NAPL PARTITIONING CALCULATIONS

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TABLE M4-1 Total Organic Carbon Concentrations in Soil

List of Acronyms

ASTM	American Society for Testing and Materials
atm-L/mol	Atmosphere-liters per mole
atm-L/mol-K	Atmosphere-liters per mole-kelvin
CSC	Casmalia Resources Site Steering Committee
K	kelvin
L/kg	liter per kilogram
mg/kg	milligram per kilogram
mg/L	milligram per liter
MIP	Membrane Interface Probe
NAPL	Non-aqueous phase liquid
SVOC	Semivolatile organic compound
TOC	Total organic carbon
USEPA	United States Environmental Protection Agency
VOC	Volatile organic compound

1.0 NAPL PARTITIONING CALCULATIONS

This attachment describes the model used to determine the potential presence of nonaqueous-phase liquid (NAPL) using soil data from selected samples collected at the Casmalia Resources Superfund Site (Site) from locations with elevated Membrane Interface Probe (MIP) responses or from locations with elevated volatile organic compound (VOC) or semivolatile organic compound (SVOC) concentrations in soil. This model is adapted from Feenstra et al. (1991) and Mariner et al. (1997). It should be noted that unvalidated data were used to perform these calculations, as validated data were not available at the time.

As described by Feenstra and Cherry (1996), this method is a simple, semiquantitative tool that enables investigators of disposal sites to assess whether soil chemical analyses indicate the presence of residual NAPLs in the subsurface. Information needed for this evaluation includes: 1) total chemical concentrations; 2) moisture content; 3) porosity; 4) sorption parameters for the chemicals of interest; and 5) physical and chemical properties of the chemicals of interest.

The chemical analysis of a soil sample generally provides a measure of the total amount of chemical of interest in the sample, expressed typically as the mass of chemical per unit dry weight of soil. The result includes chemical fractions that are: 1) dissolved in the pore water of the sample; 2) sorbed on the soil solids; 3) in the soil gas; and 4) in any NAPL phase. The analysis *cannot* indicate directly how the chemical is distributed among these phases, nor whether any NAPL is present. The method *can* be used to calculate whether a NAPL phase is *likely* present in a sample.

The hypothetical pore water concentration of the constituent of interest is calculated from the measured total soil concentration by assuming equilibrium chemical partitioning between the solid phase, the pore water, and the soil gas, and assuming that no NAPL phase is present. The pore water concentration $C_{w,i}$ (in milligrams per liter [mg/L]) can be expressed in terms of the total soil concentration $C_{t,i}$, as:

$$C_{w,i} = \frac{C_{t,i}\rho_b}{K_{d,i}\rho_b + \phi_w + H_{c,i}\phi_a} \quad \text{(eqn. 1)}$$

where:
$C_{w,i}$ = Estimated pore water concentration of component i (mg/L)
$C_{t,i}$ = Total soil concentration, dry weight basis, of component i (milligrams per kilogram [mg/kg])
ρ_b = Dry bulk density (kilograms per liter [kg/L])
$K_{d,i}$ = Distribution coefficient of component i between soil and pore water (liters per kilogram [L/kg]) = $K_{oc,i}f_{oc}$ (Feenstra et al. 1991)

where:
$K_{oc,i}$ = Organic carbon partition coefficient of component i (L/kg)
f_{oc} = Fraction organic carbon of soil (mass organic carbon per mass soil)

φ_w = Water filled porosity (volumetric)
φ_a = Air filled porosity (volumetric) = $\varphi_t - \varphi_w$

where:

φ_t = Total porosity (volumetric)

H_c = Henry's Law constant (concentration in air per concentration in pore water) = H/RT

where:
H = Henry's Law constant (atmosphere-liters per mole [atm-L/mol])
R = Gas constant = 0.08206 atmosphere-liters per mole-kelvin (atm-L/mol-K)
T = Temperature (kelvin [K])

If no NAPL is present, there is a maximum amount of chemical that can be contained in a sample of soil that contains soil solids, pore water, and soil gas. This maximum total soil concentration is determined by 1) the solubility concentration (S_i) of the chemical in water; 2) the concentration in the soil gas that would be in equilibrium with S_i; and 3) the concentration sorbed to the solids that would be in equilibrium with S_i.

It should be noted that Equation 1 is only applicable up to the solubility limit of the aqueous mixture. After solubility is reached (i.e., NAPL is present), the mass associated with the NAPL phase must also be included in this equation for an accurate estimate of pore water concentration. This supplemental calculation is addressed by several other NAPL partitioning models, including NAPLANAL (Jin et al., 1997) and SOILCALC (Mott, 1995), but was not performed in this evaluation.

Values for the chemical parameter inputs were taken from various sources, including Jin et al. 1997, Lide 2000, United States Environmental Protection Agency (USEPA) 1990, Verschueren 1983, Lyman et al. 1990, USEPA 1995, USEPA 2004a, and various websites (e.g., *ChemFinder*), or were estimated using methods in Lyman et al. (1990). For 3,3,5-trimethylcyclohexanone, isophorone was used as a surrogate for several properties (S, H, and K_{oc}).

