never reaches Earth's surface).

Anisotropy - The condition wherein soil characteristics vary differently in different directions due to an arrangement or alignment pattern within the soil.

Bulk Density (ρ_b) - The oven-dried mass of a fixed volume of soil divided by the original sample volume.

Calibration (of a model) - A process that involves varying input parameters to result in a critical output parameter (*e.g.*, ground water recharge rate) that is more reflective of natural conditions.

Capillary Fringe - A zone above the water table into which moisture is pulled due to capillary action.

Cation Exchange Capacity - The excess of cations in solution adjacent to a charged surface that replaces other cations already absorbed to that surface. The sum total of exchangeable cations that a soil can absorb.

Complexation - Any combination of cations with organic molecules or cations with anions containing free pairs of electrons

Conceptual Site Model - A generalized picture that sums up the contaminant sources, contaminant movement mechanisms, routes, end points (receptors), and other factors possibly affecting contaminants at a site.

Hydraulic Conductivity (K) - hydraulic conductivity is not a tangible measurable characteristic but rather is defined by the equation:

$K = \frac{-Q}{A(dh/dl)}$ $K = -Q / (A\, dh/dl)$

where Q is the discharge, A is the cross sectional area, and dh/dl is the hydraulic gradient. The units of K are L/T.

Constituents of Concern - Organic or inorganic contaminants that may have contaminated environmental media resulting from the activities at a facility that generated hazardous waste and/or hazardous constituents.

Co-Solvent Effects - A situation where the presence of another contaminant (*e.g.*, an organic solvent) makes a contaminant more mobile than would be expected if it were the only contaminant present.

Degradation - Biological or abiotic (*e.g.*, redox or hydrolysis reactions) breakdown or transformation of organic chemicals.

Diffusion - A transport process in which chemicals migrate in fluid due to concentration gradients, moving from areas of higher concentration to areas of lower concentration.

Dilution Attenuation Factor - Accounts for dilution of soil pore water when it mixes with ground water. Various equations are used to estimate this factor.

Disconnectedness - A catchall term used in the SESOIL model that includes effects of hysteresis and other factors that affect contaminant movement (based on soil type).

Dispersivity - A characteristic of the geological medium attributed to tortuosity and heterogeneity that affects mechanical mixing of chemicals during advection.

Effective Porosity - This is the interconnected portion of the total porosity, the part that is actually available for flow (*i.e.*, contaminant migration).

Flux - The amount of water per unit volume that passes through a defined area.

Fraction of Organic Carbon - This is the carbon in the soil that is made up of decaying plant and animal matter, humus, *etc.* It is differentiated from inorganic carbon (typically in calcium or magnesium carbonates) which does not have the same impact on contaminant movement. Generally the dominant retarding mechanism for contaminant movement in the vadose zone.

Hydraulic Conductivity - a measure of how easily water flows through (or can be pumped from) an aquifer.

Hydraulic Gradient (dh/dl) - The change in water table height (dh) over some distance (dl). The hydraulic gradient describes the direction and magnitude of ground water flow. It does not describe the velocity of ground water movement.

Hydrologic Cycle - The exchange of water among the ocean, atmosphere, and land by such processes as evaporation, precipitation, surface runoff, and groundwater infiltration.

Hydrolysis - The addition of water to a molecule.

Infiltration - The amount of water that enters the vadose zone (*i.e.*, from rainfall or irrigation).

Infinite (*vs.* Finite) Source - Used as an input assumption in some vadose models. In a finite source, the concentration of soil contamination depletes over time as contamination migrates and degrades, *etc.*, whereas an infinite source, the concentration remains relatively constant over time such as is found in a former landfill, surface impoundment, *etc.*

Isotropy - The condition wherein soil characteristics vary in a similar way regardless of direction.

K_d - Distribution coefficient, the ratio of contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium.

K_{oc} - Partitioning coefficient between organic liquid and organic carbon.

K_{ow} - Octanol water partitioning coefficient. Measures a contaminant's affinity for polar or non-polar solutions.

Leaching - The removal of constituents from a waste by the action of percolating fluids.

Ligand - Anion (*e.g.*, SO_4^{2-}) or molecule with which a cation (*e.g.*, Pb^{+2}) forms complexes.

Mass Balance - Evaluation of contamination using the total raw amount of the contaminant(s), not just the concentration in media.

Matric Potential - Also called the suction head or pore water pressure, the force of adhesion that draws water into pore space. The matric potential is inversely proportional to the pore-size of a soil.

Miscible Displacement - A contaminant transport mechanism whereby retardation of chemical movement is primarily driven by exchange reactions between inorganic contaminants and soil particles that is affected by chemistry of the solute, the pore solution, and the soil.

Mixing Zone - The vertical depth in a aquifer in which a contaminant is expected to mix (and thereby dilute).

Non-Aqueous Phase Liquid - Liquid "free product" present or potentially present in the vadose zone. Generally evaluated by comparing soil contaminant levels to soil saturation limits.

Partition Coefficient - The term that linearly relates the concentration of a contaminant in the water phase to that in the solid phase by the following equation $C_{solid} = Kd\ C_{water}$.

Partitioning - A transport process in which chemicals are distributed between solid, liquid, and gas phases, depending upon solubility, sorption, and vapor pressure characteristics.

Permeability - Ease with which a soil can transmit fluid when saturated with that fluid (*i.e.,* water).

Pore Water Velocity - The mean water flow rate in the soil pores, sometimes refered to as the Darcian velocity.

Porosity - The ratio of void space to the unit bulk volume of soil. It may be filled with water and/or air.

Recharge - The amount of infiltration water that makes it through the vadose zone down to the ground water table.

Retardation - Factors limiting pore water velocity.

Runoff - Water (*i.e.*, from rainfall or irrigation) that does not infiltrate into the vadose zone but instead "runs off" into surface water.

Sensitivity Analysis - The process of varying model input parameters over a reasonable range (range of uncertainty in the value of the model parameter) and observing the relative change in model response.

Soil Saturation Limits - A calculated value that estimates the level at which a contaminant will partition from the aqueous phase into a Non-Aqueous Phase Liquid.

Solubility - A measure of a theoretical maximum level a contaminant will dissolve in an aqueous phase before the contaminant is available as "free product."

Sorption - The chemical or physical process of sorbing chemicals to solid surfaces.

Source (instantaneous *vs*. continuous) - An input term for some vadose models that differentiates between a spill and something more like a long term leak or impact from a relatively infinite source like a landfill.

Species - The form (or valence state) of a dissolved ion, element, or molecule as it is present in a particular solution.

Tortuosity - A measure of the non-linear pathway that water molecules taken within aquifer or vadose zone materials.

Vadose Zone - The section of the Earth where soil water, soil particles, and soil gas exist in equilibrium. This zone lies between the ground surface and the top of the water table.

Vapor Pressure - The pressure exerted by a vapor in equilibrium with its solid or liquid phase.

Volumetric Water Content - Volume of water per unit volume of bulk soil.

Preface

This document was written primarily as a guidance for developing and reviewing vadose zone models that are generated by facilities to support that wastes left in soil, after meeting direct contact risk standards, will not pose a significant threat to ground water resources. In this guidance, this analysis is divided into three tiers. The tiers are characterized by increasing levels of site-specific information that is necessary to make a leaching demonstration. Division of Hazardous Waste Management personnel will use the guidance primarily to evaluate input parameters and assumptions used to develop vadose zone models for RCRA closure sites in Ohio. Division personnel may also choose to use a vadose zone model to double-check the results submitted by a facility (using the same or a different model).

Section 1.0
Introduction

1.0 Introduction

The vadose zone is defined as that section of the earth where soil water, soil particles and soil gas exist in equilibrium. This zone is important because it is there that contaminants are often introduced into the environment and eventually are transported to groundwater. An understanding of how chemicals can migrate through the vadose zone is necessary for environmental professionals to predict the impact that contamination may have on human health and the environment.

Fate and transport modeling of contaminants in the subsurface has been successfully applied to numerous environmental sites throughout the country. Models have been used to predict the time of travel and concentration of contaminants in groundwater to some point, such as a unit boundary well. However, fate and transport modeling of chemicals in groundwater has had only limited acceptance at Resource Conservation Recovery Act (RCRA) closure sites, mainly because of the uncertainties and validation practices associated with numerical modeling. In fact, guidance from the U.S. EPA has specified that only limited modeling be performed at a RCRA closure site and only under strict conditions (See Elizabeth Cotsworth Memorandum, reproduced in Ohio EPA, Closure Plan Review Guidance (CPRG), 1999 and later revisions).

Ohio EPA, Division of Hazardous Waste Management (DHWM) has allowed the use of vadose models to determine the leaching potential of contaminants that remain in soils at a closure site. In addition, groundwater modeling for engineering purposes and for the determination of an Alternate Concentration Limit (ACL) has also been accepted. Engineering applications include a determination of the number and location of pumping and extraction wells, and to determine extraction rates for ground water pump and treat systems. Soil vapor extraction systems, air sparging systems, and biological treatment systems have also been successfully modeled. The benefit of modeling is that pre-optimization of remediation systems can be performed in the office and not in the field, saving time and lowering costs.

Numerical models have also been developed that can predict the rate of intrusion of vapors and the concentration of these chemicals that can enter into buildings. Vapor intrusion into buildings is recognized as a potential pathway of human exposure and these models can also be used to judge whether vapor intrusion is a viable pathway.

All of these examples of model use are important; however, the scope of this guidance will be limited to the movement of chemicals through the unsaturated zone to the upper most aquifer to assure that leaching of chemicals is not a concern.

Vadose zone leaching models are available that cover a wide range of applications ranging from screening-level analytical models to advanced numerical models. The approach taken in the guidance document focused on the methodology outline in ASTM and U.S. EPA guidance on chemical transport through the unsaturated zone.

The application of any model will depend upon the RCRA closure objectives. Usually data collected from normal RCRA closure investigations is insufficient to support the site specific vadose zone modeling. One of the most important parts of the Data Quality Objective (DQO) process is the acquisition of a sufficient quantity of quality data as input parameters for a model. Therefore, sampling activities for a RCRA closure should reflect the DQOs needed to complete any anticipated model.

There are several useful references for data collection to support subsurface investigations and modeling including, the U.S. EPA publication, *Site Characterization for Subsurface Remediation* (1991) and *Handbook of Vadose Zone Characterization and Monitoring* (Wilson *et al*, 1994). In addition, data quality documents that should be consulted are U.S. EPA's DQO publications that can be found at US EPA's website: http://www.epa.gov/quality/qa_docs.html.

This document is divided into six sections. Section 1 is an introduction, Section 2 outlines the Tier I process, Section 3 describes the Tier II process, Section 4 describes the Tier III process and Section 5 outlines the basic approach to using numerical models and discusses reporting requirements. Section 6 is a list of references and other potentially useful sources of information. Appendix A provides background information (*i.e.*, American Society for Testing and Materials, ASTM, methods) on subsurface hydrology and other parameters of interest. Appendix B lists important physical properties for a wide variety of organic chemicals. Appendix C lists conventional methods to determine important soil physical parameters, such as dry bulk density.

1.1 Applicable uses of leaching models

Unsaturated zone modeling has wide applicability in environmental sciences and is often successfully coupled with saturated zone modeling. Because of the limitations imposed by U.S. EPA on modeling at RCRA closure sites (See Elizabeth Cotsworth Memorandum, as reproduced in Ohio EPA, CPRG, 1999 and later revisions), this document will only address the vertical movement of chemicals within the unsaturated zone to the saturated zone. **DHWM intends that the main use of unsaturated zone models at RCRA closure sites is to determine whether residual waste left in place after direct contact risk standards have been met can still pose a threat to the upper most aquifer. This assessment must be made before a closure by decontamination is deemed acceptable and the property is available for unrestricted use.**

The consequence of this use restriction is that unsaturated zone models cannot be used to determine decontamination requirements or to set initial soil clean-up standards is not allowed. DHWM believes that soil clean-up standards should be determined through the risk methodology outlined in the CPRG (1999 and later revisions). However, with the exception of sites using Generic Cleanup Numbers (GCNs), a leaching assessment may indicate that further soil remediation is necessary to protect ground water resources.

The leaching assessment, as presented in this guidance, is generally applicable to most closure sites in the state that have determined site specific clean up standards. However, there are site specific instances where this guidance will not apply. For example, the approaches presented in the following sections can not be used where Non-Aqueous Phase Liquids (NAPL) or "free product" is present. U.S. EPA guidance (1992a) should be used to evaluate this possibility. If NAPL is present, further remediation is required prior to any vadose zone modeling.

The Ohio EPA has designed a three-tiered process that will allow practitioners to use generic screening methods advocated by ASTM and U.S. EPA (Tier I), analog and/or numerical modeling using generic default parameters (Tier II), or site-specific modeling using a combination of generic defaults and site-specific data (Tier III). Figures 1 through 4 show general flow charts of the unsaturated zone modeling processes and typical decision points in the process. Each modeling tier is discussed in the following sections. A facility may choose to move through the tiers, beginning with Tier I, until they have adequately demonstrated that contaminants at their site will not leach to ground water. Alternately, a practitioner familiar with procedures in Tier I (or Tier II) may recognize the level of contaminants they are assessing will not pass that tier and choose to move directly to a higher tier.

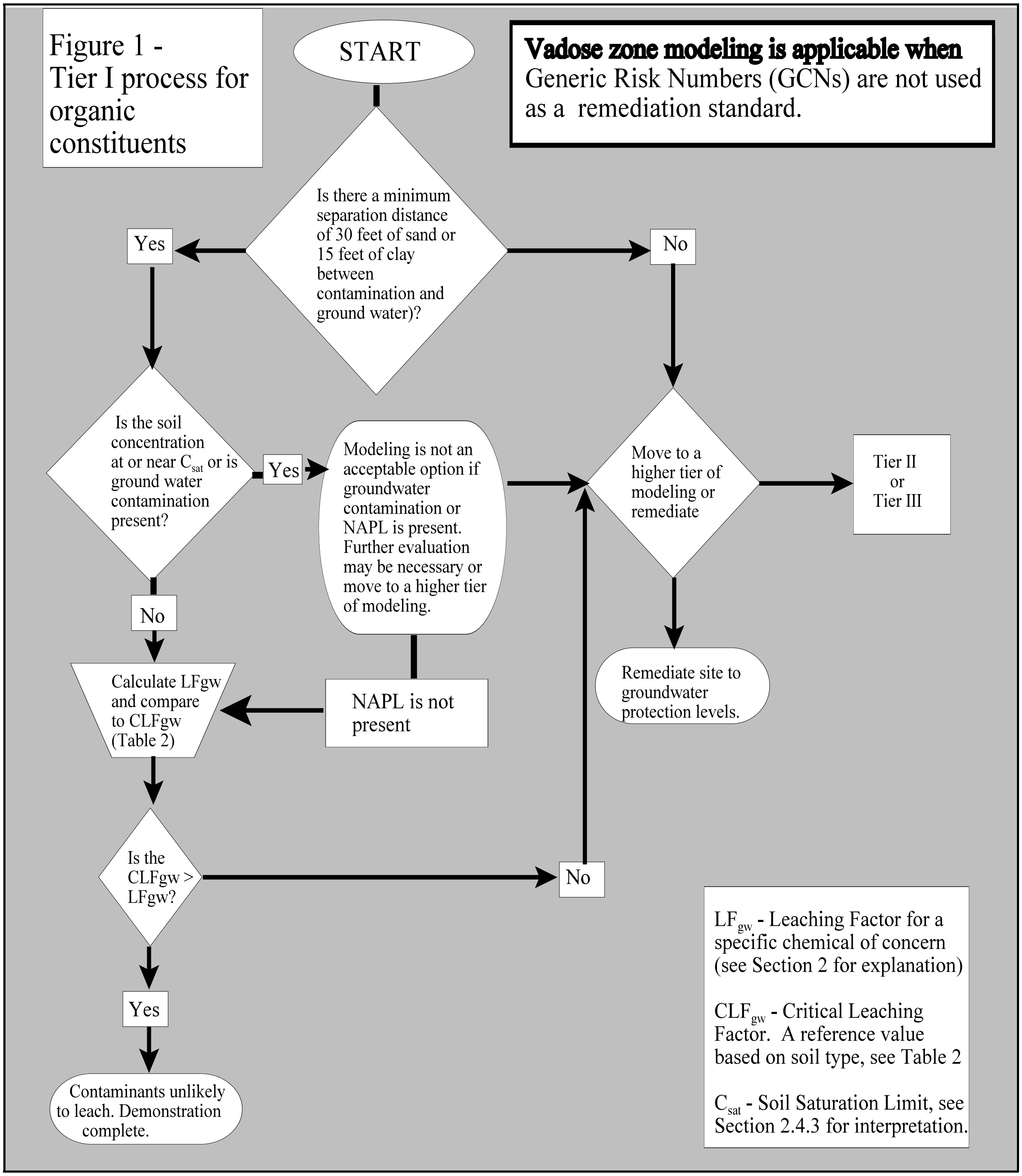

Figure 1: Tier I modeling process for organic constituents to determine whether residual soil contamination poses an unacceptable risk to ground water.

