

## **An Evaluation of Benzene Risk**

[in Risk-Based Decision-Making for Assessing Petroleum Impacts at Exploration and Production Sites, S. J. McMillen, R. I. Magaw, and R. L. Carovillano, Eds., Department of Energy and the Petroleum Environmental Research Forum, U.S. Govt. Printing Office, Chapter 11, pp. 156-173 (2001)]

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### **Introduction**

Benzene is commonly found in the environment from both human activities and natural processes. Benzene was first discovered in 1825 and isolated from coal tar in 1849, while today it is manufactured mostly from petroleum sources. Benzene is used by industry to make other chemicals such as ethylbenzene for plastics manufacture, cumene for resins, and cyclohexane for nylon and synthetic fibers [1]. Natural sources of benzene in the environment include volcanoes, forest fires, and crude oil seeps. Benzene occurs naturally in most crude oils, is a byproduct of oil refining processes, and also occurs in natural gas production condensates.

Benzene is a known human carcinogen. In workers, long-term exposure to high concentrations of benzene in air has been shown to cause cancer of the blood-forming organs. In laboratory animals, benzene has been shown to produce several types of cancer following oral or inhalation exposure. There are still questions concerning both the mechanisms of benzene carcinogenesis and the most appropriate models for developing human risk estimates. These issues are actively being studied and debated in the scientific community. In addition to cancer, benzene is also known to produce other adverse health effects, again principally on the blood-forming organs, although neurological and reproductive effects may also be of concern [1]. Most people are exposed to a small amount of benzene every day, mainly via inhalation of vapors from commercial products such as glues, paints, cigarette smoke, and vehicle exhaust. People may come into contact with benzene through the inhalation, ingestion, or dermal contact exposure pathways.

Most upstream regulatory programs (such as those in the States of Texas and Louisiana) do not routinely require benzene analysis of exploration and production (E&P) site soils and do not routinely set regulatory limits for benzene in soil. Upstream regulatory agencies in California, New Mexico, and Michigan are exceptions and do require benzene analyses for soils at E&P sites. Regulatory limits for benzene in soil are routinely set in downstream regulatory programs, such as those with jurisdiction over underground storage tank (UST)

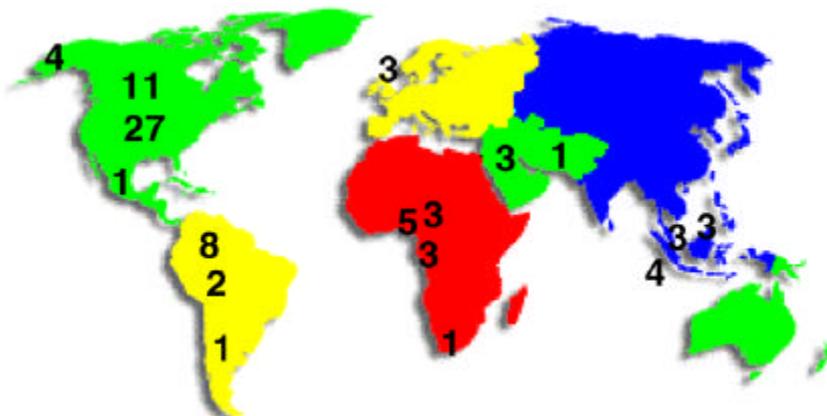
sites. Most often, these are based on Tier 1 Risk Based Screening Levels (RBSLs) developed for protecting groundwater resources. In developing RBSLs, a number of fate and transport assumptions are typically used that are now known to be overly conservative for benzene. For example, Tier 1 RBSLs have historically assumed that benzene in a complex mixture of petroleum hydrocarbons in soil behaves in the same way it would if it were the only chemical present in soil, and that there are no losses of benzene due to volatilization or biodegradation over time.

This study was conducted to improve the fate and transport assumptions typically used to derive RBSLs for benzene in soil. RBSLs are developed that take into consideration the attenuation of benzene in the vadose zone, as well as the presence of the complex petroleum mixture (expressed in terms of TPH) in soil. Additional attenuation of benzene in groundwater is not considered. The potential risk that benzene might pose at E&P sites is then evaluated by comparing these RBSLs to two estimates of potential benzene levels in E&P site soils. The first estimate is based on benzene levels found in several unweathered crude oils and condensates. The second is based on limited field data for actual benzene levels measured in E&P site soils following typical emergency response activities after spill events.

## **Benzene Concentrations in Crude Oils and Condensates**

Sixty-nine unweathered crude oils and fourteen unweathered condensate samples were analyzed for volatile aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and xylenes (BTEX) using purge and trap gas chromatography coupled with mass spectrometry (GC/MS). Samples were analyzed following a procedure based on the United States Environmental Protection Agency (USEPA) Method 8260A [2].

