PA450/1-92-002

United States Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park NC 27711

EPA-450/1-92-002 January 1992

Air/Superfund

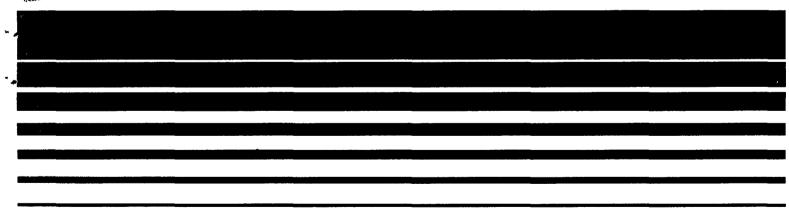


AIR/SUPERFUND NATIONAL TECHNICAL GUIDANCE STUDY SERIES

Guideline for Predictive Baseline Emissions Estimation Procedures for Superfund Sites

Interim Final





GUIDELINE FOR PREDICTIVE BASELINE EMISSIONS ESTIMATION PROCEDURES FOR SUPERFUND SITES

INTERIM FINAL

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Contract No. 68-D0-0124 Work Assignment No. 1-80 PN 5025-8

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January 1992

PREFACE

This document was developed for the U.S. Environmental Protection Agency, Region II through the Air/Superfund Technical Assistance Program. The document has been reviewed by the National Technical Guidance Study Technical Advisory Committee as well as the EPA, Region II Air Programs and Superfund staff. This document is an interim final manual offering 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.

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ACKNOWLEDGMENT

This manual was prepared for the U.S. Environmental Protection Agency by Environmental Quality Management, Inc. under Contract No. 68-D0-0124, Work Assignment No. 1-80. Mr. Craig Mann (Project Manager) and Ms. Alison Devine (Work Assignment Manager) managed the project. The principal authors were Mr. Craig Mann of Environmental Quality Management, Inc. and Mr. John Carroll of International Technology Corporation.

Mr. Joseph Padgett and his staff of the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, provided overall program direction. Peer review of the manual was provided by the Air/Superfund Technical Advisory Committee and by others including: Grace Musumeci (EPA, Region II), Donna Abrams (EPA, Region III), and Marina Stefanidis (EPA, Region II).

GUIDELINE FOR PREDICTIVE BASELINE EMISSIONS ESTIMATION PROCEDURES FOR SUPERFUND SITES

OBJECTIVE:

The objective of the following predictive procedures is to provide conservative baseline emissions estimates of air pathway contaminants for use in the Baseline Risk Assessment.

BACKGROUND/APPROACH:

In accordance with the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), the overriding purpose of an air pathway analysis (APA) is to ensure the protection of human health and the environment. Protectiveness includes compliance with Federal and State applicable or relevant and appropriate requirements (ARARs) and other nonbinding criteria to be considered (TBCs) as well as a demonstration that potential exposures are within the "acceptable risk range" for carcinogenic contaminants, and are at or below other health-based criteria for toxicants exhibiting noncarcinogenic effects. ARARs/TBCs and health-based criteria should be considered mutually exclusive. That is, ARARs/TBCs may or may not be as protective as the health-based criteria defined in the NCP. For example, many State air toxics regulations are based on occupational exposure limits (e.g., TLVs, PELs, etc.) or are simply based on best control technology with no assessment of actual exposure. In addition, risk-based ARARs may not include all pathways of exposure pertinent to the air pathway. Finally, compliance with air ARARs on a contaminant-specific basis may not prove to be protective when the risks from each pollutant are aggregated for the air pathway.

Unlike other environmental 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 times may range from only a few minutes to many years, and exposure rates may vary considerably due to the fluidity of atmospheric processes. The very nature of the air pathway, therefore, is conducive to error in the measurement or prediction of the fate of airborne contaminants over time and distance. To reduce this relative error, procedures for estimating baseline air emissions must be conservative whether the procedures incorporate measurement techniques (e.g., monitoring) or predictive modeling.

HOW TO USE THESE PROCEDURES:

These procedures are designed to be used during the RI/FS stage as a guideline to predict air pathway emissions for use in determining exposure point concentrations in the Baseline Risk Assessment. In addition, these data may also be used to demonstrate compliance or noncompliance with air ARARs and/or TBCs for the baseline case (undisturbed site).

The intent of this document is to provide the sequential series of steps necessary to accomplish the baseline air pathway analysis. These steps incorporate the preferred EPA predictive models (as of the date of publication) that may be applied to the air pathway analysis. The models herein have been extracted from various EPA sources; and therefore as a guideline, all the relevant information concerning the applicability, limitations, and assumptions of each model are not necessarily included. To properly use these procedures, the user is <u>required</u> to thoroughly understand all relevant information from the original references cited throughout this document.

These procedures utilize predictive techniques based on theoretical mass transfer and dispersion of contaminants into the atmosphere. Fate and transport models incorporate conservative values to be consistent with the "reasonable maximum exposure" scenario defined in the NCP. These models are also consistent with those described in the Risk Assessment Guidance for Superfund, Human Health Evaluation Manual, Part A, July 1989.

Use of these procedures, however, does not preclude the use of techniques for measuring emission rates and/or ambient air concentrations of airborne contaminants. Where site-specific conditions do not lend themselves to these predictive techniques (e.g., heterogeneous distribution of contaminants, inappropriate meteorological data, heightened community/State concerns, etc.), more rigorous techniques involving refined emissions and air quality modeling or measurement techniques may be necessary.

Emission and ambient air measurement techniques as well as other modeling techniques which may be more suited to site-specific conditions can be found in the Air/Superfund National Technical Guidance Study Series, Volumes I through IV, Office of Air Quality Planning and Standards, EPA-450/1-89-001, 002a, 003, and 004.

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

MAJOR STEPS:

- I. Review site background information and gather site characterization and other data to conduct the baseline emissions estimate.
- II. List all air ARARs and TBCs.
- III. Estimate air pathway emission rates of each applicable contaminant.
- IV. Estimate ambient air concentrations and/or deposition concentrations at receptors of interest.
- V. Compare ambient air concentration estimates to air ARARs and TBCs.
- VI. Organize concentration data for input to the Baseline Risk Assessment.

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 fenceline, 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)
 - Presence of soil crust and crust thickness, friability and soil particle size distribution
 - Location and distance to receptors of interest
 - Local meteorological data (annual and/or seasonal 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 for volatile compounds may include:
 - Molecular weight
 - Vapor pressure
 - Henry's Law constant
 - Diffusion coefficient in air
 - Liquid and gas-phase mass transfer coefficients (or overall mass transfer coefficient)
 - Organic carbon partition coefficient

Solubility limit in water

Reference 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, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-450/1-89-002a, NTIS PB90-270588, August 1990.

STEP II. LIST AIR ARARS AND TBCs

- 1. List All Air ARAR and TBC Acceptable Ambient Levels and Averaging Times (e.g., μ g/m³ annual average, ppmv never to exceed, etc.):
 - A. National Ambient Air Quality Standards (NAAQS) for PM₁₀, Pb, NO_x, SO₂, CO, and ozone (as applicable)
 - B. National Emission Standards for Hazardous Air Pollutants (NESHAPs) as applicable
 - C. State Ambient Air Concentration Guidelines or Standards (SAACGS)
 - D. Others as applicable

Note: Compliance with an ARAR or TBC acceptable ambient level must be demonstrated on the same averaging time basis (e.g., annual average, 24-hour average, never to exceed, etc.).

Reference for Step II, 1: CERCLA Compliance With Other Laws Manual Part II, OSWER Directive 9234.1-02, Office of Emergency and Remedial Response, Washington, D.C., EPA-540/G-89/009.

2. Develop a set of air pathway pollutants for inclusion in the analysis.

Note: It may be advantageous to reduce the number of potential airborne contaminants in the analysis or to combine certain pollutants by chemical class. In some cases, however, the time required to implement the selection/reduction procedures may exceed the time needed to simply carry all potential airborne pollutants through the analysis. The procedures described in the following reference should be used for selection of potential pollutants. Particular attention should be given to applying these procedures to the air pathway.

Reference for Step II, 2: Risk Assessment Guidance for Superfund (RAGS), Volume 1, Human Health Evaluation Manual (Part A), Sections 5.8 - 5.9, Office of Emergency and Remedial Response, Washington, D.C., EPA-540/1-89-002. December 1989.

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

Background:

Predictive modeling techniques include calculation of theoretical emission rates for both gaseous and particulate matter contaminants. Emission rate models predict emission rates as a function of contaminant concentration and contaminant physical and chemical properties within the surrounding media (e.g., within soils, surface water, etc.) and through measured or theoretically derived mass transfer coefficients. Some models have been evaluated against pilot-scale and field test results. Because these models attempt to predict complex physical and chemical phenomena, their potential relative error may be considered to span perhaps one order of magnitude.

It should be noted that many of these emission rate models require physical data about the surrounding media (e.g., soil porosity, moisture content, etc.) as well as physical and chemical properties of the contaminants (e.g., Henry's Law constants, diffusivity in air, etc.). In addition, proper use of these emission rate models assumes that a thorough site characterization has been accomplished and that media-specific concentrations of all contaminants have been adequately determined within the site volume in all three dimensions (i.e., all contaminant-specific "hot spots" have been identified to a known depth). The emission rates calculated from these models must accurately represent the site or gross under/overprediction of the resulting ambient air concentrations will result.

Gaseous Emissions from Subsurface Soils:

A. For air release potential of contaminants from subsurface soils, measure contaminant-specific soil gas concentrations. As an alternative, soil bulk concentrations can also be used for predicting air release potential of contaminants; however, soil gas measurements are preferred. Care must be taken to ensure adequate site coverage.

