

# **Appendix B**

## **Parameter Guidance**

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## Parameter Guidance

This appendix provides you with guidance on all parameter values needed to run IWAIR. This guidance covers all parameters that you may enter in text boxes and most selections from drop-down boxes. It does not include most option buttons, as those are covered in the operational guidance in Sections 4 and 5. However, a few options are covered here, as well as in Sections 4 and 5.

This appendix is organized by screen. Some parameters are applicable only to risk mode or allowable concentration mode; those are so noted.

### B.1 Method, Met. Station, WMU (Screen 1A)

Most of the options on Screen 1A are covered in the operational guidance in Sections 4 and 5. There are only two parameters for this screen: zip code and latitude/longitude. You will only need to enter data for one or the other.

**Zip Code.** This is the 5-digit zip code for the physical location of your facility. IWAIR uses this zip code to assign the most appropriate meteorological station to your site; therefore, you should not use the zip code from a mailing address, such as a post office box or a company headquarters. The zip code database includes zip codes established through 1999. If your facility has a new zip code that was established more recently, you will get an error message indicating that it is not a valid zip code, because it is not in IWAIR's database. If this occurs, you can use your old zip code, use a nearby zip code, or select a meteorological station using latitude and longitude.

**Latitude and Longitude.** These are the latitude and longitude coordinates for the physical location of your facility. At a minimum, the program requires that degrees for latitude and longitude be entered. If available, the minutes and seconds should be supplied to ensure that the most appropriate station is selected for a site. Latitude and longitude can be obtained from most maps of the area where your facility is located.

## B.2 Wastes Managed and Add/Modify Chemicals (Screens 2A and 2B)

### B.2.1 Wastes Managed

Sections 4 and 5 cover the selection of chemicals for your waste. There is only one parameter to be entered on Screen 2A: waste concentration. This is only needed for risk calculations.

**Waste Concentration (mg/L or mg/kg).** This is the concentration of each chemical in your waste. It should reflect the waste or influent going into your unit, not the concentration within the unit. For surface impoundments, it should be in mg/L or ppm. For land application units, landfills, and waste piles, it should be in mg/kg or ppm. This value must be greater than zero; the sum of all concentrations entered must be less than or equal to one million.

### B.2.2 Add/Modify Chemicals (Screen 2B)

The ADD/MODIFY CHEMICALS screen requires you to enter numerous chemical-specific parameters. These are organized below into chemical identifiers, physical-chemical properties, and health benchmarks.

#### B.2.2.1 Chemical Identifiers

**Chemical Name.** If you are entering a new chemical, you can enter the chemical name here. If you are modifying or making a new entry for an existing chemical, you will not need to enter a chemical name; IWAIR will fill it in automatically. Do not add any user designation to the end of the chemical name you enter—IWAIR will do that automatically. Enter the chemical name exactly as you would like it to sort and display. For example, if you want 1,2,4-trichlorobenzene to sort under T instead of 1, enter it as “trichlorobenzene, 1,2,4-“.

**CAS Number.** If you are entering a new chemical, you can enter the Chemical Abstracts Service (CAS) number here. If you are modifying or making a new entry for an existing chemical, you will not need to enter a CAS number; IWAIR will fill it in automatically. IWAIR does not use leading zeros on CAS numbers; therefore, for consistency with the data provided with IWAIR, it is recommended that you use leading spaces instead of leading zeros for CAS numbers shorter than the maximum length.

**B.2.2.2 Physical-Chemical Properties.** Data on many physical-chemical properties can be obtained from the following sources:

- EPA's Superfund Chemical Data Matrix (SCDM) (U.S. EPA, 1997b),
- The Merck Index (Budavari, 1996),
- The National Library of Medicine's Hazardous Substances Databank (HSDB), available on TOXNET (U.S. NLM, 2001),

- Syracuse Research Corporation's CHEMFATE database (SRC, 1999),
- CambridgeSoft.com's ChemFinder database (CambridgeSoft, 2001), and
- Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles (ATSDR, 2001).

In addition, a useful source of data on chemical properties for dioxins is EPA's *Dioxin Reassessment* (U.S. EPA, 2000a).

**Molecular Weight (g/mol).** Molecular weight is used to estimate emissions. Values can be obtained from the literature, including from the SCDM; HSDB; and CHEMFATE. This value must be greater than or equal to 1 g/mol (the molecular weight of a single hydrogen ion). No maximum limit is enforced. IWAIR has been tested for molecular weights between 1 and 400 g/mol.

**Density (g/cm<sup>3</sup>).** IWAIR uses density to determine if chemicals present in organic phase in surface impoundments are likely to float (if they are less dense than water) or sink (if they are more dense than water). Unless the value is very near 1 g/cm<sup>3</sup> (the density of water), the model is not sensitive to variations in the value. Values can be obtained from the literature, including from the SCDM; Merck Index; and HSDB. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for densities between 0.01 and 14 g/cm<sup>3</sup>.

**Vapor Pressure (mmHg).** Vapor pressure and the mole fraction in the liquid phase are used to calculate the constituent's partial vapor pressure. The partial vapor pressure is subsequently used as the partition coefficient for organic-phase wastes and aqueous-phase wastes with chemicals present above solubility or saturation limits. Values can be obtained from the literature, including from the SCDM and HSDB. Vapor pressure may be reported in other units, such as atmospheres or torr; torr is equivalent to mmHg, but data in atmospheres will need to be converted. Different vapor pressures may be reported for the same chemical at different temperatures. For best results, choose a vapor pressure reported at a temperature around 20–25°C. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for vapor pressures between 0 and 5,300 mmHg.

**Henry's Law Constant (atm-m<sup>3</sup>/mol).** Henry's law constant reflects the tendency of chemicals to volatilize from dilute aqueous solutions; it is used as the partition coefficient for aqueous-phase wastes with chemicals present below solubility or saturation limits. Values can be obtained from the literature, including from the SCDM; 2000 *Dioxin Reassessment* (for dioxins); HSDB; CHEMFATE; and ChemFinder. If Henry's law constant is not available, it can be calculated from the chemical's vapor pressure, molecular weight, and solubility using the following equation (Lyman et al., 1990):

$$H = \frac{\left(\frac{VP}{760}\right)}{\left(\left(\frac{S}{MW}\right) \times \left(\frac{1000}{1000}\right)\right)}$$

where

H	=	Henry's law constant (atm-m <sup>3</sup> /mol)
VP	=	vapor pressure (mmHg)
S	=	solubility (mg/L)
MW	=	molecular weight (g/mol)
760	=	unit conversion (mmHg/atm)
1000	=	unit conversion (L/m <sup>3</sup> )
1000	=	unit conversion (mg/g).

The value for Henry's law constant must be greater than zero. No maximum limit is enforced. IWAIR has been tested for Henry's law constants between 4E-11 and 1.2 atm-m<sup>3</sup>/mol-K.

**Solubility (mg/L).** This is the solubility of the individual chemical in water. Solubility is used for surface impoundments to identify wastes that may be supersaturated so that emissions equations may be based on the most appropriate partition coefficient (Henry's law for aqueous-phase wastes below saturation or solubility limits, and partial vapor pressure for wastes above saturation or solubility limits and organic-phase wastes). Values can be obtained from the literature, including from the SCDM; Merck Index; *Dioxin Reassessment* (for dioxins); HSDB; and CHEMFATE. This value must be greater than zero and less than or equal to one million. IWAIR has been tested for solubilities from 1.93E-5 to 1,000,000 mg/L.

**Soil Biodegradation Rate (s<sup>-1</sup>).** The soil biodegradation rate is a first-order rate constant used to estimate soil biodegradation losses in land application units, landfills, and waste piles. The tendency to biodegrade in soil is often reported as half-life; this is not comparable to biodegradation rate and should not be used in IWAIR. However, you can calculate the soil biodegradation rate from the half-life as follows:

$$k_s = \frac{\ln(2)}{t_{1/2}}$$

where

$k_s$	=	soil biodegradation rate (s <sup>-1</sup> )
$\ln(2)$	=	natural log of 2
$t_{1/2}$	=	half-life (s).

An excellent reference for soil biodegradation data (and the one used for all soil biodegradation rates included with IWAIR) is Howard et al. (1991). This reference provides both high-end and low-end half-life data for soil biodegradation. The high-end values were used in IWAIR. In general, half-lives are reported in hours. Values for very short half-lives are given in minutes or seconds. All values, except the ones already given in seconds, must be converted to seconds before using the above equation to convert to biodegradation rate. The soil biodegradation rate may be zero if the chemical does not biodegrade; however, because a zero value would cause IWAIR to try to divide by zero, IWAIR converts values entered as zero to 1E-20, which results

in negligible biodegradation. No maximum limit is enforced. IWAIR has been tested for soil biodegradation rates from  $1\text{E}-20$  to  $0.0004\text{ s}^{-1}$ .

**Antoine's Constants: A, B, or C.** Antoine's constants are used to adjust vapor pressure and Henry's law constant to ambient temperature. While not explicitly reported with units, they are intended to adjust vapor pressure in mmHg based on temperature in degrees Celsius. Values for Antoine's constants are available in Reid et al. (1977). A and B must be greater than or equal to zero. C may be negative. No maximum limits are enforced. IWAIR has been tested for A values from 0 to 14; B values from 0 to 5,400; and C values from 0 to 292.

**Diffusivity in Water ( $\text{cm}^2/\text{s}$ ).** Diffusivity in water is used to estimate emissions. Diffusivity in water can be calculated from the chemical's molecular weight and density, using the following correlation equation based on Water9 (U.S. EPA, 2001c):

$$D_w = 0.0001518 \times \left( \frac{T + 273.16}{298.16} \right) \times \left( \frac{\text{MW}}{\rho} \right)^{-0.6}$$

where

$D_w$	=	diffusivity in water ( $\text{cm}^2/\text{s}$ )
T	=	temperature ( $^{\circ}\text{C}$ )
273.16	=	unit conversion ( $^{\circ}\text{C}$ to $^{\circ}\text{K}$ )
MW	=	molecular weight ( $\text{g}/\text{mol}$ )
$\rho$	=	density ( $\text{g}/\text{cm}^3$ ).

If density is not available, diffusivity in water can be calculated using the following correlation equation based on U.S. EPA (1987b):

$$D_w = 0.00022 \times (\text{MW})^{-\left(\frac{2}{3}\right)}$$

The value for diffusivity in water must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of diffusivity in water from  $5\text{E}-6$  to  $3\text{E}-5\text{ cm}^2/\text{s}$ .

