APPENDIX D

MODEL DERIVATION

Derivation of a Screening Model for
VOC Emissions From Soils Handling Activities

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Screening Model for VOC Emissions from Soils Handling Activities
APPENDIX A - MODEL DERIVATION

A.1 INTRODUCTION

Background information about the modeling problem is presented in this appendix followed by a presentation of an emission model for estimating VOC emissions from the excavation of contaminated soil. A simplified version of the model is developed, then the models are evaluated.

Objective

Develop simple predictive model for estimating VOC emissions from soils handling activities, such as excavation.

Intended Use

The model will be used for assessing potential emissions during remediation of Superfund sites. At a minimum, the model should provide an emission factor to estimate emissions per unit time or unit operation. Ideally, it should also be appropriate for evaluating the effect of different remediation scenarios, e.g. starting waste concentrations, excavation rates, and control efficiencies.

Requirements

1. Model should be conservative, since the data may be used in some cases for health risk assessment.

2. Model should require as few input parameters as is feasible for ease of use.

Assumptions

1. During excavation, the surface area of soil in contact with the atmosphere is greatly increased. This results in up to one-third of the soil gas being released to the atmosphere. In dry soils containing very low levels of VOCs, most of the contaminants are present in the soil pore spaces, thus the percentage of the VOCs emitted is relatively high.

2.	Once the soil has been dumped into place, the organic liquid to soil gas equilibrium is quickly re-established. The emissions can be estimated by a modification of the RTI landtreatment model. [1]

3.	The freshly dumped soil is soon covered by relatively deep layers of subsequently excavated soil. These layers of soil result in longer-term emissions from the deeper layers being diffusion controlled, i.e., low. Therefore, the significant period for emissions is during excavation and the first six minutes or so afterwards. Subsequent (i.e. $t > 6$ min) emissions from this material are assumed to be zero.

4.	The total exposed surface area of contaminated soil is assumed to remain constant. New material is exposed at the same rate that previously exposed material is covered.

5.	The emissions from the pit are approximately equivalent to the emissions from the pile of excavated soil. The emissions from the soil in the backhoe bucket are negligible.

6.	Wet soils are assumed to have relatively low levels of VOC emissions, even if the soil VOC concentrations are high. Wet soils may have little air-filled porosity and therefore the rate of diffusion of VOCs through wet soils is relatively low.

Possible Excavation Scenarios

Two general scenarios are followed during excavations at waste sites.

1.	Soil is excavated using a backhoe and placed into a short-term storage pile. The soil is later picked up from the pile and dumped directly into transport vehicles (e.g. trucks or railcars) that are subsequently covered to minimize further emissions. Overall, each m^3 of soil is excavated and dumped two times.

2.	Soil is excavated using a backhoe and placed into a temporary storage pile. The soil is moved from the pile using a front-end loader (and/or backhoe) to a staging area where a large storage pile is established. The pile is typically covered to minimize leaching and air emissions. The soil is eventually re-excavated and dumped into transport vehicles (e.g. trucks or railcars) that are subsequently covered to minimize further emissions. Alternatively, the soil may be re-excavated and fed to an on-site treatment system. Overall, each m^3 of soil is excavated and dumped three times.

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[1]p. 5-14 and 5-15 of EPA-450/3-87-026 (NTIS PB88-198619), November 1987.

It is rarely feasible or efficient to dig soil and immediately transfer the soil directly to transport vehicles or treatment systems. The excavation scenario and the emission equations shown below are designed to predict the emissions from a single soil handling event. To predict the total emissions from excavation, the equations must be sequentially applied to each event where the soil is handled (i.e., two or three times in most cases). The values for certain input parameters to the equations, such as the concentration of the contaminant in the soil and the bulk density of the soil, will be altered by the act of excavation and a separate (different) value will be required for these parameters when modeling each soil handling event of the overall excavation process.

Details of Excavation Scenario

Soil is excavated for 50 min/hour[2]. Each scoop of soil contains 2 m^3 of material and has dimensions of 1m x 2m x 1m. The cycle time is 40 seconds[3], so 75 scoops are moved per hour (= 150 m^3 of soil moved per hour). The excavation pit, after one hour of operation, has dimensions of 10m x 15m x 1m.

