



# **AIR/SUPERFUND NATIONAL TECHNICAL GUIDANCE STUDY SERIES**

## **Guideline for Predictive Baseline Emissions Estimation for Superfund Sites**

Interim Final



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**GUIDELINE FOR PREDICTIVE  
BASELINE EMISSIONS ESTIMATION  
FOR SUPERFUND SITES  
ASF-21**

by

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## **PREFACE**

This document was developed for the U.S. Environmental Protection Agency, Air/Superfund Program and offers technical guidance for use by EPA Air and Superfund staff, remedial and removal contractors, and potentially responsible parties. Because assumptions and judgments are required in many parts of the analysis, the user of this manual needs a strong technical background in emissions and atmospheric dispersion modeling.

It is envisioned that this manual will be periodically updated to incorporate new data and information on air pathway analysis procedures. The Agency reserves the right to act at variance with these procedures and to change them as new information becomes available without formal public notice.

## **DISCLAIMER**

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## CONTENTS

Preface	ii
Disclaimer	iii
Figures	vi
Tables	vi
Acknowledgment	vii
Objective	1
Background and Purpose	1
Screening Versus Refined Estimates	2
Model Sampling Requirements	3
How to Use These Procedures	5
How the Document is Organized	5
Major Steps in the Air Pathway Analysis	6
Summary	6
Major Steps	
Step I - Review Site Background and Gather Data Necessary to Conduct the Baseline Emissions Estimate	8
Step II - Develop a Site Modeling Plan	10
Step III - Estimate Emission Rates of Each Applicable Site Contaminant	13
Part 1 - Vapor-Phase Emissions From Surface and Subsurface Soils Without Landfill Gas Generation	14
Part 2 - Vapor-Phase Emissions From Subsurface Soils With Landfill Gas Generation	36
Part 3 - Gaseous Emissions From Nonaerated Surface Impoundments, Open Top Wastewater Tanks and Containers, and Aqueous-Phase Contaminants Pooled at Soil Surfaces	40
Part 4 - Nonvolatile and Semivolatiles Emitted as Particulate Matter	44

## CONTENTS (continued)

Step IV - Estimate Ambient Air Concentrations at Receptor Locations of Interest	56
Step V - Organize Exposure Point Concentrations for Input to the Baseline Risk Assessment	61
Appendices	
A. Recharge Estimates by Hydrogeologic Settings	A-1
B. Example Calculations	B-1

## FIGURES

<u>Number</u>		<u>Page</u>
1	Wind erosion model decision flow chart	45
1a	Threshold friction velocity versus aggregate size distribution	47
1b	Increase in threshold friction velocity with $L_c$	49
2	Function curve used in "unlimited reservoir" model	51
3	Thornthwaite's precipitation - evaporation index (PE) for State climatological divisions	53

## TABLES

<u>Number</u>		<u>Page</u>
1	Parameter Estimates for Calculating Average Soil Moisture Content ( $\Theta_w$ )	16
2	Viscosity of Water at Temperature ( $\eta_w$ )	23
3	Additive Volume Increments for Calculating the LeBas Molar Volume ( $V_B'$ )	24

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## **GUIDELINE FOR PREDICTIVE BASELINE EMISSIONS ESTIMATION FOR SUPERFUND SITES**

### **OBJECTIVE:**

The objective of the following guidance is to provide standardized procedures as well as acceptable fate and transport models for estimating air pathway exposure point concentrations when applied to the baseline risk assessment.

### **BACKGROUND AND PURPOSE:**

Part of the human health evaluation, the baseline risk assessment is an analysis of the potential adverse health effects (current and future) caused by hazardous substance releases from a site in the absence of any actions to control or mitigate these releases. An integral part of the baseline risk assessment is the exposure assessment, whereby estimates are made of the magnitude of actual and/or potential human exposures, the frequency and duration of these exposures, and the pathways by which humans are potentially exposed.

Exposure point concentrations are estimated using monitoring data and/or chemical transport and environmental fate models. Modeling may be used to estimate future chemical concentrations in media that are currently contaminated or that may become contaminated, and current concentrations in media and/or locations for which there are no monitoring data. In some instances, it may not be appropriate to use monitoring data alone, and models may be required to estimate concentrations. Specific instances where monitoring data alone may not be adequate are as follows:

- Where exposure points are spatially separate from monitoring or sampling points (e.g., air dispersion)
- Where temporal distribution of data is lacking (e.g., potential future exposure)
- Where monitoring data are restricted by the limit of quantitation.

Under circumstances such as these, monitoring data must be supplemented with modeling estimates or modeling substituted for monitoring to derive exposure point concentrations.

The purpose of this document is to provide guidance on applying chemical fate and transport models for the air pathway. Unlike other media, the air pathway is characterized by short migration times, relatively large exposure areas, and a virtual inability to mitigate the consequences of a release after the contaminants enter the atmosphere. Exposure durations may range from only a few minutes to many years and exposure point concentrations may vary widely due to the fluidity of atmospheric processes. In addition, the air pathway exposure point concentration associated with a cancer risk of 1 in 1,000,000 for some chemicals is below current detection limits in ambient air. For these reasons, the use of predictive models may be advantageous in estimating exposure point concentrations.

## **SCREENING VERSUS REFINED ESTIMATES:**

Screening estimates of exposure point concentrations may be used in the baseline risk assessment during the identification of exposure pathways. During this phase of the baseline risk assessment, screening-level air pathway analyses may be used to help select those contaminants that will be evaluated further in the detailed analysis or to eliminate completely a specific air pathway (e.g., inhalation of fugitive dust). Such a justification could be based on one of the following:

- The exposure resulting from the pathway is much less than that from another pathway involving the same medium at the same exposure point
- The potential magnitude of the risk is low ( $< 1 \times 10^{-6}$  for carcinogens and/or  $< 1$  for noncarcinogens)
- The probability of the exposure occurring is very low and the risks associated with the occurrence are low

Use of professional judgement and experience must be exercised to make these decisions. Before such a decision is made, the site RPM must be consulted.

If a screening-level approach suggests a potential health concern, the estimates of exposure should be modified to reflect more probable exposure conditions. While screening-level analyses typically involve the use of conservative models and conservative default model variables and assumptions, refined estimates are made using more sophisticated models and site-specific data as input variables. This necessarily requires a larger site characterization data set.

Sophisticated modeling required to achieve refined exposure point concentration estimates typically requires that the three dimensional media-specific concentration of contaminants within the site volume be determined. In addition, other model parameters will require site-specific data collection (e.g., soil organic carbon content, temperature, and meteorological data).

Because screening-level analyses typically require less data, they may be performed earlier in the process and require less resources than do refined analyses. Screening-level procedures are designed to provide bounding estimates of exposure which are compared to point-of-departure human health benchmarks. Therefore, all air pathways and air contaminants for which screening-level modeling exceed a risk-level of  $1 \times 10^{-6}$  for carcinogens and meet or exceed a hazard quotient of 1 for noncarcinogens, warrant refined analyses.

## **MODEL SAMPLING REQUIREMENTS:**

As discussed previously, contaminant release, transport, and fate models are often needed to supplement monitoring data or in lieu of monitoring data when estimating exposure point concentrations. Therefore, a preliminary site modeling strategy should be developed during the scoping phase of the Remedial Investigation (RI)/Feasibility Study (FS) to allow model input data requirements to be incorporated into site characterization sampling plans.

Both screening and refined models require physical data about the media incorporating the contamination as well as data about the transporting media. In addition, physical and chemical property data are required for each contaminant exhibiting a potential for air release. Finally, the extent of contamination within the incorporating media must be determined to varying degrees depending upon the assumptions and limitations of the model(s) selected. For example, screening-level models which estimate emissions of volatile contaminants from soils typically assume an infinitely deep source of homogenous contamination, while refined models estimate emissions from a finite source of contamination. Soil sampling requirements for the screening-level model will therefore necessitate less extensive sampling. The site modeling strategy should be integrated with the site sampling plan such that sampling data are sufficient for each modeling phase.

It must be recognized that in general, fate and transport models are inherently conservative because they attempt to predict inter-media mass transfer of contaminants based on theoretical processes and/or empirical relationships. In addition, some vectors of contaminant loss (e.g., transformation) may not be taken into account because such mechanisms are not completely understood. Model validation is often limited to bench or pilot-scale studies, and to a lesser extent, to field-scale studies. Therefore, model predications of exposure point concentrations should be accompanied by an assessment of model uncertainties. To reduce the relative error and uncertainty of model predictions, values of critical model input parameters should be as accurate as resources and time constraints allow. Where possible, model predictions should be compared with monitoring and/or sampling data to reduce overall uncertainty.

The degree of sampling required to adequately determine model input parameter values will depend on the modeling objectives and the heterogeneity of the media incorporating the contaminants. For example, sampling for contaminants in surface and

subsurface soils presents potential difficulties in that the soil medium is not a well mixed compartment. Typically, contaminant concentrations as well as soil properties are not homogeneously distributed within the three-dimensional site volume. Therefore, the site sampling plan should be designed to estimate the spatial and statistical distribution of contaminants within specified limits.

The recommend approach for developing the site sampling plan is to use the Data Quality Objectives (DQO) process. The DQO process is a systematic data collection planning process developed by EPA to ensure that the right type, quality, and quantity of data are collected to support Agency decisionmaking. The DQO process generates quantitative and qualitative statements (DQOs) that clarify the purpose of the data collection effort; define the most appropriate type of data and the conditions under which the data should be collected; and specify quantitative performance criteria for using the data. This process is based on the scientific method and usually results in a statistical sampling plan that allows the site manager to draw valid inferences about contamination levels over areas of the site.

The DQO process employs statistical concepts for developing either a probalistic or nonprobalistic sampling plan. Consequently, the DQO process is most successful when the investigating team includes a member who is knowledgeable in statistics. This will help ensure that existing data and other information about the site are used most effectively in designing the sampling plan.

The following EPA documents are useful for developing an adequate site sampling plan in support of the site modeling plan:

*Data Quality Objectives for Superfund: Interim Final Guidance*, U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C. EPA/540/R-93/071, Publication 9255.9-01, NTIS PB94-963203, 1993.

*Guidance for Data Usability in Risk Assessment (Part A)*, U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C. Publication 9285.7-09A, NTIS PB94-963203, 1993.

*Supplemental Guidance to RAGS: Calculating the Concentration Term*, U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C. Publication 9285.7-08I, NTIS PB92-963373, 1992.

*Technical Background Document for Soil Screening Guidance: Review Draft*. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C. EPA/540/R-94/102, Publication 9355.4-14-1, NTIS PB95-963530, 1994.

*Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA*, U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C. EPA-540/G-89-004, OSWER Directive 9355.3-01, NTIS PB89-184626, 1989.

## **HOW TO USE THESE PROCEDURES:**

The intent of this document is to provide the sequential series of steps necessary to estimate exposure point concentrations for use in the baseline risk assessment. The models herein have been extracted from various references; and therefore as a guideline, all of the relevant information concerning the applicability, assumptions, and limitations of each model are not necessarily included. To properly use these procedures, the user must thoroughly understand all relevant information from the original references cited throughout this document.

Use of these procedures does not preclude the use of techniques for measuring actual emission rates or ambient air concentrations of airborne contaminants. Where site-specific conditions do not lend themselves to the use of predictive models, more rigorous procedures involving measurement techniques may be required. Emissions measurement and ambient air sampling techniques as well as other modeling techniques which may be more suited to site-specific conditions can be found in the EPA Air/Superfund Technical Guidance Study Series. These guidance documents cover a wide range of air issues associated with the characterization and remediation of Superfund sites. Copies of these documents are available through the National Technical Information Service (NTIS) in Port Royal, Virginia.

Finally, it should be understood that these procedures are hierarchical in nature, building upon preceding steps. Mistakes or inaccurate data in individual steps will cause the final estimated values to exhibit considerable relative error. If problems or questions arise, contact your EPA Regional Air/Superfund Coordinator for assistance.

## **HOW THE DOCUMENT IS ORGANIZED:**

This guideline is organized around the major steps required to conduct the air pathway analysis for the baseline risk assessment, with emphasis placed on the modeling procedures appropriate for the exposure assessment. The user should be familiar with the EPA procedures and guidance described in the Risk Assessment Guidance for Superfund, Human Health Evaluation Manual, Part A, July 1989 and associated documents.

The body of this document is divided into two main sections: 1) use of emission models, and 2) use of atmospheric dispersion models. The emission modeling section is further organized into subsections describing how to estimate emissions from specific media (e.g., volatile emissions from lagoons or subsurface soils). Each subsection

provides both screening-level and refined modeling procedures. Like the emission modeling section, the atmospheric dispersion modeling section also provides both screening-level and refined procedures.

For ease of use, the procedures are organized in *outline* form. Within each subsection, the appropriate model solution is given including a legend of model parameters. Solutions to model parameters which must be calculated are given either within the legend or as separate equations. Notes on model application are also provided after the equations as well as model references. It is strongly recommended that every effort be made to obtain cited references to ensure that each model is used properly and that assumptions and limitations are understood. The references cited are also valuable for the analysis of uncertainty required in the baseline risk assessment.

Finally, Appendix B to this document provides example calculations for each model. In application, these models are typically executed within a computer spreadsheet or similar program. The appendix solutions can be used to perform quality assurance checks on spreadsheet calculations.

#### **MAJOR STEPS IN THE AIR PATHWAY ANALYSIS:**

- I. Review site background information and gather data necessary to conduct the baseline emissions estimate.
- II. Develop a site modeling plan.
- III. Estimate emission rates of each applicable site contaminant.
- IV. Estimate ambient air concentrations at receptor locations of interest.
- V. Organize exposure point concentrations for input to the baseline risk assessment.

#### **SUMMARY:**

As with most fate and transport models, the refined model algorithms provided in this guidance are intrinsically conservative, and when properly applied, may be said to exhibit a relative error of perhaps one order of magnitude. The screening-level models provided herein are even more conservative because of model assumptions and because the default model parameter values provided represent high-end values of known or theoretical distributions. Screening-level models, therefore, produce bounding estimates which may be used to eliminate contaminants and/or pathways from further evaluation. With site-specific model parameter values and with adequate site characterization data (i.e., contaminant concentrations and distributions), the refined models may be used to estimate exposure point concentrations consistent with reasonable maximum exposure

(RME) assumptions. To be consistent with present EPA guidance, the refined modeling procedures predict long-term average exposure point concentrations. These concentrations are subsequently used with high-end chronic exposures (i.e., intake and duration) to derive RME for both current and future land-use assumptions.

## **STEP I. REVIEW SITE BACKGROUND AND GATHER DATA NECESSARY TO CONDUCT THE BASELINE EMISSIONS ESTIMATE**

1. Review the nature of contamination at the site and identify potential air exposure pathways and receptors (e.g., inhalation of volatile organics by an adult resident 100 m from the fence line, etc.).
2. Assemble all relevant site data. This information may include but is not limited to:
  - Site configuration and features (maps)
  - List of identified chemical contaminants
  - Sampling concentration data for each media (soil, water, and/or air)
  - Spatial coordinates of each sample in three dimensions
  - Soils data (porosity, bulk density, and/or particle density, moisture content, etc.)
  - Presence of soil crust and crust thickness, friability and soil aggregate size distribution
  - Location and distance to receptors of interest
  - Local meteorological data (annual average temperature, windspeed and prevailing direction, if applicable)
  - Extent of surface vegetation and/or surface coverings.
3. Assemble chemical property data for all site contaminants. Data requirements will vary depending on the type of compound and specific emission rate equation(s) used in Step III. Chemical properties required for modeling may include:
  - Molecular weight
  - Vapor pressure
  - Henry's law constant
  - Diffusion coefficient in air
  - Diffusion coefficient in water
  - Organic carbon partition coefficient
  - Solubility in water.



References for Physical and Chemical Properties of Contaminants:

*Air/Superfund National Technical Guidance Study (NTGS) Series, Volume II - Estimation of Baseline Air Emissions at Superfund Sites.* Appendices F and G, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-450/1-89-002a, NTIS PB90-270588, August 1990.

*CHEMDAT8 Data Base of Compound Chemical and Physical Properties.* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards Technology Transfer Network (TTN), CHIEF Bulletin Board, Research Triangle Park, North Carolina, TTN Data Number: (919) 541-1447, SYSOP Number: (919) 541-4814.

*Environmental Fate Constants for Organic Chemicals Under Consideration for EPA's Hazardous Waste Identification Projects.* U.S. Environmental Protection Agency, Office of Research and Development, Athens, Georgia, EPA/600/R-93/132, NTIS PB93-221646, August 1993.

*Estimation Programs Interface (EPI) PC-Program or individual estimation modules.* Syracuse Research Corp., Syracuse, New York, EPI and modules have been assessed by the U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. Syracuse Research Corp.

*Technical Background Document for Soil Screening Guidance, Review Draft.* U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/R-94/102, NTIS PB95-963530, November 1994.

## **STEP II. DEVELOP A SITE MODELING PLAN**

1. Based on process knowledge, historical records, or prior sampling, subdivide the site into regions where the contaminant variability is likely to be similar within each region.
2. Further subdivide each site region identified in No. 1 above, into square air pathway exposure areas (EAs). An air pathway EA is the smallest area over which an individual can reasonably be expected to move over a period of time and be exposed to air contaminants.
  - A. For residential future land-use, EPA has determined that each EA should be no larger than 0.5 acres.
  - B. For commercial/industrial or other future land-uses, determine the high-end EA (approximately the 10th percentile area) using historic land-use data for the site geographic region.
  - C. For ground-level air release from surface water bodies, the future land-use EA will normally be equivalent to the soil EA(s) adjacent to the source of emissions.
3. For surface soils ( $\leq 6$  inches deep), develop a site sampling plan to determine the 95% upper confidence limit (UCL) of the arithmetic mean concentration of each contaminant within each EA.
4. Develop a site sampling plan for subsurface soils:
  - A. Determine the 95% UCL of the arithmetic mean concentration of each contaminant within each EA soil volume (i.e., in three dimensions) using the DQO process,  

OR
  - B. Drill at least two to three boreholes within each EA and sample in 2-foot intervals from 6 inches below the ground surface until no further contamination or the ground water table is encountered.
    1. Average the analysis results of the discrete samples (volatiles) or combine discrete samples into a composite sample (semivolatiles and nonvolatiles) for each borehole. If composite sampling is used for semivolatiles and nonvolatiles, only samples within the zone of contamination should be used (i.e., do not mix clean soil with contaminated soil).

2. With discrete sampling, use the highest depth-weighted average borehole concentration within each EA to represent the mean concentration of each contaminant.

Note: The number and location of subsurface soil sampling (i.e., borehole) locations within each EA should be based on knowledge of likely soil contamination patterns and subsurface conditions. This usually means that core samples be taken directly beneath areas of high surface contamination. Thus, surface soil samples and field measurements (e.g., soil gas surveys) will provide information to help locate core sampling. Note that there may be sources buried in subsurface soils that are not discernible at the surface.

If time and resource constraints prevent a determination of the 95% UCL of the arithmetic mean concentrations to depth (i.e., Step 4.A.), the alternative sampling strategy presented in Step 4.B. is designed to provide conservative estimates of subsurface soil contaminant concentrations within each EA. This prescribed subsurface soil sampling procedure will not be sufficient to fully characterize the extent of contamination and the mean concentration of subsurface contaminants because it does not account for contaminant variability. For this reason, it is conservatively assumed that the highest average borehole concentration underlies the entire exposure area.

Composite sampling of surface and subsurface soils may be appropriate for nonvolatile and semivolatile contaminants. Discrete sampling is required for volatile contaminants to avoid loss of the analytes. Volatile contaminants may be said to have a vapor pressure > 0.1 mm Hg and boiling points < 120°C.

5. For aqueous systems, develop a sampling plan to determine the 95% UCL of the arithmetic mean concentration of each contaminant.
6. After sampling is complete, determine which air pathways or air contaminants are suitable for screening-level estimates of exposure point concentrations.

Note: One option is to perform screening-level analyses for all air pathways and contaminants. If a screening-level analysis is not performed, a refined analysis must be substituted.