Figure 1 illustrates the sample locations for the 69 crude oils and 14 condensates. The American Petroleum Institute (API) gravity range for the crude oils in this study is 9 to 46°, and the range is 45 to 70° for the condensates. While all of the samples were analyzed for BTEX as discussed above, only the benzene values are presented here. Toluene, ethylbenzene, and xylenes (TEX) do not typically present a risk management concern at petroleum release sites. They are non-carcinogenic compounds and they are addressed as part of the petroleum mixture as a whole. TEX are included in the non-carcinogenic TPH RBSLs presented in Chapter 8. The analytical results for TEX are provided in Chapter 4.



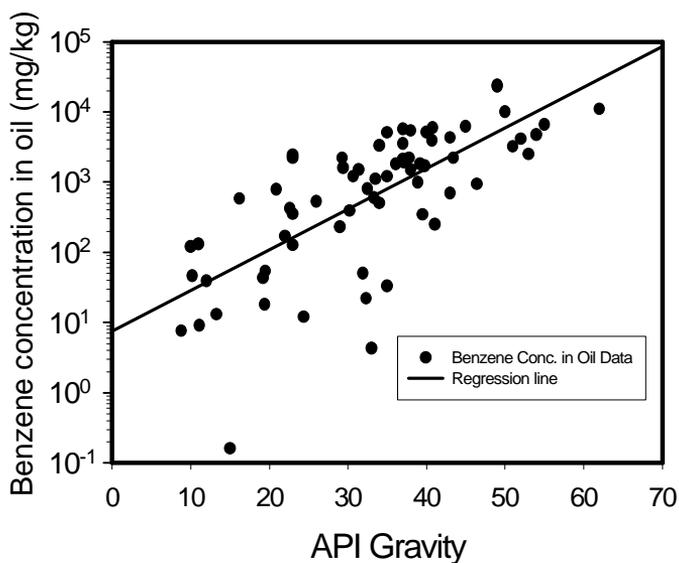
**Figure 1.** Sample locations for the crude oils and condensates. Twelve of the condensates were from the United States (excluding Alaska and Hawaii).

As shown in Table 1, the highest observed concentration of benzene in the 69 crude oils was 5900 mg/kg of oil or 0.59 wt %, and the mean concentration of benzene in the crude oils was 1,340 mg/kg. Two crude oils contained less than 1.2 mg/kg benzene (the detection limit for the analytical method). In general, higher API gravity crude oils and condensates tend to contain more benzene as shown in Figure 2. The condensates contained more benzene than the crude oils, with the maximum concentration being 35,600 mg/kg of condensate (3.56 wt %). The mean concentration of benzene for the 14 condensates was 10,300 mg/kg. There is roughly 10 times more benzene on average in the analyzed condensates than in the analyzed crude oils.

**Table 1.** Concentrations of benzene in crude oils and condensates analyzed in this study.

# of Samples	API Gravity Range (°)	Concentration of Benzene (mg/kg Oil)				Number of Samples With Benzene = ND
		Mean	Median	Minimum	Maximum	
69 Crude Oils	8.8–46.4	1,340	780	ND*	5900	2
14 Condensates	45–70.1	10,300	6400	1470	35,600	0

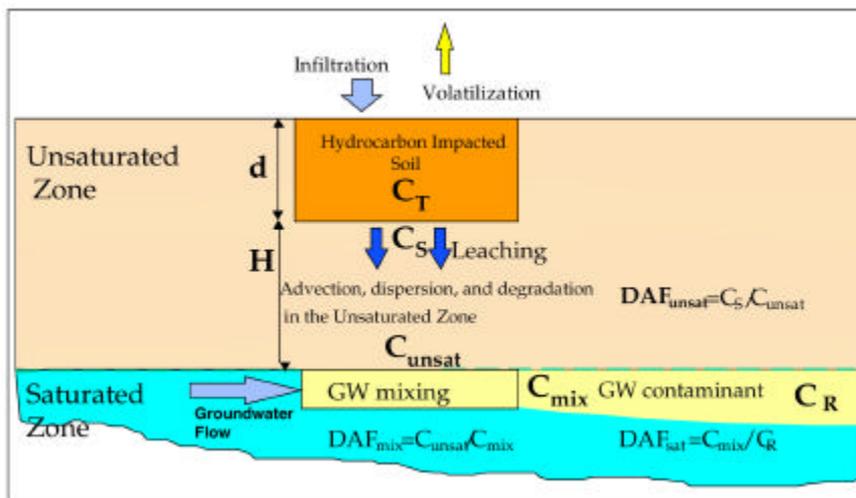
ND = Non-detect, with the sample detection limit = 0.32 mg benzene/kg oil.



**Figure 2.** Benzene concentrations versus API gravity for 61 crude oils and 14 condensates (API gravity data were unavailable for 8 crude oils).