**Diffusivity in Air ( $\text{cm}^2/\text{s}$ ).** Diffusivity in air is used to estimate emissions. Diffusivity in air can be calculated from the chemical's molecular weight and density, using the following correlation equation based on Water9 (U.S. EPA, 2001c):

$$D_a = \frac{0.00229 \times (T + 273.16)^{1.5} \times \sqrt{0.034 + \left( \frac{1}{\text{MW}} \right)} \times \text{MW}_{\text{cor}}}{\left( \left( \frac{\text{MW}}{2.5 \times \rho} \right)^{0.333} + 1.8 \right)^2}$$

where

$D_a$	=	diffusivity in air (cm <sup>2</sup> /s)
$T$	=	temperature (°C)
273.16	=	unit conversion (°C to °K)
MW	=	molecular weight (g/mol)
$\rho$	=	density (g/cm <sup>3</sup> ).
$MW_{cor}$	=	molecular weight correlation:

$$MW_{cor} = (1 - 0.000015 \times MW^2)$$

If  $MW_{cor}$  is less than 0.4, then  $MW_{cor}$  is set to 0.4.

If density is not available, diffusivity in air can be calculated using the following correlation equation based on U.S. EPA (1987b):

$$D_a = 1.9 \times \left( MW^{-\left(\frac{2}{3}\right)} \right)$$

For dioxins, diffusivity in air can be calculated from the molecular weight using the following correlation equation based on EPA's *Dioxin Reassessment* (U.S. EPA, 2000a):

$$D_a = \left( \frac{154}{MW} \right)^{0.5} \times 0.068$$

Diffusivity in air values must be greater than or equal to zero. No maximum limit is enforced. IWAIR has been tested for values of diffusivity in air from 0 to 0.25 cm<sup>2</sup>/s.

**Octanol-Water Partition Coefficient (log  $K_{ow}$ ).**  $K_{ow}$  is used to estimate emissions and to calculate the soil saturation concentration limit for land application units, landfills, and waste piles. Because  $K_{ow}$  can cover an extremely wide range of values, it is typically reported as the log of  $K_{ow}$  and should be entered as the log in IWAIR. Values can be obtained from the literature, including the SCDM. Log  $K_{ow}$  is unitless. Log  $K_{ow}$  may have negative values, reflecting  $K_{ow}$  values less than 1. Due to model limitations, log  $K_{ow}$  may not be less than -10 or greater than 10; IWAIR has been tested for this entire range.

**Hydrolysis Constant ( $s^{-1}$ ).** This value, which is used to estimate losses by hydrolysis, is the hydrolysis rate constant at neutral pH. An excellent source of data on hydrolysis rate constants (and the one used for all hydrolysis rate constants included with IWAIR) is Kollig (1993). The hydrolysis constant may be zero if the chemical does not hydrolyze; it cannot be less than zero. No maximum limit is enforced. IWAIR has been tested for values of hydrolysis constants from 0 to 22 s<sup>-1</sup>.

**$K_1$  (L/g-h).**  $K_1$  is used to estimate biodegradation losses in surface impoundments. There are very few literature sources for  $K_1$ . The primary source of data is Coburn et al. (1988). Values for  $K_1$  in CHEMDAT8 and IWAIR were taken from this source. If you have rate study data at very low concentrations, that rate can be used for  $K_1$ .  $K_1$  may be zero if the chemical does not biodegrade; it cannot be less than zero. No maximum limit is enforced. IWAIR has been tested for values of  $K_1$  from 0 to 25 L/g-h.

**$K_{max}$  (mg volatile organics/g-h).**  $K_{max}$  is used to estimate biodegradation losses in surface impoundments. There are very few literature sources for  $K_{max}$ . The primary source of data is Coburn et al. (1988). Values for  $K_{max}$  in CHEMDAT8 and IWAIR were taken from this source. If you have rate study data at very high concentrations, that rate can be used for  $K_{max}$ .  $K_{max}$  may be zero if the chemical does not biodegrade; it cannot be less than zero. No maximum limit is enforced. IWAIR has been tested for values of  $K_{max}$  from 0 to 100 mg VO/g-h.

### B.2.2.3 Health Benchmarks

**Cancer Slope Factor (CSF) (mg/kg/d)<sup>-1</sup>.** The inhalation CSF is used to evaluate risk for carcinogens. The CSF is an upper-bound estimate (approximating a 95 percent confidence limit) of the increased human cancer risk from a lifetime exposure to an agent. Inhalation CSFs are used in the model for carcinogenic constituents, regardless of the availability of an RfC. If a value for the inhalation CSF is not available, you should enter "NA" in the CSF field, rather than zero. IWAIR must have a numeric value for either the inhalation CSF or RfC to calculate risk or allowable concentration. If a numeric value is entered, it must be greater than zero. No maximum limit is enforced. IWAIR has been tested for CSF values from 0.00001 to 150,000 (mg/kg/d)<sup>-1</sup>.

**Reference Concentration (RfC) (mg/m<sup>3</sup>).** The RfC is used to evaluate noncancer hazards posed by inhalation exposures to chemicals. The RfC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is unlikely to pose an appreciable risk of deleterious noncancer effects during an individual's lifetime. If a value for the RfC is not available, you should enter "NA" in the RfC field, rather than zero. IWAIR must have a numeric value for either the inhalation CSF or RfC to calculate risk or allowable concentration. If a numeric value is entered, it must be greater than zero. No maximum limit is enforced. IWAIR has been tested for RfC values from 0.00001 to 40 mg/m<sup>3</sup>.

Human health benchmarks contained in databases developed by EPA were used whenever available. Benchmarks were obtained in the following order of preference:

- Integrated Risk Information System (IRIS) (U.S. EPA, 2001b)
- Superfund Technical Support Center Provisional Benchmarks (U.S. EPA, 1998b, 1999a, 1999b, 2000b)
- Health Effects Assessment Summary Tables (HEAST) (U.S. EPA, 1997a)



- Agency for Toxic Substances and Disease Registry (ATSDR) minimal risk levels (MRLs) (ATSDR, 2001)
- California Environmental Protection Agency (CalEPA) chronic inhalation reference exposure levels (RELs) and cancer potency factors (CalEPA, 1999a, 1999b, 2000)
- EPA health assessment documents (U.S. EPA, 1986, 1987a, 1998a)
- Various other EPA health benchmark sources.

### **B.3 WMU Data for CHEMDAT8 (Screens 3A through 3D)**

#### **B.3.1 WMU Data for CHEMDAT8 – Surface Impoundment (Screen 3A)**

**B.3.1.1 Meteorological Station Parameters.** These inputs are used only for the emissions modeling, not the dispersion modeling, which uses hourly meteorological data, not annual averages. Therefore, changes to these inputs will not affect the dispersion factors.

**Wind Speed (m/s).** IWAIR uses wind speed to select the most appropriate empirical emission correlation equation in CHEMDAT8; there are several of these correlations, and each one applies to a specific range of wind speeds and unit sizes. By default, IWAIR uses the average annual wind speed from the meteorological station that was assigned to your location. However, you may wish to override the default if you have site-specific data on wind speed. If you do override, you should use an overall annual average in all directions, not any measure of peak wind speed or average only in the prevailing wind direction. Also, wind speed is often reported in knots or mph. However, for use in IWAIR, wind speed must be converted to m/s. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of wind speed from 0.01 to 100 m/s; however, a realistic range for average annual wind speed is about 2 to 10 m/s.

**Temperature (°C).** IWAIR uses temperature to correct various temperature-dependent chemical properties used in emissions modeling (Henry's law constant and vapor pressure) from a standard temperature to the ambient temperature. By default, IWAIR uses the average annual temperature from the meteorological station that was assigned to your location. However, you may wish to override the default if you have site-specific data on temperature. If you do override, you should use an annual average temperature. Temperature may be reported in degrees Fahrenheit (°F); however, for use in IWAIR, temperature must be converted to degrees Celsius (°C). This value must be greater than or equal to -100°C. No maximum limit is enforced. IWAIR has been tested for values of temperature from 0 to 50°C.

#### **B.3.1.2 SI Dimensions, Loading Information**

**Biodegradation (on/off).** This option, in conjunction with the ACTIVE BIOMASS input, allows you to determine what type of biodegradation is modeled for your unit. In biologically active surface impoundments, two processes occur: growth of biomass, which provides a growing

matrix for chemical adsorption and loss through settling, and direct biodegradation of chemical constituents as the bacteria that compose the biomass consume constituent mass. Direct biodegradation cannot occur if there is no active biomass. If an impoundment is biologically active, it may go through a transitional period during which there is active biomass (so adsorption and settling losses occur) but the biomass is not yet adapted to consume the specific chemicals present (so direct biodegradation is not occurring). This transitional period will usually end as the biomass acclimate and adapt to the chemicals present.

Setting biodegradation to |OFF| turns off direct biodegradation. It does not affect adsorption loss. Setting active biomass to zero turns off biomass growth, so that adsorption losses are limited to adsorption to inlet solids. Setting active biomass to zero also turns off direct biodegradation (in fact, if you have set biodegradation |ON| and then set active biomass to zero, IWAIR will automatically reset the biodegradation option to |OFF|). If you set biodegradation to |OFF|, IWAIR will remove the default value for active biomass, and you will have to enter a value (typically zero, but this is not required, and it may be greater than zero if you wish to model the transitional period before direct biodegradation occurs).

If your impoundment is biologically active, it is recommended that you leave biodegradation set to |ON| (the default). If your impoundment is not biologically active, it is recommended that you set biodegradation to |OFF| and active biomass to zero.

**Operating Life (yr).** This parameter is the expected remaining operating life of your unit, from the time you are modeling until you expect it to be closed. Operating life does not affect emissions estimates for surface impoundments, which are modeled at steady state. However, operating life may affect exposure duration. IWAIR uses default exposure durations of 30 years for residents and 7.2 years for workers. However, proper closure of a surface impoundment typically ends all exposures. Therefore, if the operating life you specify is less than 30 or 7.2 years, IWAIR caps the exposure duration at the operating life. Values in excess of 30 years will not affect the results for residents, and values in excess of 7.2 years will not affect the results for workers. Operating life should be entered in years. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of operating life from 0.01 to 100 years.

**Depth of Unit (m).** This is the average depth of your unit in meters (m). If your unit is not a constant depth, use the average or most typical depth. If you have depth reported in units such as feet, you will need to convert them to meters. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of depth from 0.01 to 30 m.

**Area of Unit (m<sup>2</sup>).** This is the total surface area of your unit in m<sup>2</sup>. Areas may be reported in acres or hectares; these values will need to be converted to m<sup>2</sup> for use in IWAIR. This value must be greater than or equal to 81 m<sup>2</sup> and less than or equal to 8,090,000 m<sup>2</sup>; these are the smallest and largest areas for which IWAIR can interpolate dispersion factors for ground-level sources. IWAIR has been tested for this full range.

**Annual Flow of Waste (m<sup>3</sup>/yr).** This is the total amount of waste that flows through your impoundment in a year, in m<sup>3</sup>/yr. Flow is often reported in millions of gallons per day (MGD) or

other units; you will need to convert to  $\text{m}^3/\text{yr}$  for use in IWAIR. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of annual flow of waste from 0.01 to 10,000,000  $\text{m}^3/\text{yr}$ .