7. Perform screening-level analyses, as appropriate, and estimate risks for each air contaminant and air pathway.

8. Document the results of the screening-level analyses and prepare an assessment of model uncertainties.
9. Perform a refined analysis for all air pathways and air contaminants for which screening-level analyses exceed a risk-level of  $1 \times 10^{-6}$  for carcinogens and meet or exceed a hazard quotient of 1 for noncarcinogens.
10. Document the results of the refined analyses and prepare an assessment of model uncertainties.

### STEP III. ESTIMATE EMISSION RATES OF EACH APPLICABLE SITE CONTAMINANT

This section includes both screening-level and refined emissions modeling procedures for the following emission scenarios:

1. Vapor-phase emissions from surface and subsurface soils without landfill gas generation
2. Vapor-phase emissions from subsurface soils with landfill gas generation
3. Vapor-phase emissions from aqueous-phase contaminants in impoundments, open-top tanks, and pooled at soil surfaces
4. Semivolatile and nonvolatile contaminants emitted as particulate matter due to wind erosion.

Model predictions of emissions for these four scenarios are to open spaces. If vapor-phase intrusion of site contaminants into indoor spaces via subsurface soils is likely for either current or future land-use, the following references should be consulted to assess any associated risks:

*Air/Superfund National Technical Guidance Study (NTGS) Series, Assessing Potential Indoor Air Impacts for Superfund Sites.* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-451/R-92-002, NTIS PB93-122257, September 1992.

Johnson, P. C., and R. A. Ettinger. 1991. *Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors Into Buildings.* Environ. Sci. Technol., 25(8):1445-1452.

*Technical Background Document for Soil Screening Guidance, Review Draft.* Appendix B. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/R-94/102, NTIS PB95-963530, November 1994.

Little, J. C., J. M. Daisey, and W. W. Nazaroff. 1992. *Transport of Subsurface Contaminants Into Buildings, An Exposure Pathway for Volatile Organics.* Environ. Sci. Technol., 26(11):2058-2066.

### STEP III. PART 1 - VAPOR-PHASE EMISSIONS FROM SURFACE AND SUBSURFACE SOILS WITHOUT LANDFILL GAS GENERATION

Vapor-phase emissions from surface and subsurface soils without the generation of landfill gas are a function of the rate of diffusion through the soil matrix and the initial contaminant soil concentration at the time of sampling. Emissions may be estimated using either the initial vapor-phase concentration (i.e., soil gas analysis) or the initial bulk concentration which includes all phases within the soil matrix. Soil gas analysis, however, can only account for the vapor-phase soil concentration at the time of sampling and cannot account for the amount of contamination sorbed to soil particles, in solution with soil moisture, or in residual phase within the soil matrix. Therefore, emission estimates using soil gas analysis incorporate steady-state equilibrium assumptions (i.e., an infinite source of emissions). Soil gas analysis is used for screening-level emission estimates, while bulk samples may be used for screening-level or refined estimates.

#### Estimating Emissions Using Bulk Soil Concentrations:

1. If soil bulk concentrations are to be used to calculate emission rates, estimate the saturation concentration ( $C_{sat}$ ) of each contaminant in the vadose zone.  $C_{sat}$  for each contaminant is the concentration at which the adsorptive limit of the soil plus the theoretical solubility limit of the liquid-phase contaminant in the available soil moisture have been reached. Concentrations  $> C_{sat}$  indicate potential nonaqueous-phase liquids (NAPLs) or solids within the soil matrix.

$$C_{sat,i} = \frac{S_i}{\beta} (K_{d,i} \beta + \theta_w + H'_i \theta_a) \quad (1)$$

- where
- $C_{sat,i}$  = Soil saturation concentration of component i, mg/kg - soil
  - $K_{d,i}$  = Soil/water partition coefficient of i, L/kg (Equation 3)
  - $H'_i$  = Henry's law constant of i, unitless (=  $H_i \times 41$ , where 41 is a units conversion factor at standard conditions)
  - $H_i$  = Henry's law constant of i, atm - m<sup>3</sup>/mol
  - $\theta_a$  = Air-filled soil porosity, unitless (=  $\theta_t - \theta_w$ )
  - $\theta_w$  = Average long-term volumetric soil moisture content, L-water/L-soil (Equation 2)

- $\Theta_t$  = Total soil porosity, unitless ( $= 1 - \beta / \rho_s$ )  
 $\rho_s$  = True soil or particle density, kg/L-soil (default = 2.65 kg/L)  
 $S_i$  = Solubility in water of i, mg/L-water  
 $\beta$  = Average soil dry bulk density, kg/L-soil.

Estimation of average long-term volumetric soil moisture content ( $\Theta_w$ ):

$$\theta_w = \theta_t (I/K_s)^{1/(2b+3)} \quad (2)$$

- where
- $\Theta_w$  = Average long-term volumetric soil moisture content, L-water/L-soil  
 $\Theta_t$  = Total soil porosity, unitless (Equation 1 legend)  
 $I$  = Average water infiltration rate, m/yr (Appendix A)  
 $K_s$  = Soil saturated hydraulic conductivity, m/yr (Table 1)  
 $1/(2b+3)$  = Soil-specific exponential parameter, unitless (Table 1).

Values for  $K_s$  and the exponential term  $1/(2b+3)$  are shown in Table 1 by soil texture class. Average long-term soil moisture content should be approximated as the average from the soil surface to the bottom of contamination.

TABLE 1. PARAMETER ESTIMATES FOR CALCULATING AVERAGE SOIL MOISTURE CONTENT ( $\Theta_w$ )

Soil texture	$K_s$ , m/yr	$1/(2b+3)$
Sand	1,830	0.090
Loamy sand	540	0.085
Sandy loam	230	0.080
Silt loam	120	0.074
Loam	60	0.073
Sandy clay loam	40	0.058
Silt clay loam	13	0.054
Clay loam	20	0.050
Sandy clay	10	0.042
Silt clay	8	0.042
Clay	5	0.039

The average water infiltration rate (I) may be estimated using hydrogeologic settings by assuming the infiltration rate is equivalent to the recharge rate. Appendix A gives the estimated recharge rates by hydrogeologic setting for the continental United States.

Reference for Equation Nos. 1 and 2, Table 1, and Appendix A: Technical Background Document for Draft Soil Screening Level Guidance, Review Draft. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/R-94/102, Publication 9355.4-14-1, NTIS PB95-963530, November 1994.

Estimation of  $K_d$  if not available in the scientific literature or not estimated using the references for Step I.3:

$$K_{d,i} = K_{oc,i} \times f_{oc} \quad (3)$$

where  $K_{d,i}$  = Soil/water, partition coefficient of component i, L/kg (or  $\text{cm}^3/\text{g}$ )  
 $K_{oc,i}$  = Organic carbon partition coefficient of i, L/kg (or  $\text{cm}^3/\text{g}$ )



$f_{oc}$  = Fraction of organic carbon in soil, mg/mg (default = 0.006).

Estimation of  $K_{oc}$  if not available in the scientific literature:

Use one of the following equations based on the chemical class closest to the subject contaminant. If the contaminant does not fit any given class, use Equation No. 4 (based on largest sampling):

Based on a wide variety of contaminants (mostly pesticides):

$$K_{oc} = 10^{(0.544 \log K_{ow} + 1.377)} \quad (4)$$

Based on aromatics, polynuclear aromatics, triazines, and dinitroaniline herbicides:

$$K_{oc} = 10^{(0.937 \log K_{ow} - 0.006)} \quad (4a)$$

Based on aromatics or polynuclear aromatics:

$$K_{oc} = 10^{(1.00 \log K_{ow} - 0.21)} \quad (4b)$$

Based on s-triazines and dinitroaniline herbicides:

$$K_{oc} = 10^{(0.94 \log K_{ow} + 0.02)} \quad (4c)$$

Based on insecticides, herbicides, and fungicides:

$$K_{oc} = 10^{(1.029 \log K_{ow} - 0.18)} \quad (4d)$$

Based on substituted phenylureas and alkyl-N-phenylcarbamates:

$$K_{oc} = 10^{(0.524 \log K_{ow}) + 0.855} \quad (4e)$$

where  $K_{oc}$  = Organic carbon partition coefficient, L/kg (or cm<sup>3</sup>/g)

$K_{ow}$  = Octanol/water partition coefficient, L/kg (or cm<sup>3</sup>/g).

Reference for Equation Nos. 3-4e: *Superfund Exposure Assessment Manual*, Section 3.5.2.4, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/1-88/001, April 1988.

Reference for Value of  $f_{oc}$  in Equation No. 3: *Technical Background Document for Soil Screening Level Guidance, Review Draft*. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/R-94/102, Publication 9355.4-14-1, NTIS PB95-963530, November 1994.

## Volatile Emissions from Surface Soils When NAPL is Present

2. With measured bulk concentrations  $\geq C_{\text{sat}}$  (Equation 1), calculate the emission flux from surface soils for each contaminant.

Note: Under this scenario, nonaqueous-phase liquids (NAPLs) or solids may exist in the unsaturated portion of the vadose zone, usually as an immiscible layer or discrete film. The following model should be used in the absence of clean soil above the contamination.

### Screening-Level and Refined Procedures:

When nonaqueous-phase liquids or solids are present, the screening-level and refined procedures are identical. The emission model operates under the assumption of steady-state conditions (infinite source) over the averaging period.

$$\bar{F}_i = \beta C_{o,i} \left( \frac{2 C_{v,eq} D_{e,i}}{\beta C_{o,i} \tau} \right)^{1/2} 0.116 \quad (5)$$

- where
- $\bar{F}_i$  = Average maximum emission flux of component i from surface soils over exposure averaging period  $\tau$ , g/m<sup>2</sup>-s
  - $\beta$  = Average soil dry bulk density, g/cm<sup>3</sup>-soil
  - $C_{o,i}$  = Initial soil concentration of i, g/g-soil
  - $C_{v,eq}$  = Equilibrium vapor concentration when NAPL is present in the soil, g/cm<sup>3</sup>-vapor (Equation 6)
  - $D_{e,i}$  = Maximum effective diffusion coefficient of i when NAPL is present, cm<sup>2</sup>/d (Equation 7)
  - $\tau$  = Exposure averaging period, days (for residential land-use  $\tau = 10,950$  days)
  - 0.116 = Factor to convert g/cm<sup>2</sup>-d to g/m<sup>2</sup>-s.

Calculation of equilibrium vapor concentration when NAPL is present ( $C_{v,eq}$ ):

$$C_{v,eq} = \frac{X_i P_i MW_i}{RT} \quad (6)$$

- where
- $C_{v,eq}$  = Equilibrium vapor concentration of i when NAPL is present, g/cm<sup>3</sup>-vapor
  - $X_i$  = Mole fraction of i in the residual mixture, g/mol per g/mol
  - $P_i$  = Pure component vapor pressure of i, mm Hg
  - $MW_i$  = Molecular weight of i, g/mol
  - $R$  = Molar gas constant, 62,361 mm Hg-cm<sup>3</sup>/mol-°K
  - $T$  = Average in situ soil temperature, °K.

Calculation of maximum effective diffusion coefficient when NAPL is present ( $D_{e,i}$ ):

$$D_{e,i} = \left( \frac{\theta_a^{10/3}}{\theta_t^2} D_{a,i} \right) + \frac{1}{H'_i} \left( \frac{\theta_w^{10/3}}{\theta_t^2} D_{w,i} \right) \quad (7)$$

- where
- $D_{e,i}$  = Maximum effective diffusion coefficient of component i when NAPL is present, cm<sup>2</sup>/d
  - $\theta_a$  = Air-filled soil porosity unitless (Equation 1 legend)
  - $\theta_t$  = Total soil porosity, unitless (Equation 1 legend)
  - $D_{a,i}$  = Diffusion coefficient of i in air, cm<sup>2</sup>/d (Equation 9)
  - $H'_i$  = Henry's law constant of i, unitless (Equation 1 legend)
  - $\theta_w$  = Water-filled soil porosity, unitless (Equation 2)
  - $\beta$  = Average soil dry bulk density, g/cm<sup>3</sup>-soil
  - $D_{w,i}$  = Diffusion coefficient of i in water, cm<sup>2</sup>/d (Equation 10).

## Volatile Emissions from Subsurface Soils When NAPL is Present

3. For measured bulk concentrations  $\geq C_{\text{sat}}$  (Equation 1), calculate the emission flux from subsurface soils for each contaminant.

Note: Under this scenario, nonaqueous-phase liquids (NAPLs) or solids may exist in the unsaturated portion of the vadose zone, usually as an immiscible layer or discrete film. The following model should be used when a layer of clean soil is above the contamination.

### Screening-Level and Refined Procedures:

When nonaqueous-phase liquids or solids are present, the screening-level and refined procedures are identical, the emission model operates under the assumption of steady-state conditions (infinite source) over the averaging period.

$$\bar{F}_i = \left( \frac{\beta C_{o,i}}{\tau} \right) \left[ \left( d_c^2 + \frac{2 C_{v,eq} D_{e,i} \tau}{\beta C_{o,i}} \right)^{1/2} - d_c \right] 0.116 \quad (8)$$

- where
- $\bar{F}_i$  = Average maximum emission flux of component i from subsurface soils over exposure averaging period  $\tau$ , g/m<sup>2</sup>-s
  - $\beta$  = Average soil dry bulk density, g/cm<sup>3</sup>-soil
  - $C_{o,i}$  = Initial soil concentration of i, g/g-soil
  - $\tau$  = Exposure averaging period, days (for residential land-use  $\tau = 10,950$  days)
  - $d_c$  = Distance from soil surface to top of contamination, cm
  - $C_{v,eq}$  = Equilibrium vapor concentration when NAPL is present in the soil, g/cm<sup>3</sup>-vapor (Equation 6)
  - $D_{e,i}$  = Maximum effective diffusion coefficient of i when NAPL is present, cm<sup>2</sup>/d (Equation 7)
  - 0.116 = Factor to convert g/cm<sup>2</sup>-d to g/m<sup>2</sup>-s.

Estimation of diffusion coefficient of component i in air ( $D_{a,i}$ ) if not available from the scientific literature or not estimated using the references in Step I.3:

$$D_{a,i} = \frac{0.001 T^{1.75} \sqrt{\frac{1}{MW_i} + \frac{1}{MW_a}}}{P_{ab} [(\sum V_i)^{1/3} + (\sum V_a)^{1/3}]^2} (8.64 \times 10^4) \text{ sec/day} \quad (9)$$

where  $D_{a,i}$  = Diffusion coefficient of component i in air,  $\text{cm}^2/\text{d}$

$T$  = Average temperature,  $^{\circ}\text{K}$

$MW_i$ ;  $MW_a$  = Molecular weight of component i and air (28.8), respectively, g/mole

$P_{ab}$  = Absolute pressure, atmospheres

$\sum V_i$ ;  $\sum V_a$  = Molecular diffusion volumes of component i and air (20.1), respectively,  $\text{cm}^3/\text{mol}$ . This is the sum of the atomic diffusion volumes of the compound's atomic constituents.

Atomic diffusion volumes for use in estimating  $D_{a,i}$ :

C = 16.5	Cl = 19.5	Aromatic ring = -20.2
H = 1.98	Br = 35.0	Heterocyclic ring = -20.2
O = 5.48	F = 25.0	
N = 5.69	S = 17.0	

Example of calculating  $\sum V_i$  for benzene,  $\text{C}_6\text{H}_6$ :

$$\begin{array}{rcl}
 \text{C} & = & 6 \times 16.5 = 99.00 \\
 \text{H} & = & 6 \times 1.98 = +11.88 \\
 & & \underline{110.88} \\
 \text{Aromatic ring} & = & -20.20 \\
 & & \underline{90.68 \text{ cm}^3/\text{mol}}
 \end{array}$$

Note: Equation No. 9 may not be appropriate for polar compounds. Where possible, values of  $D_{a,i}$  in the scientific literature should be used.

Estimation of diffusion coefficient of component i in water ( $D_{w,i}$ ) if not available from the scientific literature or not estimated using the references in Step I.3:

$$D_{w,i} = \frac{13.26 \times 10^{-5}}{\eta_w^{1.14} (V'_{B,i})^{0.589}} (8.64 \times 10^4 \text{ sec/day}) \quad (10)$$

where  $D_{w,i}$  = Diffusion coefficient of component i in water,  $\text{cm}^2/\text{d}$

$\eta_w$  = Viscosity of water at average in situ soil temperature, centipoise (Table 2)

$V'_{B,i}$  = LeBas molar volume of i,  $\text{cm}^3/\text{mol}$  (Table 3).

TABLE 2. VISCOSITY OF WATER AT TEMPERATURE ( $\eta_w$ )

$^{\circ}\text{C}$	$\eta_w(\text{cp})$	$^{\circ}\text{C}$	$\eta_w(\text{cp})$	$^{\circ}\text{C}$	$\eta_w(\text{cp})$
0	1.787	11	1.271	21	0.9779
1	1.728	12	1.235	22	0.9548
2	1.671	13	1.202	23	0.9325
3	1.618	14	1.169	24	0.9111
4	1.567	15	1.139	25	0.8904
5	1.519	16	1.109	26	0.8705
6	1.472	17	1.081	27	0.8513
7	1.428	18	1.053	28	0.8327
8	1.386	19	1.027	29	0.8148
9	1.346	20	1.002	30	0.7975
10	1.307				

TABLE 3. ADDITIVE VOLUME INCREMENTS FOR CALCULATING THE LeBas MOLAR VOLUME ( $V_B'$ )

Atom	Increment, $\text{cm}^3/\text{mol}$	Atom	Increment, $\text{cm}^3/\text{mol}$
C	14.8	Br	27.0
H	3.7	Cl	24.6
O (except as noted below)	7.4	F	8.7
In methyl esters and ethers	9.1	I	37.0
In ethyl esters and ethers	9.9	S	25.6
In higher esters and ethers	11.0	Ring	
In acids	12.0	3-Membered	-6.0
Joined to S, P, N	8.3	4-Membered	-8.5
N		5-Membered	-11.5
Double bonded	15.6	6-Membered	-15.0
In primary amines	10.5	Naphthalene	-30.0
In secondary amines	12.0	Anthracene	-47.5

Example of calculating  $V_B'$  for aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ :

$$\begin{array}{rcl}
 \text{C} & = & 6 \times 14.8 = 88.8 \\
 \text{H} & = & 7 \times 3.7 = 25.9 \\
 \text{N} & = & 1 \times \text{N-primary amine} = 10.5 \\
 & & \hline
 & & 125.2
 \end{array}$$

$$\begin{array}{rcl}
 \text{6-membered ring} & & -15.0 \\
 & & \hline
 & & 110.2 \text{ cm}^3/\text{mol}
 \end{array}$$

Reference for Equation Nos. 5, 6, 7, and 8: *Emergency Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*. American Society for Testing and Materials, Philadelphia, Pennsylvania. ASTM ES38-94, December 1994.

Reference for Equation No. 9: *Superfund Exposure Assessment Manual*, Section 2.3.2. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/1-88/001, April 1988.



Reference for Equation No 10: Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. *Handbook of Chemical Property Estimation Methods*. American Chemical Society, Washington, D.C., 1990.

## Volatile Emissions from Surface Soils When NAPL is Not Present

4. For measured bulk concentrations  $< C_{sat}$  (Equation 1), calculate the emission flux from surface soils for each contaminant.

Note: Under this scenario, all contaminants are assumed to be in equilibrium between aqueous-phase, sorbed-phase, and vapor-phase (fully incorporated). The following model should be used in the absence of clean soil above the contamination.

### Screening Procedures:

$$\bar{F}_i = \beta C_{o,i} \left( \frac{4 D_{A,i}}{\pi \tau} \right)^{1/2} 0.116 \quad (11)$$

- where  $\bar{F}_i$  = Average maximum emission flux of component i from surface soils over exposure period  $\tau$ , g/m<sup>2</sup>-s
- $\beta$  = Average soil dry bulk density, g/cm<sup>3</sup>-soil
- $C_{o,i}$  = Initial soil concentration of i, g/g-soil
- $D_{A,i}$  = Apparent diffusion coefficient of i in soil, cm<sup>2</sup>/d (Equation 12)
- $\pi$  = 3.1416
- $\tau$  = Exposure averaging period, days (for residential land-use  $\tau = 10,950$  days)
- 0.116 = Factor to convert g/cm<sup>2</sup>-d to g/m<sup>2</sup>-s.