Note: For baseline conditions, relatively shallow soil gas measurements can be taken. Soil gas measurements at greater depths will be advantageous if soil excavation is contemplated during remediation. Measurements should be made during periods of stable atmospheric pressure to avoid "barometric pumping" effects. Great care must be taken not to disturb soil equilibrium conditions and thus dilute the sample. For both soil gas and bulk concentration samples, use the 95 percent upper confidence limit (UCL) on the arithmetic mean for each homogeneous

subsection of the area of contamination unless this concentration is greater than the maximum detected concentration. In this case, the maximum observed value should be used. Data used in calculating contaminant concentrations for this analysis should include all detected concentrations of a substance plus half the quantitation limit for each sample in which that substance was not detected. Only substances that were detected in at least one sample from the site should be included in this analysis.

Reference for Step III, 1, A: RAGS Part A, Sections 5-6. December 1989.

B. If soil bulk concentrations are to be used to calculate emission rates, estimate the saturation concentration (C_{sat}) for 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 dissolution limit of the contaminant in the available soil moisture has been reached. Concentrations $> C_{sat}$ indicate "free-phase" contaminants within the soil matrix.

$$C_{sat} = (K_d \times S \times n_m) + (S \times \theta_m) \tag{1}$$

where C_{sat} = Saturation concentration, mg/kg (ppm)

K_d = Soil/water partition coefficient, I/kg (or ml/g)

s = Solubility of contaminant in water, mg/l-water

n_m = Soil moisture content expressed as a weight fraction, kg-water/kg-soil

 Θ_m = Soil moisture content, l-water/kg-soil (or ml/g).

Reference for Equation No. 1: Risk Assessment Guidance for Superfund (RAGS), Volume I, Human Health Evaluation Manual (Part B, Development of Risk-based Preliminary Remediation Goals), Interim, Section 3.3.1, Office of Emergency and Remedial Response, Washington, D.C., EPA Publication No. 9285.7-01B, October 1991.

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

$$K_d = K_{oc} \times f_{oc} \tag{2}$$

where K, = Soil/water, partition coefficient, I/kg (or ml/g)

 K_{pc} = Organic carbon partition coefficient, I/kg (or ml/g)

f_{sc} = Fraction of organic carbon in soil, mg/mg (default = 0.02).

Estimation of K_{∞} 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. 3 (based on largest sampling):

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

$$K_{oc} = 10^{((0.544 \log K_{out}) + 1.377)}$$
 (3)

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

$$K_{oc} = 10^{((0.937 \log K_{out}) - 0.006)}$$
 (3a)

Based on aromatics or polynuclear aromatics:

$$K_{oc} = 10^{((1.00 \log K_{ow}) - 0.21)}$$
 (3b)

Based on s-triazines and dinitroaniline herbicides:

$$K_{oc} = 10^{((0.94 \log K_{ou}) + 0.02)}$$
 (3c)

Based on insecticides, herbicides, and fungicides:

$$K_{ac} = 10^{((1.029 \log K_{ext}) - 0.18)}$$
 (3d)

Based on substituted phenylureas and alkyl-N-phenylcarbamates:

$$K_{cc} = 10^{((0.524 \log K_{cc}) + 0.855)}$$
 (3e)

where K_c = Organic carbon partition coefficient, I/kg (or ml/g)

K_{bw} = Octanol/water partition coefficient, I/kg (or ml/g).

Reference for Step III, 1, Equation Nos. 2-3e: Superfund Exposure Assessment Manual (SEAM), Section 3.5.2.4, Office of Emergency and Remedial Response, Washington, D.C., EPA-450/1-88-001, 1988.

Reference for Values of K, and logK, in Step III, 1, B: Superfund Public Health Evaluation Manual (SPHEM), Exhibit A-1, Office of Emergency Remedial Response, Washington, D.C., EPA-540/1-86-060, October 1986.

- C. From the vapor-phase contaminant concentrations (soil gas) or from bulk concentrations determined in "A" above, calculate an emission rate for each contaminant.
 - 1. With measured soil gas concentrations:

$$E_{i} = \frac{D_{i} C_{i} A (P_{t}^{4/3})}{d_{ec}}$$
 (4)

where E_i = Emission rate of component i, g/s

D_i = Diffusion coefficient of component i in air, cm²/s (scientific literature or Equation No. 7)

C_i = Vapor concentration of component i measured in the soil pore spaces, g/cm³ (Equation No. 4a)

A = Exposed surface area, cm²

P_t = Total soil porosity, dimensionless (Equation No. 6). P_t assumes dry soil (worst-case); if soil is wet more often than dry, substitute the term (P_a^{10/3}/P_t²) for the term P_t^{4/3} (see Equation No. 6a)

d_{sc} = Effective depth of soil cover, cm (from sample depth to soil surface).

If soil gas measurements are given in ppm on a volume per volume basis, use the following equation to convert to a weight per volume basis:

$$C_i = C_{SG} \times \frac{MW_i}{2.404 \times 10^{10}}$$
 (4a)

where C_i = Vapor concentration of component i in the soil pore spaces, g/cm³

C_{sc} = Measured soil gas concentration of component i, ppmv

MW_i = Molecular weight of component i, g/mole.

2. With measured <u>bulk concentrations</u> $\geq C_{sat}$ (Equation No. 1):

Note: Under this scenario, "free-phase" contaminants exist in the soil vadose zone, usually as a liquid-phase waste layer or discrete film. Representative concentration measurements should be used from the discrete waste layer at depth and not from composite samples.

$$E_i = D_i C_{si} A(P_t^{4/3}) \frac{M_i}{d_{sc}}$$
 (5)

where $E_i = Emission rate of component i, g/s$

D_i = Diffusion coefficient of component i in air, cm²/s (scientific literature or Equation No. 7)

C_{si} = Saturation vapor concentration of component i, g/cm³ (Equation No. 8)

A = Exposed surface area, cm²

P_t = Total soil porosity, dimensionless (Equation No. 6). P_t assumes dry soil (worst-case); if soil is wet more often than dry, substitute the term (P_a^{10/13}/P_t²) for the term P_t^{4/3} (see Equation No. 6a).

M = Mole fraction of component i in the waste, gmole/gmole

d_{sc} = Effective depth of soil cover, cm.

Note: When calculating M_i, include the number of moles of all contaminants plus the water within the waste. Do not include the number of moles of soil because soil is assumed to be nonvolatile.

Calculation of total soil porosity (Pt):

$$P_t = 1 - \frac{\beta}{\rho} \tag{6}$$

where P, = Total soil porosity, dimensionless

β = Soil bulk density, g/cm³: generally between 1.0 and 2.0 g/cm³ (default = 1.5 g/cm³)

ρ = Particle density, g/cm³: usually 2.65 g/cm³ for most mineral material.

Note: P_t assumes dry soil and thus worst-case diffusion conditions. If the soil cover is wet more often than dry on a long-term basis, air-filled porosity (P_a) may be substituted for P_t. For estimation, P_t can be

assumed to be between 0.55 for dry, noncompacted soils and 0.35 for compacted soils.

Calculation of air-filled porosity (Pa):

$$P_a = P_t - \theta_m \beta \tag{6a}$$

where P_a = Air-filled soil porosity, dimensionless

P, = Total soil porosity, dimensionless (Equation No. 6)

 Θ_m = Soil moisture content, cm³-water/g-soil (or ml/g)

 β = Soil bulk density, g/cm³.

Estimation of diffusion coefficient of component i in air (D_i) if not available from the scientific literature:

$$D_i = \frac{0.001T^{1.75} \sqrt{\frac{1}{MW_i} + \frac{1}{MW_a}}}{P_{ab} \left[\left(\sum V_i \right)^{1/3} + \left(\sum V_a \right)^{1/3} \right]^2}$$
 (7)

where D_i = Diffusion coefficient of component i in air, cm²/s

T = Absolute temperature of ambient air, °K (annual average)

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

 P_{ab} = Absolute pressure, atmospheres

 ΣV_i ; ΣV_a = Molecular diffusion volumes of component i and air (20.1), respectively, cm³/mole. This is the sum of the atomic diffusion volumes of the compound's atomic constituents.

Atomic diffusion volumes for use in estimating D:

C = 16.5	CI = 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 ΣV_i for carbon tetrachloride, CCl_a :

$$C = 16.5$$

 $Cl_4 = 4x19.5 = \frac{78.0}{94.5} + \frac{1}{2}$

Note: Equation No. 7 may not be appropriate for polar compounds. Where possible, values of D_i in the scientific literature should be used.

Calculation of saturation vapor concentration (Csi):

$$C_{si} = \frac{p \ MW_i}{R \ T} \tag{8}$$

where C_{si} = Saturation vapor concentration of component i, g/cm³

p = Vapor pressure of the chemical i, mm Hg

R = Molar gas constant, 62,361 mm Hg-cm³/mole-o K

T = Absolute temperature of waste (in situ), ° K

MW_i = Molecular weight of component i, g/mole.

3. With measured bulk concentrations < C_{sat} (Equation No. 1):

Note: Under this scenario all contaminants are assumed to be in solution with the available soil moisture and adsorbed to soil particles within the soil matrix (fully incorporated). Soil samples should not show evidence of discrete waste layers or films.

$$E_i = \frac{A \ 2 \ D_{ei} \ \varepsilon \ K_{os} \ C_i}{\sqrt{\pi \ \alpha \ t}} \tag{9}$$

where E = Average emission rate of component i for exposure interval t, g/s

 D_{ei} = Effective diffusivity of component i, cm²/s (= $D_i \epsilon^{0.33}$)

D_i = Molecular diffusivity of component i in air, cm²/s (scientific literature or Equation No. 7)

K_{ss} = Soil/air partition coefficient, g/cm³ (Equation No. 9b)

C_i = Bulk soil concentration of component i, g/g

t = Exposure interval, s (exposure time x exposure frequency x exposure duration in seconds)

 ϵ = Soil porosity, dimensionless. ϵ = P_t for dry soil or ϵ = P_a when soil is more often wet than dry (see Equation Nos. 6 and 6a)

A = Exposed surface area, cm^2 .

and:

$$\alpha = \frac{D_{ei} \, \varepsilon}{\varepsilon + (\rho)(1 - \varepsilon)/K_{es}} \tag{9a}$$

where ρ = Particle density, g/cm³ (default = 2.65 g/cm³).