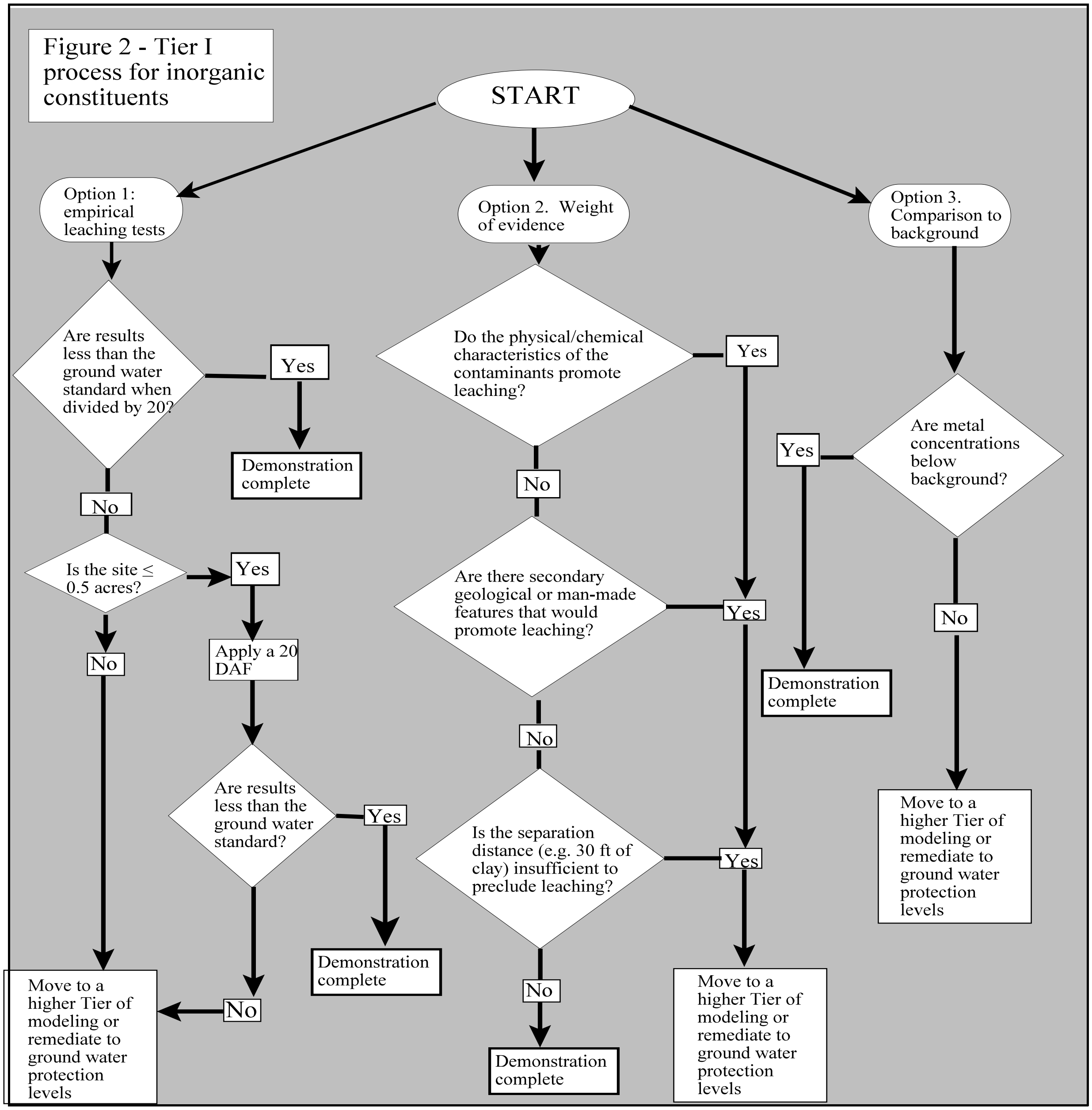

Figure 2. Tier I modeling process for inorganic constituents to determine whether residual soil contamination poses an unacceptable risk to ground water.

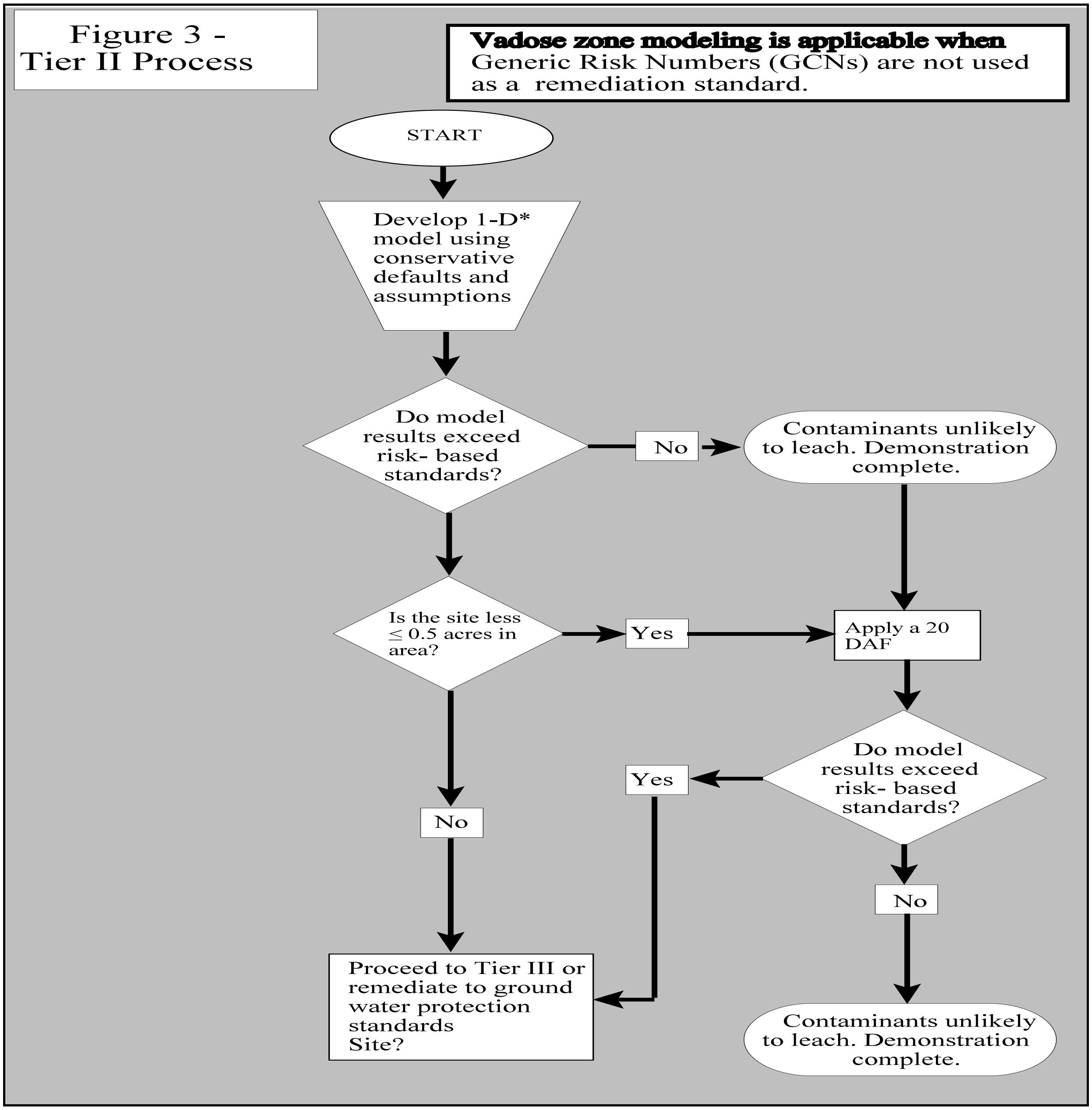

Figure 3: Tier II modeling process used to determine whether residual soil contamination poses an unacceptable risk to ground water.

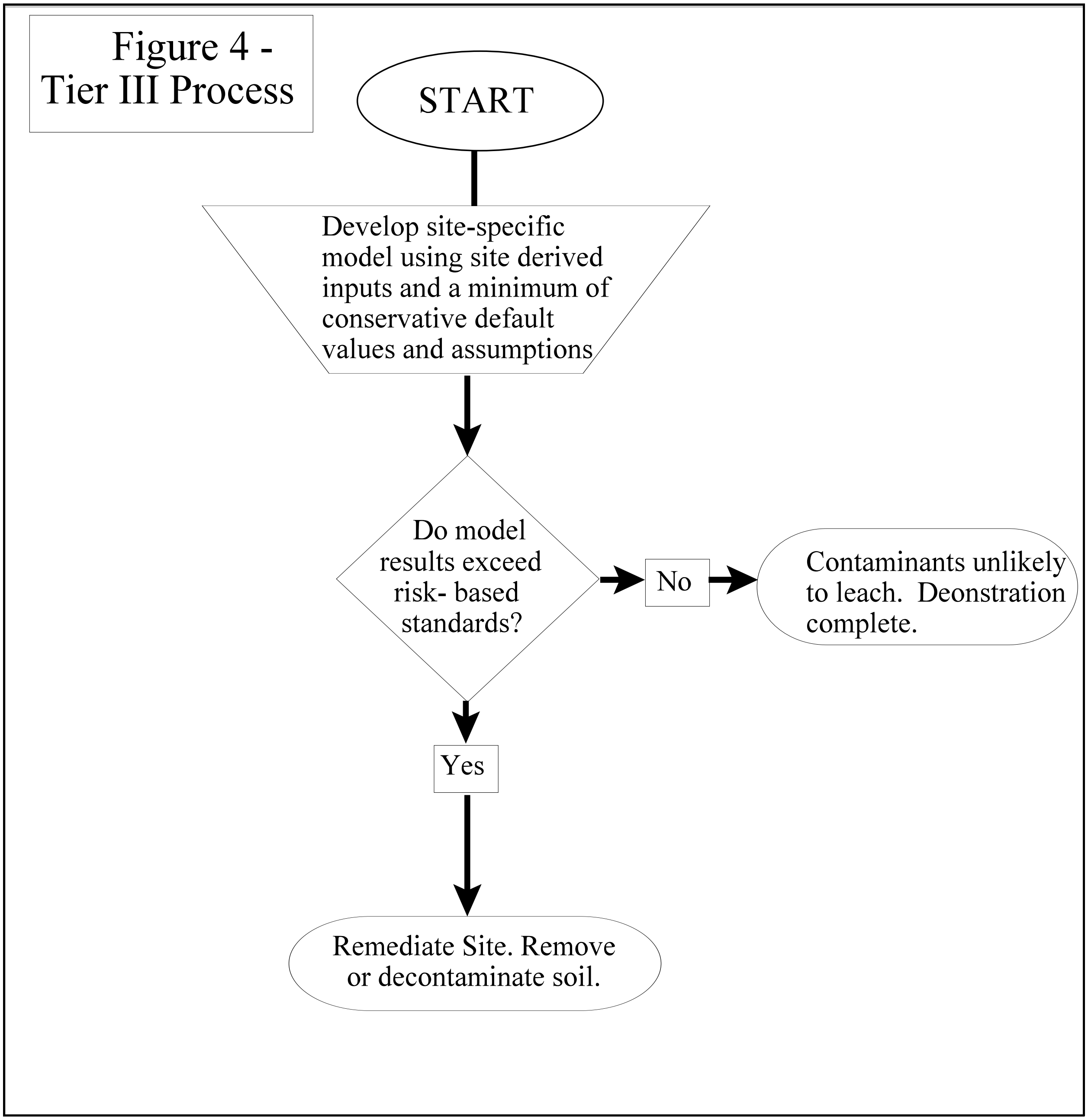

Figure 4: Tier III modeling process used to determine whether residual soil contamination poses an unacceptable risk to ground water.

Section 2.0
Tier I

2.0 Tier I: Leaching factors screening process

Human receptors can be exposed to contaminants through multiple pathways, including exposure to chemicals leaching from soils to ground water. Factors that affect the leaching of organic chemicals to ground water include, but are not limited to, infiltration rates, soil type, separation distance between the contaminated soil and ground water, organic carbon content of the soil, and characteristics of the contaminant (such as volatility). Various methods, from simple equations to complex models, are available to evaluate contaminant migration through soil to ground water. The models are based on the premise that it is possible to simulate the natural processes involved in vadose zone fate and transport of chemicals. This is accomplished by using the hydrological, mathematical, and operational characteristics of the models.

The Tier I process for organic chemicals is based upon ASTM's Risk Based Corrective Action (RBCA,1995) approach and is designed to provide a quick determination whether chemicals at a site could leach to ground water. The process outlined in this tier presents a very conservative estimate for a leaching evaluation; however, this approach does give a facility an option that requires a minimum site specific data. For example, this tier does not require the use of concentration data to make a leaching evaluation. Leaching Factors (LF) are compared to Critical Leaching Factors (CLF) to determine the potential for ground water leaching of organic chemicals. This method is designed to provide a fast and reasonable way to determine whether organic contaminants remaining at a RCRA facility closure unit could leach to ground water above applicable standards. If a necessary, a more quantitative evaluation of leaching potential is left for Tier II and Tier III. The reader is reminded that the Tier I evaluation is for demonstration purposes after a site has been evaluated as meeting risk-based clean standards (direct contact standards). **The Tier I process cannot be used to assess whether a ground water pathway should be excluded from the risk evaluation process.** The methodology for pathway analysis is presented in the CPRG (1999 and later revisions).

2.1 Organic constituents: generic leaching factors

The Tier I evaluation is designed for organic contaminants based on the partitioning equation contained in the U.S. EPA Soil Screening Guidance (Equation 24 in 1996a) and in the Risk Based Corrective Action process guidance (ASTM, 1995). The evaluation is based upon determining leaching factors for contaminants of concern and then comparing these leaching factors to a critical leaching factor. The leaching factors are designed to be conservative and protective of ground water resources.

The critical leaching factors presented in this section were determined by modeling using both the RISKPRO SESOIL™ and VLEACH unsaturated models[1] by Ohio EPA personnel. Modeling was conducted for various soils types, using a separation distance between the contaminant zone and underlying ground water of 15 to 30 feet, and for numerous chemicals. The soil concentrations used in the model simulations were assumed to be at the calculated chemical-specific soil saturation level. The recharge rates were based on the permeabilities of the respective soils and the simulations covered 100 years of percolation through the soil. The SESOIL and VLEACH modeling efforts were then compared to the leaching factors calculated from the partitioning equation to develop the critical leaching factors, below which, leaching from soils to ground water is not expected to occur.

The conceptual model that is used to simulate leaching of chemical contamination to ground water is illustrated in Figure 5.

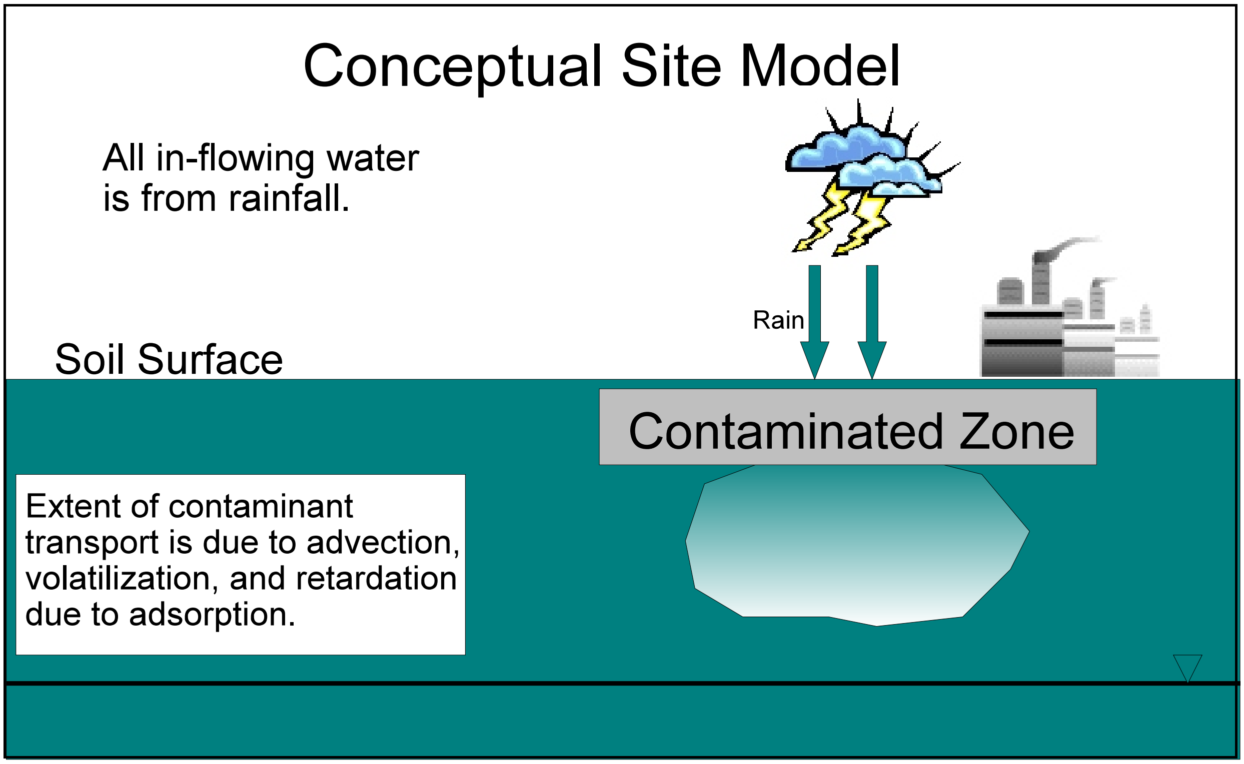

Figure 5: Conceptual model for the Tier I leaching process

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[1] SESOIL and VLEACH model results are discussed in more detail in the supporting documentation. Voluntary Action Program (VAP) Technical Decision Compendium VA30010.98.012 (VA30010.98.012 - VAP FAQ #11)

The conceptual model represents an open system. This model assumes that organic contaminants are sequestered uniformly near the soil surface. The concentration of all contaminants in the soil is assumed to be at or below their soil saturation limit. Therefore, the source term for contamination is assumed to be finite, but also at levels that exceed contamination amounts found in most site investigations. Another important aspect of selecting the soil saturation limit as the upper-most concentration boundary is that, at or near this limit, NAPL may be present. The conceptual model assumes that NAPL is not present and contaminants are transported only by advection/diffusion processes due to in-flowing rain water. In addition, flow of NAPL is not accounted for in the conceptual model. For these reasons, the potential or actual presence of a NAPL precludes the use of Tier I.