Calculation of apparent diffusion coefficient ( $D_{A,i}$ ):

$$D_{A,i} = \left[ \left( \theta_a^{10/3} D_{a,i} H_i' + \theta_w^{10/3} D_{w,i} \right) / \theta_t^2 \right] / \left( \beta K_{d,i} + \theta_w + \theta_a H_i' \right) \quad (12)$$

- where  $D_{A,i}$  = Apparent diffusion coefficient of component i in soil, cm<sup>2</sup>/d

- $\Theta_a$  = Air-filled soil porosity, unitless (Equation 1 legend)
- $D_{a,i}$  = Diffusion coefficient of i in air,  $\text{cm}^2/\text{d}$  (Equation 9)
- $\Theta_w$  = Water-filled soil porosity, unitless (Equation 2)
- $D_{w,i}$  = Diffusion coefficient of i in water,  $\text{cm}^2/\text{d}$  (Equation 10)
- $\Theta_t$  = Total soil porosity, unitless (Equation 1 legend)
- $\beta$  = Average soil dry bulk density  $\text{g}/\text{cm}^3$ -soil
- $K_{d,i}$  = Soil/water partition coefficient of i,  $\text{cm}^3/\text{g}$  (Equation 3)
- $H_i'$  = Henry's law constant of i, unitless (Equation 1 legend).

**Refined Procedures:**

$$\bar{F}_i = \frac{1}{\tau} \int_0^t F_{i(t)} dt \quad (13)$$

- where
- $\bar{F}_i$  = Average emission flux of component i over exposure averaging period  $\tau$ ,  $\text{g}/\text{m}^2\text{-s}$
  - $\tau$  = Exposure averaging period, days (for residential land-use  $\tau = 10,950$  days)
  - $F_{i(t)}$  = Instantaneous emission flux of i at time = t,  $\text{g}/\text{m}^2\text{-s}$
  - t = Time, days.

Integration of Equation No. 13:

Note: In order to numerically integrate Equation 13, the instantaneous emission flux must be calculated for a series of time-steps from  $t=0$  to  $t=\tau$  (Equation 15). For acceptable resolution, a minimum of 100 time-steps is required for extended exposure averaging periods (e.g., 30 years). Therefore:

$$\bar{F}_i = \frac{1}{\tau} \left[ \frac{h}{2} (F_o + 2F_1 + 2F_2 + \dots + 2F_{n-1} + F_n) \right] \quad (14)$$

- where
- $\tau$  = Exposure averaging period, days (Residential = 30 yr = 10,950 days)
  - $h$  = Time-step interval for  $t_o$  to  $t_n$ , days (=  $\tau/n$ )
  - $n$  = Number of time-step intervals (default = 100)
  - $F_{0,1,2,\dots,n}$  = Emission flux of  $i$  at time-zero ( $t_o$ ) and each succeeding time-step, g/m<sup>2</sup>-s (Equation 15)

Time-zero ( $t_o$ ) should be set equal to 0.25 days.

Calculation of emission flux from surface soils at each time-step (i.e., contamination begins at soil surface):

$$F_{i(t)} = \beta C_{o,i} \left( \frac{D_{A,i}}{\pi t} \right)^{1/2} \left[ 1 - \exp \left( - \frac{L_c^2}{4 D_{A,i} t} \right) \right] 0.116 \quad (15)$$

- where
- $F_{i(t)}$  = Emission flux of component  $i$  from surface soils at each time-step, g/m<sup>2</sup>-s
  - $\beta$  = Average soil dry bulk density, g/cm<sup>3</sup>-soil
  - $C_{o,i}$  = Initial soil concentration of  $i$ , g/g-soil
  - $D_{A,i}$  = Apparent diffusion coefficient of  $i$  in soil, cm<sup>2</sup>/d (Equation 12)
  - $\pi$  = 3.1416.
  - $t$  = Cumulative time at each time-step, days
  - $L_c$  = Depth from soil surface to bottom of contamination, cm
  - 0.116 = Factor to convert g/cm<sup>2</sup>-d to g/m<sup>2</sup>-s.

**IMPORTANT NOTE:**

Equation 14 is a numerical evaluation of the integral in Equation 13. Errors may result for volatilization fluxes from chemicals with large Henry's law constants in combination with relatively shallow depths of contamination unless extremely small time intervals are used in the numerical integration. The errors result in overestimation of the average emission flux such that for an extremely long time period (e.g., 30 years), the cumulative mass lost through volatilization may exceed the initial mass present in the soil. To eliminate this potential error, compare the total mass lost using the refined volatilization model to the total initial mass:

$$M_{i,T}^v = \bar{F}_i A_c \tau \quad (16)$$

$$M_{i,T} = C_{o,i} \beta A_c L_c \quad (17)$$

where	$M_{i,T}^v$	= Total mass of component i lost by volatilization over the exposure averaging period, g
	$M_{i,T}$	= Total initial mass of i, g
	$\bar{F}_i$	= Calculated average emission flux of i over the exposure averaging period $\tau$ , g/m <sup>2</sup> -s
	$A_c$	= Area of contamination, m <sup>2</sup>
	$\tau$	= Exposure averaging period, s
	$C_{o,i}$	= Initial soil concentration of i, g/Mg-soil (= mg/kg)
	$\beta$	= Average soil dry bulk density, Mg/m <sup>3</sup> -soil (= g/cm <sup>3</sup> )
	$L_c$	= Average depth to the <u>bottom</u> of contamination, m.

Note: In the case of buried waste, substitute the thickness of contamination ( $w_c$ ) for the depth to the bottom of contamination ( $L_c$ ).

If

$$M_{i,T}^v > M_{i,T} ,$$

The average emission flux over the exposure averaging period (g/m<sup>2</sup>-s) is

$$\bar{F}_i = \frac{M_{i,T}}{A_c \tau} . \quad (18)$$

Note: See Step III.6 on page 33 for refined modeling computer codes.

## Volatile Emissions from Subsurface Soils When NAPL is not Present

5. For measured bulk concentration  $< C_{\text{sat}}$  (Equation 1), calculate the emission flux from subsurface soils for each contaminant.

**Note:** Under this scenario, all contaminants are assumed to be in equilibrium between aqueous-phase, sorbed-phase, and vapor-phase (fully incorporated). The following model should be used when a layer of clean soil is above the contamination.

### Screening-Level and Refined Procedures:

When the contamination is covered by clean soil, the screening-level and refined procedures are identical. The average emission flux of component  $i$  ( $\text{g}/\text{m}^2\text{-s}$ ) is calculated using Equation 13 and integrated using Equation 14.

The emission flux from subsurface soils at each time-step is calculated as:

$$F_{i(t)} = \beta C_{o,i} \left[ \frac{D_{A,i}}{\pi t} \right]^{1/2} \left[ \exp \left[ -\frac{d_c^2}{4 D_{A,i} t} \right] - \exp \left[ -\frac{(d_c + w_c)^2}{4 D_{A,i} t} \right] \right] 0.116 \quad (19)$$

- where
- $F_{i(t)}$  = Emission flux of component  $i$  from subsurface soils at each time-step,  $\text{g}/\text{m}^2\text{-s}$
  - $\beta$  = Average soil dry bulk density,  $\text{g}/\text{cm}^3\text{-soil}$
  - $C_{o,i}$  = Initial soil concentration of  $i$ ,  $\text{g}/\text{g-soil}$
  - $D_{A,i}$  = Apparent diffusion coefficient of  $i$  in soil,  $\text{cm}^2/\text{d}$  (Equation 12)
  - $\pi$  = 3.1416
  - $t$  = Cumulative time at each time-step, days
  - $d_c$  = Depth from soil surface to top of contamination, cm
  - $w_c$  = Thickness of contaminated soil, cm
  - 0.116 = Factor to convert  $\text{g}/\text{cm}^2\text{-d}$  to  $\text{g}/\text{m}^2\text{-s}$ .

**See the *IMPORTANT NOTE* after Equation 15.**

Reference for Equation Nos. 11, 12, 15, and 19: *A Comparison of Soil Volatilization Models in Support of Superfund Soil Screening Level Development*. Environmental Quality Management, Inc., developed for the Office of Emergency and Remedial Response, Washington, D.C. Contract No. 68-D3-0035, Work Assignment No. 0-25, September 1994.

Jury, W. A., D. Russo, G. Streile, and H. El Abd. 1990. *Evaluation of Volatilization by Organic Chemicals Residing Below the Soil Surface*. Water Resources Research, Vol. 26, No. 1:13-20.



## Computer Codes for Estimating Volatile Emissions from Surface and Subsurface Soils When NAPL is Not Present

6. The refined procedures specified in Step III, Part 1, Sections 4 and 5 account for a finite source of emissions. These procedures, however, do not take into account the effects of water advection in the vadose zone (i.e., surface evaporation due to capillary action or leaching to the water table). Nor do the refined procedures account for the effects of a boundary layer at the soil-air interface. The effects of water advection may be significant for highly mobile compounds (e.g., phenol), and the effect of a soil-air boundary layer will act to reduce emissions for compounds with relatively low Henry's law constants ( $\leq 2.5 \times 10^5$ ).

Two public domain PC software programs are available from the U.S. EPA which are capable of estimating time-dependent emissions of volatiles from both surface and subsurface soils and which include solutions for both water advection and a soil-air boundary layer.

The first program is called the Exposure Model for Soil-Organic Fate and Transport (EMSOF). This program is a menu-driven enhancement of the analytical solution of Jury et al. (1990) and is capable of calculating time and depth-averaged emissions and soil concentrations as well as emissions and soil concentrations versus time. The program can be used with stratified initial soil concentrations, but soil properties are assumed constant with depth. EMSOF is available at no charge from the U.S. EPA Exposure Assessment Group, Office of Health and Environmental Assessment by sending a FAX request to Amy Wilkins; the FAX number is (202) 260-1722 or FTS 8-260-1722. Software orders should include the requestor's name, organization, address, and return telephone and FAX numbers.

The second computer program is called the Vadose Zone Leaching Model (VLEACH Version 2.2). VLEACH is a numerical code ground water model that is also capable of calculating time-dependent emissions from surface and subsurface soils. Model inputs are similar to that of EMSOF, but VLEACH allows for areal distribution of soil properties as a series of polygons, each represented by a vertical stack of cells which allows for stratified contaminant distributions. VLEACH Version 2.2 is available from the Center for Subsurface Modeling Support (CSMOS) at EPA's Environmental Research Laboratory in Ada, Oklahoma by calling (405) 436-8656.

Either EMSOF or VLEACH can be used to estimate time-averaged volatile emissions from surface or subsurface soils. These models offer the most accurate emission estimates available and each is relatively user-friendly. Both models have been validated with bench-scale and, to a lesser extent, with field-scale experimental data over relatively short time-periods.

## Estimating Emissions Using Soil Gas Measurements

7. With measured soil gas concentrations, calculate the emission flux of each contaminant.

Note: Soil gas measurements account only for the vapor-phase concentration of each contaminant, and thus cannot account for the total initial concentration (g/cm<sup>3</sup> - total volume). Therefore, the assumptions under which the following emission model operates include an infinite source of emissions.

### Screening-Level and Refined Procedures:

When using soil gas analyses, the screening-level and refined procedures are identical.

$$F_i^{\max} = \left[ \frac{C_{v,i} D_i^{\text{ev}}}{d} \right] 0.116 \quad (20)$$

- where
- $F_i^{\max}$  = Maximum emission flux of component i, g/m<sup>2</sup>-s
  - $C_{v,i}$  = Measured vapor-phase concentration of i immediately above the vapor source, g/cm<sup>3</sup>-vapor (Equation 22)
  - $D_i^{\text{ev}}$  = Effective vapor-phase diffusion coefficient of i in soil, cm<sup>2</sup>/d (Equation 21)
  - $d$  = Depth from surface to immediately above the vapor source, cm
  - 0.116 = Factor to convert g/cm<sup>2</sup>-d to g/m<sup>2</sup>-s.

Calculation of Effective Vapor-phase Diffusion Coefficient ( $D_i^{\text{ev}}$ ):

$$D_i^{\text{ev}} = D_{a,i} \frac{\theta_a^{10/3}}{\theta_t^2} \quad (21)$$

where  $D_i^{ev}$  = Effective vapor-phase diffusion coefficient of component i in soil,  $\text{cm}^2/\text{d}$

$D_{a,i}$  = Diffusion coefficient of i in air,  $\text{cm}^2/\text{d}$  (Equation 9)

$\Theta_a$  = Air-filled soil porosity above the vapor source, unitless (Equation 1 legend)

$\Theta_t$  = Total soil porosity above the vapor source, unitless (Equation 1 legend).

Calculation of the Vapor-phase Concentration ( $C_{v,i}$ ) If Soil Gas Measurements are in Units of Parts-Per-Million by volume:

$$C_{v,i} = C_{sg,i} \left( \frac{MW_i}{2.404 \times 10^{10}} \right) \quad (22)$$

where  $C_{v,i}$  = Vapor-phase concentration of component i,  $\text{g}/\text{cm}^3$ -vapor

$C_{sg,i}$  = Measured soil gas concentration of i, ppmv

$MW_i$  = Molecular weight of i, g/mol.

Reference for Equations 20 and 21: *Emergency Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*. American Society for Testing and Materials. Philadelphia, Pennsylvania. ASTM ES38-94, December 1994.

### STEP III. PART 2 - VAPOR-PHASE EMISSIONS FROM SUBSURFACE SOILS WITH LANDFILL GAS GENERATION

Vapor-phase emissions from subsurface soils with landfill gas generation are a function of the convective transport rate of the gas. Codisposal sites contain toxic or hazardous wastes in combination with municipal or sanitary wastes which generate landfill gases (e.g., methane, carbon dioxide, and hydrogen gas). These "sweep" gases greatly increase the migration velocity of volatile nonmethane organic compounds (NMOCs) and their subsequent release to the atmosphere.

#### **Screening Procedures:**

The following screening-level emission model may be used for both vented and unvented landfills and operates under the assumption that the emission flux has reached steady-state conditions and that the soil column offers no further resistance to vapor flow. This model does not require quantitative determination of the soil vapor-phase concentration of each contaminant (i.e., assumes the saturation vapor concentration) but does require a determination of which NMOCs are present in the soil gas on a speciated basis.

$$F_i^{\max} = C_{sv,i} V_y 0.116 \quad (23)$$

where  $F_i^{\max}$  = Maximum emission flux of component i, g/m<sup>2</sup>-s

$C_{sv,i}$  = Saturation vapor concentration of i, g/cm<sup>3</sup>-vapor (Equation 24)

$V_y$  = Mean landfill gas velocity in the soil pores, 141 cm/d

0.116 = Factor to convert g/cm<sup>3</sup>-d to g/m<sup>2</sup>-s.

Note: For vented landfills, multiply the emission flux by the landfill area to obtain the emission rate (g/s).

Calculation of Saturation Vapor Concentration ( $C_{sv,i}$ ):

$$C_{sv,i} = \frac{P_i MW_i}{RT} \quad (24)$$

where  $C_{sv,i}$  = Saturation vapor concentration of component i, g/cm<sup>3</sup>-vapor  
 $P_i$  = Pure component vapor pressure of i, mm Hg  
 $MW_i$  = Molecular weight of i, g/mol  
 $R$  = Molar gas constant, 62,361 mm Hg-cm<sup>3</sup>/mol-°K  
 $T$  = Average absolute in situ soil temperature, °K.

**Refined Procedures:**

$$\bar{E}_i = \frac{1}{\tau} \int_0^t E_{i(t)} dt \quad (25)$$

where  $\bar{E}_i$  = Average landfill cell emission rate of component i over the exposure averaging period  $\tau$ , g/s  
 $\tau$  = Exposure averaging period, yr (for residential land-use  $\tau$  = 30 years)  
 $E_{i(t)}$  = Instantaneous emission rate of i at time = t, g/s  
 $t$  = Time, yr.

Integration of Equation No. 25:

Note: In order to numerically integrate Equation 25, the instantaneous emission rate must be calculated for a series of time-steps from  $t = 0$  to  $t = \tau$ . For acceptable resolution, a minimum of 30 time-steps is required. Therefore:

$$\bar{E}_i = \frac{1}{\tau} \left[ \frac{h}{2} (E_0 + 2E_1 + 2E_2 + \dots + 2E_{n-1} + E_n) \right] \quad (26)$$

where  $\tau$  = Exposure averaging period, yr  
 $h$  = Time-step interval for  $t_0$  to  $t_n$ , yr ( $h = 1$  yr)

$E_{0,1,2 \dots n}$  = Emission rate of i at the initial and each succeeding time-step, g/s

$n$  = Number of time-steps.

If the landfill cell year-by-year acceptance rate is known:

$$E_{i(t)} = 2 L_o R \{ \exp(-kc) - \exp(-kt) \} C_{v,i} (3.17 \times 10^{-2}) \quad (27)$$

where  $E_{i(t)}$  = Emission rate of component i at the initial and each succeeding time-step, g/s

$L_o$  = Methane generation potential,  $m^3/Mg$  (default = 125  $m^3/Mg$ )

$R$  = Average annual landfill cell acceptance rate,  $Mg/yr$

$k$  = Methane generation rate constant,  $1/yr$  (default = 0.04/ $yr$ )

$c$  = Time since landfill cell closure to each time-step,  $yr$

$t$  = Cumulative time from initial cell refuse placement to each time-step,  $yr$

$C_{v,i}$  = Measured vapor-phase concentration of i immediately above the cell vapor source,  $g/cm^3$ -vapor (Equation 22)

$3.17 \times 10^{-2}$  = Factor to convert  $m^3/yr$  to  $cm^3/s$ .

Note: For unvented landfills, divide the emission rate by the landfill cell area to obtain the emission flux ( $g/m^2$ -s).

If year-by-year landfill cell acceptance rate is unknown:

$$R = L W Z \rho_r (1.0 \times 10^{-3})(1/\tau_L) \quad (28)$$

where  $R$  = Average annual cell acceptance rate,  $Mg/yr$

$L$  = Landfill cell length,  $m$

- W = Landfill cell width, m
- Z = Landfill cell depth, m
- $\rho_r$  = Refuse density, kg/m<sup>3</sup> (default = 650 kg/m<sup>3</sup>)
- $1.0 \times 10^{-3}$  = Conversion factor
- $\tau_L$  = Total time landfill cell accepted waste, yr.

Reference for Equation 23: *Superfund Exposure Assessment Manual*, Section 2.3.2, U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/1-88/001, April 1988.

Reference for Equation 27: *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources (AP-42)*. Section 2.4. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, 1994.

**STEP III. PART 3 - GASEOUS EMISSIONS FROM NONAERATED SURFACE IMPOUNDMENTS, OPEN TOP WASTEWATER TANKS AND CONTAINERS, AND AQUEOUS-PHASE CONTAMINANTS POOLED AT SOIL SURFACES**

The following emission models are used to estimate vapor-phase emissions from aqueous wastes. The screening-level model operates under the assumption of steady-state conditions.

With aqueous-phase concentrations, calculate the emission flux of each contaminant.

**Screening Procedures:**

$$F_i = K_i C_{L,i} (1 \times 10^4) \quad (29)$$

- where
- $F_i$  = Maximum emission flux of component i, g/m<sup>2</sup>-s
  - $K_i$  = Overall mass transfer coefficient of i, cm/s (Equation 30)
  - $C_{L,i}$  = Liquid-phase concentration of i, g/cm<sup>3</sup>  
(1 mg/L = 1x10<sup>-6</sup> g/cm<sup>3</sup>)
  - $1 \times 10^4$  = Factor to convert g/cm<sup>2</sup>-s to g/m<sup>2</sup>-s.

Calculation of overall mass transfer coefficient ( $K_i$ ):

$$\frac{1}{K_i} = \frac{1}{k_{iL}} + \frac{R T}{H_i k_{iG}} \quad (30)$$

- where
- $K_i$  = Overall mass transfer coefficient of component i, cm/s
  - $k_{iL}$  = Liquid-phase mass transfer coefficient of i, cm/s  
(Equation 31)
  - $R$  = Ideal gas constant, 8.2x10<sup>-5</sup> atm-m<sup>3</sup>/mole-°K
  - $T$  = Average system absolute temperature, °K
  - $H_i$  = Henry's Law constant of i, atm-m<sup>3</sup>/mole



$k_G$  = Gas-phase mass transfer coefficient of i, cm/s (Equation 32).