### **Benzene RBSLs for Groundwater Protection**

Groundwater protection RBSLs for benzene in soil were developed for the scenario shown in Figure 3. In this scenario, a surface impoundment or a soil is impacted from a surface spill of oil (or condensate) in which the oil is confined to the unsaturated zone and does not reach groundwater, i.e., there is no free-phase oil at the water table. It is assumed that some response to the spill has already occurred and that the extent of contamination has been delineated such that the depth of contamination and level of contamination are known. The source of benzene contamination is confined to a layer of thickness,  $d$ , and the bottom of the contaminated layer is a distance,  $H$ , from the groundwater table.



**Figure 3.** A conceptual site model showing a crude oil or condensate contaminated soil in the unsaturated zone and the various dilution and attenuation processes that occur during transport to groundwater.

In general, dilution and attenuation of benzene, or other chemicals, emanating from a source can occur in the unsaturated zone, a groundwater mixing zone, and in the groundwater downstream of the source. A typical RBSL calculation assumes an infinite source of the chemical of concern, which means there are no losses over time due to volatilization, leaching, or biodegradation in the hydrocarbon impacted layer. In addition, biodegradation in the zone between the bottom of the impacted soil and the groundwater table is not typically considered. These assumptions are overly conservative for benzene, because benzene is volatile and readily biodegradable, provided that oxygen does not limit the rate of biodegradation. Accordingly, the approach presented here for developing groundwater protection RBSLs for benzene in soil considers attenuation effects in the unsaturated zone, including a conservative accounting of degradation in the unsaturated zone between the bottom of the contaminated zone and the water table, as well as losses in the source of contamination due to volatilization and leaching. These are accounted for in an unsaturated zone dilution attenuation factor (DAF),  $DAF_{unsat}$ .

In addition to these attenuation considerations, the enhanced soil-water partitioning that occurs for benzene, due to the presence of a complex petroleum mixture in soil is also considered (i.e., the petroleum mixture keeps more of the benzene in the oily soil phase). Present approaches for calculating individual chemical RBSLs assume that partitioning occurs to native soil organic matter only.

The RBSL for benzene in soil that is protective of groundwater,  $RBSL_{s-gw}$ , was calculated using the following equation:

$$RBSL_{s-gw} = C_T = K_T * DAF_o * C_R \quad (1)$$

where:

$C_T$  = The total concentration of benzene in soil based on the groundwater exposure pathway (g/g-soil)

$C_R$  = The acceptable concentration of benzene in groundwater at the groundwater receptor (g/cm<sup>3</sup>-water)

$C_R$  is either a risk-based screening level for water,  $RBSL_w$ , or a groundwater regulatory standard (in the United States, the maximum contaminant level for benzene in groundwater is  $5 \times 10^{-9}$  g/cm<sup>3</sup>-water; the State of New Mexico has a groundwater standard =  $1.0 \times 10^{-8}$  g/cm<sup>3</sup>-water).

If appropriate,  $RBSL_w$  (g/cm<sup>3</sup>-w) can be calculated for benzene, a carcinogen, according to the following equation:

$$RBSL_w = \frac{TR * BW * AT_c * 365 * 10^{-6}}{IR_w * ED * EF * SF_o} \quad (2)$$

where:

TR = Target excess individual lifetime cancer risk ( $10^{-5}$ )

BW = Adult body weight (70 kg)

$AT_c$  = Averaging time for carcinogens (70 years)

$SF_o$  = Oral cancer slope factor [mg/kg-day]<sup>-1</sup> (0.029 for benzene)

$IR_w$  = Adult daily water ingestion rate (2 L/day)

EF = Exposure frequency for residents (350 days/year)

ED = Exposure duration for adult residents (30 years)

$K_T$  = The total partition coefficient for benzene. It is the ratio of total soil concentration to pore water concentration in the source zone of the contamination (cm<sup>3</sup>-water/g-soil).

$DAF_o$  = The overall dilution attenuation factor (unitless) which is defined as:

$$DAF_o = DAF_{unsat} * DAF_{mix} * DAF_{sat} \quad (3)$$

where:

$DAF_{unsat} = C_s / C_{unsat}$  = Unsaturated zone dilution attenuation factor (unitless)

$DAF_{mix} = C_{unsat}/C_{mix}$  = Groundwater mixing zone dilution attenuation factor (unitless)

$DAF_{sat} = C_{mix}/C_R$  = Dilution attenuation factor in groundwater downstream of the source (unitless)

$C_s$  = Concentration in pore water at the source of contamination ( $g/cm^3$ -w)

$C_{unsat}$  = Concentration in pore water at the bottom of the unsaturated zone ( $g/cm^3$ -w)

$C_{mix}$  = Concentration in groundwater at the downstream edge of the mixing zone ( $g/cm^3$ -w)

Equations for determining the overall soil-water partition coefficient and the various DAFs are presented in the paragraphs below.