Each scoop of dumped soil is assumed to maintain its 1x2x1 dimensions, so that the pile of dumped soil is equivalent to a series of stacked blocks. After one hour, a pile 5m x 10m x 3m high is established. The total exposed surface area of the pile is 140 m^2 and the bottom of the pit has another 150 m^2 of exposed area (the sides of the excavation pit are assumed to be clean overburden). The exposed surface areas are assumed to remain constant during further hours of operation with any additional area being covered with some type of impermeable cover that acts as a barrier to further emissions.

A.2   DERIVATION OF EMISSION MODELS

The models are based on adding the emissions resulting from the release of soil-gas (pore space gas) to the atmosphere when excavation soil is dumped onto a storage pile to the emissions resulting from diffusion from contaminated soil present in the excavation pit and in the storage pile. A discussion of the input parameters and typical input values are given in Sections A.4 and A.5. Limitations of the models are also given in those sections.

Pore-Space Gas Model

The general form of the equation used to estimate the emission rate from the pore space gas for any given compound is the ideal gas law:

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[2]Page 8-35 of the Excavation Handbook by H.K. Church (MCGraw-Hill, 1981) states that excavation equipment can be assumed to be in use for 30 to 50 minutes per hour.

[3]Page 12-38, op cit, gives a cycle time of 0.67 minutes for a 25 foot hoist distance and a 90° angle of swing return.

$$P\,V = nR\,T \qquad\qquad \text{(Eq. A-1)}$$

where: P   =   Vapor pressure of compound i (mm Hg);
        V   =   Volume (cm^3);
        n   =   Number of moles of gas;
        R   =   Gas constant; and
        T   =   Temperature (°K).

The mass of contaminants present in the pore space of soil can be determined as follows. First substitute M_{PS}/MW for n and then solve for M_{PS}:

$$\text{(Eq. A-2)} \qquad M_{PS} = \frac{P\,V\,MW}{R\,T}$$

where: M_{PS} =   Mass of pore space contaminants (g); and
        MW   =   Molecular weight of species i (g/g-mole).

Then substitute soil volume and air-filled porosity terms for V to account for the volume of air within a given volume of soil. Air-filled porosity is the fraction of the total soil volume that is air. A factor of 10^6 to convert from cm^3 to m^3 is also needed:

$$\text{(Eq. A-3)} \qquad M_{PS} = \frac{P\,MW}{RT}\,(10^6)(E_a)(S_V)$$

where: E_a =   Air-filled porosity (dimensionless);
        10^6 =   Conversion factor (cm^3/m^3);
        S_V =   Volume of soil moved (m^3); and
        R   =   Gas constant, 62,361 (mm Hg - cm^3/g-mole °K).

        To derive an emission rate, Equation A-3 must be modified to account for the rate at which soil is being moved and to account for the percentage of soil gas that is released or exchanged with the atmosphere:

$$\text{(Eq. A-4)} \qquad ER_{PS} = \frac{P\,MW}{RT}\,(10^6)(E_a)(Q)(ExC)$$

where: ER_{PS} =   Average emission rate from the pore space gas (g/sec);
        ExC   =   Soil gas to atmosphere exchange constant (%/100); and
        Q   =   Excavation rate (m^3/sec).

        The excavation rate term, Q, is equal to S_V divided by the total time period in seconds over which the given volume of soil is being moved. Equation A-4 assumes that the

instantaneous emission rate is equivalent throughout the excavation cycle, whereas the emissions from each scoop of soil are probably due primarily to two emission puffs: one when the backhoe bucket enters the soil and initially disturbs the soil and the second, larger puff, when the bucket dumps the soil onto the storage pile. Equation A-4 also assumes that the pore space is saturated with the contaminant vapor.

