

## **Development of Soil Cleanup Standards for Explosive Residues on Military Ranges**

Jay Clausen AMEC Earth & Environmental  
Joe Robb AMEC Earth & Environmental  
Mahalingham Ravichandran AMEC Earth & Environmental  
Susan Taylor US Army Corps of Engineers, Engineer Research and  
Development Center

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### **Abstract**

Fate-and-transport models such as SESOIL have been used extensively to develop soil cleanup standards for chlorinated solvents, petroleum hydrocarbons, SVOCs, pesticides, and herbicides. However, very little fate-and-transport modeling has been conducted to determine soil cleanup standards for explosive residues at military sites. The limited modeling work done to date utilizes codes that take into account only the equilibrium solubility concentration and not dissolution rates. Since explosive residues on ranges are typically introduced to the environment as solid particulates, the dissolution rates of energetic compounds are likely to be much lower than their aqueous solubility limits. Soil cleanup standards that do not take into account the site-specific dissolution rates are likely to be overly conservative. As a consequence, the DoD may be responsible for cleaning up a larger volume of soil than is necessary. This poster will illustrate cleanup numbers developed for RDX using SESOIL following the standard equilibrium solubility approach. Cleanup numbers were also calculated utilizing a reverse fate-and-transport modeling approach based on groundwater mass and flux estimates derived from monitoring well data from an anonymous site. A third approach was to be attempted using RDX particulate surface area measurements from detonation of a 81mm mortar coupled with dissolution rate kinetics to derive a mass loading rate. This work is yet to be completed. In addition, geostatistical techniques coupled with GIS tools were utilized to estimate current RDX soil mass and correlate this information with groundwater concentrations to derive a soil cleanup value. The different approaches to derive soil cleanup values will be discussed with the pros and cons of each method weighed against each other.

### **Introduction**

Several different approaches were evaluated for determining appropriate soil cleanup numbers for a military site that would result in no impacts to the underlying aquifer. The groundwater criteria used for the basis of developing a soil cleanup number was the US Environmental Protection Agency's Health Advisory for RDX of 2 ug/L. The approaches considered for this analysis were threefold;

- 1) Use of SESOIL through a trial and error approach to determine the maximum soil concentration that will not result in a groundwater exceedance for RDX,
- 2) Derivation of a groundwater loading rate based on existing groundwater contamination, and
- 3) Derivation of groundwater loading rate based on RDX residues and size of particulates produced from high order detonation of high explosives coupled with use of an analytical dissolution model.

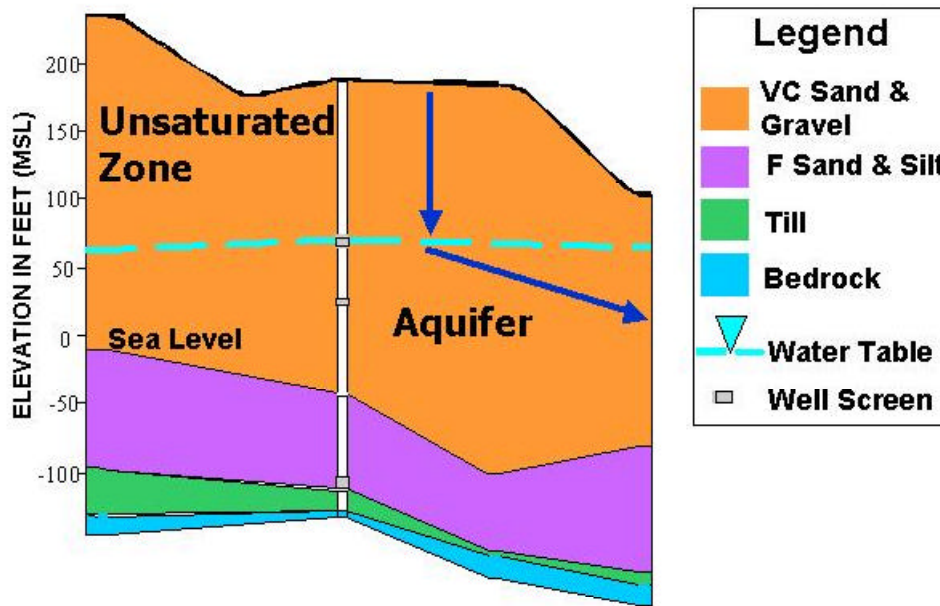
## **Geology**

Fine to coarse-grained sands form a broad outwash plain for the study site. Using the U. S. Department of Agriculture (USDA) soil classification scheme, surface soils at the site range from sands to silt loams. The lithologic material in the unsaturated zone primarily consists of very coarse sand and gravel with some silt and clay lenses. Depth to the water table is approximately 120 ft in most locations.