### **Soil-Water Partition Coefficient, $K_T$**

The overall soil-water partition coefficient,  $K_T$ , is given by:

$$K_T = \frac{C_T}{C_S} = \frac{q_w + K_d r_b + K_a q_a + K_o q_o}{r_b} \quad (4)$$

where:

$C_T$  = Total concentration of chemical in soil ( $g/g$  soil)

$C_S$  = Concentration in pore water at the source of contamination ( $g/cm^3$ -w)

$\rho_b$  = Soil bulk density ( $g$ -soil/ $cm^3$ -soil)

$\theta_w$  = Volumetric water content in vadose zone soils ( $cm^3$ -w/ $cm^3$ -soil)

$K_d$  = Soil-water sorption coefficient for chemical ( $cm^3$ -w/ $g$ -soil)

$K_a$  = Air-water partition coefficient (dimensionless Henry's Law constant) for chemical ( $cm^3$ -w/ $cm^3$ -air)

$\theta_a$  = Volumetric air content in vadose zone soils ( $cm^3$ -air/ $cm^3$ -soil)

$K_o$  = Oil-water partition coefficient ( $cm^3$ -w/ $cm^3$ -oil)

$\theta_o$  = Volumetric oil content in vadose zone soils ( $cm^3$ -oil/ $cm^3$ -soil)

Note that in Equation (4) partitioning of the chemical to residually trapped oil in the soil is included. This represents additional partitioning that occurs when a residual oil phase is present. Thus the levels of benzene that are acceptable in the soil depend on the oil content in the soil. The oil-water partition coefficient can be determined from Raoult's Law [3,4,5] as:

$$K_o = \frac{r_o MW_i}{S_i MW_o} \quad (5)$$

where:

$\rho_o$  = Density of oil phase (g-o/cm<sup>3</sup>-o)  
 $MW_i$  = Molecular weight of contaminant (g<sub>i</sub>/mole)  
 $MW_o$  = Molecular weight of oil phase (g-o/mole)  
 $S_i$  = Solubility of pure chemical in water (g<sub>i</sub>/cm<sup>3</sup>-w)

The volumetric oil content in the soil can be related to the residual TPH concentration with the following equation:

$$q_o = \frac{r_b C_{TPH}}{r_o} \quad (6)$$

where:

$C_{TPH}$  = Residually trapped TPH concentration in soil (g/g-soil)

Substituting Equations (5) and (6) for  $K_o\theta_o$ , Equation (4) becomes:

$$K_T = \frac{q_w + K_d r_b + K_d q_a + \frac{r_b MW_i C_{TPH}}{S_i MW_o}}{r_b} \quad (7)$$

Thus, the overall partition coefficient,  $K_T$ , will be dependent upon the level of residual TPH in the soil. (Note that the residual TPH level is the amount in excess of the sorbed TPH level which is nominally <100 mg/kg for a low organic carbon content soil.)

### **Summary of DAF<sub>unsat</sub>**

The attenuation in the unsaturated zone is due to the following factors:

- 1) Biodegradation of the contaminant in the region beneath the source of contamination and the groundwater table.
- 2) Depletion of the concentrations in the source of contamination due to losses associated with leaching, volatilization, and biodegradation.

A commonly used approach for modeling vadose zone transport is that of Ünlü et al. [6] which uses the equation of van Genuchten and Alves [7]. This equation is also the basis for modeling unsaturated zone transport in the computer model VADSAT [6]. To determine DAF<sub>unsat</sub> values for the RBSLs presented here a simpler model was used. This model is based on treating the contaminated zone and the unsaturated zone beneath the contaminated zone (see Figure 3) as two separate, completely mixed zones. (The Ünlü model treats the

source zone as a completely mixed zone, but models advection and dispersion in the region below the source zone.) This completely-mixed model approach was used here because it is computationally easy to use (it is possible to develop a simple algebraic expression for  $DAF_{unsat}$ ) and retains the essential parameters of the Ünlü et al. model. For completely-mixed conditions, the  $DAF_{unsat}$  can be determined from the following equation:

$$DAF_{unsat} = \frac{Hr_b K_{T,unsat}}{u} \frac{a-b}{\left(\frac{a}{b}\right)^{b-a} - \left(\frac{a}{b}\right)^{a-b}} \quad (8)$$

where:

$$a = \frac{\frac{u}{H} + I_{unsat}}{r_b K_{T,unsat}} \quad (9)$$

and

$$b = \frac{I_V + \frac{u}{d} + I_S}{r_b K_{T,S}} \quad (10)$$

$DAF_{unsat}$  in Equation 8 is equal to the ratio  $C_{so}/C_{unsat}$ , where:

$C_{so}$  = The initial concentration in the pore water at the source of contamination ( $g/cm^3$ -w)

$C_{unsat, max}$  = Maximum pore water concentration at the bottom of the unsaturated zone ( $g/cm^3$ -w)

