Fate and Transport Modeling of Chloride and Volatile Constituents in Drilling/Reserve Pits in New Mexico

1. Introduction

Daniel B. Stephens and Associates, Inc. (DBS&A) has been asked by The Industry Committee to review the Draft regulation revisions concerning drilling pit closure practices in New Mexico. We have been asked to focus on subsurface fate and transport issues, especially for chloride and volatile organics. DBS&A has conducted saturated and unsaturated modeling of chloride transport from drilling/reserve pits closed in place. DBS&A has also used conducted unsaturated modeling of selected volatile constituents: benzene and tetrachloroethylene (PCE).

Understanding the nature of movement of soil water in the vadose zone is highly relevant to developing regulations dealing with potential migration of chloride and other chemicals from pits. Key processes include precipitation, infiltration, redistribution, evapotranspiration and drainage which lead to net infiltration below the root zone which potentially becomes recharge to groundwater if that percolating water reaches the water table.

In areas of low precipitation, on a regional basis or on a basin scale, natural recharge occurs primarily along mountain fronts and local areas where water is standing on the land surface, and to a lesser extent in other areas. Thus, we consider three primary recharge mechanisms: mountain front, local and diffuse natural recharge. Mountain front recharge occurs largely where snow melt and storm runoff flow across alluvial fans and percolates into permeable alluvium. Local recharge sources include seepage from ephemeral flood flows in arroyos and standing water in ponds above a deep water table, including playa lakes. Diffuse natural recharge may take place in areas in between where mountain front and local recharge occur.

Diffuse natural recharge is the recharge process most relevant to pit waste management regulations. In accordance with these proposed regulations, pits must be at least 100 feet from a water body or water course. Consequently, the pit will not be located in a mountain front or an area of channelized surface water. Instead, if recharge occurs beneath a pit closed in place, it would be considered diffuse natural recharge. Studies of diffuse natural recharge are summarized by Stephens, 1996, Stephens, et al., 1996, and Hogan, et al., 2004. In New Mexico, typical diffuse natural recharge rates are roughly a few to less than ten millimeters per year, that is, fractions of an inch per year.

Factors enhancing diffuse natural recharge include soil texture, slope, and vegetation. Sandy soils tend to allow the majority of precipitation to infiltrate, but then the water beneath the surface is largely prevented from escaping as the soil surface dries and inhibits upward liquid transport by evaporation out of the soil. Soil surfaces which are concave upward (form bowls), tend to enhance soil moisture beneath these areas, thus increasing hydraulic conductivity and the tendency for downward water migration. Sparse or poorly vegetated landscapes allow more of the infiltrated water to escape transpiration by plants.

The natural recharge rates today are much less than they were historically, during cooler climates ten thousand years ago or so. Evidence for this is found in the distribution of natural chloride found in soil in areas of low precipitation. A common spatial pattern, known as a "chloride bulge" is where high concentrations of chloride are found a few feet below land surface, sometimes at concentrations up to 540 mg/kg. The natural chloride is derived from low concentrations in precipitation that slowly over time are concentrated because of evapotranspiration processes of native plants which remove the infiltrated soil water but not the chloride. The more evapotranspiration, the less deep percolation is available to migrate below the root zone and the more concentrated will be the remaining pore water. Thus, chloride in the soil deposited by high precipitation ten thousand years ago will be much lower in concentration than that which occurs during the more recent low precipitation period. This relatively older water lies just below the chloride bulge in the soil profile, while the more recently infiltrated water lies within and above the chloride bulge.

The areas where chloride bulges are found in soil demonstrate that water thousands of years old and younger has not yet reached the water table. At rates of natural recharge of a few millimeters per year, infiltrated water would take centuries to reach the water table in most areas where the water table is a few tens of feet below land surface; and at lower recharge rates the time would be even longer. The chloride bulge also suggests that although the concentration of salts in the pore water may cause the density of the water to exceed that of fresh water, the chloride in the pore water has not migrated downward, owing to the very low hydraulic conductivity of the soil at the in situ water content.