### **B.3.1.3 Aeration Option Information**

**Type of Aeration.** This option allows you to identify whether your impoundment is aerated and, if so, the specific type of aeration. IWAIR can model no aeration (quiescent), diffused air aeration, mechanical aeration, and both (diffused air and mechanical).

If your impoundment is not aerated, choose NO AERATION.

If your impoundment is aerated only by mechanical aerators (these are rotating impellers), choose MECHANICAL AERATION.

If your impoundment is aerated only by diffused air flow from submerged aerators, choose DIFFUSED AIR AERATION.

If your impoundment is aerated by both mechanical aerators and diffused air aerators, choose BOTH (DIFFUSED AIR & MECHANICAL).

**Fraction of Surface Area Agitated.** Unless you chose NO AERATION, you will need to enter the fraction of surface area agitated. If you have data on agitated area, you can divide the agitated area by the total area (in the same units) to obtain this fraction. Alternatively, you can estimate this visually. This input is a unitless fraction and must be greater than zero and less than or equal to one. IWAIR has been tested with values of fraction agitated from 0.01 to 1.

**Submerged Air Flow ( $\text{m}^3/\text{s}$ ).** Submerged air flow is used for diffused air systems; you will need to enter a value if you chose either DIFFUSED AIR AERATION OR BOTH (DIFFUSED AIR & MECHANICAL). This is the total air flow of all diffusers in the impoundment. For example, if you had two diffusers, each with an air flow of 0.1  $\text{m}^3/\text{s}$ , you would enter 0.2  $\text{m}^3/\text{s}$  here. If you enter a value here, it must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of submerged air flow from 0.01 to 100  $\text{m}^3/\text{s}$ .

### **B.3.1.4 Waste Characteristics Information**

**Type of Waste.** In order to generate an accurate estimate of a constituent's volatile emissions, you must define the physical and chemical characteristics of the waste you are modeling. In particular, you must identify whether or not the waste is best described as a

**Aqueous-phase waste:** a waste that is predominantly water, with low concentrations of organics. All chemicals remain in solution in the waste and are usually present at concentrations below typical solubility limits. However, it is possible for the specific components of the waste to raise the effective solubility level for a chemical, allowing it to remain in solution at concentrations above the typical solubility limit.

**Organic-phase waste:** a waste that is predominantly organic chemicals, with a high concentration of organics. Concentrations of some chemicals may exceed solubility, causing those chemicals to come out of solution and form areas of free product in the WMU. In surface impoundments, this can result in a thin organic film over the entire surface.

dilute mixture of chemical compounds (aqueous) or if the waste should be considered organic, containing high levels of organic compounds or a separate nonaqueous organic phase. These two different types of waste matrices influence the degree of partitioning that will occur from the waste to the air. Partitioning describes the affinity that a contaminant has for one phase (for example, air) relative to another phase (for example, water) that drives the volatilization of organic chemicals. Your choice of waste matrix will significantly affect the rate of emissions from the waste. The following discussion is intended to provide background on emissions modeling as it relates to waste type, guidance on making this selection, and clarification of the modeling consequences of choosing AQUEOUS VERSUS ORGANIC in IWAIR. Note that you will only be asked to choose a waste type for risk calculations; for allowable concentration calculations, IWAIR calculates emission rates for both aqueous and organic waste types and selects the one that achieves the target risk or HQ at the lowest concentration applicable to the waste type.

A WMU contains solids, liquids (such as water), and air. Individual chemical molecules are constantly moving from one of these media to another: they may be absorbed to solids, dissolved in liquids, or assume a vapor form in air. At equilibrium, the movement into and out of each medium is equal, so that the concentration of the chemical in each medium is constant. The emissions model used in IWAIR, CHEMDAT8, assumes that equilibrium has been reached.

Partitioning refers to how a chemical tends to distribute itself among these different media. Different chemicals have differing affinities for particular phases—some chemicals tend to partition more heavily to air, while others tend to partition more heavily to water. The different tendencies of different chemicals are described by partition coefficients or equilibrium constants.

Of particular interest in modeling volatile emissions of a chemical from a liquid waste matrix is the chemical's tendency to change from a liquid form to a vapor form. As a general rule, a chemical's vapor pressure describes this tendency. The pure component vapor pressure is a measure of this tendency for the pure chemical. A chemical in solution in another liquid (such as a waste containing multiple chemicals) will exhibit a partial vapor pressure, which is the chemical's share of the overall vapor pressure of the mixture; this partial vapor pressure is lower than the pure component vapor pressure and is generally equal to the pure component vapor pressure times the constituent's mole fraction (a measure of concentration reflecting the number of moles of the chemical per total moles) in the solution. This general rule is known as Raoult's law.

Most chemicals do not obey Raoult's law in dilute (i.e., low concentration) aqueous solutions, but exhibit a greater tendency to partition to the vapor phase from dilute solutions than would be predicted by Raoult's law. These chemicals exhibit a higher partial vapor pressure than the direct mole fraction described above would predict.<sup>1</sup> This altered tendency to partition to the vapor phase in dilute solutions is referred to as Henry's law. To calculate the emissions of a

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<sup>1</sup> There are some exceptions to this behavior in dilute solutions. A notable exception is formaldehyde, which has lower activity in dilute aqueous solution, which means that formaldehyde will have greater emissions in a high concentration, organic-phase waste.

constituent from a dilute solution, a partition coefficient called Henry's law constant is used. Henry's law constant relates the partial vapor pressure to the concentration in the solution.

To account for these differences in the tendency of chemicals to partition to vapor phase from different types of liquid waste matrices, CHEMDAT8 models emissions in two regimes: a dilute aqueous phase, modeled using Henry's law constant as the partition coefficient, and an organic phase, modeled using the partial vapor pressure predicted by Raoult's law as the partition coefficient. In fact, there is not a clear point at which wastes shift from dilute aqueous phase to organic phase; this is a model simplification. However, several rules of thumb may be used to determine when the Raoult's law model would be more appropriate. The clearest rule is that any chemical present in excess of its solubility limit in a wastewater has exceeded the bounds of "dilute aqueous" and is more appropriately modeled using Raoult's law. Chemicals exceeding solubility limits will typically come out of solution and behave more like pure, organic-phase component. However, solubility limits can vary depending on site-specific parameters, such as temperature and pH of the waste. In addition, waste matrix effects<sup>2</sup> can cause chemicals to remain in solution at concentrations above their typical solubility limit. This scenario (an aqueous-phase waste with concentrations above typical solubility limits) is also best modeled using Raoult's law. Another rule of thumb is that a waste with a total organics concentration in excess of about 10 percent (or 100,000 ppm) is likely to behave more like an organic-phase waste than a dilute aqueous-phase waste and be more appropriately modeled using Raoult's law.

For surface impoundments, where the waste is a liquid, the model uses an approach that considers the resistance to mass transfer (i.e., movement of chemical mass from one phase to the other) in the liquid and gas phases at the surface of the impoundment. Emissions are calculated using an overall mass transfer coefficient, which is based on the partition coefficient (as described above), the liquid-phase mass transfer factor (which accounts for resistance to transfer in the liquid phase), and the gas-phase mass transfer factor (which accounts for resistance to transfer in the gas phase). This is referred to as the two-film model. For organic-phase wastes, the mass transfer is dominated by the gas-phase resistance and the partition coefficient; the liquid-phase mass transfer resistance is negligible and is, therefore, omitted from the calculation. This is referred to as the one-film model, or the oily film model.

In the two-film model for surface impoundments, the gas-phase and liquid-phase mass transfer coefficients are strongly affected by the turbulence of the surface impoundment surface. Turbulence may be caused by mechanical aeration or, to a lesser extent, diffused air aeration. Therefore, whether the impoundment is aerated or not and how it is aerated are important inputs.

When in allowable concentration calculation mode, IWAIR calculates both aqueous-phase and organic-phase emission rates. However, aqueous-phase emission rates, as discussed above, are only applicable up to the solubility limit. If the use of the aqueous-phase emission

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<sup>2</sup> "Waste matrix effects" refers to the effect that the composition of the waste has on a constituent's solubility in the waste or the tendency for the chemical to evaporate from the waste. For example, hexane has a solubility in distilled water of approximately 12 mg/L; however, its solubility in methanol is much higher (more than 100,000 mg/L) (Perry and Green, 1984). Therefore, it is likely that hexane will remain dissolved in a solution of 10 percent methanol in water at higher concentrations than the aqueous solubility limit of 12 mg/L suggests.

rate results in an allowable concentration in excess of the solubility limit, IWAIR will use the organic-phase rate instead.

**Molecular Weight of Waste (g/mol) (Only for Risk Calculation).** If you choose to model an organic-phase waste, you will need to enter the average molecular weight of the waste. This may be calculated from the molecular weights of the component constituents as follows:

$$MW_{\text{waste}} = \frac{\sum (C_i) \times (1 \text{ m}^3)}{\sum (C_i/MW_i) \times (1 \text{ m}^3)}$$

where

$MW_{\text{waste}}$	=	molecular weight of waste (g/mol)
$C_i$	=	waste concentration of contaminant $i$ (mg/L = g/m <sup>3</sup> )
$MW_i$	=	molecular weight of contaminant $i$ (g/mol).

This assumes that the average molecular weight of the unspecified fraction of the organic waste matrix has the same average molecular weight as the specified fraction (i.e., the input contaminant concentrations). Appendix C provides values for molecular weight for all IWAIR chemicals.

This value must be greater than or equal to 1 (the molecular weight of a hydrogen ion). No maximum limit is enforced. IWAIR has been tested for values from 1 to 400 g/mol.

**Density of Waste (g/cm<sup>3</sup>) (Only for Risk Calculation).** If you choose to model an organic-phase waste, you will need to enter the density of the waste. It is best to use a measured value for this, but you can estimate it as follows:

$$\rho_{\text{waste}} = \frac{\sum (C_i)}{\sum (C_i/\rho_i)}$$

where

$\rho_{\text{waste}}$	=	density of waste (g/cm <sup>3</sup> )
$C_i$	=	waste concentration of contaminant $i$ (mg/L = g/m <sup>3</sup> )
$\rho_i$	=	density of contaminant $i$ (g/cm <sup>3</sup> ).

Appendix C provides values for density for all IWAIR chemicals.

This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values from 0.01 to 3 g/cm<sup>3</sup>.

**Active Biomass (g/L).** This input, in conjunction with the BIODEGRADATION option, allows you to determine what type of biodegradation is modeled for your unit. In biologically active

surface impoundments, two processes occur: growth of biomass, which provides a growing matrix for chemical adsorption and loss through settling, and direct biodegradation of chemical constituents as the bacteria that compose the biomass consume constituent mass. Direct biodegradation cannot occur if there is no active biomass. If an impoundment is biologically active, it may go through a transitional period during which there is active biomass (so adsorption and settling losses occur) but the biomass is not yet adapted to consume the specific chemicals present (so direct biodegradation is not occurring). This transitional period will usually end as the biomass acclimate and adapt to the chemicals present. See also the discussion in Section B.3.1.2 on biodegradation and how active biomass interacts with the biodegradation setting.