To evaluate the presence of a single component NAPL, the value of $C_{w,i}$ would be compared with the individual constituent's aqueous solubility (S_i). At the Site, however, soil and groundwater samples contain numerous chemicals of concern, and any NAPLs that may be present are likely to be multicomponent NAPLs. For *multicomponent* NAPLs, the value of $C_{w,i}$ calculated according to Equation 1 for one of the components of interest must be compared not to the pure-phase solubility (S_i) of that component, but rather to the estimated effective solubility of that component from the *mixture* (Feenstra et al., 1991).

Analogous to Raoult's Law for gases, the effective solubility of component i in equilibrium with the NAPL phase equals the mole fraction of the component in the NAPL phase times the aqueous solubility of the pure component (Feenstra et al., 1991):

$S_{e,i} = x_i S_i$ (eqn. 2)

$S_{e,i}$ = Effective solubility of component i or the aqueous solubility of component i (mg/L)
x_i = Mole fraction of component i in the NAPL (dimensionless)
S_i = Aqueous solubility of pure component i (mg/L)

When an NAPL sample from a location has not been located, neither x_i nor $S_{e,i}$ is known. However, they can be estimated using the following equations, assuming NAPL is present. From the definition for mole fraction, the following is known (Mariner et al., 1997):

$$\sum_i x_i = 1 \quad \text{(eqn. 3)}$$

Equations 2 and 3 combine to form the following equation, which assumes that NAPL is present (Mariner et al., 1997):

$$\sum_i \frac{S_{e,i}}{S_i} = 1 \quad \text{(eqn. 4)}$$

At the solubility limit, the pore water concentration ($C_{w,i}$) calculated using Equation 1 is equal to the effective solubility for that component ($S_{e,i}$) (Mariner et al., 1997). Therefore Equation 4 becomes:

$$\sum_i \frac{C_{w,i}}{S_i} = 1 \quad \text{(eqn. 5)}$$

For purposes of this report, $C_{w,i}/S_i$ is called the "fraction of solubility for component i," and the sum of these fractions is called the "total fraction of solubility." When the total fraction of solubility is less than 1, this indicates that the estimated pore water concentrations are less than the effective solubilities and that no NAPL is present. When the total fraction of solubility is greater than or equal to 1 using equation 5, this indicates the potential presence of NAPL. As described above, the pore water concentrations estimated using equation 1 are not accurate representations of expected pore water concentrations when the total fraction of solubility exceeds 1, as this equation does not include terms to account for the mass in NAPL.

The spreadsheets included in this attachment include all of the input parameters used in the calculations. Assumptions that were used to complete the calculations include the following:

- Measured soil concentrations on a dry-weight basis were assumed to be the total soil concentrations.
- The analysis only included constituents on the VOC and SVOC target compound lists (Table A-3 of the *Remedial Investigation/Feasibility Study Work Plan* (RI/FS Work Plan) [Casmalia Resources Site Steering Committee (CSC), 2004]) and not Tentatively Identified Compounds.
- When multiple detections of the same compound were reported for the same sample (typically due to multiple sample dilutions in the laboratory), the highest of the detections was used.
- Non-detects were not included; however, reported analytical values that were below reporting limits, but above method detection limits, were used.
- Phase I RI soil samples were analyzed for total organic carbon (TOC) by the Walkley-Black method with a detection limit of 1,500 mg/kg. All the Phase I soil sample results were non-detect for TOC. Consequently, half the detection limit (750 mg/kg) was initially used for soil partitioning calculations using Phase I soil data (as reported in the *Interim Progress Report* [CSC, 2005]). This calculation method produced overly conservative estimates of NAPL presence. The CSC completed organic carbon sampling in spring/summer 2006 as part of the Phase II RI sampling to support this NAPL evaluation. The results of that sampling are included in Table M4-1 (found at the end of

this Attachment). Eleven samples were collected from areas that are generally located near the eastern and western property boundaries of the Site, away from areas that are impacted by organic chemicals (see Figure M-1). As shown in Table M4-1, each sample was analyzed twice (as a result of the need to perform a method detection limit study that was not identified until after the initial analyses were completed). The median value of the reanalyzed TOC results was 0.472%. For the purposes of this report, the CSC has used TOC values from the Phase II sampling efforts because the American Society for Testing and Materials (ASTM) D2974 method provided a wider range of TOC values (both above and below the 1,500 mg/kg detection limit previously achieved in the Walkley-Black method), and were more characteristic of TOC values that would be expected for an organic weathered mudstone of the Sisquoc Formation. The Sisquoc Formation, which, similar to the underlying Monterey Formation, is an organic-rich marine mudstone, derived from both marine and mixed marine-continental organic matter
(http://energy.cr.usgs.gov/ 1995OGData/Region2/PROV13.pdf).

- Most soil samples evaluated were collected within weathered claystone. The total porosity was assumed to be 0.45, for silt or clay (USEPA, 1998).
- Water-filled porosity for saturated samples was assumed to be equal to total porosity. Samples collected from within 5 feet of the water table were assumed to be saturated, based on the anticipated capillary forces within these fine-grained soils.
- Location of the water table was determined from Figure 2-23 of the RI/FS Work Plan (CSC, 2004).
- Water-filled porosity for vadose samples was assumed to be 0.15 (USEPA, 2004b; USEPA, 1996).
- Dry bulk density was assumed to be 1.86 kg/L for all samples (USEPA, 1998).
- The model assumes no sorption onto clay minerals.
- The effects of cosolvency were neglected.

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