There are other important limitations to using the Tier I methodology. Tier I assumes that organic contaminant compounds do not react in the soil system. Therefore, abiotic and biotic transformations are not taken into account. However, volatilization and sorption of constituents are included in the conceptual model and modify the extent and rate of solute transport. The model also assumes that open boundaries exist for water to flow into, and out of, the system. All in-flowing water is assumed to be incident precipitation, so that transient infiltration conditions exist. Leachate leaves the system at the point that it enters the saturated zone. As a result, the model does not account for constant flux boundary conditions such as would be applicable to water infiltrating from a waste lagoon. This conceptual model is designed to provide a conservative approach.

2.2 Applicability/limitations

Several site condition and model limitations exist for practitioners applying the Tier I process for organic constituents. These limitations are presented below:

1) Contaminant Phase: Liquid free product (NAPL) should not be present or suspected to be present. Sampling results can be evaluated for the potential presence of NAPL using methods found in U.S. EPA (1992a). The reason for this restriction is that the methodology used to develop the Tier I leaching factors did not consider NAPL flow.

2) Contaminant Loading: The contaminants must be sequestered within the soil column and the source of contamination must not be a continuous source (*i.e.* a continuous drip or leak). The source term for contamination is therefore finite.

3) Co-Solvent Effects: The methodology described in this guidance for the assessment of leaching of contaminants in the soil to ground water is based on the assumption that the behavior of one chemical is independent of other chemical constituents present in the unsaturated zone. In addition, interactions between

chemicals in the soil, or changes to the partitioning of one chemical between soil and water caused by the presence of a co-solvent, are not considered in the modeling for the leaching factors. Such interactions can have important effects upon the mobility of a chemical. This guidance, including the critical leaching factors (CLF_{gw}) contained in Section 2 (Table 2), can only be reasonably applied at sites without substantial co-contamination by other chemicals which may impact the migration of low-mobility compounds.

The circumstances which give rise to co-solvent effects include two plausible mechanisms: (1) the dissolution of one soil-borne chemical contaminant into the soil pore water occurs at levels sufficient to increase the pore water solubility of one or more soil-borne contaminants; and (2) NAPL flow can result in the increased mobility of one or more soil-borne contaminants due to the direct impact of the free product solvent upon other contaminants. Residual levels of multiple contaminants at or below soil saturation concentrations (C_{sat}) in the unsaturated zone could result in the first of these two mechanisms. The movement of NAPL within the unsaturated zone can promote the second mechanism.

As an example, DHWM is aware of a contaminated site where co-solvent effects seem to have affected the mobility of constituents. Releases of 2,3,7,8-tetrachlordibenzodioxin (dioxin) and other related polychlorinated dibenzodioxins and dibenzofurans resulted from by-products of phenolic plastic manufacturing; the same facility used benzene as a feedstock material and solvent for resin production. It is reasonable to expected that the dioxin in the surface soils would exhibit limited mobility within the unsaturated zone due to its low solubility and high organic carbon coefficient (K_{oc}) values. However, polychlorinated dioxins have been found at soil depths indicative of a greater mobility than predicted on the basis of dioxin solubility alone. A plausible explanation of the increased mobility of dioxin in the presence of benzene is the high solubility of dioxin in benzene, which facilitates the transport of dioxin to greater depths than those predicted for dioxin alone.

Significant co-solvent effects that may enhance the mobility of contaminants may occur even if NAPL is not present. In addition, site history can have a bearing on the legitimacy of vadose zone modeling. The historical release of any free product to the unsaturated zones should also be considered when developing a model. The historical presence of free product may have contributed to a greater vertical migration (of otherwise low mobility constituents dissolved in the free product) than would have otherwise been predicted.

4) Soil Contaminant Concentrations: Concentration ceilings are the maximum concentrations of the Constituents of Concern (COCs) found at a site, or the 95% Upper Confidence Limit (UCL) of the arithmetic mean. In some cases, the

maximum contaminant level can be used in lieu of the 95% UCL. See Ohio EPA, DHWM CPRG (Ohio EPA, 1999) for details on calculating the 95% UCL (reproduced from U.S. EPA, 1992b) and appropriate use of the maximum contaminant level. These values are also used to assess whether constituents are at or near the soil saturation limit (C_{SAT}).

5) Secondary Features: The potential for discrete features in the unsaturated zone (both unconsolidated and consolidated deposits) to act as conduits or barriers to chemical movement to the water table must be assessed qualitatively. Therefore, the presence, character, and density of any faults, fractures, joints, subsidence fissures, solution channels, significant sand seams or clay layers, and other similar features should be evaluated. In the presence of such features, generic methodology found in Tier I may not be acceptable. For this case, site-specific modeling as covered in Tiers II and III may be more applicable.

6) Man-Made Deposits or Features: The modeling approach used to develop this guidance assumed that precipitation infiltrates directly into natural soils and migrates to the saturated zone. Man-made deposits, such as fill material, coal piles, ash or slag heaps, or gravel piles, could have far different hydrology and geochemistry characteristics than that used in the modeling to define the critical leaching factors and would not be appropriate for use with Tier I. In addition, other anthropogenic influences (*e.g.*, sewer pipes, conduits for utilities, *etc.*) that may impact the geology/hydrogeology leading to preferential flow pathways should be evaluated when addressing leaching to the ground water pathway. These types of influences can also invalidate standard model assumptions.

7) Contaminant Location: Tier I methodology is not appropriate if the sequestered contaminants in the soil are less than 15 feet from the ground water zone.

8) Time of Release: Limiting the evaluation to the Tier I process based only on surficial soil contamination may not be sufficient when there are indications of continuous releases over a number of years. In this situation, ground water monitoring data may be needed to support that past releases have not already impacted ground water.

9) Ground Water Sampling: Tier I should not be used if ground water screening indicates that sources from the property have contaminated the ground water. Sampling is recommended to determine whether the target ground water concentration is exceeded unless at least 30 feet of clay/till material separates the contaminated soils and the ground water (see Table 2).

2.3 Tier I: Evaluation of organic constituents leaching to ground water

Tier I evaluates the likelihood that an organic chemical could leach to ground water. This tier does not require the use of chemical concentrations to determine critical leaching critical factors, but does require basic knowledge of the physical/chemical properties of the chemicals that are present, and basic geotechnical information on the vadose zone materials. The practitioner is reminded that the Tier I evaluation is for demonstration purposes after a site has been evaluated as meeting risk-based clean standards (direct contact standards). **The Tier I process cannot be used to assess whether a ground water pathway should be excluded from the risk evaluation process.** The CPRG (1999 and later revisions) has methodology to perform pathway analyses. Tier I compares a Leaching Factor (LF_{gw}), generated for a chemical of concern at a site, to a Critical Leaching Factor CLF_{gw}. This comparison is used to determine whether a qualitative assessment is sufficient or whether a quantitative evaluation is needed. This evaluation is similar to ASTM (1995). The Ohio EPA, DHWM will also allow the use of equilibrium partitioning as described in U.S. EPA's *Soil Screening Guidance* (1996). However, DHWM expects that chemical physical/chemical parameters and other parameters used in this equation use data given in this guidance and in DHWM's CPRG.

As specified in the Application/limitations section, general restrictions for all three tiers exist for determining that the leaching pathway is not a concern. For example, the process should not be used if NAPL is present or suspected. The C_{sat} values used to make this NAPL determination correspond to the contaminant concentrations in the soil at which the absorptive limits of the soil particles, the solubility limits of the soil pore water and saturation of soil pore air have been reached. Above this concentration, the soil contaminant may be present in free phase, *i.e.* NAPLs, for contaminants that are liquid at ambient soil temperatures and pure solid phases for compounds that are solid at ambient soil temperatures.

In addition, the Tier I process should not be applied where a continuous release to the vadose zone exists (*e.g.*, continued leaching from a waste lagoon),or secondary features are present that may channel the contaminants. Tier I is not applicable if less than 15 feet of separation exists between the contaminated soils and the saturated zone. If this is the case, ground water sampling may be necessary to confirm that the ground water is currently meeting the target ground water concentration. Usually ground water sampling will be determined in the site investigation phase of a unit's closure and additional empirical data will not be necessary.

2.3.1 The Tier I process for organic constituents

Tier I utilizes leaching factors (LF_{gw}) and compares these values to critical leaching factors. The needed information and the steps necessary to perform a Tier I leaching evaluation are summarized in the following text.

2.3.2 Step 1. Determine a chemical-specific LF_{gw}

Equation 1 provides a means of calculating LF_{gw} for a wide variety of organic chemicals. The generic LF_{gw} values can be calculated as follows (equation based on an equation in ASTM, 1995 and equation #24 in U.S. EPA, 1996a):

$$LF_{gw} = \frac{\rho_b}{\left[\theta_w + K_d \rho_b + H'\theta_a\right]} \times \frac{cm^3 \cdot kg}{gm \cdot L} \tag{1}$$

where:

LF_{gw} = leaching factor (kg/L)
ρ_b = dry bulk density (g/cm^3)
θ_w = fraction of water filled porosity
θ_a = fraction of air filled porosity
K_d = partitioning constant for the soil = K_{oc} X f_{oc} (cm^3/g)
H' = Henry's Law constant (dimensionless, chemical-specific)

This equation requires values for the air-filled porosity, water-filled porosity, organic carbon content, and dry soil bulk density, Henry's Law Constant, and partitioning constant. The result of this equation predicts how likely a chemical is to leach (*i.e.*, higher numbers are more likely) using default constituent of concern input values. Table 1 provides the default inputs used to calculate these leaching factors.

Table 1: Parameter defaults used to develop the generic leaching factors.

Parameter	Defaults for the Generic LF_{gw}	
bulk density (ρ_b)	*Default for Tier I = 1.6	
air-filled porosity (θ_a)	0.26	(ASTM, 1995)
water-filled porosity (θ_w)	0.12	(ASTM, 1995)
fraction of organic carbon (f_{oc})	0.2% (0.002)	(DHWM,CPRG, 1999)
Henry's Law Constant (H')	Chemical-specific.	
partitioning constant (K_d)	Chemical-specific.	

2.3.3 Step 2: Determine the vadose zone material and its thickness.

The user needs to determine the appropriate soil category and depth between the soil contamination and ground water. This information should be determined by boring data and field/laboratory tests.

Soil types have been divided into three main categories. These are as follows:

Soil Type I: Vadose zone soil type I is characterized by a vertical hydraulic conductivity (K_v) ranging from 1 x 10^{-3} to 1 x 10^{-4} cm/s, a net recharge rate ranging from approximately eight to fourteen inches per year ,and a mean annual depth to ground water greater than five feet below grade. This soil type may include vertically continuous well-graded sand and gravel, fine sand, silty coarse sands that are typical of glacial outwash, buried valley aquifers, beach ridges and coarse alluvial deposits.

Soil Type II: Vadose zone soil type II is characterized by a K_v ranging from 1 x 10^{-4} to 1 x 10^{-5} cm/s, a net recharge ranging from approximately four to eight inches per year and a mean annual depth to ground water greater than five feet below grade. This soil type may include interbedded sand and gravel lenses with silts and clays, silty/clayey sand and gravel, and poorly-graded sands that can be found in some buried valley aquifers, glacial end moraine deposits and alluvial deposits.

Soil Type III: Vadose zone soil type III is characterized by a K_v less than 1 x 10^{-5} cm/s, a net recharge of less than approximately four inches per year, and a mean annual depth to ground water greater than five feet below grade. This soil type may include silts, clays, silty clays, and silty clayey gravels that can be found in glacial till, lacustrine sediments, flood plain deposits and thick colluvial deposits.

2.3.4 Step 3: Ensure that the measured soil chemical concentrations do not indicate the presence of NAPL.

The Tier I methodology does not account for movement of free product through soils. Therefore, it is necessary to ensure that the soil concentrations are not near or exceed a ceiling value established by a chemical's solubility limit. For chemicals that are liquid at ambient temperatures, the ceiling value is the soil saturation limit (C_{sat}). There are no ceiling values for chemicals that are solid at ambient temperatures, but co-solvent effects need to be evaluated and presented as part of the demonstration that leaching to ground water is unlikely.

Generic C_{sat} limits are provided in the CPRG (1999 and later revisions), and are available on the internet at http://epa.ohio.gov/portals/32/pdf/2008CPRG.pdf

These values were derived from the following equation obtained from U.S. EPA (1996b):

$$C_{sat} = \frac{S}{\rho_b}\left(K_d \rho_b + \theta_w + H^{'} \theta_a\right) \tag{2}$$

where:

C_{sat} = Soil Saturation Limit (mg/kg)
S = solubility in water (mg/L)
ρ_b = dry soil bulk density, (gm/cm^3)
θ_w = fraction of water filled porosity
θ_a = fraction of air filled porosity
K_d = partitioning constant, $K_{oc} \times f_{OC}$ (cm^3/g)
H' = Henry's Law constant for the COC, (dimensionless)

The defaults for the physical parameters are listed in Table 2, and Appendix A. The chemical-specific values for K_d and solubilities are found in the CPRG (1999 and later revisions).

2.3.5 Step 4: Compare chemical-specific leaching factor with the critical leaching actor

Table A.3 provides critical leaching factors for three soil types and separation distances between contaminated soils and ground water for which it is indicated that leaching to ground water is likely. The user can compare the chemical-specific LF_{gw} (generated in Step 1) with the critical leaching factors to determine whether leaching to ground water is expected to occur. Chemicals with LF_{gw} values below the appropriate CLF_{gw} value in Table 2 can be safely assumed not to leach to ground water. Chemicals with LF_{gw} above the thresholds may leach to ground water unless evidence to the contrary is shown. This requires using Tier II or Tier III to demonstrate that residual contamination in the soils will not leach above a target ground water concentration. As an example, if benzo(a)pyrene has an LF_{gw} value of 5.16E-04 (kg/L), it would not be expected to penetrate 15 ft. of sand when modeled for a 100 year period. In contrast, benzene (LF_{gw} of 4.25E+00), would be likely to penetrate a clay layer of 15 feet in thickness within that time frame.

Table 2: Critical leaching factors for ground water contamination.

Soil Type	CLF_{gw} (kg/L)
30 feet, Soil Type I	0.1
15 feet, Soil Type I	0.08
30 feet, Soil Type II	0.2
15 feet, Soil Type II	0.1
30 Feet, Soil Type III	0.6
15 feet, Soil Type III	0.4

2.3.6 Tier I Process Summary

Site-specific information for Tier I:

1) Ground water sampling and analysis is recommended (if less than 15 feet of clay or 30 feet of sand is between contamination and ground water).

2) COC soil concentrations must be low enough to assure no NAPLs are present (see U.S. EPA, 1992a).

3) Assessment of thickness and type of vadose material (*e.g.*, visual description, grain size analysis, vertical hydraulic conductivity).

4) Assessment of the site for the presence and extent of preferential flow paths.

Process Summary for Tier I:

1) Determine the nature and extent of soil contamination using sampling and laboratory analysis.

2) Determine the vadose zone thickness and material type through boring data and field/laboratory tests.

3) Evaluate whether concentrations of any constituent or COC may indicate the presence of NAPL or indicate significant co-solvent effects that could modify the mobility potential of COCs (see Section 2.2, Item #3).

4) Calculate the chemical-specific LF_{gw} factor (using Equation 1) to determine default values for a particular soil type.

5) Compare the calculated LF_{gw} factor for each constituent of concernto the appropriate Critical Leaching Factor - CLF_{gw} factor in Table 2 based on soil type and thickness to determine if the COC is likely to leach.

6) If chemicals are not likely to leach, ensure that the site conditions do not promote the migration of chemicals.

7) If chemicals are likely to leach, remove or decontaminate affected media or proceed to Tier II and/or Tier III.

2.4 Tier I: Evaluation of inorganic constituents leaching to ground water

2.4.1 Introduction

This section recommends an approach for evaluating what levels of inorganic compounds can be left in the soil and be protective of ground water.

2.4.2 Discussion

Metals such as iron, cadmium, lead and chromium are naturally occurring constituents of the soil. The concentrations of these metals in an uncontaminated soil are mainly the result of weathering processes of primary minerals found in rocks. Metals that have been introduced to the environment by anthropogenic activities may provide an elevated health risk to human health and ecological communities.

Some of the primary mechanisms of exposure to inorganic chemicals are through ingestion of ground water. Therefore, an understanding of how metals are transported to the ground water is important to understanding the health risks of metal contamination. Metals may be transported within the soil environment to a ground water zone by any of several mechanisms including advection, diffusion, and colloidal transport. Metals rarely move with the same velocity as infiltrating water; instead, the transportation of metals is usually retarded when compared with the water movement. This retardation effect results from metal being “trapped” on exchangeable sites on soil minerals, adsorbed to soil organic matter, or precipitated as a new solid phase. Transport by volatilization must also be considered for certain metals, such as mercury (Hg), selenium (Se), and arsenic (As), which also may interact with soil biota and form methylated compounds.

In addition, metals may occur in a variety of oxidation states and complexes - all of which may affect a given metal’s solubility. The major variables (*i.e.,* physico-chemical characteristics) that predict the solubility of metals are the pH, temperature, alkalinity, reduction-oxidation potential (REDOX), the type and abundance of minerals and organic matter that the solution interacts with, and the concentration of complexing ligands, such as dissolved organic acids. The solubility of metals is also dependent upon the solubility of the solid phase composition of the contaminant in the soil. Therefore, the composition of the waste that produced the soil contamination will also significantly influence the mobility of metal constituents.

The partitioning behavior of metals between a solvent (water) and a sorbent (soil minerals or organic matter) is usually described by the use of a distribution coefficient or K_d. The K_d can be defined mathematically by the following relationship:

$$K_d = C_{solid} / C_{sol} \qquad (3)$$

where: C_{solid} = the concentration of metal absorbed to the solid material.
C_{sol} = the concentration of a metal dissolved in the soil solution.

This equation implies that the sorptive behavior of a metal is a linear relationship between the dissolved component and the sorbed component. This relationship is approximately true for dilute solutions.