Diffusion Model

The general form of the equation used to estimate the emission rate from the contaminated soil in the excavation pit and in the storage pile is the RTI landtreatment model:

(Eq. A-5)

$$EF = \frac{M_o}{1} \left[\frac{1}{\left(\frac{E_a}{K_{eq} \, k_g}\right) + \left(\frac{\pi \, t}{D_e \, K_{eq}}\right)^{\frac{1}{2}}} \right] e^{-t/tb}$$

where:

EF	=	Emission flux through the soil at some time t $(g/cm^2\text{-sec})$;
M_o	=	Initial loading of contaminant in soil (g/cm^2);
l	=	Depth to which contaminant is mixed in soil (cm);
K_{eq}	=	Weight fraction of VOC in air space (dimensionless);
k_g	=	Gas-phase mass transfer coefficient (cm/sec);
D_e	=	Effective diffusivity (cm^2/sec);
t	=	Time since start of excavation of soil of interest (sec); and
t_b	=	Time constant for biological decay of contaminant i (sec).

Several modifications to the model were made to make it applicable to excavation. First, the biological expoential decay term $(e^{-t/tb})$ was set equal to one since the timeframes of interest are very short. Second, the initial loading term (M_o) and the depth to which the waste is mixed term (l) were combined into a waste loading term, designated C. Third, a factor of 10,000 was added to convert the emission units from mass per cm^2 to mass per m^2. Fourth, a term was added to account for the surface area of the emitting soil. The resulting equation is:

(Eq. A-6)

$$ER_{Diff} = \frac{(C)(10,000)}{\left(\frac{E_a}{K_{eq} \, k_g}\right) + \left(\frac{\pi \, t}{D_e \, K_{eq}}\right)^{\frac{1}{2}}} [SA]$$

where:

ER_{Diff}	=	Instantaneous emission rate from diffusion through the soil (g/sec);
C	=	Soil concentration of species of interest (g/cm^3);
10,000	=	Conversion factor (cm^2/m^2); and
SA	=	Surface area of emission source (m^2).

The surface area term, SA, includes the area of the exposed contaminated soil for both the excavation pit and the storage pile. It is assumed that the surface area of the emission source remains constant, i.e., excavation was already underway before the particular soil being modeled was handled and excavated soil is moved off-site or covered to reduce emissions at the same rate that new soil is being uncovered and excavated. To model the case where no contaminanted soil is initially exposed, the surface area term in Equation A-6 can be divided by a factor of two to yield an average amount of exposed surface area.

A.3   EMISSION MODELS

The overall emission rate equation is formed by adding Equations A-4 and A-6. Note that the timeframes of the two equations as shown are not equivalent. Equation A-4 describes the emissions over the course of excavating and dumping one scoop of soil (40 seconds in the assumed scenario), while Equation A-6 gives an instantaneous emission rate at some time t since the contaminated material was first exposed to the air. An average value for t is discussed in Section A.4 and the timeframe of the two models are reconciled so that they yield an average emission rate.

The general form of the emission models for estimating an "average" emission rate for the excavation of contaminated soil is given as Equation A-7 and a worst-case emission rate is given as Equation A-8. It is a simple matter to modify either of these equations to calculate an emission flux (i.e., rate per area) or total emissions for a given period of time.

Emission Rate

An emission rate in g/sec for excavation was derived in the previous section and is:

(Eq. A-7)

$$ER = \frac{P\ MW}{RT}(10^6)(E_a)(Q)(ExC) + \frac{(C)(10{,}000)}{\left(\dfrac{E_a}{K_{eq}k_g}\right) + \left(\dfrac{\pi\ t}{D_e\ K_{eq}}\right)^{\frac{1}{2}}}(SA)$$

Worst-Case Emission Rates

The worst-case (i.e., maximum) instantaneous emission rate, ER_{MAX}, for contaminated soil occurs when the exposed surface area is at a maximum and immediately after a bucket load of soil is dumped onto the storage pile. This emission rate can be approximated by considering the case where a pure chemical is exposed to the atmosphere. This emission rate can be determined from Equation A-6 (there is no need to consider pore space gas concentrations and diffusion since the pure chemical is already exposed to the atmosphere). Set the time term, t, equal to zero and replace the K_{eq} term with the equivalent expression: $P*MW*E_a/R*T*C$. Equation A-6 then reduces to:

D-8

(Eq. A-8)
$$ER_{MAX} = \frac{(k_g)(P)(MW)(SA)(10,000)}{RT}$$

A.4   SIMPLIFIED EMISSION MODELS

The first half of Equation A-7 is simplified first, followed by simplification of the second half of Equation A-7.