Some chloride bulges have also been explained by upward moving soil water. In places, especially where the water table is relatively shallow and there is an abundance of drought tolerant and deep rooted native plants, water can move upward from the water table to the land surface. This upward water transport is facilitated by the natural geothermal gradient that causes soil temperature to increase with depth below land surface (Walvoord and Scanlon, 2004). Natural recharge would not occur in areas where soil water moves naturally upward. Stephens and Coons, 1994 found upward hydraulic head gradients at a site near Sunland Park, New Mexico.

A pit closed in place is superimposed on these natural recharge processes. It is important to take the natural recharge, or lack of it, into account to predict the extent of potential impacts to groundwater. Pits are encapsulated with reinforced LLDPE liners that have a lifespan of 270 years or more (Kroerner et al 2005). By the time the liner fails, the sites are vegetated with native vegetation and the site has returned to the natural recharge conditions. With this in mind, we have conducted simulations of the potential impacts of chloride in pits on groundwater.

2. Closure Operations

2.1 Current Drilling/Reserve Pit Practices

2.1.1 Northwest New Mexico

In northwest New Mexico, the operating drilling/reserve pit has banks with a 2:1 slope and is typically excavated to a depth of 10 feet below grade. Excavated soil is placed around the pit to form an above-grade berm. A minimum 12-mil reinforced linear LLDPE plastic liner is placed along the bottom and sides of the excavated pit. Current practice in northwest New Mexico is to close the pit in-place. Once pit operations cease and the pit is allowed to dry out, the pit is stabilized by mixing with berms and clean soil at a ratio of 1:1 or greater. After mixing, the liner is folded over the top of the pit contents encapsulating the pit on the top, sides and bottom. The amount of pit contents varies but is generally about 700 cubic yards before mixing/stabilization with the excavated native soil. The 1:1 mixed pit thickness is about 7 feet and has a volume of 1426 yd^3. The mixed pit contents will cover an area of approximately 100 ft by 55 ft (0.13 acres). The pit is then covered by three feet of soil. The total volume of the closed pit and cover is about 1.3 acre-ft (2037 yd^3).

2.1.2 Southeast New Mexico

Wells in southeast New Mexico are on average deeper than in northwest New Mexico and generate more pit material. The drilling/reserve pit is used during drilling operations. Current closure practice in southeast New Mexico is to mix the pit contents with clean soil at a 1:1 or greater ratio, place the mixture in a minimum 12-mil reinforced LLDPE plastic lined trench, cover the mixture by folding the two layers of liner, and then cover the top liner with four feet of clean soil. The typical pit volume is 1600 yd^3 and after mixing at a 1:1 ratio with clean soil is about 3,260 yd^3, which fills a 15 ft deep trench that is 200 ft in length by 40 feet in width (0.18 acres) to a depth of about 15 feet. The total volume of the soil-pit mixture and the soil cover is about 2.8 acre-ft.

3. Model Scenarios

3.1 Maximum Chloride Concentration Limit that is Protective of Ground Water

Modeling was conducted using a combination of an unsaturated flow and transport model (VADSAT), and ground water flow (MODFLOW), and contaminant transport (MT3D) models to predict the peak concentration of chloride in a hypothetical monitoring well located at the downgradient edge of a pit site. Based on the EPA secondary chloride standard (250 mg/L) and the background concentration of chloride in the aquifer (66 mg/L in the southeast (USGS, 2003) and 15 mg/L in the northwest (maximum reported by Walvoord et al 1999)), the model results can be scaled to predict the maximum chloride concentration allowed in the pits that is protective of groundwater. Simulations were performed only for the current closure practices in the southeast since the pits are larger and the background chloride concentration is greater than in the northwest. It is assumed that liners instantaneously and completely fail after 270 years, which corresponds with the average lifespan of geomembranes at 25°C (Koerner et al 2005).