A more general approach to describe the relationship between the sorbed and dissolved metal components is to use isotherms. Isotherms receive their name from the adsorption behavior of various metals at constant temperature, pressure and ionic strength over a large concentration range. Mathematical analyses of isotherms therefore express the nonlinear behavior of dissolved metal/solid interaction and are useful when predicting the retardation of metals at varying concentrations.

The conceptual approach taken here or in this document is to establish K_d values that are representative of a variety of soil conditions. The assumptions that are inherent in this approach are that the contaminants have reached equilibrium with the soil, mass movement of contaminants is through advection and diffusion processes resulting from infiltrating rain water; and the soil displays the commonly accepted range of organic matter (0 to 0.2%), clay content (0 - 40%), bulk density (1.3 to 1.7 g/cm^3), and a moisture content of 20% or less. Consequently, where the soil properties fall far outside these boundary conditions or where influx of other solvents, such as acid spills, is present, the methods outlined in Tier I are not valid and require the user to develop site-specific methods and models for potential leachability of inorganic compounds.

2.4.3 Application/limitations

This paper presents three options for evaluating leaching of metals through soil (described in Section 2.4.5). Limitations exist for the use of Options 1 and 2 which include:

1) Solvent Effects: Many metals can have enhanced solubility and mobilization potential if subjected to either very low or high aqueous pH conditions. An example would be the release of an acid from a process line that could mobilize metal contaminants in soil. The distribution coefficients presented in this paper are not applicable for these situations where mobilization is from enhanced solvation. The K_d values presented in this paper assume that relatively dilute solution conditions are present, that a narrow range of soil moisture content is applicable and that a consistent range of soil organic matter is present. If these basic assumptions are not met, site-specific determination of the leaching of inorganic substances is warranted.

2) Secondary Features: The potential for discrete features in the unsaturated zone (both unconsolidated and consolidated deposits) to act as conduits to the water table must be assessed qualitatively. The presence, character, and density of any faults, fractures, joints, subsidence fissures, solution channels, significant sand seams, and other similar features should be evaluated. In the presence of such features, generic methodology is not acceptable.

3) Soil Stratigraphy: To select the appropriate leaching values, the horizontal and vertical variation in soil properties and horizons should be evaluated. This should also include evaluating the continuous profile of the stratigraphic units beneath the facility including the thickness and lateral extent of each stratigraphic unit. The effects of stratification on saturated and unsaturated flow should also be considered.

4) Man-made Deposits and Features: The modeling approach used to develop this guidance assumed that the precipitation infiltrates directly into natural soils. Man-made deposits, such as coal piles, ash or slag heaps, or gravel piles could potentially alter the chemistry of the infiltrating rain water (*e.g.*, pH, hardness, organic and metallic content), resulting in different rates of leaching than predicted by these models. In addition, anthropogenic influences (*e.g.,* sewer pipes, conduits for utilities, *etc.*) may impact the geology/hydrogeology leading to preferential pathways. Thus the presence these features could alter the leaching process. If any such features are present, then a site-specific analysis would be necessary to determine their effects on the leaching process. The leaching potential of metals developed in this guidance should be used with great caution at such sites.

NOTE: Note that Ohio EPA, Division of Solid Waste Management does not consider mine spoil a "man-made deposit" for the purpose of ground water monitoring at solid waste facilities. Because mine spoil is extensive enough to be mapped in many areas of Ohio and has not been physically or chemically altered, transformed, or used during a manufacturing process, mine spoil is considered to be a formation (Division of Drinking and Ground Water Policy 02-05-100).

5) Soil-Water System Equilibrium: This assumption is inherent in geochemical aqueous transport models because the fundamental equations of mass action and mass balance are equilibrium based. Therefore, any possible influence of adsorption (or desorption) rate limits is not considered. Because the model is being used to simulate metal sorption from the solid substrate, if equilibrium conditions are not met, the sorption or desorption reactions will prevent the Tier I model from making accurate predictions.

6) Reduction-Oxidation (REDOX) Potential: The REDOX potential of the system is not considered in a Tier I model. It is assumed that a normal range of soil REDOX conditions exists. These conditions range from 0.0 volts to 0.5 (Dragun, 1988). Reactions involving redox species are often biologically mediated and the concentrations of REDOX species are not as likely to reflect thermodynamic equilibrium as other inorganic constituents. To provide a conservative estimate of metal mobility, the oxidation state of the redox-sensitive metals (chromium, arsenic, and selenium) that would provide increased mobility was used to define leaching factors and K_d values.

2.4.4 Behavior of specific metals

Certain metals may have more than one oxidation state or may commonly exist in the soil environment in a complexed state. Very often one oxidation state or metal-organic complex will be more mobile in the soil than other oxidation states or metal ions. The valence state of the element can affect its toxicity as well as its mobility in the vadose zone. The following information will provide some context for evaluating assertions submitted with vadose zone modeling reports:

1) **Arsenic (As)**

Arsenic is toxic to humans and animals and occurs in the environment in a variety of oxidation states and as oxygenated compounds. The mobility of arsenic is enhanced because arsenic forms oxy-ions in typical soil environments. In the soil, arsenic generally occurs as the arsenate ion (As V, AsO_4^{3-}) or the arsenite ion (As III, AsO_2^{-1}). The toxicity of arsenic is a function of the oxidation state with the arsenite form being the most toxic of the pair. The solubility and mobility of arsenic are also dependent upon the oxidation state of arsenic. Based upon thermodynamic considerations, arsenite can be up to 10 times more soluble than arsenate. The mobility of arsenic in the soil is therefore highly dependent on the oxidation potential, with arsenic being fairly immobile under oxidizing conditions and mobile under reducing conditions. The pH of the soil solution can also greatly influence the mobility of arsenic compounds. Arsenate (As V) compounds have adsorption maxima in the low acidic (4-6 pH) range (Anderson *et al.*, 1976). Arsenite compounds also show an adsorption maxima for near neutral pHs (7-8 pH) soils. The mobility of arsenite is also dependent upon volatilization. Arsine, (AsH_3) gas and methylarsenite compounds may volatilize from the soil especially where high microbial activity is present.

2) Selenium (Se)

Selenium may exhibit a variety of oxidation states in the soil environment. In alkaline soils under slightly oxidizing conditions, the selenate (Se VI, SeO_4^{2-}) ion predominates. Conversely, if soils are acidic but conditions are still oxidizing, the selenite (Se IV, SeO_3^{2-}) ion predominates. The form of the dominant ion is an important consideration when addressing selenium mobility. Selenate is significantly mobile in soils. Neal and Sposito (1989) observed little adsorption of the selenate ion over a pH range of 5.5-9.0. Therefore, selenium mobility is favored in oxidizing environments under alkaline conditions. Other significant attenuation mechanisms include co-precipitation of selenite ion with ferric oxyhydroxides and with phosphate minerals. Selenium can be reduced by bacteria and may form volatile methylated compounds.

3) Chromium (Cr)

Chromium exists as either trivalent Cr(III) or as hexavalent Cr(VI) under most soil conditions. Most naturally-occurring chromium exists as Cr(III) in the mineral chromite ($FeCr_2O_4$) or as a trace constituent in other minerals including clays. Naturally-occurring Cr(VI) is extremely rare and is encountered in the mineral crocoite ($PbCrO_4$) formed by the alteration of lead deposits by chrome-bearing hydrothermal solutions. Such mineral deposits are not documented within Ohio. Chrome refractory materials typically contain Cr(III) and are unlikely to contain Cr(VI).

Hexavalent chromium is generally the most mobile form of chromium due to the anionic nature of the ions. Anionic compounds will interact sparingly with positive charged soil surfaces and will display adsorption only at higher pH ranges. Of the hexavalent species, $HCrO_4^{-1}$ predominates in acidic soils and CrO_4^{-1} in alkaline soils. Dichromate ($Cr_2O_7^{2-}$) ions will be the dominant hexavalent species at elevated concentrations. Trivalent Chromium generally forms hydroxyl complexes, including $Cr(OH)_2^{+}$, $Cr(OH)^{2+}$, $Cr(OH)^{o}$, and $Cr(OH)_4^{-1}$. These complexes are sparingly soluble and are easily sorbed to soils.

4) Lead (Pb)

The ubiquitous presence of lead is primarily due to dispersion by human activities, such as addition of tetraethyl lead to gasoline. It is also a common constituent of concern at waste sites. Lead is found in a zero valence state and in the +2 oxidation state in most soils and ground waters. It commonly forms hydroxide and carbonate species in water and therefore lead mobility is enhanced in alkaline subsurface environments. However, under normal, near neutral soil and ground water conditions, lead mobility is low. Lead mobility may also be enhanced under acidic conditions. The principal mineral form of lead in soil will depend on the environment and concentration of anions from which lead solid species may precipitate. Principally, solid hydroxides, and carbonates will dominate the lead minerals. However, insoluble phosphates and sulfides may also occur depending on the chemistry of the soil environment. Lead will also sorb to clay minerals and organic matter which will retard the movement of lead in the soil environment.

5) **Manganese (Mn)**

Manganese is one of the most common elements in the earth's crust. Manganese has three principal oxidation states, Mn^{2+}, Mn^{3+}, Mn^{4+}. Therefore, manganese can exhibit a wide variety of mixed-oxide compounds. Under normal conditions in ground water, Mn^{3+} is unstable and two Mn^{3+} ions will disproportionate to form one Mn^{2+} and Mn^{4+} ion. The Mn^{2+} ion will generally predominate under a pH range of near neutral (*e.g.*, 6 to 8).

6) **Mercury (Hg)**

Mercury occupies the elemental state under standard temperature and pressure conditions at the earth's surface. Elemental mercury is a liquid; therefore, its physical state enhances the dispersion of mercury in the environment. The principal form of mercury in the subsurface is mercury in the zero valence state and occurs as aqueous Hg^0. Aqueous mercury has a theoretic solubility of 25 µg/L under normal ground water conditions (Hem, 1970). However, the volatility of mercury and its tendency to form chloride and hydroxide complexes in some ground water environments may significantly lower its saturation levels. Mercury also may form more soluble organic complexes, such as methylmercury, when in contact with methane-producing bacteria. Organo-mercury complexes can remain in the food-chain for long periods of time which may result in significant bio-amplification.

7) **Uranium (U)**

Uranium may exist in a variety of oxidation states including the +3, +4, +5, and +6 oxidation states. Under normal environmental conditions the +4 and +6 oxidation states predominate. Uranium (IV) tends to form insoluble precipitates and has an observed adsorption maximum within a pH range of 5 to 6. In an oxidizing environment where uranium (VI) predominates, maximum adsorption will also occur in near neutral conditions. However, in alkaline conditions Uranium (VI) adsorption is poor. Uranium (IV) is much less mobile than uranium (VI).

8) **Vanadium (V)**

Vanadium is a transition metal and occurs in three oxidations states, V (III), V(IV), V (V) in normal soil and ground water environments. Vanadium will form stable oxy-anion complexes in alkaline and oxidizing ground water environments. The tendency to form stable complexes under these conditions tends to enhance vanadium solubility. The less highly oxidized forms of vanadium are less soluble under neutral pH conditions and sub-oxic environments. However, the solubility of vanadium is enhanced in acidic environments. Turekian (1969) determined the average river water concentration for total vanadium to be 0.9 µg/L.

9) **Zinc (Zn)**

Zinc has one principal oxidation state, Zn^{2+}, in ground water. It tends to form zinc hydroxide and carbonate species under alkaline conditions. Zinc species are retarded in the soil environment by sorption to mineral and organic matter surfaces. In addition, zinc can be removed from the soil solution phase and from ground water by co-precipitation with iron and manganese oxyhydroxides.

2.4.5 Tier I options for evaluating leaching of metals

Three options in Tier I are available for screening sites contaminated with inorganic constituents. These options are presented in the following sections. Each of these options allows a user to evaluate the potential for leaching of metals to ground water. In some cases, the use of more than one option may be necessary to demonstrate that metal leaching is unlikely. These options may be used only where applicable (see section 2.4.3). If site conditions exist that are not part of the generic site scenario a more thorough investigation (*i.e.* Tier II or Tier III) will be warranted.

Option 1: batch extraction test

A screening-level evaluation of the potential for leaching of inorganic contaminants to ground water can be made using the Toxicity Characteristic Leaching Procedure (TCLP, SW-846 Method 1311) or the Synthetic Precipitation Leaching Procedure (SPLP, SW-846 Method 1312). In general, the TCLP is intended to model hazardous constituents comingled with solid wastes in a landfill environment. The SPLP is intended to simulate leaching by acidic rainfall. A single method should be selected to model all the inorganic constituents in one impacted area. Sampling should be directed to represent conditions in areas of suspected highest concentration.

The inherent limitations of these tests should be recognized since they were designed to test the leachability and classification of waste materials rather than be used as “soil

leaching tests." The analyses prescribes maximum particle size requirements, vigorous mixing during testing, and the use of a 20:1 liquid extractant to solid ratio.
To utilize the TCLP (or SPLP) as a soil leaching test, it is assumed that the contaminant concentration found in the laboratory extractant is equivalent to the concentration of a metal leaching from the soil into ground water with a 20 dilution factor. To determine whether unacceptable leaching may occur, the concentration of contaminants should be multiplied by 20. Then, these transformed concentrations must be compared to ground water risk-based standards or the maximum contaminant levels (MCLs) allowed for drinking water. A dilution/attenuation factor of 20 may be applied if the site meets acceptable criteria of size as defined by U.S. EPA's Soil Screening Guidance (1996). This guidance stipulates a 20 DAF for source sizes less than 0.5 acres and a DAF of 1 for larger areas. If contaminant concentrations exceed the drinking water criteria, dynamic column leaching tests can be used to more accurately simulate leaching through soil. It should also be noted that if a waste sample exceeds the TCLP criteria found in Ohio Administrative Code (OAC) 3745-51-24 then that waste (or excavated soil) would be classified as a Hazardous Waste per Ohio Hazardous Waste Rules if the soil were exhumed.

Option 2: weight-of-evidence and modeling

A "weight-of-evidence" approach may be used to make the demonstration that the ground water is/will be protected from leaching above the ground water standard(s). The following information must be considered when providing a "weight-of-evidence" approach to determine that the metals present beneath the property will not impact ground water above the applicable standard(s). The amount of information necessary to make the demonstration is dependent on the levels of remaining contamination, the type of chemicals present, and specific physical and chemical parameters of the affected soil.

1) Contaminant type and characteristic of waste: A discussion of the particular speciation(s) of metal contaminants that are expected in the environment and their mobility should be included as part of the weight of evidence. Full characterization of the extent of contamination must be presented.

2) Separation distance between "contaminated" soils and ground water and material type: Thirty (30) feet of clay is sufficient to indicate that leaching of metals to ground water is unlikely. However, this separation could be less depending on the information provided. For example, if ground water sampling indicates that the ground water meets the standard, and historical information indicates that the contaminants have been present for decades, then 15 feet or less of separation may be adequate. In addition, secondary pathways (*e.g.*, fractures) become very important when evaluating the leaching potential to shallow saturated zones. An evaluation of secondary porosity features is therefore a necessary component of this demonstration.

3) Presence of conditions that may change the mobility of the metal: The user should evaluate whether conditions exist (both natural and anthropogenic) at the property which may cause the metal to be mobilized. For example, reducing environments may affect the pH of the environment and mobilize some metal species. Sites containing battery acids may also cause an increase in acidity (*i.e.,* decrease in pH) and a corresponding increase in metals' mobility.

Fluctuating water tables may also cause remobilization of metal species. Therefore, seasonal variation may need to be evaluated.

Option 3: comparison to background

Leaching to ground water would not be considered to be a problem if it can be demonstrated through sufficient sampling that concentrations in the foot print of the source area are representative of background (ambient) concentrations. If metals concentrations are at, or below, background levels, Option 3 can be used to exit the process. The sampling, analysis and data interpretation of background soils is discussed in DHWM's CPRG (1999 and later revisions).

Section 3.0
Tier II

3.0 Tier II: Modeling ground water pathway viability using generic default parameters and a dilution and attenuation factor.

Tier II gives practitioners more options for developing both numeric and analog models for a leaching determination. This tier uses conservative assumptions and default input parameters to develop a leaching model. DHWM created this tier because it recognizes the effort and data requirements for detailed unsaturated zone modeling and realizes that many facilities would not desire to develop input parameters for such site-specific models. This tier allows practitioners to develop models that use limited site data, such as contaminant concentration values, and default soil property values as long as the conservative assumptions and certain representative default values (see Appendix A) are used. The model developed may be either an analytical model, like that presented in U.S. EPA's *Soil Screening Guidance* (1996a) or numerical models like SESOIL, VLEACH or CHEMFLO. It should be noted that if U.S. EPA's *Soil Screening Guidance* is used, DWHM would require that the default input values listed in U. S. EPA's document be changed to those presented in this manual and its appendices.

No matter which type of model is chosen, it must be appropriate for site conditions and types of contaminants that are present. For example, it would be inappropriate to use a model designed and verified for leaching of organic chemicals for a site that wishes to model inorganic chemicals. Other situations may also preclude the use of certain models, including large differences in permeability of soil strata, and preferential pathways that may promote the migration of contaminants.

Tier II modeling should be performed using a minimum of site-specific parameters and without calculated dilution or attenuation factors. The intent of Tier II modeling is to demonstrate through conservative input parameters that leaching to ground water above acceptable regulatory or risk-based levels will not occur. The following sections list specific default assumptions and parameters that should be incorporated into numerical models used for Tier II.

3.1 Specific model assumptions for generic unsaturated zone modeling

For this tier of modeling, the DHWM requires that the following conservative inputs and assumptions be used for modeling. Attenuation and dilution is accounted for using a generic Dilution and Attenuation Factor (DAF) that can be applied to the modeling results according to the rationale present in U.S. EPA's Soil Screening Guidance (1996). A 20 DAF may be applied to sites that are 0.5 acres or less and a DAF of 1 to larger sites. Other dispersion, attenuation and dilution input parameters are not allowed in Tier II. The generic model assumptions for Tier II and some limitations are outlined below.