Calculation of soil/air partition coefficient (Ks):

$$K_{as} = (H/K_d) \times 41 \tag{9b}$$

where K = Soil/air partition coefficient, g/cm³

H = Henry's Law constant of component i, atm-m³/mole

 K_{I} = Soil/water partition coefficient, ml/g or cm³/g (Equation No. 2)

= Conversion factor to change H to dimensionless form.

Reference for Step III, 3: Development of Advisory Levels for Polychlorinated Biphenyl (PCB) Cleanup, Office of Research and Development, Exposure Assessment Group, Washington, D.C. EPA-600/6-86-002, 1986.

Reference for Step III, 3: RAGS Part B, Section 3.3.1, October 1991.

- 2. Gaseous Emissions From Nonaerated Surface Impoundments and Contaminants (In Solution) Pooled at Soil Surfaces:
 - A. For air release potential of contaminants from nonaerated surface impoundments and for diluted contaminants pooled at soil surfaces, measure contaminant-specific liquid-phase concentrations of each contaminant.
 - 1. Take sufficient samples to ensure representative sampling of the impoundment/pool.
 - 2. Conduct analysis of samples to quantify content on a contaminantspecific basis.
 - B. From the liquid-phase contaminant concentrations determined in "A" above, calculate an emission rate for each contaminant:

$$E_i = K_i C_s A \tag{10}$$

where E = Emission rate of component i, g/s

Κ = Overall mass transfer coefficient, cm/s (Equation No. 11)

C_s = Liquid-phase concentration of component i, g/cm³ (1 mg/l = 1x10⁶ g/cm³)

A = Exposed surface area, cm².

Calculation of overall mass transfer coefficient (K):

$$\frac{1}{K_i} = \frac{1}{k_{iL}} + \frac{R T}{H_i k_{iG}} \tag{11}$$

where K = Overall mass transfer coefficient, cm/s

k_L = Liquid-phase mass transfer coefficient, cm/s (Equation No. 12)

R = Ideal gas constant, 8.2x10⁻⁵ atm-m³/mole-o K

T = Absolute temperature, ° K

H = Henry's Law constant of component i, atm-m³/mole

 k_{ig} = Gas-phase mass transfer coefficient, cm/s (Equation No. 13).

Estimation of liquid-phase mass transfer coefficient (k,):

$$k_{iL} = \left(\frac{MWo_2}{MW_i}\right)^{0.5} \left(\frac{T}{298}\right) (k_L, O_2)$$
 (12)

where $k_{\scriptscriptstyle L}$ = Liquid-phase mass transfer coefficient, cm/s

MWo₂; MW_i = Molecular weights of oxygen (32.0) and component i, respectively, g/mole

T = Absolute temperature, ° K

k, O₂ = Liquid-phase mass transfer coefficient for oxygen at 25°C, cm/s (default = 0.002 cm/s).

Estimation of gas-phase mass transfer coefficient (kg):

$$k_{iG} = \left(\frac{MW_{H_2O}}{MW_i}\right)^{0.335} \left(\frac{T}{298}\right)^{1.005} (k_{iG}, H_2O)$$
 (13)

where k_G = Gas-phase mass transfer coefficient, cm/s

MW_{H 0}; MW_i = Molecular weights of water (18.0) and component i, respectively, g/mole

T = Absolute temperature, ° K

k_G, H₂O = Gas-phase mass transfer coefficient of water vapor at 25°C, cm/s (default = 0.833 cm/s).

Reference for Default Values of k₁,O₂ and k₃,H₂O: Evaluation and Selection of Models for Estimating Air Emissions From Hazardous Waste Treatment, Storage, and Disposal Facilities, Section 2, Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA-450/3-84-020, NTIS PB85-156115, December 1984.

3. Volatile Nonmethane Organic Compound (NMOC) Emissions From Codisposal Landfills:

Codisposal sites contain toxic wastes in combination with municipal or sanitary wastes which generate landfill gases (e.g., methane, hydrogen gas, and carbon dioxide). These "sweep" gases greatly increase the upward migration of volatile NMOCs and their subsequent release to the atmosphere. In fact, the landfill gas velocity becomes the controlling factor so that soil and gas-phase diffusion become essentially insignificant.

- A. Measure soil gas concentrations of each volatile NMOC.
- B. From the soil gas concentrations determined in "A" above, calculate an emission rate for each volatile NMOC:

$$E_i = C_i V_{\nu} A \tag{14}$$

where ξ = Emission rate of component i, g/s

C_i = Concentration of component i in the soil pore spaces, g/cm³

 V_y = Mean landfill gas velocity in the soil pore spaces, cm/s (default = 1.63x10⁻³ cm/s average)

A = Exposed surface area, cm².

Note: The default value of V_{γ} is an average value. Various site factors such as saturated soils will tend to reduce the rate of volatilization. The degree to which this model is able to accurately predict release rates under conditions of moist or wet soils is unknown. Under such conditions, emission flux measurements at soil surfaces may be necessary.

Reference for Step III, 1, 2, & 3: SEAM, Section 2.3.2.1., April 1988.

4. Free-phase Volatile Contaminants Directly Exposed to the Atmosphere:

For any and all free-phase volatile contaminants directly exposed to the atmosphere, in-depth 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 free product exists.

- 5. Solids and Semivolatiles Emitted as Particulate Matter:
 - A. For solids and semivolatile contaminants with air release potential (e.g., metals, semivolatiles, and pesticides adsorbed to fugitive dust, etc.), measure contaminant-specific bulk concentrations of erodible <u>surface</u> materials.

Note: If onsite data are not available, assume that the contaminant concentrations measured from bulk samples of surface materials are constant across the entire soil particle size range.

For estimating emissions from wind erosion, either of two emission flux (g/m²-h) models are used depending on the erodibility classification of the site surface material. These two models are: 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 flowchart (Figure 1) is used to determine: 1) whether no

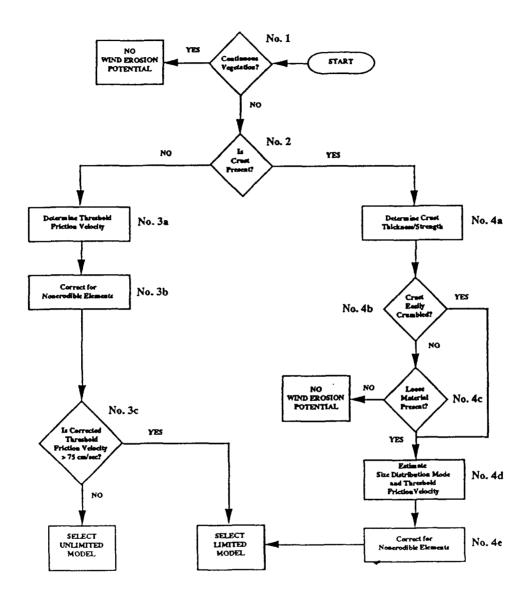


Figure 1. Decision flowchart.

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 flowchart are detailed in the list of steps following the flowchart.

It should be noted that the two emission flux models (Equations 15 and 18) 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 particle 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 Flowchart:

No. 1 Continuous Vegetation?

Continuous vegetation means "unbroken" vegetation covering 100 percent of the site or site sector to be analyzed.

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 site particles are suspended. To determine u_t , the mode of the surface aggregate size distribution must be determined. The distribution mode is the particle size containing the highest percentage of material from a representative sample. This can be determined with a field sieving procedure as follows:

- 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',) in cm/s from the relationship in Figure 1a.

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 cm² as viewed from overhead but half-buried in the soil, would have a frontal projected area of 5 cm². 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 is not available, a conservative default value of 0.01 may be used for nonsmooth soil surfaces. This results in a correction factor of approximately 1.5.

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.

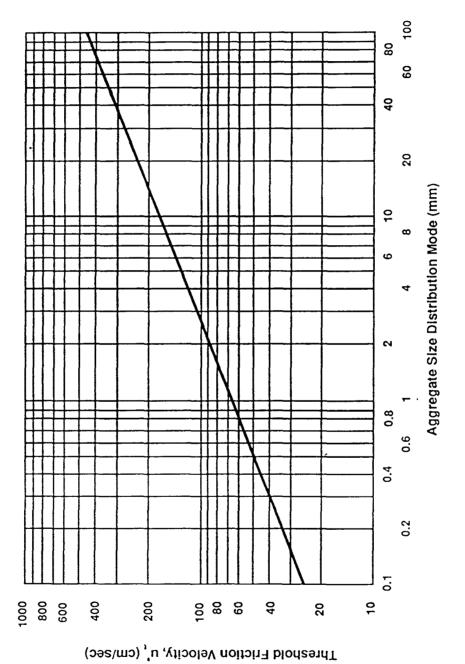
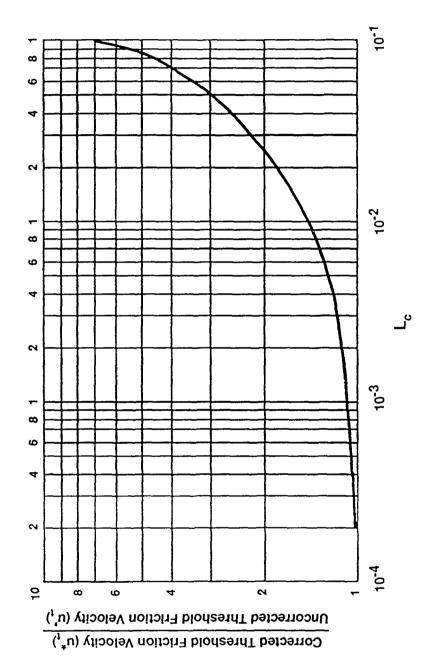


Figure 1a. Threshold friction velocity versus aggregate size distribution.



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- No. 4c Loose Material Present?