Although pit contents are mixed with clean soils at ratios of 1:1 up to 1:6, the chloride transport modeling conservatively assumes no mixing and that the volume of pit contents is double the original amount from drilling operations (e.g., the undiluted pit contents in the southeast have a 1:1 mix volume of 3,260 yd^3). The leachate concentration determined by modeling for the unmixed pit contents is then adjusted based on the mixed ratio.

Based on industry estimates, the soil in the pit contains about 12% clay and 80% sand with the remaining 8% as silt, which by the USDA classification would be loamy sand. The pit and native soils (vadose zone and aquifer) are assumed to have the same hydraulic properties. The soils are assumed to be uniform in texture from the pit bottom down to the groundwater, which will increase the rate of infiltration. Soil parameters used in the model including saturated hydraulic conductivity, total porosity, residual water content, bulk density, and the van Genuchten empirical parameters were obtained from the averages reported by Carsel and Parrish (1988). Parameters from Carsel and Parrish (1988) are widely accepted and are provided with HYDRUS-1D and VADSAT (API, 1995). The saturated hydraulic conductivity used in the model is 11.5 ft/day, which is consistent with the geometric mean hydraulic conductivity of 6.8 ft/day for the Ogallala (Blandford et al 2003) and the hydraulic conductivity range of 3 - 3000 ft/day for the alluvium in the San Juan basin (Walvoord et al 1999). The same value of saturated hydraulic conductivity was used in the vadose zone and the aquifer. Bulk densities were calculated from the total porosity provided by Carsel and Parrish 1988 and an assumed rock grain density of 2.65 gram/cm^3 by Domenico and Schwartz (1998). The effective porosity of the aquifer was assumed as 0.3 based on the specific yield of sand reported by Domenico and Schwartz, 1998.

The pit overlies an aquifer with uniform flow at a gradient of 0.004 ft/ft (Blandford et al 2003). The aquifer has a thickness of 50 feet that is the median value found for the Ogallala in New Mexico (e.g., Blandford et al 2003). For modeling purposes, the depth to water was assumed to be 50 feet. Depth to water influences the timing of impacts but has little influence on the peak impact.

The transport of chloride from the pit considers advection and dispersion. Retardation of chloride is not considered. The vertical dispersivity in the vadose zone is based on the distance from the ground surface to the water table. The VADSAT manual (API, 1995) provides an equation from Gelhar et al., 1985 to estimate the dispersivity in the vadose zone, which gives an estimated vertical dispersivity of 1.05 feet based on depth to water of 50 feet. The longitudinal dispersivity in the saturated zone will be set to a value of 7.06 feet based on a transport distance of 100 feet and equation 14b in Xu and Eckstein 1996, which is based on measurements of scale and dispersivity provided by Gelhar (1992). The lateral and vertical dispersivities will be 1/10 and 1/100 of longitudinal, which are 0.71 feet and 0.07 feet, respectively. Although dispersivity is usually a sensitive parameter for contaminant transport, it is not expected to be sensitive for these simulations since the receptor is located along the centerline of the plume.

A recharge rate of 2.5 mm/yr was used in all simulations, which is the intermediate value reported by Phillips et al (1988) for recharge in Las Cruces, NM using three techniques: tritium peak, chlorine-36 peak, and chloride mass balance. The recharge rates estimated by the tritium peak, chlorine-36 peak, and chloride mass balance techniques were 9.5 mm/yr, 2.5 mm/yr and 1.5 mm/yr, respectively. The rate of 2.5 mm/yr is above the upper range of recharge values (0.25 - 2.29 mm/yr) published for the San Juan basin by API, 1996 (after Stone, 1986). All of these rates are greater than the upper end of the range estimated by Walvoord and Scanlon, 2004 (0.03 to 0.1 mm/yr) for interplaya regions of the southwest where plants are well established in sufficiently deep soils.