This input refers to the biomass concentration within the surface impoundment. Most of the biodegradation rate constants use mixed-liquor volatile suspended solids (MLVSS) as the measure of bioconcentration. Therefore, MLVSS in the impoundment is the preferred source for this input if you have those data available. If not, you can approximate this (in order of preference) using biomass concentration in the impoundment, mixed-liquor suspended solids (MLSS) in the impoundment, MLVSS in the effluent, biomass concentration in the effluent, or MLSS in the effluent. Alternatively, you may choose to use the IWAIR default of 0.05 g/L; however, this default is only appropriate for biologically active impoundments. If you are modeling a biologically inactive impoundment, this value should be set to zero, which turns off direct biodegradation and biomass growth, so that adsorption losses are limited to adsorption to inlet solids. This value must be greater than or equal to zero and less than or equal to 1,000 g/L. IWAIR has been tested for this full range.

**Total Suspended Solids in Influent (g/L).** Total suspended solids (TSS) is used, in conjunction with total organics, to estimate growth of solids in the impoundment. This input is the TSS in the impoundment influent, not within the impoundment. If those data are not available, you can approximate this (in order of preference) using total solids in the influent, MLSS in the influent, MLVSS in the influent, biomass concentration in the influent, TSS within the impoundment, total solids within the impoundment, or MLSS within the impoundment. Alternatively, you may choose to use the IWAIR default of 0.2 g/L. This value must be greater than or equal to zero and less than or equal to 1,000 g/L. IWAIR has been tested for this full range.

**Total Organics into WMU (mg/L).** Total organics is used, in conjunction with TSS, to estimate new biomass growth, so it most accurately refers to biodegradable organics. For this reason, the most preferred data source is biological oxygen demand (BOD) in the influent. If BOD is not available, you can estimate this using chemical oxygen demand (COD) or total organic carbon (TOC) in the influent. Values of BOD, COD, or TOC in the effluent may be used if influent values are not available, but these need to be adjusted up to account for removal in the impoundment by dividing by (1 - removal efficiency). Alternatively, you can use the IWAIR default value of 200 mg/L. This value must be greater than or equal to the sum of the concentrations you entered for organic chemicals in the WASTES MANAGED screen and must be less than or equal to 1,000,000 mg/L. IWAIR has been tested for this full range.

**Total Biorate (mg/g biomass-h).** This is the degradation rate of total organics in the impoundment. Total biorate can be measured from the maximum oxygen uptake rate from respirometry studies, converting the oxygen uptake rate to grams carbon assuming mineralization (formation of CO<sub>2</sub>). Alternatively, you can use the IWAIR default value of 19 mg/g biomass-h. This value must be greater than or equal to zero. No maximum limit is enforced. IWAIR has been tested for values from 0 to 100 mg/g biomass-h.

### **B.3.1.5 Mechanical Aeration Information**

These inputs are needed for only if you selected MECHANICAL AERATION OR BOTH (DIFFUSED AIR & MECHANICAL).

**Oxygen Transfer Rate (lb O<sub>2</sub>/h-hp).** This is the oxygen transfer rating of your aerator, measured using water, and should be available from the design specifications of your aerator. If no data are available, you can use the IWAIR default of 3.0 lb O<sub>2</sub>/h-hp. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values from 0.01 to 3 lb O<sub>2</sub>/h-hp.

**Number of Aerators.** This is the number of impellers in your impoundment. You should be able to count them visually if you do not have these data readily available. This value must be greater than or equal to 1 and should be an integer. No maximum limit is enforced. IWAIR has been tested for values from 1 to 150.

**Total Power (hp).** This is the power from all impellers in the impoundment combined. You can calculate it by summing the power of each impeller (make sure they are all in the same units first). Impeller power should be part of the design specifications for your aerators. In a survey of surface impoundments managing nonhazardous wastes (U.S. EPA, 2001a), the reported average power per aerator ranged from 4 to 100 hp. If you cannot determine the power of your aerators, you can estimate aerator power. Aeration and mixing power requirements often depend on the volume of liquid needing aeration or mixing, although the range of appropriate values can be wide. Additionally, many impoundments are aerated near the unit's influent, but a large portion of the impoundment may remain unaerated. Consequently, the lower limit for aeration may be more difficult to assess than the upper limit. A reasonable upper limit for aeration power based on high aeration requirements is approximately 150 hp per million gallons of impoundment volume (Metcalf and Eddy, 1979). This factor can be applied to the total volume of the unit to assess a maximum power limit. A lower limit based on mixing is approximately 10 hp/million gallons; this factor can be applied to the unit volume times the fraction aerated to yield a lower limit. The minimum value for total power must be greater than 0.25 hp. No maximum limit is enforced. IWAIR has been tested for values from 0.26 to 3,000 hp.

**Power Efficiency (fraction).** Power efficiency is a misnomer that is carried over from CHEMDAT8. This input is really the oxygen correction factor for the liquid-phase turbulent mass transfer coefficient. The actual power efficiency, used in the equation for gas-phase turbulent mass transfer coefficient, is hardwired to a value of 0.85 in CHEMDAT8. In order to maintain consistency with CHEMDAT8, IWAIR also terms this input "power efficiency" but



uses it as the oxygen correction factor, and hardwires the real power efficiency with a value of 0.85.

This correction factor is used to adjust the oxygen transfer rate input (which applies to pure water) for application to wastewaters. A value for your aerator should be available from your aerator supplier. If no data are available, you can use the IWAIR default of 0.83; this value is consistent with its use as the oxygen correction factor. This value must be greater than zero and less than or equal to 1. IWAIR has been tested for values from 0.01 to 1.

***Impeller Diameter (cm).*** This is the diameter of each impeller, from one end of the impeller to the other. If you have different impellers of different diameters, use either an average or the most typical. If this value is in meters, feet, or inches, it must be converted to centimeters for use in IWAIR. If you cannot determine the diameter of your impellers, you can use the IWAIR default value of 61 cm. This value must be greater than zero and less than 100 times the square root of the area of the unit in  $m^2$  (i.e., the impeller cannot be longer than the side length of the unit, assuming the unit is square, which maximizes the smallest side length). IWAIR has been tested for this full range.

***Impeller Speed (rad/s).*** This is a measure of rotational speed (in radians per second). It should be part of the specifications of your aerators, although it may be reported in rotations per minute (rpm). If so, you will need to convert it to radians per second. One rotation is equal to 360 degrees, or 6.28 radians. If your aerators have different speeds, use an average or the most typical value. If you cannot determine the speed of your impellers, you can use the IWAIR default value of 130 rad/s. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for a range from 0.01 to 1,000 rad/s.

### **B.3.2 WMU Data for CHEMDAT8 – Land Application Unit (Screen 3B)**

**B.3.2.1 Meteorological Station Parameters.** These inputs are used only for the emissions modeling, not the dispersion modeling, which uses hourly meteorological data, not annual averages. Therefore, changes to these inputs will not affect the dispersion factors.

***Wind Speed (m/s).*** IWAIR uses wind speed to select the most appropriate empirical emission correlation equation in CHEMDAT8; there are several of these correlations, and each one applies to a specific range of wind speeds and unit sizes. By default, IWAIR uses the average annual wind speed from the meteorological station that was assigned to your location. However, you may wish to override the default if you have site-specific data on wind speed. If you do override, you should use an overall annual average in all directions, not any measure of peak wind speed or average only in the prevailing wind direction. Also, wind speed is often reported in knots or mph. However, for use in IWAIR, wind speed must be converted to m/s. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of wind speed from 0.01 to 100 m/s; however, a realistic range for average annual wind speed is about 2 to 10 m/s.

***Temperature (°C).*** IWAIR uses temperature to correct various temperature-dependent chemical properties used in emissions modeling (Henry's law constant and vapor pressure) from

a standard temperature to the ambient temperature. By default, IWAIR uses the average annual temperature from the meteorological station that was assigned to your location. However, you may wish to override the default if you have site-specific data on temperature. If you do override, you should use an annual average temperature. Temperature may be reported in degrees Fahrenheit (°F); however, for use in IWAIR, temperature must be converted to degrees Celsius (°C). This value must be greater than or equal to -100°C. No maximum limit is enforced. IWAIR has been tested for values of temperature from 0 to 50°C.

### **B.3.2.2 Waste/Soil Mixture Porosity Information**

**Total Porosity (volume fraction).** Porosity refers to the spaces in a soil or waste matrix that are not soil particles. These spaces may be filled with air or water. Total porosity is the sum of both air- and water-filled porosity. Sometimes porosity is referred to as saturated water content. Porosity values are used in the emissions model, and they can be used to estimate soil saturation concentration limits. If measured data on porosity are not available, porosity can be estimated from the bulk density and particle density of the waste as follows:

$$\epsilon_t = 1 - \text{BD}/\rho_s$$

where

- $\epsilon_t$  = total porosity (unitless)
- BD = bulk density of waste (g/cm<sup>3</sup>)
- $\rho_s$  = particle density of waste (g/cm<sup>3</sup>).

If particle density is not available, a typical value for mineral material is 2.65 g/cm<sup>3</sup> (Mason and Berry, 1968).

Porosity must be greater than zero and less than 1. IWAIR has been tested for values from 0.01 to 0.99.

**Air Porosity (volume fraction).** Air-filled porosity is the porosity that is filled with air instead of water. This can be calculated from volumetric moisture content (which is equivalent to water-filled porosity) and total porosity as follows:

$$\epsilon_a = \epsilon_t - \epsilon_w$$

where

- $\epsilon_a$  = air-filled porosity (unitless)
- $\epsilon_t$  = total porosity (unitless)
- $\epsilon_w$  = water-filled porosity = volumetric water content (unitless).

Air-filled porosity must be greater than zero and less than or equal to the total porosity. IWAIR has been tested for this full range.

### **B.3.2.3 LAU Dimensions and Loading Information**

**Biodegradation (on/off).** This option lets you choose whether to model biodegradation losses in the unit. Land application units are designed to biodegrade wastes; therefore, the biodegradation option is turned on by default. Biodegradation rates can be very site-specific. If you believe that the actual rates in your unit are different than those included in the IWAIR chemical properties database, the best choice would be to enter user-defined chemical entries using your own soil biodegradation rates and select biodegradation |ON|. However, if you wish to model a land application unit without biodegradation, you can select biodegradation |OFF|.