- For Tier II modeling, dispersion of water and chemical movement in the vadose zone does not occur. This implies that a one dimensional model, such as CHEMFLO, needs to be used to describe the movement of chemicals in the subsurface.

- Biodegradation is not accounted for in Tier II (Tier III must be used).

- Abiotic transformation processes, such as hydrolysis of organic compounds are assumed to not occur in Tier II (Tier III must be used).

Tier II modeling requires a fixed set of conservative input parameters and assumptions. The input parameters and default assumptions are listed below.

- The modeler must show that the basic site conditions allow a particular model to be used. For example, a model developed and verified for uniform soil stratigraphy should not be applied to a site with layered stratigraphy that displays highly differing permeabilities or soil properties. In addition, a model developed for the movement of chemicals through porous media should not be applied to a site where fracture flow or conduit flow may be present. See Section 5 for model verification and reporting requirements.

- Chemical-specific data, including solubility parameters and Henry's Law constants, must acknowledge a reference source. DHWM commonly uses U.S. EPA's *Soil Screening Guidance* (1996A and 1996b) as a reference source for Henry's Law Constants. In addition, Henry's Law constants are found in the GCN tables in DHWM's CPRG (1999 and later revisions). This table will be continually updated and may be found through the Internet: http://www.epa.state.oh.us/dhwm/cprg.

- Physical parameters adjusted for site-specific soil types that are used in vadose zone transport equations must either use the default parameters supplied with the model or the modeler may use data supplied in Appendix A of this document.

- Organic carbon content should either be set to 0.2 percent (*i.e.,* 0.002 g/g) or data found in Table A.3 of Appendix A should be used to determine the average default carbon content for a particular soil type. If a particular model requires the percent organic matter content, the modeler should note that the mean organic carbon content listed in the table can be converted to an estimate for the percent organic matter by multiplying the organic carbon content by 1.724 (Nelson and Sommers, 1996).

- Infiltration rate data should be calibrated to ground water default recharge rates of 18 cm/year for sandy soils, 12 cm/year for silty soils, and 8 cm/year for clays unless site-specific information is available.

- Maximum soil contamination values or 95 % UCL for a data distribution may be used for concentration inputs. The Ohio EPA will not accept the statistical manipulation of bimodal data sets consisting of heavily censored data (greater than 50% non-detected data) and detectable contaminant concentrations above risk-based standards. If needed, the DHWM District Closure Coordinator can assist with the appropriate use of site data for modeling.

- DHWM considers Tier II screening models to be infinite source models.

- A generic DAF factor of 20 can be applied to sites equal to or less than 0.5 acres in area. Larger sites can have a DAF of 1. These criteria are defined in U.S. EPA's Soil Screening Guidance (1996a and 1996b).

- Modeling cannot be used to set initial soil clean-up standards. However after initial risk standards (*i.e.*, direct contact) are met, the model results can be used to back-calculate additional remediation standards if the results show that ground water may be impacted at unacceptable levels.

- K_d values should be from a referenced source. DHWM would prefer that the methodology presented in section 3.1.1 and 3.1.2 be used or default K_d values. Other K_d values may be used but the modeler must reference the source of the value.

3.1.1 Determining the partition coefficient (K_d) value for organic constituents

The partitioning coefficient, K_d, for organic constituents can be derived in a variety of ways for organic constituents. The most common method is to utilize the following relationship between the organic carbon partitioning coefficient and the fraction of organic carbon found in the soil.

$$K_d = K_{oc} \text{ X } f_{oc} \tag{4}$$

Where:

K_d = The distribution coefficient
K_{oc} = The organic carbon partition coefficient, and
f_{oc} = The fraction of organic carbon in the soil

K_d and K_{oc} values may be found in the Generic Cleanup Number tables found in the appendix to DHWM's CPRG (1999 and later revisions). In addition, U.S. EPA's Soil Screening Guidance lists K_d and K_{oc} values for a variety of constituents. DHWM would prefer that the values listed in CPRG and in this document be used in models submitted to the Agency. The model documentation should list the source for the K_d and K_{oc} values.

3.1.2 Determining appropriate partition coefficient (K_d) values for inorganic constituents:

The methodology presented in this section was derived from Battelle Memorial Institute's, Multimedia Environmental Pollutant Assessment System (MEPAS; 1989). This system was selected for use because it allows for varying soil pH ranges and clay contents. The appropriate K_d value can be selected using the following information.

- Select the pH Range

  The selection of an appropriate K_d value, from the table of pH-dependent K_d values, should be made on the basis of the pH of the contaminant waste or by the pH of the soil. For example, if the contamination resulted from a waste spill of an alkaline solution, select the $\geq$ 9 pH category for the metal of interest. If the pH of the contamination is unknown or if the metal has had a significant period of time to equilibrate with the soil, select the 5 - 9 pH range; this range is typical of most soils. If an acidic waste spill is known or if the soil is acidic, select the $\leq$ 5 pH range.

- Select the Fine % Range

  The effect of differing soil types on the K_d value of metals is accounted for in Table 3 for certain inorganic constituents by identifying K_d values for soil types categorized by the Fines Percent (Fines %). The Fines % accounts for the total weight percent of clay, organic matter, iron, manganese, and aluminum hydroxides. These materials account for most of the primary adsorption sites in most soils. Values for this parameter are split into three ranges: <10 percent, 10-30 percent, and > 30% fines. These categories approximate sandy soils (<10%), loam (10 - 30%), and clay rich soils (> 30%).

Table 3: **Generic K_d Values for selected inorganic constituents.**

K_d Values Varying with Soil pH Ranges										
soil pH range	**>9**			**5-9**			**<5**			Ref.
Fines[1] %	<10	10-30	>30	<10	10-30	>30	<10	10-30	>30	
Antimony (Sb)	0	1	1	2	6	15.9	2	5	15.9	A
Arsenic (As III)	33.8			29.2			23			B
Arsenic (As V)	0.6	2.0	2.0	5.9	19.4	19.4	5.9	19.2	24.9	A
Barium (Ba)	5.3E2	2.8E3	1.6E4	5.3E2	2.8E3	1.6E4	53	2.8E2	1.6E3	A
Beryllium (Be)	7	1.4E2	8.0E2	70	1.4E3	8.0E3	7	1.4E2	8.0E2	A
Cadmium	3	42.9	100	14.9	423	567	3	42.9	100	A
Chromium (Cr^+ VI)	1	1	7.9	16.8	5.65E1	360	1	1	7.9	A
Chromium (Cr III)	6300			6300			6.3			C
Copper	4.19	9.2	33.6	41.9	92.2	336	4.2	9.2	33.6	A
Cyanide (CN^-)	0.7			0.7			0.7			C
Lead	230	597	1830	234	597	1830	10	10	12.1	A
Mercury (Hg)	322	580	5.28E3	322	580	5.28E3	30	60	500	A
Methyl Mercury	501			501			501			C
Nickel (Ni)	1.22	5.86	65	12.2	58.6	650	1.2	5.86	65	A
Selenium (Se IV)	5.91	14.9	14.9	5.91	14.9	14.9	6.9	6.87	35.8	A
Selenium (Se VI)	1			4.3			17			B
Silver (Ag)	0.4	4	40	0.4	4	40	0.4	4	39.3	A
Thallium (Tl)	123			74.5			35			B
Tin (Sn II)	2.5	5	5	5	10	10	2.5	5	5	A
Tin (Sn IV)	25	50	50	50	100	100	25	50	50	A
Uranium (U IV)	100	100	138	100	200	963	10	43	43	A
Uranium (U VI)	0	5	50	0	50	500	0	5	50	A
Vanadium (V)	50			50			50			C
Zinc (Zn)	12.7	143	1460	12.7	939	1460	3	280	280	A

References: A = Strenge and Peterson (1989); B = Loux *et al.* (1990); C = U.S. EPA (1999c). If data is present, K_d values for % fines is included. If no information is present, a singular K_d value for each pH range is presented.

The use of the % Fines parameter requires that the weight percent of the fine material in the soil is known or can be determined. The preferred hierarchy of data for this parameter is 1) site-specific information, 2) use of Soil Conservation Service (SCS) County Survey Maps for surficial soil ($\leq$ 3 feet depth), or 3) use of 0.2% organic matter as a default organic percentage. By assuming the only adsorbing surface is organic matter, the Fines % category will default to the most conservative K_d value. For certain constituents, little information is available for K_d variation with Fines Percent. For these constituents, the work of Loux *et al.* (1990) was used to generate pH range-dependent K_d values. In some cases, pH dependent K_d relationships were not listed in Loux *et al.* (1990). In these cases, a pH independent value, based upon empirical data summarized by U.S. EPA (1999c), was selected.

The reader is reminded that all assumptions, their appropriateness and the input values must be discussed in a detailed modeling report. See Section 5 for guidance and report requirements.

3.2 Criteria for assessing generic model results

The practitioner is responsible for assessing the validity and appropriateness of the model results. Part of this process is to discuss additional data or modeling requirements and any limitations that can affect the interpretation of the model results. The model results should be presented in a report to the agency that details: the site conditions, a conceptual site model, how the model that was used was developed, what assumptions were used in developing the vadose model, the rationale for the acceptability of the chosen model, the model input parameters with references, calibration of the model, and the model results. See Section 5 for details on the reporting requirements.

Once the model results have been assessed and have been found acceptable, the modeler can compare the model output data to the following criteria:

- Risk-based standards (including Generic Cleanup Numbers), as defined in DHWM's Closure Plan Review Guidance, or ground water Maximum Contaminant Limits (MCL), whichever are lower.

If the modeling process shows that leaching above unacceptable levels in ground water may occur, the participant may choose to back-calculate a new clean-up standard to assure that ground water resources will not be impacted. Conversely, the participant may choose to move to Tier III and acquire site-specific data through sampling to demonstrate that contamination left in place will not adversely impact ground water. The next section outlines the Tier III process.

Section 4.0
Tier III

4.0 Tier III: Modeling using both generic defaults and site-specific data

Tier III modeling is intended to examine the potential for leaching by using a minimum of conservative default values for soil properties and a majority of sampling derived data to accurately model the movement of chemicals through the vadose zone at a specific site. Therefore, site-derived data for soils, biodegradation rates and other abiotic attenuation processes can be incorporated into a Tier III model. Dilution and attenuation calculations may be included in a Tier III model; however, site-derived data must be acquired to support these calculations. Conversely, the modeler may use certain constraints on commonly used dilution and attenuation calculations.

There are several situations where detailed site-specific modeling is required or desirable. These situations include sites with layered soils, sites with expansive clay soils, sites having soils with high spatial heterogeneities in physical and chemical properties, or sites where fracture flow is present. In addition, site-specific models must be used if biodegradation or attenuation is to be considered. Therefore, DHWM expects that this level of modeling should include a majority of site-specific derived data.

The practitioner should follow U.S. EPA's guidance on data quality objectives to define the data needs before attempting to construct a model. The methods used to meet the data quality objectives for modeling must be clearly defined. **Special attention should be paid in determining the necessary number of samples to define the spatial distribution of model input parameters over the horizontal and vertical extent of the affected area**. For example, the organic carbon content of surficial soil samples horizontally distributed may not be representative of soils at depth and sampling would have to be conducted to define the vertical distribution of organic matter. In addition, organic carbon content is one of the most sensitive parameters in vadose zone modeling. The correct determination of organic carbon content in a soil horizon is therefore an important consideration. The practitioner should strive to collect input parameters that represent site conditions as best as possible.

4.1 Site-specific input parameters

Site-specific input parameters used for Tier III models should include:

- Infiltration rate data. Site-specific infiltration rates should be determined from a minimum of 5 years of yearly rainfall data. This length of time is generally sufficient to average out low rainfall or high rainfall years. Rainfall data may either be collected from facility records or taken from the nearest gauge station that is associated with the National Climate Data Center (http://www.ncdc.noaa.gov/ol/climate/climateresources.html). Infiltration rates and ground water recharge can be determined from the methods described in U.S. EPA (1998a and 1998b).

- Recharge rate data. The methods, assumptions, calculations and data must be included in a modeling report to support aquifer recharge input parameters. In lieu of site-derived data, ground water recharge rates of 18 cm/year for sandy soils, 12 cm/year for silty soils, and 8 cm/year for clays may be used in a model.

- Fraction of organic carbon, f_{OC}. Organic carbon and matter contents of soils can have a significant impact on fate and transport results. Therefore, the accurate determination of these input parameters are important and sampling and analysis should be performed with great care. For site-specific modeling, the practitioner should endeavor to collect a representative number of samples, both horizontally and vertically, over the affected area. Analytical methods to determine organic matter can be found in ASTM D2974-87, or Soil Science Society of America Methods (Nelson and Sommers, 1996). Commonly, modified ground water methods for total organic carbon are used by commercial laboratories and, in general, these methods can overestimate the amount organic carbon in soils. This is because inorganic carbon is not distinguished by the analytical method. The practitioner is directed to the methods of analysis outlined by Nelson and Sommers (SSSA, 1996) which will give an accurate account of soil organic carbon content. Methods such as SW-846 Method 9060 (Total Organic Carbon) should not be used to determine the organic carbon content of soils without modification.

- Partition coefficient, K_d. The partition coefficient is an important parameter for determining retardation of chemical movement in the vadose zone. The partition coefficient can vary over several orders of magnitude for heterogenous soils, so sampling and analysis activities should be constructed to represent the range of site conditions. Methods for the determination of the partition coefficient can be found in U.S. EPA's, Understanding Variation in Partition Coefficient, K_d, Values, Vol. 1 and Vol. 2 (1999a and 1999b). If appropriate, isotherm data can be derived that quantifies non-linear adsorption characteristics of the soil. Data for the determination of isotherms should be submitted with the modeling report to Ohio EPA. In lieu of site-specific organic carbon coefficients (K_{oc}), values from Table B can be used in conjunction with a default fraction organic carbon (f_{OC}) of 0.002 to determine partition coefficients for organic chemicals. The method in Section 3.1.2 can be used for inorganic constituents.

- Biodegradation. The Ohio EPA will not accept literature values for biodegradation of organic chemicals. If biodegradation rates are included in a model, site-specific data, including the methods used, number of samples, and laboratory data reports must be supplied to verify these input parameters.

- Site-specific soil parameters. These parameters include, among others, bulk density, porosity, and permeability.

4.2 Determining appropriate dilution attenuation factors

For site-specific models, a Dilution Attenuation Factor (DAF) may be calculated to account for the effect of mixing between water leaching though the vertical zone of contamination and ground water migrating laterally through the aquifer. There are many ways to calculate DAFs. One common method is the Summers Model which is also incorporated into some numerical models such as Riskpro's SESOIL®. The Summers Model is based on the hydrogeologic water-balance relationship and is expressed as:

$$C_{gw} = \frac{(Q_r)(C_p) + (Q_{gw})(C_a)}{(Q_{gw}) + (Q_r)} \qquad (5)$$

Where:

C_{gw}= concentration of the contaminant in the saturated zone, µg/ml
Q_r = volumetric flow rate of infiltration (soil water) to the aquifer, cm^3/d
Q_{gw}= volumetric flow rate of ground water beneath the contaminated area, cm^3/d
C_a = upgradient concentration of the pollutant in the aquifer (if any), µg/ml
C_p = contaminant concentration in the soil pore water, µg/ml

If C_a is equal to zero (*i.e.*, ambient ground water is not contaminated), then Equation 5 simplifies to Equation 6 and the DAF becomes:

$$DAF = \frac{(Q_{gw}) + (Q_r)}{(Q_r)} \qquad (6)$$

This equation can be expressed as hydraulic conductivity (K), hydraulic gradient (i), mixing zone thickness (d), recharge rate (r), and the length of the source parallel to ground water flow (L). (Note: Q_r = r*L*w, and Q_{gw} = K*i*d*w, where w = the length of the source perpendicular to ground water flow.)

$$DAF = 1 + \frac{Kid}{rL} \qquad (7)$$

The parameters for the above dilution model must be determined in the following manner:

Hydraulic conductivity (K or K_v) values must be derived from actual field testing. Hydraulic conductivity values can be derived from site-specific field calculations or from other measured values documented for other sites in the vicinity. If off-site data is used, the practitioner must demonstrate continuity between the reported values and the hazardous waste unit.

The ground water recharge rate (r) (referred to in U.S. EPA's *Soil Screening Guidance*, 1996a as effective infiltration rate (I)) denotes the flux of soil leachate received by the aquifer from the soil system. These values should be derived from site-specific information by field testing or assuming ground water recharge rates of 18 cm/year for sandy soils, 12 cm/year for silty soils, and 8 cm/year for clays.

The hydraulic gradient (i) should be derived from site-specific information based on a minimum of 3 wells installed in the saturated zone. If the site-specific K value is less than or equal to 1×10^{-1} cm/sec, the gradient can default to 0.002. If a site-specific gradient is calculated, it must be demonstrated that the gradient is not under the influence of any pumping wells.

The source length parallel to ground water flow (L) must be based upon the knowledge of ground water flow direction and size of the contaminated area. Equation 7 is taken from Equation 30 in US EPA's *Soil Screening Guidance* (1996a). However, U.S. EPA used data from larger CERCLA to derive the equation. The Ohio EPA, DHWM has encountered several situations at small closure units where the application of Equation 7 will result in very large dilution factors. Therefore, a minimum default value for the source length of 145 feet (approximately 0.5 acre site) must be used in developing a DAF from Equation 6. If the source length is larger, the value used to determine a DAF must be based on results of soil sampling in conjunction with professional judgement. If ground water flow direction is not known then the length should default to the square root of the source area.

The mixing zone depth (d): A mixing zone with a thickness of 10 feet (typical well screen interval) can be used as a default. Site-specific mixing zone depth may be calculated using the equation provided below. The input parameters used in the mixing zone equation must be verified with site-specific data. There is a potential that the calculation of the mixing zone could be thicker than the aquifer. If this equation is utilized for determining site-specific mixing zone depth, then the user should default to the aquifer thickness when the equation calculates a mixing zone thickness greater than the aquifer thickness.