Table 1. Model parameters for chloride transport simulations

Parameter	Southeast Pit
Source	
Source width (ft)	40
Source length (ft)	200
Pit thickness (ft)	11
Cover thickness (ft)	4
Depth to groundwater from pit bottom (ft)	35
Initial saturation (fraction pore space; cm^3/cm^3)	100%
Aquifer	
Recharge (mm/yr)	2.5
Depth to groundwater from grade (ft)	50
Aquifer thickness (ft)	50
Hydraulic gradient magnitude (ft/ft)	0.004
Background chloride (mg/L)	66
Soil	
Soil type	Loamy sand
Saturate hydraulic conductivity (ft/d)	11.5
residual water content (cm^3/cm^3)	0.057
saturated water content (cm^3/cm^3)	0.41
van Genuchten n parameter (- -)	2.28
van Genuchten α parameter (1/cm)	0.124
Dispersion	
Vadose zone vertical dispersivity (ft)	1.05
Aquifer longitudinal dispersivity (ft)	7.06
Aquifer lateral dispersivity (ft)	0.71
Aquifer vertical dispersivity (ft)	0.07

3.2 Fate of Volatile Organic Compounds in Pits after Closure

Before closure in place, the pit contents are well mixed and aerated with clean soil. The pits are then left open for months before they are finally encapsulated with liners, which allows VOCs sufficient time to volatilize. The fate of VOCs was estimated using two selected compounds: benzene and tetrachloroethylene (PCE). Benzene has a low groundwater quality standard (0.01 mg/L in Section 20.6.2.3103 NMAC) and is commonly associated with petroleum. PCE is not commonly found in pits and was anomalously detected in one pit sample collected by the Industry Committee (2007) sampling. The groundwater quality standard for PCE is 0.02 mg/L (Section 20.6.2.3103 NMAC). The gas diffusion constant for benzene was 7.7E-06 m^2/sec and 7.6E-06 m^2/sec for PCE (Reid et al 1987). Adsorption was simulated using an assumed fraction of organic carbon (0.001) and the organic carbon partitioning coefficients (Koc) of 0.089 m^3/kg for benzene and 0.364 m^3/kg for PCE (Reid et al 1987). The dimensionless Henry's constants ($C_{gas}/C_{aqueous}$) at 20°C were 0.179 for benzene and 0.628 for PCE (Reid et al 1987). The simulations were conducted using the HYDRUS-1D software. Modeling conservatively used initial concentrations of 1,000 mg/kg each of PCE and benzene, which is orders of magnitude greater than the maximum concentrations detected by the Industry Committee sampling (Industry Committee, 2007).

4. Results

4.1 Maximum chloride concentrations in pit soils

The maximum chloride concentrations in pits are a function of the mass of chloride in the pit (e.g., thickness and length of the pit), recharge rate, groundwater flow rate, aquifer thickness and initial saturation. The maximum concentration is not sensitive to the distance to the downgradient receptor, depth to water, liner failure rate, and dispersivity, which tend to influence the timing of impacts rather than the maximum impact. Soil concentrations in mg/kg were converted to leachable aqueous concentrations in mg/L from the Synthetic Precipitation Leaching Procedure (EPA SW846 method 1312) using a factor of 20. The table below summarizes the leachable concentrations based on modeling results and soil mixing ratios that are protective of the environment.

Recommended Soil Mixing Ratio	**SPLP Leachate Chloride Standard (mg/L)[1]**
None	1240
1:1	2480
2:1	3720
3:1	4960
4:1	6200
Average	3720

4.2 Fate of benzene and PCE concentrations in pit soils

Once the liners fail, benzene and PCE will quickly volatilize through the vadose zone up to the atmosphere. After less than 1 day, the initial concentrations of 1,000 mg/kg of PCE and benzene were no longer present in the model simulations due to volatilization from the well mixed and aerated pit contents.

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