Methodology for Establishing Cleanup Levels for Contaminated Sites

Introduction: In Oklahoma, appropriate cleanup levels for a specific site are provided by the Department of Environmental Quality (DEQ). Achieving these cleanup levels will allow sites to accomplish Risk-Based Closure. This document explains DEQ's methodology for determining appropriate cleanup levels for sites which will be protective of human health and the environment. It is in the best interest of the property owner or prospective purchaser to meet with DEQ prior to expending significant resources on the evaluation of a particular site. This will allow all parties to apply their resources in the most economical and useful manner. Preliminary Remediation Goals (PRGs) for the site are provided by the DEQ on request from a facility based on the identified chemicals of concern. Section I explains the methods used to derive PRGs for surface soil and groundwater. Section II includes the rationale behind the determination of soil cleanup levels to protect groundwater. The soil cleanup levels derived from the use of these equations will protect groundwater from chemicals leaching through soil. These equations are most useful for anthropogenic organic compounds and should be used when enough information is available about the hydrogeology of the site. When little is known about the hydrogeology, very conservative default assumptions about groundwater are used in the equations to calculate soil cleanup levels to protect groundwater.

There are many considerations which must go into the calculation of cleanup levels. A facility may use the Soil Screening Level Guidance published by EPA's Office of Solid Waste and the Maximum Contaminant Levels promulgated by the EPA under the Safe Drinking Water Act as screening levels. These levels are based on population exposures and may be more conservative than is suitable for an industrial site, but are adequate as screening tools. The Oklahoma Water Resources Board has criteria for discharge to surface water which can be used to screen releases which may reach surface water. There are several other regional lists which are frequently cited. Use of any other lists for screening should be approved by DEQ before any chemicals are excluded as Chemicals of Concern (COC) at the site.

Section I Risk-Based Cleanups

1. **Site Information Needed to Determine Appropriate Land Use Category**
   Determination of cleanup levels will be based on site specific characteristics and land use, both present and projected. Information needed includes location of the site, type of activities which occur at the site, and historical information regarding past activities at the site (manufacturing processes, chemicals used, waste sources, etc.). Site location information should include a facility layout, adjacent land use, topographical information, sampling locations, waste source locations, water well locations in the vicinity, and depth to groundwater (if known).

2. **Exposure Pathways**

For each site, cleanup levels must be established which will protect both human and ecological receptors. Potential human exposure pathways include: ingestion of soil and dust, inhalation of volatiles and particulates, dermal contact with soil or groundwater contaminated by those chemicals, ingestion of contaminated groundwater, consumption of crops contaminated with soil or water from the site, and surface water runoff.

Residential or Industrial Worker

Differing types of land use indicate different exposure durations for residents or industrial workers. Default values for durations of exposure and consumption patterns have been published by EPA (Exposure Factors Handbook, Risk Assessment Guidance for Superfund, Volumes A, B, and C, [RAGs]). The goal of considering land use is to arrive at a Reasonable Maximum Exposure (RME) for actual land use, both present and future. Zoning, availability of public water supplies, other development in the area, and proposed institutional controls are considered in the determinations of land use.

Lead Contamination

Cleanup levels for lead contaminated soils are based on protecting the most sensitive population, very young children. EPA has developed an Integrated Exposure Uptake Biokinetic (IEUBK) model for residential soils and a cleanup level for industrial sites based on the Bowers model which would be protective of the developing infant of a pregnant working women.

3. **Brownfields Redevelopment Projects**

In many cases, the future use of the property is industrial, and limited cleanup may be allowed. When limited cleanup for industrial use is allowed, institutional controls will be required to ensure that use of the property is consistent with the cleanup level scenario which has been proposed.

4. **Protection of Groundwater**

Soil contaminants have different potentials to impact groundwater under a site. In most cases, groundwater under the site is considered a potential drinking water source. For groundwater cleanup, the Maximum Contaminant Levels as defined by the Safe Drinking Water Act will apply. Alternate Concentration Limits which are higher than MCLs will be approved only after the facility completes a Risk Assessment which explores the potential uses and migration pathways of groundwater. Soil cleanup levels for contaminants in soil which may leach to groundwater have been calculated for many organic chemicals and will be provided where appropriate. Details of the models used to calculate these numbers are included in Section II of this document. It is also important to determine if the area is a groundwater recharge zone, or whether groundwater is discharging to surface water in the area.

5. **Protection of Surface Water**

The Oklahoma Water Resources Board has established Surface Water Quality Standards for certain chemicals. These standards are intended to prevent deterioration of any "Waters of the State" which could be caused by discharge of these chemicals into lakes, rivers or streams. Where appropriate, these standards will also apply.