Estimation of liquid-phase mass transfer coefficient ( $k_L$ ):

$$k_{iL} = \left( \frac{MW_{O_2}}{MW_i} \right)^{0.5} \left( \frac{T}{298} \right) (k_L, O_2) \quad (31)$$

where  $k_L$  = Liquid-phase mass transfer coefficient of component i, cm/s

$MW_{O_2}$ ;  $MW_i$  = Molecular weights of oxygen (32.0) and component i, respectively, g/mol

T = Average system absolute temperature, °K

$k_L, O_2$  = Liquid-phase mass transfer coefficient of oxygen at 25° C, 0.002 cm/s.

Estimation of gas-phase mass transfer coefficient ( $k_G$ ):

$$k_{iG} = \left( \frac{MW_{H_2O}}{MW_i} \right)^{0.335} \left( \frac{T}{298} \right)^{1.005} (k_G, H_2O) \quad (32)$$

where  $k_G$  = Gas-phase mass transfer coefficient of component i, cm/s

$MW_{H_2O}$ ;  $MW_i$  = Molecular weights of water (18.0) and component i, respectively, g/mol

T = Average system absolute temperature, °K

$k_G, H_2O$  = Gas-phase mass transfer coefficient of water vapor at 25° C, 0.833 cm/s.

Note: The screening-level procedures are for quiescent systems. If agitated or dynamic systems are encountered, refer to the refined procedures that follow.

Reference for Equations 29, 30, 31, and 32: *Superfund Exposure Assessment Manual*, Section 2.3.2.1, U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/1-88/001, April 1988.

### ***Refined Procedures:***

The refined procedures for estimating vapor-phase emissions from aqueous systems can be found in the following document:

*Air Emissions Models for Waste and Wastewater.* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-453/R-94-080A, November 1994.

The procedures for estimating emissions due to volatilization from aqueous systems have been incorporated into a PC-based expert system entitled the Wastewater Treatment Compound Property Processor and Air Emissions Estimator (WATER8). Both the document referenced above and the WATER8 program are available free of charge from the EPA Office of Air Quality Planning and Standards (OAQPS) Technology Transfer Network (TTN) Bulletin Board. The TTN data telephone number is (919) 541-1447; the SYSOP number is (919) 541-4814. The reference document and WATER8 can be found within the Clearinghouse for Inventories and Emission Factors (CHIEF) section of the TTN under the subsection entitled "AP-42 and File Transfers" followed by the subsection entitled "Emission Estimation Software."

Of particular application to baseline conditions at Superfund sites, are the sections of the reference document entitled Disposal Impoundments with Quiescent Surfaces, Oil Film Surfaces, and Stationary Tank Storage. It should be kept in mind, however, that the reference document and the WATER8 model are most applicable to dynamic aqueous systems. Care must be taken to ensure that the correct model is applied to actual site conditions (e.g., steady-state versus plug flow, etc.). In addition, the user should note that transformation processes (e.g., biodegradation) are included in some models. Unless site-specific data are available on transformation rates, these processes should not be included in the model predictions (i.e., transformation rate constants should be set equal to zero).

Finally, the WATER8 model incorporates the chemical and physical property data base CHEMDAT8, which includes data for over 900 chemicals. If WATER8 is used along with other emission estimation procedures outlined in this document, chemical and physical properties must be held constant. This may require revising data for specific chemicals within the CHEMDAT8 data base for consistency.

### **Nonaqueous-phase Volatile Contaminants Directly Exposed to the Atmosphere :**

For any and all nonaqueous-phase volatile contaminants directly exposed to the atmosphere, in-depth air pathway analysis (APA) is warranted. Source monitoring is recommended to determine emission rates, supplemented by ambient monitoring and/or refined modeling. Applicable situations include open drums/containers, fresh spills, etc. where residual-phase contamination exists.

### STEP III. PART 4 - NONVOLATILES AND SEMIVOLATILES EMITTED AS PARTICULATE MATTER

The following procedures are used to estimate the emissions of nonvolatile contaminants and semivolatile contaminants adsorbed to soils as fugitive dust generated by wind erosion. Concentrations used in the emission models should be from erodible surface materials (surface to 6 inches). In the case of screening-level estimates, no mass balance is performed for semivolatiles emitted as particulate matter and also emitted in vapor-phase from soils. For refined estimates, the average residual concentration within each exposure area due to wind erosion over the exposure period may be calculated and this concentration used as the initial concentration for estimating vapor-phase emissions.

#### **Screening-Level Procedures:**

For screening-level estimates, use Equation 33 from the refined procedures section which follows. Set the equivalent threshold value of windspeed at a 7 meter anemometer height ( $u_t^7$ ) to 11.32 m/s. This value of  $u_t^7$  was calculated assuming a corrected threshold friction velocity ( $u_t^*$ ) of 0.625 m/s and a typical roughness height ( $z_0$ ) for open terrain of 0.5 cm.

#### **Refined Procedures:**

For estimating emissions from wind erosion, either of two emission flux ( $\text{g}/\text{m}^2\text{-s}$ ) models are used depending on the erodability classification of the site surface material. These two models are the: 1) "unlimited reservoir," and 2) "limited reservoir." Each site surface of homogeneous contaminant concentration must be placed into one of these two classifications. The following decision flow chart (Figure 1) is used to determine: 1) whether no wind erosion potential exists, or 2) which of the two emission flux models is applicable for site conditions. The instructions within each box of the flow chart are detailed in the list of steps below.

It should be noted that the two emission flux models (Equations 33 and 35) represent average annual emissions. This assumes continuous emissions over time. In actuality, emissions do not occur except during periods when the windspeed meets or exceeds the threshold friction velocity for the given soil aggregate size. A continuous average emission flux is calculated to account for a continuous exposure interval (i.e., hours/day x days/year x years).

#### Detailed Steps for Flow Chart:

No. 1      Continuous Vegetation?

Continuous vegetation means "unbroken" vegetation covering 100 percent of the emission source area to be analyzed.

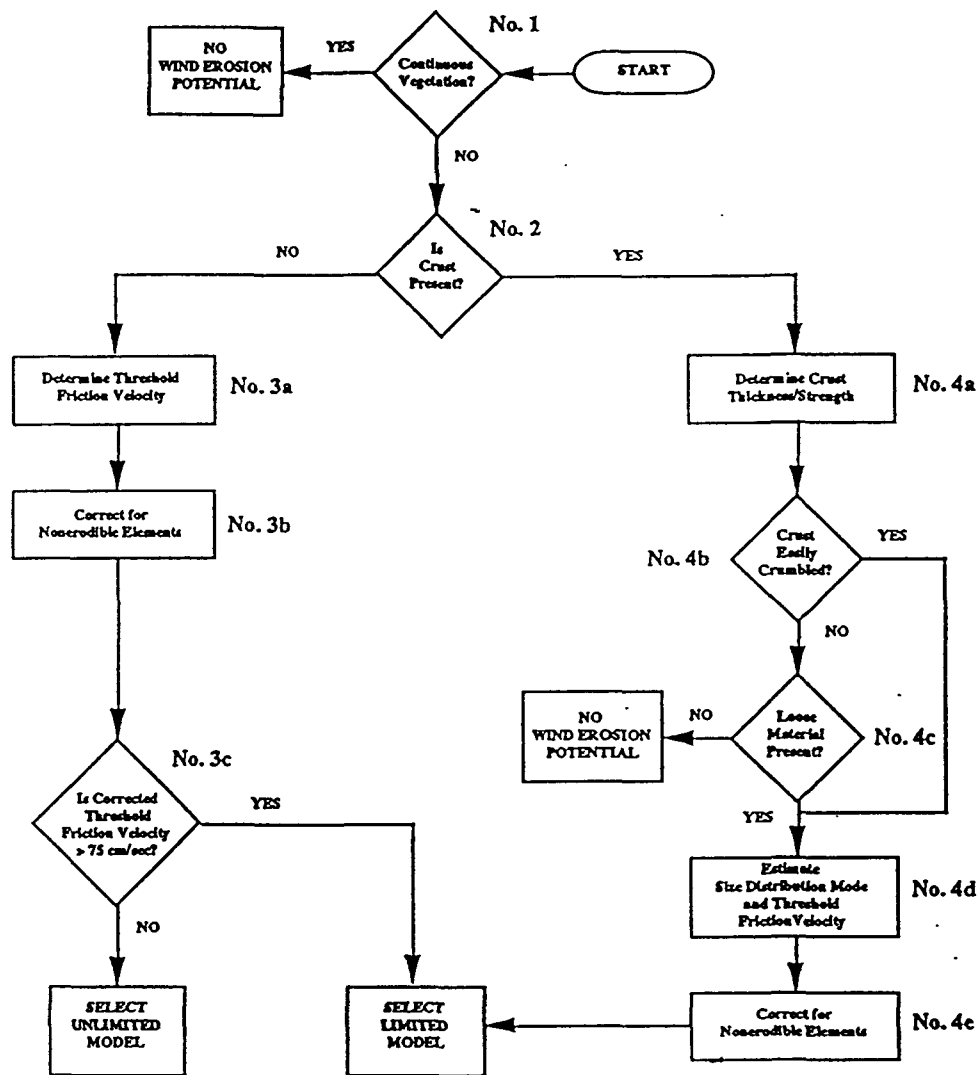


Figure 1. Wind erosion model decision flow chart.

No. 2      Is Crust Present?

Crusted surfaces are regarded as having a "limited reservoir" of erodible particles. Check for crust thickness/strength during the site inspection.

No. 3a      Determine Threshold Friction Velocity

Threshold friction velocity ( $u_t'$ ) is that wind velocity at which erodible surface particles are suspended. To determine  $u_t'$ , the mode of the surface aggregate size distribution must be determined. The distribution mode is the aggregate size containing the highest percentage of material from a representative sample. This can be determined with a field sieving procedure as follows:

1. Prepare a nest of sieves with the following openings: 4 mm, 2 mm, 1 mm, 0.5 mm, and 0.25 mm. Place a collector pan below the bottom sieve (0.25 mm opening).
2. Collect a sample representing the surface layer of loose particles (approximately 1 cm in depth for an uncrusted surface), removing any objects larger than about 1 cm in average physical diameter (nonerodible material). The area to be sampled should not be less than 30 cm x 30 cm.
3. Pour the sample into the top sieve (4 mm opening), and place a lid on top.
4. Rotate the covered sieve/pan by hand using broad sweeping arm motions in the horizontal plane. Complete 20 rotations at a speed just necessary to achieve some relative horizontal motion between the sieve and the particles.
5. Inspect the relative quantities of catch within each sieve and determine where the mode in the aggregate size distribution lies, i.e., between the opening size of the sieve with the largest catch and the opening size of the next largest sieve (e.g., 0.375 mm lies between the 0.5 mm and the 0.25 mm sieve).

With the aggregate size distribution mode, determine the threshold friction velocity ( $u_t'$ ) in cm/s from the relationship in Figure 1a. A conservative default is 50 cm/s.

Note:      Soil particle size distribution determined by laboratory methods cannot be used to determine the in-situ soil aggregate size distribution.

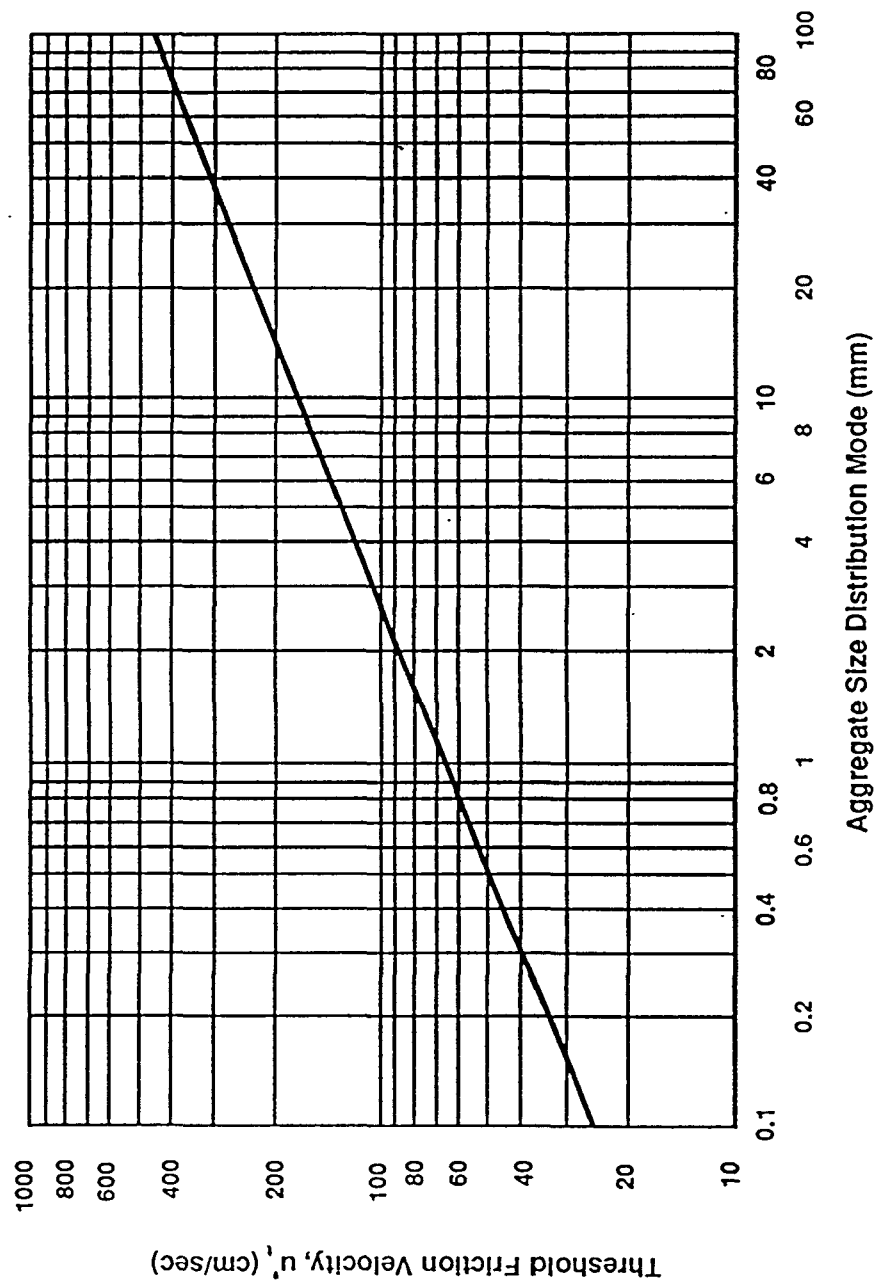


Figure 1a. Threshold friction velocity versus aggregate size distribution.

No. 3b Correct for Nonerodible Elements

Mark off a representative site area 1m x 1m and determine the fraction of total area, as viewed from directly overhead, that is occupied by nonerodible elements (e.g., stones, clumps of grass, etc.). Nonerodible elements can be said to exceed 1 cm in diameter. Correct the overhead fractional area of nonerodible elements to the equivalent projected frontal area. An example would be that a spherical stone with an area of 10 cm<sup>2</sup> as viewed from overhead but half-buried in the soil, would have a frontal projected area of 5 cm<sup>2</sup>. Determine the ratio of the frontal projected area of nonerodible elements to the total overhead area of the erodible soil. This ratio ( $L_c$ ) is used with the relationship shown in Figure 1b to determine the appropriate correction factor. Multiply  $u_t^*$  by the correction factor to obtain the corrected threshold friction velocity ( $u_t^*$ ).

Note: If data for determining  $L_c$  is not available, a conservative default value of 0.003 may be used for nonsmooth soil surfaces. This results in a correction factor of approximately 1.25.

No. 3c Is Corrected Threshold Friction Velocity >75 cm/s?

75 cm/s is an empirical number determined through observation of actual soil types.

No. 4a Determine Crust Thickness/Strength  
and

No. 4b Crust Easily Crumbled?

If the crust thickness is <0.6 cm or if the crust can be easily crumbled by hand pressure it exhibits a potential for wind erosion.

No. 4c Loose Material Present?

Determine if there is loose erodible material above any hardened crust.

No. 4d Estimate Size Distribution Mode and Threshold Friction Velocity

Estimate the aggregate size distribution mode of the loose material above the hardened crust and determine the threshold friction velocity ( $u_t^*$ ) (Step 3a).

No. 4e Correct for Nonerodible Elements ( $u_t^*$ )

(Step 3b)



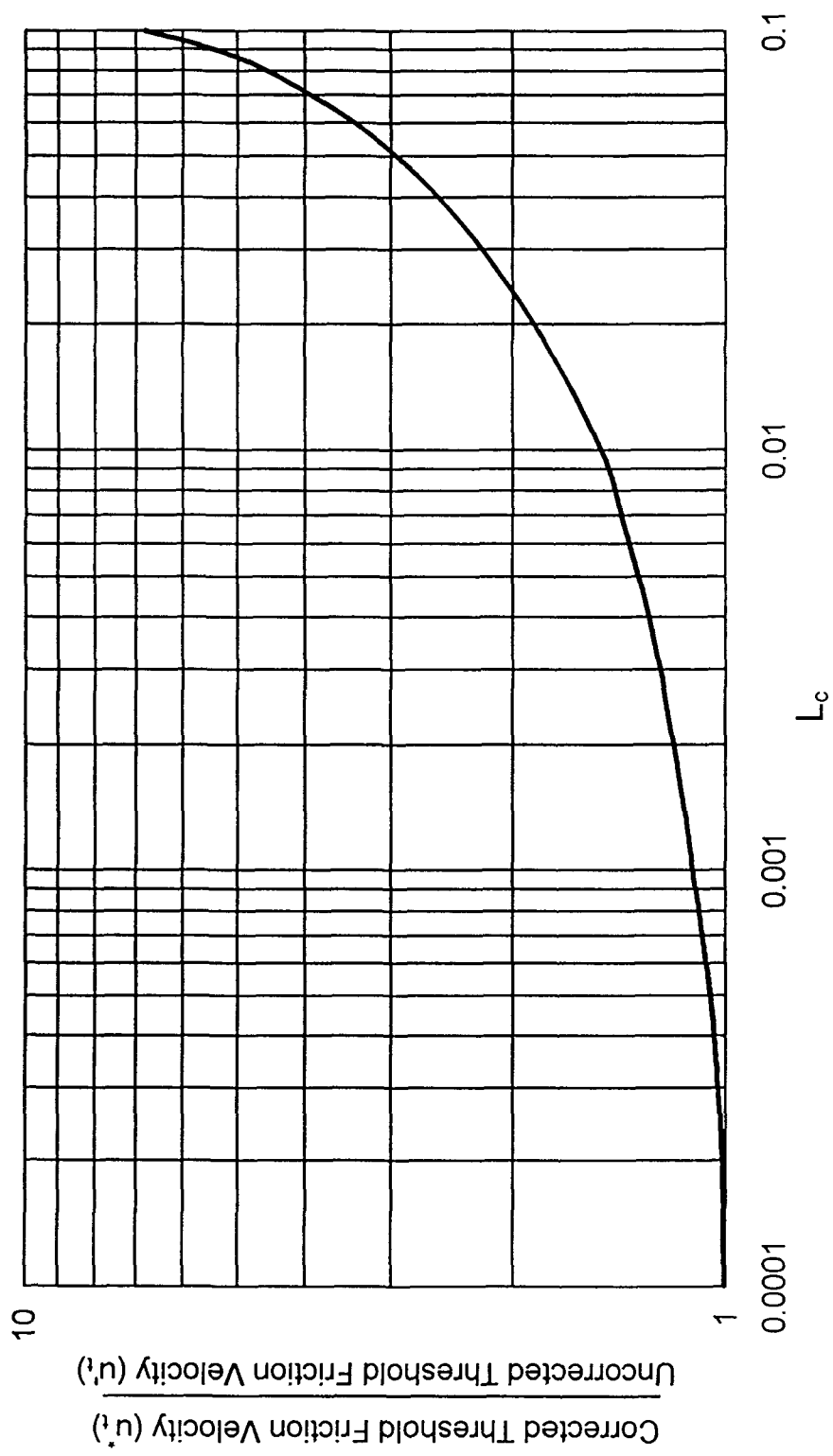


Figure 1b. Increase in threshold friction velocity with  $L_c$ .