The parameter  $\alpha$  ( $day^{-1}$ ) represents the effect of biodegradation in the unsaturated zone on  $DAF_{unsat}$  and the parameter  $\beta$  ( $day^{-1}$ ) represents the effect of the various source losses on  $DAF_{unsat}$ . The following parameters that make up  $\alpha$  and  $\beta$  are:

- $u$  = The infiltration rate (cm/day)
- $H$  = Distance from the bottom of the contaminated source region to the water table (cm)
- $d$  = Depth of the source of contamination (cm)
- $\lambda_{unsat}$  = Degradation constant in unsaturated zone beneath the source zone ( $day^{-1}$ )
- $\lambda_S$  = Degradation constant in the source zone ( $day^{-1}$ )

- $K_{T,unsat}$  = The overall soil-water partition coefficient for the unsaturated zone (cm<sup>3</sup>-water/g-soil)  
 $K_{T,S}$  = The overall soil-water partition coefficient for the source zone (cm<sup>3</sup>-water/g-soil)  
 $\lambda_V$  = Volatilization rate constant for the source zone (day<sup>-1</sup>)  
 $\rho_b$  = Bulk density of the soil (g-soil/cm<sup>3</sup>-soil)

The volatilization rate constant,  $\lambda_V$ , can be estimated from:

$$I_V = \frac{p^2 D_{wT,S}}{4d^2} \quad (11)$$

where:

$D_{wT,S}$  = Total effective diffusion coefficient defined in terms of a chemical's concentration gradient in water (cm<sup>2</sup>/day)

$D_{wT,S}$  is defined mathematically as:

$$D_{wT,S} = D_{w,eff} + K_a D_{a,eff} + K_o D_{o,eff} \quad (12)$$

The effective diffusion coefficients were determined as follows [8]:

$$D_{w,eff} = D_{wm} \frac{q_w^{3.33}}{f^2}; \quad D_{a,eff} = D_{am} \frac{q_a^{3.33}}{f^2}; \quad \text{and} \quad D_{o,eff} = D_{om} \frac{q_o^{3.33}}{f^2} \quad (13)$$

where  $D_{wm}$ ,  $D_{am}$ , and  $D_{om}$  are the molecular diffusion coefficients (cm<sup>2</sup>/sec.) of the given chemical in the water, air, and residual oil phases, respectively. The following values were used for benzene:  $D_{wm} = 1.10E-05$  cm<sup>2</sup>/sec. [9],  $D_{am} = 0.093$  cm<sup>2</sup>/sec. [9],  $D_{om} = 3.4E-05$  cm<sup>2</sup>/sec. [10]. In general, the contribution of the oil phase diffusion term to  $D_{wT,S}$  was not significant.

The expression for the first order volatilization rate constant,  $\lambda_V$ , was determined from the solution for transient diffusion at long times from a slab of thickness,  $d$ , with a pore water concentration equal to zero at the top surface and zero flux at the bottom surface [11]. We have therefore assumed that there is no additional resistance to mass transfer at the soil-air interface. The boundary layer mass transfer resistance will be small relative to the diffusion resistance in the soil, so it is reasonable to neglect this resistance. If an overburden layer exists, then its thickness can be added to the parameter  $d$  in Equation 11. This assumes that the overburden properties are similar to the source region. This would be a conservative assumption with respect to source depletion, since the partitioning

would be lower in the overburden layer than in the source region due to the presence of residual hydrocarbon in the source versus the overburden layer.

Biodegradation of benzene in subsurface soils can be limited by the mass transfer of oxygen. As a result, the first step in evaluating attenuation of benzene due to degradation was to determine whether there would be sufficient oxygen present from the bottom of the contaminated source region downward through the unsaturated zone to the groundwater table. When oxygen concentrations are above a threshold concentration, then a conservative first order reaction rate constant can be used to estimate the attenuation of benzene in the unsaturated zone. In developing the benzene RBSLs, a conservative first order pore water-based biodegradation rate constant =  $0.01 \text{ day}^{-1}$  was assumed when the source thickness was less than a critical value.<sup>1</sup> For a sandy soil this critical source thickness was estimated to be  $d \cong 5 \text{ ft}$  (calculations are not presented here). A pore water-based biodegradation rate constant =  $0.01 \text{ day}^{-1}$  translates to a soil based degradation constant,  $\lambda_{\text{unsat}} = 0.00094 \text{ day}^{-1}$  for a sandy soil with a volumetric water content,  $\theta_w = 0.094 \text{ cm}^3\text{-w/cm}^3\text{-soil}$ .

Note that Equation (8) assumes that the  $\text{DAF}_{\text{unsat}}$  is based on the maximum aqueous concentration that will reach the groundwater table. It is therefore conservative, since the average concentration in water observed over a typical exposure period would be significantly lower.