6. **Chemicals of Concern**

All chemicals identified in the initial sampling should be carried forward in the site specific determination of cleanup levels. Some of those chemicals may not exceed naturally occurring background levels of chemicals in soil or water or the levels listed in the SSL/MCL documents or the Preliminary Soil Remediation Goals provided by DEQ. Chemicals which do not exceed those levels may be "Screened Out" from further testing. Agreement must be reached between the facility and DEQ before any contaminants are dropped from further evaluation. In cases where EPA verified toxicological information is lacking, chemicals with similar structures or activity patterns to those which are present at the site may be used to determine surrogate cleanup goals. This occurs frequently for hydrocarbon spills, and for polycyclic aromatic hydrocarbons (PAHs). The facility should discuss any such proposals with Waste Management staff. EPA technical staff may also serve as resources for the most current, but unpublished information about Chemicals of Concern. DEQ staff will assist in obtaining information from these sources.

Tiered Approach to Developing Cleanup Levels

A. Use of the Soil Screening Level (SSL) guidance or published background levels for inorganic chemicals in soils or MCL values for groundwater may be a first step in screening for contaminants which might require remediation at a site. While the presence of site contaminants at concentrations lower than these published values may not warrant a cleanup action, there is no guarantee that further action will not be required at a site. There may be Ecological or other special concerns with the site, or inadequate characterization results may trigger further action. For chemicals not listed in the SSL document, or which do not have MCLs, DEQ will supply screening levels for a site based on the calculations used to determine PRGs, with a factor of .25 included in the calculations to account for mixtures of chemicals present, and for possibly limited information about subsurface environmental conditions.

B. For Chemicals of Concern which exceed screening levels, Preliminary Remediation Goals (PRGs) for the site will be supplied by the DEQ. These goals will be conservatively protective of human health and the environment. Cleanup goals are calculated based on formulae included in RAGs, Part B.

C. If the calculated soil cleanup levels to be protective of groundwater, or cleanup levels calculated according to RAGs methods are higher than other benchmarks, the most protective numbers will be used as the Preliminary Remediation Goals.

D. Should the facility wish to provide more information about the site, some of the default factors used to calculate the Preliminary Remediation Goals may be amended to make the cleanup levels *more site specific*. This information could include more detailed hydrogeologic information which demonstrates that groundwater at the site is not impacted. Well surveys for the area may demonstrate whether or not there are off-site receptors for groundwater in the area of concern. More information about the site and the underlying hydrogeology may provide confidence that a slightly higher cleanup level will still be protective of human health and the environment. Note: In some cases the cleanup level calculated with the more site-specific data may be more restrictive (lower cleanup values) than the PRGs.

E. Should cleanup levels calculated using these amended factors still be unacceptable to the facility, a Risk Assessment, as detailed in RAGs, may be performed. An outline of the proposed Risk Assessment, as well as any site specific assumptions the facility wishes to propose must be submitted to DEQ. Approval for any variance from the default assumptions must be secured in advance. Performing a Risk Assessment does not guarantee that further remediation will not have to occur, and may result in more stringent cleanup levels.

Section II

Soil Cleanup Levels for Groundwater Protection

Remediation levels may be necessary for soils to prevent leaching of chemicals in those soils to underlying groundwater. These Soil Cleanup Levels for Groundwater Protection were calculated using a set of analytical equations representing partitioning of contaminants between soil, water, and air. The methodology is based on a simplified conceptual model about the release and transport of chemicals in the subsurface environment. There are various basic assumptions (detailed in Addendum I) which affect the validity of the model results. One assumption is that the leachate is moving through a porous/non-fractured soil matrix. Another assumption concerns the amount and occurrence of dilution where leachate enters the groundwater and where groundwater discharges to surface water. Conservative default values are applied to assumptions for soil, hydrologic, and chemical characteristics to develop the Soil Cleanup Levels for Groundwater Protection. As more site specific information is gathered, the basic default values of the equations can be modified so that more accurate site specific cleanup levels can be determined. For example, the default value for dilution factor of leachate entering groundwater is 20. However, it may be modified by calculating the dilution factor based on site specific infiltration rate and groundwater flow rate. In some cases, cleanup levels determined using this methodology may not be appropriate due to violations of the basic assumptions of the conceptual model, such as where there is an aquitard which prevents soil contaminants from reaching groundwater. Conversely, where Non-Aqueous Phase Liquids (NAPLs) are present, or the aquifer has a fractured formation, other factors may require different cleanup levels.