Using either the "unlimited reservoir" or the "limited reservoir" model as determined from Figure 1, calculate an annual average emission flux (g/m<sup>2</sup>-s) for each contaminant found in the erodible surface material.

A. Using the "unlimited reservoir" model

Emission flux for inhalable particles  $\leq 10 \mu\text{m}$  (PM<sub>10</sub>):

$$\bar{F}_i = \left[ 0.036 (1-V) \left( \frac{[u]}{u_t^7} \right)^3 F(x) C_i \right] \frac{1}{3600} \quad (33)$$

where  $\bar{F}_i$  = PM<sub>10</sub> annual average emission flux of component i, g/m<sup>2</sup>-s

V = Fraction of contaminated surface with continuous vegetative cover (equals 0 for bare soil)

[u] = Mean annual windspeed, m/s (from local climatological data)

$u_t^7$  = Equivalent threshold value of windspeed at a 7 m anemometer height, m/s (Equation 34)

$C_i$  = Fraction by weight of component i from bulk samples of surface material

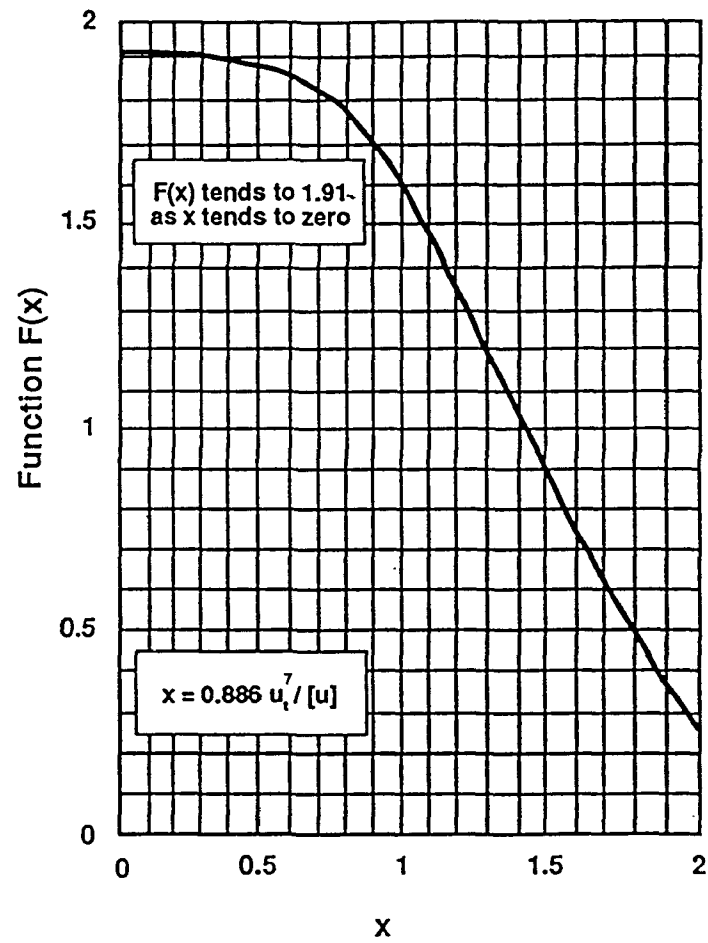
F(x) = Function obtained from the relationship in Figure 2 (x=0.886  $u_t^7$ /[u], dimensionless ratio).

Calculation of the equivalent threshold value of windspeed at a 7 m anemometer height ( $u_t^7$ ):

$$u_t^7 = \left[ \frac{u_t^*}{0.4} \ln \left( \frac{700}{z_o} \right) \right] / 100 \quad (34)$$

where  $u_t^7$  = Equivalent threshold value of windspeed at a 7 m anemometer height, m/s

$u_t^*$  = Threshold friction velocity corrected for nonerodible elements, cm/s (Step 3b)



NOTE: If  $x > 2$ ,  
 $F(x) = 0.18 (8x^3 + 12x) e^{-x^2}$

Figure 2. Function curve used in "unlimited reservoir" model.

$z_0$  = Surface roughness height, cm (default = 0.5 cm for flat terrain).

See also the Note after Equation 37.

B. Using the "limited reservoir" model.

Emission flux for inhalable particles  $\leq 10 \mu\text{m}$  ( $\text{PM}_{10}$ ):

$$\bar{F}_i = 0.5 \left[ \sum_{i=1}^N \frac{P_i (1-V)}{(PE/50)^2} \right] C_i \left[ \frac{1}{31,536,000 \text{ s/yr}} \right] \quad (35)$$

where  $\bar{F}_i$  =  $\text{PM}_{10}$  annual average emission flux of component i,  $\text{g/m}^2\text{-s}$

0.5 = Particle size multiplier for  $\text{PM}_{10}$

N = Number of surface material disturbances per year (default = 12/yr for sites with no activity)

$P_i$  = Erosion potential of component i corresponding to the observed or probable highest windspeed for the ith period between disturbances,  $\text{g/m}^2$

$C_i$  = Fraction by weight of component i from bulk samples of surface material

V = Fraction of continuous vegetative cover

PE = Thornthwaite's Precipitation - Evaporation Index used as a measure of soil moisture content (Figure 3).

Note: Values of the PE from Figure 3 which are  $\leq 50$  should be set equal to 50.

Calculation of the erosion potential ( $P_i$ ):

$$P_i = 58 (u^* - u_t^*)^2 + 25 (u^* - u_t^*), P_i = 0 \text{ for } u^* \leq u_t^* \quad (36)$$

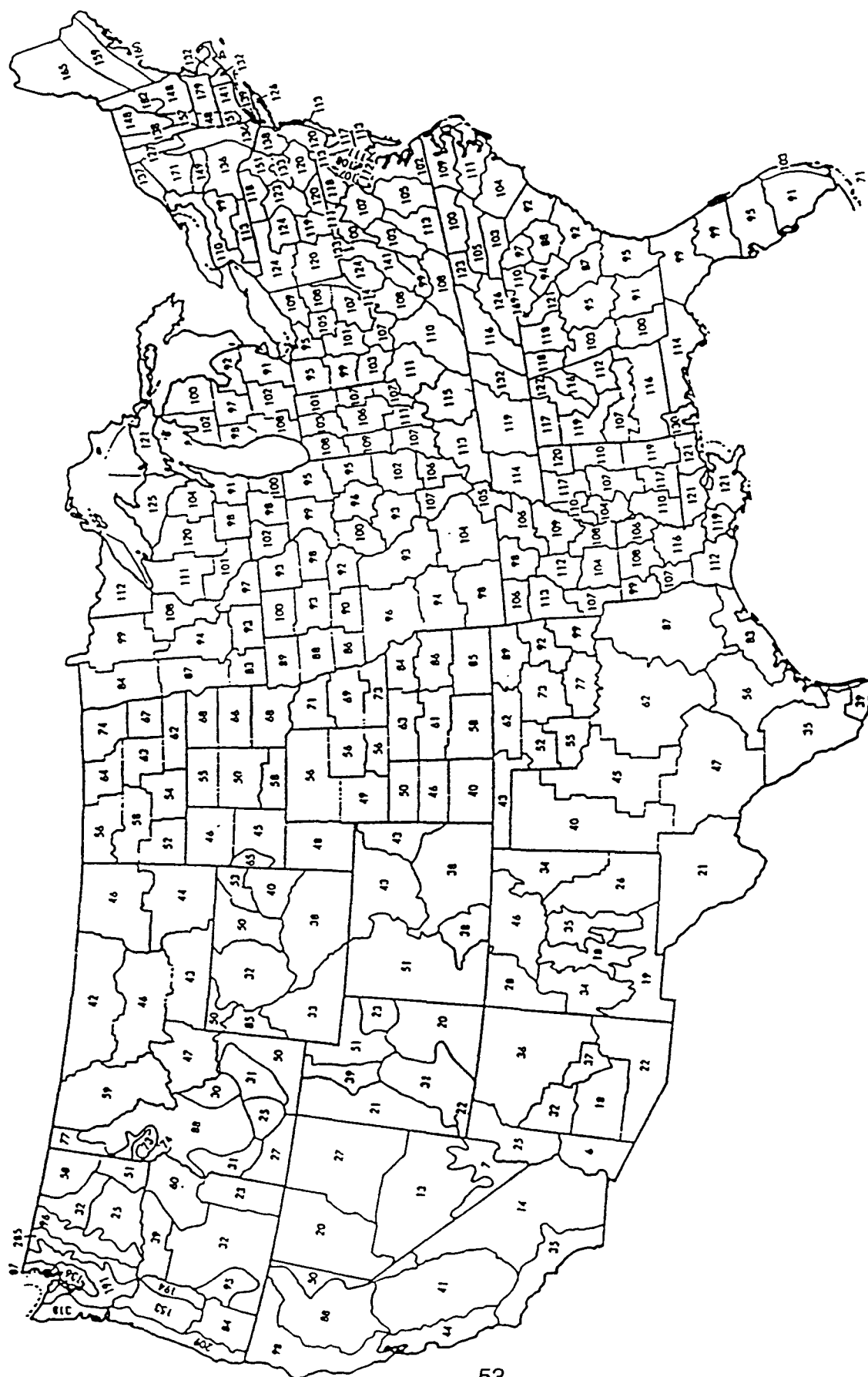


Figure 3. Thornthwaite's Precipitation-Evaporation Index (PE) for State Climatological Divisions.

where  $u^*$  = Windspeed at surface roughness height  $z_0$  of the observed or probable highest windspeed for the  $i$ th period between disturbances, m/s (Equation 37)

$u^*$  = Threshold friction velocity corrected for nonerodible elements, m/s (Step 3b)

Calculation of  $u^*$ :

$$u^* = \frac{u_z 0.4}{\ln(z/z_0)} \quad (37)$$

where  $u^*$  = Observed or probable windspeed at roughness height  $z_0$ , m/s

$u_z$  = Observed or probable windspeed at anemometer height  $z$ , m/s

$z$  = Anemometer height, cm

$z_0$  = Surface roughness height, cm

Note: Equation 35 calculates the total yearly erosion potential ( $\text{g}/\text{m}^2$ ) as a function of the number of disturbances ( $N$ ) and the highest windspeed between disturbances. The erosion potentials of all events are summed and divided by a one year averaging time in seconds. This calculation yields an average emission flux (including periods of zero emissions) to account for continuous exposure. Therefore, the calculated annual average emission flux and subsequent ambient air concentration are not appropriate for exposure averaging times less than one year. Actual short-term concentrations (e.g., minutes to hours) will be considerably higher.

Equation 35 may also be used for sites with an unlimited reservoir of erodible particles by assuming  $N$  = number of hourly meteorological windspeed observations per year where the resulting windspeed at the surface roughness height (Equation 37) is greater than or equal to the value of the corrected threshold friction velocity ( $u^*$ ).

Reference for Equation No. 33: *Rapid Assessment of Exposure to Particulate Emissions from Surface Contamination Sites*, Sections 1 - 4.1.2. Office of Health and Environmental Assessment, Washington, D.C. EPA-600/8-85/002, NTIS PB85-192219, February 1985.

Reference for Equation Nos. 35 and 36: Adapted from *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources, and Supplements (AP-42)*. Office of Air Quality Planning and Standards, Research Triangle Park, N.C., 1985.

## **STEP IV. ESTIMATE AMBIENT AIR CONCENTRATIONS AT RECEPTOR LOCATIONS OF INTEREST**

### **Background:**

Once emission rates have been calculated for all sources, atmospheric dispersion models are used to estimate exposure point ambient air concentrations at receptors of interest. The following dispersion models have been determined to yield the best estimates of long-term average concentrations given the types of emission sources and source/receptor geometry typically encountered at Superfund sites under baseline or undisturbed conditions.

At the time of publication of this document, the screening-level and refined models specified herein for area sources of emissions are regulatory models. Testing has confirmed that for area source emissions, these algorithms produce better concentration estimates for near-field receptors (i.e., within one side-length of the area source). In addition, these algorithms also allow on-site receptors, critical for most future land-use scenarios (e.g., future residential or commercial/industrial receptors within the area of contamination).

### ***Screening-Level Procedures:***

The screening-level procedures use the TSCREEN dispersion model (dated 95260) amended with the new SCREEN3 model area source algorithm. Due to these revisions in the TSCREEN model, ambient air impacts for scenarios that use the new revised area source algorithm are different than those obtained from the previous version of TSCREEN (dated 94133). The TSCREEN files and associated documentation can be obtained from the U.S. EPA Office of Air Quality Planning and Standards (OAQPS) Technology Transfer Network (TTN). See page 42 for details on how to access the OAQPS TTN.

The TSCREEN files can be found within the Support Center for Regulatory Air Models (SCRAM) section of the TTN. All executable files and associated document files should be downloaded and uncompressed as necessary using the file PKUNZIP.EXE which is also available on the TTN.



## Current Land-Use :

Estimates of risk for current land-use involve estimating long-term average exposure point air concentrations at contemporaneous receptors. Such receptors might include actual residences, commercial/industrial properties or other types of receptors near the site. When more than one receptor exists it may be necessary to estimate concentrations at each receptor. These concentrations along with the respective exposure assumptions will determine which receptor controls the risk.

1. On a site plot plan or other map drawn to scale, divide the site into the square exposure areas (EAs) previously determined for sampling and for emission estimation.
2. Locate on the map used in Step 1, the location of each potential receptor.
3. Measure and record the distance from the center of each EA to the first receptor.
4. Use the TSCREEN model to estimate the combined air concentration contributed by each EA at the first receptor. Run the model for area sources with the following specifications:
  - A. Set the "Initial Form of Release" as a "Superfund Release Type."
  - B. Set the "Superfund Release Type" to "Soil Excavation."
  - C. Answer Yes to "Is the Emission Rate ( $Q_m$ ) known (Y/N)."
  - D. Enter as the emission rate, the area of one EA in square meters (e.g., an EA of one-half acre is 2023.5 m<sup>2</sup>).
  - E. Under "Release Parameter," enter as the "Area of the Emitting Source (A)" the area of one EA in square meters (i.e., the same area as in Step 4.D. above).
  - F. Specify the "Urban/Rural Classification."
  - G. Under "Fenceline Distance," enter the shortest distance between the center of each EA and the receptor as determined in Step 3.
  - H. "Receptor Height above Ground ( $Z_r$ )" should remain zero.
  - I. Answer Yes to "Do you have specific locations where you would like pollutant concentrations to be calculated (Y/N)."

- J. Enter the remaining EA-to-receptor distances as determined in Step 3. If more than 30 distances are required, two or more model runs will be necessary.
  - K. After the model has run, record the estimated concentrations for each discrete receptor distance entered. These are normalized concentrations based on an emission flux of 1 g/m<sup>2</sup>-s.
5. For each contaminant, multiply the actual screening-level emission flux estimates for each EA by the corresponding normalized concentration as determined in Step 4.K. The product is the corrected concentration contributed by each EA.
  6. For each contaminant, sum the corrected concentrations and multiply each sum by 0.08 to convert the one-hour TSCREEN estimate to an annual average concentration.
  7. Repeat steps 4 through 6 for each additional receptor.
  8. For each contaminant, the highest receptor annual average concentration is used as the screening-level exposure point concentration for current land-use.

#### **Future Land-Use:**

Estimates of risk for future land-use involve estimating long-term average exposure point air concentrations at potential future receptor locations. Typically, the potential future receptor that will experience the highest long-term air concentration contributed by the site will be located directly above the center of the exposure area with the highest emission flux of each contaminant. In addition to the emissions from this exposure area, the contribution of the emissions from the remaining exposure areas at this location must also be considered.

1. On a site plot plan or other map drawn to scale, divide the site into the square exposure areas (EAs) previously determined for sampling and emission estimation.
2. Locate on the map used in Step 1, the center of the EA with the highest emission flux of the first contaminant.
3. Measure and record the distance from the center of each remaining EA to the center of the EA determined in Step 2.

4. Use the TSCREEN model to estimate the combined air concentration as contributed by each exposure area at the center of the exposure area determined in Step 2. Run the model for area sources with the following specifications:
  - A. Duplicate the model inputs previously specified for the current land-use scenario (Step 4, A-F).
  - B. Under "Fenceline Distance," enter 1 meter. This entry is used to estimate the concentration at the center of the EA with the highest emission flux.
  - C. "Receptor Height above Ground ( $Z_r$ )" should remain zero.
  - D. Answer Yes to "Do you have specific locations where you would like pollutant concentrations to be calculated (Y/N)."
  - E. Enter the remaining distances from the center of each EA to the center of the EA determined in Step 2.
  - F. After the model has run, record the estimated concentrations for each discrete receptor distance entered including the 1 meter distance. These are normalized concentrations based on an emission flux of 1 g/m<sup>2</sup>-s.
5. Perform Steps 5 and 6 as specified for the current land-use scenario.
6. Repeat Steps 4 and 5 above for each contaminant.
7. The combined annual average air concentration estimated at the center of the EA with the highest emission flux of each contaminant is used as the screening-level exposure point concentration for future land-use.

Note: For emissions from vented storage tanks, use the "Stacks, Vents, Conventional Point Sources" gaseous release type as the "Initial Form of Release." Set the exit velocity (Exit V) equal to 0.01 m/s; set the emission rate ( $Q_m$ ) equal to 1 g/s.

For emissions from vented landfills, use the "Municipal Solid Waste Landfills" gaseous release type as the "Initial Form of Release." Set the emission rate ( $Q_m$ ) equal to 1 g/s; set the release height above ground equal to the height of the vents.

References for Step IV, Screening-Level Procedures: Adapted from *A Tiered Modeling Approach for Assessing the Risks Due to Sources of Hazardous Air Pollutants*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-450/4-92-001, 1992.

*User's Guide to TSCREEN: A Model for Screening Toxic Air Pollutant Concentrations*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-454/B-94-023, 1994.

### ***Refined Procedures:***

Refined dispersion modeling procedures use refined dispersion models to estimate exposure point concentrations at receptors of interest. Refined dispersion models use meteorological data representative of site conditions and are capable of simultaneously estimating contributions from multiple sources of emissions with different emission rates. For area sources of emissions, the refined procedures specify the use of the Industrial Source Complex Model Version 3 in the Short-Term mode (ISCST3). Similar to the algorithms incorporated into the new TSCREEN model used for screening-level analysis, the ISCST3 model algorithms have been shown to produce better concentration estimates for near-field receptors and also allow on-site receptors.

The ISCST3 model can be used with five years of one-hour meteorological data from the nearest National Weather Service (NWS) station which is representative of site conditions; or may be used with one year of quality-assured onsite one-hour meteorological data. Both the ISCST3 model and NWS meteorological data are available on the Support Center for Regulatory Air Models (SCRAM) bulletin board of the Office of Air Quality Planning and Standards (OAQPS) Technology Transfer Network (TTN). See page 42 for details on how to access the OAQPS TTN. Setup and execution of this model must follow the procedures specified in the references for this section.

As with the screening-level procedures, the refined procedures are used to estimate exposure point air concentrations for both current and future land-use scenarios. Annual average air concentrations estimated using the refined emission and dispersion modeling procedures are used as exposure point concentrations in the baseline risk assessment.

References for Step IV, Refined Procedures: *Guideline on Air Quality Models (Revised)*. U.S. Environmental Protection Agency, Office of Air Quality Planning Standards, Research Triangle Park, North Carolina, EPA-450/2-78-027R, 1988.

*User's Guide for the Industrial Source Complex (ISC3) Dispersion Models, Volumes 1 and 2*. U.S. Environmental Protection Agency, Office of Air Quality Planning Standards, Research Triangle Park, North Carolina, EPA-454/B-95-003a and b, 1995.