### **Summary of $\text{DAF}_{\text{mix}}$**

The DAF in the mixing zone can be determined from the following equation:

$$\text{DAF}_{\text{mix}} = 1 + \frac{U_{\text{gw}} d_{\text{gw}}}{IL} \quad (14)$$

where:

$U_{\text{gw}}$  = Groundwater Darcy velocity (cm/year)

$I$  = Infiltration rate of water through soil (cm/year)

$L$  = Length of source area parallel to groundwater flow direction (cm)

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<sup>1</sup> A review of aerobic degradation studies of benzene inferred 1<sup>st</sup> order degradation rate constants ranging from  $0.02\text{-}2 \text{ day}^{-1}$  for high benzene concentrations, i.e.,  $100 \text{ mg/L}$  [12]. These rate constants were based on water phase concentrations and were obtained from a review of several laboratory microcosm and column studies and some field measurements for which hydrocarbon and oxygen concentration profiles in the unsaturated zone were determined. Apparent 1<sup>st</sup> order degradation constants will be higher than these values for lower benzene pore water concentrations [12].

$\delta_{gw}$  = Groundwater mixing zone thickness (cm)

A  $DAF_{mix}$  value = 8.7 was used to calculate benzene RBSLs. This is the value used in the recently developed New Mexico UST Guidelines for Corrective Action [9]. For comparison, using the ASTM [13,14] default parameters for  $U_{gw}$ , I, L, and  $\delta_{gw}$  yields a  $DAF_{mix}$  = 12.1.

### **Summary of $DAF_{sat}$**

A  $DAF_{sat}$  value = 1 has been assumed which is equivalent to no attenuation downstream of the source due to dispersion and degradation. This would be valid if the receptor is located at the downstream edge of the source. If the receptor is located some distance away from the source,  $DAF_{sat}$  will increase because of dispersion and biodegradation of the chemical in groundwater. Values of  $DAF_{sat}$  developed for a recently developed soil screening guidance program are shown in Table 2. Biodegradation in groundwater was neglected for the values shown in Table 2. Accounting for the typical biodegradation rates for benzene that occur in groundwater will result in higher  $DAF_{sat}$  values than those shown in Table 2. Equations such as that of Domenico [15] with appropriate soil and chemical parameters can be used for calculating screening level estimates of  $DAF_{sat}$ .

**Table 2.** Dilution Attenuation Factors ( $DAF_{sat}$ ) (1).

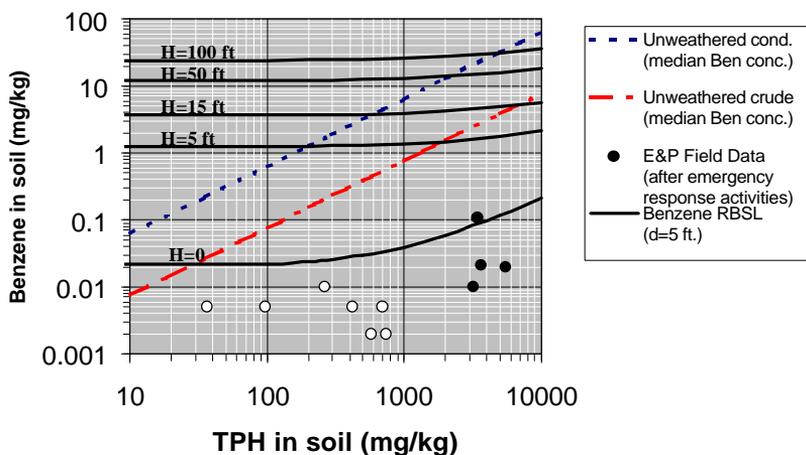
<u>Distance From Edge of Mixing Zone (Ft)</u>	<u><math>DAF_{sat}</math> (Without Degradation)</u>
0	1.0
50	1.1
100	2.2
150	4.2
250	11
500	41
1000	163

(1) From Table 4-14, New Mexico Environmental Department Guidelines for Corrective Action [9].

### **Benzene RBSL<sub>s-gw</sub> Curves**

Benzene RBSL<sub>s-gw</sub> were calculated using the equations described above for several values of TPH, H (distance from the bottom of the contaminated source zone to the water table) and a constant value of d (thickness of the contaminated source zone). No degradation in the groundwater (saturated zone) downstream of the source area was included in these calculations. If degradation were

included (meaning  $DAF_{\text{sat}} > 1$ ), the RBSLs would be greater than those shown in Figure 4.



**Figure 4.** Comparison of soil RBSLs for benzene with a) predicted soil levels for unweathered crude oils and condensates and b) actual soil levels after emergency response activities at a few E&P sites. Open (white) symbols represent detection levels for benzene. Soil RBSLs for benzene are for the groundwater exposure pathway. Calculations were based on a sandy soil type and include vadose zone attenuation due to volatilization and leaching from the source and biodegradation beneath the source (see Figure 3).  $H$  = the distance from the bottom of the contaminated soil zone to the groundwater table.