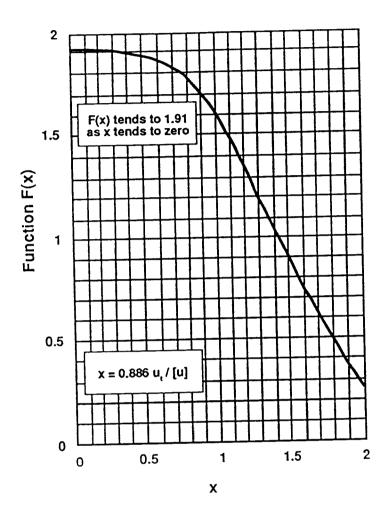
 Determine if there is loose erodible material <u>above</u> any hardened crust.
- No. 4d Estimate Size Distribution Mode and Threshold Friction Velocity

 Estimate the aggregate size distribution mode of the loose material above the hardened crust and determine the threshold friction velocity (u'₁) (Step 3a).
- No. 4e Correct for Nonerodible Elements (u*_t) (Step 3b)
 - B. Using either the "unlimited reservoir" or the "limited reservoir" model as determined from Figure 1, calculate an annual average emission flux (g/m²-h) for each contaminant found in the erodible surface material.
 - 1. Using the "unlimited reservoir" model
 - a. Emission flux for inhalable particles \leq 10 μ m (PM₁₀):

$$E_{10} = 0.036 (1-V) \left(\frac{[u]}{u_t}\right)^3 F(x) C$$
 (15)

where $E_{10} = PM_{10}$ annual average emission flux of component i, g/m^2 -h

- V = Fraction of contaminated surface with continuous vegetative cover (equals 0 for bare soil)
- [u] = Mean annual windspeed at 10 m anemometer height, m/s (from local climatological data)
- Equivalent threshold value of windspeed at 7 m anemometer height,
 m/s (Equation No. 16)
- C = Fractional percent by weight of component i from bulk samples of surface material
- F(x) = Function obtained from the relationship in Figure 2 (x=0.886 μ /[μ], dimensionless ratio).



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

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

Calculation of the equivalent threshold value of windspeed at a 7 m anemometer height (4):

$$u_t = 18.1 \ (u^*t)/100$$
 (16)

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

(u*_t) = Threshold friction velocity corrected for nonerodible elements, cm/s (5.A, detailed Steps 3a and 3b)

Note: This calculation is based on an assumed roughness height for flat terrain of 0.5 cm, between natural snow (0.1) and a plowed field (1.0). Refer to the reference for Step III.5. to calculate u if a roughness height of 0.5 cm is not appropriate for site-specific conditions.

b. Emission flux for particles $\leq 30 \,\mu$ m (for deposition modeling):

$$E_{30} = E_{10} \times 2 \tag{17}$$

where E_{30} = Annual average emission flux of component i as particles $\leq 30 \,\mu\text{m}$, g/m²-h

 $E_{10} = PM_{10}$ annual average emission flux of component i, g/m^2 -h (Equation No. 15).

- 2. Using the "limited reservoir" model.
 - a. Emission flux for inhalable particles $\leq 10 \,\mu \text{m}$ (PM₁₀):

$$E_{10} = 0.83 \frac{(f) P(u^{+}) (1-V) (C)}{(1000) (PE/50)^{2}}$$
 (18)

where $E_{10} = PM_{10}$ annual average emission flux of component i, g/m^2-h

- f = Frequency of disturbances per month (1/month for abandoned sites or sites with no activity)
- u⁺ = Observed (or probable) fastest mile of wind (at 10 m anemometer height) for the period between disturbances, m/s (from local climatological data)
- P(u⁺) = Erosion potential, i.e., quantity of erodible particles at the surface prior to the onset of erosion, g/m² (Equation No. 19 or 19a)
- Fraction of surface area covered by continuous vegetation (equals O for bare soil)
- C = Fractional percent by weight of component i from bulk samples of surface material
- PE = Thornthwaite's Precipitation-Evaporation Index used as a measure of soil moisture content (Figure 3).

Calculation of erosion potential [P(u⁺)]:

$$P(u^*) = 6.7 (u^* - u_t) \text{ for } u^* \ge u_t$$
 (19)

$$P(u^*) = O \text{ for } u^* < u_t \tag{19a}$$

where $P(u^+)$ = Erosion potential, g/m^2

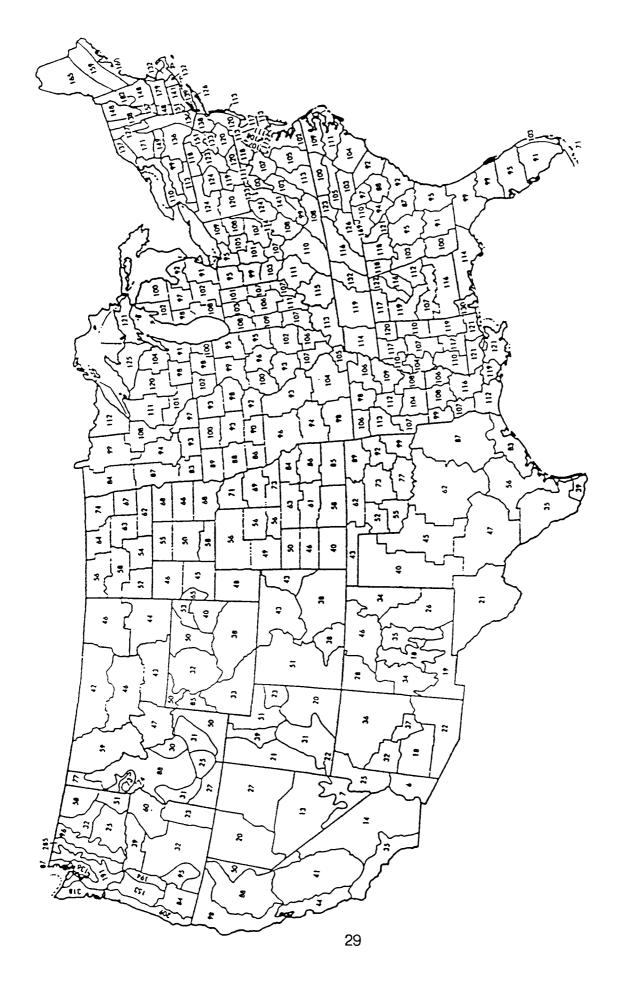


Figure 3. Thornthwaite's Precipitation-Evaporation Index (PE) for State Climatological Divisions.

- u⁺ = Observed (or probable) fastest mile of wind (at 10 m anemometer height) for the period between disturbances, m/s (from local climatological data)
- = Equivalent threshold value of windspeed at a 7 m anemometer height,
 m/s (Equation No. 16).
 - b. Emission flux for particles \leq 30 μ m (for deposition modeling):

$$E_{30} = E_{10} \times 2 \tag{20}$$

where E_{30} = Annual average emission flux of component i as particles $\leq 30 \,\mu\text{m}$, g/m²-h

 $E_{10} = PM_{10}$ annual average emission flux of component i, g/m^2 -h (Equation No. 18).

Reference for Step III.5: Rapid Assessment of Exposure to Particulate Emissions from Surface Contamination Sites, Sections 1 - 4.1.2. Office of Health and Environmental Assessment, Washington, DC. EPA-600/8-85/002. February 1985.

C. Calculate a total emission rate (g/s) of each contaminant from the emission flux rate using the following formula:

$$E_T = \frac{E_x A}{3600} \tag{20a}$$

where E_{τ} = Annual average emission rate of component i for particles $\leq x \mu m$, g/s

 $E_x = E_{10}$ or E_{30} emission flux obtained from Equation Nos. 15, 17, 18, or 20, g/m^2 -h

A = Contaminated surface area, m^2 .

STEP IV. ESTIMATE AMBIENT AIR CONCENTRATIONS AND/OR DEPOSITION CONCENTRATIONS AT RECEPTOR LOCATIONS OF INTEREST

Background:

Once emission rates have been calculated, atmospheric dispersion models are used to predict ambient air concentrations and/or deposition concentrations at receptors of interest. Dispersion models may include simple hand calculations or special computer models. Upper bound values can be approached by making conservative modeling assumptions (e.g., worst-case meteorological conditions, source configuration, etc.). A number of other more refined EPA-approved dispersion models may be substituted for models in the procedures listed below if an in-depth APA is warranted. Use of the procedures below should generally produce a more conservative estimate.

- 1. Model the emissions of each contaminant (gaseous or particulate) for each source using the appropriate EPA atmospheric dispersion model and source configuration data (i.e., size, location, height, etc.).
 - A. Determine if the release is negative, positive or neutrally buoyant.

Note:

Under various release scenarios more applicable to CERCLA Removal Actions (e.g., sudden release of dense gases) negatively buoyant releases may be encountered. Impacts from negatively buoyant releases are likely to be most severe during stable atmospheric conditions and light windspeeds. Under these conditions, buoyancy effects may dominate atmospheric turbulent energy reducing dispersion and resulting in higher concentrations close to the site. If negatively buoyant releases are anticipated, perform the calculations referenced below to determine if negative buoyancy effects are applicable.

Reference for Step IV.1.A: A Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants (Workbook), Section 5.1. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/4-88-009. NTIS PB89-134340. September 1989.

Note:

The Workbook contains hand calculation procedures for estimating emission rates, dispersion parameters, and ambient air concentrations for 18 different release scenarios typically found at treatment, storage, and disposal (TSDF) facilities (e.g., pipe leaks, tank leaks, etc.). These procedures may be used in conjunction with or in lieu of the procedures described herein if the baseline case accurately approximates one of the 18 scenarios described in the Workbook. Care should be taken, however, to carefully analyze and compare the emission rate scenarios in the Workbook with that of the baseline case to ensure that the Workbook emission scenarios are appropriate. The Workbook procedures have been converted to a PC-based system called TSCREEN. TSCREEN is available free of charge from the EPA Support Center for Regulatory Air Models (SCRAM) Bulletin Board System at (919) 541-5742.

B. For neutral or positively buoyant point or area source emissions, use the EPA SCREEN atmospheric dispersion model to predict short-term (if applicable) downwind ambient air concentrations (μg/m³). The SCREEN model predicts one hour average concentrations at receptors, independent of wind direction, for point, area, and flare sources. Because the SCREEN model can accommodate only one source for each run, model each source separately and aggregate the predicted concentrations at the receptors of interest. Aggregating will yield a conservative one hour average estimate. The following reference should be reviewed to fully understand the capabilities and limitations of the SCREEN dispersion model. SCREEN may be obtained free of charge from the SCRAM Bulletin Board at (919) 541-5742.