## **STEP V. ORGANIZE EXPOSURE POINT CONCENTRATIONS FOR INPUT TO THE BASELINE RISK ASSESSMENT**

1. In tabular form, list the long-term (annual average) ambient air concentrations of each potential airborne contaminant derived from Step IV. Include these air concentrations in the summary of exposure point concentrations for all pathways.

Note: For baseline conditions, long-term concentration averages representative of the reasonable maximum exposure scenario are most applicable for the baseline risk assessment. If emission potentials are significant, however, short-term or acute concentration estimates (e.g., 1-h, 3-h, 8-h, or 24-h average) may be required.

2. List all variables and assumptions used in the emission and dispersion modeling analyses and discuss the uncertainty associated with each as well as how this uncertainty may affect the final estimates.

Reference for Step V: *Risk Assessment Guidance for Superfund; Volume I, Human Health Evaluation Manual (Part A), Interim Final*. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., EPA/540/1-89/002, December 1989.

**APPENDIX A**

**RECHARGE ESTIMATES BY HYDROGEOLOGIC SETTINGS**

## Recharge Estimates for DRASTIC Hydrogeologic Settings

from (Newell et al., Hydrogeologic Database for Ground Water Modeling, 1989)

Mountain slope and mountain flank settings are not included.

Region	Setting	Recharge (m/yr)		
		Min.	Max.	Avg.
<i>Western Mountain Ranges</i>				
	Alluvial Mountain Valleys Facing East	0.00	0.05	0.03
	Alluvial Mountain Valleys Facing West	0.05	0.10	0.08
	Glacial Mountain Valleys	0.10	0.18	0.14
	Wide Alluvial Valleys Facing East	0.05	0.10	0.08
	Wide Alluvial Valleys Facing West	0.10	0.18	0.14
	Coastal Beaches	0.25	0.38	0.32
	Swamp/Marsh	0.10	0.18	0.14
	Mud Flows	0.18	0.25	0.22
	Regional Average :			0.14
<i>Alluvial Basins</i>				
	Alluvial Mountain Valleys	0.00	0.05	0.03
	Alluvial Fans	0.00	0.05	0.03
	Alluvial Basins with Internal Drainage	0.00	0.05	0.03
	Playa Lakes	0.00	0.05	0.03
	Swamp/Marsh	0.05	0.10	0.08
	Coastal Lowlands	0.25	0.38	0.32
	River Alluvium With Overbank Deposits	0.18	0.25	0.22
	River Alluvium Without Overbank Deposits	0.25	0.38	0.32
	Mud Flows	0.18	0.25	0.22
	Alternating Sandstone and Shale	0.18	0.25	0.22
	Continental Deposits	0.00	0.05	0.03
	Regional Average :			0.14
<i>Columbia Lava Plateau</i>				
	Alluvial Mountain Valleys	0.05	0.10	0.08
	Lava Flows: Hydraulically Connected	0.05	0.10	0.08
	Lava Flows: Not Hydraulically Connected	0.05	0.10	0.08
	Alluvial Fans	0.05	0.10	0.08
	Swamp/Marsh	0.00	0.05	0.03
	River Alluvium	0.10	0.18	0.14
	Regional Average :			0.08
<i>Colorado Plateau and Wyoming Basin</i>				
	Resistant Ridges	0.00	0.05	0.03
	Consolidated Sedimentary Rocks	0.00	0.05	0.03
	River Alluvium	0.10	0.18	0.14
	Alluvium and Dune Sand	0.00	0.05	0.03
	Swamp/Marsh	0.18	0.25	0.22
	Regional Average :			0.09
<i>High Plains</i>				
	Ogalalla	0.00	0.05	0.03
	Alluvium	0.00	0.05	0.03
	Sand Dunes	0.00	0.05	0.03
	Playa Lakes	0.00	0.05	0.03
	Braided River Deposits	0.10	0.18	0.14
	Swamp/Marsh	0.18	0.25	0.22
	River Alluvium with Overbank Deposits	0.00	0.05	0.03
	River Alluvium without Overbank Deposits	0.00	0.05	0.03
	Alternating Sandstone, Limestone, and Shale Sequences	0.00	0.05	0.03
	Regional Average :			0.06

## Recharge Estimates for DRASTIC Hydrogeologic Settings

from (Newell et al., Hydrogeologic Database for Ground Water Modeling, 1989)

Mountain slope and mountain flank settings are not included.

Region	Setting	Recharge (m/yr)		
		Min.	Max.	Avg.
<i>Non-Glaciased Central Region</i>				
	Alluvial Mountain Valleys	0.10	0.18	0.14
	Alternating Beds of Sandstone, Limestone, or Shale Under Thin Soil	0.10	0.18	0.14
	Alternating Beds of Sandstone, Limestone, or Shale Under Deep Regolith	0.10	0.18	0.14
	Solution Limestone	0.25	0.38	0.32
	River Alluvium with Overbank Deposits	0.18	0.25	0.22
	River Alluvium without Overbank Deposits	0.18	0.25	0.22
	Braided River Deposits	0.10	0.18	0.14
	Triassic Basins	0.10	0.18	0.14
	Swamp/Marsh	0.10	0.18	0.14
	Blocks	0.00	0.05	0.03
	Unconsolidated and Semi-Consolidated Aquifers	0.00	0.05	0.03
	Regional Average :			0.15
<i>Glaciased Central Region</i>				
	Till Over Bedded Sedimentary Rock	0.10	0.18	0.14
	Till Over Outwash	0.10	0.18	0.14
	Till Over Solution Limestone	0.10	0.18	0.14
	Till Over Sandstone	0.10	0.18	0.14
	Till Over Shale	0.10	0.18	0.14
	Outwash	0.18	0.25	0.22
	Rock	0.25	0.38	0.32
	Outwash Over Solution Limestone	0.25	0.38	0.32
	Moraine	0.18	0.25	0.22
	Buried Valley	0.18	0.25	0.22
	River Alluvium with Overbank Deposits	0.10	0.18	0.14
	River Alluvium without Overbank Deposits	0.25	0.38	0.32
	Glacial Lake Deposits	0.10	0.18	0.14
	Thin Till Over Bedded Sedimentary Rock	0.18	0.25	0.22
	Beaches, Beach Ridges, and Sand Dunes	0.25	0.38	0.32
	Swamp/Marsh	0.10	0.18	0.14
	Regional Average :			0.20
<i>Piedmont Blue Ridge Region</i>				
	Alluvial Mountain Valleys	0.18	0.25	0.22
	Regolith	0.10	0.18	0.14
	River Alluvium	0.18	0.25	0.22
	Mountain Crests	0.00	0.05	0.03
	Swamp/Marsh	0.10	0.18	0.14
	Regional Average :			0.15
<i>Northeast and Superior Uplands</i>				
	Alluvial Mountain Valleys	0.18	0.25	0.22
	Glacial Till Over Crystalline Bedrock	0.18	0.25	0.22
	Glacial Till Over Outwash	0.18	0.25	0.22
	Outwash	0.25	0.38	0.32

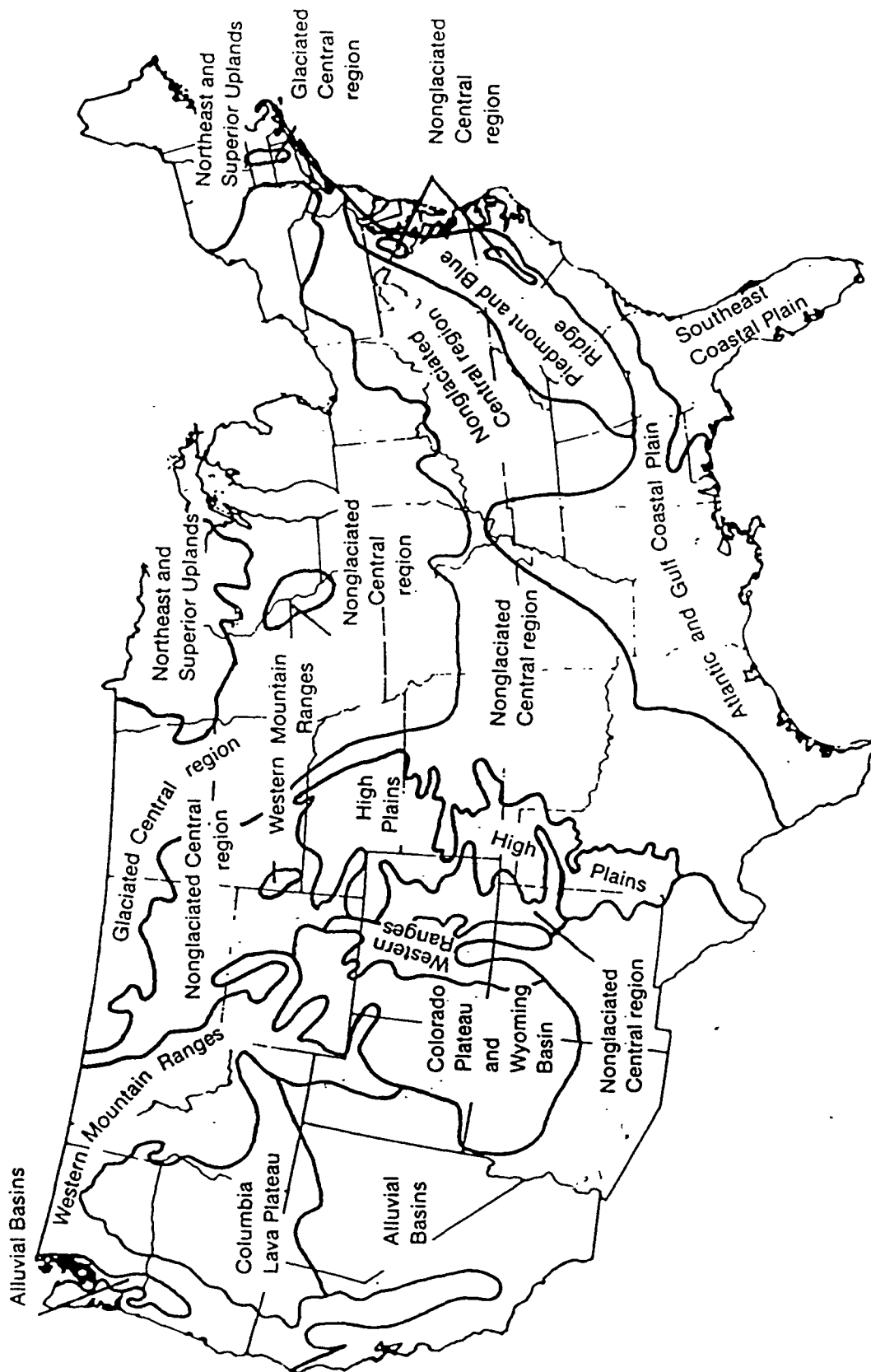


## Recharge Estimates for DRASTIC Hydrogeologic Settings

from (Newell et al., Hydrogeologic Database for Ground Water Modeling, 1989)

Mountain slope and mountain flank settings are not included.

Region	Setting	Recharge (m/yr)		
		Min.	Max.	Avg.
	Moraine	0.18	0.25	0.22
	River Alluvium with Overbank Deposits	0.18	0.25	0.22
	River Alluvium without Overbank Deposits	0.25	0.38	0.32
	Swamp/Marsh	0.10	0.18	0.14
	Bedrock Uplands	0.10	0.18	0.14
	Glacial Lakes/Glacial Marine Deposits	0.10	0.18	0.14
	Beaches, Beach Ridges and Sand Dunes	0.25	0.38	0.32
	Regional Average :			0.22
<i>Atlantic and Gulf Coast</i>				
	Regional Aquifers	0.00	0.05	0.03
	Unconsolidated and Semi-Consolidated			
	Shallow Surficial Aquifers	0.25	0.38	0.32
	River Alluvium with Overbank Deposits	0.18	0.25	0.22
	River Alluvium without Overbank Deposits	0.25	0.38	0.32
	Swamp	0.25	0.38	0.32
	Regional Average :			0.24
<i>Southeast Coastal Plain</i>				
	Solution Limestone and Shallow Surficial			
	Aquifers	0.25	0.38	0.32
	Coastal Deposits	0.25	0.38	0.32
	Swamp	0.25	0.38	0.32
	Beaches and Bars	0.25	0.38	0.32
	Regional Average :			0.32



**APPENDIX B**  
**EXAMPLE CALCULATIONS**

## EXAMPLE 1

### Calculate the Soil Saturation Concentration ( $C_{sat}$ ) of Benzene

#### Soil/Site Properties:

- Site is located in Maine.
- Hydrogeologic setting is "outwash."
- Soil type is "sandy loam."
- Soil dry bulk density ( $\beta$ ) = 1.5 kg/L.
- Soil particle density ( $\rho_s$ ) = 2.65 kg/L (default).
- Fraction of organic carbon in soil ( $f_{oc}$ ) = 0.006 (default).

#### Chemical Properties of Benzene:

- Henry's law constant ( $H_i$ ) = 5.4 E-03 atm-m<sup>3</sup>/mol.
- Solubility in water ( $S_i$ ) = 1,780 mg/L.
- Organic carbon partition coefficient ( $K_{oc}$ ) = 57 L/kg.

- A. Estimate average long-term volumetric soil moisture content ( $\Theta_w$ ) using Equation 2:

$$\theta_w = \theta_t (I/K_s)^{1/(2b+3)}$$

$$\Theta_t = 1 - \beta/\rho_s \text{ (Equation 1 legend)}$$

$$\Theta_t = 1 - 1.5/2.65$$

$$\Theta_t = 0.434$$

$$I = 0.32 \text{ m/yr (Appendix A)}$$

$$K_s = 230 \text{ m/yr (Table 1)}$$

$$1/(2b+3) = 0.080 \text{ (Table 1)}$$

$$\text{Therefore, } \Theta_w = 0.434 (0.32/230)^{0.080}$$

$$\Theta_w = 0.256$$

- B. Calculate the soil saturation concentration using Equation 1:

$$C_{sat,i} = \frac{S_i}{\beta} (K_{d,i} \beta + \theta_w + H_i' \theta_a)$$

where

$$\begin{aligned}
 K_{d,i} &= K_{oc} \times f_{oc} \text{ (Equation 3)} \\
 K_{d,i} &= 57 \times 0.006 \\
 K_{d,i} &= 0.342 \\
 \\ 
 \theta_a &= \theta_t - \theta_w \text{ (Equation 1 legend)} \\
 \theta_a &= 0.434 - 0.256 \\
 \theta_a &= 0.178 \\
 \\ 
 H'_i &= H_i \times 41 \text{ (Equation 1 legend)} \\
 H'_i &= 5.4 \text{ E-03} \times 41 \\
 H'_i &= 0.2214
 \end{aligned}$$

Therefore,

$$C_{sat,i} = \frac{1780}{1.5} (0.342 \times 1.5 + 0.256 + 0.2214 \times 0.178)$$

$$C_{sat,i} = 959 \text{ mg/kg}$$

## EXAMPLE 2

### Calculate the Average Emission Flux ( $\bar{F}_i$ ) of Benzene From Surface Soils When NAPL is Present

Site, soil, and chemical properties are the same as in Example 1.

Also:

- Diffusion coefficient of benzene in air ( $D_{a,i}$ ) = 7,517 cm<sup>2</sup>/d.
- Diffusion coefficient of benzene in water ( $D_{w,i}$ ) = 0.847 cm<sup>2</sup>/d.
- Exposure averaging period ( $\tau$ ) = 30 yr = 10,950 days.
- Mole fraction of benzene in the residual mixture ( $X_i$ ) = 0.02.
- Pure component vapor pressure of benzene ( $P_i$ ) = 95.2 mm Hg at 25° C.
- Molecular weight of benzene ( $MW_i$ ) = 78 g/mol.
- Average in situ soil temperature ( $T$ ) = 52° F = 284.11° K.
- Initial soil concentration ( $C_{o,i}$ ) = 5,000 mg/kg = 0.005 g/g.

- A. Calculate the equilibrium vapor concentration of benzene ( $C_{v,eq}$ ) when NAPL is present using Equation 6:

$$C_{v,eq} = \frac{X_i P_i MW_i}{RT}$$

$$C_{v,eq} = \frac{0.02 \times 95.2 \times 78}{62,361 \times 284.11}$$

$$C_{v,eq} = 8.38 \text{ E-06 g/cm}^3\text{-vapor}$$

- B. Calculate the maximum effective diffusion coefficient ( $D_{e,i}$ ) when NAPL is present using Equation 7:

$$D_{e,i} = \left( \frac{\theta_a^{10/3}}{\theta_t^2} D_{a,i} \right) + \frac{1}{H'_i} \left( \frac{\theta_w^{10/3}}{\theta_t^2} D_{w,i} \right)$$

$$D_{e,i} = \left( \frac{0.178^{10/3}}{0.434^2} 7,517 \right) + \frac{1}{0.2214} \left( \frac{0.256^{10/3}}{0.434^2} 0.847 \right)$$

$$D_{e,i} = 127.56 \text{ cm}^2/\text{day}$$

- C. Calculate the average emission flux from surface soils using Equation 5:

$$\bar{F}_i = \beta C_{o,i} \left( \frac{2 C_{v,eq} D_{e,i}}{\beta C_{o,i} \tau} \right)^{1/2} 0.116$$

$$\bar{F}_i = 1.5 \times 0.005 \left( \frac{2 \times 8.38 \text{ E-06} \times 127.56}{1.5 \times 0.005 \times 10,950} \right)^{1/2} 0.116$$

$$\bar{F}_i = 4.44 \text{ E-06 g/m}^2\text{-s}$$

### EXAMPLE 3

#### Calculate the Average Emission Flux ( $\bar{F}_i$ ) of Benzene from Subsurface Soils When NAPL is Present

Site, soil, and chemical properties are the same as given in Examples 1 and 2.

Also:

- Distance from soil surface to top of contamination ( $d_c$ ) = 100 cm.

A. Calculate the emission flux from subsurface soils using Equation 8:

$$\bar{F}_i = \left[ \frac{\beta C_{o,i}}{\tau} \right] \left[ \left[ d_c^2 + \frac{2 C_{v,eq} D_{e,i} \tau}{\beta C_{o,i}} \right]^{1/2} - d_c \right] \quad 0.116$$

$$\bar{F}_i = \left[ \frac{1.5 \times 0.005}{10,950} \right] \left[ \left[ 100^2 + \frac{2 \times 8.38 \text{ E-}06 \times 127.56 \times 10,950}{1.5 \times 0.005} \right]^{1/2} - 100 \right] \quad 0.116$$

$$\bar{F}_i = 1.16 \text{ E-}06 \text{ g/m}^2\text{-s}$$

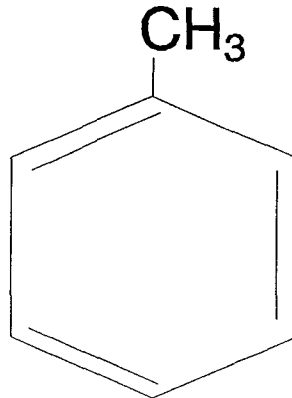


#### EXAMPLE 4

Estimate the Diffusion Coefficients in Air ( $D_{a,i}$ ) and in Water ( $D_{w,i}$ ) of Toluene

Given:

- Chemical structure of toluene ( $C_7H_8$ ) shown below.



- Molecular weight ( $MW_i$ ) of toluene = 92.14 g/mol.
- Absolute pressure ( $P_{ab}$ ) = 1 atm.
- Average temperature ( $T$ ) = 25°C = 298°K.