Simplified Pore-Space Gas Model

The first half of Equation A-7 can be simplified as follows. Assume the following:

R   =   62,361;
MW   =   100;
T   =   298;
ExC[4]   =   0.33.

Substituting these values into the first half of Equation A-7 yields an emission rate for pore space gas, ER_{PS}, of:

(Eq. A-9)
$$ER_{PS} = \frac{P\ MW}{RT}(10^6)(E_a)(Q)(ExC) = \frac{(P)(E_a)(Q)(100)(10^6)(0.33)}{(62,361)(298)}$$

(Eq. A-10)
$$ER_{PS} = \left(\frac{5.4\ g/m^3}{mm\ Hg}\right) * P * E_a * Q * 0.33$$

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[4]Assume ExC = 0.33 for dry, sandy soils and ExC = 0.10 for wet soils or those with a high clay content.

Vapor pressures for most VOCs of interest are available in tabluated physical constants in Appendix B. These values are for 25°C, but P can be estimated at other temperatures[5]. According to SEAMs, the air-filled porosity (E_a) can be assumed to be:

E_a	Soil Conditions
0.35	Wet, or compacted soil
0.55	Dry, uncompacted soil

E_a can be assumed to be 0.05 for sludges, tarry wastes, and saturated soils. Alternatively, E_a can be calculated as follows:

(Eq. A-11)
$$E_a = 1 - \left[\frac{\beta + (\beta)(M_{FRAC})}{p} \right]$$

where: β = Bulk density of soil (g/cm³);
M_{FRAC} = Moisture fraction in soil (Wt.% Moisture/100); and
p = Particle density (g/cm³).

Default values are as follows. Bulk density (β) usually is in the range of 1.0 to 2.0 and can be assumed to be about 1.5 for uncompacted soils prior to excavation. After excavation, the bulk density is lower and a value of 1.2 may be assumed. Particle density (p) is typically about 2.65 $\pm$ 5% for soils. These default values yield an E_a for dry soil of 0.43 before excavation and 0.55 after excavation.

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[5]Vapor pressure can be roughly estimated at temperatures other than 25°C by the following equation:

$$P = P^o e^{\left(\frac{-21 T_B}{1.987} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right)}$$

(Eq. A-12)

where: P = Vapor pressure of compound i at temperature T (mmHg);
P^o = Vapor pressure of compound i at temperature T_o (mmHg);
T_B = Normal boiling point of compound i (°K);
T = Temperature (°K);
T_o = Reference Temperature (°K) - Usually 298°K;
1.987 = Gas constant (cal/g-mol °K); and
21 = Heat of vaporization constant (cal/g-mol °K).

Using the SEAMS value for E_a (0.55), Equation A-10 for dry soil then reduces down to:

(Eq. A-13)
$$ER_{PS} = P * Q * 0.98 \text{ g/mmHg}-m^3$$

Equation A-13 is the simple screening model. If desired, it can be further reduced. Using the excavation scenario described above, Q can be assumed to be 150 m³/3600 sec. Equation A-13 for dry soil then reduces down to:

$$ER_{PS} = (0.04 \text{ g/mm Hg})*P \qquad\qquad \text{(Eq. A-14)}$$

Simplified Landtreatment Model

The second half of Equation A-7 can be simplified as follows. The following equations[6,7] can be used to describe the terms K_{eq} and D_e, which appear in Equation A-7:

(Eq. A-15)
$$K_{eq} = \frac{P \ MW \ E_a}{RT \ C}$$

(Eq. A-16)
$$D_e = \frac{D_a \ (E_a)^{3.33}}{(E_T)^2}$$

where: D_a = Diffusivity in air of species i (cm²/sec); and
E_T = Total porosity (dimensionless).

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[6]The equation shown for calculating K_{eq} assumes that the contaminant is an oily waste. For dilute aqueous wastes, K_{eq} = H/RT, where H = Henry's Law constant in mm Hg-cm³/g-mol.

[7]Strictly speaking, the concentration term, C, in Equations A-15 and A-7 should be adjusted to account for the mass of contaminant lost with the pore-space gas. This adjustment has not been included in the model for the sake of simplicity.