Reference for Step IV.1.B: Screening Procedures for Estimating the Air Quality Impacts of Stationary Sources. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/4-88-010. NTIS PB89-159396. August 1989.

C. As applicable, estimate 3-, 8-, 24-hour, or annual average concentrations (e.g., to demonstrate compliance with ARARs/TBCs of the same averaging times) at receptors of interest by multiplying one hour concentrations (µg/m³) by the following factors:

Averaging time	Multiplying factor
3 hours	0.9
8 hours	0.7
24 hours	0.4
annual	0.025 (for point sources only)

Reference for Step IV.1.C: Workbook. Appendix E.

Reference for Annual Point Source Multiplying Factor: Estimation of Air Impacts From Air Stripping of Contaminated Water. Air/Superfund NTGS Series, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/1-91-002. NTIS PB91-21888, May 1991. (The referenced value is presently under review and subject to change.)

- D. Estimate downwind annual average concentrations for <u>area</u> sources using the following procedures:
 - 1. Estimate the combined area source size by summing the sizes of all individual area sources.
 - 2. Determine the square area of the combined area source (example: $2,500 \text{ m}^2 = 50 \text{ m} \times 50 \text{ m}$).
 - 3. Determine the total annual emission rate for the combined area source and convert to kg/m²-yr.
 - 4. From the set of curves in Figure 4, locate the χ/Q value for the appropriate downwind receptor distance and source size.
 - 5. Multiply the χ/Q value (10⁻⁹ yr/m) by the annual emission rate per square meter, Q (kg/m²-yr) to derive the annual average concentration, χ (μ g/m³) for the combined source.

Note: For downwind distances <50 meters and for onsite receptors, the model presented in the following step (Step IV,1,E) may be used.

Reference for Step IV.1.D: Hazardous Waste TSDF-Fugitive Particulate Matter Air Emissions Guidance Document, Appendix C. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-89-019. NTIS PB90-103250. May 1989.

E. If the receptor is located at the edge of the area source or within the contaminated area, use the following procedure to estimate the annual average concentration at the <u>center</u> of the area source.

Given the horizontal dimension of the square area source (X in meters) and the total source emission rate (Q_r in g/s):

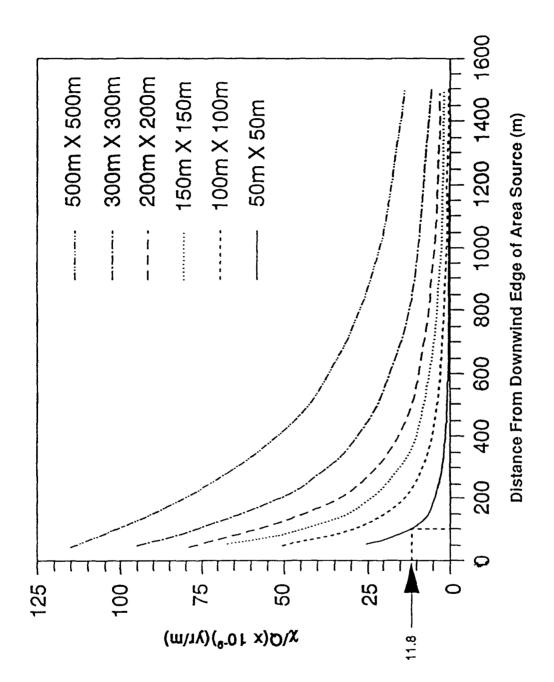


Figure 4. X/Q versus distance for six area source sizes.

- 1. Determine the natural logarithm of the horizontal dimension of the subject area source (lnX).
- 2. Enter the value produced in (1) above into the following polynomial equation to produce the natural logarithm of the normalized concentration:

$$ln(C/Q_T) = 13.0 - 0.261(lnX) - 0.241(lnX)^2 + 0.0124(lnX)^3$$

3. Take the exponential of the value produced in (2) above to produce the normalized concentration:

$$C/Q_T = e^{\ln(C/Q_T)}$$

4. Multiply the normalized concentration by the emission rate to produce the long-term (annual average) concentration in $\mu g/m^3$:

$$C = (C/Q_T)Q_T$$

Note: The above polynominal equation is based on the modeling results of progressively larger square area sources utilizing the U.S. EPA Point-Area-Line (PAL) dispersion model. A single receptor was located at the center of each source negating the effects of wind direction. Windspeed was set at 2 m/s and atmospheric stability was set at Pasquill-Gifford class D (neutral) as typical average annual values. Emissions are assumed to be continuous, uniform over the surface of the area, nonbuoyant, inert, and emitted at a concentration less than approximately one percent (10,000 ppmv), so that density differences relative to air are not important. These procedures may not be conservative for sites in very sheltered locations where windspeeds may average less than 2 m/s and/or where very stable conditions may be typical. In these cases, refined modeling and/or monitoring may be required.

The procedures in Step IV,1,D and E are presently under review and subject to change.

Reference for Step IV.1.E: Memorandum from Robert Wilson, U.S. EPA, Region X Meteorologist, to Pat Cirone, Chief, Health and Environmental Assessment Section. June 1991.

2. If the Baseline Risk Assessment ultimately indicates that the incremental or aggregate risk for carcinogenic contaminants from onsite incidental ingestion of contaminated soil exceeds the acceptable risk range (i.e., 10⁻⁴ to 10⁻⁶) or if the

Hazard Index for noncarcinongenic contaminants for the same pathway exceeds unity, determine the deposition concentration (g/m²) of each applicable contaminant at receptors of interest. Deposition concentrations are used to calculate exposures from atmospheric deposition of contaminants. Applicable pathways may include incidental ingestion of soil, uptake in edible biota, indoor exposures due to track-in of outdoor dustfall, etc.

A. Model the particulate emissions of each applicable contaminant using the EPA Industrial Source Complex (ISC) model or the EPA Fugitive Dust Model (FDM) to determine deposition concentrations.

Reference for Step IV.2.A. User's Guide for the Fugitive Dust Model (FDM) (Revised), User's Instructions, U.S. EPA, Region X, Seattle, Washington. EPA-910/9-88-202R. NTIS PB90-215203, PB90-502410 (program diskette). January 1991.

Reference for Step IV.2.A: Industrial Source Complex (ISC) Dispersion Model User's Guide-Second Edition (Revised), Volumes I, II, and User's Supplement. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/4-88-002a and 002b. NTIS PB88-171475, PB88-171483, and PB88-171491. December 1987.

Note: The most recent and fully capable editions of ISC and FDM may be obtained free of charge from the SCRAM Bulletin Board at (919) 541-5742.

B. For sites that are suspected of having deposited contaminants (especially low mobility contaminants) offsite over an extended period of time, measure contaminant-specific concentrations of surface materials at receptors of interest. The potential contributions from other sources in the area (if any) should be considered and separated from the analysis.

STEP V. COMPARE AMBIENT AIR CONCENTRATIONS TO AIR ARARS AND TBCs

1. From dispersion modeling results performed in Step IV, compare estimated ambient air concentrations with air ARARs and/or TBCs listed in Step II. Comparisons must be made on a chemical-specific basis and estimated concentrations must represent the same averaging time(s) as the ARARs/TBCs (e.g., annual average, 24-h average, etc.).

Note: Most ARAR's specify that the applicable standard must be complied with at the point of public access. For ground level nonbouyant sources this will be the site fenceline. For such ARARs, dispersion modeling must include such a receptor whether or not the receptor also represents the maximum exposed individual.

2. If any air ARAR or TCB is exceeded, an in-depth air pathway analysis is warranted which may include in-depth modeling and/or air monitoring.

STEP VI. ORGANIZE CONCENTRATION DATA 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. In addition, deposition concentration estimates (g/m²) may be applicable (see Step IV, 1, B and Step IV, 2).

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.

APPENDIX A CASE EXAMPLE

PREDICTIVE BASELINE EMISSIONS ESTIMATION FOR CASEX SITE

STEP I. REVIEW SITE BACKGROUND AND GATHER NECESSARY DATA

Background:

hypothetical Casex Superfund site is located in mixed The а rural/residential/commercial area of a northeastern state. The site contains an inactive scrap metals and polymer processing facility. Wastes from the polymer reclamation process were stored in underground storage tanks, and other wastewaters were discharged to a ditch located onsite. The facility was in operation for approximately 25 years and was closed in 1985. Removal actions were conducted in 1990 to remove tanks, drums, and debris.

Various volatile and semivolatile organics and metals have been identified in the soils and groundwater. Soil gas survey data for volatile organic compounds (VOCs) is available in addition to soil boring sample data.

1. Review the nature of contamination at the site and identify potential exposure pathways and receptors.

The primary air exposure pathways are:

- Inhalation of volatile contaminants released from near-surface and subsurface soils
- o Inhalation of metals and semivolatile contaminants (adsorbed to soil particles) released as fugitive particulate matter from surface soils.

The potential receptors are residents located at a house on the property east of the areas of contamination, and residents of apartments located just south of the property. Distances will be tabulated in the site data to follow. A secondary potential exposure pathway is ingestion of metals and semivolatile contaminants redeposited offsite from fugitive dust.

Assemble all relevant site data.

The site consists of 17.5 acres of which about one-half is wooded. The plant area contains five buildings on the west side of the property and the major areas of soil contamination. This area is fenced and contains approximately 5 acres. Figure 1 shows the general site map.

The list of chemicals identified in soils, the 95 percent UCL of the arithmetic mean of the bulk concentrations and soil gas concentrations, and sampling depths were assembled and are shown in Table 1. The reference chemical properties are also shown in this table. Figure 2 will be used to define the limits of volatile organic contaminants in soils as measured in the soil gas. The fenceline represents the approximate limits of metal contamination in surface soils. Surface vegetation in these areas was not reported.