A. Estimate the diffusion coefficient in air using Equation 9:

$$D_{a,i} = \frac{0.001 T^{1.75} \sqrt{\frac{1}{MW_i} + \frac{1}{MW_a}}}{P_{ab} [(\sum V_i)^{1/3} + (\sum V_a)^{1/3}]^2} (8.64 \times 10^4) \text{ sec/day}$$

$$D_{a,i} = \frac{0.001 \times 298^{1.75} \sqrt{\frac{1}{92.14} + \frac{1}{28.8}}}{1[(111.14)^{1/3} + (20.1)^{1/3}]^2} (8.64 \times 10^4)$$

$$D_{a,i} = 7,151 \text{ cm}^2/\text{day}$$

where:  $\Sigma V_i$  calculated as:

$$\begin{array}{rcl} \text{C (7 x 16.5)} & = & 115.50 \\ \text{H (8 x 1.98)} & = & \underline{+15.84} \\ & & 131.34 \\ \text{Aromatic ring} & = & \underline{-20.20} \\ & & 111.14 \end{array}$$

B. Estimate the diffusion coefficient in water using Equation 10:

$$D_{w,i} = \frac{13.26 \times 10^{-5}}{\eta_w^{1.14} (V'_{B,i})^{0.589}} (8.64 \times 10^4 \text{ sec/day})$$

From Table 2,  $\eta_w = 0.8904$  at 25°C

From Table 3,  $V'_B$  is calculated as:

$$\begin{array}{rcl} \text{C (7 x 14.8)} & = & 103.6 \\ \text{H (8 x 3.7)} & = & \underline{+29.6} \\ & & 133.2 \\ \text{6-Membered ring} & = & \underline{-15.0} \\ & & 118.2 \end{array}$$

Therefore:

$$D_{w,i} = \frac{13.26 \times 10^{-5}}{0.8904^{1.14} (118.2)^{0.589}} (8.64 \times 10^4)$$

$$D_{w,i} = 0.7866 \text{ cm}^2/\text{day}$$

## EXAMPLE 5

### Calculate the Average Maximum Emission Flux ( $\bar{F}_i$ ) of Benzene from Surface Soils When NAPL is Not Present (Screening-Level Procedures)

Site and soil conditions are the same as in Examples 1 and 2. Chemical properties are also the same as in Examples 1 and 2.

Also:

- ° Initial soil concentration ( $C_{o,i}$ ) = 50 mg/kg = 5.0 E-05 g/g.

- A. Calculate the apparent diffusion coefficient ( $D_{A,i}$ ) using Equation 12:

$$D_{A,i} = \left[ \left( \theta_a^{10/3} D_{a,i} H'_i + \theta_w^{10/3} D_{w,i} \right) / \theta_t^2 \right] / \left( \beta K_{d,i} + \theta_w + \theta_a H'_i \right)$$

$$D_{A,i} = \frac{\left[ (0.178^{10/3} \times 7,517 \times 0.2214 + 0.256^{10/3} \times 0.847) / 0.434^2 \right]}{(1.5 \times 0.342 + 0.256 + 0.178 \times 0.2214)}$$

$$D_{A,i} = 34.93 \text{ cm}^2/\text{day}$$

- B. Calculate the screening-level average maximum emission flux using Equation 11:

$$\bar{F}_i = \beta C_{o,i} \left( \frac{4 D_{A,i}}{\pi \tau} \right)^{1/2} 0.116$$

$$\bar{F}_i = 1.5 \times 5.0E-5 \left( \frac{4 \times 34.93}{3.1416 \times 10,950} \right)^{1/2} 0.116$$

$$\bar{F}_i = 5.54 \text{ E-07 g/m}^2\text{-s}$$

## EXAMPLE 6

### Calculate the Average Emission Flux ( $\bar{F}_i$ ) of 1,2,4-Trichlorobenzene From Surface Soils When NAPL is Not Present (Refined Procedures)

Given:

- Initial soil concentration ( $C_{o,i}$ ) = 50 mg/kg
- Area of contamination ( $A_c$ ) = 1,000 m<sup>2</sup>
- Depth to the bottom of contamination ( $L_c$ ) = 300 cm
- Soil dry bulk density ( $\beta$ ) = 1.5 g/cm<sup>3</sup>-soil
- Soil water-filled porosity ( $\Theta_w$ ) = 0.256 cm<sup>3</sup>/cm<sup>3</sup>
- Soil air-filled porosity ( $\Theta_a$ ) = 0.178 cm<sup>3</sup>/cm<sup>3</sup>
- Soil total porosity ( $\Theta_t$ ) = 0.434 cm<sup>3</sup>/cm<sup>3</sup>
- Soil organic carbon fraction ( $f_{oc}$ ) = 0.006
- Organic carbon partition coefficient ( $K_{oc}$ ) = 1,540 cm<sup>3</sup>/g
- Diffusion coefficient in air ( $D_a$ ) = 2,592 cm<sup>2</sup>/d
- Diffusion coefficient in water ( $D_w$ ) = 0.711 cm<sup>2</sup>/d
- Henry's law constant ( $H'$ ) = 0.0582
- Exposure averaging period ( $\tau$ ) = 30 yr = 10,950 days
- Number of time-steps ( $n$ ) = 100
- Time-zero ( $t_0$ ) = 0.25 days.

A. Calculate the time-step interval for  $t_0$  to  $t_n$ :

$$h = \tau/n \text{ (Equation 14 legend)}$$

$$h = 10,950/100$$

$$h = 109.5 \text{ days}$$

- B. Calculate the emission flux of 1,2,4-Trichlorobenzene for 100 time-steps using Equation 15:

$$F_{i(t)} = \beta C_{o,i} \left( \frac{D_{A,i}}{\pi t} \right)^{1/2} \left[ 1 - \exp \left[ - \frac{L_c^2}{4 D_{A,i} t} \right] \right] \quad 0.116$$

*Emission flux at time-zero ( $t_0$ ):*

$$F_{i(0)} = 1.5 \times 5.0 \text{ E-05} \left( \frac{0.184}{3.1416 \times 0.25} \right)^{1/2} \left[ 1 - \exp \left[ - \frac{300^2}{4 \times 0.184 \times 0.25} \right] \right] \quad 0.116$$

$$F_{i(0)} = 4.21 \text{ E-06 g/m}^2\text{-s}$$

•  
•  
•

*Emission flux at the last time-step ( $t_{100}$ ):*

$$F_{i(100)} = 1.5 \times 5.0 \text{ E-05} \left( \frac{0.184}{3.1416 \times 10,950.25} \right)^{1/2} \left[ 1 - \exp \left[ - \frac{300^2}{4 \times 0.184 \times 10,950.25} \right] \right] \quad 0.116$$

$$F_{i(100)} = 2.01 \text{ E-08 g/m}^2\text{-s}$$

- C. Integrate the emissions of 1,2,4-Trichlorobenzene across the 100 time-steps to derive the average emission flux using Equation 14:

$$\bar{F}_i = \frac{1}{T} \left[ \frac{h}{2} (F_0 + 2F_1 + 2F_2 + \dots + 2F_{n-1} + F_n) \right]$$

- D. Compare the total mass lost from volatilization ( $M_{i,T}^v$ ) to the initial mass ( $M_{i,T}$ ) and compute the final average emission flux using Equations 16, 17, and 18.

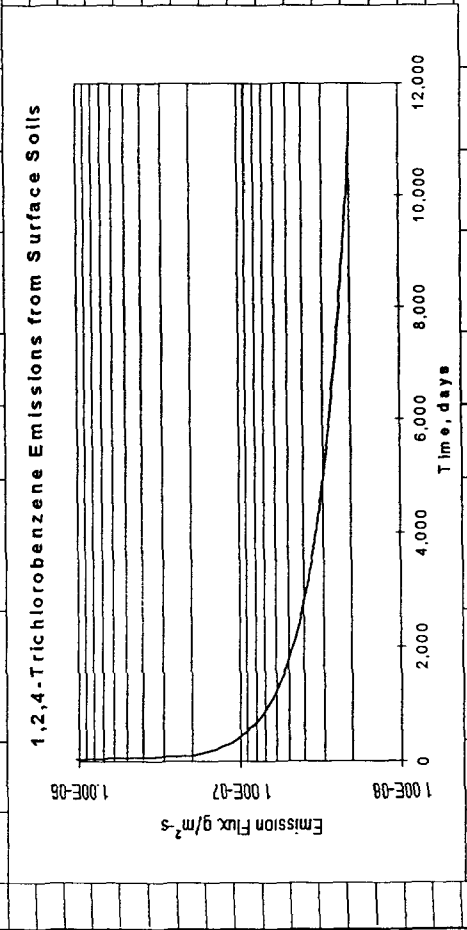
Note: These calculations are best performed using a computer spreadsheet program. The following MICROSOFT EXCEL 5.0 computer printout shows the solution for this example.

# Calculation of 1,2,4-Trichlorobenzene Emissions from Surface Soils Using Refined Procedures

Row	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
	Initial soil conc., $C_0$ (mg/kg)	Soil dry bulk density, $\rho$ (g/cm <sup>3</sup> )	Area of contamination, $A_c$ (m <sup>2</sup> )	Depth to bottom of contamination, $L_c$ (cm)	Soil particle density, $P_s$ (g/cm <sup>3</sup> )	Soil porosity, $\theta_w$ (unitless)	Water-filled soil porosity, $\theta_w$ (unitless)	Total soil porosity, $\theta_s$ (unitless)	Air-filled soil porosity, $\theta_a$ (unitless)	Soil organic carbon, $f_{oc}$ (fraction)	Organic carbon part. coeff., $K_{oc}$ (cm <sup>3</sup> /g)	Soil/water part. coeff., $K_d$ (cm <sup>3</sup> /g)	Diffusivity in air, $D_a$ (cm <sup>2</sup> /d)	Diffusivity in water, $D_w$ (cm <sup>2</sup> /d)	Henry's law constant, $H'$ (unitless)	Apparent diffusion coefficient, $D_a$ (cm <sup>2</sup> /d)	Time-step, $t$ (days)	Emission flux, $F_i$ (g/m <sup>2</sup> -s)		
Col.	$C_0$	$\rho$	$A_c$	$L_c$	$P_s$	$\theta_w$	$\theta_w$	$\theta_s$	$\theta_a$	$f_{oc}$	$K_{oc}$	$K_d$	$D_a$	$D_w$	$H'$	$D_a$	$t$	$F_i$		
No	(mg/kg)	(g/cm <sup>3</sup> )	(m <sup>2</sup> )	(cm)	(g/cm <sup>3</sup> )	(unitless)	(unitless)	(unitless)	(unitless)	(fraction)	(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(cm <sup>2</sup> /d)	(cm <sup>2</sup> /d)	(unitless)	(cm <sup>2</sup> /d)	(days)	(g/m <sup>2</sup> -s)		
7	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	0.25	4.21E-06		
8	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	109.75	2.01E-07		
9	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	219.25	1.42E-07		
10	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	328.75	1.16E-07		
11	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	438.25	1.01E-07		
12	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	547.75	8.99E-08		
13	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	657.25	8.21E-08		
14	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	766.75	7.60E-08		
15	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	876.25	7.11E-08		
100	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10183.75	2.09E-08		
101	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10293.25	2.07E-08		
102	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10402.75	2.06E-08		
103	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10512.25	2.05E-08	Total mass	
104	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10621.75	2.04E-08	lost from	
105	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10731.25	2.03E-08	volatilization, $M_{1,T}$	
106	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10840.75	2.02E-08	$M_{1,T}$	
107	50	5E-05	1,000	300	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10950.25	2.01E-08	(g)	
108																	Calculated average flux =	5.83E-08	5.52E-04	2.25E+05
109																	Final average flux =	5.83E-08 g/m <sup>2</sup> -s		

Spreadsheet equation for calculated average flux =  $(1/Q107)*((109.5/2)*(R7+(2*SUM(R8,R106)))+(R107))$   
 Spreadsheet equation for final average flux =  $IF(S108>1108,(1108/(C107*Q107*3600*24)),R108)$

NOTE: Not all time-steps are shown.



## EXAMPLE 7

### Calculate the Average Emission Flux ( $\bar{F}_i$ ) of 1,2,4-Trichlorobenzene From Subsurface Soils When NAPL is not Present (Refined Procedures)

Soil, chemical properties, and initial soil concentration are the same as in Example 6.

Also:

- Depth to the top of contamination (d) = 30 cm
- Thickness of contaminated soil ( $w_c$ ) = 100 cm
- The exposure averaging period ( $\tau$ ) = 30 yr = 10,950 days
- Number of time-steps (n) = 100
- Time-zero ( $t_0$ ) = 0.25 days
- The time-step interval =  $\tau/n$  = 109.5 days.

- A. Calculate the emission flux of 1,2,4-Trichlorobenzene for 100 time-steps using Equation 19:

$$F_{i(t)} = \beta C_{o,i} \left[ \frac{D_{A,i}}{\pi t} \right]^{1/2} \left[ \exp \left[ - \frac{d_c^2}{4 D_{A,i} t} \right] - \exp \left[ - \frac{(d_c + w_c)^2}{4 D_{A,i} t} \right] \right] \quad 0.116$$

Emission flux at time-zero ( $t_0$ ):

$$F_{i(0)} = 1.5 \times 5.0 \text{ E-05} \left[ \frac{0.184}{3.1416 \times 0.25} \right]^{1/2} \\ \times \left[ \exp \left[ - \frac{30^2}{4 \times 0.184 \times 0.25} \right] - \exp \left[ - \frac{(30 + 100)^2}{4 \times 0.184 \times 0.25} \right] \right] \quad 0.116$$



$$F_{i(0)} = 0 \text{ g/m}^2\text{-s}$$

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Emission flux at the last time-step ( $t_{100}$ ):

$$F_{i(100)} = 1.5 \times 5.0 \text{ E-05} \left[ \frac{0.184}{3.1416 \times 10,950.25} \right]^{1/2} \\ \times \left[ \exp \left[ -\frac{30^2}{4 \times 0.184 \times 10,950.25} \right] - \exp \left[ -\frac{(30 + 100)^2}{4 \times 0.184 \times 10,950.25} \right] \right] 0.116$$

$$F_{i(100)} = 1.55 \text{ E-08 g/m}^2\text{-s}$$

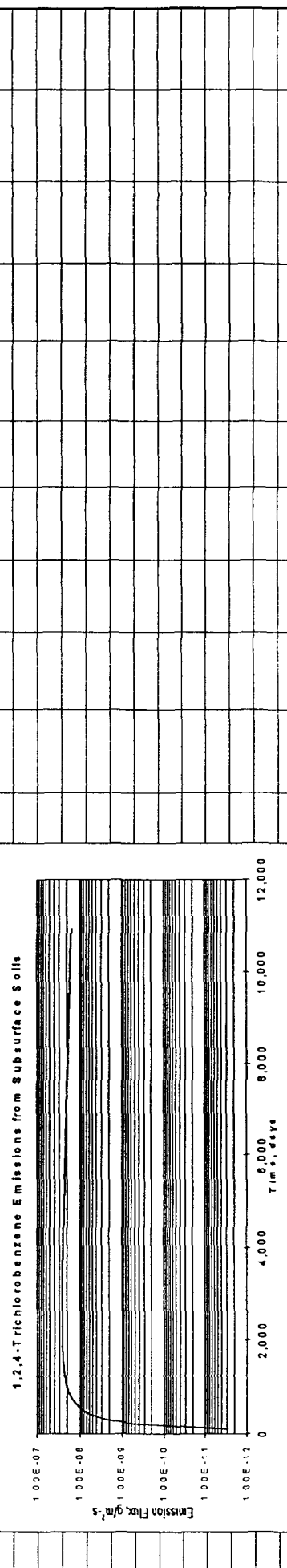
- B. Integrate the emissions of 1,2,4-Trichlorobenzene across the 100 time-steps to derive the average emission flux using Equation 14:

$$\bar{F}_i = \frac{1}{T} \left[ \frac{h}{2} (F_0 + 2F_1 + 2F_2 + \dots + 2F_{n-1} + F_n) \right]$$

- C. Compare the total mass lost from volatilization ( $M_{i,T}^V$ ) to the initial mass ( $M_{i,T}$ ) and compute the final average emission flux using Equations 16, 17, and 18.

Note: These calculations are best performed using a computer spreadsheet program. The following MICROSOFT EXCEL 5.0 computer printout shows the solution for this example.

Row	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
	Initial soil conc., C <sub>o</sub> (mg/kg)	Initial soil conc., C <sub>o</sub> (g/g)	Area of contam A <sub>c</sub> (m <sup>2</sup> )	Depth to top of contam d <sub>c</sub> (cm)	Thickness of contam w <sub>c</sub> (cm)	Soil dry bulk density, β (g/cm <sup>3</sup> )	Soil particle density, ρ <sub>s</sub> (g/cm <sup>3</sup> )	Water-filled soil porosity, θ <sub>w</sub> (unitless)	Total soil porosity, θ <sub>t</sub> (unitless)	Air-filled soil porosity, θ <sub>a</sub> (unitless)	Soil organic carbon, f <sub>oc</sub> (fraction)	Organic carbon part. coeff., K <sub>oc</sub> (cm <sup>2</sup> /g)	Soil/ water K <sub>d</sub> (cm <sup>3</sup> /g)	Diffusivity in air, D <sub>a</sub> (cm <sup>2</sup> /d)	Diffusivity in water, D <sub>w</sub> (cm <sup>2</sup> /d)	Henry's law constant, H' (unitless)	Apparent diffusion coefficient, D <sub>a</sub> (cm <sup>2</sup> /d)	R t (days)	S F <sub>i</sub> (g/m <sup>2</sup> -s)	T	U
7	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	0.25	0.00E+00		
8	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	109.75	2.87E-12		
9	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	219.25	5.34E-10		
10	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	328.75	2.80E-09		
11	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	438.25	6.15E-09		
12	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	547.75	9.62E-09		
13	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	657.25	1.27E-08		
14	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	766.75	1.54E-08		
15	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	876.25	1.76E-08		
100	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10163.75	1.63E-08		
101	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10293.25	1.62E-08		
102	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10402.75	1.61E-08		
103	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10512.25	1.60E-08	Total mass	
104	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10621.75	1.59E-08	lost from	Total
105	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10731.25	1.57E-08	volatilization,	Initial mass,
106	50	5E-05	1,000	30	100	1.5	2.65	0.256	0.434	0.178	0.006	1540	9.240	2592	0.711	0.0582	1.84E-01	10840.75	1.56E-08	M <sub>i,r</sub> <sup>v</sup>	M <sub>i,r</sub>
107	50	5E-05	1,000	30	100	1.5	2.65	0.256	0												



## EXAMPLE 8

### Calculate the Maximum Emission Flux ( $F_i^{\max}$ ) of Benzene Using Soil Gas Concentrations

Given:

- Measured soil gas concentration ( $C_{sg,i}$ ) = 500 ppmv.
- Soil air-filled porosity ( $\Theta_a$ ) = 0.178.
- Soil total porosity ( $\Theta_t$ ) = 0.434.
- Depth to immediately above the vapor source ( $d$ ) = 220 cm.
- Chemical properties of benzene are the same as in Examples 1 and 2.

A. Calculate the vapor-phase diffusion coefficient ( $D_i^{ev}$ ) using Equation 21:

$$D_i^{ev} = D_{a,i} \frac{\Theta_a^{10/3}}{\Theta_t^2}$$

$$D_i^{ev} = 7,517 \frac{0.178^{10/3}}{0.434^2}$$

$$D_i^{ev} = 127.34 \text{ cm}^2/d$$

B. Convert the measured soil gas concentration from ppmv to g/cm<sup>3</sup>-vapor using Equation 22:

$$C_{v,i} = C_{sg,i} \left[ \frac{MW_i}{2.404 \times 10^{10}} \right]$$

$$C_{v,i} = 500 \left( \frac{78}{2.404 \times 10^{10}} \right)$$

$$C_{v,i} = 1.62 \text{ E-06 g/cm}^3\text{-vapor}$$

C. Calculate the maximum emission flux using Equation 20:

$$F_i^{\max} = \left[ \frac{C_{v,i} D_i^{\text{ev}}}{d} \right] 0.116$$

$$F_i^{\max} = \left[ \frac{1.62 \text{ E-06} \times 127.34}{200} \right] 0.116$$

$$F_i^{\max} = 1.20 \text{ E-07 g/m}^2\text{-s}$$

## EXAMPLE 9

### Calculate the Maximum Emission Flux ( $F_i^{\max}$ ) of Benzene from Subsurface Soils with Landfill Gas Generation (Screening-Level Procedures)

Giver:

- ° The chemical properties of benzene are the same as in Examples 1 and 2.
- ° Temperature ( $T$ ) =  $25^\circ\text{C} = 298^\circ\text{K}$ .