**Operating Life (yr).** This parameter is the expected remaining operating life of your unit, from the time you are modeling until you expect it to be closed. Operating life does not affect exposure duration for land application units the way it does for other unit types, because exposures can continue postclosure for land application units. Operating life does affect average emission rates for land application units. Emissions are estimated for each year of operation plus 30 years postclosure, and then the maximum 7- and 30-year averages are calculated. For land application units, IWAIR uses default exposure durations used by IWAIR of 30 years for residents and 7.2 years for workers, regardless of operating life. Operating life should be entered in years. This value must be greater than zero. No maximum limit is enforced; however, see the discussion below under number of applications per year on how operating life affects the maximum number of applications per year. IWAIR has been tested for values of operating life from 0.01 to 100 years.

**Tilling Depth of Unit (m).** This is the depth to which your land application unit is tilled and the depth to which wastes are mixed with soil; once constituents get below this depth, they are no longer mixed with newly applied waste. Tilling depth should be entered in m; if it is in other units, it must be converted to m. Tilling depth must be greater than zero. No maximum limit is enforced. IWAIR has been tested for tilling depths from 0.01 to 1 m.

**Area of Unit (m<sup>2</sup>).** This is the total surface area of your unit in m<sup>2</sup>. Areas may be reported in acres or hectares; these values will need to be converted to m<sup>2</sup> for use in IWAIR. This value must be greater than or equal to 81 and less than or equal to 8,090,000 m<sup>2</sup>; these are the smallest and largest areas for which IWAIR can interpolate dispersion factors for ground-level sources. IWAIR has been tested for this full range of values.

**Annual Waste Quantity (Mg/yr).** This is the total amount of waste that you manage in your land application unit in a year, in Mg/yr. You may need to estimate this by multiplying the waste quantity applied per application by the number of applications per year. This value must be greater than zero. The maximum limit depends on the other inputs. The waste quantity, number of applications per year, bulk density, and area imply a depth of application as follows:

$$d_{\text{app}} = Q / (N_{\text{appl}} \times \text{BD} \times A)$$

where

$d_{app}$	=	depth of application (m)
$Q$	=	annual waste quantity (Mg/yr)
$N_{appl}$	=	number of applications per year ( $yr^{-1}$ )
$BD$	=	bulk density of waste ( $g/cm^3 = Mg/m^3$ )
$A$	=	area of unit ( $m^2$ ).

This depth of application may not exceed the tilling depth and, realistically, should be considerably less than the tilling depth. IWAIR has been tested for values of annual waste quantity from 0.01 to 10,000,000 Mg/yr.

**Number of Applications per Year.** This is the number of times you apply waste to the land application unit per year. You may need to convert a frequency of application to the corresponding number of applications per year. For example, if you apply waste weekly, you would enter 52 applications per year in IWAIR. This value must be an integer greater than or equal to 1. The maximum number of applications per year depends on the operating life you specified. IWAIR models land application unit emissions in time steps equal to the time between applications (so, if you entered 52 applications per year, IWAIR would model in 1-week time steps), for a period equal to the operating life of the unit plus 30 years. The total number of time steps modeled is thus:

$$N_{steps} = (t_{life} + 30) \times N_{appl}$$

where

$N_{steps}$	=	total number of time steps modeled (unitless)
$t_{life}$	=	operating life of unit (yr)
$N_{appl}$	=	number of applications per year ( $yr^{-1}$ ).

This total number of time steps,  $N_{steps}$ , cannot exceed 32,766 because of code limitations for integer variables. This is unlikely to result in practical limitations, unless the operating life is very long and the number of applications per year very high. For example, you could have daily applications (365 applications/year) for 59 years and still be just within this limitation. IWAIR has been tested for values from 1 to 52.

**Waste Bulk Density ( $g/cm^3$ ).** This is the overall, or bulk, density of your waste. This should be available from measurements. Bulk density must be in  $g/cm^3$ . This value must be greater than zero. IWAIR has been tested for values from 0.01 to 14  $g/cm^3$ .

### **B.3.2.4 Waste Characteristics Information (Only for Risk Calculation)**

**Type of Waste.** In order to generate an accurate estimate of a constituent's volatile emissions, you must define the physical and chemical characteristics of the waste you are modeling. In particular, you must identify whether or not the waste is best described as a dilute mixture of chemical compounds (aqueous) or if the waste should be considered organic, containing high levels of organic compounds or a separate nonaqueous organic phase. These two different types of waste matrices influence the degree of partitioning that will occur from the waste to the air. Partitioning describes the affinity that a contaminant has for one phase (for example, air) relative to another phase (for example, water) that drives the volatilization of organic chemicals. Your choice of waste matrix will significantly affect the rate of emissions from the waste. The following discussion is intended to provide background on emissions modeling as it relates to waste type, guidance on making this selection, and clarification of the modeling consequences of choosing AQUEOUS VERSUS ORGANIC in IWAIR. Note that you will only be asked to choose a waste type for risk calculations; for allowable concentration calculations, IWAIR calculates emission rates for both aqueous and organic waste types and selects the one that achieves the target risk or HQ at the lowest concentration applicable to the waste type.

**Aqueous-phase waste:** a waste that is predominantly water, with low concentrations of organics. All chemicals remain in solution in the waste and are usually present at concentrations below typical saturation limits. However, it is possible for the specific components of the waste to raise the effective saturation level for a chemical, allowing it to remain in solution at concentrations above the typical saturation limit.

**Organic-phase waste:** a waste that is predominantly organic chemicals, with a high concentration of organics. Concentrations of some chemicals may exceed saturation limits, causing those chemicals to come out of solution and form areas of free product in the WMU.

A WMU contains solids, liquids (such as water), and air. Individual chemical molecules are constantly moving from one of these media to another: they may be absorbed to solids, dissolved in liquids, or assume a vapor form in air. At equilibrium, the movement into and out of each medium is equal, so that the concentration of the chemical in each medium is constant. The emissions model used in IWAIR, CHEMDAT8, assumes that equilibrium has been reached.

Partitioning refers to how a chemical tends to distribute itself among these different media. Different chemicals have differing affinities for particular phases—some chemicals tend to partition more heavily to air, while others tend to partition more heavily to water. The different tendencies of different chemicals are described by partition coefficients or equilibrium constants.

Of particular interest in modeling volatile emissions of a chemical from a liquid waste matrix is the chemical's tendency to change from a liquid form to a vapor form. As a general rule, a chemical's vapor pressure describes this tendency. The pure component vapor pressure is a measure of this tendency for the pure chemical. A chemical in solution in another liquid (such as a waste containing multiple chemicals) will exhibit a partial vapor pressure, which is the chemical's share of the overall vapor pressure of the mixture; this partial vapor pressure is lower than the pure component vapor pressure and is generally equal to the pure component vapor

pressure times the constituent's mole fraction (a measure of concentration reflecting the number of moles of the chemical per total moles) in the solution. This general rule is known as Raoult's law.

Most chemicals do not obey Raoult's law in dilute (i.e., low concentration) aqueous solutions, but exhibit a greater tendency to partition to the vapor phase from dilute solutions than would be predicted by Raoult's law. These chemicals exhibit a higher partial vapor pressure than the direct mole fraction described above would predict.<sup>3</sup> This altered tendency to partition to the vapor phase in dilute solutions is referred to as Henry's law. To calculate the emissions of a constituent from a dilute solution, a partition coefficient called Henry's law constant is used. Henry's law constant relates the partial vapor pressure to the concentration in the solution.

To account for these differences in the tendency of chemicals to partition to vapor phase from different types of liquid waste matrices, CHEMDAT8 models emissions in two regimes: a dilute aqueous phase, modeled using Henry's law constant as the partition coefficient, and an organic phase, modeled using the partial vapor pressure predicted by Raoult's law as the partition coefficient. In fact, there is not a clear point at which wastes shift from dilute aqueous phase to organic phase; this is a model simplification. However, several rules of thumb may be used to determine when the Raoult's law model would be more appropriate. The clearest rule is that any chemical present in excess of its soil saturation concentration has exceeded the bounds of "dilute aqueous" and is more appropriately modeled using Raoult's law. Chemicals exceeding saturation limits will typically come out of solution and behave more like pure, organic-phase component. However, saturation limits can vary depending on site-specific parameters, such as temperature and pH of the waste. In addition, waste matrix effects<sup>4</sup> can cause chemicals to remain in solution at concentrations above their typical saturation limit. This scenario (an aqueous-phase waste with concentrations above typical saturation limits) is also best modeled using Raoult's law. Another rule of thumb is that a waste with a total organics concentration in excess of about 10 percent (or 100,000 ppm) is likely to behave more like an organic-phase waste than a dilute aqueous-phase waste and be more appropriately modeled using Raoult's law.

For land application units, where the waste is either a solid or mixed with a solid (such as soil), the CHEMDAT8 emissions model considers two-phase partitioning of the waste into the liquid (either aqueous or organic) phase and the air phase, using the partition coefficients described above, to estimate the equilibrium vapor composition in the pore (or air) space within the WMU. Emissions are subsequently estimated from the WMU by calculating the rate of diffusion of the vapor-phase contaminant through the porous waste/soil media.

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<sup>3</sup> There are some exceptions to this behavior in dilute solutions. A notable exception is formaldehyde, which has lower activity in dilute aqueous solution, which means that formaldehyde will have greater emissions in a high concentration, organic-phase waste.

<sup>4</sup> "Waste matrix effects" refers to the effect that the composition of the waste has on a constituent's solubility in the waste or the tendency for the chemical to evaporate from the waste. For example, hexane has a solubility in distilled water of approximately 12 mg/L; however, its solubility in methanol is much higher (more than 100,000 mg/L) (Perry and Green, 1984). Therefore, it is likely that hexane will remain dissolved in a solution of 10 percent methanol in water at higher concentrations than the aqueous solubility limit of 12 mg/L suggests.

When in allowable concentration calculation mode, IWAIR calculates both aqueous-phase and organic-phase emission rates. However, aqueous-phase emission rates, as discussed above, are only applicable up to the saturation limit. If the use of the aqueous-phase emission rate results in an allowable concentration in excess of the saturation limit, IWAIR will use the organic-phase rate instead.

**Molecular Weight of Waste (g/mol).** If you choose to model an organic-phase waste, you will need to enter the average molecular weight of the waste. This may be calculated from the molecular weights of the component constituents as follows:

$$MW_{\text{waste}} = \frac{\sum (C_i) \times (1 \text{ Mg})}{\sum (C_i/MW_i) \times (1 \text{ Mg})}$$

where

$$\begin{aligned} MW_{\text{waste}} &= \text{molecular weight of waste (g/mol)} \\ C_i &= \text{waste concentration of contaminant } i \text{ (mg/kg = g/Mg)} \\ MW_i &= \text{molecular weight of contaminant } i \text{ (g/mol)}. \end{aligned}$$

This assumes that the average molecular weight of the unspecified fraction of the organic waste matrix has the same average molecular weight as the specified fraction (i.e., the input contaminant concentrations). This value must be greater than or equal to 1 (the molecular weight of a single hydrogen ion). No maximum limit is enforced.