Soil types include mainly sand and loamy sand. Grain size analyses of surface soils and average soil moisture content (2%) of subsurface (vadose zone) soils were obtained, but other properties such as soil porosity were not reported. The grain size analysis for surface soils is shown in Table 2. Permanent groundwater is present at a depth of 15 to 20 feet, and the land is relatively flat.

The following were taken from Figures 1 and 2:

For volatile and semivolatile organics and metals:

Area of contamination = $150 \text{ m} \times 150 \text{ m} = 22,500 \text{ m}^2$

Distance to house = 175 m E Distance to apartments = 210 m S

TABLE 2. GRAIN SIZE ANALYSIS FROM SURFACE SOIL SAMPLES

Soil type	Grain size, mm	Average fraction, %
Gravel Coarse sand Medium sand Fine sand Silt Clay	2.00 - 4.75 0.42 - 2.00 0.25 - 0.42 0.075 - 0.25 0.006 - 0.075 < 0.006	6.5 12.3 36.6 28.1 6.6 9.9
		100.0

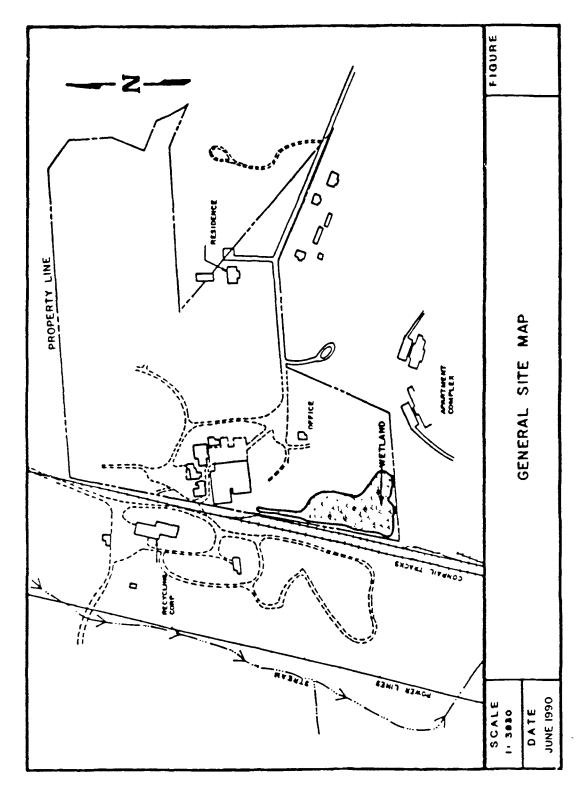


Figure 1. General site map.

TABLE 1. SAMPLING DATA AND CHEMICAL PROPERTIES

COMPOUND	95% UCL		BULK CONC. (ug/kg)	95% S01L	UCL GAS						
VOLATILE ORGANICS	DEPTH 1 ft.	DEPTH 4 ft.	DEPTH 11 ft.	CONC. (ppbv)	DEPTH ft.	(g/mol)	VP (mm Hg)	Di (cm2/s)	Hi Koc (atm-m3/mol) (m1/g)	Koc (ml/g)	Solubility (mg/l)
Methylene chloride Trichloroethene Benzene Tetrachloroethene 1,1-Dichloroethane 1,1,1-Trichloroethane Toluene Ethylbenzene Xylenes (total)	23 33 12 12 75 100	2000 2000 67000 3600	170 5300 2500 220 220 250 25 1800 71000 72000	96654 106654 106654 17500 1343 9735 20111 24905 20702	 0004400444	85 131 166 99 133 106 106	362 362 95.2 17.8 182 123 28.1 10	1.00E-01 7.90E-02 7.90E-02 7.20E-02 9.10E-02 7.80E-02 7.50E-02 7.17E-02	2.03E-03 9.10E-03 5.59E-03 2.59E-02 4.31E-03 1.44E-02 6.43E-03 7.04E-03	35.0 126.0 83.0 364.0 364.0 30 152 300 1100 240	20000 1100 1750 1750 150 5500 535 152 152 198
Phenol Benzoic Acid Napthalene Dimethylphthalate Fluorene Anthracene Di-n-butylphthalate Fluoranthene Pyrene Bis(2-ethylhexyl)pthalate	4700 3300 830 720 720 52 400 23000 2500 1700		7100 7400 3600 5700 1400 76000 76000 630000 1700			94 128 128 128 116 178 202 202 202 203 391 391	0.341 0.5 1.00E-04 1.00E-05 5.00E-06 2.50E-06		4.54E-07 4.80E-04	7300 7300 170000 38000 38000	30
INORGANICS Arsenic Barium Cadmium Chromium Mercury	1.07E+06 2.43E+05 5.80E+04 1.30E+04 1.40E+03 1.30E+04					75 137 112 52 201 59	0.002				

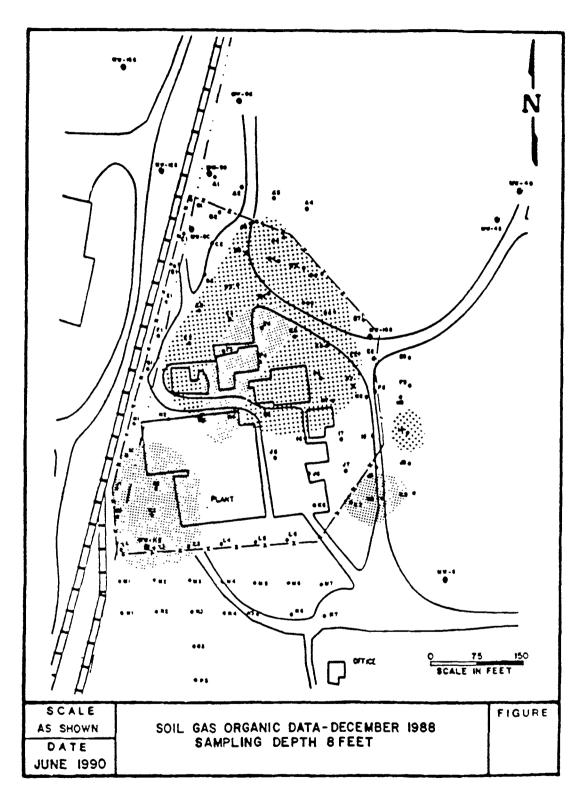


Figure 2. Areas of volatile organics in soil gas.

Available meteorological data:

Mean annual temperature = 54.7° F (13° C)

Average wind direction:

October - April

NW

May - August

SW SE

September :

Windspeed data taken from National Climatic Data Center Publications is shown in Table 3. The nearest representative station available was within 5 miles of the site.

3. Assemble reference chemical property data for all contaminants.

This information is included in Table 1.

TABLE 3. LOCAL CLIMATOLOGICAL DATA

	TABLE 3. LOCAL CLIMATO	LOGICAL DATA
	Windspeed da	ta
	Normal mean	
mi/h	m/s	Direction
9.6	4.29	WSW
	Fastest mile data ((1983)
	Faste	st mile
Month	mi/h	m/s
January	27	
February	36	
March	31	
April	28	
May	26	
June	26	
July	23	
August	34	
September	24	
October	26	
November	30	
December	35	
Mean	28.83	12.89

STEP II. LIST AIR ARARS AND TBCs

- 1. List All Air ARARs and TBC Acceptable Ambient Levels and Averaging Times:
 - A. NAAQS for applicable site contaminants:

PM₁₀:

 $50 \mu g/m^3$ annual average $150 \mu g/m^3$ 24-h average

Ozone:

0.12 ppm 1-h average

B. NESHAPs:

Not applicable.

C. State Ambient Air Concentration Guidelines or Standards:

The State does not publish specific AALs for air toxics but does require control of air emissions from industrial processes that emit more than 0.1 lb/h (45.4 g/h) of each of 11 toxic volatile organic substances. The following site contaminants are included in the State's list of toxic air pollutants:

Benzene Tetrachloroethene Trichloroethene.

This rule is not an ARAR under baseline conditions, but may be a potential TBC and will be evaluated as such.

D. Others as applicable.

No other ARARs or TBCs were identified.

2. Develop a set of air pathway pollutants for inclusion in the analysis.

The set of contaminants with the highest site concentrations and lowest levels of concern are of greatest interest and should be carried through the analysis. Therefore, for each contaminant, the concentration in the soil was divided by the ambient health level of concern for that contaminant. Volatile organic compounds (soil gas concentrations) were assessed separately from metals and semivolatiles (surface soil bulk concentrations). The resulting quotients were summed and the percent contribution of each contaminant was computed to provide a relative indication of the importance of that contaminant. Contaminants contributing less

than one percent of the total of the ratios of concentration in soil to level of concern were eliminated. This operation is shown in Table 4. The remaining contaminants, or indicator compounds, are listed in Table 5 along with the health levels of concern and the ARARs/TBCs.

Note: The procedure used in (2) above was developed to simplify the calculations for this case example and should <u>not</u> necessarily be used as guidance.

TABLE 4. CALCULATIONS FOR SELECTION OF INDICATOR COMPOUND

	PRELIMINARY HEALTH LEVEL OF CONCERN (ug/m3) *	BASIS	CONC. (ppb or ug/kg)	CONC./ HLOC	CONTRIBUTION (%)	INDICATOR CHEMICAL
VOLATILE ORGANICS						
Methylene chloride 1,1-Dichloroethane 1,1,1-Trichlorothane Trichloroethene Benzene Tetrachloroethene Toluene Ethylbenzene Xylenes (total)	2.13 500 1000 0.588 0.12 1.92 2000 1000 300	10-6 Risk RfC RfC 10-6 Risk 10-6 Risk 10-6 Risk RfC RfC RfC	96654 1343 9735 10640 40714 17500 20111 24905 20702	45377.46 2.69 9.74 18095.24 339283.33 9114.58 10.06 24.91 69.01	0.0060	X X X
SEMIVOLATILES/METALS			-	411987.01	100.0000	
Phenol Benzoic acid Napthalene Dimethylphthalate Fluorene Anthracene Di-n-butylphthalate Fluoranthene Pyrene Bis(2-ethylhexyl)phtha Benzo(a)pyrene Arsenic Barium Cachium Cachium Mercury Nickel	2100 14000 14 3500 140 1050 350 140 105 0.00059 0.00059 0.00056 8.3E-05 0.3 0.0042	Oral RfD Ora	1.00	2.24 0.24 59.29 0.21 0.37 0.38 65.71 2.64 23.81 2520000.00 2881355.93 4652173913.04 486000.00 103571428.57 156626506.02 4666.67 3095238.10	3.1826	x x x

^{*} Oral RfDs or oral slope factors are used ONLY to derive preliminary health levels of concern for indicator compound analysis.