A. Calculate the saturation vapor concentration ( $C_{sv,i}$ ) of benzene using Equation 24:

$$C_{sv,i} = \frac{P_i MW_i}{RT}$$

$$C_{s,vi} = \frac{95.2 \times 78}{62,361 \times 298}$$

$$C_{s,vi} = 4.00 \text{ E-04 } g/cm^3\text{-vapor}$$

B. Calculate the maximum emission flux using Equation 23:

$$F_i^{\max} = C_{sv,i} V_y 0.116$$

$$F_i^{\max} = 4.00 \text{ E-04} \times 141 \times 0.116$$

$$F_i^{\max} = 6.54 \text{ E-03 } g/m^2\text{-s}$$

## EXAMPLE 10

### Calculate the Average Landfill Emission Rate ( $\bar{E}_i$ ) of Benzene with Landfill Gas Generation (Refined Procedures)

Given:

- A single cell codisposal landfill with a maximum capacity of 75,000 Mg.
- Methane generation potential ( $L_0$ ) = 125 m<sup>3</sup>/Mg (default).
- Average annual landfill acceptance rate (R) = 5,000 Mg/yr.
- Methane generation rate constant (k) = 0.04/yr (default).
- Time since landfill closure (c) = 5 yr (i.e., time-zero or  $t_0$  = 5 yr).
- Time from initial refuse placement in landfill (t) = 20 yr at time-zero.
- Measured vapor-phase benzene concentration ( $C_{v,i}$ ) = 500 ppmv = 1.62 E-06 g/cm<sup>3</sup>.
- Exposure averaging period ( $\tau$ ) = 30 yr.
- Time-step interval (h) = 1 yr.

- A. Calculate the emission rate of benzene for 30 one-year time-steps using Equation 27:

$$E_{i(t)} = 2 L_0 R \{ \exp(-kc) - \exp(-kt) \} C_{v,i} (3.17 \times 10^{-2})$$

*Emission rate at time-zero ( $t_0$ ):*

$$E_{i(t_0)} = 2 \times 125 \times 5,000 \{ \exp(-0.04 \times 5) - \exp(-0.04 \times 20) \} \times 1.62 \text{ E-06 } (3.17 \times 10^{-2})$$

$$E_{i(t_0)} = 2.37 \text{ E-02 g/s}$$

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*Emission rate at the last time-step ( $t_{30}$ ):*

$$E_{i(30)} = 2 \times 125 \times 5,000 \{ \exp(-0.04 \times 35) - \exp(-0.04 \times 50) \} \times 1.62 \text{ E-05 } (3.17 \times 10^{-2})$$

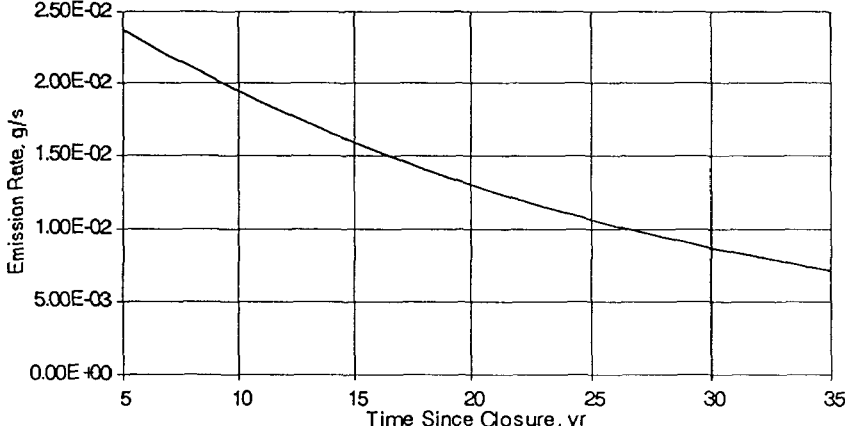
$$E_{i(30)} = 7.14 \text{ E-03 g/s}$$

- B. Integrate the emissions of benzene across the 30 time-steps to derive the average emission rate using Equation 26:

$$\bar{E}_i = \frac{1}{\tau} \left[ \frac{h}{2} (E_0 + 2E_1 + 2E_2 + \dots + 2E_{n-1} + E_n) \right]$$

Note: These calculations are best performed using a computer spreadsheet program. The following MICROSOFT EXCEL 5.0 computer printout shows the solution for this example.

# Calculation of Average Landfill Emission Rate of Benzene with Landfill Gas Generation

Row	A	B	C	D	E	F	G
	Measured	Average	Methane	Methane		Time from	
	vapor-phase	annual	generation	generation	Time	initial	
	conc.,	acceptance	potential,	rate	since	refuse	Emission
	$C_{v,i}$	rate,	$L_0$	constant,	closure,	placement,	rate,
		R		k	c	t	$E_i(t)$
Col.	(g/cm <sup>3</sup> -vapor)	(Mg/yr)	(m <sup>3</sup> /Mg)	(1/yr)	(yr)	(yr)	(g/s)
8	1.62E-06	5,000	125	0.04	5	20	2.37E-02
9	1.62E-06	5,000	125	0.04	6	21	2.28E-02
10	1.62E-06	5,000	125	0.04	7	22	2.19E-02
11	1.62E-06	5,000	125	0.04	8	23	2.10E-02
12	1.62E-06	5,000	125	0.04	9	24	2.02E-02
13	1.62E-06	5,000	125	0.04	10	25	1.94E-02
14	1.62E-06	5,000	125	0.04	11	26	1.87E-02
15	1.62E-06	5,000	125	0.04	12	27	1.79E-02
16	1.62E-06	5,000	125	0.04	13	28	1.72E-02
17	1.62E-06	5,000	125	0.04	14	29	1.65E-02
18	1.62E-06	5,000	125	0.04	15	30	1.59E-02
19	1.62E-06	5,000	125	0.04	16	31	1.53E-02
20	1.62E-06	5,000	125	0.04	17	32	1.47E-02
21	1.62E-06	5,000	125	0.04	18	33	1.41E-02
22	1.62E-06	5,000	125	0.04	19	34	1.35E-02
23	1.62E-06	5,000	125	0.04	20	35	1.30E-02
24	1.62E-06	5,000	125	0.04	21	36	1.25E-02
25	1.62E-06	5,000	125	0.04	22	37	1.20E-02
26	1.62E-06	5,000	125	0.04	23	38	1.15E-02
27	1.62E-06	5,000	125	0.04	24	39	1.11E-02
28	1.62E-06	5,000	125	0.04	25	40	1.07E-02
29	1.62E-06	5,000	125	0.04	26	41	1.02E-02
30	1.62E-06	5,000	125	0.04	27	42	9.84E-03
31	1.62E-06	5,000	125	0.04	28	43	9.45E-03
32	1.62E-06	5,000	125	0.04	29	44	9.08E-03
33	1.62E-06	5,000	125	0.04	30	45	8.72E-03
34	1.62E-06	5,000	125	0.04	31	46	8.38E-03
35	1.62E-06	5,000	125	0.04	32	47	8.05E-03
36	1.62E-06	5,000	125	0.04	33	48	7.74E-03
37	1.62E-06	5,000	125	0.04	34	49	7.43E-03
38	1.62E-06	5,000	125	0.04	35	50	7.14E-03
				Calculated average emission rate =			1.38E-02
Spreadsheet equation for average emission rate = $(1/30)*(1/2*(G8 + (2*SUM(G9:G37)) + G38))$							
<div>Landfill Emissions of Benzene</div> 							



## EXAMPLE 11

### Calculate the Emission Flux ( $F_i$ ) of Benzene from a Quiescent Surface Impoundment (Screening-Level Procedures)

Given:

- Chemical properties of benzene are the same as in Examples 1 and 2.
- Liquid-phase benzene concentration ( $C_{L,i}$ ) = 800 mg/L = 8.0 E-04 g/cm<sup>3</sup>.
- Average impoundment temperature ( $T$ ) = 13°C = 286°K.

- A. Calculate the liquid-phase mass transfer coefficient ( $k_{iL}$ ) of benzene using Equation 31:

$$k_{iL} = \left( \frac{MW_{O_2}}{MW_i} \right)^{0.5} \left( \frac{T}{298} \right) (k_L, O_2)$$

$$k_{iL} = \left( \frac{32}{78} \right)^{0.5} \left( \frac{286}{298} \right) (0.002)$$

$$k_{iL} = 1.23 \text{ E-03 cm/s}$$

- B. Calculate the gas-phase mass transfer coefficient ( $k_{iG}$ ) of benzene using Equation 32:

$$k_{iG} = \left( \frac{MW_{H_2O}}{MW_i} \right)^{0.335} \left( \frac{T}{298} \right)^{1.005} (k_G, H_2O)$$

$$k_{iG} = \left( \frac{18}{78} \right)^{0.335} \left( \frac{286}{298} \right)^{1.005} (0.833)$$

$$k_{iG} = 4.89 \text{ E-01 cm/s}$$

C. Calculate the overall mass transfer coefficient ( $K_i$ ) of benzene using Equation 30:

$$\frac{1}{K_i} = \frac{1}{k_{iL}} + \frac{R T}{H_i k_{iG}}$$

$$\frac{1}{K_i} = \frac{1}{1.23 \text{ E-03}} + \frac{8.2 \text{ E-05} \times 286}{5.4 \text{ E-03} \times 4.89 \text{ E-01}}$$

$$\frac{1}{K_i} = 821.89$$

$$K_i = 1.22 \text{ E-03 cm/s}$$

D. Calculate the emission flux of benzene using Equation 29:

$$F_i = K_i C_{L,i} (1 \times 10^4)$$

$$F_i = 1.22 \text{ E-03} \times 8.0 \text{ E-04} \times (1 \times 10^4)$$

$$F_i = 9.76 \text{ E-03 g/m}^2\text{-s}$$

## EXAMPLE 12

### Calculate the $PM_{10}$ Annual Average Emission Flux ( $\bar{F}_i$ ) of Cadmium Due to Wind Erosion Using the "Unlimited Reservoir" Model

Given:

- The mean annual windspeed ( $[u]$ ) = 5.2 m/s.
- Fraction by weight of cadmium in surface soils ( $C_i$ ) = 5.0 E-04.
- Fraction of contaminated surface with continuous vegetation ( $V$ ) = 0.1.
- The aggregate size distribution mode of surface material = 0.3 mm.
- Surface roughness height ( $z_o$ ) = 0.5 cm (default).

A. Estimate the threshold friction velocity ( $u_t'$ ) from Figure 1a:

- From Figure 1a, the value of  $u_t'$  corresponding to an aggregate size distribution mode of 0.3 mm = 40 cm/s

B. Correct the value of  $u_t'$  for nonerodible elements:

- With no other data, assume the default correction factor of 1.25.
- Calculate the threshold friction velocity corrected for nonerodible elements ( $u_t^*$ ) as:

$$u_t^* = u_t' \times \text{Correction Factor}$$

$$u_t^* = 40 \text{ cm/s} \times 1.25$$

$$u_t^* = 50 \text{ cm/s}$$

C. Calculate the equivalent threshold value of windspeed at a 7 m anemometer height ( $u_t^7$ ) using Equation 34:

$$u_t^7 = \left[ \frac{u_t^*}{0.4} \ln \left( \frac{700}{z_o} \right) \right] / 100$$

$$u_t^7 = \left[ \frac{50}{0.4} \ln \left( \frac{700}{0.5} \right) \right] / 100$$

$$u_t^7 = 9.06 \text{ m/s}$$

D. Estimate the value of F(x) using Figure 2:

$$\begin{aligned} \text{- From Figure 2: } x &= 0.886 (u_t^7 / [u]) \\ x &= 0.886 (9.06 / 5.2) \\ x &= 1.54 \end{aligned}$$

$$\text{- From Figure 2: } F(x) \approx 0.83$$

E. Calculate the average annual emission flux of cadmium using Equation 33:

$$\bar{F}_i = \left[ 0.036 (1 - V) \left( \frac{[u]}{u_t^7} \right)^3 F(x) C_i \right] \frac{1}{3600}$$

$$\bar{F}_i = \left[ 0.036 \times (1 - 0.1) \times \left( \frac{5.2}{9.06} \right)^3 \times 0.83 \times 5.0 \text{ E-04} \right] \frac{1}{3600}$$

$$\bar{F}_i = 7.06 \text{ E-10 g/m}^2\text{-s}$$

### EXAMPLE 13

**Calculate the  $PM_{10}$  Annual Average Emission Flux ( $\bar{F}_i$ ) of Cadmium Due to Wind Erosion Using the "Limited Reservoir" Model**

Given:

- Number of site disturbances per year ( $N$ ) = 12 (default).
- Fraction by weight of cadmium in surface soils ( $C_i$ ) =  $5.0 \times 10^{-4}$ .
- Fraction of contaminated surface with continuous vegetation ( $V$ ) = 0.1.
- Site is located on the southeastern coast of North Carolina.
- The threshold friction velocity corrected for nonerrodible elements ( $u_t^*$ ) =  $50 \text{ cm/s} = 0.50 \text{ m/s}$ .
- The fastest windspeed between each disturbance ( $u_z$ ) =  $14.5 \text{ m/s}$  at a  $10 \text{ m}$  anemometer height ( $z = 1000 \text{ cm}$ ).
- Surface roughness height ( $z_o$ ) =  $0.5 \text{ cm}$ .

- A. Calculate the fastest windspeed between disturbances at the surface roughness height ( $u^*$ ) using Equation 37:

$$u^* = \frac{u_z 0.4}{\ln(z/z_o)}$$

$$u^* = \frac{14.5 \times 0.4}{\ln(1000/0.5)}$$

$$u^* = 0.76 \text{ m/s}$$

- B. Calculate the erosion potential ( $P_i$ ) for each period between disturbances using Equation 36:

$$P_i = 58 (u^* - u_t^*)^2 + 25 (u^* - u_t^*), \quad P_i = 0 \text{ for } u^* \leq u_t^*$$

Since  $u^* > u_t^*$ ,  $P_i \neq 0$ , therefore

$$P_i = 58 (0.76 - 0.50)^2 + 25(0.76 - 0.50)$$

$$P_i = 10.42 \text{ g/m}^2$$

B. Estimate the Thornthwaite's Precipitation-Evaporation Index (PE) from Figure 3:

$$PE = 104$$

C. Calculate the  $PM_{10}$  annual average emission flux of cadmium using Equation 35:

$$\bar{F}_i = 0.5 \left[ \sum_{i=1}^N \frac{P_i (1-V)}{(PE/50)^2} \right] C_i \left[ \frac{1}{31,536,000 \text{ s/yr}} \right]$$

Because the fastest windspeed between each of the 12 disturbances per year is the same value, calculate the emission flux for the first disturbance and multiply by 12 to derive the annual average emission flux:

$$F_i = 0.5 \left[ \frac{10.42 (1-0.1)}{(104/50)^2} \right] 5.0 \text{ E-04} \left[ \frac{1}{31,536,000} \right]$$

$$F_i = 1.72 \text{ E-11 g/m}^2\text{-s}$$

$$\bar{F}_i = 1.72 \text{ E-11 g/m}^2\text{-s} \times 12$$

$$\bar{F}_i = 2.06 \text{ E-10 g/m}^2\text{-s}$$

## EXAMPLE 14

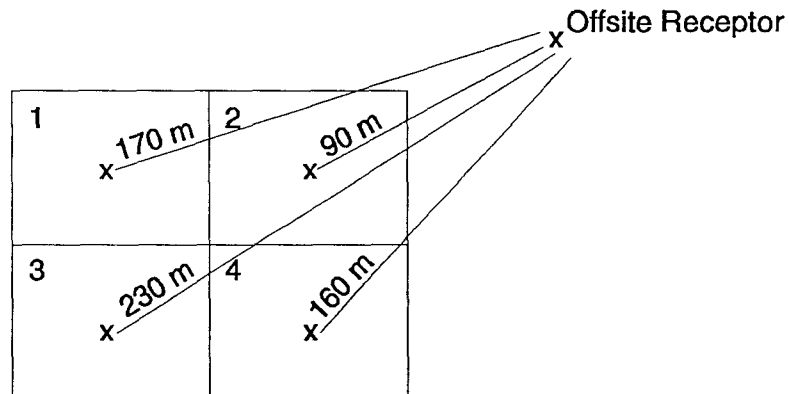
### Estimate the Current Land-Use Exposure Point Concentration of Benzene Using the Screening-Level Dispersion Modeling Procedures

Given:

- The emissions of benzene are from surface soils over an urban 2 acre area of contamination.
- Dividing the area of contamination into 4 - 1/2 acre square exposure areas (EAs), the predicted emission flux from each EA is:

<u>Source No.</u>	<u>Emission flux, g/m<sup>2</sup>-s</u>
1	2.60 E-08
2	4.88 E-07
3	3.75 E-07
4	1.25 E-07

- The site layout and source-to-receptor distances are shown below.



Run the TSCREEN dispersion model as specified for current land-use in Step IV. The results are shown below.

Source No.	Distance to receptor, m	TSCREEN normalized concentration, $\mu\text{g}/\text{m}^3$ per $\text{g}/\text{m}^2\text{-s}$	Predicted emission flux, $\text{g}/\text{m}^2\text{-s}$	Corrected concentration, $\mu\text{g}/\text{m}^3$
2	90	0.5983 E + 07	4.88 E-07	2.92
4	160	0.2626 E + 07	1.25 E-07	0.33
1	170	0.2393 E + 07	2.60 E-08	0.06
3	230	0.1483 E + 07	3.75 E-07	0.56
Total				3.87

Convert the total 1-h concentration to an annual average:

$$3.87 \mu\text{g}/\text{m}^3 \times 0.08 = 0.31 \mu\text{g}/\text{m}^3$$

The average long-term exposure point concentration for current land-use is predicted to be  $0.31 \mu\text{g}/\text{m}^3$ .



## EXAMPLE 15

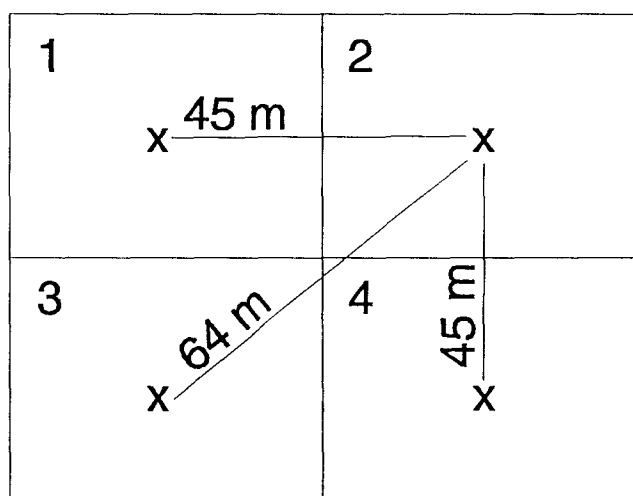
### Estimate the Future Land-Use Exposure Point Concentration of Benzene Using the Screening-Level Dispersion Modeling Procedures

Given:

- ° Emissions data are the same as in Example 14.

Because emission source No. 2 has the highest emission flux, the future land-use receptor is located at the center of source No. 2. The emission contribution of all four sources will therefore be estimated at this receptor.

Site layout and source-to-receptor distances are shown below.



Run the TSCREEN dispersion model as specified for future land-use in Step IV. The results are shown below.

Source No.	Distance to receptor, m	TSCREEN normalized concentration, $\mu\text{g}/\text{m}^3$ per $\text{g}/\text{m}^2\text{-s}$	Predicted emission flux, $\text{g}/\text{m}^2\text{-s}$	Corrected concentration, $\mu\text{g}/\text{m}^3$
2	1	0.3413 E+08	4.88 E-07	16.66
4	45	0.1623 E+08	1.25 E-07	2.03
1	45	0.1623 E+08	2.60 E-08	0.42
3	64	0.9520 E+07	3.75 E-07	3.57
Total				22.68

Convert the total 1-h concentration to an annual average:

$$22.68 \mu\text{g}/\text{m}^3 \times 0.08 = 1.81 \mu\text{g}/\text{m}^3$$

The average long-term exposure point concentration for future land-use is predicted to be  $1.81 \mu\text{g}/\text{m}^3$ .

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