A practitioner may calculate a property-specific mixing zone depth using the following equation and parameter determinations:

$$d = (0.0112\, L^2)^{0.5} + d_\alpha (1 - \exp[(-Lr) / (Kid_\alpha)] \qquad (8)$$

Where:

d = depth of mixing zone (m)
d_α = aquifer thickness (m)
L = source length parallel to ground water flow (m)
r = effective infiltration rate or ground water recharge rate (meters/year)
K = horizontal hydraulic conductivity (m/yr)
i = hydraulic gradient (m/m)
exp = the inverse of the natural log

For aquifer thickness, if site-specific information can not be reasonably obtained, then a judgement can be made based on area Ohio Department of Natural Resources (ODNR) well logs, ODNR Ground Water Resource Maps, and other published literature on the hydrogeology of the site/local area. Other parameters should be determined as described above.

References for methods for other common model input parameters are listed in Table 4.

Table 4: Methods to determine common model input parameters

Input Parameter	Reference
Bulk Density (ρ)	Methods of Soil Analysis 1986, Chap. 13; ASTM 2937, ASTM D1556, ASTM D2167, and ASTM D 2922
Cation Exchange Capacity	SW-846 Methods 9080 and 9081
Field Capacity	Methods of Soil Analysis 1986, Chap. 36
Field Capacity Soil Tension	Methods of Soil Analysis 1986, Chap. 36
Particle Density	ASTM D854-91
Porosity	Methods of Soil Analysis 1986, Chap. 18
Soil Water Characteristic Curve	ASTM D2325-74; Methods of Soil Analysis 1986, Chap. 26
Volumetric Water Content (θ_w)	Methods of Soil Analysis 1986, Chap. 21

Other helpful references and methods are included in the reference section (Section 6).

4.3 Criteria for assessing generic model results

The practitioner is responsible for assessing the validity and appropriateness of the model results. Part of this process is to discuss further data or modeling requirements and any limitations that can affect the interpretation of the model results. Once the model results have been assessed and have been found acceptable, the modeler can compare the model output data to the following criteria:

- The criteria used to assess whether concentrations of contaminants in waste left in place at a closure facility do not pose a threat to ground water resources are either risk-based standards (as defined in DHWM's Closure Plan Review Guidance) or ground water Maximum Contaminant Limits (MCL), whichever is lower.

- The criteria that are used to assess whether leaching may impact ground water or whether a viable ground water pathway exists are either risk-based standards or ground water Maximum Contaminant Limits (MCL), whichever is lower.

At this point, the participant should back-calculate a new risk-based clean-up standard to assure that ground water resources will not be impacted by remaining contaminants.

Section 5.0
Model Requirements

5.0 Modeling requirements

5.1 Conceptual model development

To simulate the behavior of water flow and transport of contaminants at a site, it is necessary to develop an understanding of the site conditions. A Conceptual Site Model (CSM) is a simplified representation of the hydrogeological and geologic conditions that can affect the flow of water and chemicals at a particular site. The purpose of a conceptual model is to develop an understanding of the hydrogeologic system, based on which the available data can be organized and used to analyze the system by modeling. Thus, the conceptual site model introduces the assumptions and qualitative interpretation of the flow and transport processes operating at that site.

Development of a CSM should consolidate the data into a set of assumptions and concepts that can be evaluated quantitatively. The major components should include: the hydrogeologic framework, boundary conditions, contaminant sources, distribution and concentrations, and properties that affect the transport of the contaminants. The conceptual model should also include a narrative with appropriate block diagrams and/or cross sections. The CSM should be continually refined as more data are defined.

The specific details necessary to provide a conceptual understanding of the area being modeled may be dependent on many factors, such as: purpose of the modeling exercise, type of model, known site conditions, complexity of the site, and potential risk to human health or the environment. The components of the CSM should be summarized in a report. However, references can be made to other site documents for additional detail.

5.2 Site criteria

The data requirements for vadose zone modeling may require additional information than is usually available from an initial site investiagtion. Some of the most important parameters for both vadose zone and ground water modeling are listed below:

Site characterization information including:

- Regional geologic data depicting subsurface geology.
- Topographic data (including surface water elevations).
- Presence of surface water bodies and measured stream-discharge (base flow) data.
- Identification of chemicals of concern.
- Vertical and horizontal extent of contamination.
- Identification of down-gradient receptors.

Soil description information including:

- Geologic cross-sections drawn from soil borings and well logs.
- Well or boring construction diagrams and soil boring logs.
- Soil texture, water content, air entry pressure, unsaturated conductivity (with water content).
- Appropriate field soil parameters (*e.g.*, organic carbon content, bulk density, CEC, porosity).

Ground water data including:

- Measured hydraulic-head data.
- Estimates of hydraulic conductivity derived from aquifer and/or slug test data.
- Location and estimated flow rate of ground water sources and sinks.
- Direction and rate of contaminant migration.
- Appropriate saturated or unsaturated zone hydrological parameters.
- Appropriate geochemical field parameters (*e.g.*, dissolved oxygen, pH, Eh).

Contaminant data including:

- Appropriate bio-geochemical indicator parameters (*e.g.*, electron acceptors and degradation by-products).
- Identification of transformation products (*i.e.,* TCE to Vinyl Chloride).
- Location, history, and mass loading or removal rate for contaminant sources or sinks.

The appropriate sections should be discussed in the modeling report with clear statements on the reasons for modeling and a listing of the criteria used to assess the results of the model.

5.3 Model selection

The selected model should be capable of simulating conditions encountered at the site. The following general guidelines should be used in assessing the appropriateness of a particular model:

- In general, analytical models should be used where field data show that vadose zone flow or ground water flow and transport processes are relatively simple.

- Models that do not account for dispersion (such as **one-dimensional models**) should be used primarily for sites where the degree of heterogeneity or anisotropy is not known, known to be isotropic, or sites where a potential receptor is immediately downgradient from a contaminant source.

- **Two-dimensional models** (where dispersion is accounted for) are only allowed for advanced Tier III modeling and should be used for problems which include one or more ground water sources/sinks (*e.g.*, pumping or injection well, drain, river, *etc.*), where the direction of water flow is in two dimensions (*e.g.*, radial flow to a well or a single aquifer with relatively small vertical hydraulic head or contaminant concentration gradients), for sites in which the aquifer has distinct variations in its hydraulic properties, or where the impacts of transverse dispersion are important.

- **Three-dimensional flow and transport models** should generally be used where the hydrogeologic conditions are well known, multiple aquifers are present, or the vertical movement of water or contaminants is important.

The rationale for selection of the model software, its applicability, and fulfillment of site objectives should be discussed in the model documentation report.

5.4 Model criteria

If the selected model can provide an adequate representation of the conditions at the property, the modeling code must also be examined for code verification, whether it is being used for its intended purpose, and whether the model has been verified under actual field conditions. These concepts are discussed below.

5.4.1 Code-verification

The practitioner must code-verify the model. Code-verification is the process of checking the accuracy of the algorithms used to solve the governing equations, thereby demonstrating that the model actually approximates the process equations for which it is being applied. This can be accomplished by solving a problem with the model and comparing the results to those obtained from an analytical solution or to another numerical model that has been verified. The publication of a model or its availability for sale does not necessarily mean that the model has been verified. However, if the model has been code-verified in the literature or user’s manual, evidence of this should be presented. The results of the code-verification should be presented in the report.

5.4.2 Consistent use

The model objectives must be consistent with the selected model’s abilities. For example, a model specifically designed to describe the fate and transport of organic compounds should not be used to model metals. In addition, when using a commercially available or public domain model, it is important to install the model properly on a system similar to that used or recommended by the model documentation. If a model is altered to run on another system, modifications should be discussed in the professional report. To ensure that installation has been properly completed, one should recreate example problems (if available) given in the documentation.

5.5 Model-specific design (input parameters)

The report should detail all of the parameters that were used to develop the calibrated model. Assuming a digital file of the model is submitted, this report section should emphasize the rationale for modeled parameter values. Listing of all variations of a parameter throughout the model is not necessary. Data gaps, anomalies, or uncertainties should be discussed in the modeling report.

5.6 Model calibration

A model calibration consists of changing values of model input parameters in an attempt to match field conditions within some acceptable criteria. For vadose zone models, calibration involves calculating an appropriate water budget for ground water run off.

Data describing field conditions may consist of measured water content to unsaturated hydraulic conductivity, hydraulic heads, ground water or stream flow rates, or contaminant plume migration rates. A model calibration requires that field conditions at a site be properly characterized. Lack of proper site characterization may result in a model calibrated to a set of conditions that are not representative of actual field conditions.

At a minimum, comparisons between model-simulated conditions and field conditions should be made. These comparisons may consist of:

- Soil moisture content
- Ground water flow direction
- Hydraulic head gradients
- Water balance
- Contaminant migration rates (if appropriate)
- Contaminant migration directions (if appropriate)
- Contaminant concentrations (if appropriate)

These comparisons should be present in maps, tables, or graphs. Each modeler and model reviewer will need to use their professional judgment in evaluating the calibration results. There are no universally accepted "goodness-of-fit" criteria that apply in all cases. However, it is important that the modeler make every attempt to minimize the difference between model-simulated and field conditions.

For initial assessments, it is possible to obtain useful results from models that are not calibrated. The application of uncalibrated models can be very useful as a screening tool or in guiding data collection activities.

5.7 Model verification.

The model must be field-verified, if possible, to further ensure that favorable comparisons exist between the modeled results and observed field data for the area being modeled. Model verification is the process in which the calibrated model is shown to be capable of reproducing a set of field observations independent of that used in the model calibration (*e.g.*, historical matching). The degree of verification necessary for a model is dependent on the purpose of the modeling exercise, type of model used, results of the sensitivity analysis, and the complexity of the site. An uncertainty analysis is conducted by assigning distributions to parameters which are demonstrated to have the most variability at a site and are the most sensitive to the model output. The range in error of the model calibration should be considered when drawing conclusions about the results. [Note: If the model cannot be verified and/or validated, then more emphasis should be placed on the sensitivity and uncertainty analyses.]

5.8 Sensitivity analysis

A sensitivity analysis is the process of varying model input parameters over a reasonable range (range of uncertainty in the value of the model parameter) and observing the relative change in model response. Typically, the observed changes in hydraulic head, flow rate, or contaminant transport are noted. The purpose of the sensitivity analysis is to demonstrate the sensitivity of the model simulations to by varying input values of the model. The sensitivity of one model parameter versus other parameters is also evaluated. If some change in a parameter or boundary condition causes significant changes in output, then the model is sensitive to that parameter or boundary. Sensitivity analyses are also beneficial in determining the direction of future data collection activities. Data for which the model is relatively sensitive would require future characterization, as opposed to data for which the model is relatively insensitive, which would not require further field characterization.

5.9 Modeling report contents

If modeling at a RCRA site is applicable, then information must be supplied that will lead the regulatory authority through the modeling process. A model documentation report is required. The report must detail the process by which the model was selected, developed, calibrated, verified and used. The modeling report is important because site-specific goals, chemical and physical inputs, and rationale for non-default inputs are critical factors in analyzing results and as such, need to be evaluated along with model results.

The report must include the following information:

- A description of the purpose and scope of the model application (*i.e.*, the CSM).
- Presentation (or reference) of the data used to characterize the site.
- Documentation of the sources (with references) of all data used in the model, whether derived from published sources or measured or calculated from field or laboratory tests.
- Identification of the model, its applicability, and limitations, including an evaluation of:
  - The questions that the model should answer;
  - Whether modeling is the best way to answer the questions;
  - Whether an analytical or numerical model is needed; and,
  - Whether enough site data has been collected to conduct the modeling.
- A discussion of the modeling approach.
- Documentation of all calculations.
- Documentation of calibration of the model (where appropriate).
- Presentation of all the model input parameters.
- Summary of all model calibration information and sensitivity analysis results.
- Present all model predictive simulation results as a range of probable results given the range of uncertainty in values of model parameters.

Other criteria not listed above should also be included as appropriate.

Section 6.0
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6.0 References

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Appendix A
Soil Hydrology

A.1 Soil hydrology background information

The study of the water movement through the soil is an important consideration for environmental scientists because of the understanding it imparts to predicting the transportation of chemical contaminants. Chemical movement is highly complex and solute transport is dependent upon the chemical properties of the contaminant, the physical make-up of the soil, and climatic factors. This section will focus on some of these input parameters that are commonly used in vadose zone modeling. Fortunately, there is a large body of investigatory data, derived from studies conducted over the last half century, that have generated an understanding of soil water and chemical movement that we can draw on to predict the potential impact of contamination to ground water resources. Some important factors that must be considered in vadose zone modeling are listed in Table A.1. Each of these factors deserve special consideration but because of the limited scope of this document, will not be discussed. This appendix will focus on soil properties and water movement in the vadose zone.

Table A.1: **Factors affecting chemical movement in the vadose zone**

1. **Contaminant Properties** (examples, not presented in this paper)
a. K_{oc}/ K_{ow}/K_d b. Henry's Law c. Viscosity d. Solubility e. Soil water properties
2. **Soil Properties**
a. Soil properties b. Amount of organic material c. Porosity (along with interconnectiveness –> hydraulic conductivity) d. Cationic exchange capacity e. pH

3. **Climatic/Environmental Factors** (including vegetation patterns)
a. Water mass flow b. Rainfall/runoff relationships c. Evapotranspiration of soil water

A.1.1 Contaminant movement through the soil

There are two basic processes that control the movement of chemicals through the soil. These processes are diffusive movement and advective flow of chemicals. Both of these processes are relevant to environmental scientists. Diffusive movement results when chemicals move along an energy or chemical gradient. Advective flow results when chemicals are dissolved in water and move through the soil column with the infiltrating water. Site-specific information may indicate that one movement process predominates over another. In reality, a combination of these processes usually work together to move a chemical through the environment. The rate of diffusion or advective flow is dependent upon the physical properties of the environment and porous medium, and the chemical properties of the contaminants.

Environmental factors include climatological parameters and vegetation patterns. These parameters affect the amount of infiltrating water available for mass flow, rainfall-runoff relationships, and evapotranspiration of soil water. These factors can limit the amount of water that actually flows through the vadose zone and reaches the ground water table.

Physical properties of the porous media include the pore-size distribution, amount of organic matter, porosity, hydraulic properties, cation exchange capacity (CEC), and pH. Porosity and the interconnectiveness between pores can determine the transmission rate, or hydraulic conductivity, of soil water. The soil media parameters such as the organic matter content, pH and CEC can retard chemical movement by chemical interacting with contaminants. Therefore, the soil can act as a sink to contaminants, retarding and sequestering them, until other processes slowly release them.

In the proceeding sections, an examination of soil textural relationships, properties of porous media, soil-water relationships, and the various approaches to predict the unsaturated hydraulic conductivity are presented.

A.1.2 The soil system

The soil system can be described as a heterogeneous system, composed of solid, liquid and gaseous phases. Each of these phases can influence the movement of water and chemicals in the soil system. The solid phase of the soil is composed of minerals, organic matter and biological components such as plant matter, bacteria and fungus. The primary liquid phase in the soil system is water. The water phase contains dissolved solutes through the interaction with soil minerals or from the addition of solutes into the soil. The soil water is also attracted to the soil mineral surfaces and, if conditions are right, may be held tightly in place and endure little movement. Conversely, water may rapidly percolate into the soil by mass flow processes or through macropores, such as fractures. The gaseous phase occupies the pore space not taken up with water. It primarily consists of a mixture of water vapor and CO_2. Depending on the volatility of contaminant substances, a substantial amount of other gaseous components may also occupy the pore space.

These components are held in equilibrium by chemical and physical forces; however, the equilibrium is only transitory and will change as any of the three soil components are added to or subtracted from the system. Equilibrium will re-establish itself as time passes until the soil system is stressed again in the future. Generally, the soil water component can change rapidly as rain water infiltrates into the system or water is removed by evaporation or transpiration. Other physical factors such as temperature change can also exert a major influence on soil component equilibrium. The soil system has been variously referred to as the unsaturated zone, the zone of aeration, or the vadose zone. These terms are intended to convey the concept there is an equilibrium between the three soil phases and that all the pore space is not filled with water. The unsaturated zone has been divided into three major regions or zones. These zones are illustrated in Figure A.1.

The root zone or rhizosphere consists of the first one to three feet of the subsurface influenced by plant roots and bacteria associated with plants. This zone is usually characterized by higher organic matter content and CO_2 compared to the rest of the unsaturated zone. The root zone can influence water movement and water infiltration by direct uptake of water by plants. Plants can significantly alter the soil texture by the growth of roots. These new paths are termed macropores and water may conducted very rapidly to lower regions of the unsaturated zone through these pores.

The middle zone between the root zone and the capillary fringe is termed the intermediate zone. The composition of clay minerals, soil texture and water content can vary substantially with depth within this zone. If local impermeable layers exist, water percolating through the soil may be trapped and a perched water table may result. In addition, certain trees which are deep rooting may locally influence soil properties and soil water content.