These soils permit rapid recharge of percolating water and facilitate air exchange with the atmosphere. Hence the soils are aerobic and have a moderate-to-high resistivity. Measurements of sixty-one surface soil samples show low average values for organic matter (1.8 percent or 18,000 milligrams per kilogram [mg/kg]) and pH (4.6), features that limit biodegradation. Total organic carbon (TOC) levels across the site range from 31 to 247,000 mg/kg, with a mean of 11,055 mg/kg. The mean TOC value for samples from 0 to 2 ft was 16,000 mg/kg and approximately 1,500 mg/kg for depths greater than 2 ft. A few soil horizons have a more developed organic layer present but in most locations, an organic-rich surface soil is absent. Although the pH increases with depth, the quantity of organic matter and the moisture content decrease significantly. The surface soils contained less than 4 percent clay-sized particles. Clay-sized particles (traces in most samples) and CEC (8-10 millequivalents [meq]/100g), factors affecting sorption processes, are low in the surface soils and lower still in deeper soils. The data are reflective of highly weathered glacio-fluvial sediments primarily consisting of coarse sand and gravel. These highly weathered soils have low concentrations of soluble salts (e.g. base cations such as calcium and magnesium as well as sodium and chloride) because these ions have been removed by leaching.

## **Hydrogeology**

Except on extreme slopes, surface water runoff at the site is virtually nonexistent due to the highly permeable nature of the sand and gravel underlying the area (Figure 1).



**Figure 1.** Generalized Lithologic Cross-Section for the site.

### Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, Royal Demolition Explosive or cyclonite) belongs to a class of compounds known as nitramines (Table 1). RDX is a crystalline solid at room temperature with a molecular weight of 222 g/mol (Figure 2). RDX has a low water solubility (42 mg/L) and vapor pressure and its  $K_{ow}$  indicates a low affinity for hydrophobic substances. Under intense anaerobic conditions (e.g. approximately -150 mv) and a near-neutral pH biodegradation can be an efficient removal mechanism, although toxic intermediates (nitrosamines) are formed during the process. Degradation is not an important process under the aerobic conditions present at the site. Adsorption is a function of soil clay content, but is typically a relatively minor process. Adsorption is reversible and the occurrence of covalent bonding of amino transformation products has not been demonstrated. Sorption at the site is limited because site soils are relatively coarse-grained (<4 percent clay based on grain size measurements) and contain little (~1.8 percent) organic matter.

Migration of RDX to groundwater is limited by a relatively slow dissolution rate. The principal fate-and-transport mechanisms in soil, therefore, are dissolution, advection, dispersion, and diffusion unless anaerobic conditions exist. Once dissolved, RDX is a persistent and mobile chemical in aerobic aquatic environments.

**Figure 2.** SESOIL input parameters for RDX.

**Table 1.** RDX physiochemical properties.

## **SESOIL**

The Seasonal Soil Compartment Model (SESOIL) is a one-dimensional finite-difference vertical transport code for simulating contaminant movement in the vadose soil zone (Bonazountas and Wagner, 1984 and Hetrick et al. 1993). SESOIL was designed as a screening-level tool, utilizing less soil, chemical, and meteorological input data than most similar models. The model can simulate water movement, sediment transport, and pollutant fate (i.e. degradation), and can be applied to generic environmental scenarios for purposes of evaluating the general behavior of chemicals in the vadose zone (**Figure 3**). SESOIL is designed to estimate contaminant concentrations in the soil following direct application at the surface and/or interaction with other media (i.e., deposition from air). The model was developed for USEPA's Office of Water and the Office of Toxic Substances in 1981 with updates following in 1984, 1986, 1988, 1989, and 1995. SESOIL has been compared with other models, field data, and undergone sensitivity analysis in a number of studies. The model has been used in a number of states and accepted by regulatory bodies for determining cleanup levels in soils (Bonazountas et al. 1997).

The output of SESOIL includes the volumetric flow rate of infiltration into the aquifer (leachate) and the concentrations of contaminants in soil moisture (leachate) before entering the aquifer (**Figure 4**). The volumetric flow rate of infiltration is a function of soil physical properties (porosity, bulk density, permeability, disconnectedness index) and climate data (precipitation, storm intensity, etc). The predicted concentration of contaminants in soil moisture is a function of the volumetric flow rate of infiltration, initial source concentration, contaminant chemical properties (solubility, Henry's Constant, soil-water partition coefficient, etc.) and the source area size.