1. **Soil Cleanup Levels for Groundwater Protection**

These levels are based on simple analytic equations which include factors such as the current MCL, the Henry's Law constant for the chemical, and the K_d (soil-water distribution coefficient). The K_d is calculated by multiplying the K_{oc} (organic carbon/water partitioning coefficient) for the chemical of concern times the fraction organic carbon in soil (0.006 $g_{organic\ carbon}/g_{soil}$ is the default). Other default assumptions are the water filled soil porosity (T_w = 0.3 L_{water}/L_{soil}), air filled soil porosity (T_a = 0.13 L_{air}/L_{soil}), and the dry bulk soil density (p_b = 1.5 kg/L). The equations are attached as Addendum 1. For inorganic contaminants, K_d values can be determined from published literature, or established empirically.

2. **Simple Site Specific Soil Remediation Goals to Protect Groundwater**

These levels will allow the facility to use more site specific inputs into the equations and to calculate a dilution factor based on the hydraulic conductivity, hydraulic gradient, mixing zone depth, infiltration rate, source length parallel to groundwater flow. More site specific information regarding dry bulk soil density, aquifer hydraulic conductivity, and the K_d values for inorganics can be established through laboratory testing. The equations are attached as Addendum 2. Any variations from default values will require DEQ approval.

Summary

This paper is a brief discussion of the methods used by the DEQ to arrive at soil cleanup levels which are risk-based. Varying levels of effort are required for the facility to develop site specific inputs for the various equations used in these determinations. For many facilities, cleanup to Preliminary Remediation Goals will be the most protective and least costly methodology. For other sites, more time and effort will be needed to complete the sampling and hydrogeologic mapping required to determine more site specific cleanup levels. Cleanup to statistically established background levels is also an acceptable option, and may be proposed by the facility.

Waste Management staff will work with the facility to ensure that the process is accomplished in a timely manner, protective of human health and the environment, and is cost-effective for the facility. Since toxicological and chemical information does change as new research is performed and validated, cleanup levels developed for one site cannot necessarily be used for future cleanups at other sites or from other states where different methodologies are used. As laws and rules change, this will continue to be a dynamic process.

Addendum 1:
Soil-Water Partitioning Equation to Protect Ground Water - Generic Option

$$C_g = C_w\,[K_d + (T_w + T_a H)/p_b] \times 20 \qquad (1)$$

C_g = cleanup level in soil (mg/kg).
C_w = acceptable drinking water concentration (mg/L).
K_d = soil-water distribution coefficient (L/kg). $K_d = K_{oc} \times f_{oc}$. where ($K_{oc}$) is the soil organic carbon/water partitioning coefficient and (f_{oc}) is the fraction of organic carbon of the soil.
T_w = water-filled soil porosity (L_{water}/L_{soil}).
T_a = air-filled soil porosity (L_{air}/L_{soil}).
H = Henry's law constant, (atm-M^3/mol x 41) expressed unitless.
p_b = dry soil bulk density (g/cm^3).
Note: the number 20 in equation (1) is the default value for Dilution Factor.

Required parameter values for calculating PRGs are as follows:

C_w = chemical specific MCL or PMCL in mg/L.
K_{oc} = chemical-specific value (L/mg).
f_{oc} = 0.006 g/g (Default value).
T_w = 0.3 L_{water}/L_{soil} (Default value for loam soil).
T_a = 0.13 L_{air}/L_{soil} (Default value for loam soil).
H = chemical specific value in (atm-m^3/mol) X 41 (conversion factor) unitless.
p_b = 1.5 g/cm^3 (Default value for typical soil).

Use of this equation requires assumptions to be made about environmental factors that affect the fate and transport of contaminants in the subsurface. Although actual conditions seldom meet these assumptions completely, they are generally representative of most situations and generate conservative solutions.

Major assumptions about soil / water partitioning theory are as follows:

1. There is no contaminant loss due to volatilization or degradation.
2. Adsorption is linear with concentration.
3. The system is at equilibrium with respect to adsorption.
4. Adsorption is reversible.

Simplifying Assumptions: Conceptual Model of Contaminant Migration to Groundwater

1. Source is infinite (Steady State conditions).
2. Contaminants are uniformly distributed in the zone of contamination.
3. Soil Contamination extends from the surface to the water table.
4. No chemical or biological degradation occurs in the unsaturated zone.
5. Equilibrium soil/water partitioning is instantaneous and linear.
6. Receptor well is at edge of source area.
7. Aquifer is unconsolidated and unconfined.
8. Aquifer properties are homogeneous and isotropic.
9. No attenuation of contaminants occurs in the groundwater / aquifer.
10. NAPLs are not present.