The calculation of RBSLs considers the following important factors: 1) degradation in the unsaturated zone between the source of contamination and the groundwater table, 2) source losses due to volatilization and leaching, and 3) enhanced partitioning of benzene in soils due to the presence of TPH. Parameters that determine the relative importance of these factors include the depth to groundwater, the thickness of the source of contamination, and the soil type. All of these three factors significantly contribute to higher acceptable levels of benzene in soil than would be acceptable if attenuation and increased partitioning in the vadose zone were not considered.

The RBSL curves presented in Figure 4 are based on a sandy soil type; a biodegradation constant,  $\lambda_{\text{unsat}} = 9.4\text{E-}04 \text{ day}^{-1}$ ; a hydrocarbon impacted layer of thickness,  $d=5 \text{ ft}$ ; and a groundwater standard =  $0.010 \text{ mg/L}$ . Values of other parameters for determining the curves in Figure 4 are listed in Table 3.

**Table 3.** Parameters used for benzene  $DAF_{\text{unsat}}$  and  $RBSL_{s-gw}$  calculations.

Soil or Contaminant Parameter	Source Layer (1)	Unsaturated Zone Layer Beneath Source
$u$ (cm/yr)	20	20
$\phi$ ( $\text{cm}^3\text{-pores}/\text{cm}^3\text{-soil}$ )	0.349(2)	0.349(2)
$\theta_w$ ( $\text{cm}^3\text{-w}/\text{cm}^3\text{-soil}$ )	0.094(3)	0.094(3)
$\theta_o$ ( $\text{cm}^3\text{-o}/\text{cm}^3\text{-soil}$ )	0.019(1)	0.0
$\theta_a$ ( $\text{cm}^3\text{-a}/\text{cm}^3\text{-soil}$ )	0.236(1)	0.255
$D_{wm}$ ( $\text{cm}^2/\text{sec.}$ )	1.10E-05	1.10E-05
$D_{am}$ ( $\text{cm}^2/\text{sec.}$ )	0.093	0.093
$D_{om}$ ( $\text{cm}^2/\text{sec.}$ )	3.40E-05	-
$K_a$ ( $\text{cm}^3\text{-w}/\text{cm}^3\text{-a}$ )	2.20E-01	2.20E-01
$K_o$ ( $\text{cm}^3\text{-w}/\text{cm}^3\text{-o}$ )	2.01E+02	-
$f_{oc}$ (g oc/g soil)	2.00E-03	2.00E-03
$K_{oc}$ ( $\text{cm}^3\text{-w}/\text{g oc}$ )	83	83
$\rho_b$ (g soil/ $\text{cm}^3$ soil)	1.73(2)	1.73(2)
$\rho_o$ (g oil/ $\text{cm}^3$ oil)	0.90	-
$D_{wT,S}$ ( $\text{cm}^2/\text{sec.}$ )	1.36E-03(1)	-
$K_{T,S}$ ( $\text{cm}^3\text{-w}/\text{g soil}$ )	2.47(1)	-
$K_{T,\text{unsat}}$ ( $\text{cm}^3\text{-w}/\text{g soil}$ )	-	0.252
$MW_i$	78	78
$MW_o$	200	-
$\lambda_s$ ( $\text{day}^{-1}$ )	0	-
$\lambda_{\text{unsat}}$ ( $\text{day}^{-1}$ )	-	9.4E-04
$d$ (ft)	5	-

- (1) Values shown are for TPH = 10,000 mg/kg-soil.
- (2) From Brakensiek et al. [16].
- (3) Determined from  $u = 20$  cm/yr and Brooks-Cory parameters from Brakensiek et al. [16] and saturated hydraulic conductivities from Carsel and Parrish [17].

In Figure 4 RBSLs are shown for benzene as a function of TPH in the soil and for distance to groundwater,  $H$ . The following key points can be made regarding this figure:

#### ***Effect of TPH on Benzene $RBSL_{s-gw}$***

The presence of TPH increases the benzene RBSL due to increased partitioning. At short depths to groundwater, the presence of TPH has the greatest effect on the RBSL. When only the sorption of benzene to soil particles is considered (TPH <100 mg/kg), for  $H = 0$  the  $RBSL = 0.022$  mg/kg. A level of TPH of

10,000 mg/kg results in an increase in the RBSL to 0.21 mg/kg. There is less effect of TPH on RBSLs at greater depths, H, because higher TPH levels result in relatively less attenuation from source losses.

### ***Effect of Depth to Groundwater, H, on Benzene RBSL<sub>s-gw</sub>***

When  $H = 0$ , there is no attenuation in the unsaturated zone ( $DAF_{\text{unsat}} = 1$ ). As H increases, attenuation occurs between the bottom of the contaminated zone and the groundwater table. This is a result of degradation over depth H and of losses due to volatilization and leaching in the hydrocarbon impacted layer of thickness, d. As H increases, attenuation increases, and the RBSL increases. For  $d=5$  ft, the increase in RBSL is due to increased degradation with contributions from losses due to volatilization and leaching in the contaminated region.