K_{eq} represents the relative saturation of the soil-gas with respect to a given compound and cannot realistically exceed 1. Calculated values of K_{eq} using Equation A-15 will exceed 1 if the soil-gas is below saturation with respect to that compound. If the output of Equation A-15 is $K_{eq} > 1$, then a value of $K_{eq} = 1$ should be used in all equations having a K_{eq} term. Alternatively, K_{eq} could be determined by field measurements of the pore space concentration in the soil ratioed to the total concentration of the contaminant in the soil.

E_T can be calculated by Equation A-11 if the moisture fraction is set to zero.

Assume the following:

$$
\begin{aligned}
R &= 62{,}361; \\
MW &= 100; \\
T &= 298; \\
D_a &= 0.1; \\
E_a &= 0.55; \\
E_T &= 0.625;
\end{aligned}
$$

Substitute these values into Equations A-15 and A-16 to yield:

(Eq. A-17)
$$
K_{eq} = \frac{P}{C\ 332{,}200}
$$

$$
D_e = 0.035 \qquad\qquad \text{(Eq. A-18)}
$$

The second half of Equation A-7 can then be simplified by inserting Equations A-17 and A-18, and by assuming that $E_a = 0.55$ and that $k_g = 0.15$. Equation A-7 then reduces to:

(Eq. A-19)
$$
ER_{Diff} = \frac{(C)(10{,}000)}{\left(1.22\text{x}10^6\ \dfrac{C}{P}\right) + \left(2.98\text{x}10^7\ \dfrac{C\ t}{P}\right)^{\frac{1}{2}}}\ (SA)
$$

Equation A-19 provides an instantaneous emission rate at time $= t$. It is assumed that emissions from freshly excavated soil are significant for a period of 360 seconds, after which the soil is covered by subsequent layers of excavated material. The emission rate versus time over this 360 second period for a given scoop of soil will generally exhibit an exponential decay. The exact shape of this decay curve will vary as the input parameters such

as vapor pressure and air-filled porosity vary. Therefore, it is necessary to determine at what time t the instantaneous emission rate approximates the average emission rate over the 360 second period. This can be done by calculating the instantaneous emission rates at $t = 0$ second, $t = 15$ seconds, $t = 30$ seconds, and so on. The emission rate is calculated for every 15 second period up to $t=360$ and the results plotted. The average emission rate is calculated by summing the instantaneous emission rates and dividing the sum by the number of data points (in this example, 24). The value for the average emission rate is then found on the plot of emission rate versus time, and the corresponding time found on the x-axis. This time t is then used in Equation A-19. For the typical case, the instantaneous rate at $t = 60$ seconds is a good approximation of the overall emission rate for the first 360 seconds. Using this value Equation A-19 yields the simple screening equation:

(Eq. A-20)

$$ER_{Diff} = \frac{(C)(10,000)}{\left(1.22 \times 10^6 \dfrac{C}{P}\right) + \left(1.79 \times 10^9 \dfrac{C}{P}\right)^{\frac{1}{2}}} (SA)$$

Equation A-20 assumes that the emission flux arising from diffusion is equal for both the excavation pit and the excavated soil in the storage pile. Equation A-20 will overpredict emissions if $K_{eq} > 1$. P at temperatures other than $25\,^\circ$C can be estimated using Equation A-12. From the excavation scenario described earlier, SA can be assumed to be 290 m^2.

Assuming a typical bulk density of undisturbed soil, C can be modified to a weight basis as follows:

(Eq. A-21)

$$C' = C * \frac{1 \text{ cm}^3}{1.5 \text{ g}} * 10^6 \ \mu g/g$$

where: C'   =   Concentration of species in soil (μg/g).

The overall emission rate is determined by adding Equations A-13 and A-20. This estimated value should be checked to see whether or not it exceeds the total mass of contaminants present in the soil that is moved, which is equal to the theoretical maximum emissions (not considering emissions from the un-excavated soil in the pit). To do this, the emission rate should be multiplied by 3,600 seconds to get the total emissions over a reasonably long period of time, one hour. The mass of contaminants present in the soil can be determined by:

$$C_{TOT} = C * S_V * 10^6 \text{ cm}^3/\text{m}^3 \qquad\qquad \text{(Eq. A-22)}$$

where: C_{TOT} =   Total starting mass of contaminant in excavated soil (g).