The objectives of the modeling were to (1) assess the potential for compounds detected in soil to impact the underlying aquifer and (2) determine the concentration that can be left in the soil without exceeding regulatory standards for groundwater. Vadose zone flow and transport modeling was conducted using SESOIL. Leachate impacts to groundwater were evaluated using the Summers groundwater mixing zone model. Model runs to evaluate the potential for compounds to reach groundwater were intentionally conservative to assist in the identification of compounds of concern (COCs). Once COCs were identified, a more refined model that more closely resembled site conditions was used to evaluate soil concentrations that are protective of groundwater. Model results indicate the mobility potential of explosives and propellants depends on the chemical properties of the individual compounds.

**Figure 3.** SESOIL Fate and Transport Processes Simulated.

**Figure 4.** SESOIL Flow Process.

The following sensitivity analysis were conducted to assess the impact on modeled output.

- Vary source size to match average groundwater concentration
- Vary initial soil concentration to match average groundwater concentration
- Vary source size until mass flux predicted by SESOIL = mass flux predicted by saturated zone model
- Vary source size until mass flux predicted by SESOIL = observed mass flux, based on plume mass, age

### **Summers Model**

The Summers model is a public domain, screening-level program used to predict groundwater concentrations resulting from leaching of contaminants through the vadose zone. The Summers model solves the following equation to estimate the concentration of a contaminant in groundwater:

$$1) \quad C_{gw} = [(Q_p C_p) + (Q_a C_a)] / (Q_a + Q_p)$$

Where

- $C_{gw}$  = concentration of contaminant in groundwater,
- $Q_p$  = volumetric flow rate of infiltration into the aquifer (from SESOIL),
- $Q_a$  = volumetric flow rate of groundwater in the mixing zone (from SESOIL),  
 $V_a D_a W_a$ ,
- $V_a$  = groundwater flow velocity,
- $D_a$  = thickness of groundwater mixing zone,
- $W_a$  = width of groundwater mixing zone,
- $C_p$  = concentration of contaminant in soil moisture (leachate) before entering aquifer, and
- $C_a$  = background concentration of the contaminant in the aquifer (assumed to be zero).

Equation 1 is the basis for how the SESOIL and Summers Models are used together to estimate groundwater concentrations. The volumetric flow rate of infiltration into the aquifer and the concentration of contaminant in soil moisture ( $Q_p$  and  $C_p$ ) are output values from SESOIL. The terms that define the volumetric flow rate of groundwater in the mixing zone ( $D_a$ ,  $W_a$  and  $V_a$ ) and the background concentration of the contaminant in the aquifer are input parameters for the Summers model. The volumetric flow rate of groundwater in the mixing zone ( $Q_a$ ) is a function of the depth and width of the mixing zone and the groundwater velocity, which in turn is a function of porosity, hydraulic conductivity and hydraulic gradient.

The following is a list of assumptions and limitations of the SESOIL and Summers models in the context of vadose zone modeling conducted.

1. SESOIL assumes equilibrium distribution of mass in the soil moisture, soil gas, and sorbed phases. This assumption does not account for factors that could limit the dissolution rate of source material such as weathering of explosive particles, ambient temperature, explosive particle surface area, and the intensity and duration of precipitation events.
2. The explosives literature indicates photodegradation can be an important mechanism for explosives at the land surface if standing water is present. However, the SESOIL model does not explicitly account for photodegradation of contaminants.
3. The explosive literature indicates compounds such as TNT, DNT, and possibly RDX can be irreversibly transformed in soil. SESOIL assumes equilibrium partitioning and does not account for irreversible transformation.
4. The Summers Model assumes instantaneous mixing in a “mixing zone” below the source area. In reality, mixing does not occur instantaneously in groundwater. At the water table beneath the source, the concentration will be that of the leachate. As the leachate migrates with groundwater the source concentrations dilute due to dispersion, diffusion, and retardation.