### B.3.3 WMU Data for CHEMDAT8 – Landfill (Screen 3C)

**B.3.3.1 Meteorological Station Parameters.** These inputs are used only for the emissions modeling, not the dispersion modeling, which uses hourly meteorological data, not annual averages. Therefore, changes to these inputs will not affect the dispersion factors.

**Wind Speed (m/s).** IWAIR uses wind speed to select the most appropriate empirical emission correlation equation in CHEMDAT8; there are several of these correlations, and each one applies to a specific range of wind speeds and unit sizes. By default, IWAIR uses the average annual wind speed from the meteorological station that was assigned to your location. However, you may wish to override the default if you have site-specific data on wind speed. If you do override, you should use an overall annual average in all directions, not any measure of peak wind speed or average only in the prevailing wind direction. Also, wind speed is often reported in knots or mph. However, for use in IWAIR, wind speed must be converted to m/s. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of wind speed from 0.01 to 100 m/s; however, a realistic range for average annual wind speed is about 2 to 10 m/s.

**Temperature (°C).** IWAIR uses temperature to correct various temperature-dependent chemical properties used in emissions modeling (Henry's law constant and vapor pressure) from a standard temperature to the ambient temperature. By default, IWAIR uses the average annual

temperature from the meteorological station that was assigned to your location. However, you may wish to override the default if you have site-specific data on temperature. If you do override, you should use an annual average temperature. Temperature may be reported in degrees Fahrenheit (°F); however, for use in IWAIR, temperature must be converted to degrees Celsius (°C). This value must be greater than or equal to -100°C. No maximum limit is enforced. IWAIR has been tested for values of temperature from 0 to 50°C.

### **B.3.3.2 Waste Porosity Information**

**Total Porosity (volume fraction).** Porosity refers to the spaces in a soil or waste matrix that are not soil particles. These spaces may be filled with air or water. Total porosity is the sum of both air- and water-filled porosity. Sometimes porosity is referred to as saturated water content. Porosity values are used in the emissions model, and they can be used to estimate soil saturation concentration limits. If measured data on porosity are not available, porosity can be estimated from the bulk density and particle density of the waste as follows:

$$\epsilon_t = 1 - \text{BD}/\rho_s$$

where

- $\epsilon_t$  = total porosity (unitless)
- BD = bulk density of waste (g/cm<sup>3</sup>)
- $\rho_s$  = particle density of waste (g/cm<sup>3</sup>).

If particle density is not available, a typical value for mineral material is 2.65 g/cm<sup>3</sup> (Mason and Berry, 1968).

Porosity must be greater than zero and less than 1. IWAIR has been tested for values from 0.01 to 0.99.

**Air Porosity (volume fraction).** Air-filled porosity is the porosity that is filled with air instead of water. This can be calculated from volumetric moisture content (which is equivalent to water-filled porosity) and total porosity as follows:

$$\epsilon_a = \epsilon_t - \epsilon_w$$

where

- $\epsilon_a$  = air-filled porosity (unitless)
- $\epsilon_t$  = total porosity (unitless)
- $\epsilon_w$  = water-filled porosity = volumetric water content (unitless).

Air-filled porosity must be greater than zero and less than or equal to the total porosity. IWAIR has been tested for this full range.



### **B.3.3.3 Landfill Dimensions and Loading Information**

**Biodegradation (on/off).** This option lets you choose whether to model biodegradation losses in the unit. Landfills are generally not designed to biodegrade wastes; therefore, the biodegradation option is turned off for landfills by default. However, biodegradation may occur in your landfill. If you believe it does and want to model it, you can select biodegradation |ON|. Soil biodegradation rates can be very site-specific. If you believe that the actual rates in your unit are different than those included in the IWAIR chemical properties database, you can enter user-defined chemical entries using your own soil biodegradation rates.

**Operating Life (yr).** This parameter is the expected remaining operating life of your unit, from the time you are modeling until you expect it to be closed. For landfills, this value is used in emissions calculations. In addition, it affects exposure duration. IWAIR uses default exposure durations of 30 years for residents and 7.2 years for workers. However, proper closure of a landfill typically ends all exposures. Therefore, if the operating life you specify is less than 30 or 7.2 years, IWAIR caps the exposure duration at the operating life. Values in excess of 30 years will not affect the results for residents, and values in excess of 7.2 years will not affect the results for workers. Operating life should be entered in years. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of operating life from 0.01 to 100 years.

**Total Area of Landfill (m<sup>2</sup>).** This is the total surface area of your unit in m<sup>2</sup>. Be sure to enter total area and not just the area of the active cell. Areas may be reported in acres or hectares; these values will need to be converted to m<sup>2</sup> for use in IWAIR. This value must be greater than or equal to 81 and less than or equal to 8,090,000 m<sup>2</sup>, which are the smallest and largest areas for which IWAIR can interpolate dispersion factors for ground-level sources. IWAIR has been tested for this full range of values.

**Total Depth of Landfill (m).** This is the average depth of your unit in meters (m). If your unit is not a constant depth, use the average or most typical depth. If you have depth reported in units such as feet, you will need to convert them to m. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of depth from 0.01 to 30 m.

**Total Number of Cells in Landfill.** Landfills are typically filled one cell at a time. This input is the total number of cells in your landfill. IWAIR models one open cell at a time, with each cell open for a period equal to the operating life divided by the total number of cells. This value must be greater than or equal to 1. No maximum limit is enforced. IWAIR has been tested for values from 1 to 10,000.

**Annual Quantity of Waste Disposed in Landfill (Mg/yr).** This is the total amount of waste that you manage in your landfill in a year, in Mg/yr. This value must be greater than zero. The maximum limit depends on other inputs. The waste quantity, operating life, area, and depth imply a loading rate as follows:

$$L = (Q \times t_{\text{life}}) / (A \times D)$$

where

L	=	loading rate ( $\text{Mg}/\text{m}^3 = \text{g}/\text{cm}^3$ )
Q	=	annual waste quantity ( $\text{Mg}/\text{yr}$ )
$t_{\text{life}}$	=	operating life (yr)
A	=	area of landfill ( $\text{m}^2$ )
D	=	depth (m).

This loading rate may not exceed the bulk density of the waste. IWAIR has been tested for values of annual waste quantity from 0.01 to 10,000,000 Mg/yr.

**Bulk Density of Waste ( $\text{g}/\text{cm}^3$ ).** This is the overall, or bulk, density of your waste. This should be available from measurements. Bulk density must be in  $\text{g}/\text{cm}^3$ . This value must be greater than zero. IWAIR has been tested for values from 0.01 to 14  $\text{g}/\text{cm}^3$ .

#### **B.3.3.4 Waste Characteristics Information (Only for Risk Calculation)**

**Type of Waste.** In order to generate an accurate estimate of a constituent's volatile emissions, you must define the physical and chemical characteristics of the waste you are modeling. In particular, you must identify whether or not the waste is best described as a dilute mixture of chemical compounds (aqueous) or if the waste should be considered organic, containing high levels of organic compounds or a separate nonaqueous organic phase. These two different types of waste matrices influence the degree of partitioning that will occur from the waste to the air. Partitioning describes the affinity that a contaminant has for one phase (for example, air) relative to another phase (for example, water) that drives the volatilization of organic chemicals. Your choice of waste matrix will significantly affect the rate of emissions from the waste. The following discussion is intended to provide background on emissions modeling as it relates to waste type, guidance on making this selection, and clarification of the modeling consequences of choosing AQUEOUS versus ORGANIC in IWAIR. Note that you will only be asked to choose a waste type for risk calculations; for allowable concentration calculations, IWAIR calculates emission rates for both aqueous and organic waste types and selects the one that achieves the target risk or HQ at the lowest concentration applicable to the waste type.

**Aqueous-phase waste:** a waste that is predominantly water, with low concentrations of organics. All chemicals remain in solution in the waste and are usually present at concentrations below typical saturation limits. However, it is possible for the specific components of the waste to raise the effective saturation level for a chemical, allowing it to remain in solution at concentrations above the typical saturation limit.

**Organic-phase waste:** a waste that is predominantly organic chemicals, with a high concentration of organics. Concentrations of some chemicals may exceed saturation limits, causing those chemicals to come out of solution and form areas of free product in the WMU.

A WMU contains solids, liquids (such as water), and air. Individual chemical molecules are constantly moving from one of these media to another: they may be absorbed to solids, dissolved in liquids, or assume a vapor form in air. At equilibrium, the movement into and out

of each medium is equal, so that the concentration of the chemical in each medium is constant. The emissions model used in IWAIR, CHEMDAT8, assumes that equilibrium has been reached.

Partitioning refers to how a chemical tends to distribute itself among these different media. Different chemicals have differing affinities for particular phases—some chemicals tend to partition more heavily to air, while others tend to partition more heavily to water. The different tendencies of different chemicals are described by partition coefficients or equilibrium constants.

Of particular interest in modeling volatile emissions of a chemical from a liquid waste matrix is the chemical's tendency to change from a liquid form to a vapor form. As a general rule, a chemical's vapor pressure describes this tendency. The pure component vapor pressure is a measure of this tendency for the pure chemical. A chemical in solution in another liquid (such as a waste containing multiple chemicals) will exhibit a partial vapor pressure, which is the chemical's share of the overall vapor pressure of the mixture; this partial vapor pressure is lower than the pure component vapor pressure and is generally equal to the pure component vapor pressure times the constituent's mole fraction (a measure of concentration reflecting the number of moles of the chemical total moles) in the solution. This general rule is known as Raoult's law.

Most chemicals do not obey Raoult's law in dilute (i.e., low concentration) aqueous solutions, but exhibit a greater tendency to partition to the vapor phase from dilute solutions than would be predicted by Raoult's law. These chemicals exhibit a higher partial vapor pressure than the direct mole fraction described above would predict.<sup>5</sup> This altered tendency to partition to the vapor phase in dilute solutions is referred to as Henry's law. To calculate the emissions of a constituent from a dilute solution, a partition coefficient called Henry's law constant is used. Henry's law constant relates the partial vapor pressure to the concentration in the solution.

To account for these differences in the tendency of chemicals to partition to vapor phase from different types of liquid waste matrices, CHEMDAT8 models emissions in two regimes: a dilute aqueous phase, modeled using Henry's law constant as the partition coefficient, and an organic phase, modeled using the partial vapor pressure predicted by Raoult's law as the partition coefficient. In fact, there is not a clear point at which wastes shift from dilute aqueous phase to organic phase; this is a model simplification. However, several rules of thumb may be used to determine when the Raoult's law model would be more appropriate. The clearest rule is that any chemical present in excess of its soil saturation concentration has exceeded the bounds of "dilute aqueous" and is more appropriately modeled using Raoult's law. Chemicals exceeding saturation limits will typically come out of solution and behave more like pure, organic-phase component. However, saturation limits can vary depending on site-specific parameters, such as temperature and pH of the waste. In addition, waste matrix effects<sup>6</sup> can cause chemicals to

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<sup>5</sup> There are some exceptions to this behavior in dilute solutions. A notable exception is formaldehyde, which has lower activity in dilute aqueous solution, which means that formaldehyde will have greater emissions in a high concentration, organic-phase waste.