TABLE 5. AIR PATHWAY COMPOUNDS AND LEVELS OF CONCERN

					
CASEX AIR PATHWAY	COMPOUNDS	AND LEVE	LS OF CO	NCERN	Ţ=
Compound	Preliminary health level of concern, μ g,m³	Basis	ARAR, µg/m³	TBC emissions	Basis
VOLATILE ORGANICS					
Methylene chloride	2.13	10-6 Risk	NA		
Trichloroethene	0.588	10-6 Risk	NA	45.4 g/h	SAACGS
Benzene	0.12	10-6 Risk	NA	45.4 g/h	SAACGS
Tetrachloroethene	1.92	10-6 Risk	NA	45.4 g/h	SAACGS
INORGANICS					
Arsenic	0.00023	10-6 Risk	NA		
Cadmium	0.00056	10-6 Risk	NA		
Chromium	8.3E-05	10-6 Risk	NA		

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

- Gaseous Emissions from Subsurface Soils:
 - A. Obtain contaminant-specific soil gas or soil bulk concentrations.

Both soil gas and bulk samples were taken for this site (at different locations). Emissions calculations will be made using both sets of data for comparison purposes. The higher emission rates will be used for the indicator compounds.

B. Estimate the saturation concentration (C_{set}) for each contaminant in the vadose zone.

For methylene chloride (dichloromethane) C_{sat} is calculated from Equation 1 as:

$$C_{sat} = (K_d \times s \times n_m) + (s \times \theta_m)$$

where
$$K_{r} = K_{re} \times f_{re}$$
 (Equation 2).

Without site-specific data, the value of f_{∞} is assumed to be the default value of 0.02. The values of K_{∞} and s were taken from the Superfund Public Health Evaluation Manual, Exhibit A-1.

Therefore
$$K_d = 35.0 \times 0.02 = 0.7$$

and,

$$C_{sat} = (0.7 \times 20,000 \times 0.02) + (20,000 \times 0.02)$$

$$C_{sat} = 680 \text{ ppm} = 680,000 \text{ ppb}$$

Values of C_{sat} similarly calculated for all volatile indicator compounds are given in Table 6.

TABLE 6. SATURATION CONCENTRATION FOR VOLATILE INDICATOR COMPOUNDS

COMPOUND	95%UCL BULK CONC. (ug/kg)	Kd (m1/g)	s (mg/1)	nM (fraction)	Csat (ug/kg)
Methylene chloride Trichloroethene Benzene	170 5300 2500	0.7000 2.5200 1.6600	20000 1100 1750	0.02 0.02 0.02	680000 77440 93100
Tetrachloroethene	220	7.2800	150	0.02	24840

- C. Calculate an emission rate for each volatile contaminant.
 - 1. Calculate emission rate estimates using soil gas concentration measurements with Equation 4:

$$E_i = \frac{D_i C_i A(P_t^{4/3})}{d_{sc}}$$

For methylene chloride, the soil gas was measured at 96,654 ppb by volume at a depth of 8 ft (Table 1). Convert the vapor concentration to a weight per volume basis using Equation 4a:

$$C_i = C_{SG} \times \frac{MW_i}{2.404 \times 10^{10}}$$

$$96.654 \ ppm \times \frac{85}{2.404 \times 10^{10}} = 3.42 \times 10^{-7} \ g/cm^3$$

Depth of soil cover:

$$d_{sc} = 8 \text{ ft x } 30.48 \text{ cm/ft} = 244 \text{ cm}$$

Obtain diffusion coefficients of compounds in air (D_i).

Contamination is above the permanent and seasonal groundwater table. For worst-case conditions, calculate total soil porosity, P. (Equation 6):

$$P_t = 1 - \frac{\beta}{\rho}$$

Assume bulk density $\beta = 1.5 \text{ g/cm}^3$ and particle density $\rho = 2.65 \text{ g/cm}^3$.

$$P_t = 1 - 1.5/2.65 = 0.434$$

Exposed surface area, $A = 22,500 \text{ m}^2 = 2.25 \text{ x } 10^8 \text{ cm}^2$

Using Equation 4:

$$E_i = \frac{(0.10)(3.42 \times 10^{-7})(2.25 \times 10^8)(0.434^{4/3})}{244} = 0.0104 \text{ g/s}$$

Emission rate calculations for other indicator compounds are shown in Table 7.

- 2. N/A
- All bulk concentrations are less than their respective values of C_{sat}.
 Therefore, emission rates for each contaminant will be calculated using Equation 9:

$$E_i = \frac{A \ 2 \ D_{ei} \ \varepsilon \ K_{as} \ C_i}{\sqrt{\pi \alpha t}} \tag{8}$$

- The exposed surface area, $A = 22,500 \text{ m}^2 = 2.25 \text{ x } 10^8 \text{ cm}^2$.
- ° The effective diffusivity, $D_{ei} = D_i P_t^{0.33}$.

TABLE 7. EMISSION RATE CALCULATIONS FROM SOIL GAS SAMPLES

COMPCUND	CONC.	MW (g/mol)	D ₁ (cm2/s)	Ci (g/cm3)	DEPTH dSC (cm)	POROSITY Pt (unitless)	AREA A (cm2)	Ei (g/s)
Methylene chloride Trichloroethene Benzene Tetrachloroethene	96654 10640 40714 17500	85 131 78 166	1.00E-01 7.90E-02 8.80E-02 7.20E-02	3.42E-07 5.80E-08 1.32E-07 1.21E-07	244 244 122 122	0.434 0.434 0.434 0.434	2.25E+08 2.25E+08 2.25E+08 2.25E+08	1.04E-02 1.39E-03 7.04E-03 5.28E-03
TOTALS	165508							2.41E-02

- Values of D, were obtained from the NTGS Series, Volume II, Appendices F and G.
- ° The soil/air partition coefficient, K_{ss} is calculated using Equation 9b.
- o The 95 percent UCL of the soil bulk concentrations, C; is obtained from Table 1.
- α is calculated from Equation 9a, where ϵ is calculated using the default values in Equation 6.
- The exposure interval, t = 60 s/min x 60 min/h x 24 h/day x 350 days/yr x 30 yr = 9.07 x 10⁸ s which represents upper bound residential exposure.

Table 8 gives the values of each variable in Equation 9 and the calculated emission rate for each volatile indicator compound.

TABLE 8. EMISSION RATE CALCULATIONS FROM BULK SAMPLES

COMPOUND	95%UCL BULK CONC. (ug/kg)	95%UCL BULK CONC. (g/g)	Di (cm2/s)	POROSITY Pt (unitless)	AREA A (cm2)	Dei (cm2/s)	Kas (g/cm3)	alpha	TIME t (s)	Ei (g/s)
Methylene chloride Trichloroethene Benzene Tetrachloroethene	170 5300 2500 220	1.70E-07 5.3E-06 2.5E-06 2.2E-07	1.00E-01 7.90E-02 8.80E-02 7.20E-02	0.434 0.434 0.434 0.434	2.25E+08 2.25E+08	0.075923 0.059979 0.066812 0.054664		1.99E-03 2.07E-03	9.07E+08 9.07E+08 9.07E+08 9.07E+08	3.86E-03 1.85E-03
TOTALS	8190									5.89E-03

- 2. N/A. No surface impoundments or pooled diluted volatiles at the surface.
- 3. N/A. Not a codisposal landfill.
- 4. N/A. No free-phase volatiles directly exposed.
- 5. Solids and semivolatiles emitted as PM:
 - A. Obtain bulk concentrations of metals and semivolatiles in surface soils from Table 1. Use the decision flowchart, Guideline, Figure 1, to determine if wind erosion potential exists and which emission rate model is applicable. Assume no vegetation in the areas of surface contamination at this site. Flowchart steps:
 - No. 1 Continuous vegetation? No.
 - No. 2 Is crust present? No.
 - No. 3a Determine threshold friction velocity.

 From Table 2, the aggregate size distribution mode lies between 0.25 mm and 0.42 mm. With a value of 0.3 mm for surface soil, the threshold friction velocity (Guideline, Figure 1a) is approximately 40 cm/s.
 - No. 3b Correct for nonerodible elements. Data not reported. Assume $L_c=0.01$ (default). From Guideline, Figure 1b, the correction factor is 1.5. Therefore, $u^*_{c}=1.5x40=60$ cm/s.
 - No. 3c Is threshold friction velocity >75 cm/s? No. Select "unlimited reservoir" model.
 - B. Calculate an emission flux (g/m²-h) for each contaminant found in the erodible surface material.
 - 1. Use the "unlimited reservoir" **model**
 - a. Use Equation 15 for emission flux of PM_{10} :

$$E_{10} = 0.036(1-V)\left[\frac{[u]}{u_t}\right]^3 F(x)C$$

Input variables:

V=0 (Without data, assume no vegetative cover) [u] = Mean annual windspeed (Table 3) = 4.29 m/s

Calculate equivalent threshold windspeed at 7 m height using Equation 16:

$$u_t = 18.1(u_t^*)/100$$

= 18.1(60)/100
= 10.9 m/s

Fractional percent of contaminant (example for arsenic):

$$C = 1070 \text{ mg/kg x } (1 \text{ kg/}10^6 \text{ mg})$$

= 0.00107

Obtain F(x) from Guideline, Figure 2:

$$F(x) = 0.18 (8x^{3} + 12x)e^{-x^{2}}$$

$$= 0.18 [8(2.25)^{3} + 12(2.25)]e^{-(2.25)^{2}}$$

$$= 0.1346$$

Therefore,

$$E_{10} = 0.036(1-0) \left[\frac{4.29}{10.9} \right]^3 (0.1346)(0.00107) = 3.16 \times 10^{-7} \ g/m^2 - h$$

- b. Not applicable at this time.
- C. Calculate total emission rates from the calculated emission flux rates using Equation 20a:

$$E_T = \frac{E_x A}{3600}$$

For arsenic, the contaminated surface area, $A = 22,500 \text{ m}^2$

$$E_T = \frac{(3.16 \times 10^{-7})(22,500)}{3600} = 1.98 \times 10^{-6} \text{ g/s}$$

Note: Emission rates of each indicator compound were computed from both soil gas and bulk samples. The greater of the two emission rate calculations for each indicator compound are summarized in Table 9.