Equations A-4 and A-13 are based on the assumption that the soil pore gas is saturated with the compound of interest. If this is not the case, then Equations A-4 or A-13 may overpredict the emission rate. The output from Equations A-4 or A-13 should be

multiplied by the duration of excavation and compared to the total mass of contaminants present in the soil. If Equations A-4 or A-13 gives a value that exceeds one-third of C_{TOT}, then they should be replaced with the following equation:

$$ER_{PS} = C_{TOT} * 0.33/t_{sv} \qquad \text{(Eq. A-23)}$$

where: t_{sv} =   Time to excavate a given volume of soil (sec).

A.5   MODEL EVALUATION

The emission model was evaluated to determine the sensitivity of the model to various input parameters. All the independent variables in Equation A-7 are listed in Table A-1. For each variable a typical value is given along with the range of values likely to be encountered at Superfund site excavations. The uncertainty associated with measuring each variable is also estimated in Table A-1. The range of physical properties was based on n-butane being the lightest VOC likely to be encountered at a site and naphthalene being the heaviest compound likely to be of concern. Typical physical property values were based on C6 to C8 compounds (e.g. benzene to xylene). The soil volume term was kept constant to show the variability in surface area for a given volume of soil. The gas-phase mass transfer coefficient (k_g) was estimated using the correlations given with the RTI landtreatment model and the following input values:

Parameter	Units	Minimum Value	Maximum Value	Typical Value
Wind Speed	m/sec	1.0	4.47	2.0
Viscosity of air	g/cm-sec	1.81×10^{-4}		
Density of air	g/cm^3	1.2×10^{-3}		
Diffusity in air	cm^2/sec	0.25	0.059	0.1
Diameter of excavation	m	24		

The minimum and maximum values for the independent input parameters from Table A-1 were combined to generate a best-case and worst-case set of emission scenarios. These are shown in Table A-2 along with the case using the typical input parameters. As seen in Table A-2, the three cases shown differ greatly in the estimated average emission rate.

To identify which parameters had the greatest effect on the overall emissions, a set of calculations were performed using the base or typical case as the starting point. The effect of each parameter was examined by substituting the minimum and maximum value for each into the base case conditions. The results of this first-order sensitivity analysis are shown in Table A-3. The two independent variables having the largest effect on the overall emission rate are the starting concentration of the contaminant in the soil and the vapor pressure of the contaminant. Note that temperature has a small effect, but that emissions are inversely proportional to temperature. This is, of course, contrary to the overall effect of temperature on emissions: emissions increase as temperature increases. This seeming anomaly is due to

Table A-1

Table A-2

Table A-3

main effect of temperature being to increase the vapor pressure and diffusivity terms. If these terms are not corrected for temperature, then the model will become less accurate as the temperature deviation from 25°C increases.

Equation A-7 requires the input of the time after the start of excavation (t). It was assumed earlier that the emission rate at t=60 seconds was equal to the average emission rate over t=0 to t=360 seconds. It was further assumed that after 360 seconds, the excavated soil would be covered with additional layers of soil and the diffusion of further material (emissions) would be minimal. The effect of time (t) was examined by substituting a range of times into the base case conditions. The results of these trials are given in Table A-4 and depicted in Figure A-1 and A-2.

The effect of the initial soil concentration of the contaminant on the predicted emission rate was examined by using the same base case assumptions and varying the concentration from 1 ppbw to 10,000 ppmw. These results are shown in Table A-5 and are plotted in Figure A-3. As the concentration increases, the percentage of the total mass of material emitted decreases. Also, the relative contribution of pore-space gas to the total emissions also decreases. The effect of vapor pressure (and molecular weight) was examined by inserting the values for vapor pressure and molecular weight for several common organic species into the base case. All compounds were assumed to be present at 100 ppmw in the soil. These results are shown in Table A-6.