<sup>6</sup> "Waste matrix effects" refers to the effect that the composition of the waste has on a constituent's solubility in the waste or the tendency for the chemical to evaporate from the waste. For example, hexane has a solubility in distilled water of approximately 12 mg/L; however, its solubility in methanol is much higher (more than

remain in solution at concentrations above their typical saturation limit. This scenario (an aqueous-phase waste with concentrations above typical saturation limits) is also best modeled using Raoult's law. Another rule of thumb is that a waste with a total organics concentration in excess of about 10 percent (or 100,000 ppm) is likely to behave more like an organic-phase waste than a dilute aqueous-phase waste and be more appropriately modeled using Raoult's law.

For landfills, where the waste is either a solid or mixed with a solid (such as soil), the CHEMDAT8 emissions model considers two-phase partitioning of the waste into the liquid (either aqueous or organic) phase and the air phase, using the partition coefficients described above, to estimate the equilibrium vapor composition in the pore (or air) space within the WMU. Emissions are subsequently estimated from the WMU by calculating the rate of diffusion of the vapor-phase contaminant through the porous waste/soil media.

When in allowable concentration calculation mode, IWAIR calculates both aqueous-phase and organic-phase emission rates. However, aqueous-phase emission rates, as discussed above, are only applicable up to the saturation limit. If the use of the aqueous-phase emission rate results in an allowable concentration in excess of the saturation limit, IWAIR will use the organic-phase rate instead.

**Molecular Weight of Waste (g/mol).** If you choose to model an organic-phase waste, you will need to enter the average molecular weight of the waste. This may be calculated from the molecular weights of the component constituents as follows:

$$MW_{\text{waste}} = \frac{\sum (C_i) \times (1 \text{ Mg})}{\sum (C_i/MW_i) \times (1 \text{ Mg})}$$

where

$$\begin{aligned} MW_{\text{waste}} &= \text{molecular weight of waste (g/mol)} \\ C_i &= \text{waste concentration of contaminant } i \text{ (mg/kg = g/Mg)} \\ MW_i &= \text{molecular weight of contaminant } i \text{ (g/mol)}. \end{aligned}$$

This assumes that the average molecular weight of the unspecified fraction of the organic waste matrix has the same average molecular weight as the specified fraction (i.e., the input contaminant concentrations). This value must be greater than or equal to 1 (the molecular weight of a single hydrogen ion). No maximum limit is enforced.

### B.3.4 WMU Data for CHEMDAT8 – Waste Pile (Screen 3D)

**B.3.4.1 Meteorological Station Parameters.** These inputs are used only for the emissions modeling, not the dispersion modeling, which uses hourly meteorological data, not annual averages. Therefore, changes to these inputs will not affect the dispersion factors.

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100,000 mg/L) (Perry and Green, 1984). Therefore, it is likely that hexane will remain dissolved in a solution of 10 percent methanol in water at higher concentrations than the aqueous solubility limit of 12 mg/L suggests.

**Wind Speed (m/s).** IWAIR uses wind speed to select the most appropriate empirical emission correlation equation in CHEMDAT8; there are several of these correlations, and each one applies to a specific range of wind speeds and unit sizes. By default, IWAIR uses the average annual wind speed from the meteorological station that was assigned to your location. However, you may wish to override the default if you have site-specific data on wind speed. If you do override, you should use an overall annual average in all directions, not any measure of peak wind speed or average only in the prevailing wind direction. Also, wind speed is often reported in knots or mph. However, for use in IWAIR, wind speed must be converted to m/s. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of wind speed from 0.01 to 100 m/s; however, a realistic range for average annual wind speed is about 2 to 10 m/s.

**Temperature (°C).** IWAIR uses temperature to correct various temperature-dependent chemical properties used in emissions modeling (Henry's law constant and vapor pressure) from a standard temperature to the ambient temperature. By default, IWAIR uses the average annual temperature from the meteorological station that was assigned to your location. However, you may wish to override the default if you have site-specific data on temperature. If you do override, you should use an annual average temperature. Temperature may be reported in degrees Fahrenheit (°F); however, for use in IWAIR, temperature must be converted to degrees Celsius (°C). This value must be greater than or equal to -100°C. No maximum limit is enforced. IWAIR has been tested for values of temperature from 0 to 50°C.

#### **B.3.4.2 Waste Porosity Information**

**Total Porosity (volume fraction).** Porosity refers to the spaces in a soil or waste matrix that are not soil particles. These spaces may be filled with air or water. Total porosity is the sum of both air- and water-filled porosity. Sometimes porosity is referred to as saturated water content. Porosity values are used in the emissions model, and they can be used to estimate soil saturation concentration limits. If measured data on porosity are not available, porosity can be estimated from the bulk density and particle density of the waste as follows:

$$\epsilon_t = 1 - \text{BD}/\rho_s$$

where

- $\epsilon_t$  = total porosity (unitless)
- BD = bulk density of waste (g/cm<sup>3</sup>)
- $\rho_s$  = particle density of waste (g/cm<sup>3</sup>).

If particle density is not available, a typical value for mineral material is 2.65 g/cm<sup>3</sup> (Mason and Berry, 1968).

Porosity must be greater than zero and less than 1. IWAIR has been tested from 0.01 to 0.99.

**Air Porosity (volume fraction).** Air-filled porosity is the porosity that is filled with air instead of water. This can be calculated from volumetric moisture content (which is equivalent to water-filled porosity) and total porosity as follows:

$$\epsilon_a = \epsilon_t - \epsilon_w$$

where

- $\epsilon_a$  = air-filled porosity (unitless)
- $\epsilon_t$  = total porosity (unitless)
- $\epsilon_w$  = water-filled porosity = volumetric water content (unitless).

Air-filled porosity must be greater than zero and less than or equal to the total porosity. IWAIR has been tested for this full range.

#### **B.3.4.3 Waste Pile Dimensions and Loading Information**

**Biodegradation (on/off).** This option lets you choose whether to model biodegradation losses in the unit. Waste piles are generally not designed to biodegrade wastes; therefore, the biodegradation option is turned off for waste piles by default. However, biodegradation may occur in your waste pile, particularly if residence times of waste in the waste pile are long (on the order of 60 days to one year). With such residence times, naturally occurring microorganisms could potentially acclimate and degrade contaminants within the waste pile. If you believe that biodegradation does occur in your waste pile and you want to model it, you can select biodegradation |ON|. Soil biodegradation rates can be very site-specific. If you believe that the actual rates in your unit are different than those included in the IWAIR chemical properties database, you can enter user-defined chemical entries using your own soil biodegradation rates.

**Operating Life (yr).** This parameter is the expected remaining operating life of your unit, from the time you are modeling until you expect it to be closed. Operating life does not affect emissions estimates for waste piles, which are modeled at steady state. However, operating life may affect exposure duration. IWAIR uses default exposure durations of 30 years for residents and 7.2 years for workers. However, proper closure of a waste pile typically ends all exposures. Therefore, if the operating life you specify is less than 30 or 7.2 years, IWAIR caps the exposure duration at the operating life. Values in excess of 30 years will not affect the results for residents, and values in excess of 7.2 years will not affect the results for workers. Operating life should be entered in years. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of operating life from 0.01 to 100 years.

**Height of Waste Pile Unit (m).** This is the average height of your waste pile in meters (m). If your waste pile is not a constant height, use the average or most typical height. If you have height reported in units such as feet, you will need to convert them to m. This value must be greater than or equal to 1 m and less than or equal to 10 m; these are the smallest and largest heights for which IWAIR can interpolate dispersion factors for waste piles. IWAIR has been tested for this full range.

**Area of Unit ( $m^2$ ).** This is the total surface area of your unit in  $m^2$ . Areas may be reported in acres or hectares; these values will need to be converted to  $m^2$  for use in IWAIR. This value must be greater than or equal to 20 and less than or equal to 1,300,000  $m^2$ ; these are the smallest and largest areas for which IWAIR can interpolate dispersion factors for waste piles. IWAIR has been tested for this full range of values.

**Average Quantity of Waste in Waste Pile (Mg/yr).** This is the average amount of waste in your waste pile over a year, in Mg/yr. This value must be greater than zero. No maximum limit is enforced. IWAIR has been tested for values of annual waste quantity from 0.01 to 10,000,000 Mg/yr.

**Bulk Density of Waste ( $g/cm^3$ ).** This is the overall, or bulk, density of your waste. This should be available from measurements. Bulk density must be in  $g/cm^3$ . This value must be greater than zero. IWAIR has been tested for values from 0.01 to 14  $g/cm^3$ .

#### **B.3.4.4 Waste Characteristics Information (Only for Risk Calculation)**

**Type of Waste.** In order to generate an accurate estimate of a constituent's volatile emissions, you must define the physical and chemical characteristics of the waste you are modeling. In particular, you must identify whether or not the waste is best described as a dilute mixture of chemical compounds (aqueous) or if the waste should be considered organic, containing high levels of organic compounds or a separate nonaqueous organic phase. These two different types of waste matrices influence the degree of partitioning that will occur from the waste to the air. Partitioning describes the affinity that a contaminant has for one phase (for example, air) relative to another phase (for example, water) that drives the volatilization of organic chemicals. Your choice of waste matrix will significantly affect the rate of emissions from the waste. The following discussion is intended to provide background on emissions modeling as it relates to waste type, guidance on making this selection, and clarification of the modeling consequences of choosing AQUEOUS VERSUS ORGANIC in IWAIR. Note that you will only be asked to choose a waste type for risk calculations; for allowable concentration calculations, IWAIR calculates emission rates for both aqueous and organic waste types and selects the one that achieves the target risk or HQ at the lowest concentration applicable to the waste type.

**Aqueous-phase waste:** a waste that is predominantly water, with low concentrations of organics. All chemicals remain in solution in the waste and are usually present at concentrations below typical saturation limits. However, it is possible for the specific components of the waste to raise the effective saturation level for a chemical, allowing it to remain in solution at concentrations above the typical saturation limit.

**Organic-phase waste:** a waste that is predominantly organic chemicals, with a high concentration of organics. Concentrations of some chemicals may exceed saturation limits, causing those chemicals to come out of solution and form areas of free product in the WMU.

A WMU contains solids, liquids (such as water), and air. Individual chemical molecules are constantly moving from one of these media to another: they may be absorbed to solids, dissolved in liquids, or assume a vapor form in air. At equilibrium, the movement into and out

of each medium is equal, so that the concentration of the chemical in each medium is constant. The emissions model used in IWAIR, CHEMDAT8, assumes that equilibrium has been reached.