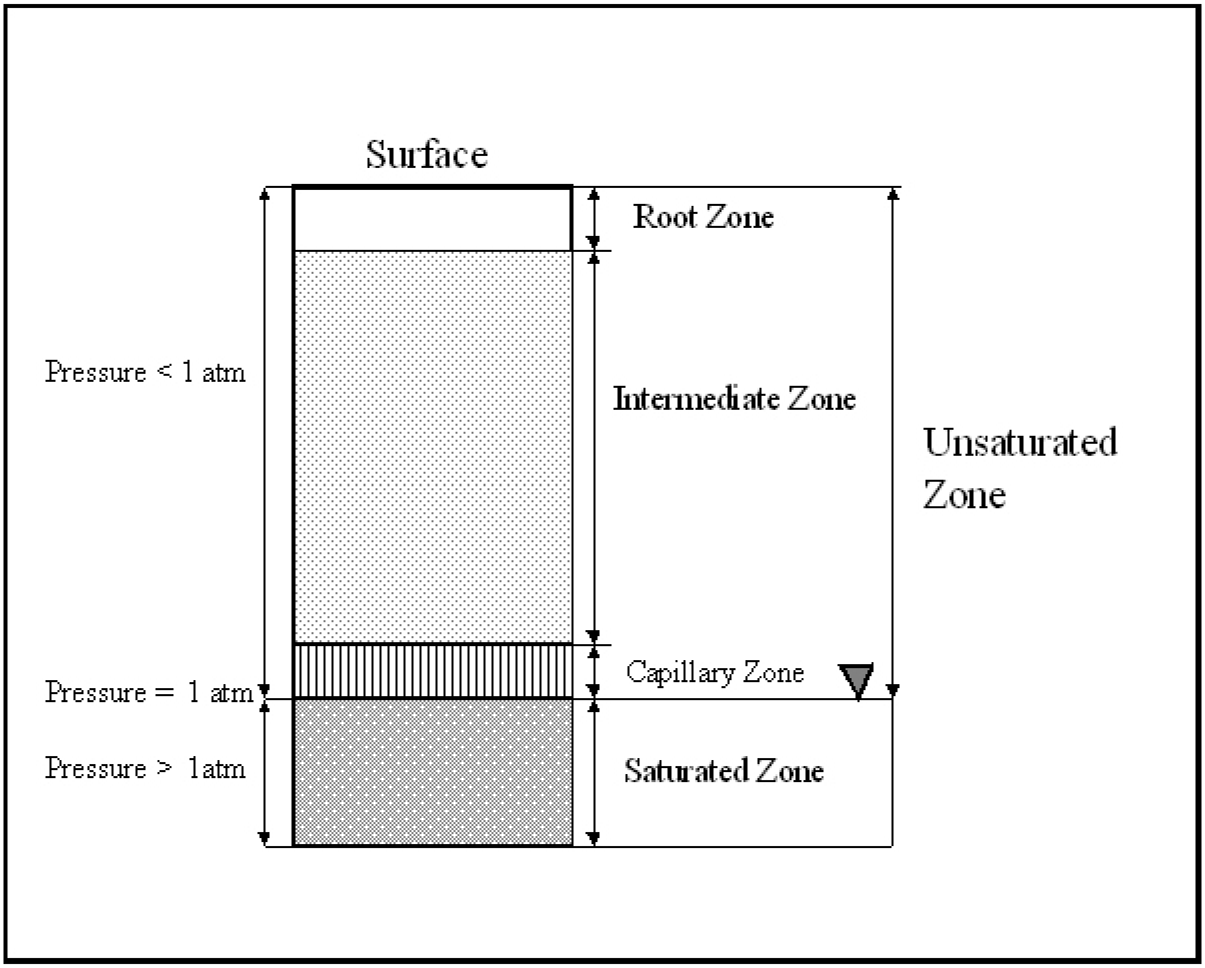

Figure A.1. The three components of the unsaturated zone: the root zone, the intermediate zone, and the capillary fringe. Pressure refers to the matrix potential indicating that in the unsaturated zone water is imbibed into the subsurface due to a variety of physical forces.

The capillary zone or capillary fringe is located between the intermediate zone and the saturated zone or ground water table. Water is drawn upward into the capillary zone from the ground water table producing a wetter region as compared to the intermediate zone. The thickness of the capillary zone will vary due to the soil texture. Fine-grained soils may have capillary zones that approach 10 feet. Coarse grained soils, composed of sands, may have a capillary zone of an inch or less. Other factors such as barometric pressure and infiltrating water can depress or inflate the capillary fringe.

The pressure in the unsaturated zone is defined as negative, thus infiltrating water is drawn into the unsaturated zone. The reference pressure is usually taken as atmospheric pressure. Therefore, the boundary between the unsaturated zone and saturated zone is defined as a gauge pressure of 0. The forces that are responsible for the negative pressure in the unsaturated zone are briefly defined in later sections of this document.

A.1.3 Soil texture

The physical arrangement of soil particles can have a profound influence on the movement of water, solutes and gases through the soil. Soil scientists specify the physical constituent of the soil by classifying the soil texture. The soil texture is defined by the size, shape, and arrangement of soil particles and pore space. The major grain-size classes for soils include sand grains (2 mm to 0.05 mm), silts (0.05 mm to 0.002 mm) and clay (less than 0.002 mm). Using the size relationship and the amount of organic matter, soil scientists have developed a texture-based system to classify soils. There are many such systems, but in this document the United States Department of Agriculture's system will be used. The relationship between grain-size percentage and classification is shown in Figure A.2.

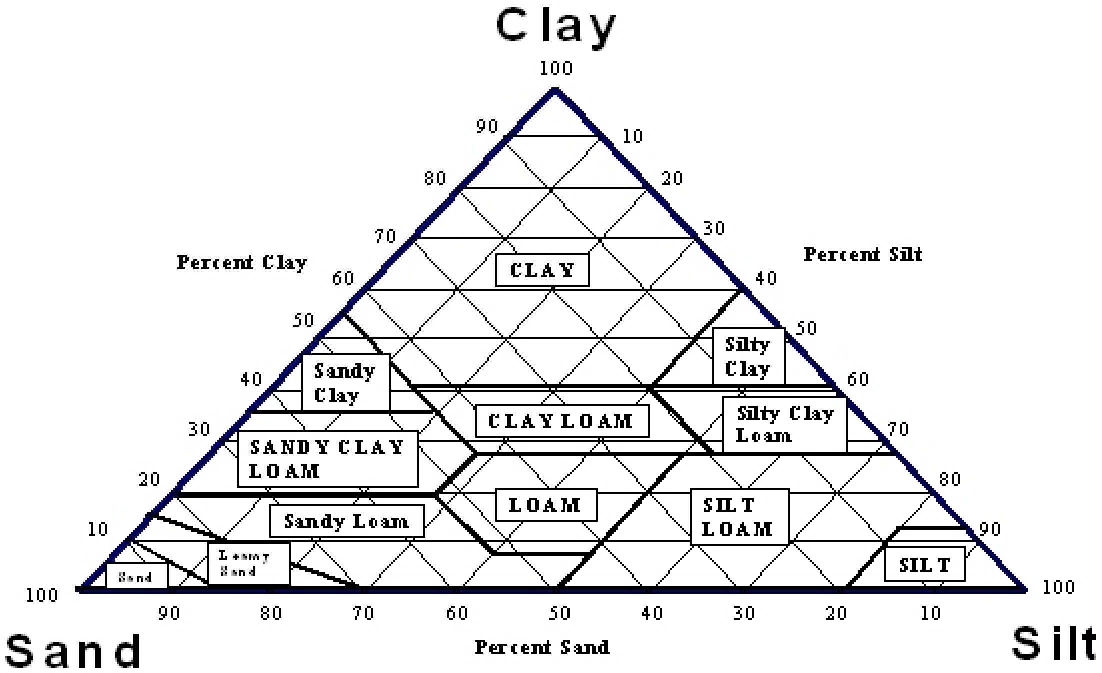

Figure A.2. Soil texture classification diagram. The different soil texture classes are defined by the percentage of sand, silt and clay. The classification system is based upon the United States Department of Agriculture Classification system.

The textural classification system is based upon the percentage of sand-, silt- and clay-sized particles in a soil sample. Soils containing predominately one grain-size are classified by the dominant grain-size class, such as sand. Soils containing mixtures of sand, silt, and clay are called loams. Techniques for particle size analysis can be found in Soil Science Society of America's Methods of Soil Analysis (1986).

Pores can also be classified, usually by pore width. A classification of pore size given by Brewer (1964) is listed in Table A.2. Pores may be classed as macropores, mesopores, micropores, ultramicropores and cryptopores based upon the diameter of the pore space. In practical terms the pore spaces are rarely classified because of the difficulty in measurement and the normal heterogeneity found in soil systems.

Table A.2: **Table of pore-size classification** (Brewer, 1964)

Class	Subclass	Class Diameter Limits (μm)
Macropores	Coarse Medium Fine Very Fine	>5000 2000-5000 1000-2000 75-1000
Mesopores		30-75
Micropores		5-75
Ultramicropores		0.1-5
Cryptopores		<0.1

The pore-size is generally governed by the size of the particles in the soil medium. For example, soils predominately made up of sand will have a higher porosity than soils made up of silt-size particles. This is because larger grains will pack together less tightly leaving larger pore space compared to finer-grained material. Loams therefore will have intermediate porosities reflecting the percentages of sand, silt and clay. Soils with higher clay contents can form aggregates, which soil scientists term "peds". Peds may separate from each other by natural processes such as dessication forming large macropores, that will be substantially different in size than the normal pore-size range due to simple packing of soil grains.

Porosity (ϕ) can be calculated by a variety of means. The most common method is to calculate the percentage of total soil volume occupied by pores. This is done by first calculating a soil's bulk and particle density (Methods of Soil Analysis, 1986) and then using the following equation:

$$\text{Porosity } (\phi) = [1 - (\text{bulk density}/\text{particle density})] \qquad \text{(A1)}$$

The bulk density is defined as the ratio of the mass of dry solids to the bulk volume of the soil and the particle density is the ratio of the solid particle mass to their total volume. Typical porosities and bulk densities for various soil types are listed in Table A.3. In addition, typical values for organic matter are also presented. On average, particle densities of 2.65 g/cm^3 are typical of sandy soils but decrease as the clay and organic matter content rise.

Table A.3: Physical properties of soils

Soil	Bulk Density (g/ml)	REF.	Porosity (ϕ) (Mean Value)	REF.	Percent Organic Carbon (Mean Value)	REF.
Sand	1.59 - 1.65	A	0.349	B	0.71	C
Loamy Sand		A	0.410	B	0.61	C
Sandy Loam	1.20 - 1.47	A	0.425	B	0.71	C
Silt Loam	1.47	A	0.484	B	0.58	C
Loam			0.452	B	0.52	C
Sandy Clay Loam			0.406	B	0.19	C
Silty Clay Loam			0.473	B	0.13	C
Clay Loam	1.20 - 1.36	A	0.476	B	0.10	C
Sandy Clay			0.426	D	0.38	C
Silty Clay	1.26	A	0.492	D		
Clay			0.475	B	0.38	C

A: Jury, W.A. (1986). Vadose Zone Modeling of Organic Pollutants. S.C Hern and S.M Melancon, eds., Lewis Publishers, Chelsea, MI.

B: McCuen, R.H., W.J. Rawls, and D. L. Brakensiek (1981). Statistical analysis of the Brooks-Corey and the Green-AMPT parameter across soil textures. Water Resources Research, Vol. 17, No. 4, pp.1005-1013.

C: Rawls, W.J. (1983). Estimating bulk density from particle size analysis and organic matter content. Soil Science, Vol. 135, No. 2, pp.123-125.

D: Li, E.A., V.O. Shanholtz, and E.W. Carson, (1976). Estimating saturated hydraulic conductivity and capillary potential at the wetting front. Dept. of Agricultural Eng. Virginia Polytechnical Institute and State University.

A.1.4 Soil-water relationships

By definition the pore space in the unsaturated zone is partially filled with water. The volume of the pore space that is filled with water will vary both spatially within the unsaturated zone and through time. It may seem logical that as a soil drys it should lose all the water in the pore spaces. This is true up to a point. Water will drain from the larger pore spaces, but soil will rarely dry completely. This is because of surface and capillary forces that will hold some water in the soil. Primarily this water occupies smaller pore spaces and is also held as a thin film on mineral surfaces.

These cohesion and adsorption forces are very important for soil water movement. The cohesive forces can be compared to capillary action of water in tubes. For example, physics tells us that if small diameter straws are placed vertically into a pan of water, water will rise up into the straws. The smaller the diameter of the straw, the higher the water will rise. This is due to the greater negative pressure head in the smaller diameter straw. Just like in this simple example, water in the soil system will be drawn into and held by stronger force in pores with smaller diameters. The pressure head on water in smaller pores will be more negative and it is more difficult to remove water from finer pores compared to larger ones.

Soil scientists refer to this as the suction head, pore water pressure, or matric potential (ψ_m). These forces are responsible for pulling water into pores of the soil system, facilitating movement at high volumetric water contents, and retaining water in pores at low water contents. Soil scientists commonly refer to this retained water as being under held under tension, because an external force must be applied to remove the water.

The matric potential in a soil will therefore vary based upon the amount of water filling the pore spaces. Pore water pressure values will be less negative when the pores are partially filled and more negative when the pore are mostly empty. The pore water pressure or matric potential can be expressed in a variety of units, including head units, measured in *centimeters of water*. Pressure units are also commonly found in the literature and include the *standard atmosphere* or *bar*. One standard atmosphere is defined as 1.013×10^6 dynes $\cdot$ cm^{-2} or 14.7 $lb \cdot in^{-2}$. In addition, more recent literature values also list the kilopascal (kPa) as a pressure unit. The conversion factors for different units are listed in Table A.4.

Table A.4: Conversion factors for common pressure and head units

Conversion Factors for Common Pressure and Head Units
1. ψ = -1 atm. = -1034 cm water
2. ψ = - 1 bar = -0.9872 atm = -1020 cm water
3. ψ = 1 kPa = 10 cm of water

Other forces also affect the potential movement of water. These forces are the osmotic potential, the gravitation potential, and the pressure potential. The osmotic potential can decrease the total potential of soil water due to dissolved salts. The osmotic potential will always lower the total potential energy of water. The gravitation potential causes water to move from higher elevation to lower elevation. The gravitation potential must be assessed using some reference point, usually taken to be either the soil surface or the water table. Unlike osmotic potential, the gravitational potential may be either negative or positive depending on the datum. The pressure potential is the change in total potential energy of soil water due to the application of an external force. This external force may be surficial loading such as a building or changes in barometric pressure. Detailed descriptions of these forces are outside of the scope of this text and can be found in Jury *et al*. (1991) or Hillel (1998).

The retention of water in soils will greatly affect the movement of water and solutes through a soil column. Soil scientists have established relationships between pore water pressure and water retention by constructing soil water retention curves. Measurements of this type start with a soil sample saturated with water (volumetric water content $\theta = \theta_s$). Pressure is applied to the sample. The pressure where water is released is termed the air entry pressure ($-\psi_A$). The air entry pressure is the pressure where air will begin to enter pore spaces and the soil is defined as being unsaturated. The air entry pressure will be close to atmospheric value for most soils. As pressure is increased, more water will be drained from the soil. Water retention will be dominated by capillary forces to about a pore water pressure of a negative atmosphere and by surficial forces at greater pressures. At some pressure, no further water will drain from the sample. The water content at this pressure is termed the *irreducible water content* (sometimes referred to as residual water content) and is given the symbol θ_r. A typical pore water retention curve is shown in Figure A.3.

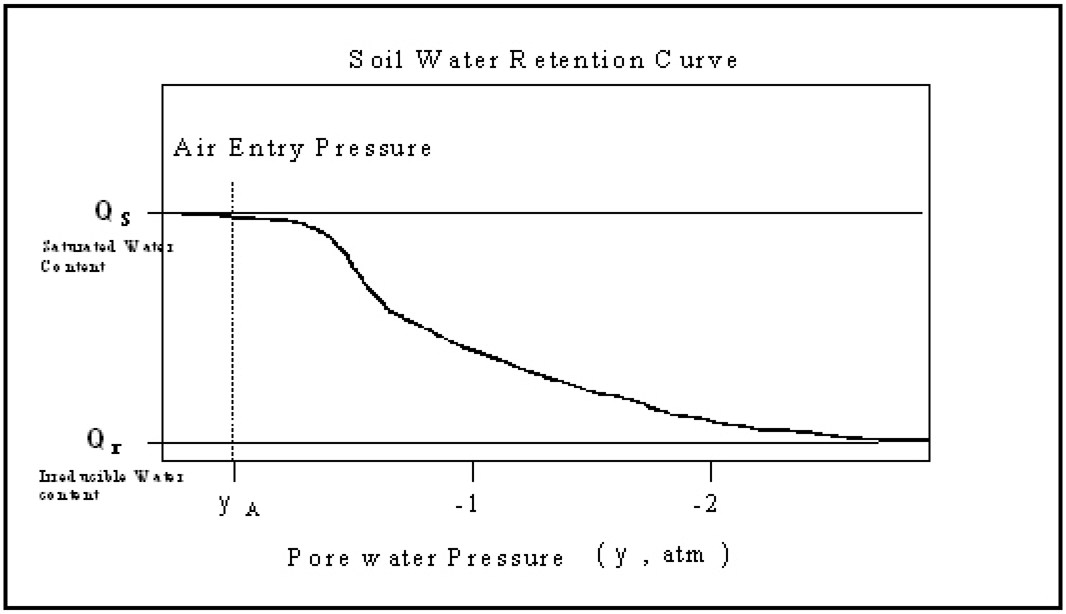

Figure A.3. A typical pore water retention curve. Water is held under increasing tension as the volumetric pore water decreases. At pressures between 0 and -1 atm, capillary forces dominate water retention. At pore water pressure less than -1 atm, surficial forces act to hold water in the soil.

The air entry pressure and irreducible water content for different soil types are listed in Table A.5.

Table A.5: Typical values for the irreducible water content and air entry pressure for common soils.

Soil Type	Irreducible Water Content, θ_r	Air Entry Head (ψ_a, cm)
Sand	0.045	6.9
Loamy Sand	0.057	8.06
Sandy Loam	0.065	13.33
Silt Loam	0.067	50
Loam	0.078	27.78
Sandy Clay Loam	0.1	16.95
Silty Clay Loam	0.089	100
Clay Loam	0.095	52.63

Soil Type	Irreducible Water Content, θ_r	Air Entry Head (ψ_a, cm)
Sandy Clay	0.1	37.04
Silty Clay	0.07	200
Clay	0.068	125

Carsel, R.F. and R.S. Parrish (1988). Variation within texture classes of soil water characteristics. Water Resource Res., Vol. 24, pp.755-769. Note: air entry values were derived from average values presented in Carsel and Parrish using the equation [α (cm^{-1}) = $-1/\psi_a$].