A final check of the models was made by comparing model predictions to field data[8]. Comparisons of both the detailed (Equation A-7) and simple models (Equations A-13 and A-20) to field data are shown in Table A-7. Total emissions for twenty minute sampling periods are shown for two different field sites. The detailed model using site-specific input data agrees with the field measurements within a factor of five in all but two cases. The simplified model shows equally good agreement.

The equations presented here are a first attempt to model emissions from soils handling operations. The equations are limited by a lack of laboratory or field data to define certain key relationships between the variables. For example, the excavation rate and the total exposed area are assumed in the equations to have a direct linear relationship with the emission rate. No data, however, exist to support this assumption. Similarly, the effects of temperature, scoop size, and surface area to volume ratio on emissions have not been investigated. Another limiting assumption is that 33% of the pore space gas is exchanged with the atmosphere. This value is arbitrary and was selected since it fit reasonably well with the very limited field data that are available.

Measurements of emission rates from dynamic processes such as excavation are very difficult to perform and are of limited accuracy. Limitations exist for dispersion models used in indirect approaches (e.g., transect) and in the sampling and analytical precision when

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[8]Eklund, et al. Field Measurement of VOC Emissions From Soils Handling Operations at Superfund Sites. EPA Contract No. 68-02-4392, Work Assignment 64. September 1990.

attempting to determine emission rates using a mass balance approach. Emerging measurement technologies, such as remote optical sensing, may allow more detailed evaluation of the effect of these parameters in the future.

Table A-4.

Effect of Time (t) on Emissions

Time (sec)	Diffusion Emission Rate (mg/sec)	Total Emission Rate (mg/sec)
0	81.9	83.1
5	11.0	12.1
10	8.09	9.23
20	5.89	7.03
30	4.87	6.01
40	4.25	5.39
50	3.83	4.96
60	3.51	4.65
90	2.89	4.02
120	2.51	3.65
180	2.06	3.20
240	1.79	2.93
300	1.61	2.74
360	1.47	2.61
420	1.36	2.50
480	1.28	2.41
540	1.20	2.34
600	1.14	2.28
1200	0.81	1.95
1800	0.66	1.80
2400	0.58	1.71
3000	0.51	1.65
3600	0.47	1.61

Figure A-1. Emission Rate vs. Time for Base Case Conditions for 0 to 360 seconds.

Figure A-2. Emision Rate vs. Time for Base Case Conditions for 0 to 60 Minutes.

Table A-5.

Effect of Conc. (C) on Emissions

Conc (ug/Kg)	Log Conc (ug/Kg)	Pore Gas Emission Rate (g/sec)	Diffusive Emission Rate (g/sec)	Total Emission Rate (g/sec)	Emissions* Vs. Total Mass (%)
1	1	1.88×10^{-5}	4.52×10^{-5}	6.40×10^{-5}	114
10	2	1.88×10^{-4}	4.52×10^{-4}	6.40×10^{-4}	114
100	3	1.87×10^{-3}	4.52×10^{-3}	6.40×10^{-3}	114
1000	4	0.019	0.045	0.06	114
10000	5	0.188	1.14	1.33	236
100000	6	1.138	3.51	4.65	82.6
1000000	7	1.138	10.15	11.29	20.1
10000000	8	1.138	25.32	26.46	4.7

* Includes only mass of contaminants in excavated soil

Figure A-3. Emission Rate vs. Time as Soil Concentration Increases.

Table A-6.

Effect of Molecular Weight (MW) + Vapor Pressure (P) on Emissions

Conc (ug/Kg)	Molecular Weight (g/g-mol)	Vapor Pressure (mm Hg)	Diffusive Emission Rate (g/sec)	Total Emission Rate (g/sec)
Alkanes				
butane	58.12	1820	4.52	6.40 *
pentane	72.15	513	4.52	6.40 *
hexane	86.18	150	4.52	6.40 *
heptane	100.2	46	4.05	5.55
octane	114.23	17	2.57	3.21
nonane	128.26	4.3	1.30	1.48
Aromatics				
benzene	78.12	95.2	5.18	7.06
ethylbenzene	106.16	10	1.87	2.21
o-xylene	106.2	7.0	1.54	1.78

* Pore space emissions equal the total mass of contaminant present divided by 3.

table A-7