A sensitivity analysis showed that the model was sensitive to the use of laboratory derived site-specific  $K_d$  values or  $K_{oc}$  values. Initial model runs used an RDX literature reported  $K_{oc}$  value of 70.8 L/kg. Based on a shallow soil  $f_{oc}$  of 0.005 and a deep soil  $f_{oc}$  of 0.0001, the shallow and deep  $K_d$  values were 0.35 and 0.007 L/kg, respectively. Using the literature  $K_{oc}$  and site-specific  $f_{oc}$  values, the model predicted an RDX soil concentration of 0.52 mg/kg would not exceed 0.002 mg/L RDX in groundwater. However, it should be kept in mind that  $K_{oc}$  is not a good predictor of RDX partitioning because of the polar nature of the molecule. The model was then run with  $K_d$  instead of a  $K_{oc}$  value and  $f_{oc}$  values. In this case, the  $K_d$  value was based on the University of Texas study (Speitel et al. 2002), where the laboratory determined an average site-specific RDX  $K_d$  value of 0.385 L/kg (average of all 120-hour tests) for the surface soils and 0.049 L/kg for deeper soils. The shallow site-specific  $K_d$  value is almost identical to the  $K_{oc}$ -based  $K_d$  value (0.385 vs. 0.35 L/kg), and the deep site-specific  $K_d$  value is higher than the  $K_{oc}$ -based  $K_d$  value (0.049 vs. 0.007 L/kg). Using the University of Texas  $K_d$  values, the model predicted a soil concentration of 0.50 mg/kg would not exceed 0.002 mg/L RDX in groundwater.

The difference between the results based on the literature  $K_{oc}$  versus the lab-measured  $K_d$  values is only 3.8 percent. At least for the case of RDX, therefore, there is not a significant difference between laboratory and literature estimates of sorption.

In summary, through a trial and error approach SESOIL yielded soil cleanup numbers in the range of 0.2 to 2 mg/kg. The difference in results is primarily a function in the selected solubility and partitioning coefficient values used, source size, and groundwater mixing zone thickness. All of these parameters have some degree of uncertainty associated with their values.

### **Groundwater Derived Soil Cleanup Numbers**

The 2<sup>nd</sup> approach involved utilizing the extent of groundwater contamination and determining the mass of RDX dissolved in groundwater and then estimating a mass flux rate. The saturated zone model, MODFLOW, was utilized to calculate the mass of RDX which yielded a range of 13 to 36 kg. Because of uncertainties in hydraulic properties, namely porosity a range of RDX was calculated. The next step involved using MODFLOW coupled with MT3D to conduct a transport simulation. Mass was added to the model at the source until a reasonable match was obtained between model simulated groundwater plume and the actual plume. Once this was achieved the model was then used to determine the flux rate of RDX to groundwater, which turned out to be approximately 0.1 kg/year. The next step involved using the flux rate as a mass loading rate to soil with the SESOIL model. The size of the soil source area was adjusted until the resultant model predicted groundwater concentrations agreed with actual groundwater concentrations. Then through trial and error the mass loading rate was adjusted until the RDXA HA of 2 ug/L was not exceeded. The resultant mass loading rate was converted to a soil concentration, which was approximately 5.5 mg/kg. The one apparent flaw in this approach was the unrealistic source size derived from this approach.

### **Analytical Calculations Using the RDX Dissolution Rate**

#### **CONCLUSIONS**

The modeled approaches require a source loading term as either mass or concentration. As illustrated in [Table 2](#) the heterogeneous distribution of RDX coupled with the uncertainty in soil concentration is problematic. Depending on the methodology employed to come up with a realistic soil concentration the values could range over five orders of magnitude. Other findings include;

- Continuous source results in concentration profile more consistent with site conditions,
- Comparing *maximum* leachate concentration and mass flux, the two approaches produce essentially the same calibration,
- Both approaches use source area of  $2E+5 \text{ cm}^2$  to predict maximum mass flux = 0.5 kg/yr and maximum leachate concentration equal to solubility (38 mg/L),
- Solubility controls source area size due to soil concentrations greater than solubility, and
- Sensitivity analyses shows similar results when aqueous concentrations do not approach the solubility limit.

Critical vadose zone modeling parameters requiring site-specific data and or measurement, in order of priority include:

1. **Dissolution Rates** - The largest uncertainty in vadose zone modeling is the relationship between the mass of explosives in soil and mass flux from surface soils through the vadose zone to the aquifer. In SESOIL and other fate and transport models, flux rates are calculated from the solubility of contaminant in pure phase under equilibrium conditions. None of the existing vadose zone models have a provision to account for dissolution rate which is a function of surface area of particles from which contaminants are being dissolved, which severely limits their applicability to HE fate-and-transport. As a consequence, all existing vadose models, including SESOIL, will over-predict the transport of HE through the vadose zone.
2. **Contaminant Concentrations in Vadose Zone Soil Moisture** - The concentration of contaminants dissolved in soil moisture in the vadose zone has not been characterized at some areas due to elevated detection limits associated with soil sampling. Without knowledge of how much mass is dissolved in soil moisture in the vadose zone and the distribution of this mass in the vadose zone, the potential impact of surface soil remediation is not known. **REFERENCES**

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