Partitioning refers to how a chemical tends to distribute itself among these different media. Different chemicals have differing affinities for particular phases—some chemicals tend to partition more heavily to air, while others tend to partition more heavily to water. The different tendencies of different chemicals are described by partition coefficients or equilibrium constants.

Of particular interest in modeling volatile emissions of a chemical from a liquid waste matrix is the chemical's tendency to change from a liquid form to a vapor form. As a general rule, a chemical's vapor pressure describes this tendency. The pure component vapor pressure is a measure of this tendency for the pure chemical. A chemical in solution in another liquid (such as a waste containing multiple chemicals) will exhibit a partial vapor pressure, which is the chemical's share of the overall vapor pressure of the mixture; this partial vapor pressure is lower than the pure component vapor pressure and is generally equal to the pure component vapor pressure times the constituent's mole fraction (a measure of concentration reflecting the number of moles of the chemical per total moles) in the solution. This general rule is known as Raoult's law.

Most chemicals do not obey Raoult's law in dilute (i.e., low concentration) aqueous solutions, but exhibit a greater tendency to partition to the vapor phase from dilute solutions than would be predicted by Raoult's law. These chemicals exhibit a higher partial vapor pressure than the direct mole fraction described above would predict.<sup>7</sup> This altered tendency to partition to the vapor phase in dilute solutions is referred to as Henry's law. To calculate the emissions of a constituent from a dilute solution, a partition coefficient called Henry's law constant is used. Henry's law constant relates the partial vapor pressure to the concentration in the solution.

To account for these differences in the tendency of chemicals to partition to vapor phase from different types of liquid waste matrices, CHEMDAT8 models emissions in two regimes: a dilute aqueous phase, modeled using Henry's law constant as the partition coefficient, and an organic phase, modeled using the partial vapor pressure predicted by Raoult's law as the partition coefficient. In fact, there is not a clear point at which wastes shift from dilute aqueous phase to organic phase; this is a model simplification. However, several rules of thumb may be used to determine when the Raoult's law model would be more appropriate. The clearest rule is that any chemical present in excess of its soil saturation concentration has exceeded the bounds of "dilute aqueous" and is more appropriately modeled using Raoult's law. Chemicals exceeding saturation limits will typically come out of solution and behave more like pure, organic-phase component. However, saturation limits can vary depending on site-specific parameters, such as

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<sup>7</sup> There are some exceptions to this behavior in dilute solutions. A notable exception is formaldehyde, which has lower activity in dilute aqueous solution, which means that formaldehyde will have greater emissions in a high concentration, organic-phase waste.



temperature and pH of the waste. In addition, waste matrix effects<sup>8</sup> can cause chemicals to remain in solution at concentrations above their typical saturation limit. This scenario (an aqueous-phase waste with concentrations above typical saturation limits) is also best modeled using Raoult's law. Another rule of thumb is that a waste with a total organics concentration in excess of about 10 percent (or 100,000 ppm) is likely to behave more like an organic-phase waste than a dilute aqueous-phase waste and be more appropriately modeled using Raoult's law.

For waste piles, where the waste is either a solid or mixed with a solid (such as soil), the CHEMDAT8 emissions model considers two-phase partitioning of the waste into the liquid (either aqueous or organic) phase and the air phase, using the partition coefficients described above, to estimate the equilibrium vapor composition in the pore (or air) space within the WMU. Emissions are subsequently estimated from the WMU by calculating the rate of diffusion of the vapor-phase contaminant through the porous waste/soil media.

When in allowable concentration calculation mode, IWAIR calculates both aqueous-phase and organic-phase emission rates. However, aqueous-phase emission rates, as discussed above, are only applicable up to the saturation limit. If the use of the aqueous-phase emission rate results in an allowable concentration in excess of the saturation limit, IWAIR will use the organic-phase rate instead.

**Molecular Weight of Waste (g/mol).** If you choose to model an organic-phase waste, you will need to enter the average molecular weight of the waste. This may be calculated from the molecular weights of the component constituents as follows:

$$MW_{\text{waste}} = \frac{\sum (C_i) \times (1 \text{ Mg})}{\sum (C_i/MW_i) \times (1 \text{ Mg})}$$

where

- $MW_{\text{waste}}$  = molecular weight of waste (g/mol)
- $C_i$  = waste concentration of contaminant  $i$  (mg/kg = g/Mg)
- $MW_i$  = molecular weight of contaminant  $i$  (g/mol).

This assumes that the average molecular weight of the unspecified fraction of the organic waste matrix has the same average molecular weight as the specified fraction (i.e., the input contaminant concentrations). This value must be greater than or equal to 1 (the molecular weight of a single hydrogen ion). No maximum limit is enforced.

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<sup>8</sup> "Waste matrix effects" refers to the effect that the composition of the waste has on a constituent's solubility in the waste or the tendency for the chemical to evaporate from the waste. For example, hexane has a solubility in distilled water of approximately 12 mg/L; however, its solubility in methanol is much higher (more than 100,000 mg/L) (Perry and Green, 1984). Therefore, it is likely that hexane will remain dissolved in a solution of 10 percent methanol in water at higher concentrations than the aqueous solubility limit of 12 mg/L suggests.

## B.4 User-Override Emission Rates (Screens 4A and 4B)

**Override Emission Rates.** You may choose either to enter your own emission rates for all chemicals modeled or to override IWAIR's calculated emission rates for some or all of the chemicals modeled. Override emission rates may be based on measured data or modeled results from an emissions model outside of IWAIR, but regardless of source, should reflect a long-term average, not a short-term peak.

This input has different units in risk calculation mode versus allowable concentration mode:

- In risk mode, this input should be the actual measured or modeled emissions from your unit, normalized on area (in  $\text{g}/\text{m}^2/\text{s}$ ). If emission rates are based on modeled rates, they should correspond to the actual waste concentrations in your unit. Emissions in  $\text{g}/\text{s}$  should be normalized to area by dividing by the area of the unit.
- In allowable concentration mode, the emission rate should either be based on modeled emissions corresponding to a waste concentration of  $1 \text{ mg}/\text{kg}$  or  $1 \text{ mg}/\text{L}$ , or they should be normalized to concentration by dividing by the actual waste concentration present when the emissions were measured or modeled. The units for allowable concentration mode emission rates ( $\text{g}/\text{m}^2\text{-s}$  per  $\text{mg}/\text{kg}$  or  $\text{mg}/\text{L}$ ) reflect this. Emissions measured or modeled in  $\text{g}/\text{s}$  should also be normalized to area by dividing by the area of the unit.

You may input one override emission rate per chemical. In risk mode, IWAIR assumes this emission rate corresponds to the waste type (aqueous or organic) you chose on Screen 3, WMU DATA FOR CHEMDAT8. In allowable concentration mode, IWAIR assumes this emission rate corresponds to an aqueous waste. As a result, IWAIR will not output concentrations in concentration mode in excess of each chemical's solubility or saturation limit if you have entered user-override emission factors.

**Source and Justification for User-Override Values.** If you enter override emission factors, you must document their source in this field. The justification field may not be left blank.

## B.5 ISCST3 or User-Override Dispersion Factors (Screen 5A)

**Distance to Receptor (m).** This is the distance from the edge of your unit to the receptor for whom you want to estimate risk or allowable concentration. You must choose from one of the six values available in IWAIR: 25, 50, 75, 150, 500, or 1,000 m. Choose the distance that best approximates the location of your receptors. If you are using IWAIR's dispersion factors, they will correspond to the distance you select; selecting a distance smaller than the actual distance to receptors near your unit will overestimate risk, and selecting a distance larger than the actual distance will underestimate risk. If you enter your own dispersion factors, this input is only for your reference and is not used in calculations. Therefore, you should select the distance that most closely approximates the distance your dispersion factor applies to.

**Receptor Type.** Two different types of exposed individuals, worker and resident, can be modeled with IWAIR. The dispersion factors do not vary with receptor type; however, receptor type is chosen here for convenience. The difference between these two receptor types lies in the exposure factors, such as body weight and inhalation rate, used to calculate risk for carcinogens. There is no difference between them for noncarcinogens because calculation of noncarcinogenic risk does not depend on exposure factors. The assumptions for residents reflect males and females from birth through age 30; it is important to consider childhood exposures because children typically have higher intake rates per kilogram of body weight than adults. The actual exposure duration used for residents is the smaller of 30 years or the operating life of the unit that you entered (except for land application units, for which the exposure duration for residents is always 30 years regardless of operating life). Exposure for residents starts at birth and continues for the length of the exposure duration, using the appropriate age-specific exposure factors. The assumptions for workers reflect a full-time, outdoor worker; all exposure is assumed to occur as an adult. The exposure duration for workers is the smaller of 7.2 years or the operating life of the unit (except for land application units, for which the exposure duration for workers is always 7.2 years regardless of operating life). For more information on the specific exposure factors used for residents and workers, see the *IWAIR Technical Background Document*.

**User-Override Dispersion Factors.** You may choose either to enter your own dispersion factors for all receptors modeled or to override IWAIR's calculated dispersion factors for some or all of the receptors modeled. Note that dispersion factors are not chemical-specific, nor are they specified to receptor type (resident or worker). Dispersion factors may be based on measured air concentrations or air concentrations modeled outside of IWAIR. If based on modeled air concentrations, they should correspond to an emission rate of  $1 \mu\text{g}/\text{m}^2\text{-s}$ . If based on measured air concentration data, they should be normalized to emission rate by dividing by the actual emission rate measured or modeled. The units for dispersion factors ( $\mu\text{g}/\text{m}^3$  per  $\mu\text{g}/\text{m}^2\text{-s}$ ) reflect this. Note that when you enter your own dispersion factors, you are not limited to the six receptor distances included in IWAIR. In this circumstance, those distances are for your reference only.

**Source and Justification for User-Override Values.** If you enter override dispersion factors, you must document their source in this field. If your receptor distances differ from the distances available in IWAIR, it may be useful to document here the actual receptor distances for each numbered receptor. The justification field may not be left blank.

## B.6 Results Screen (Screen 6)

### B.6.1 Target Risk and Hazard Quotient Value

These inputs are needed for allowable concentration mode only. In risk mode, risk and HQ are calculated by IWAIR.

**Risk Value for Carcinogens.** Choose one of the five values available. A higher risk value represents greater risk and will result in lower allowable concentrations. This value is not required if no carcinogens are being modeled (i.e., CSF is NA for all chemicals modeled).

**Hazard Quotient Value for Noncarcinogens.** Choose one of the five values available. A higher HQ value represents greater likelihood of health effects and will result in lower allowable concentrations. This value is not required if no noncarcinogens are being modeled (i.e., RfC is NA for all chemicals modeled).

## B.6.2 Health Benchmarks

Parameter guidance for health benchmarks is provided in Section B.2.2.3.

## B.7 References

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