Addendum 2:

Soil-Water Partitioning Equation to Protect Ground Water - Simple Site-Specific Option

$$C_{ss} = C_w [K_d + (T_w + T_a H)/p_b] \times DF \qquad (2)$$

where:

C_{ss} = site-specific cleanup level in soil (mg/kg).
C_w = chemical-specific acceptable drinking water concentration, MCL or Health Based Level (mg/L).
K_d = soil-water distribution coefficient (cm^3 /g). For organic contaminants, $K_d = K_{oc} \times f_{oc}$ where (K_{oc}) is the soil organic carbon/water partitioning coefficient and (f_{oc}) is the fraction of organic carbon of the soil. For inorganic contaminants, K_d values may be determined on a site specific basis by performing partitioning tests.
T_w = water-filled soil porosity (L_{water}/L_{soil}). Default = 0.30.
T_a = air-filled soil porosity (L_{air}/L_{soil}). Default = 0.13.
H = Henry's law constant expressed unitless, (atm-m^3 / mol) x 41.
p_b = dry soil bulk density (g/cm^3). Default = 0.15.
DF = dilution factor, calculated using equation (3).

Dilution Factor Equation for Simple Site-Specific Option

$$DF = 1 + Kid/IL \qquad (3)$$

where:

DF = Dilution Factor.
K = aquifer hydraulic conductivity (m/yr). In situ measurements of this parameter in the mixing zone area of the aquifer via pumping tests or slug testing are preferred.
i = hydraulic gradient (m/m). Water table maps generated from water level measurements in monitoring wells screened in the mixing zone of the aquifer can be used to calculate this parameter.
Note: Default value for Ki = 22 m/yr.
d = mixing zone depth (m), calculated using equation (4).
I = infiltration rate (m/yr). This value can be represented by the recharge to ground water. The infiltration rate is basically the amount of water that moves through the soil horizon and enters a ground water aquifer. Default = .13.
L = source length parallel to ground water flow (m). This value is determined by measuring the linear distance of contaminated soil in the direction of ground water flow. Default = 45 m for a square contaminated area 0.5 acres in size.

Mixing Zone Depth Equation for Simple Site-Specific Option

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

d = mixing zone depth (m). Represents the depth contaminants are dispersed into the aquifer.
K = aquifer hydraulic conductivity (m/yr).
i = hydraulic gradient (m/m).
Note: Default Ki = 22 m/yr.
d_a = aquifer thickness (m). This value can be determined from boreholes and should include the entire aquifer vertical thickness. Default = 12.
I = infiltration rate (m/yr). Default = 0.13.
L = source length parallel to ground water flow (m). Default = 45.

Note: Where the calculated mixing zone depth exceeds the aquifer thickness, aquifer thickness should be used instead of this equation.

Justification for Derivation of Equation 3- Dilution Factor

I. $m_1 + m_2 = m_3$, (Conservation of Mass) where m = mass in kg

II. $cv = m$, where c = concentration of chemical in mg/L and v = volume of solution in meters^3, assuming density of solution, p = 1000 kg/meter^3

III. $c_1 v_1 + c_2 v_2 = c_3 v_3$, [Substitution of II into I]. Let $v_3 = v_1 + v_2$ (Steady State):

IV. $c_3 = (c_1 v_1 + c_2 v_2) / (v_1 + v_2)$. Let $c_2 = 0$ (clean groundwater):

V. $c_3 = c_1 v_1 / (v_1 + v_2)$

VI. $c_1 = c_3 [(v_1 + v_2) / v_1]$

VII. $c_1 = c_3 (DF)$, where $DF = [(v_1 + v_2) / v_1]$.

VIII. $v = Q \times T$, where Q = volumetric flow rate meters^3/year and T = time in years

IX. $DF = (Q_1T + Q_2T) / Q_1T = T(Q_1 + Q_2) / Q_1T = (Q_1 + Q_2) / Q_1$

X. $DF = 1 + (Q_2 / Q_1)$, where $Q_1 = I \times A_1 = I(LW)$ and * $Q_2 = Ki\,A_2 = Ki(W \times d)$, where I = Infiltration Rate, L = Source Length, W = Source Width
i = groundwater gradient, A2 = cross sectional area perpendicular to ground water flow.

XI. $DF = 1 + [Ki(W \times d) / (I \times W \times L)]$

XII. $DF = 1 + [Kid / (I \times L)]$ (Equation 3)

* $Q_2 = Ki\,A_2$ is Darcy's Law for ground water flow.