TABLE 9. SUMMARY OF EMISSION RATE ESTIMATES

CASEX CONTAMINANT EMISSION RATE	≣S
Compound	Emission rate, g/s
VOLATILE ORGANICS	
Methylene chloride	1.04E-02
Trichloroethene	3.86E-03
Benzene	7.04 E-03
Tetrachloroethene	5.28E-03
INORGANICS	
Arsenic	1.98E-06
Cadmium	8.88E-08
Chromium	1.98E-08

STEP IV. ESTIMATE AMBIENT AIR CONCENTRATIONS AND/OR DEPOSITION CONCENTRATIONS AT RECEPTOR LOCATIONS OF INTEREST

- 1. Model the emissions of each contaminant for each source using the appropriate EPA atmospheric dispersion model and source configuration data.
 - A. The release will be neutrally buoyant.
 - B. No stack emissions, and 1-h average concentrations for area sources are not applicable (i.e., no 1-h average ARARs/TBCs).
 - C. No stack emissions, and 3, 8, and 24-h average concentrations for area sources are not applicable (i.e., no 3, 8, or 24-h average ARARs/TBCs).

Note: Calculation of less than annual average concentrations (short-term) may be necessary if potential emissions are of enough magnitude to cause ambient air concentrations to exceed subchronic or acute health-based criteria. Consult with a toxicologist or the Superfund Health Risk Technical Support Center if excessive short-term exposures are anticipated.

- D. Estimate annual average concentrations of contaminants from the area source using the following procedures:
 - 1. Total area source size = 22,500 m²
 - 2. Square area = $(150 \text{ m})^2$
 - 3. Convert the previously calculated emission rates to the form kg/m²-yr.

$$Q = \frac{E_i \ g/s \times 31,536,000 \ s/yr \times 1 \ kg/1000 \ g}{22,500 \ m^2}$$

$$Q = E_i \times 1.4016 \ kg/m^2 - yr$$

For methylene chloride, $Q = 0.0104 \times 1.4016 = 1.46 \times 10^{-2} \text{ kg/m}^2\text{-yr}$.

See Table 10 for other calculated values.

TABLE 10. CALCULATIONS FOR ANNUAL AVERAGE AMBIENT CONCENTRATION ESTIMATES

CASEX SITE					
Compound	Emission rate, g/s	Area, m²	Emissions Q, kg/m²-yr	x/Q value, 10 ⁻⁹ yr/m	Annual avg. con-centration,
VOLATILE ORGANICS					
Methylene chloride	1.04E-02	22500	1.46E-02	27.5	0.402
Trichloroethene	3.86E-03	22500	5.41E-03	27.5	0.149
Benzene	7.04E-03	22500	9.87E-03	27.5	0.271
Tetrachloro- ethene	5.28E-03	22500	7.40E-03	27.5	0.204
INORGANICS					
Arsenic	1.98E-06	22500	2.78E-06	27.5	7.65E-05
Cadmium	8.88E-08	22500	1.24E-07	27.5	3.42E-06
Chromium	1.98E-08	22500	2.78E-08	27.5	7.63E-07

- 4. Obtain χ/Q value from Guideline, Figure 4 curves. Distance from the downwind side of the source to the closest receptor is 175 m. From the curve for the 150 x 150 m area source, $\chi/Q = 27.5$ (10⁻⁹ yr/m).
- 5. Compute annual average concentration, $\chi(\mu g/m^3)$:

$$\chi = \chi/Q \times Q$$

For methylene chloride,

$$\chi$$
 = (27.5)(1.46 x 10⁻²)
 χ = 0.402 μ g/m³

See Table 10 for other calculated values.

Predict annual average concentrations of PM₁₀ contaminants.

- 1. Area source size = $22,500 \text{ m}^2$
- 2. Square area = $(150 \text{ m})^2$
- 3. Convert the emission rate to kg/m²-yr. For arsenic,

$$Q = \frac{1.98 \times 10^{-6} \ g/s}{22,500 \ m^2} \times \frac{1 \ kg}{1000 \ g} \times \frac{31,536,000 \ s}{yr} = 2.78 \times 10^{-6} \ kg/m^2 - yr$$

- 4. Obtain χ/Q value from Guideline, Figure 4 curves. Using downwind edge distance of 175 m and the 150 x 150 m area source, $\chi/Q = 27.5(10^{-9} \text{ yr/m})$.
- 5. Compute annual average concentration, $\chi(\mu g/m^3)$:

$$\chi = \chi/Q \times Q$$

For arsenic,
$$\chi$$
 = (27.5)(2.78 x 10⁻⁶)
 χ = 7.65 x 10⁻⁵ μ g/m³

Other contaminants are shown in Table 10.

- E. Not applicable.
- 2. As applicable, determine deposition concentrations (g/m²) by modeling particulate emissions of each applicable contaminant as particles \leq 30 μ m using the ISC or FDM dispersion model.

Not applicable if Baseline Risk Assessment indicates risk from onsite incidental ingestion of contaminated soil is within the acceptable risk range or if the hazard index is less than one.

STEP V. COMPARE AMBIENT AIR CONCENTRATIONS TO ARARS AND TBCs

1. Compare predicted ambient air concentrations to ARARs/TBCs.

The ARARs for PM_{10} and ozone (NAAQS) will not be approached.

The State air toxics TBCs are compared below:

Contaminant	Predicted emission rate	TBC	Status
Benzene	25.3 g/h	45.4 g/h	O.K.
Tetrachloroethene	19.0 g/h	45.4 g/h	O.K.
Trichloroethene	13.9 a/h	45.4 g/h	O.K.

STEP VI. ORGANIZE CONCENTRATION DATA FOR INPUT TO THE BASELINE RISK ASSESSMENT

- 1. List the annual average ambient air concentrations for each pollutant (indicator compound) Table 10.
- List variables and assumptions used in emission and dispersion modeling analyses and discuss their uncertainty and how this uncertainty may affect the final estimates.

The following discussion of assumptions is exemplary only. Site-specific conditions will dictate the extent to which assumptions and their possible effects on emissions and ambient concentration estimates will need examination.

- Equation 1: Both the soil/water partition coefficient (K_d) and the contaminant solubility(s) used in Equation 1 assume that each contaminant will behave in multicomponent systems (mixtures) as they would in two-component systems (i.e., one contaminant and soil/water). If mixture values of K_d and s are less than published two-component values, the value of C_{sat} will be less than that calculated in Equation 1.
- Equation 4: The 95 percent UCL soil gas concentrations (C_i) used in Equation 4 are assumed to be homogeneous across the exposed surface area (A). If significantly higher concentrations exist within this area and are closer to receptors of interest, higher ambient air concentrations are expected. Total soil porosity (P_t) used in Equation 4 was derived from Equation 6 using default values (i.e., air-filled porosity = total porosity). Use of total porosity instead of true air-filled porosity will tend to overpredict emissions.
- Equation 9: As with Equation 4, the 95 percent UCL soil bulk concentrations (C_i) and total porosity (P_t) were used in Equation 9 and will have similar effects on calculated emissions and resulting ambient air concentrations. The soil/air partition coefficient (K_{ss}) assumes that each contaminant will behave according to its Henry's Law constant in multicomponent systems (i.e., activity coefficient = 1). If a contaminant's activity coefficient is less than one, emissions will be less than calculated. Equation 9 represents the time-averaged emission rate over exposure interval t. Actual emissions, therefore, will be greater at the beginning of this interval and decrease with time.

- Equation 15: The relationships used to compute the threshold friction velocity and the function F(x) used in Equation 15 were derived from wind tunnel observations of various surface types. The annual average emission flux rates calculated using Equation 15 represent a continuous emitting source. In actuality, emissions occur only when windspeeds meet or exceed the threshold friction velocity for the given particle size. Therefore, short-term emissions will be considerably higher than the long-term average which includes a considerable period of no emissions. No site-specific information was available for extent of surface vegetation. The surface vegetation (V) was therefore set equal to zero to promote a conservative analysis.
- Step IV, 1,D: Annual average ambient air concentrations of contaminants determined from the relationship between downwind distance and χ/Q (Figure 4) are based on conservative refined modeling of fugitive emissions from several treatment, storage, and disposal facilities in the United States. The set of curves represented in Figure 4 are based on conservative modeling assumptions and upper bound data points. Actual concentrations may, therefore, be less than values predicted from this relationship.

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1. REPA-450/1-92-002		3. RECIPIENT'S ACCESSIO	N NO.	
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Guideline for Predictive Baseline Emissions Procedures for Superfund Sites	Estimation	6. PERFORMING ORGANIZ	ZATION CODE	
7. AUTHOR(S)		8. PERFORMING ORGANIZ	ZATION REPORT NO.	
Craig S. Mann				
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Quality Management, Inc. 1310 Kemper Meadow Drive, Suite 100 Cincinnati, Ohio 45240		10. PROGRAM ELEMENT	NO.	
		11. CONTRACT/GRANT N	0.	
		68-D0-0124		
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency		13. TYPE OF REPORT AND	D PERIOD COVERED	
Office of Air Quality Planning and Standards		14. SPONSORING AGENCY	ENCY CODE	
Research Triangle Park, NC 27711				
15. SUPPLEMENTARY NOTES	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~			
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