Understandably, different textural classes of soil will have different particle-size distributions and different soil retention properties. The finer grained soils will retain water through a larger range of matric pressures than coarser-grained soils. Consequently, coarser-grained soils will drain faster facilitating rapid solute movement, but the movement will not be sustained. Finer-grained soils will not drain as fast, but transport may be sustained by diffusive movement for a longer period of time compared to coarser-grained soils. A comparison of typical retention curves for various soils is shown in Figure A.4.

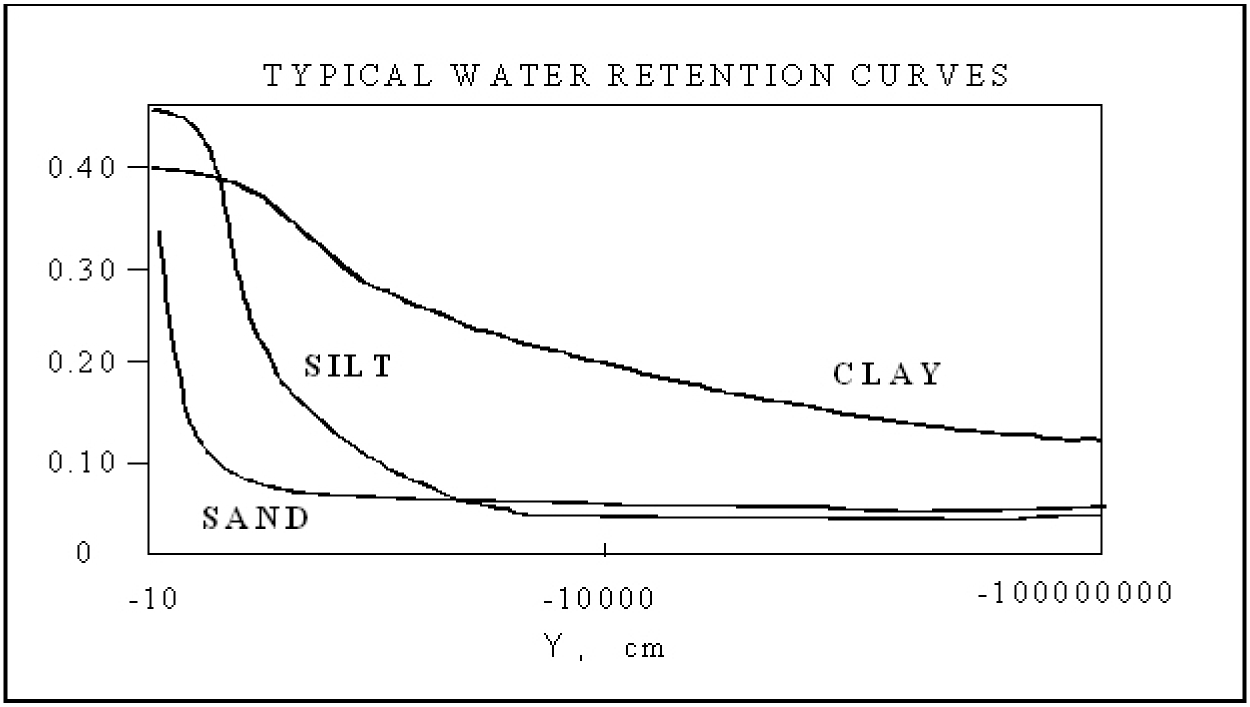

Figure A.4. Typical water retention curves for sand, silt, and clay.

A.1.5 Soil water movement

In the preceding section we observed that forces acting on water in a soil column could affect the movement of infiltrating water. These concepts can be used to develop a method to assess the unsaturated hydraulic conductivity. The first step is to examine water flow in saturated porous media and then use these concepts, along with the relationships already discussed, to develop an unsaturated flow equation.

A.1.5.1 Saturated flow

The basis of saturated flow was developed by Darcy in 1856. The equation for evaluating saturated flow of water has been formalized into Darcy's Law.

$$Q = -K_sA\ \Delta P/L \qquad (A2)$$

Where:

Q = volumetric flow rate
K_s = the saturated hydraulic conductivity
A = the cross-sectional area perpendicular to flow
ΔP = the change in hydrostatic pressure
L = length

In most texts, the difference in hydrostatic pressure is evaluated in the context of hydrostatic head. This is easily evaluated based upon water table elevations or differences in piezometric surfaces. Equation A3 can then be expressed as:

$$Q/A = q = -K_s\ (h_2-h_1)/L \qquad (A3)$$

In this case, the equation is expressed as the volumetric flow rate per unit area (q), and the difference in hydrostatic pressure per unit length is expressed as the change in head per unit length [$(h_2-h_1)/L$]. This equation is valid for uniform grain-sized granular material, a condition which is rarely encountered in nature. Most granular material is composed of a range of particle sizes that affect the flow path of water particles. Because of this, a correction factor that accounts for the non-ideal nature of the granular material is made to Equation 4. The is factor is introduced as a new term in equation A4 called the effective porosity (n_e).

$$Q/n_eA = q/n_e = v = -(K_s/n_e)\ (h2 - h1)/L \qquad (A4)$$

The new term "v" is the linear pore water velocity. Therefore, to use Darcy's Law to determine the velocity of ground water movement or determine the volumetric flux, the saturated hydraulic conductivity, the effective porosity and change in water table elevation must be determined. In Darcy's Law, the saturated hydraulic conductivity is listed as a constant. In practice, it will vary with distance based upon heterogeneities within the saturated flow system. The saturated hydraulic conductivity can therefore be thought of as a averaged property of the ground water system over the length of the flow path. Typical values for saturated hydraulic conductivity and effective porosity for various media are listed in Table A.6.

Table A.6: Typical saturated hydraulic conductivity values for various soil and rock types.

Media Type	**Saturated Hydr. Cond., K_s (cm/s)**	**Reference**	**Effective Porosity (mean) ϕ**	**Reference**
Soil Type				
Gravel	3.0E-2 to 3.0E0	A	0.42	C
Coarse Sand	9.0E-5 to 6.0E-1	A	0.28	D
Medium Sand	9.0E-5 to 5.0E-2	A	0.30	D
Fine Sand	2.0E-5 to 2.0E-2	A	0.32	D
Loamy Sand	4.1E-3	B	0.40	C
Sandy Loam	1.2E-3	B	0.41	C
Loam	2.9E-4	B	0.43	C
Silt, Loess	1.0E-7 to 2.0E-3	A		
Silt Loam	1.2E-4	B	0.49	C
Till	1.0E-10 to 2.0E-4	A		
Clay	1.0E-9 to 4.7E-7	A	0.39	C
Sandy Clay Loam	3.6E-4	B	0.33	C
Silty Clay Loam	1.9E-5	B	0.43	C
Clay Loam	7.2E-5	B	0.39	C
Sandy Clay	3.3E-5	B	0.32	C
Silty Clay	5.6E-6	B	0.42	C
Unweathered Marine Clay	8.0E-11 to 2.0E-7	A		
Sedimentary Rock				
Karst and Reef Limestone	1.0E-4 to 2.0E0	A		
Limestone, Dolomitic	1.0E-7 to 6.0E-4	A	0.001 - 0.05	A
Sandstone	3.0E-8 to 6.0E-4	A	0.005-0.1	A
Siltstone	1.0E-9 to 1.4E-6	A		
Shale	1.0E-11 to 2.0E-7	A	0.005-0.05	A

A: Domenico and Schwartz, 1990
B: Carsel and Parrish, 1988
C: Rawls *et al.*, 1992
D: U.S. EPA, 1996

The saturated hydraulic conductivity is both a function of the fluid and the porous media that fluid is flowing through. Generically, this function can be expressed as the *intrinsic permeability* of any fluid and media. The relationship between the saturated hydraulic conductivity and intrinsic permeability is expressed in Equation 5.

$$K_s = (\rho_f \, g \, \kappa)/\mu \qquad \text{(A5)}$$

Where:

ρ_f is the fluid density (0.998 g/cm^3 at 20°C),
g is the acceleration of gravity (980 cm/s^2),
κ is the intrinsic permeability (cm^2), and
μ is the dynamic viscosity (0.01 poise at 20°C)

The intrinsic permeability is commonly used as an input parameter for many vadose transport models. Saturated hydraulic conductivity values may be converted to intrinsic permeability using the following conversion factor shown in Equation A6.

At 20°C $\quad K_s\,(\text{cm/s}) \bullet 1.022\text{E-}5 = \kappa(\text{cm}^2)$ (A6)

A.1.5.2 Flow of water in unsaturated systems

Flow of water in unsaturated media is complicated by the fact that water transmission is a function of matric potential which, in turn, is a function of the volumetric water content. The volumetric water content will vary through time because of transient influx of rainwater and evaporation of water. The practical aspect of this phenomenon is that the water will be conducted through unsaturated porous media at some fraction of the saturated value, but this unsaturated hydraulic conductivity will vary through time. L. A. Richards in 1931 formulated the equivalent of Darcy's Law for unsaturated media. Richard's equation for vertical movement of water is as follows in Equation A7:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial Z}\left(K(h)\left(\frac{\partial h}{\partial Z} - 1 \right)\right) \qquad \text{(A7)}$$

Where:

$\partial\theta/\partial t$ is the change in volumetric water content through time (cm^3/cm^3),
h is the pore water pressure head (cm),
K_h is the unsaturated hydraulic conductivity (cm/day), and
$\partial h)/\partial Z$ is the change in head with depth (cm).

The unsaturated hydraulic conductivity can be evaluated using the relationships developed by Brooks and Corey (1964) or van Genuchten (1980). The closed form of the van Genuchten equation for unsaturated hydraulic conductivity for constant flux conditions is:

$$K(S) = K_s S^{1/2}[1 - (1 - S^{1/m})^m]^2 \qquad \text{(A8)}$$

and

$$\frac{\theta - \theta r}{\theta s - \theta r} = S = \left[1 + \left(\alpha |h|\right)^{n}\right]^{-m} \qquad \text{(A9)}$$

Where:
S is the reduced water content,
θ_r is the irreducible water content (Table A.5),
θ_s is the saturated water content (Table A.6, effective porosity),
K_s is the saturated hydraulic conductivity (cm/day), (Table A.6)
α is the inverse of the negative of air entry pressure (Table A.5),
n is a shape factor and m may be evaluated from the following equation.

$$m = 1 - 1/n \qquad \text{(A10)}$$

Representative values for n for various soil types is presented by Carsel and Parrish (1988) in Table A.7.

Table A.7: Representative shape factors (n) and corresponding m values for various soil types.

Soil Type	Shape Factor (n)	m
Sand	2.68	0.63
Loamy Sand	2.28	0.56
Sandy Loam	1.89	0.47
Silt Loam	1.41	0.29
Loam	1.56	0.36
Sandy Clay Loam	1.48	0.32
Silty Clay Loam	1.23	0.19
Clay Loam	1.31	0.24
Sandy Clay	1.23	0.19
Silty Clay	1.09	0.08
Clay	1.09	0.08

Appendix B

Appropriate Use of Common Default Parameters for Vadose Zone Models

B.1 Introduction

Vadose zone models use a variety of input parameters, many of which are common to both leaching and vapor intrusion models. These parameters include, but are not limited to, porosity (ϕ), dry bulk density (ρ_b), particle density (ρ_s), moisture content (%), and water-filled porosity or water content (θ_M or θ_V). These input parameters are commonly default values, based on the model literature or from guidance (Soil Screening Guidance, U.S. EPA; 1996a and 1996b). However, there are instances where site-specific input parameters are desirable. In these cases, soil samples are submitted to a geotechnical laboratory for analyses. However, data generated from laboratories should be checked to make sure that it is consistent with the correct use as intended by the model. Sometimes problems result from misapplication of the data because of different conventions used by the engineering and scientific communities. For example, moisture content may be determined upon a mass basis or upon a volume basis. The data reviewer will not necessarily know how moisture content was determined because the results for either basis are reported as a percentage. The data may be misapplied, if the moisture content determined on a mass basis was applied in a model that required a volumetric water content. For this reason, it's important for method information to be presented by the modeler to the Agency.

This appendix will discuss some of the conventions used for physical parameters in common vadose zone models.

The reader should be aware that these parameters will vary spatially across and beneath a field site. A single sample or test for a parameters is usually not sufficient to capture these variations.

B.2 Dry soil bulk density (ρ_b)

The bulk density (also called dry bulk density) is the ratio of the mass of dry solids to the bulk volume of a soil. The bulk density is therefore less than the density of particles that make up the soil, because it also includes the volume of pore space. There is no standard method for the measurement of bulk density. Most commonly, dry bulk density is measured by taking a sample of known volume, drying it at 105°C for 24 hours or until a constant weight is obtained, then weighing the dried soil sample. The dry weight divided by the volume is the bulk density of the sample.

$$\rho_b = \frac{\text{Weight of dry sample}}{\text{Volume of Sample}} \qquad \text{(B1)}$$

There are other methods to measure the bulk density including radiation techniques. The reader is referred to Blake and Hartge (SSSA, Chapter 13, 1986).

The dry bulk density will vary within certain limits for different soil types. See Appendix A, Table A.3 for representative values of bulk density for differing soil types. The bulk density is a useful parameter. It is used to by geotechnical engineers to estimate compaction of the soils. The bulk density is used in modeling to calculate between the volumetric water content and the gravimetric water content, to calculate retardation factors, and is coupled with the particle density to calculate the porosity of a soil.

B.3 Particle density (ρ_s)

The particle density is defined as the ratio of total mass of solid particles to their total volume, excluding pore space. The particle density is usually measured by pycnometry (weighing by difference). One commonly employed method is described by Danielson and Sutherland (SSSA, Chapter 18, 1993). This method is for the specific gravity of particles, but it will operationally give the particle density of a soil sample. Another method listed by Blake and Hartge (SSSA, Chapter 14, 1983) is the Submersion Method of Capek.

The particle density will vary due to the presence of different soil minerals and objects. A commonly used default for particle density is 2.65 g/cm^3 (U.S. EPA, Soil Screening Guidance, 1996a). This value is the density of the mineral quartz and would be representative of most sands. Soils composed predominately of clays would have a slightly higher particle densities approaching 2.75 g/cm^3. These relationships do not hold for anthropogenic materials such as slag or fill. For sites with anthropogenic materials, empirical measurement would be necessary to define the particle density.

B.4 Porosity

The porosity of a soil refers to the amount of void space present. The pore space and the arrangement of pore spaces within a soil sample is very complex and difficult to measure. This is because of the arrangement of soil particles influences the shape, size and orientation of pores within the soil matrix. The porosity of a soil will vary with the arrangement of particles or texture. In general, finer grained soils, rich in clay, will have the highest porosity, and coarser textured soils, rich in sand, will have lower porosity. The reader is directed to Appendix A, Table A.3 for representative values of porosity for differing soil types.

There is no one defined method for the determination of porosity. The most common approach is to use the particle density in conjunction with the bulk density of a sample to define the total porosity. This relation is defined in the following equation:

$$\text{Porosity } (\phi) = (1 - \rho_b/\rho_s) \qquad \text{(B2)}$$

Another method is to use pycnometry as described by Danielson and Sutherland (SSSA, Chapter 18, 1983).

Porosity measurements are important and are used in most vadose zone models. Porosity measurements serve as a basis for determining the water-filled porosity, air-filled and in calculations to determine the total mass of contaminants at a facility.

B.5 Water content

The water content indicates the amount of water in a soil sample. Understandably, this value will change over time as the soil water budget changes. Most vadose zone models require some measure of water content. However, there is some confusion about the basis for water content measurement and the use of the data. The most common measurement is the percent moisture content of a soil sample. The measurement is made by weighing a soil sample, then drying it at 105 °C until a constant weight is obtained, then weighing the dried soil sample. The percent moisture content is then:

$$\% \text{ Moisture} = (\text{Dry Weight})/(\text{Wet Weight}) \text{ X } 100 \qquad \text{(B3)}$$

The ratio of dry weight to wet weight of a soil sample represents the gravinometric water content or water content on a mass basis (θ_M). Unfortunately, most vadose zone models require that water content of a soil be expressed in terms of volume rather than mass. The conversion from water content based upon mass to that of a volumetric basis can be made with the following relationships:

$$\frac{\text{Vol. of water (mL)}}{\text{Vol. of soil (mL)}} = \theta_M \text{ (g/g)} \text{ X } \frac{\text{Bulk Density (g/cm}^3)}{\text{Density of water (g/cm}^3)} \qquad \text{(B4)}$$

The ratio of the volume of water to that of the soil sample in Equation B4 is the volumetric water content (θ_V). The bulk density is defined in Section B.2 and density of water is usually assumed to be 1.0 g/cm^3.

In many applications, the model prompts the user for neither the volumetric nor mass water content. Instead, the model will require water-filled porosity or the percentage that the average pore-space is filled with water. This value can be determine by first noting that:

$$\text{Volume of Pore Space (mL)} = \text{Porosity} \times \text{Volume of Soil (mL)} \quad \text{(B5)}$$

Rearranging equation B5 in terms of volume of soil and substituting this relation in equation B4, the following relationship is found:

$$\frac{\text{Vol. of water (mL)}}{\text{Vol. of pore space (mL)}} = \frac{\theta_M\ (\text{g/g})}{\text{Porosity}} \times \frac{\text{Bulk Density (g/cm}^3)}{\text{Density of water (g/cm}^3)} \quad \text{(B6)}$$

This ratio is them multiplied by 100 to determine the percentage of water in the pore space of a soil sample. For example, if a soil sample is determined to have 20% moisture content (determined on a mass basis), a dry bulk density of 1.5 g/cm^3 , a total porosity of 0.5 (i.e. 50 %) and the density of water is 1.0 g/cm^3, then

Example:

$$\text{\% of pore filled with water} = \frac{0.2}{0.5} \times \frac{1.5\ \text{g/cm}^3}{1.0\ \text{g/cm}^3} \times 100 = \underline{\mathbf{60\%}}$$