### **Benzene RBSLs for Surface Soil Exposure**

Benzene RBSLs for exposure of commercial workers to surficial soils via the pathways of ingestion, inhalation of vapors and particulates, and dermal contact (RBSL<sub>ss</sub>) were also determined for comparison with the groundwater based RBSL<sub>s-gw</sub> values and are shown in Table 4. Methods for determining RBSL<sub>ss</sub> were consistent with ASTM E1739-95 and E2081-00 guidelines [13,14].

**Table 4.** Benzene risk-based soil screening levels for exposure of a commercial worker to surficial soil (1).

Thickness of Impacted Layer, d (Ft)	RBSL <sub>ss</sub> (mg/kg Soil)
2	484
5	290
10	174

- (1) Surficial soil pathways include: ingestion, inhalation (vapor emission and particulates), and dermal contact.

The RBSL<sub>ss</sub> values in Table 4 increase as the thickness of the impacted layer (d) decreases, because a smaller thickness (d) results in a lower exposure to benzene. These RBSL<sub>ss</sub> values are greater than the benzene soil RBSL values shown in Figure 4 based on the groundwater exposure pathway (RBSL<sub>s-gw</sub>). This indicates that groundwater protection is likely to be the major risk management concern for benzene at most sites.

## Comparison of RBSLs With Expected Benzene Levels at E&P Sites

Figure 4 also presents lines for predicted benzene soil levels that would correspond to varying levels of E&P site contamination by unweathered condensates and crude oils. The lines are based on the median concentrations of benzene observed for the 69 crude oils and the 14 condensates for which composition data were summarized in Table 1. Figure 4 also presents field data from various E&P sites for benzene soil concentrations, plotted versus the corresponding TPH soil levels for these sites. Most of these data are from sites impacted by crude oils, but data from a few condensate impacted sites are also included. For these sites, soil samples were obtained soon after emergency response activities were completed.

Comparisons of the E&P field data with the unweathered crude oil and condensate data indicate that typical emergency response activities significantly reduce the levels of benzene in soils. Figure 4 also indicates that sites impacted by condensates and crude oils may not exceed benzene groundwater standards even for short distances to the water table (H). However, benzene soil levels that correspond to unweathered crude oils and especially to unweathered condensates, may present a risk to groundwater at certain TPH levels and depths to groundwater. It should be noted that the benzene RBSLs presented in this chapter do not account for attenuation in the saturated zone, which can be significant when the point of compliance is downstream of the source.

### Summary

An improved approach to developing RBSLs for benzene in soil that are protective of groundwater was developed that makes use of more realistic fate and transport assumptions than are typically used in most Tier 1 calculations. Attenuation effects were considered, including a conservative accounting of minimal biodegradation in the unsaturated zone between the bottom of the contaminated zone and the water table, as well as losses in the source of contamination due to volatilization and leaching. In addition to these attenuation considerations, the enhanced soil-water partitioning that occurs for benzene due to the presence of TPH in soil was also considered. All of these factors significantly contribute to higher acceptable levels of benzene in soil than would be estimated if attenuation and increased partitioning in the vadose zone were not considered. Additional attenuation in the saturated zone was not considered but would further increase acceptable levels of benzene in some cases.

Benzene RBSLs were found to depend on some key parameters: 1) depth to groundwater (H), 2) thickness of oil impacted layer (d), and 3) level of TPH in

the soil. These parameters determine the amount of attenuation of benzene in the vadose zone and the decreased partitioning of benzene to soil when TPH is present. An easy to use figure was presented that can be used to select the appropriate benzene RBSL for an individual site if the above factors are known. This figure illustrates that RBSLs increase by a factor of 10 to 1000 when vadose zone attenuation and increased partitioning (water to soil) due to TPH are taken into account.

The potential risk posed by benzene at E&P sites was also evaluated. Overall, the major risk management concern for benzene at most E&P sites is likely to be due to its potential to impact groundwater and not due to direct commercial worker exposure to impacted surface soils. Benzene may present a risk to groundwater at some E&P sites. The potential risk will depend on the type of oil (crude oil or condensate) spilled, the depth to groundwater, the thickness of contamination, the level of TPH in the soil, and the extent of weathering of benzene from soils that results from any emergency response activities.

The benzene RBSLs presented in this chapter are illustrative of screening levels that could be used in conjunction with TPH RBSLs to decide if further corrective action is required at a given site. To use screening levels such as these for benzene it is assumed that some response to a spill has already occurred and that the extent of contamination has been delineated such that the depth of contamination and level of contamination of benzene and TPH are known.

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